

**EGE UNIVERSITY GRADUATED SCHOOL OF
NATURAL AND APPLIED SCIENCES**

(MASTER THESIS)

**PRODUCTION OF FATTY ACID ESTERS
USED AS LUBRICANTS**

Esin DENİZ AYAN

Supervisor : Prof. Dr. Ferhan S. ATALAY

Department of Chemical Engineering

Department Code : 603.03.00

Presentation Date : 17.03.2010

Bornova-İZMİR

2010

Esin DENİZ AYAN tarafından yüksek lisans tezi olarak sunulan **“Production of Fatty Acid Esters Used as Lubricants”** başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 17.03.2010 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

Jüri Üyeleri:

İmza

Jüri Başkanı : Prof. Dr. Ferhan S. ATALAY
Raportör Üye : Assoc.Prof.Dr.Oğuz BAYRAKTAR
Üye : Asist. Prof. Dr. Serap CESUR

ÖZET

YAĞLAMA MALZEMESİ OLARAK KULLANILMAK ÜZERE YAĞ ASİTİ ESTERLERİ ELDESİ

DENİZ AYAN, Esin

Yüksek Lisans Tezi, Kimya Mühendisliği Bölümü

Tez Yöneticisi: Prof. Dr. Ferhan S. ATALAY

Mart 2010, 66 sayfa

Bu tezde yağlama malzemesi olarak kullanılmak üzere kesikli bir reaktörde yağ asidi esterleri üretimi incelenmiştir. Esterleşme reaksiyonu çalışmalarında kullanılmak üzere, zeytin yağı rafinasyonu yan ürünü olarak elde edilen yağ asidi karışımı seçilmiştir. Katalizör olarak asidik iyon değiştirici reçine olan ticari Amberlyst 15 ve derişik sülfürik asit kullanılmıştır. Reaksiyonlarda alkol olarak, 1,2 propandiol, etilen glikol, gliserin ve 1- butanol seçilmiştir.

Amberlyst 15 katalizörlüğünde yapılan çalışmalarda, 1,2 propandiol, etilen glikol, gliserin ve 1-butanol ile yağ asidi esterleri elde edilememiştir. Sülfürik asit katalizörlüğünde yapılan çalışmalarda 1-butanol ile elde edilen yağ asidi esterleri miktarı gliserinle elde edilenlerden daha fazladır. Bu nedenle sıcaklık , katalizör miktarı, alkol/yağ asitleri başlangıç mol oranları değiştirilerek yapılan parametrik çalışmalar ve kinetik çalışması 1-butanol ile yağ asitlerinin esterleşme reaksiyonu için gerçekleştirilebilmiştir. Reaksiyon ilk beş dakika içinde dengeye geldiği için reaksiyon tersinmez olarak belirlenmiştir. Reaksiyon sadece ileri reaksiyon olarak tanımlanmış ve reaksiyon derecesi 1.24 olarak belirlenmiştir.

Bütil esterlerin performans testleri OPET A.Ş. tarafından yapılmıştır ve üretilen bütil esterlerin hidrolik yağı ham maddesi ve kesme yağlarında katkı olarak kullanılabilceği tespit edilmiştir.

Anahtar sözcükler: Yağ asidi esterleri, linoleik asit bütil ester, oleik asit bütil ester, palmitik asit bütil esterleri, esterleşme, sülfürik asit, Amberlyst 15, reaksiyon kinetiği.

ABSTRACT**PRODUCTION OF FATTY ACID ESTERS
USED AS LUBRICANTS**

DENİZ AYAN, Esin

MSc in Chemical Engineering

Supervisor: Prof. Dr. Ferhan S. ATALAY

March 2010, 66 pages

In this thesis, production of fatty acid esters used as lubricants has been studied in a batch reactor. To be used in the esterification reactions fatty acid esters mixture which is a side product of olive oil refinery system was chosen. As the catalysts an acidic ion exchange resin with the brand name Amberlyst 15 and concentrated sulfuric acid were used. In the reactions 1,2- propanediol, ethylene glycol, glycerin and 1-butanol were used as alcohol.

In the studies of catalyst Amberlyst 15 with 1,2- propanediol, ethylene glycol, glycerin and 1-butanol, fatty acid esters were not obtained. In the studies of catalyst sulfuric acid with 1-butanol, the amount of obtained fatty acid esters were much more than the esters obtained from glycerin. For this reason, parametric studies with changing temperature, catalyst loading amount, and alcohol/fatty acid initial mol ratios were carried out and the kinetic study has been performed for the fatty acid esterification reaction with 1-butanol. The reaction was determined as irreversible since the reaction reached the equilibrium in five minutes. So the reaction rate was expressed only forward reaction rate with an order of 1.24.

The performance tests of butyl esters were performed by OPET A.Ş. and it was found that the produced butyl esters can be used as base material for hydraulic oils and as additive for cutting oils.

Keywords: Fatty acids, linoleic acid butyl ester, oleic butyl ester, palmitic butyl ester, butyl esters, esterification, sulfuric acid, Amberlyst 15, reaction kinetics.

ACKNOWLEDGEMENT

I sincerely would like to thank to my supervisor Prof. Dr. Ferhan S. ATALAY for his valuable suggestions, criticisms and supports during this study.

I would also like thank to Dr. Emine SERT, Chemist İlhami TAŞKIRAN, Chemist Serpil Taşkıran, Electrical Technician, Gürsel Serin, for their supports. I would like to thank to OPET A.Ş. and Esra Meriç Ökesli.

I sincerely would like to thank to my husband Bilge AYAN for his valuable support.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	v
ÖZET	vii
ACKNOWLEDGEMENT	ix
LIST OF FIGURES	xv
LIST OF TABLES	xvii
NOMENCLATURE AND ABBREVIATIONS.....	xx
1. INTRODUCTION	1
2. THEORETICAL BACKGROUND	4
2.1 Esterification	4
2.2 Fatty Acids	5
2.2.1 Properties of Fatty Acids	8
2.3 Fatty Acid Esters	11
2.4 Lubricants	14
2.4.1 Biolubricants	15
3. LITERATURE REVIEW	18
3.1 Esterification Studies with Homogeneous Catalysts	18
3.2 Esterification Studies with Heterogeneous Catalysts	20

TABLE OF CONTENTS (continued)

	<u>Page</u>
4. EXPERIMENTAL STUDY	27
4.1 Materials.....	27
4.2 Experimental Setup and Procedure	30
4.3 Analysis	32
5. RESULTS AND DISCUSSION	34
5.1 Experiments with Different Alcohols	34
5.2 Determination of Equilibrium Constant	35
5.3 Experiments for Investigation of the Effect of Temperature, Catalyst Loading Amount and Initial Mole Ratio.....	36
5.4 Kinetic Study	41
5.5 Performance Tests and Results	45
5.6 Discussion	50
6. CONCLUSION	52
7. FUTURE WORKS	53
REFERENCES	54
APPENDICES	58
Appendix I	58

TABLE OF CONTENTS (continued)

	<u>Page</u>
Appendix II	60
Appendix III	62
RESUME	65

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
2.1.1 A generic mechanism for an acid Fischer esterification	4
2.2.1 Molecular structure of different fatty acids	8
2.2.1.1 Chemical chain structure of linoleic acid	9
2.2.1.2 Chemical chain structure of oleic acid	10
2.2.1.3 Chemical chain structure of palmitic Acid	10
2.3.1 Chemical chain structure of linoleic acid butyl ester	12
2.3.2 Chemical chain structure of oleic acid butyl ester	13
2.3.3 Chemical chain structure of palmitic acid butyl ester	14
4.2.1 The experimental setup	31
4.3.1 A Sample Chromatogram	33
5.2.1 $\ln K$ vs. $1/T$	36
5.3.1 Temperature effect on conversion	37
5.3.2 Catalyst loading effect on conversion	39
5.3.3 Initial mole ratio effect on conversion	40
5.4.1 Temperature effect on conversion	41
5.4.2 $r_{\text{calculated}}$ and $r_{\text{experimental}}$ comparison	42
5.5.1 Suction filtration	45

LIST OF FIGURES (continued)

5.5.2	Vacuum distillation setup	46
-------	---------------------------------	----

LIST OF TABLES

<u>Tables</u>	<u>Page</u>
2.2.1 Fatty Acids in Commodity Oils and Fats	7
2.2.1.1 Melting and boiling points of fatty acids	8
2.2.1.2 Melting points of fatty acids	9
2.3.1 Physical properties of linoleic acid butyl ester	12
2.3.2 Physical and chemical properties of oleic acid butyl ester.....	13
2.3.3 Physical and chemical properties of palmitic acid butyl ester	14
3.1 Literature survey on the esterification reactions catalyzed by homogeneous catalysts without kinetic studies	24
3.2 Literature survey on the esterification reactions catalyzed by heterogeneous catalysts without kinetic studies	24
3.3 Literature survey on the esterification reactions catalyzed by homogeneous catalysts with kinetic studies	25
3.4 Literature survey on the esterification reactions catalyzed by heterogeneous catalysts with kinetic studies	26
3.5 Literature survey on the esterification reactions catalyzed by heteropolyacid catalysts with kinetic studies	26
4.1.1 The Properties of 1-Butanol	27

LIST OF TABLES (continued)

4.1.2	The Properties of Calcium Chloride	27
4.1.3	The Properties of Glycerin	28
4.1.4	The Properties of Methanol	28
4.1.5	The Properties of 1,2 Propanediol	29
4.1.6	The Properties of Sodium Carbonate	29
4.1.7	The Properties of Sulfuric Acid	30
4.3.1	Gas chromatograph operation conditions	32
5.1.1	Preliminary experiments	34
5.2.1	Experiments for temperature effect on equilibrium constant	35
5.2.2	Equilibrium constants, conversion values and mole of esters produced	36
5.3.1	Experiments for temperature effect on conversion	37
5.3.2	Conversion values and mole of esters produced	37
5.3.3	Experiments for catalyst loading effect on conversion	38
5.3.4	Conversion values and mole of esters produced	38
5.3.5	Experiments for initial $n_{\text{alcohol}}/n_{\text{FAMOO}}$ ratio effect on conversions	39
5.3.6	Conversion values and mole of esters produced	40
5.4.1	Experiments for initial reaction rates	43

LIST OF TABLES (continued)

5.4.2	Kinetic Model	44
5.5.1	Performance test results.....	49

NOMENCLATURE AND ABBREVIATIONS

<u>Symbols</u>	<u>Legend</u>	<u>Units</u>
A	Fatty acid	[-]
$A_{Butanol}^{\%}$	Area percent of butanol peak	[%]
$A_{Ester}^{\%}$	Area percent of ester peaks	[%]
B	Butanol	[-]
C_{A0}	Initial concentration of fatty acid mixture	$\left[\frac{mole}{L} \right]$
C_{B0}	Initial concentration of 1-butanol	$\left[\frac{mole}{L} \right]$
E	Ester	[-]
K	Equilibrium constant	[-]
K_a	Equilibrium constant of reaction based on activity	[-]
K_x	Equilibrium constant of reaction based on mole fraction in liquid phase	[-]
K_{γ}	Activity coefficient	[-]
M	Initial mole ratio of 1-butanol / fatty acid mixture	[-]
MW_E	Molecular weight of ester mixture	$\left[\frac{g}{mole} \right]$

MW_B	Molecular weight of butanol	$\left[\frac{g}{mole} \right]$
N_{A0}	Initial mole of fatty acid mixture	$[mole]$
N_{B0}	Initial mole of 1-butanol	$[mole]$
N_{E0}	Initial mole of esters	$[mole]$
N_{W0}	Initial mole of water	$[mole]$
N_E	Mole of Ester at any time	$[mole]$
v_i	Stoichiometric coefficients; (+) for products, (-) for reactants	$[-]$
W	Water	$[-]$
X_A	Conversion of fatty acid mixture	$[\%]$
xi	Mole fraction of component I	$[-]$

Abbreviations

DEGS	Diethylene glycol succinate
FAME	Fatty acid methyl esters
FAMOO	Fatty acid mixture of olive oil

1. INTRODUCTION

The industrial chemistry of oils and fats is a mature technology, with experience of years and current studies. However the processes of the fats and oils industry are well known, the environmental threats cause new, cleaner processes “green processes” and also cause new markets for new products, “biodegradable products”. As environmentally friendly “green” processes, less energy, and renewable resources; enzyme catalyzed reactions are used for new compounds (Shahidi, F., editor, 2005).

Nowadays biofuels, biodegradable plastics, biolubricants are the most popular biodegradable products. Biolubricants are formulated for a rapid biodegradability and low environmental toxicity. However petroleum-based lubricants offer cost advantages, stability and enjoy universal acceptance, petroleum-based oils are not biodegradable and a serious environmental issue is the total loss of lubricants (Benefuel, 2010).

Biolubricants are possible to obtain from vegetable oil derivatives (B'elafi-Bak'ó et al., 2004). Different types of fatty acid esters can be used in biolubricants manufacturing. Oleic acid is one of the most important fatty acids in nature. Vegetable oils comprise oleic acid and other common fatty acids.

Fatty acids are almost entirely straight chain aliphatic carboxylic acids. The most natural fatty acids are 4 carbon atoms to 22 carbon atoms, with 18 carbon atom most common. A range of fatty acid esters is being produced commercially for example, esters produced from long-chain fatty acids (12–20 carbon atoms) and short-chain alcohols (3-8 carbon atoms) have been used increasingly in the food, detergent, cosmetic and pharmaceutical industries (Bauer et al., 1990), esters prepared from the reaction of long-chain acids with long-chain alcohols (12–20 carbon atoms) also have important applications as plasticizers and lubricants (Gandhi et al., 1995).

Wide range of fatty acid esters are obtained by esterification reactions (see 2.1 Esterification) with different catalysts. Lipase enzymes, sulfuric acid or p-TSA, superacids, ion exchange resins, and heteropolyacids, are used in esterification reactions.

When the substrates are acid-resistant, the reaction is usually carried out in the presence of Bronsted acid such as HCl, HBr, H₂SO₄, NaHSO₄, and camphorsulfonic acid, etc. (Otera, 2003). Sulfuric acid is the most commonly used catalyst because it is effective and cheap. In homogenous esterification reactions para-toluene sulfonic acid is a good alternative because of its catalytic activity.

Sulfated zirconia is the most recently used superacid. They are potential catalysts for isomerization of lower alkanes. Although there are many studies on it, there is no universally accepted theory as sites of what type account for the unique catalytic activity of sulfated zirconia. Recent studies of the strength of Bronsted and Lewis acid sites do not support the early hypothesis on the superacidity of such systems (Volodin and Bedilo, 2000)

The cationic acid resins are active at low temperatures and could act as shape selective materials. Indeed, among all these materials, we can distinguish between the resins (gel-type), not really porous, and the macroporous resins. The swelling properties of a resin are due to the formation of hydrogen bonds between the sulfonic groups of the resin and the water or the alcohol molecules of the reaction mixture (Pouilloux et al., 1999).

The heteropolyacids are strong Bronsted acids widely used as catalysts, which has good thermal stability, high acidity and high oxidizing ability. Heteropolyacids are also used as redox catalysts. In combination with TiO₂, heteropolyacids can be used as photocatalysts active in visible light (Rayalu et al., 2007).

Sulfuric acid was chosen in this study as the catalyst, because it was effective and cheap. Sulfuric acid has a disadvantage in the separation process and a solid catalyst can eliminate this disadvantage but the solid catalysts have not yielded satisfactory results according to liquid ones yet. Also the effective operation conditions of solid catalysts are very limited (temperature, agitation speed and particle size, etc.).

The production of biobased products from low cost raw materials would make biobased production cost more competitive than petroleum based products. Using fatty acid mixtures of oils are a new trend and this project focused on these fatty acid mixtures. The studied fatty acids showed differences for different locations because of the dominating vegetable oil. Dominating vegetable oil in

Izmir is the olive oil, so in this project, esterification reactions have been studied on fatty acid mixtures obtained from an olive oil refinery. According to our knowledge it was not found a study in the literature on fatty acids obtained from soap stocks. Effects of temperature, catalyst loading amount, initial mole ratios of alcohol to fatty acid were investigated and also kinetic model was studied.

Section 2 gives information about esterification, fatty acids, fatty acid esters, lubricants and biolubricants. Literature review is in section 3. Section 4 gives the experimental studies; used materials, experimental set up and procedure, and also gives information about the investigated parameters. Results and discussion, equilibrium constant calculations and kinetic study are in section 5 and section 6 is conclusion.

2. THEORETICAL BACKGROUND

2.1. Esterification

Esterification is the general name for a chemical reaction in which two reactants (typically an alcohol and an organic acid) form an ester as the reaction product. Esterification is a reversible reaction and proceeds to completion only if the water is continuously removed during the course of the reaction. Generally water is eliminated as chemically, physically, or by pervaporation. According to Le Chatelier's principle to shift the equilibrium of the reaction towards the desired alkyl ester, one of the reactants usually the alcohol, has to be in excess. Excess alcohol favors the ester formation or excess water favors the carboxylic acid formation.

The esterification reaction has several reaction steps; these are shown in Figure 2.1.1.

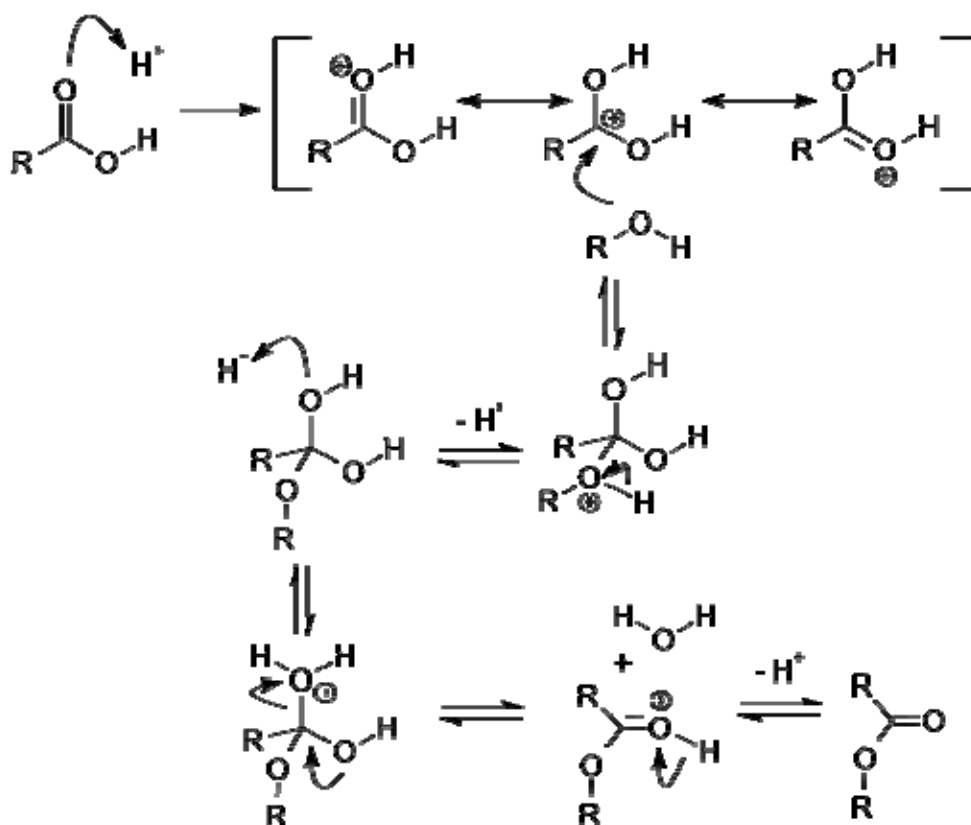


Figure 2.1.1 A generic mechanism for an acid Fischer esterification (Fischer and Speier, 1895)

The esterification reaction steps can be explained as;

1. Proton transfer from acid catalyst to carbonyl oxygen increases electrophilicity of carbonyl carbon.
2. The carbonyl carbon is then attacked by the nucleophilic oxygen atom of the alcohol.
3. Proton transfer from the oxonium ion to a second molecule of the alcohol gives an activated complex.
4. Protonation of one of the hydroxyl groups of the activated complex gives a new oxonium ion.
5. Loss of water from this oxonium ion and subsequent deprotonation gives the ester.

2.2 Fatty Acids

Fatty acids are almost entirely straight chain aliphatic carboxylic acids. The definition includes all chain lengths, but most natural fatty acids have carbon atoms between 4 to 22, with 18 carbon atoms the most common. The molecular structures of different fatty acids are shown in Figure 2.2.1. Fatty acids generally contain an even number of carbon atoms. The general formula for a saturated fatty acid is $\text{CH}_3(\text{CH}_2)_n\text{COOH}$, in which n is an even integer. If $n=16$, the result is an 18-carbon saturated fatty acid. Systematic names for fatty acids are too cumbersome for general use, and shorter alternatives are widely used. Two numbers separated by a colon give, respectively, the chain length and the number of double bonds: octadecenoic acid with 18 carbons and 1 double bond is therefore 18:1. Fatty acids in commodity oils and fats are shown in Table 2.2.1.

The natural fatty acids are obtained from the hydrolysis of hard animal fats (tallow), coconut, palm kernel, soybean oils and from the fractional distillation of crude tall oil (a byproduct of Kraft pulping of pine wood). Fatty acid market information is given by Rohm and Haas (2010), as below.

“Most new plants have been built in Southeast Asia which is the major source for coconut, palm and palm kernel oils. The market is dominated by two producers, the

Uniquema group and the Henkel group representing about 50% world market share. Other fatty acids are derived from petroleum.” (Rohm and Haas, 2010).

Table 2.2.1 Fatty Acids in Commodity Oils and Fats, (Shahidi, editor, 2005)

Fatty acid	Common name	Formula	Molecular Weight (g/mole)
4:0	Butyric	$\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$	88.11
6:0	Caproic	$\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$	116.16
8:0	Caprylic	$\text{CH}_3(\text{CH}_2)_6\text{CO}_2\text{H}$	144.21
10:0	Capric	$\text{CH}_3(\text{CH}_2)_8\text{CO}_2\text{H}$	172.26
12:0	Lauric	$\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$	200.31
14:0	Myristic	$\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$	228.37
16:0	Palmitic	$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$	256.42
18:0	Stearic	$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$	284.48
18:1 9c	Oleic	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	282.46
18:2 9c12c	Linoleic	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_2(\text{CH}_2)_6\text{CO}_2\text{H}$	280.45
18:3 9c12c15c	α -Linoleic	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{CO}_2\text{H}$	278.43
22:1 13c	Erucic	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{CO}_2\text{H}$	338.57
20:5 5c8c11c14c17c	EPA ¹	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_5(\text{CH}_2)_2\text{CO}_2\text{H}$	302.45
22:6 4c7c10c13c16c19c	DHA ²	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_6\text{CH}_2\text{CO}_2\text{H}$	328.48

¹ Eicosapentaenoic Acid² Docosahexaenoic Acid

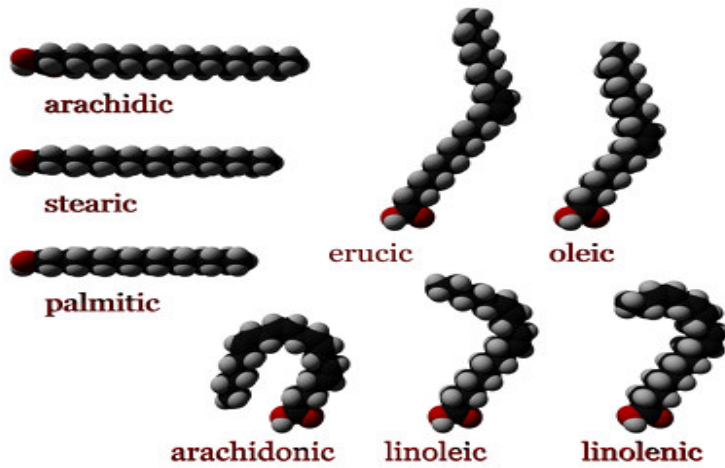


Figure 2.2.1 Molecular structure of different fatty acids (Wikipedia, 2010)

2.2.1 Properties of Fatty Acids

Fatty acids react just like any other carboxylic acid, which means they can undergo esterification and acid-base reactions. Reduction of fatty acids yields fatty alcohols. Unsaturated fatty acids can also undergo addition reactions, most commonly hydrogenation, which is used to convert vegetable oils into margarine. With partial hydrogenation, unsaturated fatty acids can be isomerized from cis to trans configuration. Melting and boiling points of various fatty acids are tabulated in Table 2.2.1.1 and Table 2.2.1.2.

Table 2.2.1.1 Melting and boiling points of fatty acids (Rohm and Haas, 2010)

		Mp (°C)	Bp (°C)
Caprylic acid	(C8)	17	240
Capric acid	(C10)	32	270
Lauric acid	(C12)	44	299
Myristic acid	(C14)	54	326
Palmitic acid	(C16)	63	352
Stearic acid	(C18)	70	376

Table 2.2.1.2 Melting points of fatty acids (Rohm and Haas, 2010)

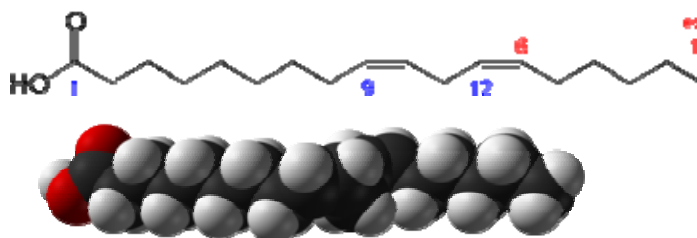
		Mp (°C)
Arachic acid	(C20)	75°C
Behenic acid	(C22)	80°C
Lignoceric acid	(C24)	84°C
Oleic acid	(cis unsaturated C18)	16°C
Linoleic acid	(diene C18)	-5°C
Erucid acid	(cis unsaturated C22)	34°C

Fatty acid mixture used in this study composes of linoleic, oleic and palmitic acids. Properties of these acids are given as follows.

Linoleic Acid

Linoleic acid is an unsaturated omega-6 fatty acid. It is a colorless liquid. In physiological literature, it is called 18:2(n-6). Chemically, linoleic acid is a carboxylic acid with an 18-carbon chain and two cis double bonds; the first double bond is located at the sixth carbon from the omega end (Figure 2.2.1.1).

The word linoleic comes from the Greek word linon (flax). Oleic means of, relating to, or derived from oil or olive or of or relating to oleic acid since removing the omega-6 double bond produces oleic acid. Linoleic acid is used in making soaps, emulsifiers, and quick-drying oils. Reduction of linoleic acid yields linoleyl alcohol.

**Figure 2.2.1.1.** Chemical chain structure of linoleic acid (Wikipedia, 2010)

Oleic Acid

Oleic acid is a mono-unsaturated omega-9 fatty acid found in various animal and vegetable sources. It has the formula $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ (Figure 2.2.1.2). The trans-isomer of oleic acid is called elaidic acid. The term oleic means related to, or derived from, oil or olive. Other names; (9Z)-Octadecenoic acid, (Z)-Octadec-9-enoic acid, *cis*-9-Octadecenoic acid, *cis*- Δ^9 -Octadecenoic acid, Oleic acid 18:1 *cis*-9.

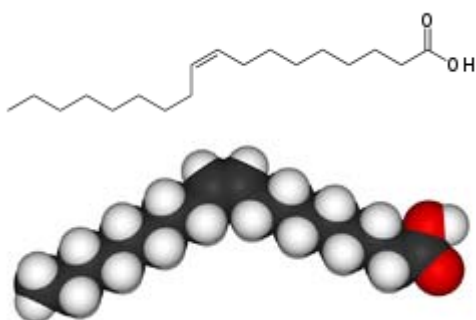


Figure 2.2.1.2. Chemical chain structure of oleic acid (Wikipedia, 2010)

Palmitic Acid

Palmitic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ or hexadecanoic acid in IUPAC nomenclature, is one of the most common saturated fatty acids found in animals and plants. As its name indicates, it is a major component of the oil from palm trees (palm oil and palm kernel oil). The word palmitic is from the French "palmitique", the pith of the palm tree. Butter, cheese, milk, olive oil and meat also contain this fatty acid. Palmitate is a term for the salts or esters of palmitic acid (Figure 2.2.1.3).



Figure 2.2.1.3 Chemical chain structure of palmitic acid (Wikipedia ,2010)

2.3. Fatty Acid Esters

Fatty acids are used in a wide variety of applications. According to market researches explained by Rohm and Haas, the demand for fatty acids has been reached about 3,000,000 metric tons per year by growing about 4% per year over the past 10 years. Fatty acids are typically present in the raw materials used for the production of biodiesel or biolubricants.

About 100,000 metric tons of the natural fatty acids are consumed in the preparation of various fatty acid esters. The simple esters with lower chain alcohols (methyl-, ethyl-, n-propyl-, isopropyl- and butyl esters) are used as emollients in cosmetics and other personal care products and as lubricants. Esters of fatty acids with more complex alcohols, such as sorbitol, ethylene glycol, diethylene glycol and polyethylene glycol are consumed in foods, personal care, paper, water treatment, metal working fluids, rolling oils and synthetic lubricants, (Rohm and Haas, 2010).

There are different kinds of fatty acid esters, produced from different alcohols. In biodiesel industry much common is methyl esters (FAME) which are used as standards for GC analysis. But, in this project butyl esters of olive oil fatty acids were obtained and the important ones (linoleic, oleic and palmitic acid butyl esters) were investigated below.

Linoleic Acid Butyl Ester (C₂₂H₄₀O₂)

Linoleic acid butyl ester is used as surfactant and lubricant and also used in pharmaceutical industry (in prophylactically effective substances which are useful in protecting mammals against staphylococcal infection).

Chemical chain structure is shown in Figure 2.3.1 and also physical properties are tabulated in Table 2.3.1.



Figure 2.3.1 Chemical chain structure of linoleic acid butyl ester

Table 2.3.1 Physical properties of linoleic acid butyl ester (Chemical Book, 2010)

Formula:	$C_{22}H_{40}O_2$
Molecular Weight:	336.55 g/mol (IUPAC)
Name(s):	12-octadecadienoic acid(z,z)-butylester; 9,12-Octadecenoic acid(Z,Z)-, butylester; butyllinoleate; n-butyl linoleate; butyl (9Z,12Z)-octadeca-9,12-dienoate; (9Z,12Z)-Octadecane-9,12-dienoic acid butyl ester
Appearance :	pale yellow clear liquid
cas number :	2634-45-9
(EINECS) number :	220-121-4
Melting point :	15.00 to 18.00 °C. @ 760.00 mm Hg
Boiling point :	360.00 to 362.00 °C. @ 760.00 mm Hg
Flash point :	349.00 °F. TCC (176.11 °C.)

Oleic Acid Butyl Ester ($C_{22}H_{42}O_2$)

Fatty acid esters of alcohols are of increasing economic interest in many industries involving a wide range of applications: bio-carburants, bio-surfactants, biolubricants, solvents, hydraulic and drilling fluids, dispersing agents, cosmetics.

Among the fatty acids, oleic acid is particularly stable to thermal-oxidation, due to the presence of only one insaturation in its structure. General usage is as plasticizer agent and solvent for polymers.

Chemical chain structure is shown in Figure 2.3.2 and also physical and chemical properties are tabulated in Table 2.3.2.

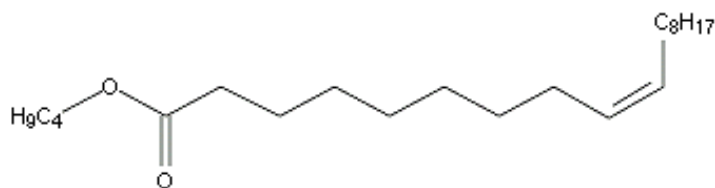


Figure 2.3.2 Chemical chain structure of oleic acid butyl ester

Table 2.3.2 Physical and chemical properties of oleic acid butyl ester (The Good Scent Company, 2010), (NIST, 2010)

Formula:	C ₂₂ H ₄₂ O ₂
Molecular Weight:	338.568 g/mol (IUPAC)
Name(s):	oleic acid butyl ester; <i>cis</i> -octadec-9-enoic acid butyl ester; butyl oleate
Appearance :	pale yellow clear liquid
cas number :	142-77-8
(EINECS) number :	205-559-6
coe number :	741
fl. number :	09.208
Boiling point :	220.00 to 222.00 °C. @ 760.00 mm Hg
Flash point :	> 200.00 °F. TCC (> 93.33 °C.)
molar refractivity :	105.80 ± 0.3 cm ³
parachor :	919.3 ± 4.0 cm ³
index of refraction :	1.456 ± 0.02
surface tension :	31.2 ± 3.0 dyne/cm
density :	0.870 ± 0.06 g/cm ³
polarizability :	41.94 ± 0.5 10 ⁻²⁴ cm ³
XlogP :	8.20
XlogP3-AA :	8.80
Δ_fH^o_{liquid}	-816.88 kJ/mol (simple calculation by NIST; no Washburn corrections)

Palmitic Acid Butyl Ester (C₂₀H₄₀O₂)

Palmitic acid butyl ester has important technical applications in a variety of areas, including medicine, cosmetics, and food industries, as well as more traditional usage as lubricants.

Chemical chain structure is shown in Figure 2.3.3 and also physical and chemical properties are tabulated in Table 2.3.3.

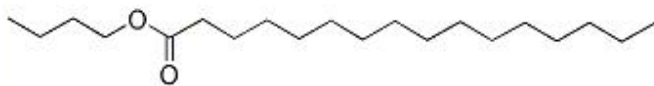


Figure 2.3.3 Chemical chain structure of palmitic acid butyl ester

Table 2.3.3 Physical and chemical properties of palmitic acid butyl ester (Chemical Book, 2010)

Formula:	C ₂₀ H ₄₀ O ₂
Molecular Weight:	312.5304000 (IUPAC)
Name(s):	palmitic acid butyl ester; butyl palmitate
Appearance :	pale yellow liquid to solid
cas number :	111-06-8
(EINECS) number :	203-829-8
fl. number :	09.331
Melting point :	15.00 to 18.00 °C. @ 760.00 mm Hg
Boiling point :	360.00 to 362.00 °C. @ 760.00 mm Hg
Flash point :	349.00 °F. TCC (176.11 °C.)
molar refractivity :	96.48 ± 0.3 cm ³
parachor :	852.5 ± 4.0 cm ³
index of refraction :	1.445 ± 0.02
surface tension :	30.7 ± 3.0 dyne/cm
density :	0.862 ± 0.06 g/cm ³
polarizability :	38.24 ± 0.5 10 ⁻²⁴ cm ³
XlogP :	7.80
XlogP3-AA :	8.70

2.4. Lubricants

Most modern lubricants are complex formulated products consisting of 70-90% base oils mixed with functional additives to modify the natural properties (i.e. cold stability, oxidation stability, hydrolytic stability, viscosity and viscosity index and corrosion) and fulfill the requirements for the fluid.

The base oil can be mineral, vegetable, synthetic or re-refined:

Mineral oils are the most commonly used today. They consist predominantly of hydrocarbons but also contain some sulfur and nitrogen compounds with traces of a number of metals.

Vegetable oils used in lubricants are mainly derived from rapeseed, sunflower, palm and coconut.

Synthetic oils include among others polyalphaolefins (PAO), synthetic esters and polyalkylene glycols (PAGs). PAOs are petrochemical derived synthetic oils that most resemble mineral oils. Synthetic esters form a large group of products, which can be either from petrochemical or oleochemical origin. Five different categories of synthetic esters can be distinguished: monoesters, di-esters, phthalate esters, polyol esters and complex esters. Polyalkylene glycols (PAGs) are polymers from petrochemical origin commonly made from ethylene oxide and propylene oxides.

Re-refined oil is the used oil that undergoes an extensive re-refining process to remove contaminants to produce fresh base oil. The base oil is then sold to blenders who add additive packages to produce lubricants.

2.4.1. Biolubricants

‘Biolubricants’ are often based on vegetable oils. In all different current discussions, biolubricants are at the least products for which formulation for (a certain extend of) rapid biodegradability and low environmental toxicity is a deliberate and primary intention. However, no universal agreement exists on the origin and chemical composition of the biolubricants. They can also be synthetic esters which may be partly derived from renewable resources (the hydrolysis of fats and oils to produce the constituent fatty acids). They can be made from a wider variety of natural sources including solid fats and low grade or waste materials such as tallows. Genetically-modified vegetable oils, such as high-oleic sunflower and rapeseed, are also at the beginning to find use in applications where higher oxidative stability is needed. According to market search of IENICA (2004) European lubricant consumption was as follows:

- “**47%**: automotive industry
- 32%**: industrial lubricants (including hydraulic oils which account for approximately 15% of total lubricant consumption)
- 11.3%**: process oils
- 9.4%**: marine and aviation

Industry claims suggest that over 90% of all lubricants could be replaced by biolubricants: this gives a potential European market of up to 9 million tonnes of biolubricants per year”.

Vegetable oils offer biodegradability and low toxicity. Obviously during the formulation of a biodegradable and low toxicity fluid, the additives must be biodegradable and have low toxicity.

The two most significant opportunities for biolubricants are:

High-risk lubricants that are in applications where there is a high probability of accidental exposure of the lubricants to sensitive environments for example hydraulic equipment in forests and by water.

Total-loss lubricants where, by the design of the equipment or application the lubricant ends up almost entirely in the environment, e.g. conveyor gears.

Benefits of Biodegradable Lubricants

- Less emissions because of higher boiling temperatures ranges of esters (Native triglycerides lead to partly gummy structures at high temperatures and can build eye irritant acroleins).
- Total free of aromatics, over, 90 % biodegradable oils, non water polluting.
- Oil mist and oil vapor reduction, leading to less inhalation of oil mist into the lung.
- Better skin compatibility, less dermatological problems.
- High cleanliness at the working place.
- At least equal and often higher tool life.
- Higher wetting tendency of polar esters lead to friction reduction.
- Higher viscosity index: their viscosity does not vary with temperature as much as mineral oil. This can be an advantage when designing lubricants for use over a wide temperature range. This can also result in lower viscosity classes for the same applications combined with easier heat transfer.

- Higher safety on a shop floor, because of higher flashpoints at the same viscosities.
- Cost savings on account of less maintenance, man power, storage and disposal costs.

Disadvantages of Biodegradable Lubricants

- Low temperature limitations. The addition of co-solvents such as synthetic fluids or mineral oils can improve the low-temperature properties of vegetable oils.
- Partly worse smell and compatibility with paintings and sealings.
- More flushing tendency because of lower viscosity.
- Less oxidation and hydrolytic stability's of vegetable oils.
- Filter clogging tendency depending on ester type and formulation.
- Depending on the ester type worse air release or foaming and corrosion protection behaviors.
- Depending on ester type yellow metal discoloration can occur.

3. LITERATURE REVIEW

3.1 Esterification Studies with Homogenous Catalysts

Mouloungui and Lacaze-Dufaure (2000) have studied catalysed (p-TSA) and uncatalysed esterifications between oleic acid and 2-ethylhexanol in a temperature range of 140°C and 170°C. The effect of amount of alcohol with respect to the fatty acid was evaluated (stoichiometric amount or twice the stoichiometric amount was studied). p-TSA monohydrate in xylene (reaction completed in 50 min at 140°C), p-TSA without xylene in concentrated alcoholic medium (93% mass concentration of esters were reached after 10 min), concentrated alcoholic medium without catalyst (reaction was completed in 280min at 170°C) cases were studied.

Bart et al. (1994) presented a general kinetic equation and obtained the results of kinetic and thermodynamic parameters of the esterification of levulinic acid with n-butanol, catalyzed by sulfuric acid. A stirred batch reactor was used for the esterification. Reaction rate constant, equilibrium constant (0.33 at 25°C, 0.75 at 50°C, 1.5 at 75°C, 2.17 at 90°C, 2.73 at 100°C), reaction order, activation energy, frequency factor, reaction enthalpy, reaction entropy, and activation enthalpy were observed as kinetic and thermodynamic parameters by changing initial molar ratios and amounts of sulfuric acid at six different temperatures (25, 50, 75, 90, 100 and 118°C). Bart et al. found that the resultant kinetic equation which follows a first-order rate expression and with respect to each component fits the experimental data well.

Aranda et al. (2007) evaluated the effect of the alcohol used, presence of water, type and concentration of catalysts in the esterification of palm fatty acids to produce biodiesel in a batch reactor. Kinetic parameters were estimated and molecular modeling was performed. Various homogeneous acid catalysts (sulfuric acid 98%, phosphoric acid 85%, trichloroacetic acid 98% and methanesulfonic acid 95%) were used in esterification experiments and methanesulfonic and sulfuric acid were found as the best catalyst. The alcohol to fatty acid molar ratio (A/FA) in reaction mixture was 3 and 0.1% wt/wt catalyst mass was loaded. The reaction conversions were calculated by the consumed NaOH amount used for titration. The conversion was increased using higher amounts of catalyst. Since ethanol presents steric hindrance in the reaction and shows higher water inhibition, it was observed that the reaction with methanol which has shorter chain and

higher polarity showed greater yields than ethanol and the reaction rate decreased with the presence of water in the reaction medium.

Bhatia et al. (2004) studied on the esterification kinetics of palmitic acid with isopropanol in a batch reactor catalyzed by p-TSA (homogeneous) and ZnA/SG (heterogeneous). The effect of reaction temperature (373-443 K), reactant molar ratio (1-5), catalyst loading ($1-5 \text{ g}_{\text{cat}} \text{ dm}^{-3}$) and effect of water concentration (0-15vol%) were investigated on various experiments. The effect of particle size of heterogeneous catalyst was also studied which did not show any significant effect on the conversion of palmitic acid. It was found that the conversions of palmitic acid over p-TSA and ZnA/SG at 443 K were 97.1%, 63.8% respectively and it was also found that the conversion was increased with the elevation of temperature. The palmitic acid conversion was enhanced with the increase of isopropanol to palmitic acid ratio and the conversion was greater with the p-TSA catalyst. A kinetic model was developed treating the esterification as a second order reversible reaction for the homogeneous system using p-TSA catalyst and the heterogeneous system using ZnA/SG was expressed in Langmuir Hinshelwood Hougen Watson model. Compared to the proposed models, the experimental values fitted quite well.

Ling and Geankoplis (1958) were studied on the esterification of isobutyl alcohol and oleic acid. The temperature effect, variation of the concentration of the catalyst (sulfuric acid) and molar ratio (alcohol/oleic acid) were investigated. The observation results of these parameters were compared with the results of the reactions using n-butyl alcohol. A second order expression was derived for the reaction to represent the experimental data.

Esterification of the free fatty acids in sunflower oil catalyzed by sulfuric acid with methanol was examined by Martin et al., 2007. Two different catalyst concentrations (5 wt% and 10 wt%) and six different molar ratios (10:1, 20:1, 40:1, 60:1, 80:1, 114.6:1) are studied. Kinetic model was found for the forward reaction as the first order, and for the reverse reaction as the second order.

A different experimental setup was used by Fernandes et al. (2008) for esterification of oleic acid with methanol in presence of the sulfuric acid catalyst, a reactor coupled with an adsorption column. Reaction temperature was higher than boiling points of both methanol and water to evaporate the water produced during the reaction. A condenser (water and methanol condense) placed above the

adsorption column, after passing the adsorption column water free methanol returned to the reactor. This water free system shifted the equilibrium to the desired FAME side of the reaction. Yield was 88.2%, using the traditional batch reactor system, but with a new system, yield was achieved as 99.7%.

The esterification of oleic acid with methanol using sulfuric acid and p-toluenesulphonic acid catalysts at elevated temperatures followed a second order reversible rate expression. According to Unnithan and Tiwari (1987), the esterification of a mixture of fatty acids containing mainly oleic and linoleic acids with methanol at elevated temperatures using sulfuric acid as catalyst also followed the same kinetics as that of pure oleic acid. p-Toluenesulphonic was found to be a better catalyst than H_2SO_4 for fatty acid esterification with methanol.

3.2. Esterification Studies with Heterogeneous Catalysts

In the study of Lee et al. (2010), a comparison of Amberlyst 15 and Amberlyst BD20 (both heterogeneous catalysts) is made by esterification of soybean oil, oleic acid and trap grease. It was found that the activity of Amberlyst BD20 remained the same with recycling however the activity of Amberlyst 15 decreased during recycling when the free fatty acid contents of oils were 50% and 99.8%. It was observed that the inhibition effect of water was great on activity of Amberlyst 15. This phenomenon was explained by the evaluation of the SEM images of Amberlyst 15 and Amberlyst BD20. Since Amberlyst BD20 had fewer pores, it was deemed to have more desirable performance in reducing the inhibition by water of the esterification.

Marchetti and Errazu (2008) studied on the esterification of the pure oleic acid using different alcohols (such as ethanol anhydrous, ethanol 96%, 1-propanol, 2-propanol and butanol) in presence of various catalysts (solid resins, zeolite and enzymes). The different effects of the parameters such as alcohol's carbon chain length, the presence of water and the location the OH group were investigated. The enzyme Lipozyme CALB had an emerging position among other catalysts studied, showing highest activity and higher final conversion (98%) after reaction time of 3 days. It was found that the presence of water was shifting the final conversion to a lower level as a negative effect. It was also obtained that, the OH group location in the alcohol used had a significant effect on the final conversion value.

Pouilloux et al. (1999) studied the preparation of monoglycerides in the presence of ion-exchange resins (K1481 “gel”, Amberlyst 15 “macroporous”, Amberlyst 16 “macroporous”, Amberlyst 31 “gel”) by using glycerol and fatty acids. The study showed that since the strong salivation on the sulfonic groups of the resins, the strong adsorption of glycerol before the reaction inhibited esterification of oleic acid. Without modifying the selectivity, the swelling of the resin in the oleic acid favoured the reaction. The elimination of water by using a molecular sieve was successful. The increase of hydrocarbon chain length of fatty acid decreased the reaction rate because of the smaller accessibility to the active sites in pores of the catalysts. Excess glycerol favoured the monoglyceride formation but lowered the degree of acid conversion.

Mouloungui et al. (1993) studied esterification of oleic acid and methanol in presence of supercritical carbon dioxide by using p-TSA, K2411 and K1481 as catalysts in the presence of solid p-TSA monohydrate and the reaction was in pseudo homogeneous phase. Kinetics of the oleic acid - methanol esterification with p-TSA was described as pseudo homogeneous reaction with the first order. The chemical activity was limited by external diffusion and desorption of reactants and products with solid catalysts.

Yadav and Mehta (1994) studied on the preparation of phenethyl acetate and cyclohexyl acetate by using heterogeneous catalysis such as Filtrol-24, Amberlyst-15, sulphated zirconia, heteropolyacids. For comparison, concentrated sulfuric acid and DTPA (homogenous) were also employed. Excess acid was used and the mole ratios of acid to alcohol were changed in the range of 1:1 and 5:1. Between the mole ratios of 1:1 and 1:3, the reaction was the second order and at larger ratios, it becomes pseudo-first order and independent of the mole ratio. The activities of catalysts were put in order as Amberlyst-15 = DTPA, Filtrol-24, sulfated zirconia, DTPA/silica, DTPA/carbon for both phenethyl alcohol and cyclohexanol.

Esterification of free fatty acids (low quality or waste raw materials) with methanol was studied by Santacesaria et al. (2007) in a tubular packed bed reactor using sulfonic acid resin catalyst, to produce biodiesel. Acidified soybean oil (with oleic acid) was used as the raw material. The alcohol acid feed ratio, overall feed flow rate and temperature effects were examined.

Goodwin Jr. et al. (2008) studied the catalytic performance of the esterification and transesterification of three thermally robust solid catalysts: titania zirconia (TiZ), sulfated zirconia (SZ), and tungstated zirconia (WZ). Tricaprylin, oleic acid and caprylic acid were reacted with anhydrous methanol and ethanol. The most active catalyst was fresh sulfated zirconia (SZ) for both of these reactions, but catalyst was not easily regenerated.

The kinetic model of the oleic acid subcritical methanol esterification with zinc acetate catalyst was studied by Hou et al. (2010). Effects of the temperature, pressure, reaction time and molar ratio of oleic acid to methanol on conversion were examined in a batch type autoclave. Oleic acid conversion reached 0.95 under the conditions of 6MPa, 220°C, 1wt% catalyst, and four times of stoichiometric amount alcohol as excess. According to the kinetic model; the reaction order was calculated as 2.2.

Bélafi-Bakó et al. (2004) carried out esterification reactions of fusel oil and oleic acid in presence of immobilised Novozym 435 lipase enzyme as a biocatalyst to investigate the effects of the water content, temperature, substrate concentration and molar ratio (oleic acid/alcohol) on the ester yield. For elimination of the water, which has a negative effect on the conversion, a pervaporation system was used. The system was found to be suitable to achieve 99.8% conversion. The final oleochemical ester obtained was an environmental-safe biolubricant which didn't have aquatic toxicity.

Esterification of butanoic acid and oleic acid with n-butanol and oleyl alcohol in presence of hexane was studied by Zaidi et al. (2002) and nylon-immobilized lipase from *Candida rugosa* was used as catalyst. They showed that synthesis of various short chain and long chain fatty acid esters was possible by using nylon immobilized lipase from *C. rugosa* in hexane. And the rate equation was ping-pong bi-bi mechanism with two substrate inhibition.

All the studies investigated above are classified and tabulated in Table 3.1 (homogeneous catalysts without kinetic study), Table 3.2 (heterogeneous catalysts without kinetic study), Table 3.3 (homogeneous catalysts with kinetic study), Table 3.4 (heterogeneous catalysts with kinetic study) and Table 3.5 (heteropolyacid catalysts with kinetic study).

Raw material variety is necessary for each industrial sector. Most effective, cheaper or more environmentally friendly raw materials are searched every day.

In the biolubricant industry, nowadays, low molecular weight alcohols are used as esterification of fatty acid esters. Generally methyl alcohol is the common low molecular alcohol used for the production. In this project, production of fatty acid esters with good lubricity starting with high molecular weight alcohols or diols was aimed. The lubricity performance of these esters was tested.

The production of biobased products from low cost raw materials would make biobased production cost more competitive than petroleum based products. Using fatty acid mixtures of oils was a new trend and this project focused on these fatty acid mixtures. There are so many studies with low molecular weight alcohols and different pure fatty acids or fatty acid mixtures of different oils (Aranda et al. (2007), Mouloungui et al. (1993), Lee et al. (2010), Santacesaria et al. (2007)).

The studied fatty acids showed differences for different locations because of the dominating vegetable oil. Dominating vegetable oil in İzmir was olive oil, so in this project esterification was studied on fatty acid mixtures obtained from olive oil refinery. According to our knowledge, there was no study on fatty acids produced from soap stock in the literature. Effects of temperature, catalyst loading amount, initial mole ratios of alcohol to fatty acid were investigated and also kinetic model was studied.

Sulfuric acid was chosen as homogeneous catalysts in spite of its disadvantages of separation from the system, because it is the most commonly used catalyst in esterification reactions and cheap. To use solid catalysts could eliminate the separation problem from reaction mixture, so in our experimental studies, Amberlyst 15 was used as solid catalyst. Unfortunately the production of esters between fatty acid mixture with different alcohols (1,2-propanediol, ethylene glycol, glycerin and 1-butanol) were not observed since the inhibition of the by product water on the activity of Amberlyst 15.

Table 3.1 Literature survey on the esterification reactions catalyzed by homogeneous catalysts without kinetic studies.

Author	Acid	Alcohol	Catalyst
Unnithan and Tiwari 1987	Oleic Acid	Methanol	p-TSA
Mouloungui and Lacaze-Dufaure 2000	Oleic Acid	2-Ethyl Hexanol	p-TSA, Uncatalyst
Fernandes et al. 2008	Oleic Acid	Methanol	Sulfuric Acid

Table 3.2 Literature survey on the esterification reactions catalyzed by heterogeneous catalysts without kinetic studies.

Author	Acid	Alcohol	Catalyst
Pouilloux et al. 1999	Oleic Acid	Glycerol	K1481, Amberlyst 16, Amberlyst 31
Marchetti and Errazu 2008	Oleic Acid	Ethanol, 1-Propanol, 2-Propanol, Butanol	Zeolite, Enzym
Mouloungui et al. 1993	Oleic Acid	Methanol	K2411, K1481, p-TSA
Belafi-Bako et al. 2004	Oleic Acid	Fusel oil ³	Novezym 435
Lee et al. 2010	Soy Bean Oil, Oleic Acid, Trap Grease	Methanol	Amberlyst 15, Amberlyst BD 20
Goodwin Jr. et al. 2008	Tricaprylin, Oleic Acid, Caprylic Acid	Methanol	Titania Zirconia, Sulfated Zirconia, Tungstated Zirconia

³ Fusel oil is a by-product of distilleries, composed of ethanol, propanol, isoamyl alcohol, isobutyl alcohol, isopropyl alcohol.

Table 3.3 Literature survey on the esterification reactions catalyzed by homogeneous catalysts with kinetic studies.

Author	Acid	Alcohol	Catalyst	Kinetic
Ling and Geankoplis 1958	Oleic Acid	Isobutyl	Sulfuric Acid	2nd order
Aranda et al. 2007	Palm Fatty Acid	Methanol	Methanesulfonic Acid, Sulfuric Acid, Phosphoric Acid, Tricloroacetic Acid	1st order with respect to FA
Bart et. al. 1994	Levunilic Acid	n-Butanol	Sulfuric Acid	1st order with respect to each component
Martin et. al. 2007	Sun Flower Oil	Methanol	Sulfuric Acid	1st order for forward reaction, 2nd order for the reverse reaction

Table 3.4 Literature survey on the esterification reactions catalyzed by heterogeneous catalysts with kinetic studies.

Author	Acid	Alcohol	Catalyst	Kinetic
Santacesaria et al. 2007	Acidified Soybean Oil	Methanol	Sulfonic Acid Resin Catalyst	2nd order
Hou et al. 2010	Oleic Acid	Subcritical Methanol	Zinc Acetate	Order of reaction is 2,2
Zaidi et al. 2001	Butanoic Acid, Oleic Acid	n-Butanol, Oleyl Alcohol	Nylon Immobilised Lipase from <i>Candida Rugosa</i>	Ping-pong bi-bi mechanism with two substrate inhibition
Bhatia et al. 2004	Palmitic Acid	Isopropanol	p-TSA, ZnA/SG	Langmuir Hinshelwood Hougén Watson Model

Table 3.5 Literature survey on the esterification reactions catalyzed by heteropolyacid catalysts with kinetic studies.

Author	Acid	Alcohol	Catalyst	Kinetic
Yadav and Mehta 1994	Acetic Acid	Phenethyl Alcohol, Cyclohexanol	Filtrol-24, Amberlyst-15, Sulphated Zirconia, Heteropolyacids, Sulfuric Acid, DTPA	2nd order, pseudo-first order ⁴

⁴ For initial mole ratios of acid to alcohol between 1:1 and 3:1, reaction order is 2nd order, for initial mole ratios of acid to alcohol higher than 3:1, reaction rate is pseudo-first order

4. EXPERIMENTAL STUDY

4.1 Materials

1- Butanol

One of the alcohols used in the experiments is 1-butanol supplied from Sigma-Aldrich. The properties are given in Table 4.1.1.

Table 4.1.1 The properties of 1-butanol

Manufacturer	Fluka (Sigma-Aldrich)
Molecular formula	C ₄ H ₁₀ O
Molar mass	74.12 g/mol
Appearance	colourless liquid
Purity	99 %
Density	0.81 g/cm ³ (298 K)
Melting point	183K
Boiling point	389-391 K
Solubility in water	7.7 g/100 mL (20 °C)
Refractive index (<i>n_D</i>)	<i>n</i> _{20/D} 1.399

Calcium Chloride

Calcium chloride was used in the experiments for eliminating water from final product before distillation which was supplied from Merck. The properties are given in Table 4.1.2.

Table 4.1.2 The properties of calcium chloride

Manufacturer	Merck
Molecular formula	CaCl ₂
CAS number	10043-52-4
Appearance	White, 6-14 mm granules
Purity	≥ 90 %
Molar mass	110.98 g/mol
Density	2.15 g/cm ³ (293K)
Melting point	1045 K
Boiling point	>1872 K
Solubility in water	(293 K) 740 g/l
pH value	8 - 10 (100 g/l, H ₂ O, 293 K)
Water absorption capacity (24 hrs., 80 % relative humidity)	≥ 20 %

Glycerin

One of the alcohols used in the experiments is glycerin supplied from Kimetsan. The properties are given in Table 4.1.3.

Table 4.1.3 The properties of glycerin

Manufacturer	Kimetsan
Molecular formula	$C_3H_5(OH)_3$
CAS number	56-81-5
Molar mass	92.10 g/mol
Appearance	colourless liquid
Purity	99 %

Methanol

The other alcohol used in the experiments is methanol supplied from UNY Chemical Materials. The properties are given in Table 4.1.4.

Table 4.1.4 The properties of methanol

Manufacturer	UNY Chemical Materials
Molecular formula	CH_3OH
Molar mass	32.04 g/mol
Appearance	colourless liquid
Density	$0.790-0.792 \text{ g/cm}^3$ (293 K)
Boiling point	337-338 K
Refractive index (n_D^{20})	1.3280-1.3300

1,2 Propanediol

The final alcohol used in the experiments is 1,2 propanediol supplied from Merck. The properties are given in Table 4.1.5.

Table 4.1.5 The properties of 1,2 Propanediol

Manufacturer	Merck
Molecular formula	C ₃ H ₈ O ₂
CAS number	57-55-6
Appearance	clear, colorless, odorless liquid
Purity	99 %
Molar mass	76.09 g/mol
Density	1.036-1.037 g/cm ³ (293K-277 K)
Melting point	254 K
Boiling point	461 K (1013 hPa)
Solubility in water	(293 K) miscible in all proportions
pH value	6 - 8 (100 g/l, H ₂ O, 293 K)

Sodium Carbonate

Sodium carbonate was used as neutralizer for the samples taken from the reactor in experimental studies and supplied from Merck. The properties are given in Table 4.1.6.

Table 4.1.6 The properties of sodium carbonate

Manufacturer	Merck
Molecular formula	Na ₂ CO ₃
CAS number	497-19-8
Appearance	White solid, hygroscopic
Purity	99.5 %
Molar mass	105.99 g/mol
Density	2.53 g/cm ³ (293 K)
Melting point	1137 K
Boiling point	1873 K (decomposition)
Solubility in water	220g/l (293 K)
pH value	11.5 (50 g/l, H ₂ O, 298 K)

Sulfuric Acid

The homogeneous catalyst used in the experiments is sulfuric acid supplied from Merck. The properties are given in Table 4.1.7.

Table 4.1.7 The properties of sulfuric acid

Manufacturer	Merck
Molecular formula	H ₂ SO ₄
CAS number	7664-93-9
Appearance	clear, colorless, odorless liquid
Purity	95-97 %
Molar mass	98.08 g /mol
Density	1.84 g/cm ³ (293K)
Melting point	253 K
Boiling point	618 K
Solubility in water	(293 K) soluble
pH value	0.3 (49 g/l, H ₂ O, 298 K)

Fatty Acid Mixture

Fatty acid mixture used for the esterification reaction with different alcohols is supplied from BALSARI Yağ Sanayi Ltd. Şti. Fatty acid mixtures includes 62% oleic acid, 29% palmitic acid, 6% linoleic acid by weight percent and it was obtained from soap stock which is a by product of the olive oil refinery plant of Tariş A.Ş.

4.2 Experimental Setup and Procedure

Experimental setup

The schematic diagram of the experimental setup for reaction studies is shown in Figure 4.2.1.

The reactor consisted of a three-necked Pyrex flask of 1000cm³ capacity fitted with a reflux condenser, a thermocouple and a sampling device. The reaction temperature is stabilized by the temperature control. The reaction mixture was magnetically stirred at about 600 rpm.

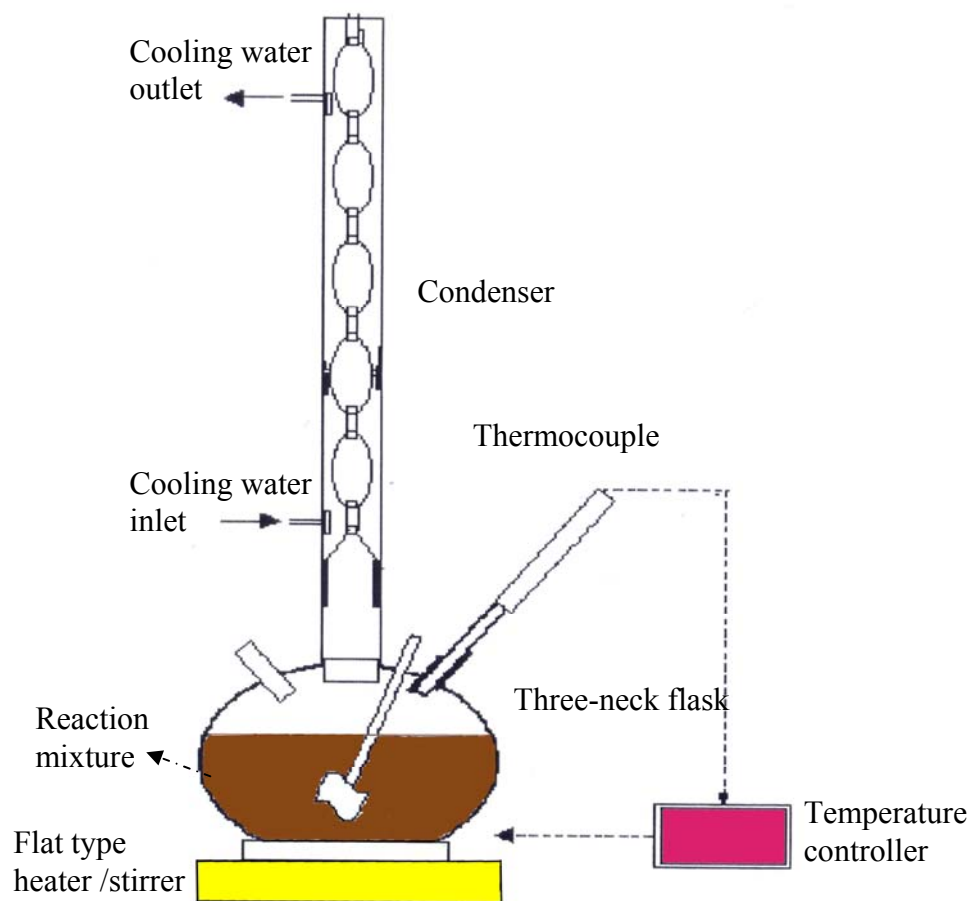


Figure 4.2.1 The experimental setup

Experimental procedure

The experimental procedure is given as below:

1. The condenser cooling water circulation gets started.
2. The predetermined amount of FAMOO is charged to the reactor and heated to the reaction temperature.
3. The alcohol is heated to the reaction temperature.
4. The alcohol and the catalyst are added to the reactor.
5. At regular intervals, 1 ml of samples are withdrawn from the reactor for analysis.

6. Samples are neutralized with Na_2CO_3 .
7. Organic phase is withdrawn by an injector and cooled.
8. Samples of the withdrawn organic phase are analyzed by GC.

4.3 Analysis

The samples are analyzed using a gas chromatograph. Conditions for analysis on the gas chromatograph are given in Table 4.3.1 and one of the chromatograms is illustrated in Figure 4.3.1.

Table 4.3.1 Gas chromatograph operation conditions

Gas Chromatograph	Hewlett-Packard 5890GC Series II
Column	DEGS
Column Dimensions	6ft* 1/8" (stainless steel)
Carrier Gas	Nitrogen
Injection Temperature (°C)	270
Detector	FID
Detector Temperature (°C)	300
Sample Amount (μl)	0.2
Oven Temperature (°C)	170 (isothermal)
Attenuation	7
Total Analysis Time (min)	110

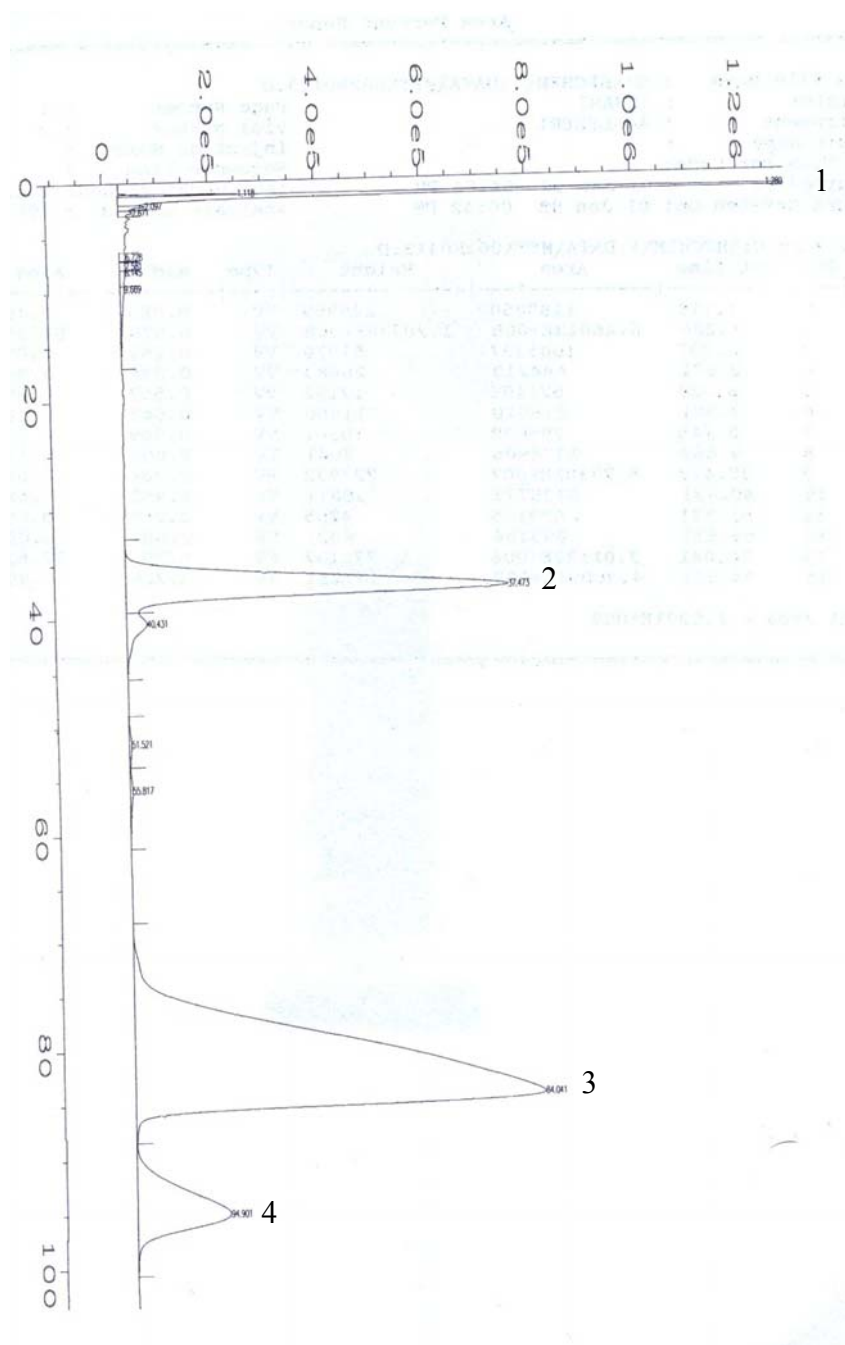


Figure 4.3.1 A sample chromatogram

1) 1-butanol, 2) palmitic acid butyl ester, 3) oleic acid butyl ester, 4) linoleic acid butyl ester

5. RESULTS AND DISCUSSION

5.1 Experiments with Different Alcohols

Different alcohols, mono, di and triols were studied with fatty acid mixture. 1-butanol was selected as mono alcohol, 1,2-propanediol and ethylene glycol were diols, glycerin was triols. Sulfuric acid was used as the homogeneous catalyst and as the solid catalyst, an acidic ion exchange resin, Amberlyst 15 was selected.

Unfortunately, no esters could be observed by esterification with 1,2-propanediol, ethylene glycol, glycerin and 1-butanol when Amberlyst 15 was used as the catalyst.

Also, the esters with 1,2 propanediol and ethylene glycol could not be obtained using sulfuric acid. Since the produced amount of esters using 1-butanol by sulfuric acid catalyst was very large when compared with glycerin, all experimental studies were carried out with 1-butanol. The experiments performed with different alcohols and different catalysts are tabulated in Table 5.1.1.

Table 5.1.1 Preliminary experiments ($\frac{n_{\text{alcohol}}}{n_{\text{FAMOO}}} = 6$, $T = 378 \text{ K}$)

Experiment Name	Alcohol	Catalyst	Ester Peaks
Set1 Experiment 1	1,2 - propanediol	Amberlyst 15	-
Set1 Experiment 2	1- butanol	Amberlyst 15	-
Set1 Experiment 3	Ethylene glycol	Amberlyst 15	-
Set1 Experiment 4	Glycerin	Amberlyst 15	-
Set1 Experiment 5	1,2 - propanediol	H ₂ SO ₄	-
Set1 Experiment 6	1- butanol	H ₂ SO ₄	Observed
Set1 Experiment 7	Ethylene glycol	H ₂ SO ₄	-
Set1 Experiment 8	Glycerin	H ₂ SO ₄	Observed

The effect of temperature, catalyst loading amount and alcohol/fatty acid mol ratios on conversion of esterification reaction between fatty acid mixture and 1-butanol were investigated.

The experiments between Set1 Experiment 1 and Set1 Experiment 8 were performed for deciding the alcohol and catalyst. Set1 Experiment 9,10 and 11 were performed for investigating the effect of temperature, Set3 experiments were

performed for investigating the effect of catalyst loading amount and Set4 experiments were performed for investigating the effect of initial mole ratio. Set2 experiments were performed for calculating the equilibrium constant and Set6 and Set7 experiments were performed for determining the kinetic model. Set5 was performed in the presence of methanol for checking if the chromatogram of the products were similar with the chromatogram of the FAME standards (see Appendix I).

5.2 Determination of Equilibrium Constant

Set2 experiments were done for the determination of equilibrium constants.

Experiments performed for observing the effect of temperature on equilibrium constants are tabulated in Table 5.2.1. The $n_{\text{alcohol}}/n_{\text{FAMOO}}$ ratio was 6, reaction time was 9.5 hours and agitation speed was 600 rpm for each experiment. Calculation of equilibrium constant and a relationship obtained from the determined equilibrium constants, which represents how K_{eq} changes with temperature, is given at Appendix III.

Table 5.2.1 Experiments for temperature effect on equilibrium constant (catalyst loading amounts, 7wt % sulfuric acid / system).

Experiment Name	FAMOO Volume (ml)	Alcohol		T (K)
		Name	Volume (ml)	
Set2 Experiment 1	157.5	1-butanol	274	363
Set2 Experiment 2	157.5	1-butanol	274	353
Set2 Experiment 3	157.5	1-butanol	274	373
Set2 Experiment 4	157.5	1-butanol	274	383

$$K_a = \left(\frac{\gamma_S^s \gamma_T^t \dots}{\gamma_B^b \gamma_C^c \dots} \right) \left(\frac{x_S^s x_T^t \dots}{x_B^b x_C^c \dots} \right) = K_\gamma K_x \quad 5.2.1$$

For ideal solutions;

$$K_a = \left(\frac{x_S^s x_T^t \dots}{x_B^b x_C^c \dots} \right) = K_x \quad 5.2.2$$

This system was assumed as ideal and K_a was calculated by using mole fractions of components (Smith, 2005). The calculated data (conversion, mole of produced esters and equilibrium constant) are tabulated in Table 5.2.2 and $\ln K$ vs. $1/T$ graph is shown in Figure 5.2.1.

Table 5.2.2 Equilibrium constants, conversion values and mole of esters produced.

	Set2 Experiment 1	Set2 Experiment 2	Set2 Experiment 3	Set2 Experiment 4
T (K)	363	353	373	383
x_A (%)	48.3	43.6	52.7	57.7
N_E (mole)	0.24	0.22	0.26	0.29
K_{Eq}	0.082	0.060	0.107	0.146

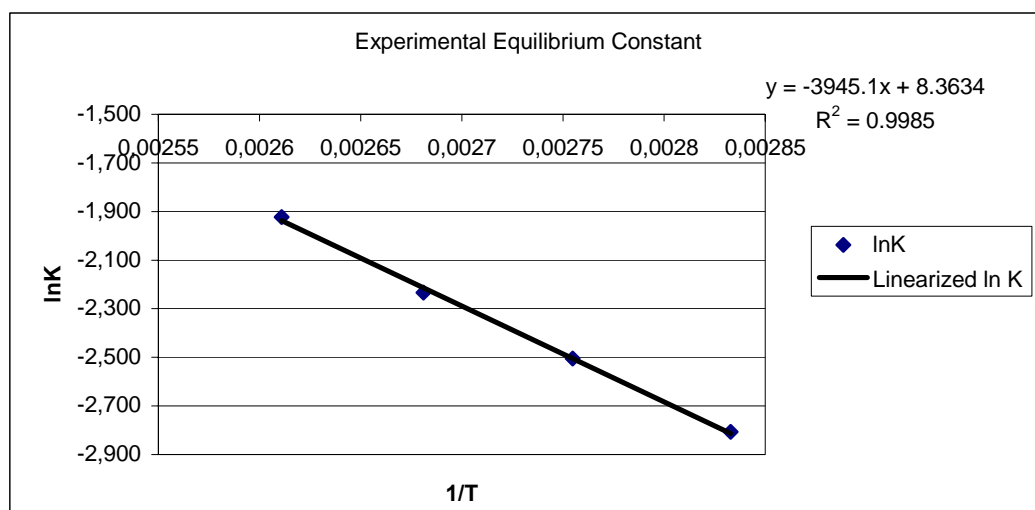


Figure 5.2.1 $\ln K$ vs $1/T$

5.3 Experiments for the Effect of Temperature, Catalyst Loading Amount and Initial Mole Ratio

Experiments performed for observing the effect of temperature on conversions are tabulated in Table 5.3.1. The calculated data (conversion and mole of produced esters) are tabulated in Table 5.3.2 and conversion vs. time graph is shown in Figure 5.3.1.

The $n_{\text{alcohol}}/n_{\text{FAMOO}}$ ratio was 6, reaction time was 6 hours and agitation speed was 600 rpm for each experiment.

Table 5.3.1 Experiments for temperature effect on conversion (catalyst loading amounts, 7wt % sulfuric acid / system).

Experiment Name	FAMOO Volume (ml)	Alcohol		T (K)
		Name	Volume (ml)	
Set1 Experiment 9	157.5	1-butanol	274	378
Set1 Experiment 10	157.5	1-butanol	274	368
Set1 Experiment 11	157.5	1-butanol	274	358

Table 5.3.2 Conversion values and mole of esters produced

Time (min)	Set1 Experiment 9		Set1 Experiment 10		Set1 Experiment 11	
	x_A (%)	N_E	x_A (%)	N_E	x_A (%)	N_E
5	45.0	0.23	40.5	0.20	36.5	0.18
20	47.6	0.24	43.3	0.22	38.0	0.19
60	51.5	0.26	47.3	0.24	43.9	0.22
120	52.9	0.26	48.7	0.24	45.5	0.23
240	54.4	0.27	49.6	0.25	45.7	0.23
360	54.7	0.27	49.9	0.25	46.2	0.23

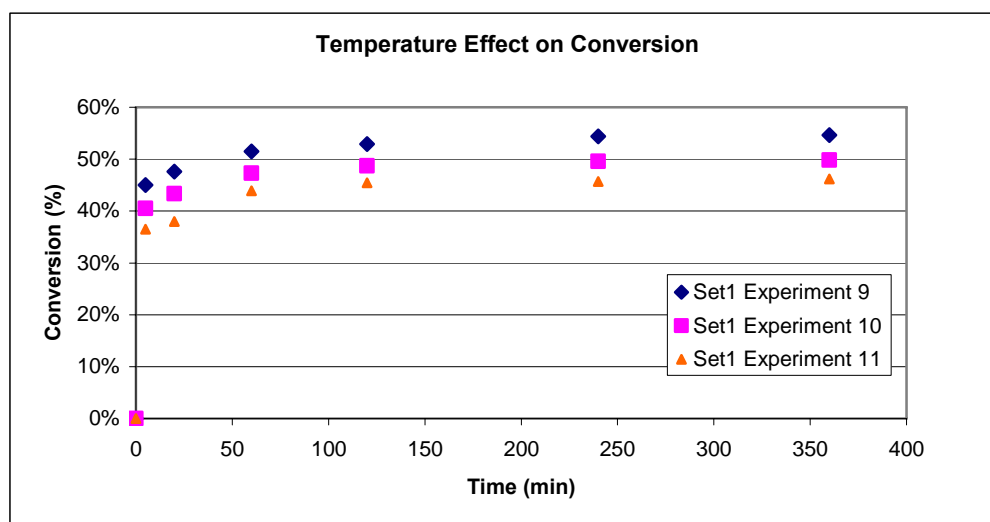


Figure 5.3.1 Temperature effect on conversion

Experiments performed for observing the effect of catalyst loading on conversions are tabulated in Table 5.3.3. The calculated data (conversion and mole of produced esters) are tabulated in Table 5.3.4 and conversion vs. time graph is shown in Figure 5.3.2.

The $n_{\text{alcohol}}/n_{\text{FAMOO}}$ ratio was 6, reaction time was 6 hours and agitation speed was 600 rpm for each experiment.

Table 5.3.3 Experiments for catalyst loading effect on conversions (reaction temperatures, 368 K).

Table 5.3.3 Experiments for catalyst loading effect on conversions (reaction temperatures, 368 K). Experiment Name	FAMOO Volume (ml)	Alcohol		Catalyst Amount (%)*
		Name	Volume (ml)	
Set1 Experiment 10	157.5	1-butanol	274	7
Set3 Experiment 1	157.5	1-butanol	274	1
Set3 Experiment 2	157.5	1-butanol	274	0.5

*wt % sulfuric acid / system

Table 5.3.4 Conversion values and mole of esters produced

Time (min)	Set1 Experiment 10		Set3 Experiment 1		Set3 Experiment 2	
	x_A (%)	N_E	x_A (%)	N_E	x_A (%)	N_E
5	40.5	0.20	38.7	0.19	28.6	0.14
20	43.3	0.22	41.1	0.21	30.5	0.15
60	47.3	0.24	43.8	0.22	33.8	0.17
120	48.7	0.24	46.6	0.23	37.3	0.19
240	49.6	0.25	48.0	0.24	40.5	0.20
300	-	-	48.1	0.24	41.3	0.21
360	49.9	0.25	48.6	0.24	41.4	0.21

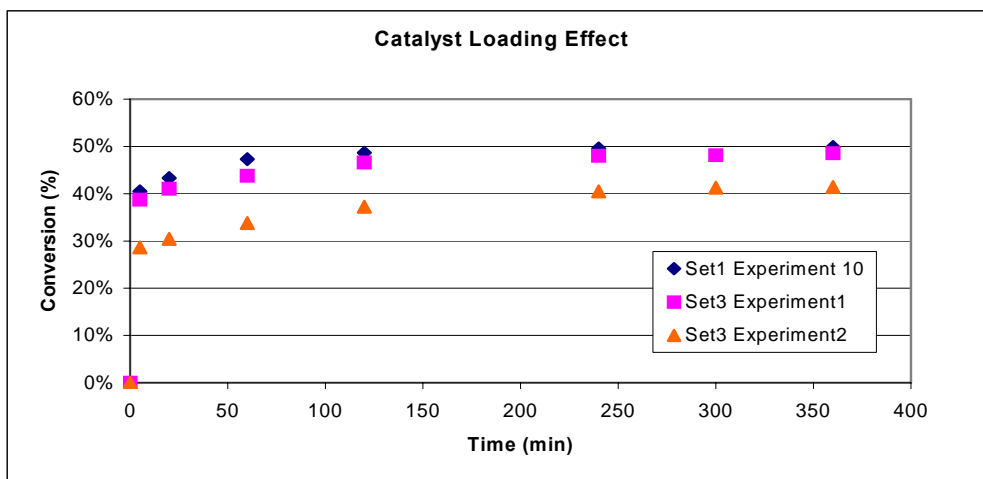


Figure 5.3.2 Catalyst loading effect on conversion

Experiments performed for observing the effect of $n_{\text{alcohol}}/n_{\text{FAMOO}}$ ratio on conversions are tabulated in Table 5.3.5. The calculated data (conversion and mole of produced esters) are tabulated in Table 5.3.6 and conversion vs time graph is shown in Figure 5.3.3.

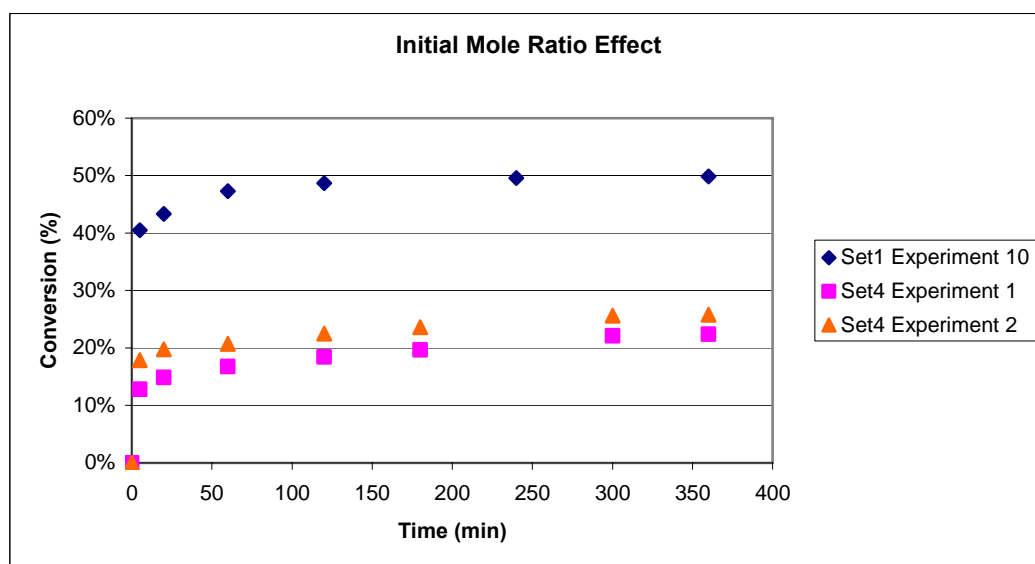
The reaction time was 6 hours and agitation speed was 600 rpm for each experiment.

Table 5.3.5 Experiments for initial $n_{\text{alcohol}}/n_{\text{FAMOO}}$ ratio effect on conversions (catalyst loading amounts, 7wt % sulfuric acid / system and reaction temperature, 368K).

Experiment Name	FAMOO Volume (ml)	Alcohol		$n_{\text{alcohol}}/n_{\text{FAMOO}}$
		Name	Volume (ml)	
Set1 Experiment 10	157.5	1-butanol	274	6
Set4 Experiment 1	157.5	1-butanol	46	1
Set4 Experiment 2	157.5	1-butanol	59.3	1.3

Table 5.3.6 Conversion values and mole of esters produced

Time (min)	Set1 Experiment 10		Set4 Experiment 1		Set4 Experiment 2	
	x_A (%)	N_E	x_A (%)	N_E	x_A (%)	N_E
5	40.5	0.20	12.8	0.06	27.5	0.14
20	43.3	0.22	14.9	0.07	28.8	0.14
60	47.3	0.24	16.8	0.08	29.5	0.15
120	48.7	0.24	18.5	0.09	30.4	0.15
180	-	-	19.6	0.10	32.1	0.16
240	49.6	0.25	-	-	-	-
300	-	-	22.1	0.11	33.1	0.17
360	49.9	0.25	22.4	0.11	33.3	0.17

**Figure 5.3.3** Initial mole ratio effect on conversion

To evaluate the peaks obtained by GC, pure butyl esters should be used to check palmitic, oleic and linoleic butyl esters. But, pure butyl esters were not supplied. So the esters of oleic, palmitic and linoleic acids with methanol were studied and the products were analyzed using a GC; and the results were checked with the GC analysis obtained from the standard of methyl esters of the fatty acids. Thus, the same GC response was assumed (See Appendix I). The initial mole ratio of methanol/ fatty acid mixture was 2, used catalyst amount was 1ml H_2SO_4 , reaction temperature was 328K, the reaction time was 3 hours and agitation speed was 600 rpm for the esterification reaction of methanol with fatty acid mixture.

5.4 Kinetic Study

Set1 experiments were performed for both determination of temperature effect on conversion and determination of the kinetic model. Kinetic model was expected as 1st order or 2nd order with respect to literature; however the model did not fit to proposed models. There was not a significant difference between the final conversion at 360min and the conversion at 5 min. Marchetti and Errazu (2008) obtained the similar results with 1-butanol and oleic acid esterification reaction as our study and also there was a similar conversion graph with Figure 5.4.1 in the study of Bart et al. (1994) with levulinic acid and n-butanol. Hence, initial reaction rates were used to define the kinetic model.

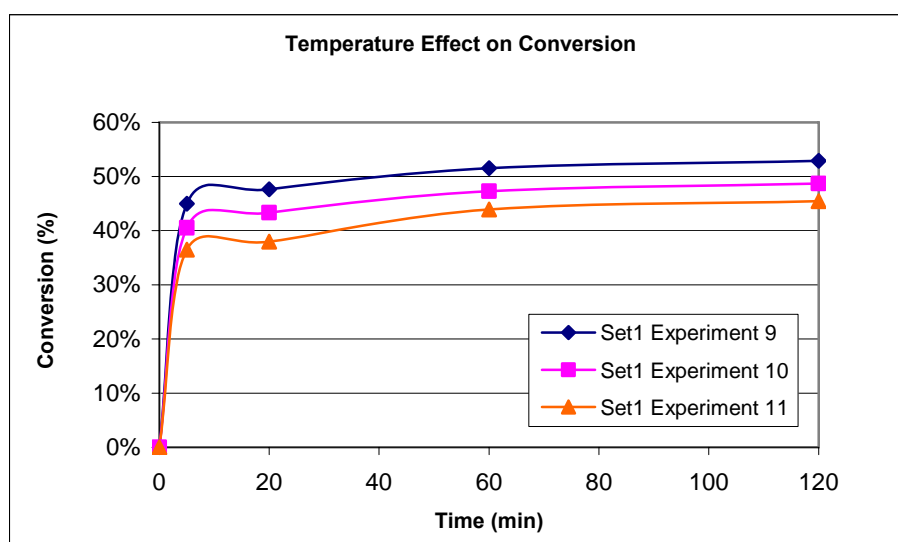


Figure 5.4.1 Temperature effect on conversion

Experiments done for observing initial reaction rates are tabulated in Table 5.4.1. The reaction time was 5 min and agitation speed was 600 rpm for each experiment.

According to the assumption of the initial reaction rate method; initially the reaction behaves as irreversible (Fogler, 1999). Sample is withdrawn at very earlier time of reaction (nearly at initial), so it is assumed that at that time no backward reaction occurred. Kinetic model is shown by equation 5.4.3 and the experimental reaction rate values are calculated using equation 5.4.4. The error value, square of difference between experimental reaction rate and calculated reaction rate from kinetic model, was 0.0001, constants k_0 , a and b were

calculated as 1.81, 0.66, 0.58 respectively. Activation energy was calculated as 12.79kJ/mol using Arrhenius equation. Kinetic model is shown at Table 5.4.2.

$$r = k[C_{A0}]^a [C_{B0}]^b \quad 5.4.1$$

$$k = k_0 e^{-\frac{E}{RT}} \quad 5.4.2$$

$$r = k_0 e^{-\frac{E}{RT}} [C_{A0}]^a [C_{B0}]^b \quad 5.4.3$$

$$r = \frac{[C_{A, t=5 \text{ min}}] - [C_{A0}]}{5 - 0} \quad 5.4.4$$

Experimental and calculated r values are plotted in figure 5.4.2. Plot shows the goodness of model predictions.

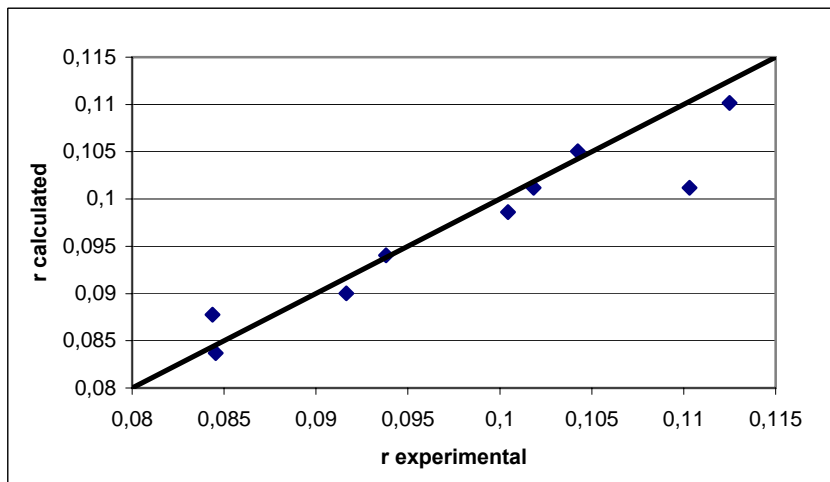


Figure 5.4.2 $r_{\text{calculated}}$ and $r_{\text{experimental}}$ comparison

Table 5.4.1 Experiments for initial reaction rates (catalyst loading amounts, 7wt % sulfuric acid / system)

Experiment Name	FAMOO Volume (ml)	Alcohol		T (K)	$n_{\text{alcohol}} / n_{\text{FAMOO}}$
		Name	Volume (ml)		
Set1 Experiment 9	157.5	1-butanol	274	378	6
Set1 Experiment 10	157.5	1-butanol	274	368	6
Set1 Experiment 11	157.5	1-butanol	274	358	6
Set6 Experiment 1	157.5	1-butanol	91.4	358	2
Set6 Experiment 2	157.5	1-butanol	91.4	368	2
Set6 Experiment 3	157.5	1-butanol	91.4	378	2
Set7 Experiment 1	157.5	1-butanol	137.5	358	3
Set7 Experiment 2	157.5	1-butanol	137.5	368	3
Set7 Experiment 3	157.5	1-butanol	137.5	378	3

Table 5.4.2 Kinetic Model

	T (K)	C_{A0} (mol/L)	C_{B0} (mol/L)	$r_{\text{experimental}}$ (mol/L.s)	r (mol/L.s)
Set1 Experiment 11	358	1.16	6.95	0.0845	$r = 1.81e^{\frac{-12796}{RT}} [C_{A0}]^{0.66} [C_{B0}]^{0.58}$
Set6 Experiment 1		2.01	4.02	0.0844	
Set7 Experiment 1		1.70	5.09	0.0916	
Set1 Experiment 10	368	1.16	6.95	0.0938	
Set6 Experiment 2		2.01	4.02	0.1004	
Set7 Experiment 2		1.70	5.09	0.1018	
Set1 Experiment 9	378	1.16	6.95	0.1042	
Set6 Experiment 3		2.01	4.02	0.1125	
Set7 Experiment 3		1.70	5.09	0.1103	

5.5 Performance Tests and Results

At the end of the batch experiment a mixture of esters, 1-butanol and fatty acids was obtained. Esters must be separated from this mixture to test the performance of esters if they could be used as biolubricants or as additives for biolubricants. Performance tests were performed by OPET A.Ş.

Distillation

Thus the separation process was chosen as vacuum distillation (Figure 5.5.2). Before the distillation, CaCl_2 particles were added to the mixture and waited for 24 hours for sorption of water on to CaCl_2 particles. Separation of the added CaCl_2 from the mixture suction filtration was done by using Büchner funnel, blue band filter paper, Büchner flask and vacuum pump (Figure 5.5.1).



Figure 5.5.1 Suction filtration

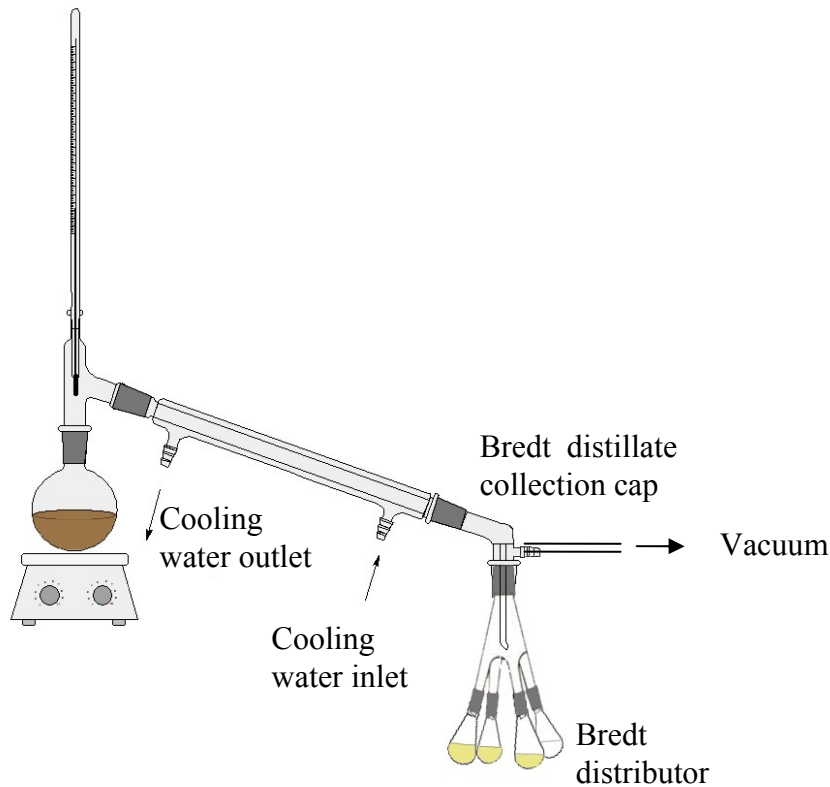


Figure 5.5.2 Vacuum distillation set up.

Performance Tests

Physical Tests

Viscosity

Viscosity describes the internal resistance of a fluid. Viscosity grade is an identifier property for classification of lubricants hence it is important in lubricity market. Each organization uses a different kinematic viscosity range numbering system. The most common classification systems are those of the SAE⁵, AGMA⁶, and ISO⁷. In these performance tests, kinematic viscosity was measured according to ASTM D 445. The measured viscosity values at 313 K and 373 K are tabulated in Table 5.5.1.

⁵ Society of Automotive Engineers

⁶ American Gear Manufacturers Association

⁷ International Organization for Standardization

Viscosity Index

Viscosity index is an arbitrary measure for the change of kinematic viscosity with temperature which is a quality indicator for lubricating oils. The viscosity index scale is set up by the SAE. The temperatures chosen arbitrarily for reference are 100 °F (40 °C) and 210 °F (100 °C). The original scale only stretched between zero (worst oil, naphthenic) and 100 (best oil, paraffinic) but since the conception of the scale better oils have also been produced, leading to viscosity indexes greater than 100. In these performance tests viscosity was calculated according to ASTM D 2270. The calculated viscosity index values are tabulated in Table 5.5.1.

Refractive Index

ASTM D 2887 test method covers the measurement of refractive index of transparent and light-colored hydrocarbons in the range of 1.3300 to 1.5000 at temperatures from 20 to 30°C by manual (optical/mechanical) or automatic (digital) procedure. The measured refractive index values of butyl esters are tabulated in Table 5.5.1.

Demulsification

ASTM D 1401 test method covers measurement of the ability of petroleum oils or synthetic fluids to separate from water. It is mainly developed specifically for steam turbine oils, but there is a wide range of application fields now. Data obtained from demulsification test are tabulated in Table 5.5.1.

Foaming Tendency Determination

ASTM D 892 test method covers the determination of the foaming characteristics of lubricating oils at 24°C and 93.5°C. Means of empirically rating the foaming tendency and the stability of the foam are described. Test values are tabulated in Table 5.5.1.

Phosphorus, Sulfur, Calcium, Zinc and Chlorine

ASTM 6481 test method covers the quantitative determination of additive elements in unused lubricating oils. It determines chlorine, phosphorus, sulfur, calcium, and zinc in lubrication oils by energy dispersive X-ray fluorescence spectroscopy. The measured P, S, Cl, Ca, Zn values are tabulated in Table 5.5.1.

Four Ball

Antiwear properties of esters were tested according to ASTM D 4172 and measured values are tabulated in Table 5.5.1.

Copper Strip Test

ASTM D 130 test method covers the determination of the corrosiveness to copper of aviation gasoline, aviation turbine fuel, automotive gasoline, cleaners (Stoddard) solvent, kerosine, diesel fuel, distillate fuel oil, lubricating oil, and natural gasoline or other hydrocarbons having a vapor pressure no greater than 124 kPa (18 psi) at 37.8°C. The produced esters are classified according to ASTM D 130 and the classification is tabulated in Table 5.5.1.

Total Acid Number

ASTM D 664 test method covers the measurement of acid concentration in a nonaqueous solution. It is determined as the amount of potassium hydroxide base required to neutralize the acid in one gram of an oil sample. The measured total acid number is tabulated in Table 5.5.1.

Base Number

This test method covers the determination of basic constituents in petroleum products by titration with perchloric acid in glacial acetic acid. The measured base number is tabulated in Table 5.5.1.

ASTM Color

ASTM D 1500 test method covers the visual determination of the color of a wide variety of petroleum products, such as lubricating oils, heating oils, diesel fuel oils, and petroleum waxes. The description of the color was tabulated in Table 5.5.1.

Table 5.5.1 Performance test results

Propety	Unit	Method	Results
Viscosity 40°C	cSt	ASTM D 445	7.2095
Viscosity 100°C	cSt	ASTM D 445	2.4116
Viscosity Index		ASTM D 2270	179
ASTM Color		ASTM D 1500	2,5
Total Acid Number	mgKOH/g	ASTM D 664	46.85
Base Number	mgKOH/g	ASTM D 2896	4.41
Copper Strip Corrosion		ASTM D 130	1a
Foaming Characteristics		ASTM D 892	10/0
Demulsification		ASTM D 1401	40/40/0 10 min
Refraktif Indeks		ASTM D 1218	1.3819
FOUR BALL	Newton		>1000
FOUR BALL	AW- μ m		784.24
P	%wt	ASTM D 6481	0
S	%wt	ASTM D 6481	0.001
Cl	%wt	ASTM D 6481	0.039
Ca	%wt	ASTM D 6481	0.001
Zn	%wt	ASTM D 6481	0.002
Mixing with water			Not miscible

Performance of the produced butyl esters was tested and the observed results were listed below.

Positive Results

Four ball test results showed that the produced butyl esters can be used as additive for cutting oils because of their positive effect on wear.

Complete separation occurred in 20 min. Miscibility with water is not a desirable property for lubricating oils so mixing with water test results were so good.

The produced butyl esters can be used as hydraulic oils according to foaming characteristics test results, no foam observed.

The produced butyl esters do not contains phosphorus, sulfur, calcium, and zinc.

Negative results

The produced butyl esters contain chlorine. Before vacuum distillation, CaCl_2 particles were added to the mixture and waited for 24 hours for sorption of water on to CaCl_2 particles. This process is the chlorine source.

The viscosity of produced butyl esters is low; it is similar to biodiesel viscosity.

Total acid number is high which will affect the oxidation stability in a negative manner. Hence the conversion of the esterification reaction between 1-butanol and fatty acid mixture was not 100%, the product contained fatty acids. These unreacted fatty acids can be eliminated to reduce the total acid number.

5.6 Discussion

The esterification reaction of fatty acid mixture obtained from soap stock and 1-butanol was studied in a batch reactor.

Acidic ion exchange resin Amberlyst 15 was studied but because of the limited operation conditions of the ion exchange resins; the esters were not produced so, more effective acid catalyst, sulfuric acid was preferred.

Experiments were performed with three different catalyst loading amounts, 0.5 wt% sulfuric acid / system, 1.0 wt% sulfuric acid / system, 7.0 wt% sulfuric acid / system for investigation of the catalyst loading effect. Conversion had a significant change with twice the catalyst amount. With 0.5 wt% sulfuric acid / system amount, achieved conversion was 41.4% and the conversion was 48.6% with 1.0 wt% sulfuric acid / system amount. When the catalyst amount increased, time to achieve equilibrium conversion decreased. Another experiment was done for 15 times of the first catalyst loading amount (Set1 Experiment 10) and although there was a change in conversion, it was not so much from twice catalyst amount (Set3 Experiment 1). By using 7.0wt% sulfuric acid / system catalyst amount, the achieved conversion was 49.9%. In the study of Bart et. al. (1994) catalyst amount effect the system in the same manner. Maximum conversion was obtained at 383 K and 7.0 wt% sulfuric acid / system.

Equilibrium constants were calculated (system assumed to be ideal solution) at different temperatures and it was seen that equilibrium constants were increasing with increasing temperature.

Experiments were performed with three different temperatures, 358 K (Set1 Experiment 11), 368 K (Set1 Experiment 10), 378 K (Set1 Experiment 9) for investigation of the temperature effect. Between 358 K and 368 K change in conversion was 8% for 10 K change in temperature and it was 9.6% for 10 K change in temperature between 368K and 378 K. The conversion was increased with temperature and also the rate of increase in conversion with temperature was bigger at higher temperatures. Bart et. al. (1994), Yadav and Mehta (1994) and Bhatia et. al.(2004) were obtained similar trends. According to these data the reaction could be named as an endothermic reaction.

Effect of acid / alcohol initial molar ratios was also studied with three experiments, 1:1 (Set4 Experiment 1), 1:1.3 (Set4 Experiment 2), 1:6 (Set2 Experiment 10). At Set4 Experiment 1, 1:1 was chosen to see the effect of Le Chatelier's principle, 1:1.3 was chosen to see if small amount of excess alcohol was able to favour the reaction to the ester side and 1:6 was chosen to simplify the kinetic study ($C_{B0} \gg C_{A0}$, no significant change in C_{B0} , $r = k \cdot C_A$). The conversions were 22.4 %, 33.3 % and 49.9 % for 1:1, 1:1.3 and 1:6 respectively. So, excess alcohols favored the reaction to the desired ester side, similar results were obtained by Hou et. al.(2010) and Bhatia et. al.(2004).

According to performance tests, the produced butyl esters can be used as hydraulic oils or as additive to cutting oils.

6. CONCLUSION

In the study of esterification reaction of fatty acid mixture of olive oil with 1-butanol effects of the temperature, the catalyst loading amount and the initial mole ratio was investigated as;

Conversion of fatty acid mixture increased with increasing temperature and also the rate of increase in conversion with temperature was higher at high temperatures.

Conversion of fatty acid mixture increased with increasing catalyst loading amount and time to achieve the equilibrium conversion decreased with increasing the catalyst amount.

Conversion of fatty acid mixture increased with increasing initial mole ratio of alcohol / fatty acid mixture.

The reaction rate was expressed only forward reaction rate with an order of 1.24.

An alternative base material for hydraulic oils and an alternative additive for cutting oils were produced.

7.0 FUTURE WORK

The esterification reaction of fatty acid mixture obtained from soap stock and 1-butanol was studied in a batch reactor, but a distillation column can be used instead of a batch reactor.

Esterification is a reversible reaction and proceeds to completion only if the water is continuously removed during the course of the reaction. In this study water was not removed from the reaction mixture, but a molecular sieve can be used in a reactive distillation column.

Amberlyst 15 could not be used because of the limited operation conditions of the ion exchange resins, but an alternative solid catalyst can be used.

The effect of catalyst loading amount was investigated by changing the catalyst amounts, but uncatalysed esterification reaction can be performed.

REFERENCES

- Aranda, D. A. G., Santos, R. T. P., Tapanes, N. C. O., Ramos, A. L. D., Antunes, O. A. C.,** 2007, Acid catalyzed homogenous esterification reaction for biodiesel production from palm fatty acids, *Catalysis Letters*, 122:20-25.
- Bahatia, S., Mohamed, A. R., Aafagi, R.,** 2004, Kinetics of esterification of palmitic acid with isopropanol using p-toluene sulfonic acid zinc ethanoate supported over silica gel as catalysts, *Journal of Chemical Technology and Biotechnology* 79:1127-1134.
- Bart, H. J., Reidetschlager, J., Schatka, K., Lehmann, A.,** 1994, Kinetics of esterification of levulinic acid with n-butanol by homogeneous catalysis, *Industrial & Engineering Chemistry Research*, 33:21-25.
- Bauer, A.R., Garbe, D., Surgurg, H.,** 1990, *Common Fragrance and Flavor Materials*, VCH, New York Second Revised Edition.
- Bélafi-Bakó, K., Dörmo, N., Bartha, L., Ehrenstein, U., Gubicza, L.,** 2004, Manufacture of environmental-safe biolubricants from fusel oil by enzymatic esterification in solvent-free system, *Biochemical Engineering Journal*, 21:229-234.
- Benefuel,** 2010, *Technology – Bio-Lubricant Processing*,
http://www.benefuel.net/bio_lube.html (Last Access 04.02.2010)
- Chemical Book,** 2010, N-BUTYL LINOLEATE basic information,
http://www.chemicalbook.com/ProductChemicalPropertiesCB7190454_EN.htm, (Last Access: 21.02.2010).
- Fernandes, F. A. N., Lucena, I. L., Silva, G. F.,** 2008, Biodiesel production by esterification of oleic acid with methanol using water adsorption apparatus, *Industrial & Engineering Chemistry Research*, 47:6885-6889.
- Fischer, E. and Speier, A.** (1895), Darstellung der Ester, *Chemische Berichte* 28: 3252–3258.

REFERENCES (continued)

- Fogler, H. S.**, 1999, Elements of Chemical Reaction Engineering, Chemical Process Design and Integration, New Jersey, Prentice Hall, Third Edition ,239.
- Gandhi, N.N., Sawant, S.B., Joshi, J.B.**, 1995, Specificity of a lipase in ester synthesis: effect of alcohol. *Biotechnology Programe*, 11:282–287.
- Goodwin Jr., J. G., Lopez, D. E., Bruce, D. A., Furuta, S.**, 2008, Esterification and transesterification using modified-zirconia catalysts, *Applied Catalysis A: General*, 339:76-83.
- Hou, X., Song, C., Qi, Y., Deng, T., Qin, Z.**, 2010, Kinetic model for the esterification of oleic acid catalyzed by zinc acetate in subcritical methanol, *Renewable Energy*, 35:625-628.
- IENICA, Interactive European Network for Industrial Crops and Applications**, 2004, Biolubricant Market Data Sheet, <http://www.ienica.net/marketdatasheets/biolubricantsmds.pdf> (Last Access 23.02.2010).
- Lee, J. S., Kim, D.K., Park, J.Y.**, 2010, Esterification of free fatty acids using water tolerable Amberlyst as a heterogeneous catalyst, *Bioresource Technology*, 101:62-65.
- Ling, W.C. and Geankoplis, C.J.**, 1958, Liquid-phase esterification of oleic acid and isobutyl alcohol, *ACS Legacy Archive*, 50:939-942.
- Marchetti, J.M. and Errazu, A.F.**, 2008, Comparison of different heterogeneous catalysts and different alcohols for the esterification reaction of the oleic acid, *Fuel*, 87:3477-3480.
- Martin, M. A., Berrios, M., Siles, J., Martin, A.**, 2007, A kinetic study of the esterification of free fatty acids in sunflower oil, *Fuel*, 86:2383-2388.
- Mouloungui, Z. and Lacaze-Dufaure, C.**, 2000, Catalysed and uncatalysed esterification reaction of oleic acid with 2-ethyl hexanol, *Applied Catalysis A: General*, 204:223-227.

REFERENCES (continued)

- Mouloungui, Z., Vieville, C., Gaset, A.,** 1993, Esterification of oleic acid by methanol catalyzed by p-toluenesulfonic acid and cation-exchange resins K2411 and K1481 in supercritical carbon dioxide, *Industrial & Engineering Chemistry Research*, 32:2065-2068.
- NIST, National Institute of Standards and Technology,** 2010, (Z)-9-Octadecenoic acid butyl ester, <http://webbook.nist.gov/cgi/cbook.cgi?ID=142-77-8&Units=SI&cTC=on>, (Last access: 21.02.2010).
- Otera, J.,** 2003, Esterification Methods, Reactions and Applications, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 303.
- Pouilloux, Y., Abro, S., Vanhove, C., Barrault, J.,** 1999, Reaction of glycerol with fatty acids in the presence of ion-exchange resins preparation of monoglycerides, *Journal of Molecular Catalysis A: Chemical* 149:243-254.
- Rayalu, S. S., Dubey, N., Chatti, R. V., Joshi, M. V., Labhsetwar, N. K., Devotta, S.,** 2007, Effect of heteropolyacid and its route of incorporation on the photocatalytic properties of zeolite-based materials, *Current Science*, 93:1376-1382.
- Rohm and Haas,** 2010, Esterification of fatty acids, http://www.amberlyst.com/fatty_acids.htm, (Last access: 21.02.2010).
- Santacesaria, E., Tesser, R., Serio, M. D., Guida, M., Gaetano, D., Agreda, A. G.,** 2007, Kinetics and mass transfer of free fatty acids esterification with methanol in a tubular packed bed reactor: A key pretreatment in biodiesel production, *Industrial & Engineering Chemistry Research*, 46:5113-5121.
- Shahidi, F.,** editor, 2005, *Bailey's Industrial Oil and Fat Products*, John Wiley & Sons, Inc., 2, New Jersey, 411.
- Smith, R.,** 2005, *Chemical Process Design and Integration*, London, John Wiley and Sons, 109.

REFERENCES (continued)

- The Good Scent Company**, 2010, butyl oleate, <http://www.thegoodscentcompany.com/data/rw1013711.html>, (Last Access: 21.02.2010).
- Unnithan, U. R. and Tiwari, K. K.**, 1987, Kinetics of esterification of oleic acid and mixtures of fatty acids with methanol using sulphuric acid and p-toluenesulphonic acid as catalysts, 1128, Kinetics of esterification of palmitic acid with isopropanol using p-toluene sulfonic acid zinc ethanoate supported over silica gel as catalysts, S. Bahatia, A.R. Mohamed, R. Aafagi (Eds), *Journal of Chemical Technology and Biotechnology* 79.
- Volodin, A. M., Bedilo, A. F.**, 2000, Unusual manifestation of benzene radical cations in ESR spectra on sulfated zirconia, *Journal of Molecular Catalysis A: Chemical*, 158: 405–408.
- Wikipedia**, 2010, fatty acids, http://en.wikipedia.org/wiki/Fatty_acids, (Last Access: 21.02.2010).
- Wikipedia**, 2010, fatty acids, http://en.wikipedia.org/wiki/Linoleic_acid, (Last Access: 21.02.2010).
- Wikipedia**, 2010, fatty acids, http://en.wikipedia.org/wiki/Oleic_acid, (Last Access: 21.02.2010).
- Wikipedia**, 2010, fatty acids, http://en.wikipedia.org/wiki/Palmitic_acid, (Last Access: 21.02.2010).
- Yadav, G. D. and Mehta, P. H.**, 1994, Heterogeneous catalysis in esterification reactions: Preparation of phenethyl acetate and cyclohexyl acetate by using a variety of solid acidic catalysts, *Industrial & Engineering Chemistry Research*, 33:2198-2208.
- Zaidi, A., Gainer, J. L., Carta, G., Mrani, A., Kadiri, T., Belarbi, Y., Mir, A.**, 2002, Esterification of fatty acids using nylon-immobilized lipase in n-hexane: kinetic parameters and chain-length effects, *Journal of Biotechnology*, 93:209-216.

APPENDIX I

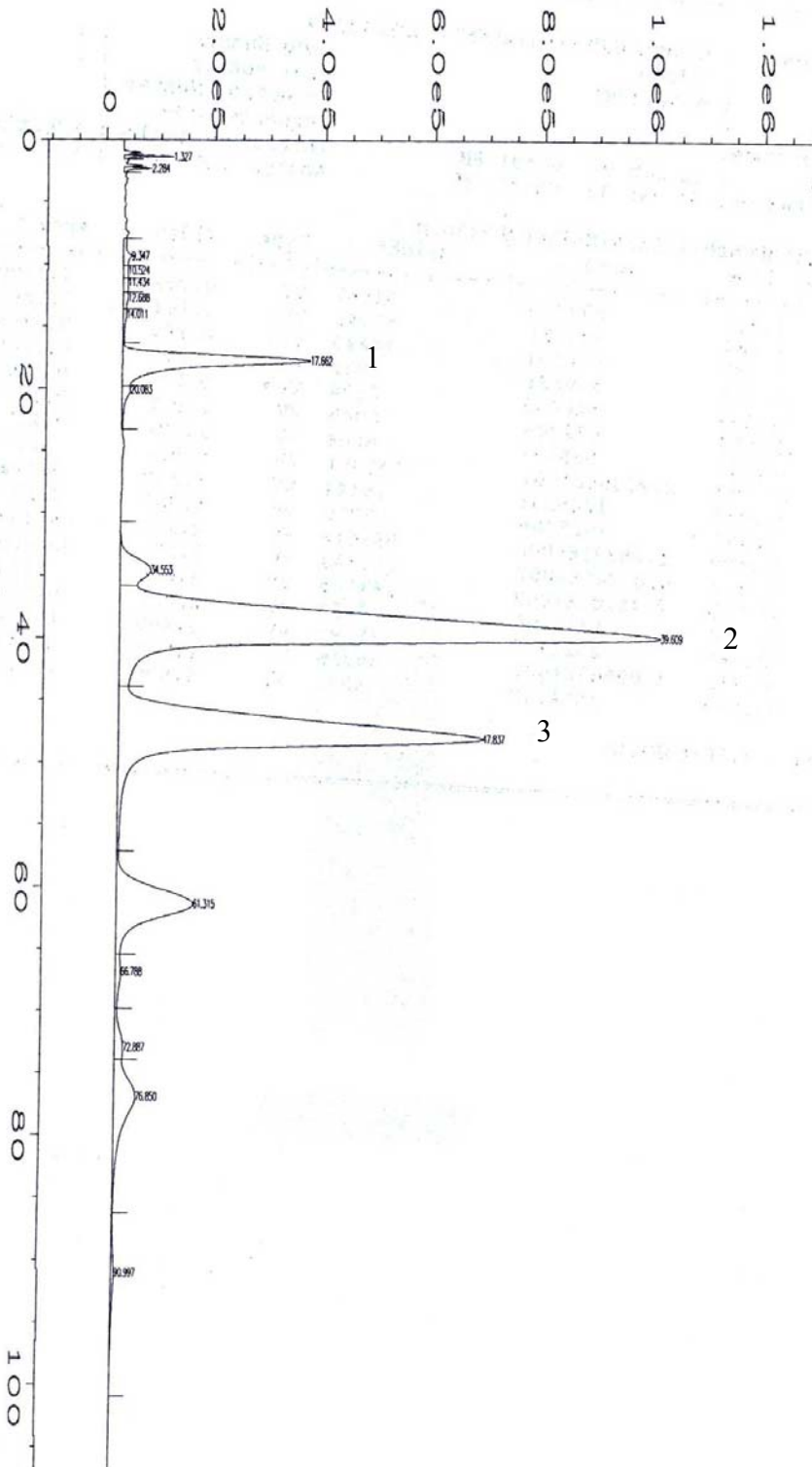


Figure AI.1 Olive oil methyl esters, control analysis

1) palmitic acid methyl ester, 2) oleic acid methyl ester, 3) linoleic acid methyl ester

APPENDIX I (Continued)

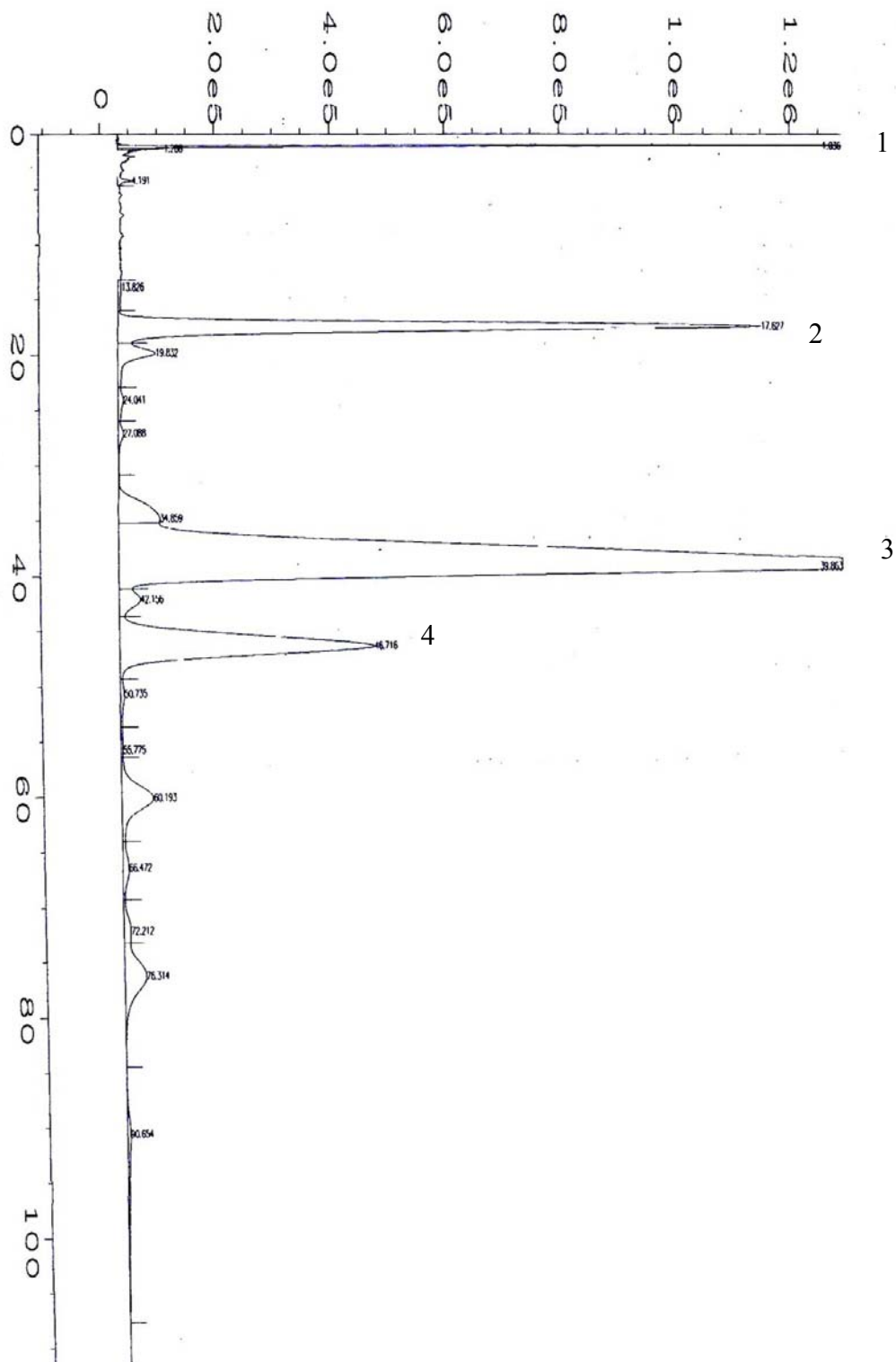


Figure AI.2 Set5 control experiment (FAMOO-methanol esterification)
1) 1-butanol, 2) palmitic acid methyl ester, 3) oleic acid methyl ester, 4) linoleic acid methyl ester

APPENDIX II

In the experiments, the weight percentages of 1-butanol, butyl linoleate, butyl oleate and butyl palmitate were measured by the GC analysis. Using these experimental data and taking into consideration the reaction, conversion of fatty acids to butyl esters were calculated. The reaction and molar amounts of components according to reaction stoichiometry are as follows;

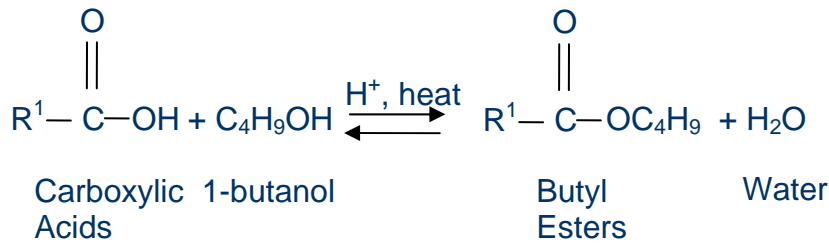


Table AII.1 Moles of the esterification reaction

	MW (g/mole)	Initial	Final
Total Fatty Acid (A)	265.9	N_{A0}	$N_{A0} * (1-x_A)$
1-butanol	74	N_{B0}	$N_{B0} - N_{A0} * x_A$
Butyl esters (E)	320	-	$N_{A0} * x_A$
Water (W)	18	-	$N_{A0} * x_A$

$$\frac{A_{Ester}^{\%}}{A_{Butanol}^{\%}} = \frac{\text{Mass of Ester}}{\text{Mass of Butanol}}$$

$$\frac{\text{Mass of Ester}}{\text{Mass of Butanol}} = \frac{N_{A0} X_A MW_{Ester}}{(N_{B0} - N_{A0} X_A) MW_{Butanol}}$$

$$X_A = \frac{\frac{A_{Ester}^{\%}}{A_{Butanol}^{\%}} N_{B0} MW_{Butanol}}{N_{A0} MW_{Ester} + \frac{A_{Ester}^{\%}}{A_{Butanol}^{\%}} MW_{Butanol} * N_{A0}}$$

AII.1

According to equation AII.1 conversions of a fatty acid mixture were calculated for every withdrawn sample.

Sample calculation;
Set1 Experiment 9

$$N_{A0}=0.5, N_{B0}=3, \frac{A_{Ester}^{\%}}{A_{Bu\ tan\ ol}^{\%}} = \frac{30.15}{69.51}$$

$$X_A = \frac{\frac{30.15}{69.51} * 3 * 74}{0.5 * 320 + \frac{30.15}{69.51} * 74 * 0.5} = 0.55$$

APPENDIX III

Experimental equilibrium constant calculation;

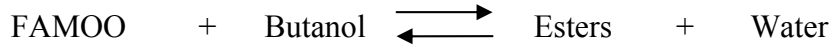


Table AIII.1 Moles and mole fractions of the esterification reaction.

Moles at initial	N_{A0}	N_{B0}	0	0
Moles at equilibrium	$N_{A0}(1 - X_{Eq})$	$(N_{B0} - N_{A0}X_{Eq})$	$N_{A0}X_{Eq}$	$N_{A0}X_{Eq}$
Total moles at equilibrium	$(N_{A0} - N_{A0}X_{Eq}) + (N_{B0} - N_{A0}X_{Eq}) + N_{A0}X_{Eq} + N_{A0}X_{Eq}$ $= N_{A0} + N_{B0}$			
Mole fractions at equilibrium	$\frac{N_{A0}(1 - X_{Eq})}{N_{A0} + N_{B0}}$	$\frac{N_{B0} - N_{A0}X_{Eq}}{N_{A0} + N_{B0}}$	$\frac{N_{A0}X_{Eq}}{N_{A0} + N_{B0}}$	$\frac{N_{A0}X_{Eq}}{N_{A0} + N_{B0}}$

$$M = \frac{N_{B0}}{N_{A0}}$$

$$K_{Eq} = \frac{\frac{N_{A0}X_{Eq}}{N_{A0} + N_{B0}} \times \frac{N_{A0}X_{Eq}}{N_{A0} + N_{B0}}}{\frac{N_{A0}(1 - X_{Eq})}{N_{A0} + N_{B0}} \times \frac{N_{A0}(M - X_{Eq})}{N_{A0} + N_{B0}}} = \frac{X_{Eq}^2}{(1 - X_{Eq})(M - X_{Eq})}$$

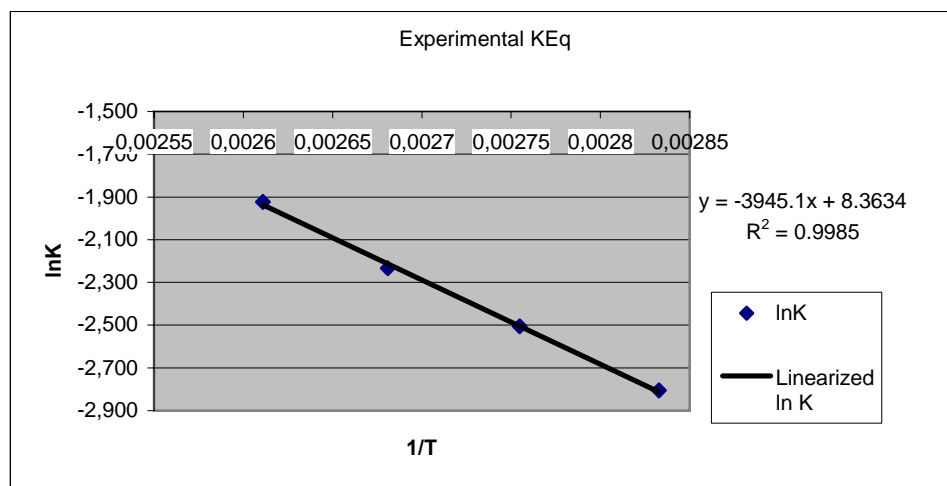
Set 2 experiments were performed for the calculation of the experimental equilibrium constant. It was assumed that after 9.5 hours, the system reached the equilibrium. Equilibrium conversions and equilibrium constants were calculated (see TableAIII.2).

$$X_{A, at t=9.5h} = X_{Eq}$$

Table AIII.2 Equilibrium constant values

	T	1/T	X_{Eq}	K_{Eq}	$\ln(K_{Eq})$
Set2 Exp1	363	0.00275	0.48	0.082	-2.505
Set2 Exp2	353	0.00283	0.43	0.060	-2.806
Set2 Exp3	373	0.00268	0.52	0.107	-2.233
Set2 Exp4	383	0.00261	0.57	0.146	-1.923

Using the calculated data Figure AIII.1 was drawn and using a regression analysis, a relationship between temperature and equilibrium constant was obtained.

**Figure AIII.1** Experimental K_{Eq} .

$$\ln(K_{Eq}) = m \times \frac{1}{T} + \ln A$$

$$y = -3945.1x + 8.3634$$

$$R^2 = 0.9985$$

All experiments are checked if they reached the equilibrium conversion. Only conversion of Set 1 Experiment 11 was above the equilibrium conversion which is impossible. It may be an experimental error.

RESUME

ESİN DENİZ AYAN

(Chemical Engineer)

Adress : 155 Sok. No:48 D:8 Hakimevleri /İZMİR
 GSM. : 0.535 407 38 22
 E - mail : esin_deniz982@hotmail.com



PERSONAL DATA

- Date of Birth : 31.03.1982
- Place of Birth : Keşan/EDİRNE
- Driving License : B class
- Marital Status : Married

EDUCATION

- **Ege University – Graduate School of Natural and Applied Sciences**
(English)
Chemical Engineering Master Program İZMİR 2009-2010
- **Ege University** (English)
Chemical Engineering Department (GPA 73.6: /100) İZMİR 2000-2004
- **Turgutlu Halil Kale Science High School**
(GPA: 4.39/5) MANİSA 1997-2000
- **Konak Anadolu High School** (English) İZMİR 1995-1997
- **Yozgat Anadolu High School** (English) YOZGAT 1993-1995

COMPLETED PROJECTS

- **Research Project**
“Chloride Formation by Using Idle Car Batteries”
MEF Dershaneleri 9th Research Project Competition 1999-2000
Jury Private Price at Branch of Chemistry

WORK EXPERIENCE

- **KİMSEL KİMYA** Sales Manager 01.12.2007- 03.12.2008
Determining sales goals. Reporting and controlling sales activities. Stock planning according to stock turnover. Product responsibility of Thor-Biocides, Evonik-Tego and DOW-HEC. Key account customers sales representation.
- **KİMSEL KİMYA** Regional Sales Manager 03.08.2007-01.12.2008
Answering technical questions of customers. Enlarging the sales of customers and adding new customers. Regular visits to customers.

- **KTS Kimya Tekstil Sanayi** Sales Engineer 02.05.2005- 01.02.2007
Answering technical questions of customers. Enlarging the sales of customers and adding new customers. Regular visits to customers. Stock planning according to stock turnover and purchasing.
- **ŞAHAN A.Ş. Toz Boya** Production Chief 15.09.2004-24.03.2005
Production planning, raw material control, production and quality control as a production chief.
- **TÜPRAŞ** Training 07.07.2003-01.08.2003
Crude Oil Unit
- **DYO İZMİR** Training 22.07.2002-16.08.2002
Car refinish paints

SKILLS

Languages: English (advanced)
Computer: MS Windows and Office Applications, Visual Basic, IntelliCAD, ChemCAD

CERTIFICATES & LICENCES

Technical Training of Biocides, THOR Chemie, Italy 2008
Quality: ISO 9001:2000, Ege University 2004
Contemporary Operational Approaches of Marketing, Ege University, 2004

INTERESTS

Hobbies; chess, volleyball

REFERENCES

- **Hakan Küçükşenlik**
Kimsel Kimya
General Manager
Tel: 02164446474
- **Kaan ŞENÇALIŞ**
KTS Kimya
Owner of the company
Tel: 05327919736
- **Semra Öztürk**
Şahan Toz Boya A.Ş.
Production Manager
Tel: 02328538739