ISTANBUL TECHNICAL UNIVERSITY * INSTITUTE OF SCIENCE AND TECHNOLOGY

EFFECT OF PYRIDINE ON THE ESTERIFICATION REACTION BETWEEN OLEIC ACID AND GLYCEROL

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Date of Submission: August 24, 1992

Date of Approval: September 9, 1992

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SEPTEMBER 1992

PREFACE

The aim of this study is to investigate the effect of pyridine on the esterification reaction between oleic acid and glycerol. Thus, the kinetics of esterification and distribution of products were examined. Reactions were carried out in the presence of pyridine and the results were compared with those obtained from the reactions without pyridine.

During this study many persons helped me. Therefore, first I wish to express my sincere gratitude to my supervisor, Prof. Dr. Ekrem EKINCI. Special thanks are due Assoc. Prof. Dr. Tuncer ERCIYES my co-advisor for his invaluable contributions, and helps. I also thank graduate students Seniha ERKAL, and Sermet KABASAKAL for their kindly assistances.

AUGUST, 1992 Mansour Masoud EMTIR

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SUMMARY

The kinetics of esterification reaction between oleic acid and glycerol has been studied under various conditions. Pyridine was used as co-solvent. Reactions were carried out at 180, 200, and 220°C. Experimental data fitted the second-order rate equation for the reaction at 180°C and third-order rate equation for the reactions at 200°C and 220°C, while for the reactions without pyridine the obtained data fitted the third-order rate equation for all temperatures. In addition to the kinetic investigation, the product distribution at 180°C with and without pyridine was studied. It was observed that pyridine has an effect on the formation of partial glycerides.

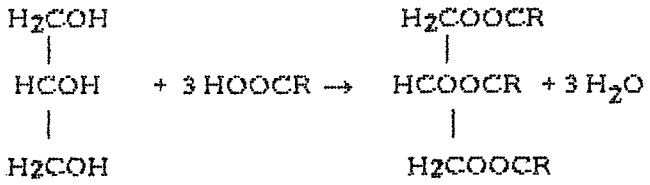
OLEIK ASİD VE GLİSEROL ARASINDAKİ ESTERLEŞME REAKSİYONUNDA PİRİDİN ETKİSİ

ÖZET

Bu çalışma da gliserin ile oleik asit arasındaki esterleşme reaksiyonu piridin ortak çözücüsü varlığında yürütülerek reaksiyon kinetiği yönünden incelenmiştir. Aynı reaksiyon, karşlaştırma amacı ile çözücüsüz olarak da yürütülmüş ve elde edilen sonuçlar karşılaştırılmıştır.

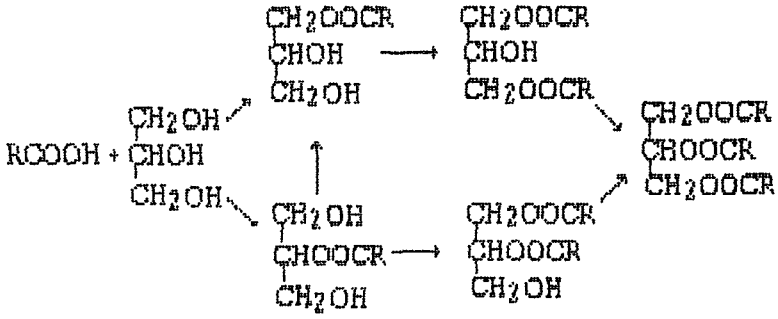
Gliserinin yağ asitleri ile esterleşmesi prosesi "yeniden esterleşme" prosesi olarak da belirtilmektedir. Bunun nedeni, yağ asitleri kaynağının doğal yağlarla vakslar oluşu ve yağ asitlerinin bu kaynaklardan hidroliz yolu ile elde edilmesidir. Homotrigliseridlerin üretiminde en basit ve o nedenle en çok arzu edilen çalışma yöntemi, direkt esterleşme yöntemidir. Buna karşılık belli konfigürasyon ve homojen yapıdaki mono- ve digliseridlerin üretiminde direkt esterleşme yöntemi uygun olmamaktadır.

Gliserinin yağ asitleriyle esterleşmesi sonucunda homotrigliserid oluşumu en basit şekliyle aşağıdaki denklemle gösterilebilir:



Gerçekte bu reaksiyon, başlangıçta monogliserid oluşumu, monogliseridin digliserid vermek üzere daha ileri esterleşmesi ve digliserin de trigliserid vermek üzere esterleşmesi kademelerinden yürümektedir. Bunlara ilave olarak böyle bir esterleşme reaksiyonu, acil gruplarının gliserin molekülündeki bir konumundan diğer konuma kaymaları nedeniyle daha da karışık olan bir mekanizma izlemektedir. Bu bilgiler de göz önüne alındığında

esterleşme reaksiyonunun ilerleyişi daha doğru olarak aşağıdaki gibi gösterilebilir.



1 ve 2-Monoglycerid Diglyserid 1,2 ve 1,3 Triglyserid

Gliserini yanlız bir hidroksil grubuna yetecek miktarda yağ asiti ile esterleşmesinden normal olarak monogliserid elde edilmesi beklenir. Ancak uygulama da söz konusu koşullarda elde edilen üründe di- ve trigliseridler de monogliserid ile birlikte bulunmaktadır. Üründe di- ve trıgliseridlerin bulunmasının nedeni, gliserin ve yağ asitlerinin birbiri içerisindeki sınırlı çözünürlüğüne dayanılarak açıklanabilir.

Yağ asitlerinin gliserindeki çözünürlüklerinin çok düşük olduğu ve yağ asitlerinin monogliseridteki çözünürlüklerinin gliserindeki çözünürlüklerinden daha fazla olduğu literatürde belirtilmektedir. Bu nedenle reaksiyonun başlamasından sonra oluşan monogliserid yağ asitleri ile daha ileri reaksiyona girecek di- ve trigliserid ürünlerini oluşturmaktadır. Bu düşüncenin temel olduğu bazı çalışmalarda esterleşme reaksiyonun da fenol ve Dowtherm gibi çözücüler ortak çözücü olarak kullanılmıştır.

Bu çalışmada gliserin-oleik asit esterleşme reaksiyonunda daha önce de belirtildiği gibi piridin ortak çözücü olarak kullanılmıştır. Piridin-su azeotropu karışımdaki suyun ayrılması daha önce geliştirilmiş bir deney düzeneği yardımıyla gerçekleştirilmiştir. Bu deney düzeneğinde katı sodyum hidroksit su tutan madde olarak kullanılmıştır. Pridin miktarı reaksiyon temperatürünü sağlayacak şekilde tespit edilmiştir. Reaksiyon 180°C, 200 °C, ve 220°C " da yürütülmüştür. Reaksiyon karışımından önceden belirlenen zaman aralıklarında alınan numunelerin çözücüleri giderildikten sonra oleik asit miktarları asit değeri tayini yapılarak belirlenmiştir. Serbest asit miktarı, ortamdan ayrılan ester suyu miktarına göre düzeltilerek kinetik eşitliklerde kullanılmıştır. Deneysel

sonuçların en iyi hangi hız eşitliğine uyduklarının testbitinde en küçük kareler yöntemini kullanan bilgisayar programı kullanılmıştır. Bu program istenilen aralıkta her mertebe için tarama yapmakta ve en uygun mertebeyi tesbit etmektedir. Deneysel sonuçların bu şekilde değerlendirilmesiyle piridin kullanılan reaksiyonun 180°C da ikinci mertebe, 200°C ve 220°C larda ise üçüncü mertebe reaksiyona uyduğu anlaşılmıştır. Çözücüsüz olarak yürütülen reaksiyonlarda elde edilen sonuçların bu şekilde değerlendirilmesiyle piridin kulllanılan reaksiyonun 180°C da ikinci mertebe, 200 ve 220°C larda ise üçüncü mertebe reaksiyona uyduğu anlaşılmıştır. Çözücüsüz olarak yürütülen reaksiyonlarda elde edilen sonuçlar yukarıda belirtilen üç temperatürde de üçüncü mertebe reaksiyon hız eştitliğine uygunluk göstermiştir.

Literatürde gliserin-yağ asiti esterleşme reaksiyonu çeşitli katalizörlerin kullanılmasıyla değişik temperatürlerde yürütülmüştur. Reaksiyonun ikinci mertebe bulunduğu gibi üçüncü mertebe olarak da bulunduğu rapor edilmiştir.

Bu çalışmada bulunan reaksiyon hız sabitleri ve aktivasyon enerjileri Tablo 1 de verilmiştir.

TABLO 1. Reaksiyon Hız Sabitleri Aktivasyon Enerjileri.

Çözücü	Hız Sabiti, k(ağ%)$^{-2}$ (dak.)$^{-1}$			Aktivasyone Enerji
	180°C	200°C	220°C	K.cal/mol
Piridin	1.10×10^{-4} (a)	3.81×10^{-6}	12.5×10^{-6}	27.46
Çözücüsüz	1.93×10^{-6}	6.40×10^{-6}	13.2×10^{-6}	21.30

(a) k nın birimi (ağ %)$^{-1}$ (dak.)$^{-1}$

Çalışmada piridin ortak çözücü olarak reaksiyon ürünlerinin dağılımına olan etkisi 180° C da yürütülen reaksiyonda incelenmiştir. Bu amaçla reaksiyon karışımından belirli zaman aralıklarında alınan numunelerin serbest asit, mono-, di-, ve trigliserid miktarları tayin edilmiştir. Aynı çalışma piridin kullanılmayan reaksiyon için de tekrarlanmıştır. Çonuçlar tablolar 2 , 3 verilmiştir.

TABLO 2 Oleik asit ile gliserol ün 180 °C de ki esterleşme reaksiyonu sonuçları *

Numune	Zaman (dak.)	Asit %	Hidroksil değeri	Monogliserid %	Digliserid %	Trigliserid %
1	6.67	89.08	37.90	12.32	0.000	00.00
2	21.83	71.93	64.96	15.84	0.240	12.06
3	37.00	64.14	73.27	16.57	0.234	19.06
4	57.92	53.80	70.85	5.08	0.607	40.51
5	77.75	50.50	53.94	7.56	0.334	41.61
6	97.75	47.03	51.18	6.26	0.348	46.36
7	127.58	42.68	40.61	6.91	0.209	50.20
8	157.67	38.06	33.70	4.38	0.220	57.34

TABLO 3 Piridinli ortamda oleik asit ile gliserol ün 180 °C de ki esterleşme reaksiyonu sonuçları *

Numune	Zaman (dak.)	Asit %	Hidroksil değeri	Monogliserid %	Digliserid	Trigliserid
1	7.75	93.37	25.40	7.30	0.027	0.00
2	22.50	83.12	47.49	9.55	0.193	7.14
3	37.83	74.30	59.40	9.67	0.321	15.71
4	77.25	59.21	67.97	5.37	0.565	34.86
5	97.00	54.68	65.81	6.49	0.502	38.33
6	127.50	48.67	66.29	4.96	0.561	45.81
7	159.25	43.38	62.47	6.62	0.461	50.46

* Analizler gliserinsiz numunelerle yapıldı.

Tablodan da görüldüğü gibi reaksiyon süresince hidroksil değerlerindeki değişme ve buna bağlı olarak mono-, di-, ve trigliseridlerin miktarlarındaki değişim piridin ve piridinsiz reaksiyonda farklı olmaktadır. Bu sonuç piridin kullanılan reaksiyonda reaktan oranlarının değiştirilmesiyle her hangi bir kısmi gliseridce zengin

ürün elde edilebileceği şeklindeki önceki çalışma sonucunu da doğrulamaktadır.

CHAPTER 1. INTRODUCTION

Mono-and diglycerides are the well known ester products of glycerol. These ester derivatives of fatty acids contain, respectively, one and two combined fatty acids, and have two and one hydroxyl groups in their molecules.

Industrial mono-and diglycerides prepared by direct esterification of glycerol are mixtures of mono-, di-, and triglycerides depending on the molar ratios applied in the reaction. Free glycerol is also present in final product. These products represent an important class of food emulsifiers and as such are used in ice cream and peanut butter. Partial glycerides are also widely used in the manufacture of oil-based binders such as alkyd resins and lirethane oils. For these reasons studies on this special subject is going on even nowadays although it began long time ago. The first comprehensive classical study of esterification of glycerol was carried out by Berthelot [1], who systematically prepared mono-, di-, and triglycerides from practically all fatty acids known at that time. Such esterification was conducted by heating a mixture of glycerol and fatty acids in a sealed tube. Because esterification is an equilibrium reaction, esterification by use of heat alone without special provisions for removal of one of the products of the reaction gives poor results both with respect to the rate and extent of esterification. One practical way of increasing the yield of esterification reaction is to remove the water as it is formed. Various methods have

been applied both in the laboratory and in industry to accomplish the removal of ester water. In esterifing high molecular weight alcohols and acids which dissolve little water, the water formed during the reaction separates in a layer. Therefore the removal of water can be accomplished easily. When glycerol and a high molecular weight acid (e.g., stearic acid, oleic acid) are esterified under reduced pressure the water can be removed by bubbling an inert gas through the mixture. Konen et al. [2] suggested the use of steam, inert gas, or sulfur dioxide to promote agitation and carry off the water formed in the esterification of fatty acids with polyhydroxy alcohols at 230 °C. Desicants such as calcium carbide [3] and activated bauxite [4] have been suggested for removal of water during esterification.

Although removal of the water from reaction medium had positive effect on the reaction equilibrium, actually they could not provide the formation of a determined partial glyceride. Consequently the end product of the reaction is always a mixture of mono-, di-, and triglycerides. This is because of the limited solubility of glycerol in fatty acids [5].

In order to increase the yield of a determined partial glycerides, the use of co-solvents has been proposed by several workers [6, 7, 8, 9]. According to Hilditch and Rigg [10] the yield of monoesters can be increased by the use of solvents in which the glycol and acid are mutually soluble. Hilditch and Rigg [10] used phenol as mutual solvent for esterification, and Eckey and Richardson [11] used dioxane as a mutual solvent for glycerolysis. Mattil and Sims [12] used pyridine as a solvent in the glycerolysis reaction. In the reaction of fat with 50 % by weight of glycerol in 4 parts of pyridine, using sodium

methoxide as a catalyst at steam bath temperature, maximum conversions of monoglyceride of appraximately 65 % were observed.

In a previous study, pyridine was used as a co-solvent in the direct esterification of glycerol with oleic acid [5]. In the present study effect of pyridine on same reaction was investigated in respect of the kinetics and product distribution by using the same set up for water removal. The obtained results were compared with those of the reaction carried out without pyridine.

CHAPTER 2. LITERATURE SURVEY

Esterification can be defined as the condensation of an acid and an alcohol to give an ester and water; the reverse reaction is hydrolysis.

$$RCOOH + R'OH \rightleftharpoons RCOOR' + HOH$$

The esters of organic and inorganic acids are formed by reaction between the ionizable hydrogen of the acid ($RCOO^{-}H^{+}$) and the hydroxyl of the alcohol ($R'-OH$) to form water; experimental evidence indicated that in the esterification reaction the alcohol yields the hydrogen and the acid the hydroxyl to form water.

The velocity constant for the forward reaction (esterification) may be written as

$$v = k\ [RCOOH]\ [R'OH]$$

the rate law for the reverse reaction may be expressed as

$$v' = k'\ [RCOOR']\ [HOH]$$

and at the equilibrium, the following equation holds

$$K = k/k' = [RCOOR']\ [HOH]/[RCOOH]\ [R'OH].$$

As the ratio of the velocity constants k and k' is a constant, it may be represented by K which is called as the equilibrium constant. The magnitude of K indicates which

substance will predominate when equilibrium is reached. If K is large, the product [RCOOR'] [HOH] will be large compared with [RCOOH] [R'OH] and, if K is small the reverse will be true. If K has a medium value, comparable concentrations of all four reactants will coexist. The equilibrium constant, applies only when all the reacting substance coexist in homogeneous solution. If one reactant or reaction product escapes, or is removed from the reaction zone, the equilibrium is readjusted according to Le Chaltalier principal.

Leyes [13] has pointed out that there is no universal manner in which all esterification reaction can be forced to completion, but from the point of view of industrial operation they can be divided into three broad classes, depending upon the volatility of the esters.

Class 1. With esters of high volatility, such as ethyl and methyl formate and methyl acetate, the boiling point of the ester is lower than the corresponding alcohol, and the ester can therefore be readily removed from the reaction mixture.

Class 2. Esters of medium volatility are capable of removing the water formed by distillation, e.g., propyl, butyl, and amyl formates; propyl, butyl, and amyl acetates; and the methyl and ethyl esters of propionic, butyric, and valeric acid. In some cases, ternary mixtures of alcohol, ester, and water are formed. This group can be further subdivided, e.g., with ethyl acetate, all of the ester is removed as a vapor mixture with alcohol and part of the water, while the balance of the water accumulates in the system; with butyl acetate all of the water formed is removed overhead with part of the ester and alcohol, and the balance of the ester accumulates in the system.

Class 3. With esters of low volatility several possibilities exist. In the case of the esters of butyl and amyl alcohols, the water is removed as a binary mixture with the alcohol, e.g., in the production of dibutyl phthalate. In the case of esters of the lower alcohols (methyl, ethyl, and propyl) it may be necessary to add a hydrocarbon such as benzene or toluene to increase the amount of water distilled over. With certain high-boiling alcohols (benzyl, furfuryl, and β-phenyl ethyl) an accessory liquid is always required to eliminate water by distillation.

There are variety of methods that have been employed for direct preparation of esters:
1-Reaction of an alcohol and an acid with elimination of water;
2-Reaction of an alcohol and an acid anhydride to form an ester and an acid;
3-Reaction of an alcohol and an acid chloride with elimination of HCL;
4-Reaction of an alkyl halide and a metal salt of an organic acid with elimination of the metal halide.

Of the direct methods, the only process of technical importance involves direct formation of the ester from alcohol and acid, because it is the simplest, cheapest, and the only practical method for large-scale industrial production of ester. Since in the present study the direct esterification was conducted, indirect methods for ester formation involving alcoholysis, transesterification, and acidolysis will not be considered. Generally, fatty acids can be esterified with low molecular weight monohydric alcohols, with higher monohydric alcohols, and with polyhydric alcohols to produce esters, since this study esterification reaction between oleic acid and glycerol was

investigated, esterification with polyhydric alcohols will be explained, but some information will be given on esterification with monohydric alcohols as well.

2.1. Esters of low molecular weight monohydric alcohols

The esterification of fatty acids with lower molecular weight monohydric alcohols is normally carried out, using a large excess of the alcohol in the presence of an acid catalyst. For preparation of methyl and ethyl esters, fatty acids are commonly refluxed for several hours in the presence of 1 to 3 % of sulfuric acid or dry hydrogen chloride. Using such excesses of methyl alcohol (15 to 35 moles per mole of fatty acid), ester yields of 95 % or higher are obtained. For analytical work it has been suggested that methyl esters can be formed by reaction of soaps with an excess of dimethyl sulfate in the presence of potassium carbonate [14]. This reaction is convenient for quantitative studies. Vacuum distillation is used to separate the methyl esters into fractions of varying boiling points and molecular size. In the esterification of lower alcohols, removal of water is difficult because of the closeness of boiling point of water and the lower alcohols. Azeotropic procedures likewise are not applicable because of the mutual solubility of alcohol-rich water-alcohol mixtures with normal azeotrope solvents. It is necessary to resort to other means to eliminate the water, for example, extraction with a water-insoluble solvent such as benzene or carbon tetrachloride, drying with potassium carbonate, or salting out.

Levesque and Craig [15] have studied the kinetics of the esterification of butanol and oleic acid with a phenol-formaldehyde-sulfonic acid resin. The reaction is

essentially second order after an initial slow period . The velosity constant is directly proportional to the surface area of the catalyst per unit weight of reactants.

2.2. Esters of Higher Monohydric Alcohols

Esterification of higher alcohols from hexyl upward can be carried out conveniently, using stoichiometric quantities of alcohol and fatty acid under azeotropic conditions with benzene, toluene, or xylene as a solvent. Direct esterification of higher fatty alcohols is practical by using a stream of inert gas such as carbon dioxide, nitrogen, or even steam to sweep out the liberated water, or alternatively a partial vacuum may be used to remove water while retaining the acid and alcohol. Higher fatty alcohol esters of saturated acids are waxy solids. Bannister [16] recommends the following procedure for making diethyl phthalate and other high-boiling esters. One equivalent of phthalic anhydride and 2.5 equivalents of ethyl alcohol are refluxed for 2 hours in the presence of 1 % of concentrated sulfuric acid (based on the acid anhydride). To produce the monoester, the excess of alcohol is distilled off at a temperature below 100°C. For the diester, a mixture of 67 % benzene and 37 % alcohol is introduced continuously below the surface of the reaction mixture and the resulting of alcohol-water-benzene ternary is distilled off and condensed. A yield of diester of over 99 % is obtained by passing 3.4 to 7 equivalents of alcohol through the mixture in 4.5 to 7 hours. Esters of stearic, benzoic, citric, caproic, malonic, succinic, cinnamic, tartaric, salicylic, malic, and fumaric acid may be made in this manner [17].

2.3. Esters of polyhydric alcohols

The most common polyhydric alcohol esters are the natural fats, or the glycerol esters of the higher fatty acids, but the esters of a number of other polyhydric alcohols have attained industrial importance and all are of scientific interest. The polyhydric alcohols that have been esterfied with various fatty acids include the diols, triols, tetrols, pentitols, and hexitols. The closely related polyhydric ethers that have been reacted with fatty acids include the polyalkylene glycols, polyglycerols, polymerized pentaerythritols, hydroxyalkyl ethers or polyhydric alcohols, as well as the simpler carbohydrates (mono-, di-, and trisaccharides) [18]. Two classes of polyhydric alcohol esters may be distinguished, namely, (a) those in which all the alcoholic hydroxyl groups have been esterified, and (b) those which are incompletely esterified. The ester formed by partial as well as by complete esterification of polyhydric alcohols are far more important than the monohydric esters.

Like monohydric alcohols, the esterification of polyhydric alcohols is affected by catalysts, temperature, agitation, and removal of water produced during the reaction. However, in the case of monohydric alcohols it is possible to use a large excess of the esterifing alcohol, removing it after the completion of the reaction. With polyhydric alcohols this is impossible. Because with an excess of polyol the fatty acid residues are distributed randomly, leaving some free hydroxyl groups and giving a product containing all possible mono-, di-, tri-, etc., esters together with the fully esterified polyol. In order to carry esterification to completion it is necessary to use only the theoretical amount or a slight excess of the

alcohol, using reaction conditions under which water is efficiently removed. The ways of water removal are:

1. Azeotropic esterification. The theoretical amounts of polyol and fatty acid are heated in the presence of refluxing xylene which carries away the water formed during the reaction. For laboratory preparations a simple trap such as the dean-stark is used for collection of water. Measurement of the water distilled during reaction offers a convenient method for following the course of the reaction. The temperature of azeotropic esterification can be closely regulated by control of solvent quantity [19]. Commercially azeotropic esterification is used, particularly for alkyd resin production. Phthalic anhydride sublimes readily at esterification temperature, and the azeotropic solvent (usually xylene) tends to dissolve and flush the sublimate back to the reaction kettle [20].

2. Esterification using an inert gas sparge. Rate and degree of esterification with polyols is improved by blowing an inert gas, such as carbon dioxide or nitrogen, through the reaction mixture [21]. Water is carried off by the gas stream, but losses of both polyol and fatty acid may occur [20].

3. Vacuum esterification. Esterification under reduced pressure offers the most efficient and practical method for esterification with polyhydric alcohols [22, 23]. A moderately rapid reaction is maintained af a lower temperature than for the other processes with good preservation of color. Glycerol, which is probably the most important polyol used for esterification, is moderately volatile at vacuum esterification temperatures. Partial condensers help minimize glycerol losses.

A combination of vacuum esterification and sparging with CO_2 or even steam gives the most practical reaction from the standpoints of rate, completeness, and product color [20].

Catalysts can be used for speeding up esterification reaction, the choice of the proper catalyst is dependent upon several factors and will vary with the system under consideration. Strong mineral acids are generally used in esterification, particularly hydrochloric and sulfuric acids, although other substances such as salts, silica gel [24], and cation-exchange resins [15] have been employed. In the laboratory, hydrogen chloride is the most widely used catalyst, but for industrial operations sulfuric acid is preferred, principally because of the corrosiveness of the former acid.

Good agitation during large scale esterification is of great importance. Paddle agitators are not normally satisfactory, but propeller or turbine types are needed to draw the heavy, fatty acid immiscible polyol from the bottom of the reaction vessel. This is practicularly important in order to avoid charring with high melting polyols, such as pentaerythritol [25].

The simplest polyhydric alcohols which can be esterified with the higher fatty acids to form polyesters are glycols. The glycols have a considerable variety of uses, e.g., in antifreeze solutions, and hydraulic fluids, as solvents and humectants, and as intermediates in the preparation of other compounds (esters, ethers, acetals, ketals, etc.). The structure of the glycols consists of hydrocarbon chain with two hydroxyl groups attached to two of the carbon atoms, they can be designated by the general

formula $C_n H_{2n} (OH)_2$. The lowest member of the series is ethylene glycol, $HOCH_2CH_2OH$ [26].

The glycols form two series of esters, namely, mono- and diesters, depending upon whether one or both hydroxyl groups are esterified. In the case of the symmetrical glycols, only one monoester can result from esterification and only one diester is possible irrespective of the similarity or dissimilarity of the acidic groups. The simple glycols, as well as polyglycols, may be esterified with fatty acids to produce mono-and diesters. Both classes of glycols may be directly esterified with fatty acids in the same manner as the monohydric alcohols. For complete direct esterification an excess of fatty acid is required, whereas for the preparation of monoesters an excess of glycol is used. The reaction velocity is increased by high temperature, the addition of catalysts, agitation, and removal of moisture.

Ruttan and Roebuck [27] and Howe [28] have described procedures for the preparation of mono-and diesters of ethylene glycol, $HOCH_2CH_2OH$, by direct esterification with palmitic, heptadecanoic (margaric), and stearic acids. The yield of monoesters can be increased by using mutul solvents in which the glycol and acid are soluble.

Kailan and Schachner [29] investigated the velocity of esterification of the acid-catalyzed reaction of ethylene glycol with valeric, caproic, and heptanoic acids and found that with hydrogen chloride as catalyst, the reaction velocity was approximately the same as with butyric acid under the same conditions; also that the retarding effect of water was much less.

Rubin [30] calculated rate constants for the esterification of fatty acid with polyhydric epoxy resins, both self-catalyzed and catalyzed with acids or salts. He found no difference in rate between litharge and lead naphthenate; but β-toluene sulfonic acid was found to be about 30 % faster. Calcium naphthenate was about 50 % slower and its rate only a little faster than that of the self-catalyzed reaction.

Feuge, Kramer, and Bailey [31] compared the effectiveness of a variety of catalysts for the esterification of fatty acids with glycerol. They found zinc or tin chlorides are the most effective and practical catalysts.

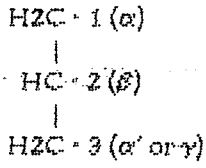
Dunlap and Heckles [32] have investigated the catalyzed esterification of ethylene glycol and oleic acid, they found that the rates of esterification using divalent metal salts are not as great as for strong acids. However, it is probable that the mechanism is similar and that the metal salts act as acids in the general sense.

Continuous methods of esterifiying glycols and other polyhydric alcohols with fatty acids at elevated temperature have been described in a series of patents [33]. The polyhydric alcohol and the fatty acid are reacted in vaporized or mist form through spray nozzles which introduce them into a reaction chamber. The ester, owing to its high boiling point, readily condenses and is collected. The reaction may be carried out in special reactor designed to allow the mixture to pass through at varying speed or temperature.

The esters of glycerol are no doubt the most important derivatives of the polyalcohols. Glycerol, $CH_2OHCHOHCH_2OH$,

contains three hydroxyl groups, the hydrogens of which may be replaced by acyl groups to form fatty acid esters. All of the natural fats consist of mixtures of the esters of glycerol; many synthetic resins are polymerized esters of glycerol; and various other synthetic glycerides, e.g., mono-and diglycerides, find a wide employment in the manufacture of numerous food and industrial products. All but a small proportion of the known organic acids can be esterified or otherwise reacted with glycerol to form esters; hence the theoretically possible number of such products is extremely large. This number is increased because the formation of position isomers is possible, and because homogenous and heterogeneous acyl substitution is possible in the case of the di-and triglycerides.

The polyhydric nature of glycerol necessitates that the positions of the hydroxyl groups be designated in order that the point of attachment of an acyl or other substituent may be specifically indicated. The glyceryl radical is preferably represented by the skeleton:



It is obvious that if acyl groups are attached at different positions of the glyceryl skeleton several isomeric structures will result. If the acyl groups are of the same species two mono-and two diglyceride, but only one tri-glyceride is possible. If only one species of acyl group is present the product may be designated as a homoglyceride; if two or three species are present the product may be designated as a heteroglyceride [34].

The preparation of pure esters of known structure is far more difficult than the simplicity of these compounds would indicate. The earliest method, and the one still most widely used, involves the direct esterification of glycerol with an acid in the presence of an appropriate catalyst. The method, however, is limited to the preparation of homotriglycerides and to mixtures of isomeric mono-and diglycerides. The inability to prepare pure monoglycerides by direct esterification is due to the fact that 2-acyl groups tend to migrate to the 1-position [35].

In 1844, approximately twenty years after Chevreul (1815) established the constitution of natural fats, Pelouze and G'elis [36] synthesized tri-butyrin by direct esterification of glycerol and butyric acid in the presence of sulfuric acid as a catalyst. Ten years later Berthelot [1] began his systematic synthesis of the glycerides in the course of which he prepared the mono-, di-, and triglycerides of practically all of the then available fatty acids.

Complete esterification. Usually refers to reaction conditions in which a specific fatty acid was present in the reaction mixture in the theoretical amount or slight excess. Investigations of esterification of glycerol with mixtures of fatty acids have been less numerous than those employing a specific acid. The esterification of glycerol with mixtures of fatty acids is the reverse of the saponification of fats and should proceed to the same equilibrium under the same conditions (time, temperature, catalyst, etc.).

Bhattacharga and Hilditch [37] prepared various triglycerides by heating a mixture of fatty acids

(about 110 g) with 80 to 90 % of the theoretical quantity of glycerol and 0.5 % of naphthalene-β-sulfonic acid at a temperature of 135°-145°C. For 5 to 6 hours under a vacuum of 1 mm Hg. Esterification under these conditions was presumed to be essentially complete and no mono-or diglycerides was present in the final product.

Tasuchiyo and Akiyama [38] esterified an equimolar mixture of stearic and oleic acids with the theoretical amount of glycerol to provide for complete esterification. The product should be a mixture of six triglycerides, namely, tristearin, triolein, two distearomonooleins, and two dioleomonostearins. Analysis of the product indicated that it contained 20% tristearin.

Incomplete Esterification. When glycerol is reacted with a fatty acid in an amount sufficient to esterify only one hydroxyl group, the product does not consist exclusively of a monoacylglyceride, but rather a mixture of mono-, di- and triglycerides, the relative proportions of which depend upon the conditions of esterification.

Bellucci [22] noted that when one mole of glycerol was reacted with one mole of palmitic, stearic, or oleic acid at 215°-220°C under a pressure of 30-40 mm. of mercury, the bulk of the fatty acids disappeared in about two hours, but an excess of glycerol remained. He observed that monoglycerides formed initially, but after the first 1/2 hour diglycerides predominated. When the reaction was continued after all of the fatty acids had reacted, the amount of monoglycerides increased and the unreacted glycerol was consumed. These observations indicate that diglycerides are an intermediate product in the formation of monoglycerides.

Hilditch and Rigg [10] found that at 160°-180°C and in the presence of naphthalene-β-sulfonic acid as catalyst. 50-70 % of the fatty acids was esterified in about 4 hours. Depending on the ratio of glycerol (1 to 10 moles) to fatty acid (1 mole) the primary product was diglyceride and only 32-46 % of the total esters formed consisted of monoglycerides. This predominance of diglycerides was explained by Hilditch and Rigg on the basis of the comparative immiscibility of glycerol and the higher fatty acids or their glycerol esters; consequently the monoglycerides which are first formed pass mainly into the fatty acid phase where they undergo reaction to form di-and even triglycerides.

It was observed that, in general, the greater the ratio of glycerol to fatty acid, the higher the yield of monoglyceride. An increase in the concentration of catalyst, temperature, or duration of the reaction increased the total amount of glycerides produced but reduced the proportion of monoglyceride. Similar behavior was observed when ethylene glycol replaced glycerol in the esterification reaction [39].

Biswas [40] investigated the esterification of pure stearic, palmitic, myristic, oleic, lauric, and linoleic acids with glycerol at 180°C by using K_2CO_3 (0.1 % on wt-of acid) as a catalyst. Samples taken in 40, 60, 120, 180, and 225 minutes were analyzed for 1- and 2-monoglyceride and the results tabulated. Significant amount of 2-glyceride were found in most cases.

In 1962 Choudhury [41] studied the direct esterification of various saturated and unsaturated fatty acids by using an excess concentration of glycerol (for maximum monoglyceride production) at 180°C reaction

temperature and in presence and absence of alkaline catalyst. The results showed that the maximum monoglyceride formed was in the range of 55-60 % of the fatty product at equilibrium stage of the reaction. The alkaline catalyst substantially increase the initial rate of reaction without appreciably lowering the time required for reaching the equilibrium concentration of monoglyceride in the resulting reaction mixture. The catalyst helps in depressing diglyceride formation.

Bailey [42] studied the inhibition of esterification by addition of pyridine. Under the experimental conditions employed an esterification of 3.1 % in 6 hours, in the absence of any negative catalyst, was reduced to about 1.7 % by addition of about 70 parts of C_5H_5N per million; but further addition (up to 800 parts per million) only reduced esterification to 1.37 %. When the effective surface was increased by the insertion of glass tubes, the total surface area of which was approximate the same as that of the vessel, esterification, in the absence of C_5H_5N, reached 4.7 %; by the addition of about 300 parts of C_5H_5N per million, the esterification was again reduced to 1.7, the addition of further C_5H_5N having comparatively little effect.

The kinetics of the direct esterification of glycerol have been studied by several workers. Feuge et al. [31] studied the esterification of glycerol and peanut-oil fat acids under reduced pressure with and without the assistance of various metal chlorides and oxides as catalysts. They found the uncatalyzed reaction is bimolecular in character but proceed in two successive stages of which the later has the lower velocity constant. Velocity constants have been determined for the initial and final stages of the reaction at intervals between 166°

and 241°C. The calculated heat of activation for the initial and final stages of the reaction are respectively, 12.3 and 10.8 kcal. per mole. The concentration of free fatty acid corresponding to the termination of the first stage decreases progressively as the temperature of the reaction is increased.

Hartman [43] investigated the esterification rate of eight commonly fatty acids at 180°C using equivalent and equimolar amounts of glycerol, with and without co-solvent. The esterification with equivalent amounts of glycerol without co-solvent followed second order kinetics and proceeded at a similar rate for all acids examined. Esterifications with equimolar amounts of glycerol were kinetically complex and their speed depended on the solubility of glycerol in individual fatty acids. Esterification with glycerol in a co-solvent (Dowtherm A) also proceeded at a similar velocity for all of the acids. The reaction slowed down appreciably or stopped after 48 hours, which may have resulted from the influence of water produced in the reaction. The velocity constants for the esterification of the individual acids with equivalent amounts of glycerol were calculated as shown in Table 2.1, assuming that the reaction was bimolecular and followed second order kinetics. In agreement with the results of Feuge et al [31] it was found that the velocity constants were greater at the initial stage of the reaction than towards its end.

TABLE: 2.1. Velocity Constants of Reaction between Equivalent Proportions of Fatty Acid and Glycerol at 180°C [43].

	Velocity constants* after reaction for:	
Acid	1 hour	5 hours
Caprylic	0.176	0.120
Capric	0.190	0.131
Lauric	0.191	0.130
Myristic	0.180	0.129
Palmitic	0.178	0.143
Stearic	0.171	0.120
Oleic	0.178	0.121
Linoleic	0.181	0.120

* Expressed as g. mole $^{-1}$ hours^{-1}

Makman [44] studied the kinetics of esterification of soap stock fatty acids with glycerol, pentaerythritol, and glycol by following the acid number of the reaction mixture. The reaction is much faster in the case of pentaerythritol and glycol were first order kinetics is obeyed, than for glycerol, where second order is found. The different behavior in the case of glycerol is explained by the difference in the reactivity of the primary and secondary hydroxyl groups.

The kinetic of esterification of glycerol with lauric acid and phthalic anhydride (as monoglyceryl H phthalate) were investigated by Tanizaki et al. [45], the reactions were third order at 170°C and 230°C. The esterification of phthalic anhydride was slower and shower higher temperature dependence (activation energy) than that of lauric acid.

Gioielli et al. [46] investigated the kinetics of esterification reaction of glycerol with palmitic acid, the esterification in the absence of catalysts proceed in two stages, first stage being the faster one. The start of the second stage coincided with an inflection in the triglyceride accumulation curve.

Gioielli et al. [47] studied fatty acids distribution with respect to glycerol during esterification. For non catalytic esterification of glycerol with mixed fatty acids (C_{14-18}), the distribution of acid residues between primary and secondary hydroxyl groups in the triglycerides formed was random.

The kinetic of zinc chloride-catalyzed esterification of glycerol with palmitic acid was investigated by Schuch et al. [48]. The esterification of glycerol with palmitic acid at 160°C or 185°C catalyzed by $ZnCl_2$ was found a second order reaction. The reaction rate was measured by determine of unreacted acid.

Trofimov et al. [49] investigated the kinetics of esterification of oleic acid with β- sitosterol (The main component of the alcohol fraction of neutral compounds in sulfate soap) at 200-250°C, reaction was a second order at molar ratio of the reactions 1:1 and a first order reaction at significant excess of oleic acid. The activation energy of the reaction was 76.2 kJ/ mol and the preexponential factor was 1.2×10^{-7}.

CHAPTER 3. THEORETICAL ASPECT OF THE STUDY

The miscibility of glycerol with fatty acids and glycerides is of theoretical and practical importance for the formation of monoglycerides. Feuge et al. [31] established the maximum amount of glycerol reactable and miscible with hydrogenated cotton seed oil, but according to Hartman [50], the actual miscibility cannot be readily assessed from their data. In 1958 Choudhury [51] reported that in the presence of 0.1 % sodium hydroxide the solubility of glycerol in a number of fats amounted to 18-24 % weight-percent of glycerol on the fat basis between 175-200°C.

Hartman's observations in his laboratory were incompatible with Choudhury's results and led to a re-examination of the data of the later author. Determinations were made of the solubility of glycerol in fats and fatty acids at 180 and 200°C. No appreciable glycerolysis or esterification occurred under the conditions used. The influence of 0.1 % sodium hydroxide on the miscibility was found to be insignificant and was therefore omitted. Some typical results are contained in Table 3.1 with Choudhury's results in parenthesis. According to Hartman the marked difference in the results, despite otherwise similar procedure, may be due to the use of high speed stirring (1000 r.p.m.) by Choudhury which produced emulsification.

TABLE 3.1. Miscibility of glycerol with fatty acids and glycrides [50].

Material	Weight-percent of dissolved glycerol on fat basis 180°C	200°C
Peanut oil, refined	0.9 (18.0 at 175°) a	1.2 (22.3) a
Coconutoil, refined	1.3 (19.8 at 175°) a	1.6 (23.8) a
Tristearin	0.9	1.2
Trilaurin	1.2	1.6
Tricaprylin	3.6	6.0
Stearic acid	5.1	7.0
Oleic acid	5.8	7.9
Palmitic acid	7.6	9.6
Myristic acid	11.7	16.5
Lauric acid	23.0	31.4
Caprylic acid	completely miscible	—
1- Monostearin	32.7	—
2- Monolaurin	completely miscible	—

[a] R.B.R Choudhury, ref. [51].

On the absolute percentage basis the molecular weight apparently has little influence on the miscibility of glycerol with triglycerides containing acids with more than 10 carbon atoms. The effect of molecular weight is more pronounced in the case of fatty acids and still greater with monoglycerides. Hartman [50] stated that the figures in Table 3.1 explain some results obtained by Choudhury [51, 41] on the preparation of monoglycerides better than his own miscibility figures.

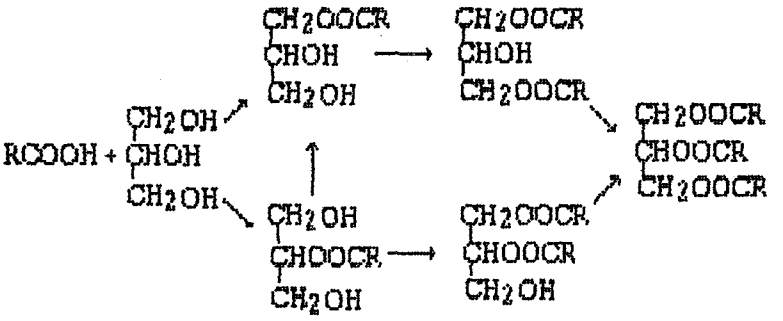
The formation of homotriglycerides by esterification of glycerol with fatty acids may be represented in its simplest form by the following equation:

$$\begin{array}{l} H_2COH \\ | \\ HCOH \\ | \\ H_2COH \end{array} + 3\,HOOCR \rightarrow \begin{array}{l} H_2COOCR \\ | \\ HCOOCR \\ | \\ H_2COOCR \end{array} + 3\,H_2O$$

Direct esterification is often the easiest and most desirable method for preparation of a homotriglyceride. However, the reaction cannot be made sufficiently specific to produce any desired mono- or diglyceride with respect either to configuration or to homogeneity, and it is not possible to produce, by direct esterification, specifically oriented triglycerides with two or three different fatty acids in the molecule, because the limiting factor determing the product composition is the comparative insolubility of glycerol in the reaction mixture [52].

Actually the reaction proceeds in stages beginning with the formation of monoglycerides which are further esterified to form diglycerides, and these in turn are esterified to form triglycerides. The esterification reaction is however, further complicated by the fact that acyl radicals tend to migrate from one position to another within the glycerol molecule. It is a well-established fact that 2-monoacylglycerides tend to rearrange to 1-monoacylglycerides and that this reaction is accelerated by heat and the presence of small quantities of acids and alkalies [53].

Martin [54] demonstrated that equilibrium between the two-monoglycerides is established at 90-92 % of 1-monoglycerides. The tendency of the 2-acylglycerides to rearrange to 1-acylglycerides is in line with the observed differences in the heat of combustion and specific heats of these two isomeric glycerides [55]. In the light of the above mentioned facts, the mechanism of the esterification reaction can, therefore, be more accurately represented by the following scheme:



In order to increase the amount of any desired partial glycerides, the reaction, as mentioned before, is carried out with a co-solvent. It is well known that pyridine and glycerol are miscible with each other, pyridine is a good solvent for the fatty acids, and esterification water is miscible with pyridine in every ratio and forms an azeotropic mixture, which has a boiling point of 94°C [5]. Taking these facts into consideration, the study of esterification reaction between glycerol and oleic acid in the presence of pyridine seemed to be worthwhile of being investigated.

CHAPTER 4. EXPERIMENTAL

4.1. MATERIALS

Merck grade oleic acid was used which had an acid value of 193-198.61. Other chemical reagents which were used such as glycerol, pyridine, and sodium hydroxide were analytical grade.

4.2. PROCEDURES

4.2.1. Esterification of oleic acid with glycerol in the presence of pyridine as co-solvent

The direct esterification reactions were run at temperatures of 180°, 200°, and 220°C. For the esterification reactions in the presence of pyridine, simultaneous removal of water from the reaction medium was necessary. For this purpose a special set of apparatus that was developed previously was used [5].

Schematic of the set up is shown in figure 4.1. As can be seen, the reaction was carried out in a four-necked flask equipped with a stirrer turning at 200-220 r.p.m., a thermometer, and a special water trap.

Water contaminated pyridine droplets coming from the condenser was contacted with solid NaOH placed at the bottom of a perforated tube, which has an angle of 45° with the horizontal. Thus, a concentrated NaOH solution is formed around the sodium hydroxide pellets. When the NaOH

solution reachs a certain concentration, it drains from the bottom holes of the tube, while the pyridine continuously returns into the reaction medium. According to this mechanism an efficient water removal is accomplished.

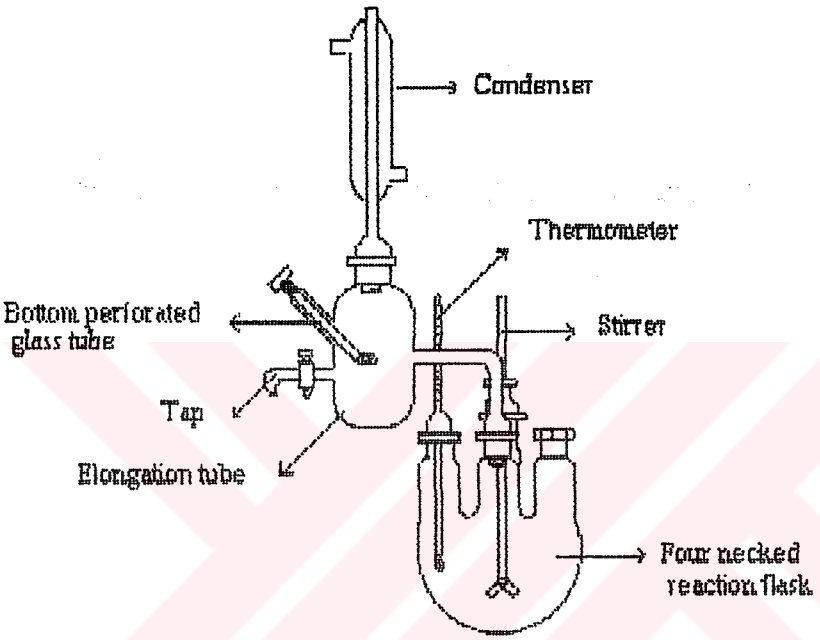


Fig. 4.1. Sketch of experimental set up for the esterification in the presence of pyridine

Esterification reactions were conducted in concentrated solution using about approximately equivalent proportions of the reactants. The oleic acid and pyridine were placed in the flask and heated to the reaction temperature. Pyridine is added in such amount that the reaction temperature was satisfied. In a separate flask glycerol was heated to reaction temperature and added immediately to the four-necked flask. In this way the reaction which might be occurred before reaching the reaction temperature is avoided.

Samples were withdrawn using a pipette at predetermined time intervals and cooled immediately by

immersing into cold water. Pyridine was removed from each sample at 20 mm Hg and 90°C by using a rotary evaporator. It was confirmed that under these conditions glycerol was not removed. Fatty acid contents of the pyridine free samples were determined [56]. Oleic acid concentrations were expressed as weight percentage as determined from the acid value and equivalent weight of the acid. A correction for loss of water was applied to each sample.

In order to investigate the effect of pyridine on product distribution at 180°C, the monoglyceride content [57] and hydroxyl value were determined [58]. From the monoglyceride content and the hydroxyl value, the composition of each sample was calculated.

4.2.2. Esterification of oleic acid and glycerol in the absence of pyridine

The esterification was also conducted without using pyridine at 180°C, 200°C and 220°C by using a different experimental setup figure 4.2. In this case water was removed from the reaction medium by the aid of an inert gas, nitrogen. The esterification takes place in a four-necked flask equipped with a stirrer turning at 200 r.p.m., a thermometer, an inert gas inlet tube and an air condenser. Nitrogen gas was allowed to enter the reaction flask at a rate of 12 litre per hour, to carry away water formed in the reaction. Samples were withdrawn at predetermined time intervals and cooled immediately by immersing into cold water. Acid values of the samples were determined [56]. Oleic acid concentration was expressed in weight percentage based on the sample corrected for loss of water. Hydroxyl values and monoglyceride contents were determined in order to estimate product distribution at 180°C [58, 57].

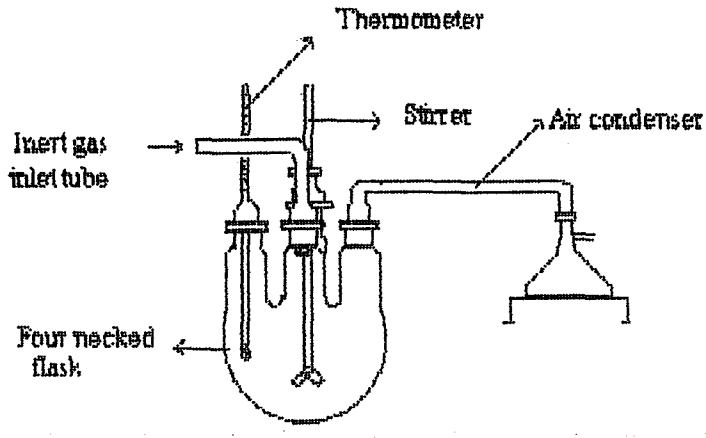


Fig. 4.2. Sketch of experimental set up for the esterification without co-solvent

CHAPTER 5. RESULTS AND DISCUSSION

In this part the kinetics results of the esterification reaction between oleic acid and glycerol is presented. The obtained experimental data is used to determine the reaction order for temperatures of 180°, 200°, and 220°C. for cases of with and without co-solvent.

In order to bring the reactants to reaction temperature, the reactants are heated in a separate flasks to avoid differences in reaction initiation times. However, during the mixing process of the reactants there may still be some little differences in the process of getting component to desired temperature.

In this study the kinetic data of the esterification reaction evaluated by the integral method of analysis in two ways; first way utilizes the acid value of the reactant mixture as the initial concentration and the acid percentage is measured with respect to time. The acid percentage as function of time is corrected for loss of water. The second way takes the first sample as the initial concentration. Similarly acid percentages are corrected for losses of water. During the course of this study various runs are done using both approaches and it was realized that both of these methods are compatible.

5.1 Esterification reactions using pyridine as co-solvent

In all experiments approximately equivalent amount of reactants are used. For the case of esterification of oleic acid and glycerol with pyridine at 180°C, 91.69 grams of oleic acid, 10.95 grams glycerol, and the amount of pyridine was 22.57-28.28 % based on fatty acid-glycerol mixture. The results of the co-solvent run at 180°C. are compiled in Table 5.1. Examining the experimental results it is observed that reaction time is taken as 163 minutes and the corrected acid percentage is 33.56 which is satisfactory level conversion for the kinetic analysis of this reaction.

For the other experiments at higher reaction temperatures higher conversions are expected. However, for the higher conversion cases the steric hindrance and the side reactions may affect the results, therefore deviations from the normal kinetic behavior may be observed.

TABLE 5.1. Esterification of Oleic acid and Glycerol in the presence of Pyridine at 180°C.

Sample number	Initial concentration according to:							
	Weighted amounts				First sample taken from reaction medium			
	Time (min)	Acid value	Acid %	Corrected acid %	Time (min)	Acid value	Acid %	Corrected acid %
—	0	173.91	89.35	89.35	—	—	—	—
1	1	162.81	83.65	83.34	0	162.81	83.65	83.65
2	5	156.22	80.27	79.79	4	156.22	80.27	80.09
3	10	149.44	76.78	76.15	9	149.44	76.78	76.44
4	15	147.25	75.66	74.98	14	147.25	75.66	75.26
5	20	140.11	71.99	71.17	19	140.11	71.99	71.44
6	30	129.94	66.76	65.78	29	129.94	66.76	66.03
7	41	121.95	62.66	61.57	40	121.95	62.66	61.80
8	56	106.45	54.69	53.47	55	106.45	54.69	53.67
9	71	101.82	52.32	51.06	70	101.82	52.32	51.26
10	87	94.79	48.70	47.43	86	94.79	48.70	47.61
11	108	85.82	44.09	42.81	107	85.82	44.09	42.97
12	129	78.87	40.52	39.26	128	78.87	40.52	39.40
13	147	70.77	36.36	35.13	146	70.77	36.36	35.26
14	163	67.67	34.77	33.56	162	67.67	34.77	33.68

Esterification reaction carried out at 200°C with pyridine was accomplished using 93.12 grams oleic acid, 9.43 grams glycerol, and the amount of pyridine was 9.01-12.85 % based on fatty acid-glycerol mixture. The results of this experiment are shown in Table 5.2. This reaction started with acid percentage of 90.81 and reduced to a corrected value of 27.75 after 151.02 minutes.

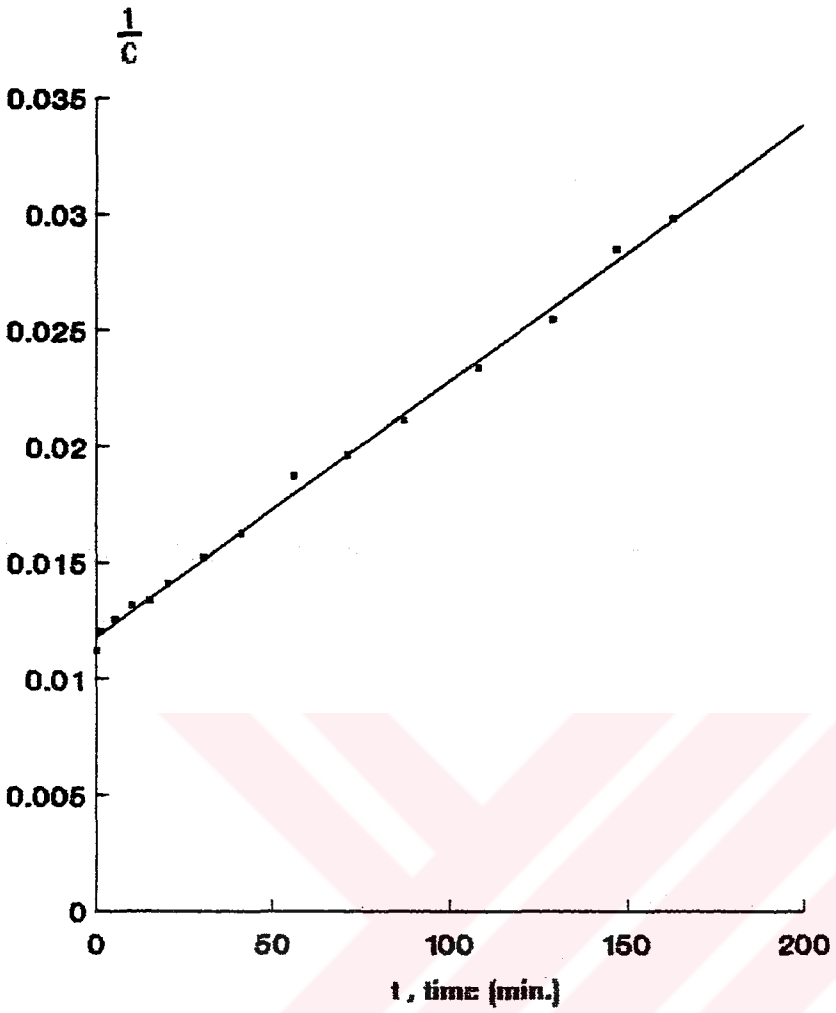


FIGURE 5.1. Rate of esterification of oleic acid and glycerol in the presence of pyridine at 180°C. Standard error of estimate = 3.6701×10^{-4}, coefficient of determination = 0.9967, and coefficient of regression = 0.9983.

TABLE 5.2. Esterification of Oleic acid and Glycerol in the presence of Pyridine at 200°C.

Sample number	Initial concentration according to:							
	Weighted amounts				First sample taken from reaction medium			
	Time (min)	Acid value	Acid %	Corrected acid %	Time (min)	Acid value	Acid %	Corrected acid %
0	0.00	177.07	90.81	90.81	—	—	—	—
1	1.18	169.81	87.08	86.87	0.00	169.81	87.08	87.08
2	6.18	151.75	77.82	77.16	5.00	151.75	77.82	77.35
3	11.10	139.53	71.55	70.65	9.92	139.53	71.55	70.89
4	16.10	131.08	67.22	66.19	14.92	131.08	67.22	66.35
5	21.18	123.79	63.48	62.35	20.00	123.79	63.48	62.51
6	31.10	111.87	57.37	56.12	29.92	111.87	57.37	56.26
7	41.35	100.52	51.55	50.24	40.17	100.52	51.55	50.36
8	51.10	93.21	47.80	46.47	49.92	93.21	47.80	46.59
9	61.02	86.29	44.25	42.93	59.83	86.29	44.25	43.03
10	76.18	79.25	40.64	39.33	75.00	79.25	40.64	39.43
11	91.35	72.55	37.21	35.93	90.17	72.55	37.21	35.02
12	111.02	65.92	33.81	32.57	109.83	65.92	33.81	32.65
13	131.27	60.87	31.22	30.03	130.08	60.87	31.22	30.10
14	151.02	56.33	28.89	27.75	149.83	56.33	28.89	27.82

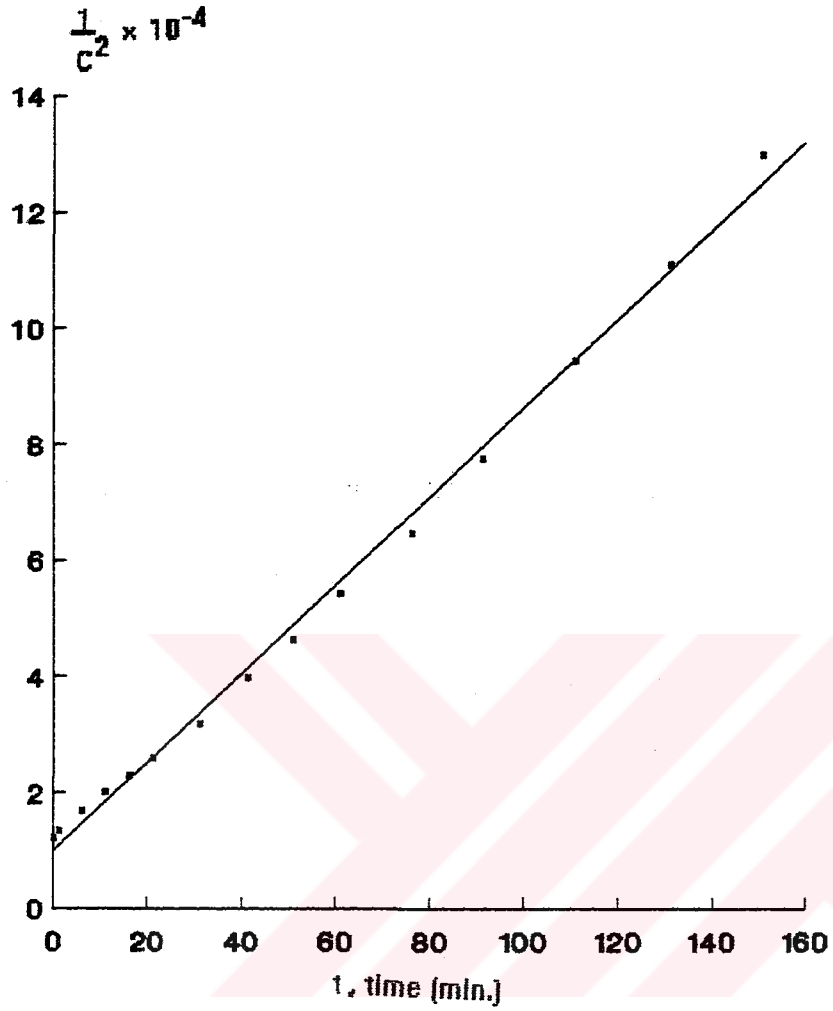


FIGURE 5.2. Rate of esterification of oleic acid and glycerol in the presence of pyridine at 200°C. Standard error of estimate = 2.4264×10^{-5}, coefficient of determination = 0.9972, and coefficient of regression = 0.9986.

The result of esterification reaction at 220°C using 108.2 grams oleic acid, 11.66 grams glycerol, and requried amount of pyridine (6.13-11.44 %) based on fatty acid-glycerol mixture shows higher conversion as shown in Table 5.3, the reaction starts with acid percentage of 90.28 and reduces to a corrected acid value of 15.73 after 153.17 minutes.

TABLE 5.3. Esterification of Oleic acid and Glycerol in the presence of Pyridine at 220°C.

Sample number	Initial concentration according to:							
	Weighted amounts				First sample taken from reaction medium			
	Time (min.)	Acid value	Acid %	Corrected acid %	Time (min.)	Acid value	Acid %	Corrected acid %
—	0.00	176.04	90.28	90.28	—	—	—	—
1	1.00	158.41	81.24	80.75	0.00	158.41	81.24	81.24
2	6.67	129.21	66.26	65.22	5.67	129.21	66.26	65.61
3	12.00	110.44	56.64	55.40	11.00	110.44	56.64	55.73
4	17.00	98.38	50.45	49.15	16.00	98.38	50.45	49.45
5	22.08	88.24	45.25	43.94	21.08	88.24	45.25	44.20
6	32.17	75.36	38.65	37.35	31.17	75.36	38.65	37.59
7	42.17	65.97	33.83	32.61	41.17	65.97	33.83	32.81
8	52.17	58.45	29.97	28.82	51.17	58.45	29.97	28.99
9	62.25	53.34	27.35	26.26	61.25	53.34	27.35	26.42
10	77.25	47.26	24.24	23.22	76.25	47.26	24.24	23.36
11	92.00	43.64	22.38	21.42	91.00	43.64	22.38	21.54
12	112.17	38.90	19.95	19.06	111.17	38.90	19.95	19.17
13	133.33	35.17	18.04	17.21	132.33	35.17	18.04	17.31
14	153.17	32.18	16.50	15.73	152.17	32.18	16.50	15.83

5.2 Esterification reaction without co-solvent

The main purpose of this part of study is to see the effect of pyridine as co-solvent on the reaction of oleic acid and glycerol. For this reason its thought necessary

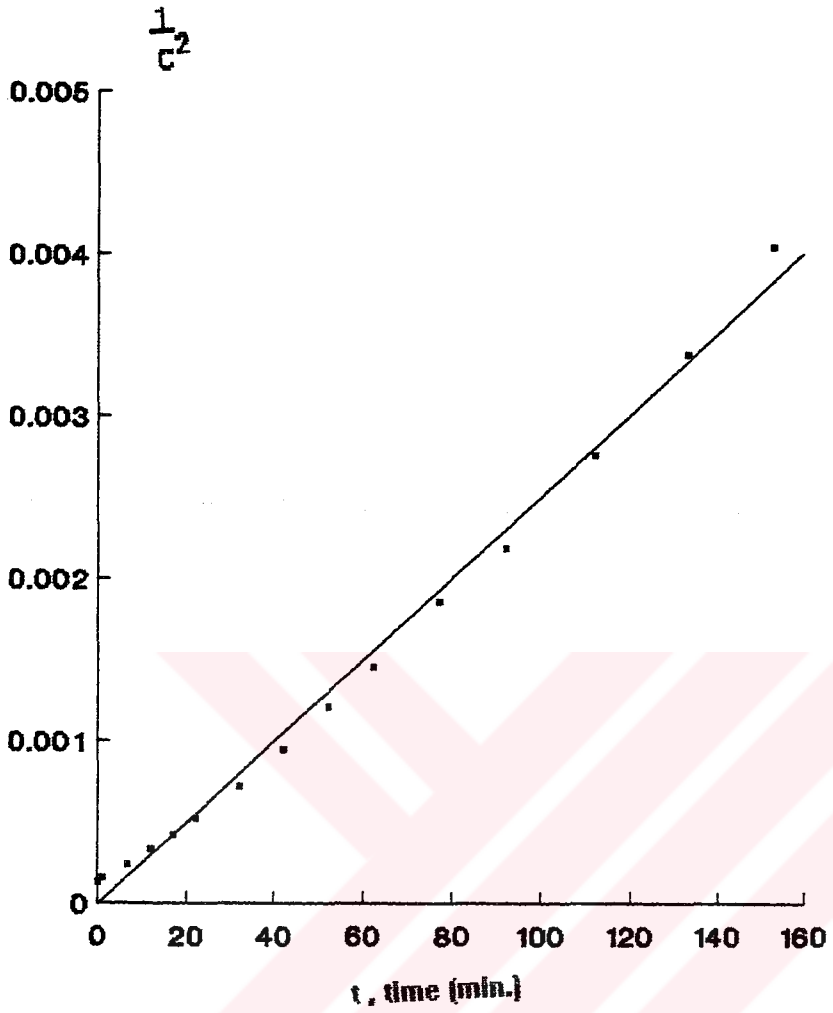


FIGURE 5.3. Rate of esterification of oleic acid and glycerol in the presence of pyridine at 220°C. Standard error of estimate = 1.0716×10^{-4}, coefficient of determination = 0.9931.and coefficient of regression = 0.9966.

to run reactions with oleic acid and glycerol in the absence of pyridine to have a base for comparison of the effect of pyridine on the esterification reaction. All the experimental runs with pyridine which are represented in section 5.1 are repeated for the case of esterification without co-solvent.

Esterification reaction at 180°C is carried out using 113.56 grams oleic acid and 11.66 grams glycerol. As seen from Table 5.4, at the start of the reaction corrected acid percentage was 90.69 which reduced to 37.55 after 155.83 minutes.

TABLE 5.4. Esterification of Oleic acid and Glycerol at 180°C.

Sample number	Initial concentration according to:							
	Weighted amounts				First sample taken from reaction medium			
	Time (min.)	Acid value	Acid %	Corrected acid %	Time (min.)	Acid value	Acid %	Corrected acid %
—	0.00	175.04	90.69	90.69	—	—	—	—
1	4.75	170.67	88.43	88.30	0.00	170.67	88.43	88.43
2	10.08	160.17	82.99	82.57	5.33	160.17	82.99	82.70
3	15.83	151.04	78.26	77.63	11.08	151.04	78.26	77.74
4	21.08	142.02	73.59	72.77	16.33	142.02	73.59	72.88
5	25.83	137.71	71.35	70.46	21.08	137.71	71.35	70.56
6	35.83	127.07	65.84	64.78	31.08	127.07	65.84	64.88
7	46.17	118.62	61.46	60.31	41.42	118.62	61.46	60.40
8	56.25	111.01	57.52	56.30	51.50	111.01	57.52	56.38
9	67.50	103.68	53.72	52.45	62.75	103.68	53.72	52.53
10	81.42	97.01	50.26	48.97	76.67	97.01	50.26	49.04
11	96.58	90.41	46.85	45.54	91.83	90.41	46.85	45.60
12	115.67	84.26	43.66	42.35	110.92	84.26	43.66	42.41
13	136.33	79.06	40.96	39.67	131.58	79.06	40.96	39.73
14	155.83	74.93	38.82	37.55	151.08	74.93	38.82	37.60

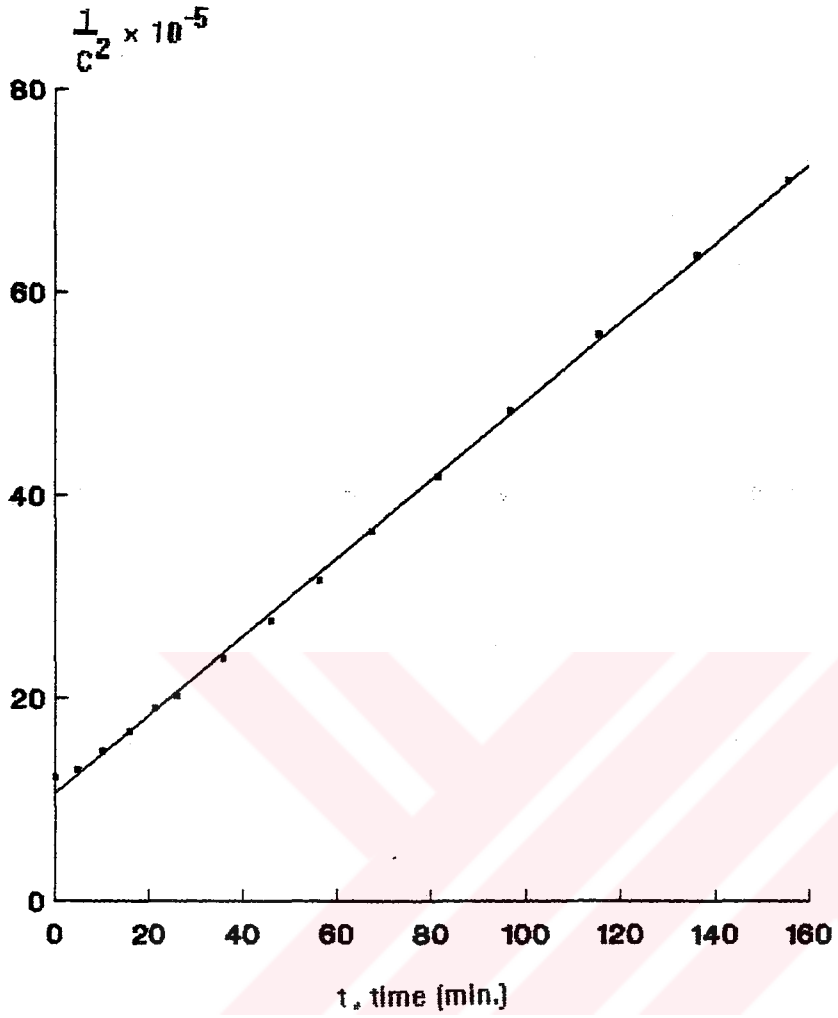


FIGURE 5.4. Rate of esterification of oleic acid and glycerol at 180°C.
Standard error of estimate = 6.4096×10^{-6},
coefficient of determination = 0.9990, and
coefficient of regression = 0.9995.

Esterification reaction at 200°C carried out with 113.56 grams of oleic acid and 11.66 grams of glycerol is shown in Table 5.5. These results show at the initial time of the reaction corrected acid percentage of 90.69, and after 158 minutes reduced to 21.76.

TABLE 5.5. Esterification of Oleic acid and Glycerol at 200°C.

Sample number	Initial concentration according to:							
	Weighted amounts				First sample taken from reaction medium			
	Time (min.)	Acid value	Acid %	Corrected acid %	Time (min.)	Acid value	Acid %	Corrected acid %
—	0.00	175.04	90.69	90.69	———	———	———	———
1	5.00	153.23	79.39	78.81	0.00	153.23	79.39	79.39
2	10.00	136.77	70.87	69.96	5.00	136.77	70.87	70.47
3	15.08	124.10	64.30	63.21	10.08	124.10	64.30	63.68
4	20.08	113.66	58.89	57.69	15.08	113.66	58.89	58.12
5	25.50	104.79	54.30	53.03	20.50	104.79	54.30	53.42
6	35.42	91.22	47.26	45.96	30.42	91.22	47.26	46.30
7	45.08	82.81	42.91	41.60	40.08	82.81	42.91	41.91
8	55.42	74.77	38.74	37.46	50.42	74.77	38.74	37.74
9	65.33	69.06	35.78	34.54	60.33	69.06	35.78	34.79
10	80.67	62.33	32.30	31.10	75.67	62.33	32.30	31.33
11	96.17	56.49	29.27	28.15	91.17	56.49	29.27	28.34
12	118.17	50.54	26.19	25.12	113.17	50.54	26.19	25.32
13	138.67	46.80	24.25	23.25	133.67	46.80	24.25	23.42
14	158.00	43.86	22.73	21.76	153.00	43.86	22.73	21.93

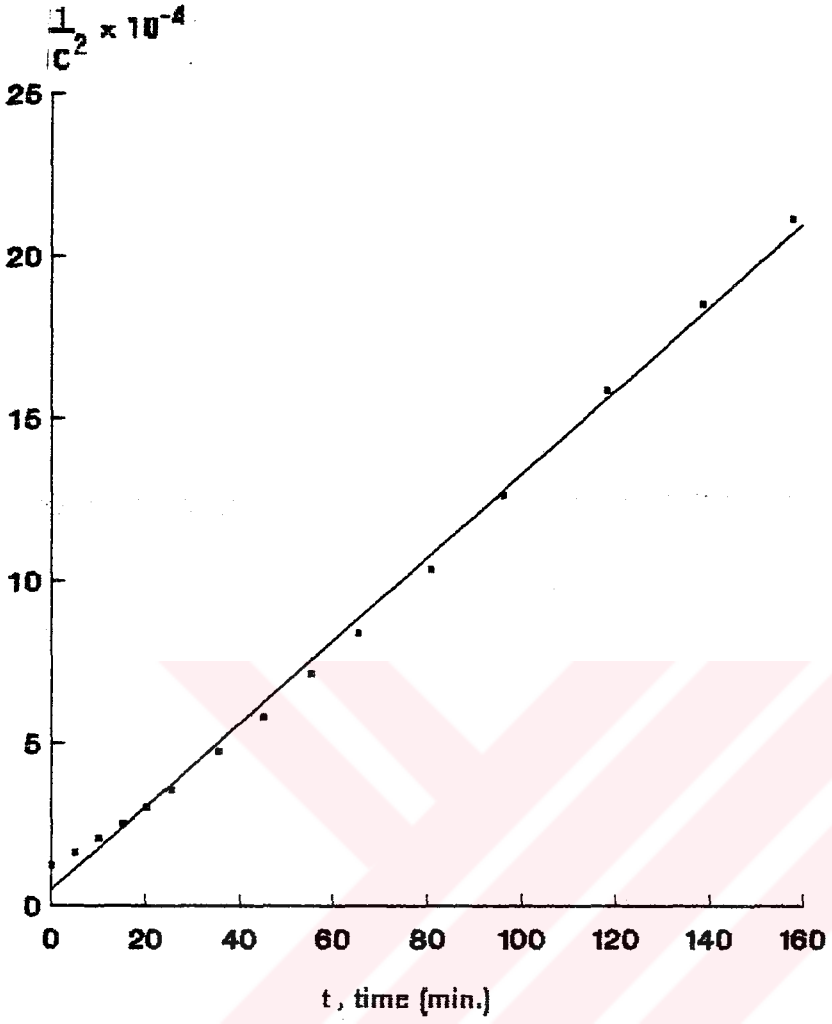


FIGURE 5.5. Rate of esterification of oleic acid and glycerol at 200°C.
Standard error of estimate = 4.0850×10^{-5}.
coefficient of determination = 0.9963.and
coefficient of regression = 0.9981.

Esterification reaction carried out at 220°C was performed using 113.56 grams oleic acid and 11.66 grams glycerol is shown in Table 5.6, the corrected initial acid percentage of 90.69 reduced to 15.58 after 155.75 minutes.

TABLE 5.6. Esterification of Oleic acid and Glycerol at 220°C.

Sample number	Initial concentration according to:							
	Weighted amounts				First sample taken from reaction medium			
	Time (min.)	Acid value	Acid %	Corrected acid %	Time (min.)	Acid value	Acid %	Corrected acid %
—	0.00	175.04	90.69	90.69	———	———	———	———
1	6.00	132.13	68.46	67.48	0.00	132.13	68.46	68.49
2	11.08	112.91	58.50	57.29	5.08	112.91	58.50	58.13
3	17.42	95.69	49.58	48.28	11.42	95.69	49.58	48.98
4	23.08	84.84	43.96	42.65	17.08	84.84	43.96	43.27
5	28.25	77.52	40.17	38.88	22.25	77.52	40.17	39.44
6	33.42	70.70	36.63	35.38	27.42	70.70	36.63	35.89
7	42.75	62.38	32.32	31.13	36.75	62.38	32.32	31.58
8	53.08	55.51	28.76	27.74	47.08	55.51	28.76	28.14
9	63.08	50.29	26.06	25.00	57.08	50.29	26.06	25.36
10	77.58	44.61	23.11	22.13	71.58	44.61	23.11	22.46
11	92.75	40.28	20.87	19.96	86.75	40.28	20.87	20.25
12	115.58	36.64	18.98	18.13	109.58	36.64	18.98	18.40
13	136.17	33.86	17.54	16.74	130.17	33.86	17.54	16.99
14	155.75	31.54	16.34	15.58	149.75	31.54	16.34	15.81

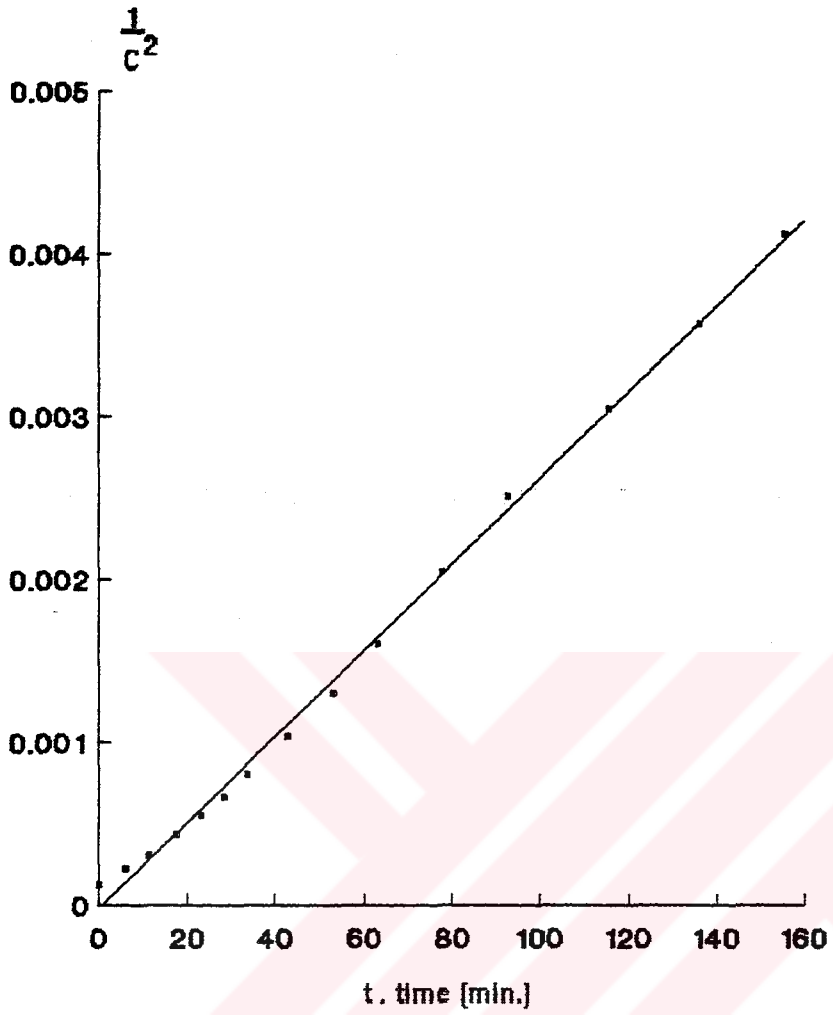


FIGURE 5.6. Rate of esterification of oleic acid and glycerol at 220°C.
Standard error of estimate = 5.3555×10^{-5}, coefficient of determination = 0.9983, and coefficient of regression = 0.9991

5.3. Kinetic studies

The experimental data which are compiled with and without co-solvent are plotted for the case of different reaction rate Equations to determine the reaction order for each of the experimental runs. A computer program utilizing least square technique which scans reaction order in the desired range was used.

The graphs for the best fit results of the computer evaluation are given in figures (5.1, 5.2, 5.3, 5.4, 5.5, and 5.6) from the reaction order determination it is found that for the case of pyridine experiments the reaction is second order at 180°C, and third order at 200°C, and 220°C. The reaction order for esterification without pyridine follows third order for all temperatures. From these results it is clear that pyridine has a distinctive effect on the reaction kinetics. The effect of pyridine on the esterification reaction may be explained in terms of the co-solvent effect of pyridine, which provides more free hydroxyls which are steric hindranced in the reaction medium without pyridine. The reason why this effect is not observed at 220°C may be explained in terms of the reduced amount of pyridine available in the reaction medium to provide the reaction temperature compare to 200°C.

Comparing the present results with literature show that the reaction order at 180°C for the esterification without co-solvent follows second order reaction. Disagreement between the present study and Hartman [43] may be due to the difference in reaction medium and procedure used in the respective studies. Contrary to this study Hartman [43] used a sealed tube and did not remove the esterification water from the medium during the course of the reaction. However, Tanizaki et al. [39] were also

reported a third order esterification reaction between glycerol and lauric acid or phthalic anhydride at 170°C and 230°C.

Dunlap and Heckles [32] carried out esterification of oleic acid with glycerol without using co-solvent and reported second order reaction, the difference between the reaction orders with this study may be explained with the use of catalyst in Dunlap and Heckles [32] study which is expected to reduce the reaction order compare to the present case.

The reaction dependence on the reactants and their concentration is well illustrated by Trafimov et al .[49] study in which case oleic acid and β-sitosterol at 200-250°C. The reaction was found to be a second order for molar ratio of the reactants being 1:1. For the case of excess oleic acid utilization the reaction order was reported to be first order.

The rate constant calculation on this study were based on second and third-order kinetics, which was appropriate for the individual case. The first and second order reactions can be represented by Equations 1 and 2, respectively.

$$kt = \frac{1}{c} - \frac{1}{c_o} \quad \cdots\cdots\cdots (1)$$

$$2kt = \frac{1}{c^2} - \frac{1}{c_o^2} \quad \cdots\cdots\cdots (2)$$

To test Equations 1 and 2. $1/c$ and $1/c^2$ were plotted against t. respectively. In view of the difficulty of establishing the concentration in mole per liter at the

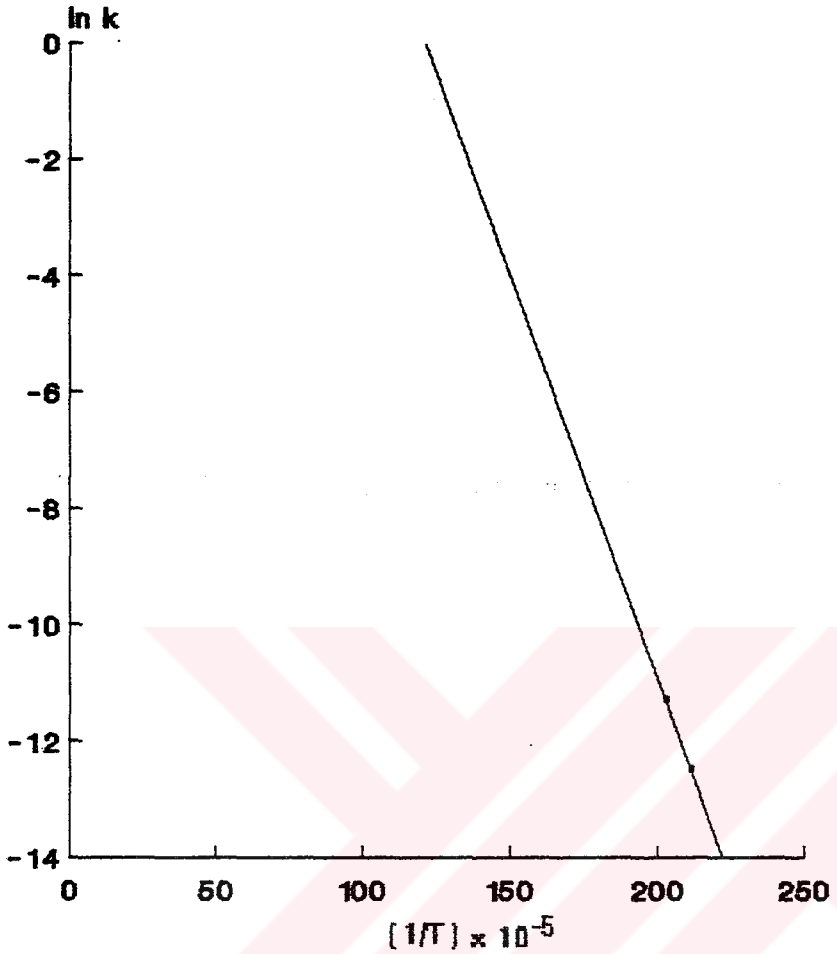


FIGURE 5.7. Plot of Arrhenius Equation for esterification of oleic acid and glycerol in the presence of pyridine.

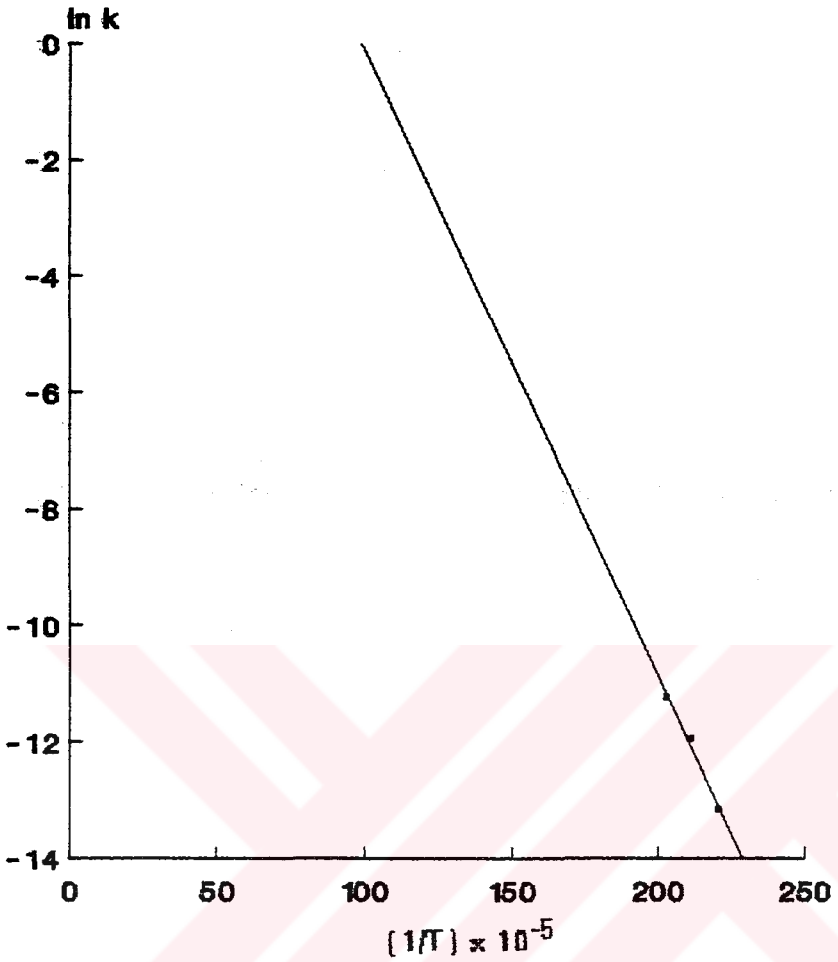


FIGURE 5.8. Plot of Arrhenius Equation for esterification of oleic acid and glycerol.

applied temperatures, the oleic acid concentration was expressed as weight percentage.

Rate constants determined from the slopes of the straight lines shown in Figures (5.7, and 5.8) are presented in Table 5.7. Activation energies are also included in Table 5.7, which are determined from Arrhenius' law [59].

$$k = k_o e^{-E/RT}$$

From Arrhenius' law a plot of ln k vs. 1/T gives a straight line, activation energy can be calculated from its slope.

TABLE 5.7. Rate Constants and Activation Energies for the Esterification of Oleic Acid and Glycerol under different Conditions.

Solvent used in the reaction	Rate Constant, $k(wt\%)^{-2}(min)^{-1}$			Activation energy, E kcal/mole
	180°C	200°C	220°C	
Pyridine	1.10×10^{-4}*	3.81×10^{-6}	12.5×10^{-6}	27.46
None	1.93×10^{-6}	6.40×10^{-6}	13.2×10^{-6}	21.30

* The unit of rate constant is $(wt\%)^{-1}(min)^{-1}$.

The product distribution of the esterifications was studied by systematic chemical analysis of mono-, di-, and triglycerides with respect to time for both reactions with and without pyridine at 180°C The results of product

TABLE 5.8. Course of Esterification Reaction between Oleic acid and Glycerol at 180°C.*

Sample number	Time (min.)	Acid %	Hydroxyl value	Monoglyceride %	Diglyceride %	Triglyceride %
1	6.67	89.08	37.90	12.32	0.000	00.00
2	21.83	71.93	64.96	15.84	0.240	12.06
3	37.00	64.14	73.27	16.57	0.234	19.06
4	57.92	53.80	70.85	5.08	0.607	40.51
5	77.75	50.50	53.94	7.56	0.334	41.61
6	97.75	47.03	51.18	6.26	0.348	46.36
7	127.58	42.68	40.61	6.91	0.209	50.20
8	157.67	38.06	33.70	4.38	0.220	57.34

TABLE 5.9. Course of Esterification Reaction between Oleic acid and Glycerol in presence of Pyridine at 180°C.*

Sample number	Time (min)	Acid %	Hydroxyl value	Monoglyceride %	Diglyceride %	Triglyceride %
1	7.75	93.37	25.40	7.30	0.027	0.00
2	22.50	83.12	47.49	9.55	0.193	7.14
3	37.83	74.30	59.40	9.67	0.321	15.71
4	77.25	59.21	67.97	5.37	0.565	34.86
5	97.00	54.68	65.81	6.49	0.502	38.33
6	127.50	48.67	66.29	4.96	0.561	45.81
7	159.25	43.38	62.47	6.62	0.461	50.46

* Analysis were carried out with the glycerol free samples.

distribution for both cases are shown in Tables (5.8, and 5.9). Investigation of these results show that the products are distributed in a different percentages during the esterification reaction. However, it is realized that these differences in the product distributions at the earlier stages of the reaction are more pronounced compared to the end of reaction. Still there is a clear product distribution differences at the end for the case of reactions with and without co-solvent. The reaction mechanism can be better understand by following the variation in hydroxyl values with time, for the experiment without pyridine hydroxyl values increase to a maximum value of 73.27 at 37 minutes and then it decreased to about 34 at the end of the experiment. The increase in the hydroxyl values is attributed to the formation of partial glycerides consumption which is stressed due to transesterification coming into operation decreased the hydroxyl value. The partial glycerides formed in the reaction dissolving at the fatty acid is believed to have the main effect on the decrease of the hydroxyl value.

In the presence of pyridine as co-solvent the hydroxyl value increase up to 127.5 minutes and show a little drop at the end of the experiment. Pyridine is the main reason for the difference in the hydroxyl profile since it acts as a solvent for all components of the reaction mixture. It includes glyceride in the transesterification reactions to keep the concentration of hydroxyl higher than the case for without pyridine. It is advisable to study other reaction stoichiometries and temperatures to stress the difference in the product distribution for preferential process conditions for both reactions.

5.4. Conclusions

The following conclusions may be drawn from the study of esterification reaction between oleic acid and glycerol with and without pyridine.

1-The reaction between oleic acid and glycerol follows third order kinetics under the conditions used in this study, for all temperatures.

2-The reaction order of the same esterification reaction using pyridine as co-solvent follows a second order at 180°C and third order at 200°C and 220°C.

3-The reaction rate constants for esterification reaction at 180, 200, and 220°C were found to be 1.93×10^{-6}, 6.40×10^{-6}, and 13.2×10^{-6} $(wt\ \%)^{-2}\ (min.)^{-1}$ respectively. For the case of esterification reaction using pyridine reaction rate constant were found to be 1.10×10^{-4} $(wt\ \%)^{-1}\ (min.)^{-1}$, 3.81×10^{-6} $(wt\%)^{-2}\ (min.)^{-1}$, and 12.5×10^{-6} $(wt\ \%)^{-2}\ (min.)^{-1}$ respectively for the same temperatures.

4-The formation of the partial glycerides with time showed different pattern for the reactions with and without pyridine and final distributions were closer to each other than the initial values.

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