

# **RECLAMATION OF USED LUBRICATING OILS USING MAGNETIC NANOPARTICLES AND CAUSTIC SODA**

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By

Timur Ashirov

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RECLAMATION OF USED LUBRICATING OILS USING MAGNETIC  
NANOPARTICLES AND CAUSTIC SODA

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We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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Hasan Tarık Baytekin (Advisor)

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Yunus Emre Türkmen

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Akın Akdağ

Approved for the Graduation School of Engineering and Science:

---

Ezhan Karaşan

Director of the Graduate School

# ABSTRACT

## RECLAMATION OF USED LUBRICATING OILS USING MAGNETIC NANOPARTICLES AND CAUSTIC SODA

Timur Ashirov

M. S. in Materials Science and Nanotechnology

Advisor: H. Tarık Baytekin

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Oils are one of the mostly used lubricants in industry. Chemical oxidation, however, causes depletion of additive materials i.e. antioxidants in lubricants and their usage life time shortens. This causes varnish and sludge problems and leaves behind tons of used oil that loses its functionality. It is reported that more than 600 tons of lubricating oil can be reclaimed from 1000 tons of used oil. One of the reclamation methods is caustic extraction, and has been known for more than 3 decades. Although caustic extraction has a very high potential because of its economic considerations, this method is not fully understood due to lack of research. We have revealed that opposite to the common belief, oxidized oils (used oils) have ester groups in contrary to carboxylic acids. Magnetic nanoparticles ( $\text{Fe}_3\text{O}_4$ ) can be used as a catalyst for hydrolysis of various esters. We have investigated the effect and mechanism of caustic extraction in combination with magnetic iron oxide nanoparticles. Using sodium hydroxide, breaks ester bonds by forming carboxylate salts and alcohols. These carboxylate salts are transferred into water and can be removed by water. Formed alcohol groups can be trapped by drying agents like  $\text{MgSO}_4$ . Further purification of reclaimed oils can be achieved using hexane or similar low molecular weight and inexpensive solvents. According to our results, properties of recovered base oils mostly compete with petroleum based and ester-based synthetic base oil properties.

Keywords: Used lubricants, used oil, magnetic nanoparticles, caustic extraction, oil reclamation

## ÖZET

# KULLANILMIŞ KAYGANLAŞTIRICI YAĞLARIN MANYETİK NANOPARÇACIKLAR VE KOSTİK SODA KULLANILARAK GERİ KAZANILMASI

Timur Ashirov

Malzeme Bilimleri ve Nanoteknoloji, Yüksek Lisans

Advisor: H. Tarık Baytekin

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Yağlar, endüstride en çok kullanılan kayganlaştırıcılardan biridir. Fakat, kimyasal oksitlenme katkı maddelerinin tükenmesine, yani kayganlaştırıcılarda antioksidanların bitmesine ve kullanım ömrünün azalmasına neden olmaktadır. Bu, cilalanma ve tortu oluşumu gibi sorunlara neden olmaktadır ve geriye tonlarca kullanılmış ve işlevini kaybetmiş yağ kalmaktadır. 1000 ton kullanılan yağdan 600 tondan fazla yağın geri kazanılabileceği bildirilmiştir. Geri kazanma yöntemlerinden birisi de kostik ekstraksiyonudur ve bu yöntem 30 yıldan uzun süredir bilinmektedir. Ekonomik nedenlerle kostik ekstraksiyon çok yüksek bir potansiyele sahip olmasına rağmen, bu yöntem araştırmaların yetersizliği nedeniyle tam olarak anlaşılamamıştır. Bu çalışmamızda, yaygın düşüncenin aksine oksitlenmiş baz yağlarda (kullanılmış yağ) karboksilik asit yerine ester oluşturduğunu keşfettik. Manyetik nanoparçacıkların ( $\text{Fe}_3\text{O}_4$ ), çeşitli esterlerin hidrolizi için katalizör olarak kullanıldığı bilinmektedir. Kostik ekstraksiyon işleminde manyetik demir oksit nanoparçacıkları kullanımının etkisini ve mekanizmasını araştırdık. Sodyum hidroksit kullanılması ester bağlarını karboksil tuzları ve alkoller oluşturarak parçalamaktadır. Bu karboksil tuzları suda çözünebilir ve su içinde karıştırılarak uzaklaştırılabilmektedir. Oluşan alkol grupları,  $\text{MgSO}_4$  gibi su tutucu maddelerle uzaklaştırılabilmekte olup, geri kazanılan yağlar hekzan veya benzer ucuz ekstraksiyon solventleri kullanılarak daha fazla arıtılabilmektedir. Sonuçlarımıza göre, geri kazanılan baz yağlarının özellikleri çoğunlukla petrol bazlı ve ester bazlı sentetik baz yağların özellikleri ile rekabet edebilir durumdadır.

Anahtar sözcükler: Kullanılmış kayganlaştırıcılar, kullanılmış yağlar, manyetik nanoparçacıklar, kostik ekstraksiyon, yağların geri kazanılması

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# Table of Contents

<b>1</b>	<b>Introduction .....</b>	<b>1</b>
1.1	Tribological Contacts.....	2
1.2	Tribological Contacts Types .....	2
1.3	Friction.....	4
1.4	Wear.....	6
1.5	Tribological lubrication .....	7
1.6	Organization of thesis .....	8
<b>2</b>	<b>Base Oil Lubricants .....</b>	<b>10</b>
2.1	Classification of Base Oils .....	12
2.2	Refining of Base Oils.....	14
2.3	Base Oils Derived from Crude Oil .....	16
2.3.1	Gas-to-Liquid Base Oils.....	16
2.3.2	Paraffinic Base Oils .....	17
2.3.3	Naphthenic Base Oils.....	17
2.3.4	White Oils .....	18
2.3.5	Very High Viscosity Index Base Oils .....	18
2.3.6	Polyalphaolefins .....	18
2.3.7	Re-refined Base Oils .....	19
2.4	Base oils naming.....	19
2.5	SN 150 Base Oil .....	20
<b>3</b>	<b>Engine Oil Lubricants .....</b>	<b>22</b>
3.1	Additives .....	22
3.1.1	Surface active additives .....	23
3.1.2	Bulk additives .....	26

3.1.3	Zinc dialkyl dithio phosphate (ZDDP) .....	28
3.2	Grades and standards of engine oil lubricants .....	30
3.2.1	Castrol Power 1 4T 10W-40 motorcycle oil .....	31
3.3	Characterization methods of engine oils .....	32
3.3.1	Lubricant base oils and additive characterization methods .....	32
3.3.2	Characterization of ZDDP on surfaces .....	35
3.4	Oxidation of lubricants .....	37
<b>4</b>	<b>Materials &amp; Methods .....</b>	<b>40</b>
4.1	Chemicals used .....	40
4.2	Procedures .....	41
4.2.1	Oxidation of SN150 base oil .....	41
4.2.2	Oxidation of Castrol Power 1 4T 10w-40 motorcycle oil .....	43
4.2.3	Preparation of magnetic iron oxide nanoparticles .....	44
4.2.4	Characterization of Magnetic nanoparticles .....	44
4.2.5	Reclamation of oxidized oils .....	47
4.2.6	Preparation of standard titration solutions for determination of total acid and base numbers .....	48
4.2.7	Titration of samples .....	48
4.3	Analytical techniques .....	48
4.3.1	Infrared spectroscopy .....	49
4.3.2	NMR spectroscopy .....	50
4.3.3	Scanning Electron Microscope .....	50
4.3.4	Zeta Sizer .....	50
<b>5</b>	<b>Results &amp; Discussion .....</b>	<b>51</b>
5.1	Results with magnetic nanoparticles in combination with radical initiators .....	51
5.2	Experiments in combination with caustic soda .....	55
5.2.1	Idea of using sodium hydroxide .....	55

5.2.2	After separation of reusable oil .....	59
5.2.3	Reaction times .....	64
5.3	NMR studies of oil .....	65
5.3.1	NMR spectrum of SN150.....	65
5.3.2	Changes after oxidation of oil .....	66
5.3.3	Changes after caustic treatment.....	67
5.3.4	Comparison with Real Used Engine Oil.....	71
5.4	Titration results.....	74
5.5	Yields of reclamation.....	76
5.6	Summary of this work.....	77
<b>6</b>	<b>Conclusion.....</b>	<b>79</b>
6.1	Advantages of our method .....	79
6.2	Oil oxidation: Carboxylic acids or Esters .....	81
6.3	Other reclamation methods .....	81
<b>7</b>	<b>References .....</b>	<b>1</b>
	<b>Appendices.....</b>	<b>9</b>
	Appendix A.....	9
	Appendix B.....	10
	Appendix C.....	11
	Appendix D.....	12
	Appendix E.....	13
	Appendix F.....	14
	Appendix G.....	15



# List of Tables

Table 2.1 Some physical and chemical properties of hydrocarbons found in base oils [1].....	11
Table 2.2 Description of base oil categorization according to API and ATIEL [8]...	12
Table 2.3 Origins and classifications of common base oils [9].....	14
Table 2.4 Relative amounts of elements in typical crude oil [9].....	15
Table 2.5 Effect of crude oil refining [9]. ....	16
Table 2.6 Characteristics and properties of Group I SN 150 Base oil [21]. ....	21
Table 3.1 Typical lubricating properties of Castrol Power 1 4T 10W-40 motorcycle oil [44]. ....	32
Table 3.2 Assignment of carbonyl peaks identified in IR spectrum given in .....	38
Table 4.1 Carbonyl peak areas of oils with respect to oxidation time. ....	42
Table 4.2 Typical IR absorption peaks of different carbonyl moieties []. ....	49
Table 5.1 Relative peak areas of IR carbonyl region of oil samples given in Figure 5.15.....	64
Table 5.2 Assignment of <sup>1</sup> H NMR peaks of untreated SN150.....	66
Table 5.3 Assignment of <sup>1</sup> H NMR regions changed after oxidation of SN150 BO...67	
Table 5.4 Assignment of peaks for <sup>1</sup> H NMR spectrum of untreated bottom phase that was obtained after the reclamation process where the used oil was treated with only NaOH at 150 °C. ....	69
Table 5.5 Assignment of peaks for <sup>1</sup> H NMR spectrum of bottom phase of reclamation process with NaOH only at 150 °C after neutralization with hydrochloric acid, HCl. ....	71
Table 5.6 Titration results of untreated, oxidized, used, neutralized and rewashed oil. ....	75
Table 5.7 TAN of oxidized base oil and neutralized base oil samples. ....	76
Table 5.8 Weight and percentage yields of reclamation processes at different conditions. ....	77

# List of Figures

Figure 1.1 Subcategories of Tribology: Friction, Lubrication and Wear [1].	1
Figure 1.2 Tribological contact observed in macroscale and in microscale [1].	2
Figure 1.3 Types of tribological contacts categorized according to contact area type [1].	3
Figure 1.4 Types of tribological contacts according to surface type [1].	3
Figure 1.5 Smoothing of rough contact surfaces with increasing of rubbing time [1].	4
Figure 1.6 Stribeck curve of lubrication regimes [3].	6
Figure 2.1 Origin and production route of base oil lubricants (PAO-polyalphaolefins) [9].	13
Figure 2.2 Left: production amounts of different base oil types, Right: production amounts worldwide with respect to regions [9].	14
Figure 2.3 Schematics of crude oil refining process [10-12].	15
Figure 2.4 Chemical structure of PAO6 (top) and PAO2 (bottom) [1].	19
Figure 3.1 Types of automotive engine oil additives according to their functions [1].	23
Figure 3.2 Chemical structure of all forms of ZDDP additive [36].	29
Figure 3.3 ZDDP antiwear film formation on the surface of metal bearing. Adapted from ref 40.	30
Figure 3.4 Mechanism of tribofilm formation on metal surface. Adapted from ref 41.	30
Figure 3.5 A typical ATR-IR spectrum of Castrol Power 1 4T 10w-40 engine oil.	33
Figure 3.6 ZDDP monitoring by time using $^{31}\text{P}$ NMR spectroscopy. Taken from ref. 52.	34
Figure 3.7 SEM images of ZDDP layer after a) 24 hours b) 48 hours c) 72 hours of growth time. Taken from ref. 55.	35
Figure 3.8 Real-time AFM images of ZDDP growth monitoring. Adapted from ref. 60.	36

Figure 3.9 SLIM images of real-time tribofilm growth monitoring on steel sphere surface. Taken from ref. 62.....	37
Figure 3.10 Color changes of lubricating oil during degradation (oxidation) [66]. ...	39
Figure 3.11 IR carbonyl (C=O) absorption region of SN150 base oil oxidized at 200 °C at 1atm for 17 hours in a round bottomed flask (rbf). ....	39
Figure 4.1 IR spectra of SN150 base oil oxidized in PARR 4838 series reactor for 4 hours. ....	42
Figure 4.2 IR spectra of Castrol Power 1 4T 10w-40 engine oil heated at 170 °C for different times. Inset right: magnified IR region of ZDDP additive. Inset left: magnified IR region of PMA based viscosity modifier. ....	43
Figure 4.3 IR spectra of untreated Fe oxide and after reaction with used oil. ....	45
Figure 4.4 EDX spectra of untreated Fe oxide np (top) and after reaction with used oils. ....	46
Figure 4.5 (A), (B) SEM images of synthesized magnetic nanoparticles, (C)-Zeta Sizer measurement result of synthesized magnetic nanoparticles. ....	47
Figure 4.6 Bruker ALPHA Platinum ATR single reflection diamond based ATR spectrometer that was used in this study. Taken from ref #72. ....	50
Figure 5.1 IR spectra of untreated and oxidized SN150 base oil in a flask, in a vial and in the PARR model 4838 reactor.....	52
Figure 5.2 Mechanism of radical formation from AIBN [77]......	53
Figure 5.3 IR spectra of reaction of oxidized SN150 base oil (BO) with magnetic np. ....	54
Figure 5.4 IR spectra of reaction of oxidized SN150 base oil (BO) with ferrocene. ....	54
Figure 5.5 IR spectra of reaction of oxidized SN150 BO with Fe <sub>3</sub> O <sub>4</sub> in presence of AIBN as a radical initiator. ....	55
Figure 5.6 IR spectra of reaction of oxidized base oil with NaOH in presence of magnetic nanoparticles at 120 °C.....	56
Figure 5.7 IR spectra of reaction of oxidized base oil with NaOH only at 120 °C. ....	57
Figure 5.8 IR spectra of reaction of oxidized base oil with NaOH in presence of magnetic np at 150 °C. ....	57
Figure 5.9 IR spectra for comparing effect of magnetic np presence for reclamation process at 120 °C.....	58
Figure 5.10 IR spectra for comparing reaction with NaOH in presence of Fe <sub>3</sub> O <sub>4</sub> at 120 °C and 150 °C.....	59

Figure 5.11 Colors observed for reclaimed oil: 1-BO oxidized at 200 °C for 17 hours, 2-Reclaimed oil (treated with NaOH in the presence of Fe <sub>3</sub> O <sub>4</sub> at 120 °C), 3-Reclaimed oil (treated with NaOH only at 120 °C), 4- Reclaimed oil (treated with NaOH in presence of Fe <sub>3</sub> O <sub>4</sub> at 150 °C), 5- Reclaimed oil (treated with NaOH only at 150 °C), 6-Untreated N150 base oil. ....	61
Figure 5.12 IR spectra of separated oil (2), that is treated with NaOH in presence of Fe <sub>3</sub> O <sub>4</sub> nps at 120 °C (top phase), prior to treatment with MgSO <sub>4</sub> and untreated SN1150 base oil (3).....	61
Figure 5.13 IR spectra of separated oil (2), that is treated with NaOH in presence of Fe <sub>3</sub> O <sub>4</sub> np at 150 °C (top phase), after treatment with MgSO <sub>4</sub> and untreated SN1150 base oil (3).....	62
Figure 5.14 IR spectrum of bottom aqueous phase after reaction with NaOH in presence of Fe <sub>3</sub> O <sub>4</sub> np at 120 °C, after separation. ....	62
Figure 5.15 IR spectra of oil samples after reclamation at different conditions. ....	63
Figure 5.16 Typical <sup>1</sup> H NMR spectrum of untreated SN150 Base oil. Inset: magnified region for observing other regions.....	65
Figure 5.17 Stacked <sup>1</sup> H NMR spectra of untreated and oxidized base oil. ....	67
Figure 5.18 <sup>1</sup> H NMR spectra of oil reclaimed using NaOH at 150 °C.....	68
Figure 5.19 <sup>1</sup> H NMR spectrum of untreated bottom phase.....	69
Figure 5.20 <sup>1</sup> H NMR of bottom aqueous phase after neutralization with HCl. ....	71
Figure 5.21 IR spectra of untreated Castrol Power 1 4T 10w-40 engine oil, used engine oil and oxidized base oil. Insets show magnified regions of: O-H stretching region (left), C=O stretching region (middle), S=O IR absorption region (right). ....	72
Figure 5.22 <sup>1</sup> H NMR spectra of unknown used oil, untreated Castrol Power 1 4T 10w-40 EO and untreated SN150 BO. ....	73
Figure 5.23 Chemical structure of PMA based additive; a) polymer, b) monomer [31]. ....	74
Figure 5.24 Summary of work presented in this thesis.....	78

# Chapter 1

## 1 Introduction

Tribology is the field of science that focuses on surface interactions that are in motion relative to each other. Major three parts covered by tribology are friction, lubrication and wear. Detailed scheme of tribology subject is described in Figure 1.1 [1]. The word “tribology” is Greek origin and means rubbing (Greek: *tribos*) [2]. Although these three parts are covered under the same roof they are totally different in mechanism of approach. Friction and wear are two correlated subjects and can be studied separately. Lubrication is an auxiliary field of tribology for friction and wear. These two can be studied in presence of lubrication or without lubricant. Tribology is one of the fundamental sciences in nature. Examples are from sliding of soap in a wet hand and toe sliding on an ice up to perfectly lubricated mechanisms. Machinery, automotive, hydraulics etc. almost all the industry is based on rubbing of surfaces. Reducing friction between these two surfaces will make machinery more energy efficient and save millions of kilowatts of energy. In the same manner reducing wear will give prolonged lifetime for moving parts producing less waste.

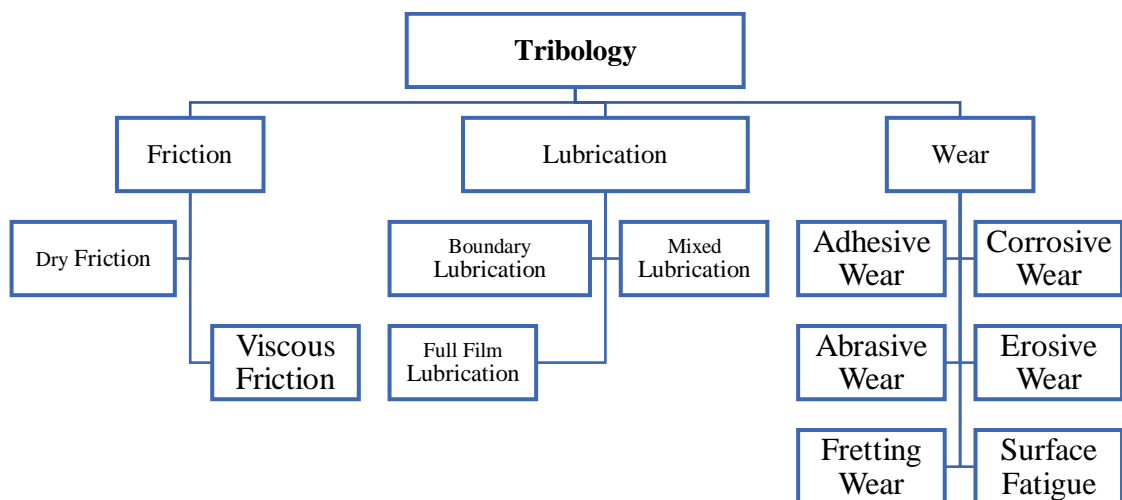


Figure 1.1 Subcategories of Tribology: Friction, Lubrication and Wear [1].

## 1.1 Tribological Contacts

When two surfaces or interfaces are rubbing relatively to each other it is called tribological contact. It can be defined with conditions of contact like: load, pressure, velocity, hardness, type of motion, humidity, temperature, surface roughness etc. In microscale or nanoscale surfaces are not rough and there is always a contact between these surfaces (Figure 1.2) [1]. Due to high strains during the microscale contact chemical bonds are broken and heat is produced. By time passage, these contacts break totally and fail to function. Due to this fact, contacts should be investigated both in nano and mesoscales. In industrial applications, due to toughness and hardness considerations, steel is the main material of fabrication. That is why many asperity contacts studies are based on steel-steel interaction. Other surfaces that are studied: polymers, yellow metal (brass) and ceramics etc.

## 1.2 Tribological Contacts Types

Tribology is the science that should be studied well in both nano and macroscales. Macroscale studies involve surface studies and the factors that affect friction is area of contact, while in microscale or in smaller scale, chemical and physical interactions start to take role. Macroscale investigations can be divided and categorized according to contact area and type of contact. Contact area can be in various forms depending on contact surface, they are basically divided in three categories: *distributed* contact, *line* contact and *point* contact. As it can be understood from their names; distributed contact is two surfaces i.e. planes rubbing each other and the contact weight, load friction is distributed evenly to whole contact area. Line and point contact is the type of contact where cylinder or sphere is rolling on a surface. In the case of cylinder, contact is line and in case of sphere, contact is point (Figure 1.3) [1].

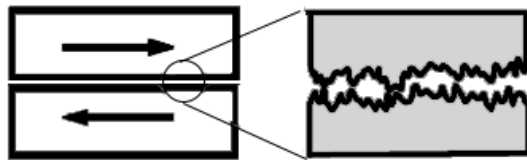


Figure 1.2 Tribological contact observed in macroscale and in microscale [1].

In three cases the main changing factor is area of contact. These three types of contact can be classified in to two types according to surface types. Distributed contact is said

to be *conformal* contact, as they have same curvature. In other words, the contact area has same curvature for both contacting objects. During line and point contacts area and surfaces have different curvature, and they are called *nonconformal* contacts (Figure 1.4).

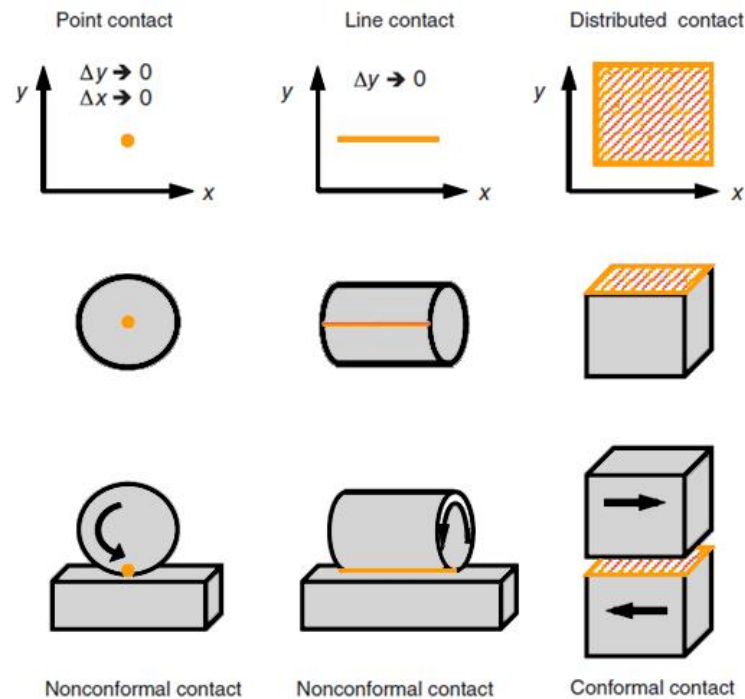


Figure 1.3 Types of tribological contacts categorized according to contact area type [1].

Distributed contacts occur in cylinders where cylinder wall and piston rub each other and have same curvature, in the same time they show conformal tribological contact. Balls in bearings show point contact and these two have different motion and show nonconformal contact. There are many other examples can be given in contact classification types.

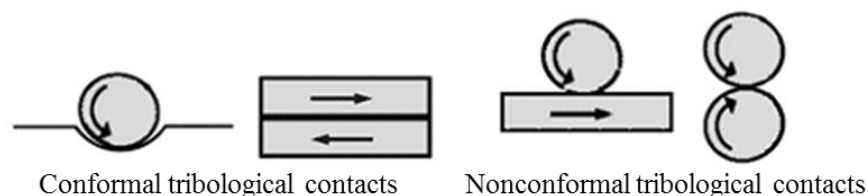


Figure 1.4 Types of tribological contacts according to surface type [1].

When focusing on microscale level local interactions become important and chemical/physical changes on these local interactions start taking a role. If lubricant is being used, all interactions with lubricants should be considered. Rubbing surfaces are not rough as we said before, and during abrasion process surfaces become rough and bond breaking cause surfaces to be rough (Figure 1.5) [1]. Lubricants keep surfaces coming into contact with each other and at the same time dissolve broken particles and wash away. This is why in every lubricating system a filter is used to recapture particles. Local interactions are hard to study to nonuniformity of surface. Local micro surfaces can get very hot due to processes such as bond breaking and formation of new bonds. Increased time of interaction on the surface yields a uniform topography and by the time, machinery starts to operate without further breakages of wear. These factors mainly depend on load applied, because of low load or absence of load surfaces may not interact and wear level is not high. While increasing load leads to chemical reactions on the surface and local deformations due to temperature increase, even moving parts may break due to weakening.



Figure 1.5 Smoothening of rough contact surfaces with increasing of rubbing time [1].

### 1.3 Friction

Friction can be explained as a resistant force for moving. When two surfaces are in contact, they have an interaction, that can be physical or chemical. These interactions are the main causes for friction. Friction can be divided into two classes: *static* and *dynamic*. Static friction is type of friction when contacting surface are at rest i.e. no motion and it transfers to dynamic when surfaces start to move. Friction is also categorized according to lubricant type used, if liquid lubricant is used it is called *viscous* friction and if there is not it is called *dry* friction. Friction is defined by friction coefficient which can be determined by the ratio of friction force to normal force (1). Friction is a vectoral quantity.

$$\mu = \frac{F}{N} \quad (\text{Eq. 1})$$



Normal force is defined by load applied and gravitational force. Normal force is always perpendicular to direction of motion, but the direction of gravitational force is always down. Friction coefficient can be calculated by knowing applied force and weight of object. Sometimes in tribological experiments, additional load is added to weight of object, in these cases weight of object can be neglected if comparably very small to applied load. In this case, simply by dividing applied force to load, friction coefficient can be calculated. This rule applies for dry friction coefficient calculations, for viscous friction i.e. lubricant is being used, shear stress of lubricant  $\tau$  should be considered. Shear stress  $\tau$  is determined by lubricant properties and depends on viscosity, velocity of movement and range.

Lubricants added decrease friction coefficient, and thus friction. Lubricated friction can be described by formation of thin film on the surface. Lubrication regime describes ratio of film thickness to surface roughness: *boundary lubrication*, *mixed lubrication* and *full-film lubrication* (Figure 1.6) [3]. Lubrication regime is derived from mechanical interaction of solid lubricating surfaces.

- *Boundary lubrication*: this the lubrication regime where surfaces are in hard contact and surface interactions are at highest level and friction is high. This regime can be defined by high friction and low speed.
- *Mixed lubrication*: in this regime surfaces are separated a little bit by lubricant. Interaction occurs partially on specific sites due to asperity contacts. This regime is between boundary lubrication and hydrodynamic regime.
- *Full-film lubrication*: in this regime surfaces are far enough to remove all surface interactions. Friction coefficient is lowest in this regime, but increases with increasing of speed. Lubricants carry additives that form thin film on the lubricated surfaces, that's why it is called full-film lubrication regime.

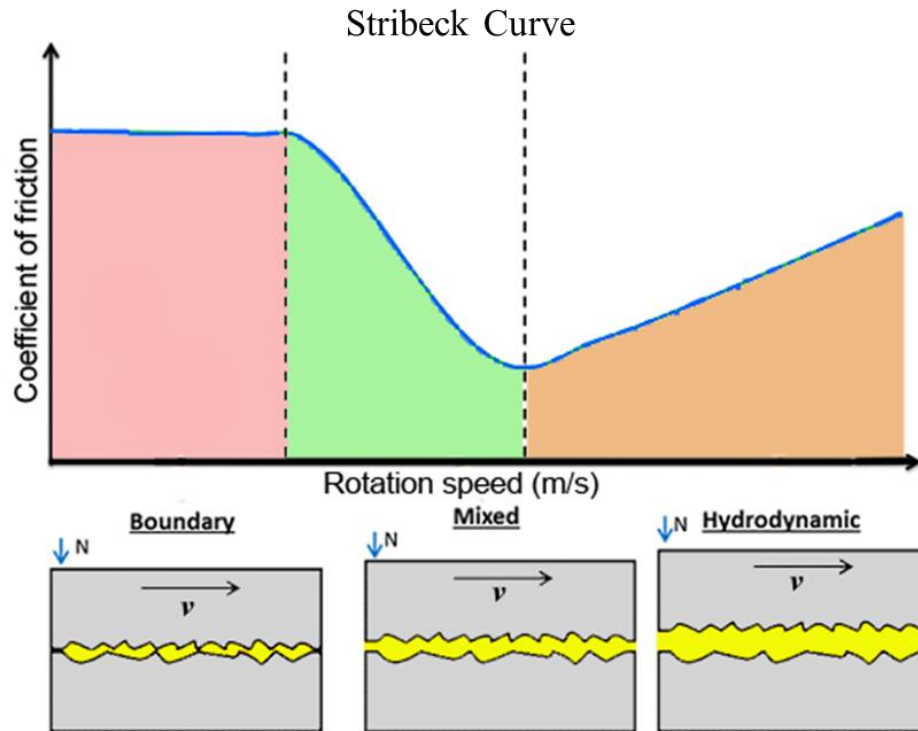


Figure 1.6 Stribeck curve of lubrication regimes [3].

## 1.4 Wear

Wear is removal of surface materials due to interaction between the surfaces. Microscale of wear is braking of bonds due to interaction with other surfaces. Wear depends on lubrication regime, lubricating parameters, operating conditions and environment. Wear types can be categorized into many classes, but these five are major classes of wear: adhesive wear, abrasive wear, surface fatigue, fretting wear and erosive wear.

- *Abrasive wear:* this type of wear occurs between interaction of hard material with softer material. Roughness on the surface of hard material makes scratches on the surface of soft material. According to number of bodies that takes place in action can be categorized to two-body or three-body interaction.
- *Adhesive wear:* this type of wear is mainly occurs due to high temperature and high pressure operating conditions. Surfaces melts and chemical reactions start, even weld into together.

- *Surface fatigue*: this type of wear occurs in cycling contacts. During cycling, due to failure of parts cycling surfaces starts to slide. Surface is deformed because of this sliding.
- *Fretting wear*: this type of wear occurs in case of small vibrations between rubbing surfaces. This cause local interactions on the surface and cause wear.
- *Erosive wear*: this type of wear occurs when small particles smash the surface and cause deformations by removing some materials from the surface.
- Other types of wear are *corrosive wear* that occurs because of chemical reaction on the surface. This can be caused by solvent, surfaces etc. This type of wear also called *tribochemical wear* or *tribocorrosion*.

## 1.5 Tribological lubrication

Lubricants are added both, to reduce friction and wear. But lubricants should be chosen according to the mechanical parts, operating conditions, operating environment etc. Choosing wrong lubricant causes lubrication failure and raise of both friction and wear. During rubbing process, two parts get heated and chemical bonds cleavage on the surfaces start [1]. By time, these parts become broken or unusable. Lubricant's main usage aim is to prolong the lifetime of moving parts by providing flow that removes broken particles from and at the same time they provide cooling effect. However, they are not good coolants and that is why in many lubricating systems cooling liquid is also flown. Many lubricants contain additives that prevent oxidation of oil and form a thin layer of film on the rubbing surfaces which is called as *tribofilm*. Other minor functions of lubricants can be categorized into following:

- Reduction of noise and vibrations.
- Prevent corrosion by blocking water and corrosive materials.
- Transferring power.
- Separation of moving parts from each other.

Lubricants are good for reduction of noise and vibrations mainly due to separation of moving parts. When moving parts touch each other, they produce noise and unwanted

vibrations, adding lubricant will separate these surfaces and thus reduce noise and vibrations. Water and other unwanted substances may increase wear rate by causing corrosive wear on surface, lubricants prevent this by removing and capturing corrosive molecules. Lubricants are one of the mostly used liquids for transferring power, for example in hydraulic systems. Due to their high viscosity, they are good power transfers and widely being applied in hydrodynamic mechanisms.

Lubricants can be divided into three categories with respect to their physical state: *liquid lubricants*, *semi-solid lubricants*, *solid and dry lubricants*. Liquid lubricant will be covered separately in next chapter in detail.

- *Solid and dry lubricants*: Solid lubricants can also be used for lubrication purposes [4]. They can be used when operating conditions, mechanical parts or other parameters does not allow liquid lubrication. Mostly used solid lubricants are: molybdenum disulfide, Teflon (PTFE), graphite etc. They can be used in combination with liquid lubricants, or sometimes additionally to reduce friction. Mainly they are used as a coating for reducing friction on surfaces.
- *Semi-liquid lubricants*: These types of lubricants can be utilized when liquid lubricants cannot be used. One of the well-known semi-solid lubricant is *grease*, they are used in many lubricating areas [5]. They are base oils composed of 5-30% with thickening material i.e. polymers, clays, soap etc.

## 1.6 Organization of thesis

In this thesis work, we will present reclamation of used lubricating oil using caustic soda (sodium hydroxide) and magnetic iron oxide nanoparticles. We have focused our work on engine oils and base oils mainly. Brief explanations for lubricants is given in this chapter and the organization of thesis will be as follows:

- Chapter 1: Short description of tribology and lubrication relation of lubrication with tribology. Types and classes of lubricants used, purposes and reason for lubrication needs are also briefly explained.

- Chapter 2: Base oil lubricants, their types, usage and production routes, their characteristics, especially base oil SN150 that was used in current study will be discussed in detail.
- Chapter 3: Additives for final oil formulation, types of additives used, purposes of usage, their depletion and especially additives used in engine oils, specifically Castrol Power 1 4T 10w-40 engine oil is focused. Also, oxidation mechanism of oils is described in detail.
- Chapter 4: Materials and Methods used for preparation of samples, chemicals that are used, procedures and instruments and analytical techniques etc. will be covered in detail.
- Chapter 5: Results on the spectroscopic measurements data, discussions that were done for the observations in the current study are presented.
- Chapter 6: Conclusion of this thesis with all suggestions will be given.

# Chapter 2

## 2 Base Oil Lubricants

Base oils, sometimes referred as base fluids are crude oils that become usable after the addition of additives. Base oils consist of hydrocarbons and there are variety of base oils. Hydrocarbons according to their type of bonds can be *saturated* or *unsaturated*. Saturated hydrocarbons obey to formula of  $C_nH_{2n+2}$  and they are hydrogen saturated unlike unsaturated hydrocarbons i.e. they contain double or triple bonds in their structures. General hydrocarbons found in base oils are naphthenes, paraffins and aromatics. These hydrocarbons can be straight, chained, cyclic or unsaturated. Base oil properties depend on type of these hydrocarbons found in. Type and chemistry of hydrocarbons found in base oils also determine the lubricating properties. General test that base oils are subjected: *viscosity index* and *viscosity*, *polarity*, *volatility*, *oxidation stability* etc.

- *Viscosity and viscosity index*: they are determined by length of hydrocarbon chain. Long chains result in high viscosity and short chains result in low viscosity base oils. Viscosity index of base oils, depend on thermal properties of hydrocarbons in. Viscosity of long chain hydrocarbons do not alter much with respect to temperature, and due to this they can be used in many high temperature applications. Presence of rings and branching in hydrocarbon structure enhances cold flow characteristics and at the same time prevent wax formation [6].
- *Polarity*: it is determined by ability to dissolve additives and interaction with surfaces. Generally, base oils are nonpolar due to long and branched hydrocarbon chains. Polarity, effects base oil properties like: air release, adsorption to surface, demulsification and foaming.

- *Volatility*: it is determined by amount of low molecular weight hydrocarbons in base oil. These low hydrocarbons evaporate at high temperatures and leave behind viscous base fluid. Engine or machinery oil operates at high temperatures [7], that is why volatility should be maintained before formulating final lubricating machinery oil. Because, these evaporated hydrocarbons can form deposits on moving parts.
- *Oxidation stability* is factor that shows resistance to chemical oxidation. Base oils that are operated at high temperatures [7] and subjected to oxidation process i.e. molecular oxygen starts to react with hydrocarbons. Detailed mechanism of lubricating oil oxidation is discussed in Chapter 3. Unsaturated hydrocarbons are more reactive towards oxygen, in other words, base oils containing unsaturated hydrocarbons can be oxidized easier. Oxidation stability shows at what temperature base fluid starts to be oxidized.

Base oil that will be used for production of final engine oil should be chosen according to above-mentioned parameters. Base fluid containing suitable ratio of paraffinic, aromatic and naphthenic hydrocarbons should be chosen. Table 2.1 summarizes some physical and chemical properties of hydrocarbons found in base oils [1].

Properties	Paraffinic	Naphthenic	Aromatic
Viscosity index	High	Low	Low
Density	Low	Low	High
Pour point	High	Low	Low
Volatility	Low	Medium	Low
Flash point	High	Low	Low/medium
Oxidation stability	High	High	Low
Thermal stability	Low	Low/medium	High
Toxicity	Low	Low	Medium
Elastomer compatibility	Shrink	Swell	Swell

Table 2.1 Some physical and chemical properties of hydrocarbons found in base oils [1].

## 2.1 Classification of Base Oils

Base oils are classified according to their usage purpose within common terminology. Base oil lubricants are mostly used in automotive industry. Engine oils are subjected to physical and chemical tests by Original equipment manufacturers (OEMs) prior to market release. OEMs have approval tests for engine oils, that oils should pass before market introduction. Base oils used in automotive industry are categorized into groups I, II, III, IV and V [8]. These categorization and descriptions are done by American Petroleum Institute (API) and Association Technique de l'Industrie Europeenne des Lubrifiants (ATIEL). Description of these groups is summarized in Table 2.2 [8] (VI stands for Viscosity Index). Group V includes all other base oils that cannot be categorized into other groups. They are not suitable for usage in engine oil applications. This classification is based on amount of hydrocarbons and sulfur content.

Group	Description
I	Saturated hydrocarbons < 90%, sulfur > 0.03%, $80 \leq VI \leq 120$
II	Saturated hydrocarbons $\geq 90\%$ , sulfur $\leq 0.03\%$ , $80 \leq VI < 120$
III	Saturated hydrocarbons $\geq 90\%$ , sulfur $\leq 0.03\%$ , $VI \geq 120$
IV	PAOs (Polyalphaolefins)
V	All others, but groups I, II, III and IV: e.g. naphthenics, synthetic and natural esters

Table 2.2 Description of base oil categorization according to API and ATIEL [8].

Base oils have other classification types according to their origin and production route. Many base oils used in industrial and automotive application are produced from petroleum. But, there are also lubricants or so called bio-lubricants that produced from vegetables or animal origin. Recent years due to increasing of environmental issues biodegradable lubricants have attracted reasonable attention. Gas to liquid (GTL) lubricants are produced from natural gas and coal. These mentioned lubricants, or environmentally adapted lubricants (EALs) are given in detail in Figure 2.1 [9].



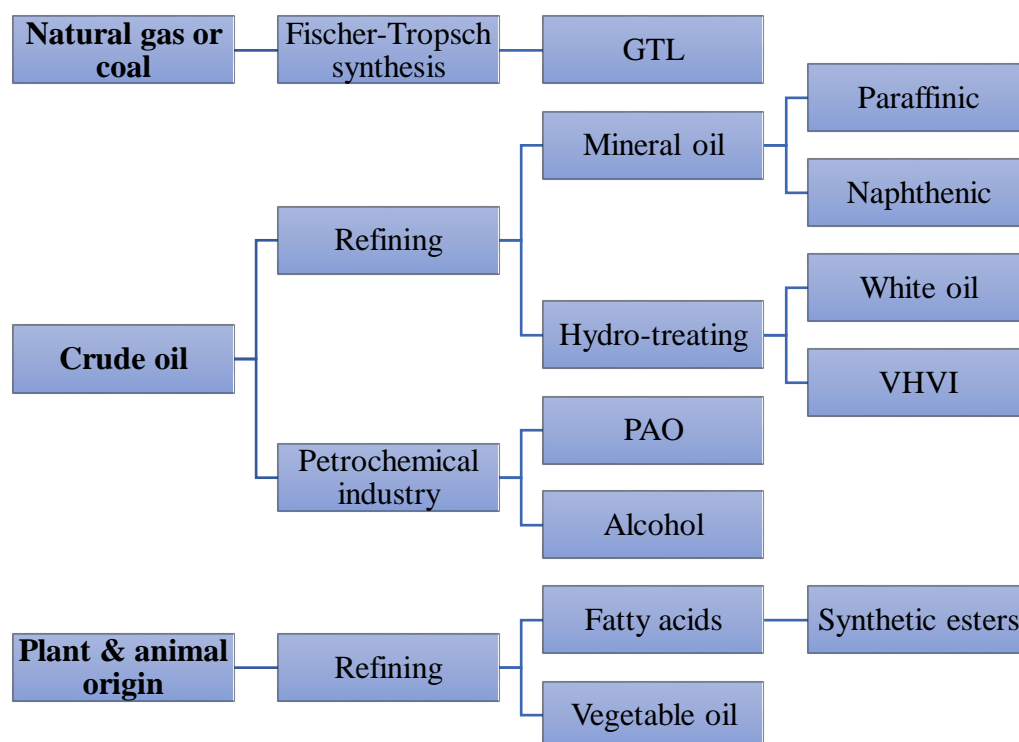


Figure 2.1 Origin and production route of base oil lubricants (PAO-polyalphaolefins) [9].

Lubricant categorization according to API and ATIEL are also shown in Figure 2.1. Generally, group numbers are not used as a base oil names, rather common names shown in Figure 2.1 are used. Common names of oils and their group belongings are summarized in Table 2.3 [9] (VHVI stands for very high viscosity index).

These lubricating base oils are produced worldwide and properties of base oils change due to hydrocarbon content and amount of sulfur of that region. As base oils are derived from petroleum, their properties depend on the petroleum properties of that region. Production amounts of base oils and production across the world is given in Figure 2.2 [9]. Most commonly produced base oils belong to Group I and Group II, and relatively small amount belong to Group III. They are used almost in every part of industry, especially in automotive and jet engine oils production. One of the biggest manufacturers of base oils is United States, second is Europe, continues with Korea and Japan. China is also one of the biggest manufacturer of base oils, minor producers of base oil are Middle East and some parts of Africa, and South America. South Asia and Australia together produce considerable amount of base oil annually.

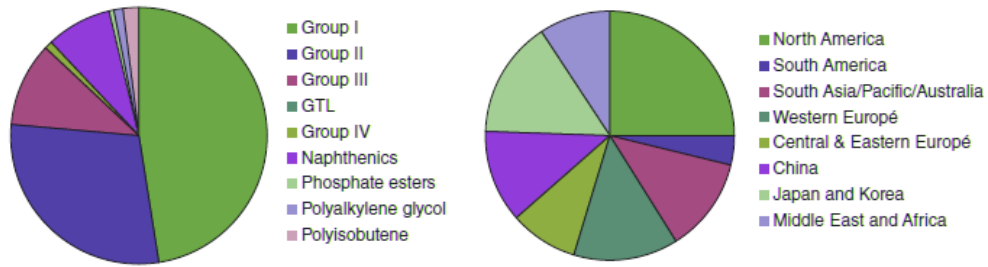


Figure 2.2 Left: production amounts of different base oil types, Right: production amounts worldwide with respect to regions [9].

API group	Description	Origin	Common name
I	Paraffinic	Crude oil	Mineral oil
I	Re-refined	Used oil	Re-refined
II	Paraffinic	Crude oil	Mineral oil
II	Re-refined	Used oil	Re-refined
II	White oil	Crude oil	White oil
III	VHVI	Crude oil	Synthetic fluid
III	GTLs	Natural gas (or coal)	GTLs
IV	PAOs	Crude oil	Synthetic fluid
V	Naphthenic	Crude oil	Mineral oil
V	Vegetable oil	Vegetable oil	Vegetable oil
V	Synthetic esters	Vegetable oil and crude oil	Ester

Table 2.3 Origins and classifications of common base oils [9].

## 2.2 Refining of Base Oils

Base oils produced from crude oil are formed by the result of process, named as *refining*. Initially crude oil contains hydrocarbon and low amount of sulfur, oxygen, nitrogen, metals and salts [9]. Relative amounts of elemental content in crude oil is given in Table 2.4 [9]. Crude oil needs to be refined in order to produce base oil with suitable lubrication properties. During refining process, desirable substances are kept and unwanted elements and molecules are removed. Sulfur is among desirable elements, as it acts as a natural antioxidant in the oils.

Component	Percent weight
Carbon	83-87
Hydrogen	11-14
Sulfur	0-3
Nitrogen	0-1
Oxygen	0-0.5
Metals and salts	0-0.2

Table 2.4 Relative amounts of elements in typical crude oil [9].

Refining process begins with atmospheric pressure distillation. At this step crude oil is heated and oil components are separated according to their boiling points. Low molecular mass components are collected on top of tower and heavy molecules stay in bottom. Detailed scheme of refining process is shown in Figure 2.3 [10-12].

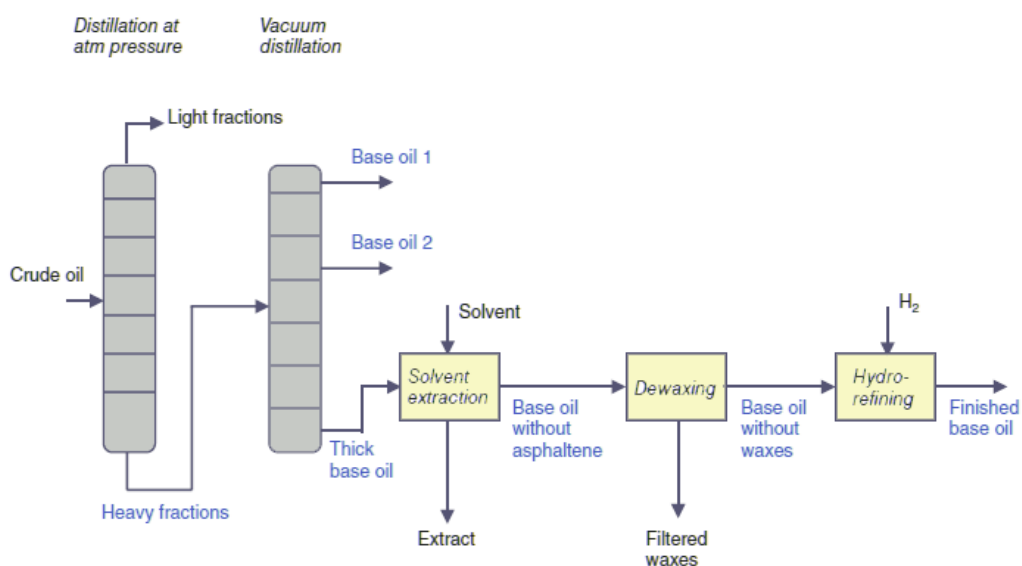


Figure 2.3 Schematics of crude oil refining process [10-12].

Low molecular weight molecules are collected constantly by distillation and further purified for production of various fuels. These fuels can be: gasoline, gases, kerosene, naphtha and light gas oil. Products left in the bottom are transferred to vacuum distillation tower and highly volatile aromatic hydrocarbons are removed in this part. Thick base oil remains after vacuum distillation process [9, 11, 12]. In this thick layer, waxes and asphaltenes are present and they are removed by solvent extraction, cooling to lower temperatures where wax crystallize [13]. Presence of wax will affect viscosity

of base oil, and wax crystallizes at high temperatures and causes failure in lubrication. At final stage, hydro-refining is applied to obtain desired oxidation stability and color. Often, directly hydro-finishing is applied, where cracking happens. Trace elements, sulfur and nitrogen are also removed in order to sustain gas emission levels. Sulfur acts as a natural antioxidant, but nitrogen catalyzes oxidation and it needs to be removed. After all of these steps, physical and chemical properties of crude oil change. Detailed change in properties of crude oil is summarized in Table 2.5 [9]. Final engine oil properties are adjusted by using additives and they will be covered in Chapter 4 in detail.

Property	Deasphalting	Dewaxing	Hydro-refining
Viscosity	Decrease	Increase	No change
Viscosity index	Increase	Decrease	No change
Density	Decrease	Increase	Decrease
Pour point	Increase	Decrease	Increase
Flash point	No change	No change	No change
Oxidation stability	Improve	No change	Improve
Additive response	Improve	No change	Improve
Color	Improve	Improve	Improve

Table 2.5 Effect of crude oil refining [9].

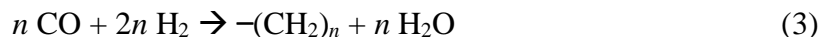
## 2.3 Base Oils Derived from Crude Oil

In this section, base oils derived from crude oil that are shown in Figure 2.1 will be discussed in detail. As seen from the figure, crude oil based base oils are: GTL, paraffinic, naphthenic, white oil, VHVI base fluids and PAOs. Also, re-refined base oil will be discussed. These names are used according to their hydrocarbon and sulfur content along with synthesis method.

### 2.3.1 Gas-to-Liquid Base Oils

Due to hardness to obtain petroleum based mineral oils, gas-to-liquid oils were invented. GTL is expensive due to difficulties in manufacturing. They were considered as an alternative for petroleum based fuels. They are produced according to Fisher-Tropsch (F-T) process by reaction of natural gas or coal with oxygen. This

procedure consists of three main steps: syngas production, its conversion and hydrotreatment. The chemical reaction pathways are shown below:



Hydrocarbon chains are produced in the end of the reactions. These hydrocarbon chains can be in various size and due to process, they do not contain aromatics, metals, olefins, sulfur and nitrogen. Their physical properties are identical with VHVI and PAO, they have suitable clod flow characteristics and low volatility. They are categorized as a synthetic base oil and belong to group III base oils according to API [14-16].

### 2.3.2 Paraffinic Base Oils

Paraffinic base oils, as it is understood from name, 45-60% consist of paraffinic hydrocarbons [1]. Due to small amount of aromatic hydrocarbon content their color is slightly yellow. During refining process, their viscosity increases and their color becomes denser. These paraffinic base oils are one of the mostly used lubricants in industry, due to suitable lubricating properties and good additive solvability. Another reason for their wide usage is stability temperature of 150 °C with oxygen presence and 200 °C without oxygen. Their physical properties at low temperatures are excellent and can be improved by using additives. When we look to Stribek curve (Figure 1.6), they can be used from boundary to full-film lubrication regime. Most of paraffinic oils are utilized in automotive industry as an engine and transmission oil, and in other industrial applications [9].

### 2.3.3 Naphthenic Base Oils

Naphthenic base fluids contain 65-75% naphthenic and 25-35% paraffinic hydrocarbon units. They make about 10% of petroleum oils. Their color is same with paraffinic oils, but they can be light yellow due to low amount of aromatic hydrocarbons. Their physical properties are same with paraffinic base fluids; thus, they are also good lubricants and have good additive response. They are used to increase additives solvability of other lubricating oils. Despite having good lubricating properties, they have indigent VI, which makes them unusable in high temperature applications [9]. One of good properties of these oils is that they do not contain wax;

thus, they have wonderful pour point characteristics. They are generally utilized in jet turbine, hydraulic and metal applications [11].

#### **2.3.4 White Oils**

Final step of refining process produces white oils that contains mixture of paraffinic and naphthenic hydrocarbons. They are purified well and contain lowest amount of aromatic hydrocarbons, sulfur and nitrogen. Therefore, they are colorless and named as white oils. Rather than paraffinic and naphthenic oils they are used in food, cosmetics applications, pharmaceutical i.e. areas where sanitation legal requirements are high. Due to production route, they are relatively high-priced and used only in specific operations [9].

#### **2.3.5 Very High Viscosity Index Base Oils**

Hydroisomerisation happens due to cracking step during hydrotreating, and changes chemical structure of molecules making them more branched. In the end of this step, very high viscosity index (VHVI) base oils are produced. Main composition of VHVI oils is paraffinic, sometimes small amount of naphthenic hydrocarbons present. They have very high viscosity; thus, good oxidation stability and low volatility. When compared to group I and II base oils, their cold flow characteristics are better. They are called as synthetic base oils and generally used in new type of engines [9, 17].

#### **2.3.6 Polyalphaolefins**

PAOs are only chemically synthesized base oils, they are produced from linear chain paraffin hydrocarbons. Chemical structure of final product can be controlled easily and base oils with good mass dispersion can be obtained. Physical properties of PAOs can be arranged accordingly. One of their drawbacks is their additive response. To overcome this problem, they are mixed with ester or naphthenic base fluids. PAOs are more valuable compared to mineral base oils, due to their extraordinary properties. Their oxidation resistance is better, viscosity is high and volatility is low. Because of being expensive they are utilized in transmission and cold start engines (0W-xx), as they have superior low temperature characteristics [9, 18]. Chemical formula of some PAOs are given in Figure 2.4 [1].

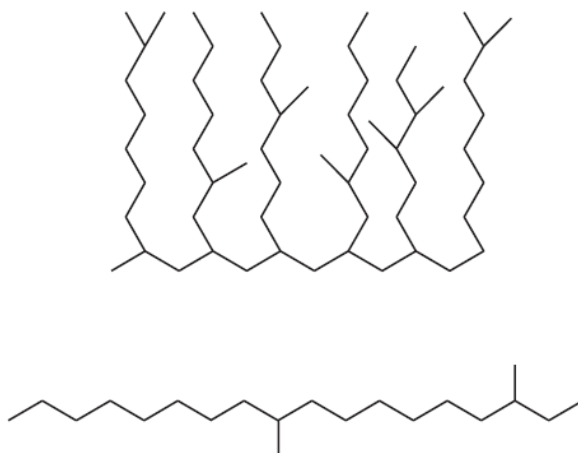


Figure 2.4 Chemical structure of PAO6 (top) and PAO2 (bottom) [1].

### 2.3.7 Re-refined Base Oils

According to EU Waste Directive, petroleum derived base oils or industrial lubricants must be re-refined instead of being burned [19]. Additives inside lubricants deplete by usage time and oxidation (degradation) of lubricating oil becomes inevitable. Beyond that, due to usage process, lubricants become contaminated with water and other particles. Lubricant after fulfilling its life needs to be changed. However, waste oils can be re-refined by moisture and contaminants removal. As a result of this process, superior quality base oils can be obtained. Re-refining cycle resembles crude oil refining process, first water is removed in distillation tower, second distillation is applied to remove volatile components like fuel and other organics, final step is used to extract base oils by using conventional solvents, and in the same way particles are removed. Re-refining is becoming more important due to oil spills around the world. It was reported that from every 1000 tons of used oil at least 600 tons can be reclaimed [20].

## 2.4 Base oils naming

Naming of base oils is made according to their physical properties, API groups and additives inside. Group I base oil are called as SN and their respective viscosity at 100 °F (37.78 °C) in Saybolt seconds units is used. Here S stands for *solvent* because solvent extraction step and N means *neutral* because of neutralization after acid washing step. Group I base oil also can be Bright Stock (BS), that means bright fluorescence because of heavy aromatic hydrocarbons is observed. Common group I base oils names: SN150, SN650, SN500 etc.

Group II base oils are referred as Neutral, they are indicated by their viscosity at 100 °F (37.78 °C) in Saybolt seconds units. Also group II base oils are named by their kinematic viscosity (KV) at 100 °C in cst units. Examples of group II base oil names: 100 N, 150 N, 600 N or Group II 4, Group II 6 etc.

Re-refined base oils are also named as Group I and Group II base oils, sometimes “Re-refined” is added in front of name and they are differentiated according to their kinematic viscosity at 100 °C in cst units.

Other group oils are named according to their kinematic viscosity at 100 °C in cst units, group III base oil are named according to their oil type, generally they are referred as VHVI and group IV as PAOs. Examples of group III and IV base oil names: VHVI 4, VHVI 6, PAO 6, PAO 10, Group V 5, Group V 10 and etc.

## **2.5 SN 150 Base Oil**

We used Group I SN 150 Bright Stock base oil in our experiments. This is most common base oil used for lubricant manufacturing. SN 150 is 90% saturated base oil, it is produced commonly by solvent refining and by KOH neutralization. Its properties depend on the production region and production process, but its sulfur content is maximum 0.3 % and VI is between 80-90 [21]. Physical and chemical properties of SN 150 base oil are given in Table 2.6 [21].



Oil property	SN 150 specification
Kinematic viscosity, mm <sup>2</sup> /sec (cSt) at:	
100 °F	27 – 31
100 °C	4.5 – 5.5
Viscosity index	90
Acid index, mg KOH/1g oil	Not normalized
Ash %	0.005
Water content, ppm	100
Flash point, °C	195
Pour point °C	
1.09 – 1.04	Minus 15
1.04 – 1.09	Minus 10
Sulfur content %	0.3
Polycyclic aromatic hydrocarbons (PAH) %	3
Appearance	Homogeneous clear fluid
Specific gravity at 15 °C, kg/m <sup>3</sup>	0.87

Table 2.6 Characteristics and properties of Group I SN 150 Base oil [21].

# Chapter 3

## 3 Engine Oil Lubricants

Base oils prior to usage are adjusted with various additives in order to satisfy international standards. Final lubricating product is named as engine oil, motor oil or lubricant. Primary functions of motor oils are to reduce friction and inhibit wear; minor activity is to remove sludge formed, prevent corrosion and finally cooling the motor [22]. Engine oils are used in internal combustion motors. Thus, they can go to very high temperatures about 160 °C in case of gasoline powered engines and to 315 °C for diesel engines [22]. As we said before, engine oils are formulated from base oils, lubricating properties and physical properties of base oils are not sufficient. Base oils can be oxidized easily at high temperatures. For preventing this, antioxidant additives are commonly used. Antioxidant additives are chosen according to application of the final motor oil. There are many other additives used during formulation such as viscosity modifiers, surfactants, friction modifiers, antiwear, extreme additives etc.

### 3.1 Additives

Additives used in automotive engine oil are classified according to their function and acting mechanism. Types of additives according to their chemical and physical functions in automotive oil are given in Figure 3.1 [1]. When taking into consideration automotive internal combustion engine, all of the reactions and interactions happen in the solid/liquid and liquid/liquid interfaces. Moving parts are solid and lubricant is liquid, oxygen is gas, lubrication occurs between these parts. Surface additives act on these interfaces and bulk additives act inside oil i.e. liquid/liquid interface.

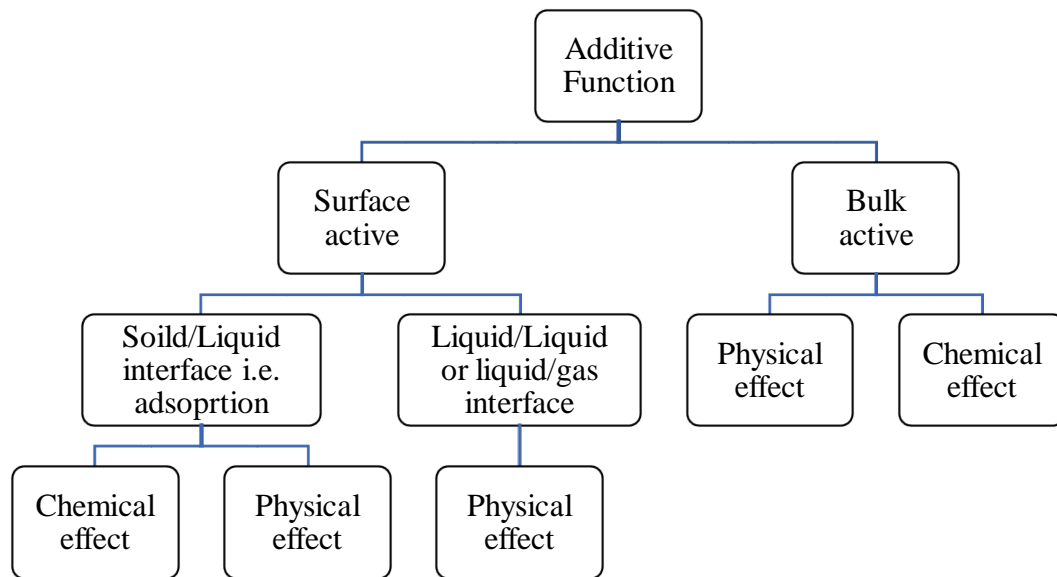


Figure 3.1 Types of automotive engine oil additives according to their functions [1].

### 3.1.1 Surface active additives

Surface additives act, interact at solid/liquid interface decrease friction and prevent solid moving parts from wear and corrosion. Their general mechanism of action is based on forming films on solid surfaces. This film can form by adsorption to surface both physically and chemically. Due to this, they are referred as film forming additives. Because of high working temperature and presence of pressurized air, metal surfaces form oxides. These oxides can bind some air and water molecules, function of surface active additives is to remove these water and air molecules by interacting with this oxide layer [23]. These types of additives are: *antiwear additives*, *corrosion inhibitors*, *EPAs (extreme pressure additives)*, *friction modifiers*.

- *Antiwear additives*: this type of additives as understood from the name are used to reduce wear in moving parts. Wear reduces lifetime of moving parts and aim of antiwear additives is to endure lifetime of engine components. They are used about 1-3% during engine oil formulation and activated at high temperatures [24-26]. They react with the surface and form chemical bonds (chemisorption). Because of strong interaction with steel surface, elements like sulfur, phosphorus, nitrogen that are chosen. Among all, phosphorus is the best candidate by providing longest lifetime to moving motor parts. One of the

mostly used antiwear additive is ZDDP (zinc dialkyldithiophosphate), it functions as an antioxidant at the same time. ZDDP will be discussed in next section in detail. Because of environmental issues new type of antiwear materials like Teflon (PTFE), graphene, DLC etc are being discovered [25-27].

- *Corrosion inhibitors:* corrosion occurs due to acids and sulfur compounds, which form because of oil oxidation. Based on their interaction mechanisms corrosion inhibitors used are neutralizers or film forming additives. The last ones are used frequently. Their mechanism is same with antiwear additives, they form protective layer on surface of metal via chemical or physical binding (adsorption). There are two types of corrosion; electrochemical and chemical corrosion. Difference is, in electrochemical corrosion electrolytes facilitate corrosion, while in chemical there is no electrolytes. In steel parts, due to high temperatures and oxidation reactions electrolytes form [28]. Additives that prevent corrosion form layer on metal surface and preserve reaching of water and oxygen to the activated surface. Some corrosion inhibitors used are: phosphates, carboxylic acids, basic&neutral sulfonates and amines.
- *Extreme Pressure Additives:* these additives are used for prevention of shuffling and corrosion of parts in case of high localized pressure. Their principle is same with corrosion and antiwear additives, formation of layer that protects from wear and decreases friction. They are used in massively weighted gears that move slowly but with high torque [26, 29]. There are two types of EPA; mild and strong. They are differentiated by activation temperature, mild is activated in lower temperatures and strong EPA needs high activation temperatures. Film formation occurs on the surface of moving parts, and it becomes polar because of hydrocarbon chains breaking at extreme pressure. Here also, elements that have high binding coefficient to iron are chosen. These elements make chemical bonds with iron and after removal of hydrocarbon moiety only thick layer of iron salts remain.
- *Friction modifiers:* friction modifier additives are needed to change friction during mixed lubrication regime during tribological contact (Figure 1.6). They are active mainly in low temperatures and desorb from the surface by

increasing of temperature. This can be prevented by using more amount of additive. Generally, about 1% of this additive is used during formulation. They can both reduce friction and control the friction, it is added in motor oils for reducing and in transmission oils for adjusting the friction [24, 28]. They have similar mechanism to other surface additives; formation of film on the surface. They are made from fatty acids, esters, amides, alcohols i.e. they contain long apolar hydrocarbon chains and oxygen or nitrogen containing functional groups. Acidic groups bind better than amines and alcohols. Hydrocarbon chain length also plays significant role in lubrication; long chains decrease friction better, while smaller chains can result in corrosion issues [24].

All of the additives mentioned above were functional on solid/liquid interface. They form films on the surface of the engine parts and prevent corrosion, wear, friction etc. But there are other group of additives that act in liquid/liquid or liquid/gas phase; *defoamers*, *demulsifiers* and *emulsifiers*.

- *Defoamers*: foams are formed during air entrance into lubricating oil, air encapsulates into base oil and foams form. These foams are stable due to pressure equality of air inside and lubricating layer outside. Defoamers have polar ends and they interact with air, which destabilize foams. After reaching desired thickness foams explode. They are used for increasing lubricant dispersity and prevention of air entering and foam formation [29]. Polymethacrylates and silicone oils are among most commonly used defoamers. They are added in very low amounts.
- *Demulsifiers*: oil is also used as a coolant, but its cooling properties are poor and water is used as a main cooling agent. During these applications water can mix oil, and increase corrosion. Emulsifiers and demulsifiers are used for adjusting water amount in lubricant. Demulsifiers contain polar hydrophilic molecules that have hydrophilic elements (oxygen, sulfur, phosphorus and nitrogen) and trap water. They are made from high molecular weight polymers and contain about 5-50% of polyethylene oxide [1].
- *Emulsifiers*: they are similar materials to demulsifiers and their aim is to separate water from oil interface. They contain same elemental groups as

demulsifiers, and reduce water droplet sizes by reducing surface tension of water droplets. Demulsifiers are used together with emulsifiers and demulsifiers are more active.

### 3.1.2 Bulk additives

Additives that were mentioned in previous part were functional at solid and liquid surfaces. Here, we will discuss additives that are added for improving oil properties itself. Some of these additives act physically (*viscosity modifiers, dispersants, pour point depressants*) and others act in chemical way (*antioxidants, detergents*). These additives will be discussed in detail.

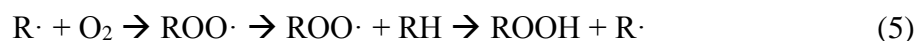
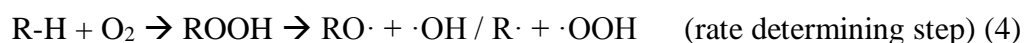
- *Viscosity modifiers*: Viscosity of base oil can operate within certain narrow range, needing seasonal change, as outside temperature changes from high positive values to negative [29-31]. Viscosity modifiers are chosen according to their low reactivity with oil and other additives, ability to increase fuel economy. Viscosity modifiers are chosen from long chain high molecular weight polymers. At low temperatures, these polymers stay in enlaced form and by increasing temperature they became linear; thus, they increase viscosity of base oil. Appropriate viscosity modifier should be chosen according to application of oil, operating temperature, needed viscosity grade etc. Commonly used viscosity modifiers are made from olefin copolymers (OCP), polyisobutylene (PIB) i.e. olefin polymers or polymethacrylates (PMA) i.e. ester polymers.

PMAs are one of most commonly used viscosity modifier additives, they easily mix with wide range of base oils and they have good thermal properties. However, their viscosity range is low compared to PIBs and OCPs, thus they are used in small viscosity range grade oil. Being ester based, PMAs have good oxidation stabilities. But, one of drawbacks is high manufacturing costs. Due to this, they are used in small quantity applications like in automotive engine lubricating oils [31]. OCPs are hydrocarbon based polymers with elementary chemical structure. Their thermal properties are good, and they are cheap. But, they are needed to be used with pour point dispersants [30]. PIBs are one of the initially discovered viscosity modifiers, they are made from butadiene and have rather simple chemistry. Their thermal stabilities are not good as desired.

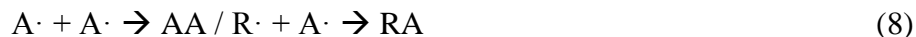
- *Dispersants*: These additives are added in order to remove and disperse sludge, soot and deposits formed. They clean moving parts by removing sludge on surface of moving parts. By removing insoluble components, they also adjust viscosity of lubricating oil. They have polar groups that attach to the surface of sludge and insoluble components, dispersant functions are same with surface additives. By attaching to sludge, they prevent agglomerates formation due of their bulk structure [28, 32]. Commonly used dispersants contain polyisobutene as a long hydrocarbon chain and succinimide as a polar moiety. Mainly, they are polymers with moderate molecular weight.
- *Pour point depressants*: During cold seasons, i.e. at low temperature, viscosity of base oils increase. After some point, base oil becomes cloudy and liquid starts to crystallize. Pour point depressants prevent this crystallization by dissolving or binding the wax. In this way, they prevent crystallization of liquid base oil [29, 32]. They have similar structures to viscosity modifiers and are composed of polymethacrylate or naphthalene polymers. But, they do not have long chains, they are rather branched and bulker. They are more effective in small polymer or monomer form rather than in polymer forms. They are used in motor oils, transmissions fluids, gear lubricants and in hydraulic applications fluids [29, 31].

Previously mentioned additives are added in order to modify physical properties of base fluids, they do not interact chemically. For adjusting chemical properties of base lubricants chemically active additives are added. They are *antioxidants* and *detergents*.

- *Antioxidants*: Lubricating engine oils operate at high temperatures and in presence of oxygen they start to be oxidized. Oxidation of lubricating oils is very complex procedure and it will be discussed in incoming chapter. In presence of oxygen, following chain reaction starts [33]:



Auto oxidation of base oil is favorable process (reactions 4-6). Antioxidants terminate the reaction with trapping free radicals [33]:



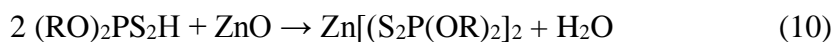
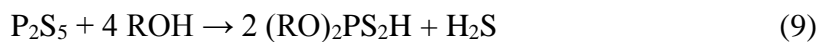
This is simple representation of antioxidant functioning. In other words, antioxidants are radical scavengers i.e. they trap radicals and prevent further reaction. They can be amine based, phenolic and sulfur-phosphorus based like ZDDP [29, 34]. ZDDP will be discussed in next section in detail.

- *Detergents*: They are basic molecules with long hydrocarbon chain. They react with acidic groups formed during oxidation of base oil. Their secondary function is to prevent further oxidation. Total number of detergents in lubricating oil is called as total base number (TBN), it is used as a sign for routine oil changes [29, 35]. They contain metal ions that neutralize acidic groups. According to their basicity they are divided into *neutral* and *overbased* detergents. Neutral detergents have same function as corrosion inhibitors and antiwear additives, they keep the metal parts surface clean. But, overbased detergents have metals that react with acidic groups and neutralize them. Generally, calcium and magnesium ions are used as a basic moiety. Salts can be phenates, sulfonates, salicylates. Among these first and third acts as an antioxidant and can be manufactured very cheaply. However, they are not basic as sulfonates [35].

### 3.1.3 Zinc dialkyl dithio phosphate (ZDDP)

ZDDP is one of the mostly used automotive engine oil additive. It is both an antiwear and antioxidant additive. It contains zinc bonded to dithiophosphoric acid. Depending on pH of the medium it can be in monomer, dimer, tetramer and polymer forms. Chemical structures of all forms of ZDDP are given in Figure 3.2 [36]. The R group in the structure determines antiwear properties. There are various types of ZDDP depending on R group moiety. They are one of the mostly added additive in lubricants with 2-15% [37]. They are produced by reaction of  $P_2S_5$  with alcohol and reaction of product formed afterwards with ZnO [38]:





It was discovered during 1940s and still being used in various types of motor oils [39].

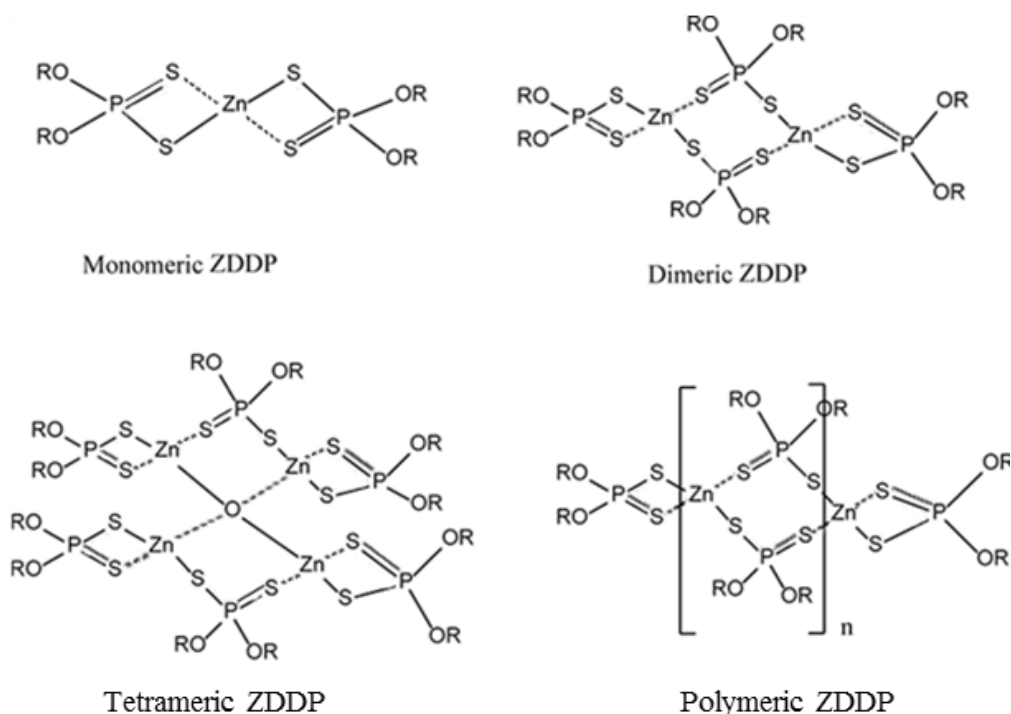


Figure 3.2 Chemical structure of all forms of ZDDP additive [36].

ZDDP acts as an antiwear additive by forming thin film on metal surface, which is named as *tribofilm*. During high temperatures, ZDDP degrades by forming ZnO and sulfur containing groups. These sulfur containing groups are chemisorbed onto iron surface (Figure 3.3) [40]. Tribofilm prevents metal parts rubbing each other and prevent scuffing. Detailed mechanism of film formation happens according to Figure 3.4 [41]. This film renews itself, and it is not stable at very high temperatures.

Tribofilm formation is a chemical process and high temperature is required in this process. Films that are formed at lower temperatures are not stable and the film is only physisorbed onto the surfaces. After heating to high temperatures, degradation of ZDDP starts and chemical reaction between iron and sulfur in ZDDP leads to formation of tribolayer. In absence of heat, however, ZDDP degradation is almost negligible, degradation happens only during high temperatures that exceed 150 °C. During even higher temperatures degradation of ZDDP increases exponentially [42, 43]. After depletion of ZDDP in lubricant, base oil starts to oxidize and tribofilm

formation is not promoted any longer. Tribofilm formed on the surface is removed by effect of heat and this is the time for oil change. The main factor for ZDDP degradation and lubricant oxidation is mainly the high engine operation temperature. Reducing temperature to lower degrees would increase lifetime of both ZDDP and lubricants.

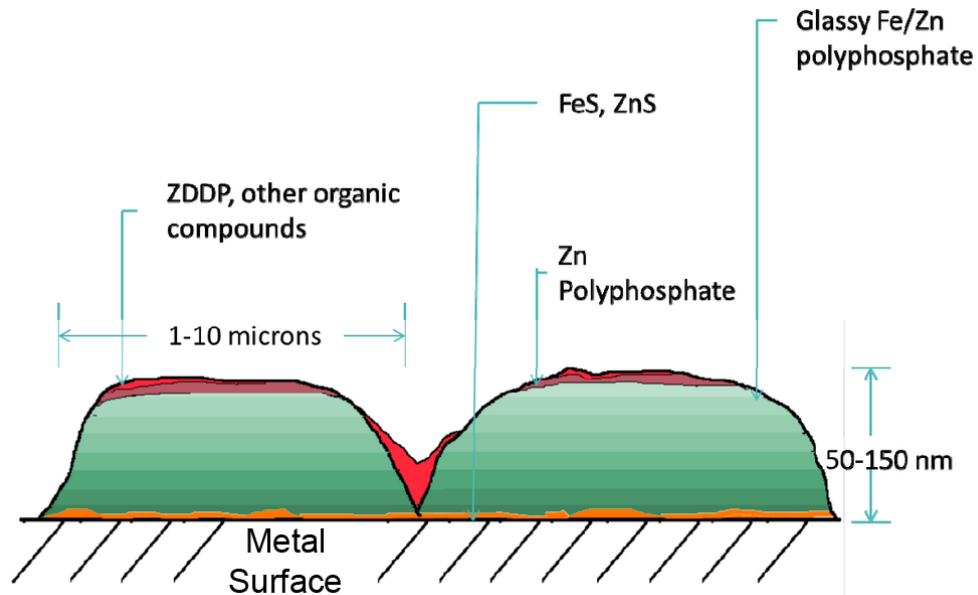


Figure 3.3 ZDDP antiwear film formation on the surface of metal bearing. Adapted from ref 40.

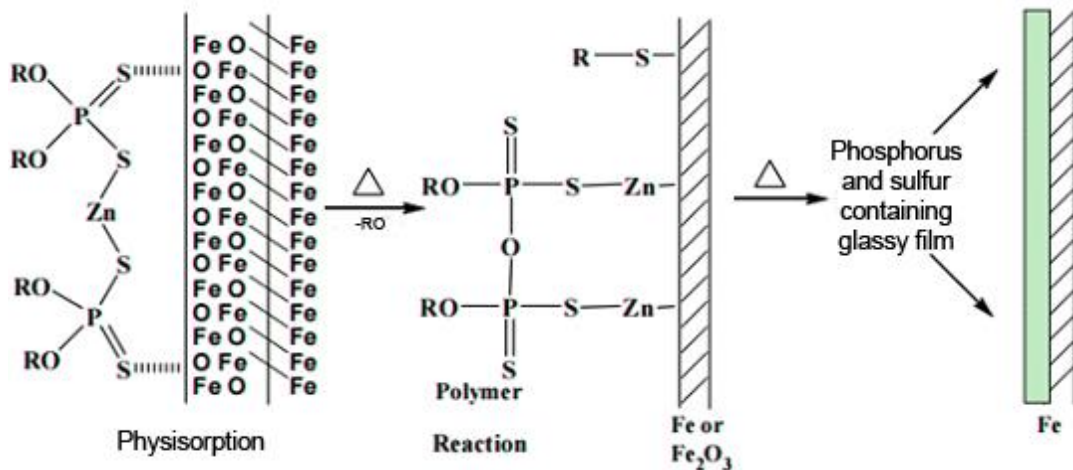


Figure 3.4 Mechanism of tribofilm formation on metal surface. Adapted from ref 41.

### 3.2 Grades and standards of engine oil lubricants

Final lubricating motor oils are classified according to their viscosity range. This numeration classification was brought to life by Society of Automotive Engineers

(SAE). Kinematic viscosity of lubricant is measured and lubricant is named with these viscosity ranges. According to their viscosity ranges engine oils are categorized as *single-grade* and *multi-grade*.

*Single grade* engine oil does not contain viscosity modifiers and they are designated only with one viscosity index. Viscosity of oils change substantially with respect to the temperature. Single grade oils have only one viscosity index, and named as 0W, 10W, 40W, all units used are centipoise (cP) and here “W” stands for winter. These oils are named as SAE 0W, SAE 10W, indicating that they are SAE tested. For oils used only in summer season, only viscosity index value is used for naming. They are named as SAE 20, SAE 50 etc. and no extra letter indication is used

*Multi-grade* oil contains viscosity index improver or viscosity modifier (part 3.1.2). It allows wide range of viscosities for lubricants, both in winter and in summer. They are named with two viscosity index ranges, like 10w-40, 20w-50 etc. Here “w” stands for winter and indicates viscosity index of lubricating oil in winter. For multi grade oils, SAE is not used and oils are categorized according to their viscosity index range.

Engine oils prior to marketing release are subjected to various physical and chemical tests. There are five biggest organizations that create testing procedures and approve final lubricants. They are API, ILSAC (International Lubricant Standardization and Approval Committee), ACEA, JASO (Japanese Automotive Standards Organization) and ASTM (American Society for Testing Materials). All of these testing and approving organizations apply almost same testing procedures. API has set minimum requirements for lubricant performance. Oils are subjected to the tests for oxidation stability, sludge formation, wear in moving parts, lubricant consumption, viscosity adjustment, shear stress, and other common tests.

### **3.2.1 Castrol Power 1 4T 10W-40 motorcycle oil**

During our experiments, we have used multi-grade Castrol Power 1 4T 10W-40 motorcycle oil. Its viscosity range is from 10-40. It is made from synthetic base oil and designed for 4 stroke motorcycle engines. It has been approved by API and JASO and being tested by ASTM standard tests. Its lubricating properties are given in Table 3.1 [44]. It is one of the most commonly used motorcycle oil both in world and in Turkey. It contains polymethacrylate based viscosity modifier and ZDDP additive.

Name	Method	Units	Typical
Density @ 15C, Relative	ASTM D4052	g/ml	Report
Appearance	Visual	-	Clear & Bright
Viscosity, Kinematic 100C	ASTM D445	mm <sup>2</sup> /s	13.0
Viscosity, Kinematic 40C	ASTM D445	mm <sup>2</sup> /s	83
Viscosity Index	ASTM D2270	None	160
Viscosity, CCS -25C (10W)	ASTM D5293	mPa.s (cP)	5000
Total Base Number, TBN	ASTM D2896	mg KOH/g	9.8

Table 3.1 Typical lubricating properties of Castrol Power 1 4T 10W-40 motorcycle oil [44].

### 3.3 Characterization methods of engine oils

Beyond testing engine oils with standard ASTM tests, during scientific research lubricants are investigated with several physical and chemical characterization methods. Characterization of lubricating oils consists of characterization of base oils itself and characterization of additives inside. Oils are being changed according to time or mileage schedule, which is commonly based on color of the lubricant on eye. From scientific viewpoint, it is very important to understand fully what happens during degradation of both lubricants and additives. Mostly used characterization methods are focused on analyzing ZDDP additive inside engine, rather than base oil. But, for characterization of both lubricant and additive Infrared spectroscopy (IR) is used [45-49]. There is also another method that is used for base oil and additive characterization; <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P Nuclear Magnetic Resonance Spectroscopy (NMR) [50, 51]. Other common characterization methods are based on investigation of only ZDDP are: <sup>31</sup>P NMR spectroscopy [52-54], X-ray Absorption Near Edge Structure spectroscopy (XANES) [55, 56] and Cyclic Voltammetry (CV) [57-59]. These methods are suitable for investigation of ZDDP in oils or equivalent solvents. But for analyzing ZDDP on surfaces, Atomic Force Microscopy (AFM) [55, 60, 61], Scanning Electron Microscope (SEM) [42, 55] and Spacer Layer Interferometry Imaging (SLIM is used) [42, 43, 62].

#### 3.3.1 Lubricant base oils and additive characterization methods

The most suitable method for analyzing long chained hydrocarbon base oils and additives inside is IR spectroscopy. As IR spectroscopy is method based on vibration of bonds, functional groups, changes in nature of bonding will provide different

signals. Principles of IR spectroscopy will be discussed in next chapter. Base oils consist of long chain hydrocarbons and in IR spectrum we will see long C-H stretching and bending at  $2800\text{--}3000\text{ cm}^{-1}$  and strong  $\text{CH}_2$  bending peaks at  $1460\text{ cm}^{-1}$ . For ester based oils C=O stretching peaks appear at  $1700\text{--}2000\text{ cm}^{-1}$ , sulfur and nitrogen content peaks also appear, nitrogen content peaks appear around  $1515\text{--}1560\text{ cm}^{-1}$  due to N-O stretching. Carbon and sulfur bond stretching peaks appear at: S=O stretching  $1200\text{--}1030\text{ cm}^{-1}$  and C-S stretching appear at  $600\text{--}800\text{ cm}^{-1}$  region. Additives have also peaks, common additive ZDDP have strong P-O-C stretching at  $970\text{ cm}^{-1}$  and P=S stretching at  $723\text{ cm}^{-1}$ . Other additives like viscosity modifiers PMAs have C=O stretching peaks at around  $1750\text{ cm}^{-1}$  [63]. Advantages of IR spectroscopy are: fast results, inexpensive, easy to monitor, suitable both for liquid and solid applications etc. Typical IR spectrum of untreated Castrol Power 1 4T 10w-40 engine oil is given in Figure 3.5. As it is seen from the spectrum, peaks are easily identified and it is easy to gather information about nature of oil used.

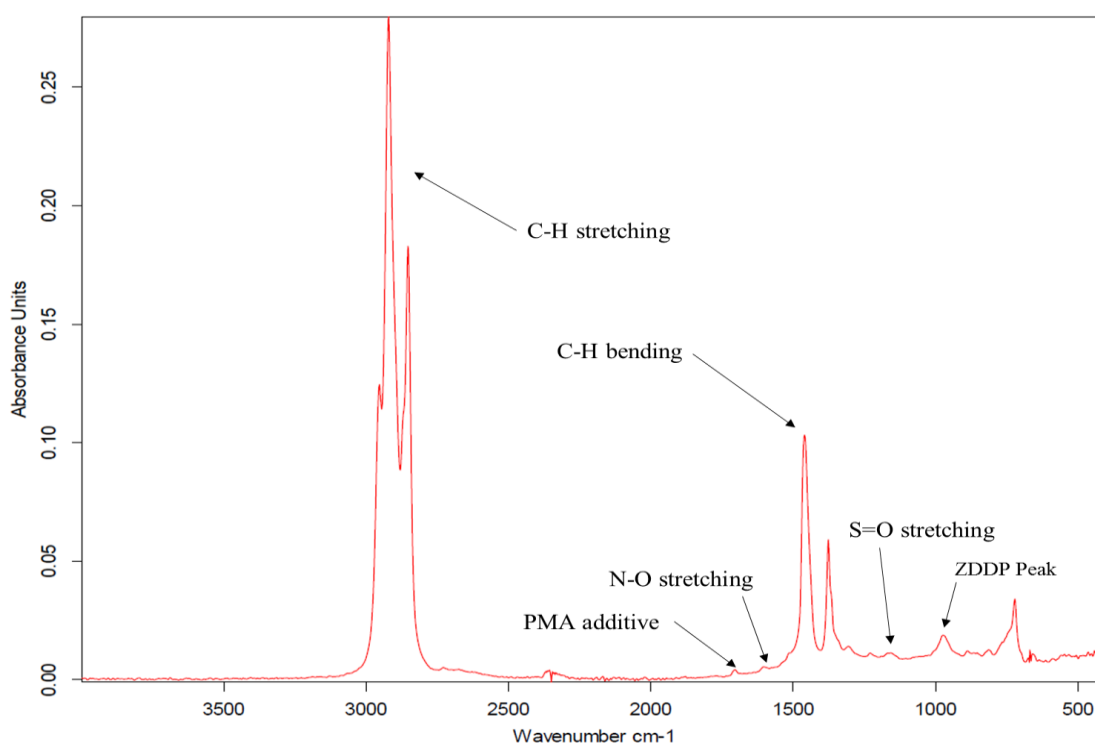


Figure 3.5 A typical ATR-IR spectrum of Castrol Power 1 4T 10w-40 engine oil.

Another method for monitoring both additive and base oil is NMR spectroscopy.  $^1\text{H}$  and  $^{13}\text{C}$  NMR can be used for monitoring base oil and phosphorus NMR can be used for ZDDP analyzing.  $^1\text{H}$  NMR provides data about nature of C-H bonds,  $^{13}\text{C}$  NMR

monitors changes in C-C bond nature.  $^1\text{H}$  and  $^{13}\text{C}$  NMR does not provide full data for oil, because of high C-H and C-C bond nature. In proton NMR, C-H bonds signals are very strong and it is very hard to distinguish changes in other regions, in  $^{13}\text{C}$  NMR there is no such problem but it needs really long scanning times. Because of these disadvantages NMR spectroscopy is minor tool for oil monitoring. However,  $^{31}\text{P}$  NMR is very handy tool for monitoring ZDDP change both in oils and in equivalent solutions. Every compound of phosphorus gives signals at different shifts and by monitoring shifts with time it is easy to monitor ZDDP. One example of ZDDP monitoring with phosphorus NMR is given in Figure 3.6 [52]. As it is seen from the figure  $^{31}\text{P}$  NMR is very handy tool for complete ZDDP monitoring in lubricants.

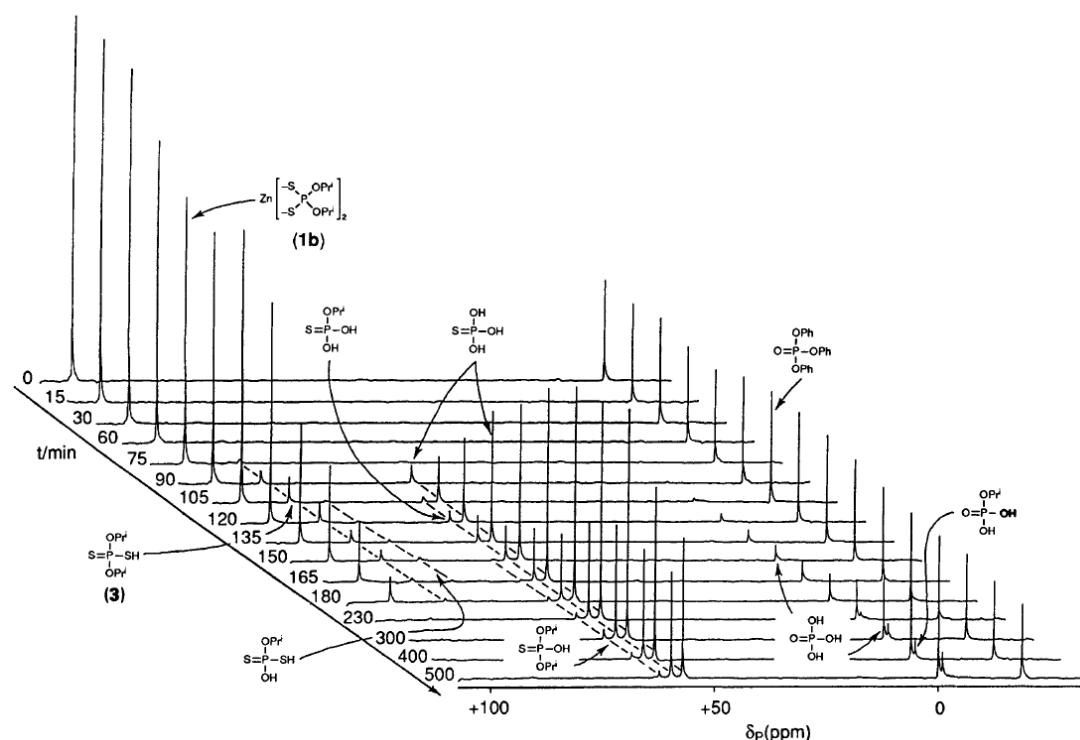


Figure 3.6 ZDDP monitoring by time using  $^{31}\text{P}$  NMR spectroscopy. Taken from ref. 52.

Another method for monitoring ZDDP in lubricant is cyclic voltammetry. CV is method based on oxidation-reduction potentials. It applies voltage either from negative to positive or from positive to negative. Applied voltage is plotted against current and a cyclic voltammogram is obtained. Every antioxidant has its own potential of oxidation/reduction. Current height depends on concentration of oxidizing/reducing specie. Generally, CV is used for monitoring antioxidant additives

in oils, as ZDDP is also additive it can be monitored using CV. By monitoring antioxidant current height, it is possible to determine concentration. Lubricant itself is not conductive and for that reason electrolytes should be used. Electrolytes need to be soluble in base oil and suitable electrolytes should be chosen.

Here, we can also discuss about XANES spectroscopy as a tool for monitoring ZDDP content in lubricants or equivalent solutions. XANES spectroscopy is based on elemental absorption of X-rays. When high energy X-rays hit atoms, photoelectrons are emitted, sometimes electron is not emitted directly, it can be emitted in forms of fluorescence with delay, that is called as Auger process. Different elements in different compounds emit different energy photoelectrons. By monitoring changes in energy of these photoelectrons it is possible to monitor changes in compounds composition [64]. During analyzing ZDDP, photoelectron emission of zinc is being monitored, because of degradation its peaks are shifted and what compounds are formed can be understood.

### 3.3.2 Characterization of ZDDP on surfaces

ZDDP growth on surface can be monitored using AFM, SEM and SLIM. Among these methods, AFM and SLIM allows real-time monitoring of ZDDP growth, but not SEM. For SEM analysis, surface should be investigated prior to growth and compared afterwards. ZDDP forms thin layer on surface of metal and it can be distinguished by SEM. Typical ZDDP growth images taken by SEM are given in Figure 3.7 [55]. ZDDP layer increases from 50 nm to 200 nm within 72 hours of growth time.

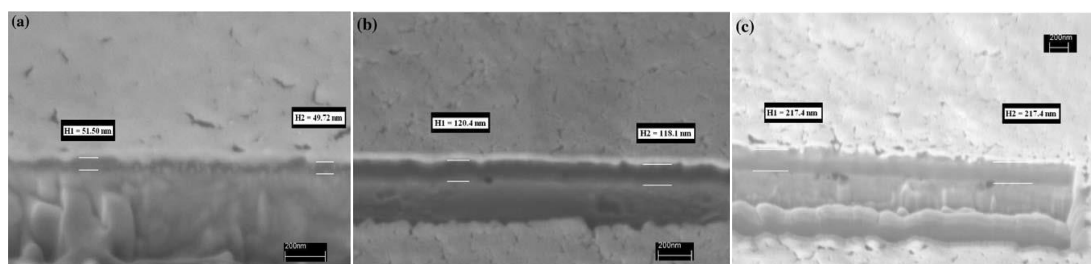


Figure 3.7 SEM images of ZDDP layer after a) 24 hours b) 48 hours c) 72 hours of growth time. Taken from ref. 55.

AFM measures thickness of tribofilm formation and recently growth of ZDDP using AFM tip and real-time monitoring of growth was reported [60]. ZDDP growth was achieved by sliding tip inside oil on top of iron layer. Typical AFM images of ZDDP

growth are shown in Figure 3.8 [60]. Tip sliding cycles were increased and in the same time tribofilm thickness increased from 0 – 30 nm. AFM is essential tool for understanding mechanism of growth in nanoscale. In the same time, effect of high pressure and high temperature on growth was investigated. It was noted that growth rate increases up to some certain pressure, beyond that wear starts. Temperature has positive effect on growth but increasing temperature too high leads to removal of film from surface [60].

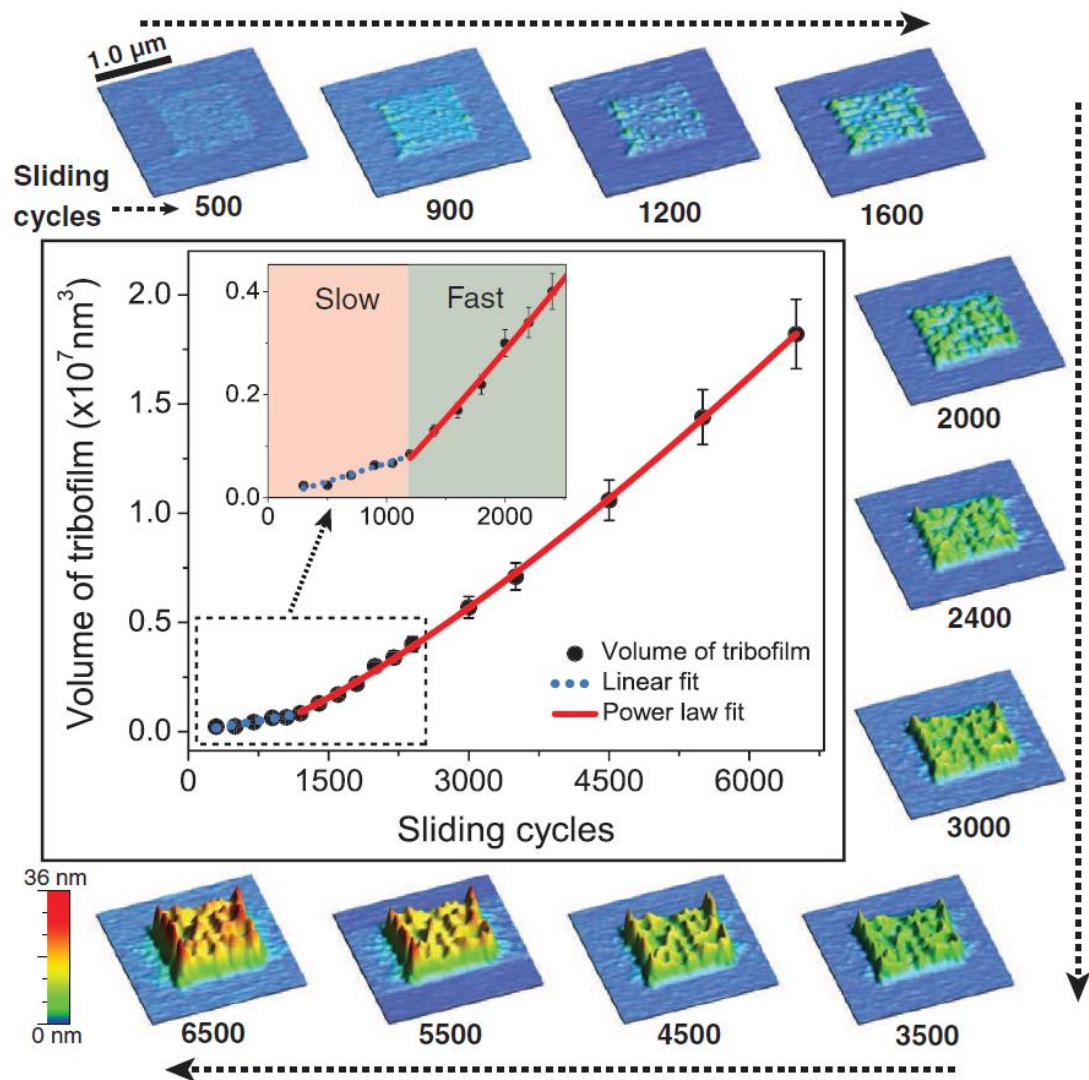


Figure 3.8 Real-time AFM images of ZDDP growth monitoring. Adapted from ref. 60.

SLIM is an imaging method where between sample and detector there is spacer layer. Spacer layer consists of glass layer on very thin chromium layer and spacer material. Beams reflect from sample and then split into two parts at the chromium layer i.e.



there will be two beams, one reflected directly from chromium layer and other from sample surface. Initially, these beams interfere, and by increasing film thickness on the surface this interference starts to change and finally leading black and white regions. Film formation changes reflecting angle, due to this some part of light interferes and some not. For interfering lights, there will be black regions and for non-interfering, white regions will occur. By using charge coupled device (CCD) camera images can be colorized [65]. Using this imaging method tribofilm growth can be monitored in real-time. Typical real-time tribofilm growth SLIM images are represented in Figure 3.9 [62]. Contrast color on the surface changes with increasing growth time. Using same technique, wear of film from the surface can be monitored. Both AFM and SLIM are suitable methods for observing small changes on tribofilm.

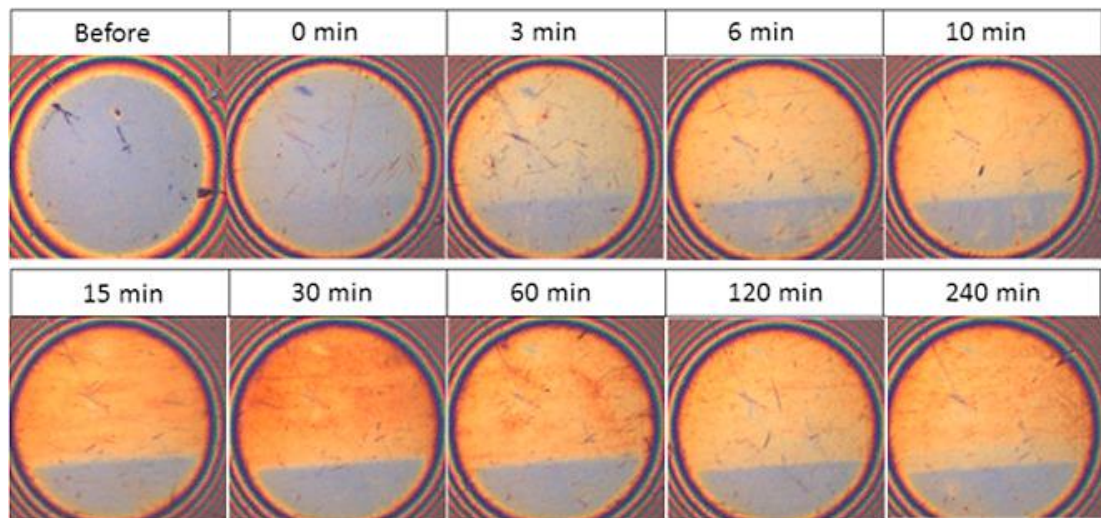
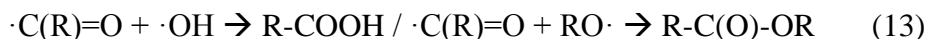
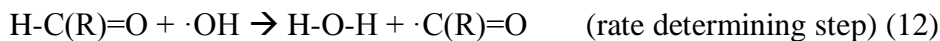
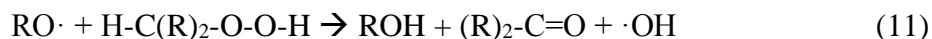


Figure 3.9 SLIM images of real-time tribofilm growth monitoring on steel sphere surface. Taken from ref. 62.

### 3.4 Oxidation of lubricants

Lubricants start to be oxidized, this can be observed by comparing color of oils. First obvious sign of lubricant oxidation is change in color. Initially, slight yellow color of oils becomes brown and consequently black (Figure 3.10) [66]. Color change of oils is mainly due to additives and sulfur content. Fully refined and desulfurized oils are colorless and called as white oils. During their oxidation, no color change is seen [67]. Prior to base oil oxidation, antioxidant degradation process happens. Antioxidants deplete at high temperatures and only after that base oils start to thermally degrade. Antioxidants block free radicals formed and terminate the chain reactions. Mechanism

of inhibition was given in previous sections. In this part, we will focus mainly what happens after depletion of antioxidant. Initially, R-H groups form R· radicals and they propagate the chain reaction. Further reactions happen in following way [33]:



Due to long chains of reactions alcohols, ketones, aldehydes, carboxylic acids and esters are formed. As more oxygen reacts, more oxygen containing products are formed and lubricant becomes more polar, losing its lubricating properties. These changes can be easily seen and identified by IR spectroscopy (Figure 3.11). Oxidation peaks appear as collection of peaks, but there are minor peaks overlapped in between. We have identified 5 different peaks: 1697, 1718, 1731, 1740 and 1773  $\text{cm}^{-1}$ . Assignment of these peaks was done using Table 4.2 and they are given in Table 3.2. There are mainly three types of carbonyl groups identified IR spectrum shown in Figure 3.11: ketones, aldehydes and esters, here we cannot identify peaks for carboxylic acids.

Peak center ( $\text{cm}^{-1}$ )	Functional group and structure	
1697	Ketone	R-(C=O)-R
1718		Ar-(C=O)-R
1731	Aldehyde	R-(C=O)-H
1740	Ester	R-(C=O)-OR
1773		R-(C=O)-OAr

Table 3.2 Assignment of carbonyl peaks identified in IR spectrum given in



Figure 3.10 Color changes of lubricating oil during degradation (oxidation) [66].

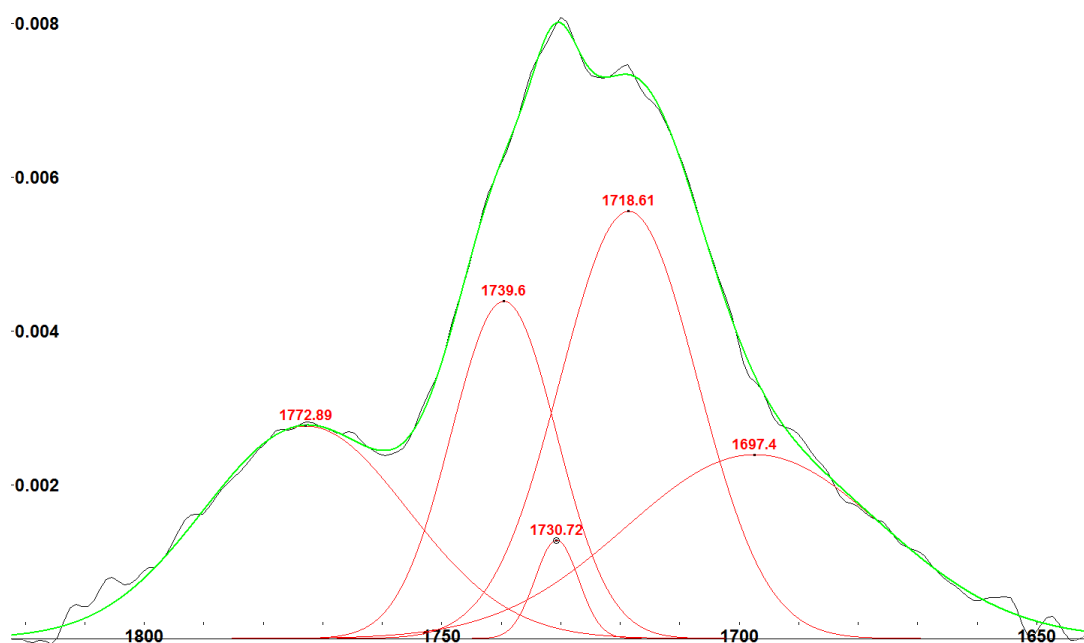


Figure 3.11 IR carbonyl (C=O) absorption region of SN150 base oil oxidized at 200 °C at 1atm for 17 hours in a round bottomed flask (rbf).

IR spectroscopy is one of the best methods for studying oxidation of lubricating motor oils, as it allows to analyze both, changes in additives and changes in base oil structure separately.

# Chapter 4

## 4 Materials & Methods

This master's thesis work presents work on reclamation of used oil, using sodium hydroxide in combination with magnetite nanoparticles. Initially, SN150 base oil was oxidized on hot plate or in the reactor for several hours and they were reacted with NaOH and Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Obtained samples were mixed with DI water and fresh re-usable oil phase was collected at the top and water miscible oxygen containing species were collected at the bottom phase.

### 4.1 Chemicals used

SN 150 base oil was obtained from Özçınarlar A.Ş. Oil Manufacturing Company in Kutahya/Turkey. Physical and chemical properties of this oil were shown in the previous chapters.

Sodium hydroxide and potassium hydroxide salts were obtained from Merck chemicals (84.0% purity: it was chosen to reduce cost of reclamation process) and used in 1:1 portions during experiments.

FeCl<sub>3</sub>·6H<sub>2</sub>O and FeCl<sub>2</sub>·4H<sub>2</sub>O solid salts were obtained from Merck chemicals, 1.0 and 2.0 M solutions were prepared in deionized water (DI) and used respectively. Concentrated (25%) ammonium hydroxide (VWR chemicals) was used with dilution.

Chloroform-d (CDCl<sub>3</sub>) was obtained from Merck chemicals (99.8% absolute for NMR grade) and used for proton (<sup>1</sup>H) and carbon (<sup>13</sup>C) NMR analysis.

In all stages; separation, washing and in all reactions in procedures DI water was used (18 µS resistivity).

For neutralization of bottom layer containing sodium salts of carboxylic acids and for preparation of other necessary solutions 37% Analar grade hydrochloric acid (VWR

Chemicals) was used. Barium hydroxide (Merck 98%) was used the preparation of basic titration standard solution.

Analar grade Isopropyl alcohol (IPA) (VWR Chemicals) and Analar grade toluene (VWR Chemicals) were used for preparation of titration solvent (in 99:100 ratio).

Titration end points were determined by laboratory grade bromothymol blue and phenolphthalein indicator solutions.

IR analyses were performed without using any solvent or additional reagent. A droplet was placed on the top of ATR crystal.

## **4.2 Procedures**

There are three main reactions procedures in total; oxidation of base oils, preparation of magnetic iron oxide nanoparticles, reclamation of used base oils using caustic soda in combination with iron oxide nanoparticles.

### **4.2.1 Oxidation of SN150 base oil**

SN150 base oil was oxidized at 200 °C under atmospheric pressure. For measuring temperature, internal probe was used and outside temperature was adjusted accordingly. Initially, base oil was oxidized on hotplate and after reactor was used for better oxidation. Oxidation process was monitored using IR spectroscopy. For observation of better oxidation peaks (changes in carbonyl region) oxygen was bubbled during heating process. Totally, three different samples were used, first oxidized with air bubbling inside 250 ml round bottomed flask at 200 °C for 17 hours. Temperature was adjusted using external probe and whole oxidation process was monitored with FTIR spectrometer. Second used sample was for control purposes and it was prepared by oxidation in PARR reactor 4838 series at 200 °C, adjusted with external probe of reactor. Air was bubbled inside at 30 LPH (liter per hour) flow rate. Whole oxidation process was continued for 4 hours and oxidation was monitored with FTIR-ATR spectrometer. The spectrum of SN150 base oil oxidation is given in Figure 4.1. Last sample was also for control, SN150 base oil was oxidized on hot plate at 200 °C without air bubbled in, temperature was adjusted using external probe of hot plate. Oxidation was continued for 36 hours and results were analyzed with FTIR and NMR spectrometers using OPUS and TOPSIN software.

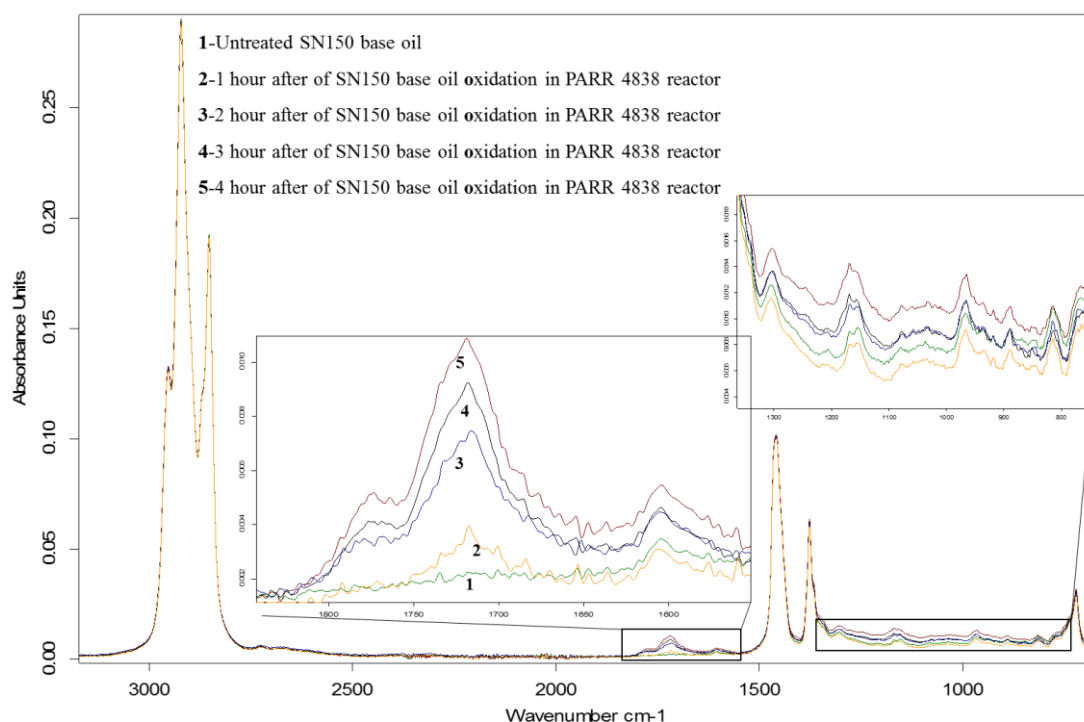


Figure 4.1 IR spectra of SN150 base oil oxidized in PARR 4838 series reactor for 4 hours.

For understanding better oxidation mechanism, we have calculated peak area increase with respect to time (Table 4.1). Untreated SN150 base oil initially does not contain any carbonyl peaks. 1 hour after the oxidation reaction, small carbonyl peak starts to appear. Interestingly, in the 2<sup>nd</sup> hour of oxidation new peaks formed. In the 3<sup>rd</sup> and 4<sup>th</sup> hours of oxidation reaction the composition of peaks did not alter, only intensity of peaks increased. Sulfur moiety peaks also increased with time. Sulfur compounds act as a natural antioxidant in oils, this explains why after 1<sup>st</sup> hour of oxidation different carbonyl peaks started to appear. Initially, sulfur moieties prevented oxidation of hydrocarbons. Only after their oxidation (after 1<sup>st</sup> hour of oxidation reaction) hydrocarbons start to be oxidized.

Sample	Carbonyl peak area
Untreated SN150 base oil	0
1 hour after oxidation	0.138
2 hour after oxidation	0.344
3 hour after oxidation	0.44
4 hour after oxidation	0.535

Table 4.1 Carbonyl peak areas of oils with respect to oxidation time.

#### 4.2.2 Oxidation of Castrol Power 1 4T 10w-40 motorcycle oil

In our studies, we have used Castrol Power 1 4T 10w-40 motorcycle oil. This engine oil was oxidized in a vial at 170 °C. The oxidation process was monitored with FTIR spectrometer (see Figure 4.2). During oxidation process, ZDDP deplete, viscosity modifier additives also deplete with time and carboxylic acid peaks start to appear. By increasing time, ZDDP additive peak is disappearing (Inset right), at that time there is no obvious change in carbonyl region (Inset left). Base oils do not contain carbonyl group initially, here carbonyl region peaks belong to PMA based viscosity index improver additive. By increasing heating time, this peak also decreases and after depletion of ZDDP starts to rise. Also, at carbonyl region new peaks start to appear. These newly formed peaks indicate that oxidation of base oils inside starts only after depletion of ZDDP additive. There is also increase in N-O region, as well as in S-O and C-S regions too. There is no obvious change in other regions. Also, during oxidation of engine oils due to depletion of viscosity modifier additive viscosity of oils start to increase. Their viscosity range changes and they become unusable.

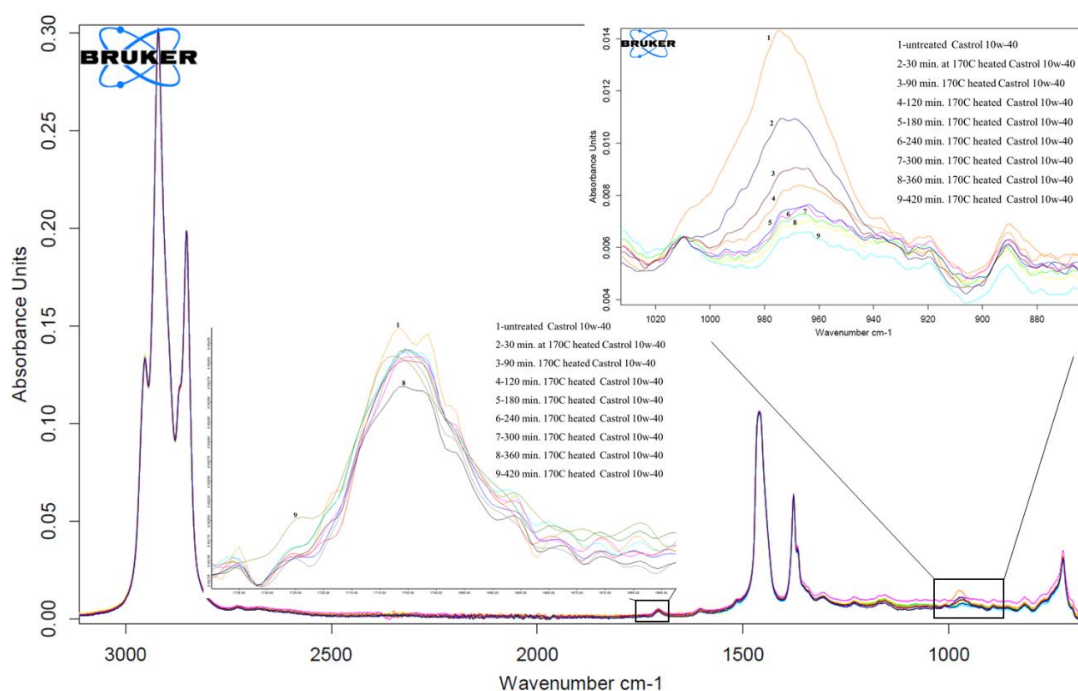
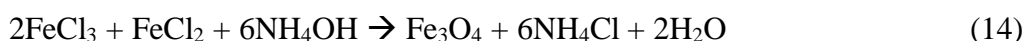


Figure 4.2 IR spectra of Castrol Power 1 4T 10w-40 engine oil heated at 170 °C for different times. Inset right: magnified IR region of ZDDP additive. Inset left: magnified IR region of PMA based viscosity modifier.

### 4.2.3 Preparation of magnetic iron oxide nanoparticles

Magnetite nanoparticles ( $\text{Fe}_3\text{O}_4$ ) were synthesized according to the method described in “Room Temperature Co-Precipitation Synthesis of Magnetite Nanoparticles in a Large pH Window with Different Bases” study [68]. From previously mentioned salts,  $\text{FeCl}_2$  and  $\text{FeCl}_3$  solutions were prepared in DI water respectively. 25%  $\text{NH}_4\text{OH}$  solution was diluted using DI water. 1.0 mL of 2.0M  $\text{FeCl}_2$  and 4.0 mL of  $\text{FeCl}_3$  were mixed in 100 mL beaker. They were vigorously mixed and 50 mL of 0.7M ammonia solution was added dropwise. Reaction proceed according to following equation:



In the end of reaction, stirbar was removed immediately and solution was put to settling down. After a few minutes liquid on top was poured off, remaining part was washed with DI water and left again for nanoparticles to settle down. This procedure was repeated several times for removing excess and unreacted salts. At last stage, magnetic nanoparticles were fixed to bottom of beaker by help of strong magnet and washed with ethanol solvent several times. This was done to remove water content completely, as nanoparticles were aimed to be used in oil samples. After washing with ethanol, samples were first dried with rotary evaporator and then further in under vacuum. Finally, dried nanoparticles were crushed with plastic spatula.

### 4.2.4 Characterization of Magnetic nanoparticles

Synthesized iron oxide magnetic nanoparticles were characterized using Scanning Electron Microscope (SEM) and Zeta Sizer (Figure 4.5). Size range of synthesized nanoparticles measured with was between 30-50 nm. After reclamation reaction, magnetic nanoparticles were also analyzed with FTIR and EDX spectroscopy. After analysis, it was observed that Fe oxide nanoparticles (np) were coated with oxidized oil molecules. When we look into IR spectra of Fe oxide np, we can see new formed peaks that belong to oxidized oil molecules (Figure 4.3).



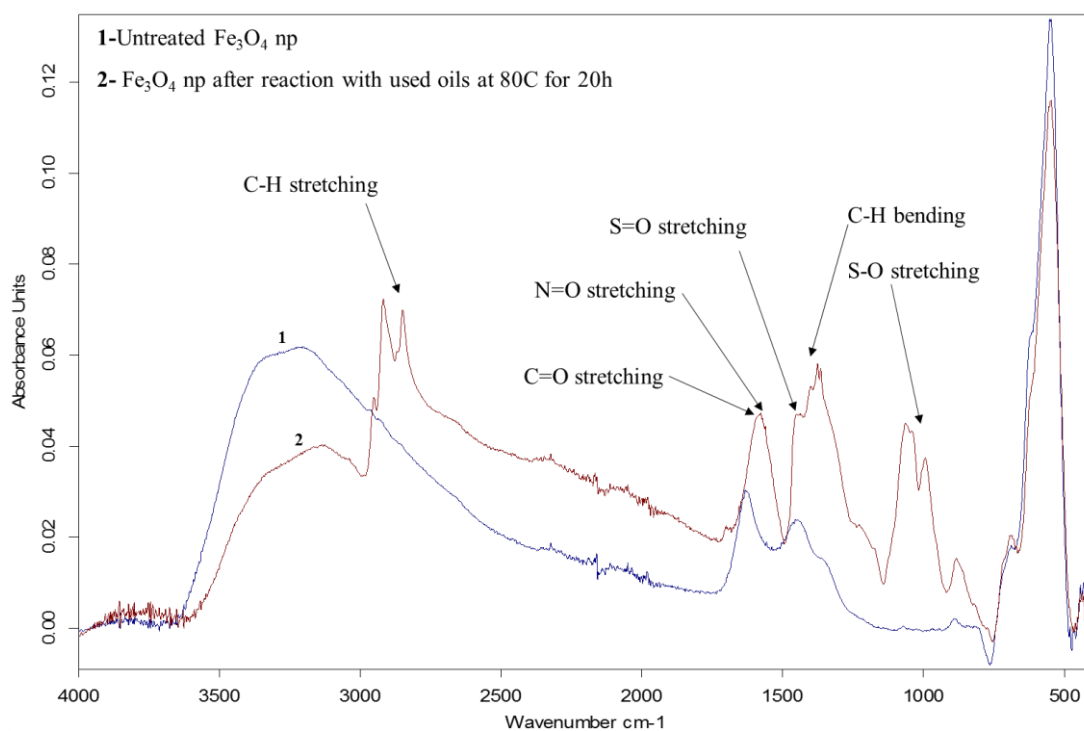


Figure 4.3 IR spectra of untreated Fe oxide and after reaction with used oil.

Also, these changes were analyzed using EDX (Energy-dispersive X-ray spectroscopy) spectrum of SEM instrument (Figure 4.4). EDX provides elemental analysis of samples that are under investigation. Initially, in EDX spectrum of untreated Fe oxide np we see oxygen and iron peaks. After reaction with used oils we see formation of carbon peak. These results indicate that after treating our np with used oils they become coated with oxidized oils molecules.

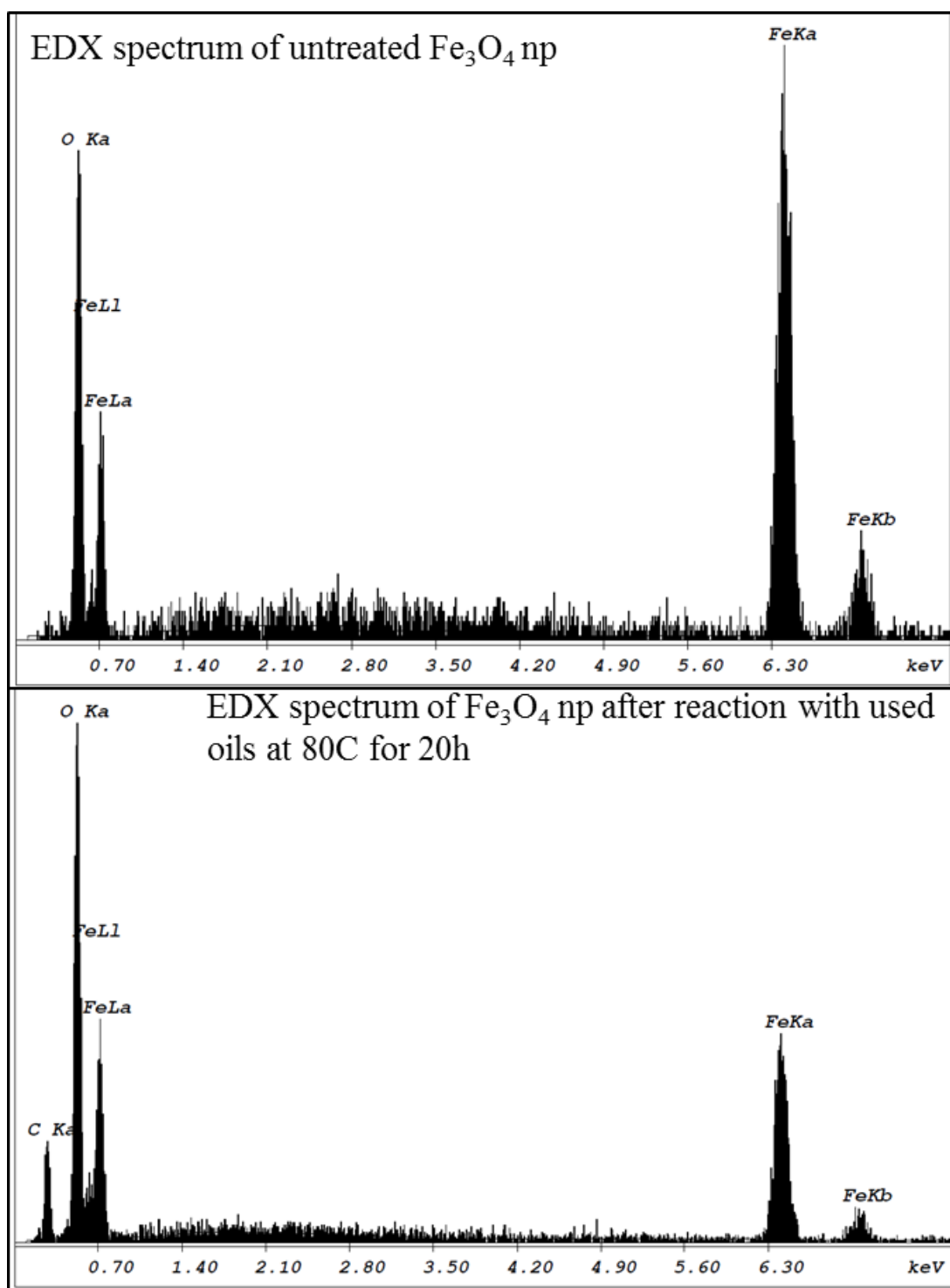


Figure 4.4 EDX spectra of untreated Fe oxide np (top) and after reaction with used oils.

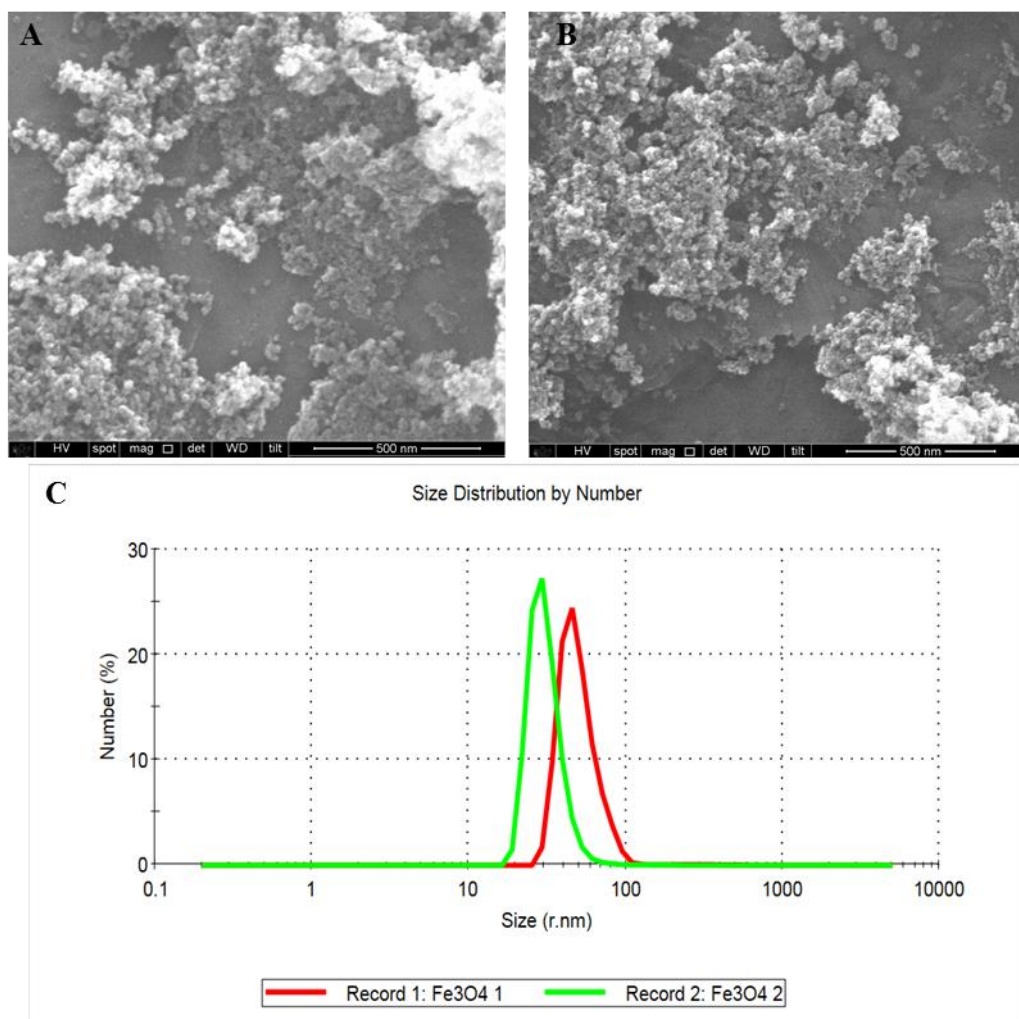


Figure 4.5 (A), (B) SEM images of synthesized magnetic nanoparticles, (C)-Zeta Sizer measurement result of synthesized magnetic nanoparticles.

#### 4.2.5 Reclamation of oxidized oils

Previously prepared oxidized oil samples were used for these experiments. Sodium hydroxide was used according to method described in US Patent [69]. According to the patent amount of sodium and potassium hydroxide mixture should be added within 5-10% of oil mass. We have added about 4.0 gr of oxidized oil sample and about 200 mg of NaOH. Cap of vial was closed tightly and coated with parafilm. Argon gas was bubbled inside of this vial for 20 mins. Sample was put on hot plate and temperature was adjusted to 120 °C. Also, argon balloon was put on samples for maintaining constant argon atmosphere. Samples were heated for very long times (120-180 hours). Second attempt was tried at 150 °C under same conditions. Trials with Fe<sub>3</sub>O<sub>4</sub> nanoparticles were done in same way, 80 mg of nanoparticle was added. Also, mixture of NaOH and KOH was used in mass ratio of 1:1. Lately, reclamation was done using

800 mg of NaOH+KOH (1:1) bases and 11.0 gr of oxidized SN150 base oil was used and heated for 160 hours.

For using only magnetic iron oxide nanoparticles, we added 20 mg of nanoparticle to 4 gr of oxidized base oil. The same procedure for maintaining argon atmosphere was applied and it was heated at 120 °C for several days. Reaction was monitored with FTIR spectrometer with certain time domain.

#### **4.2.6 Preparation of standard titration solutions for determination of total acid and base numbers**

All procedures were obeyed to ASTM D974 test procedures [70]. Initially, 0.9 mL of concentrated hydrochloric acid (HCl, specific gravity: 1.18) was taken and dissolved in 100 mL of IPA. Afterwards, 600 mg of KOH was taken and dissolved in IPA, heated to 120 °C and boiled with stirring for 15 minutes. After observation of complete dissolution, 260 mg of barium hydroxide was added and again boiled at 120 °C for additional 10 minutes. Solution was cooled and remained for several hours. After, it was filtered with fine mesh grade filter paper (MN615). After filtration, solution was directly used for titration. Titration solvent was prepared using toluene, water and IPA. These three ingredients were mixed with according to ASTM ratios (100:1:99) [70].

#### **4.2.7 Titration of samples**

Initially, two  $0.2 \pm 0.02$  g of samples were taken and mixed with titration solvent. Indicator was used methyl orange for titration of oil samples and for blank titration also same indicator was used. Samples were titrated with previously prepared standardized KOH solution. Subsequently, blank titration was performed. Calculations were done using difference of volumes that were consumed in titration blank and sample, separately.

### **4.3 Analytical techniques**

All analyzes were done using two main instruments; Bruker ALPHA Platinum Attenuated Total Reflectance (ATR) spectrometer with single reflection diamond module and Bruker AVANCE III 400 MHz/54 mm NMR spectrometer. I will briefly explain Bruker ALPHA's Platinum ATR spectrometer.

### 4.3.1 Infrared spectroscopy

Using fingerprint IR absorption energies of bonds it is possible to identify functional groups in a molecule, track changes in a spectrum and derive quantitative data. Typical fingerprint IR absorption peak changes in oils during oxidation process are given in Table 4.2. Peak analysis of other IR spectra were done with respect to this table.

Molecular Functionality	Specific Structure <sup>a</sup>	Functional Group	Frequency (cm <sup>-1</sup> )
Carboxylic acid	R-(C=O)-OH	C=O	1,710 (dimer) 1,760 (monomer)
		C=O	1,690 (dimer)
	Ar-(C=O)-OH	OH	3,000–2,500 (dimer)
			3,530 (monomer)
Ketone	R-(C=O)-R	C=O	1,715
	Ar-(C=O)-R	C=O	1,685
	Ar-(C=O)-AR	C=O	1,665
Aldehyde	R-(C=O)-H	C=O	1,735
	Ar-(C=O)-H	C=O	1,705
		(C=O)-H	2,900–2,700
Ester	R-(C=O)-OR	C=O	1,740
	Ar-(C=O)-OR	C=O	1,725
	R-(C=O)-OAr	C=O	1,770
		C-O	1,300–1,100
<sup>a</sup> R = aliphatic group, Ar = aromatic group			

Table 4.2 Typical IR absorption peaks of different carbonyl moieties [71].

#### 4.3.1.1 Bruker ALPHA Platinum ATR Spectrometer

Bruker ALPHA ATR Spectrometer is benchtop small size diamond based single reflection instrument. It contains changeable modules according to applications, ALPHA Platinum is module that contains diamond crystal with clamp, that can be used to press solid samples for better absorption. Its image is represented below in Figure 4.6 [72].



Figure 4.6 Bruker ALPHA Platinum ATR single reflection diamond based ATR spectrometer that was used in this study. Taken from ref #72.

#### **4.3.2 NMR spectroscopy**

NMR analyses were done with Bruker AVANCE III 400 MHz/54 mm NMR spectrometer. Standard 5 mm probes were used for samples. For  $^1\text{H}$  NMR analysis, 64 scans with 62.5 s of dwell time, range of 0-18 ppm was used. For  $^{13}\text{C}$  NMR analysis, 16000 scans with 220 s of dwell time, range of 0-210 ppm was used. Same samples were used for both  $^{13}\text{C}$  and  $^1\text{H}$  NMR analysis.

#### **4.3.3 Scanning Electron Microscope**

SEM images were acquired using FEI Quanta ESEM instrument. Samples were prepared directly on aluminum SEM sample holder. Images were taken at 15.0 kV energy and 2.5 spot size. EDX spectrums were obtained from survey scan at 15.0 kV energy.

#### **4.3.4 Zeta Sizer**

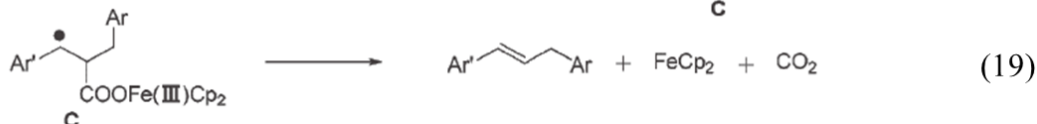
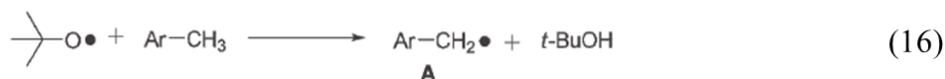
Zeta Sizer data were obtained using Malvern MAL1033437 instrument. Fe oxide np were mixed in water. Refractive index of material was chosen as 2.42. Viscosity and refractive index of dispersant were as 0.8872 cP and 1.33 respectively. 3 measurements were made and average value was chosen.

# Chapter 5

## 5 Results & Discussion

### 5.1 Results with magnetic nanoparticles in combination with radical initiators

Magnetic iron oxide nanoparticles were used in decarboxylation of carboxylic acids. The mechanism suggested was [73]:



In this mechanism rate limiting step is cleavage of  $\text{sp}^3$  C-H bond (reaction 16). Instead of nanoparticles it is possible to use ferrocene, and other iron salts. But, magnetic nanoparticles can be collected easily from solution by using strong magnet. Being inspired by this idea we treated oxidized oil with iron oxide magnetic nanoparticles (np). Reaction was monitored within certain time domains.

Prior to passing to results that were obtained by using nanoparticles, I want to show the changes that took place during the oxidation of SN150 base oil. Here the changes occur mainly in carbonyl region and minor changes were observed at sulfur region (Figure 5.1). As it is shown from the spectrum, in carbonyl region there are different overlapped peaks. Absorption signals are increased in the sulfur region. The first

observation suggests formation of ketones, aldehydes, esters and carboxylic acids [74-76]. Peak fitting of the carbonyl (C=O stretching) region indicates there are at least 3 different C=O bearing groups present (Figure 3.11). Interestingly, increasing oxidation time (i.e. in flask, in a vial or in a reactor etc.) of base oil leads to formation of similar peaks on IR spectrum. There is no any change in composition but increasing oxidation time increases intensity of peaks.

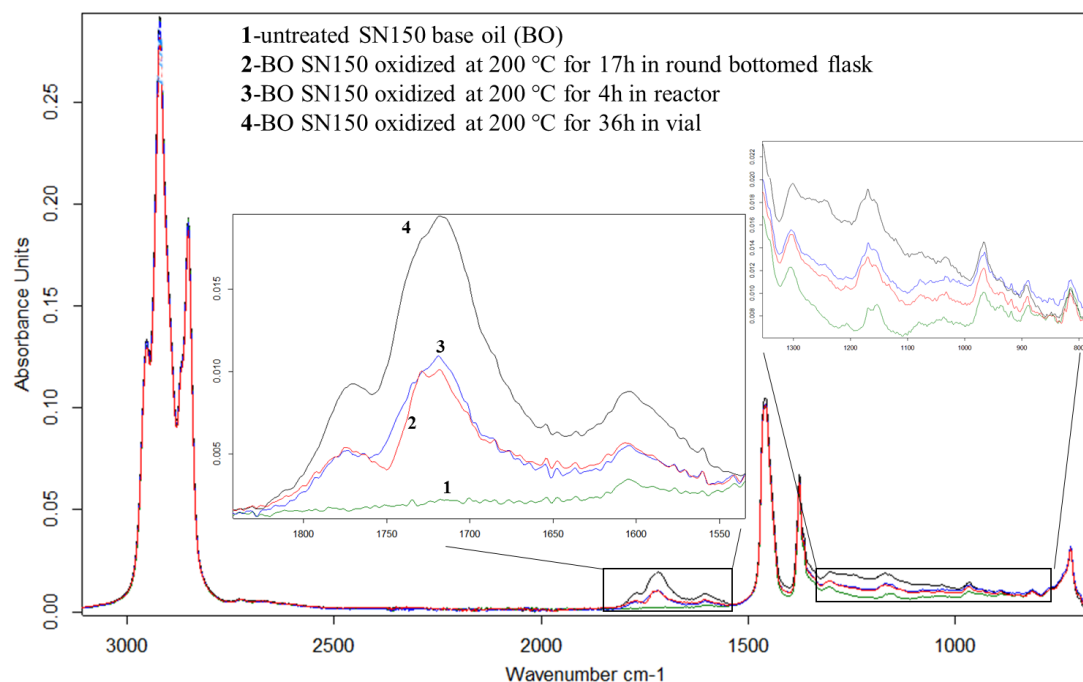


Figure 5.1 IR spectra of untreated and oxidized SN150 base oil in a flask, in a vial and in the PARR model 4838 reactor.

Iron oxide magnetic np and ferrocene experiments were carried with SN150 oil that was oxidized in PARR model 4838 reactor at 250 °C for 4 hours. During the oxidation reaction changes in carbonyl peaks were monitored with FTIR spectrometer. Results showed that both  $\text{Fe}_3\text{O}_4$  and ferrocene were effective in reducing carbonyl amount in oxidized oil (Figure 5.3 and Figure 5.4). It is seen from the figures clearly, that there is reduction in carbonyl peaks ( $\sim 1700\text{ cm}^{-1}$ ) and nitration peaks ( $\sim 1600\text{ cm}^{-1}$ ) in both in magnetic np and ferrocene. But, due to easy removal and possibility to reuse magnetic iron oxide np, they were selected for our studies. After 11 hours of reaction with magnetic np there was 10% diminishment, and after 21 hours it increased to 16%. The peak diminishment can be explained by adsorption (chemisorption and physisorption) of oxidized oil species to np surface [78]. Another advantage of magnetic np is that, they can be stirred by the help of magnetic stirrer. However,



magnetic nps don't fully eliminate carbonyl peak and not much change occurred in color of oxidized oils compared to untreated oils.

In the equations 15 and 16, given above, tert-butyl peroxide is used as radical initiator [73]. But, in our experiments with oxidized oil we did not use any radical initiator. For this purpose, we tried using azobisisobutyronitrile (AIBN) radical initiator. AIBN produces free radicals at 80 °C according to mechanism shown in Figure 5.2 [77]. After addition of AIBN with Fe<sub>3</sub>O<sub>4</sub> np, results were different from what we expected. Oxidation peaks instead of decreasing, increased as it is seen in Figure 5.5. Peaks initially increased and decreased afterwards. After 72 hours of reaction, we concluded that the treatment of used oil with radical initiator did not become effective as it was original work [73]. Within 72 hours, reaction was monitored with FTIR spectroscopy within certain time domain. We expected decrease in carbonyl peaks intensity. Initial results were opposite to expected. But reaction was continued for longer times, due to slow reaction rates in long hydrocarbon chains.

After these series of experiments, we concluded that magnetic np is not enough itself for oil recovering or regeneration, as we inspired from the literature study on “iron-catalyzed direct alkenylation of sp<sup>3</sup>(C–H) bonds via decarboxylation of cinnamic acids under ligand-free conditions” [73].

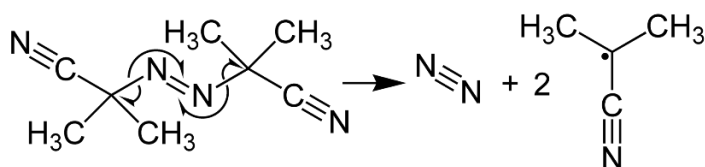


Figure 5.2 Mechanism of radical formation from AIBN [77].

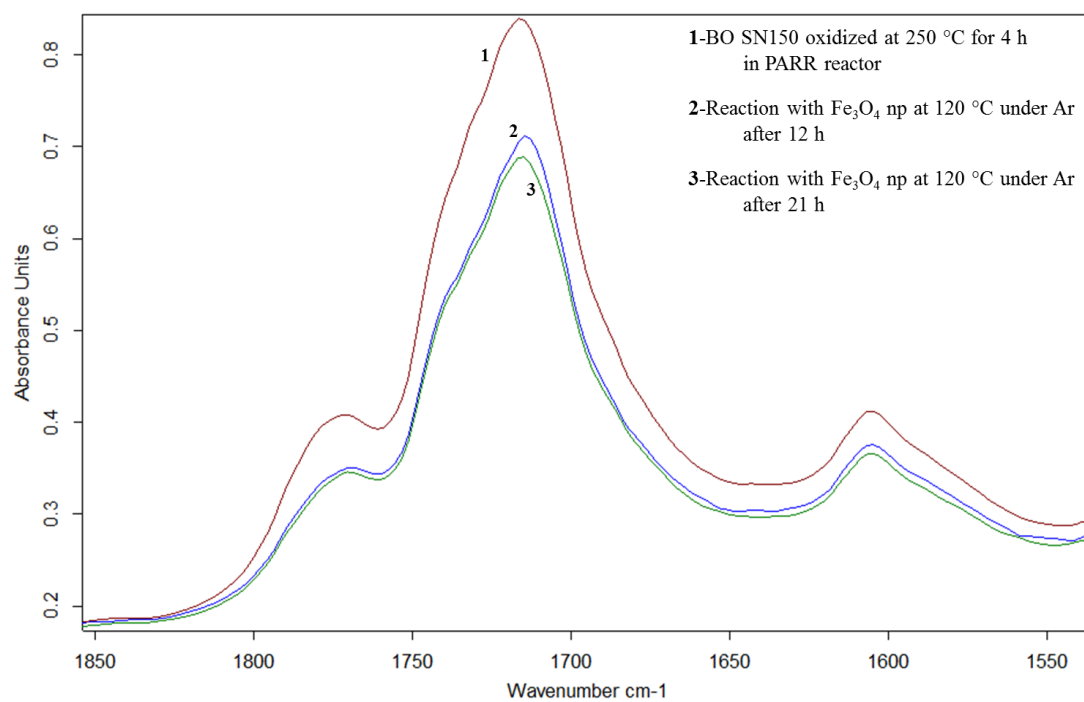


Figure 5.3 IR spectra of reaction of oxidized SN150 base oil (BO) with magnetic np.

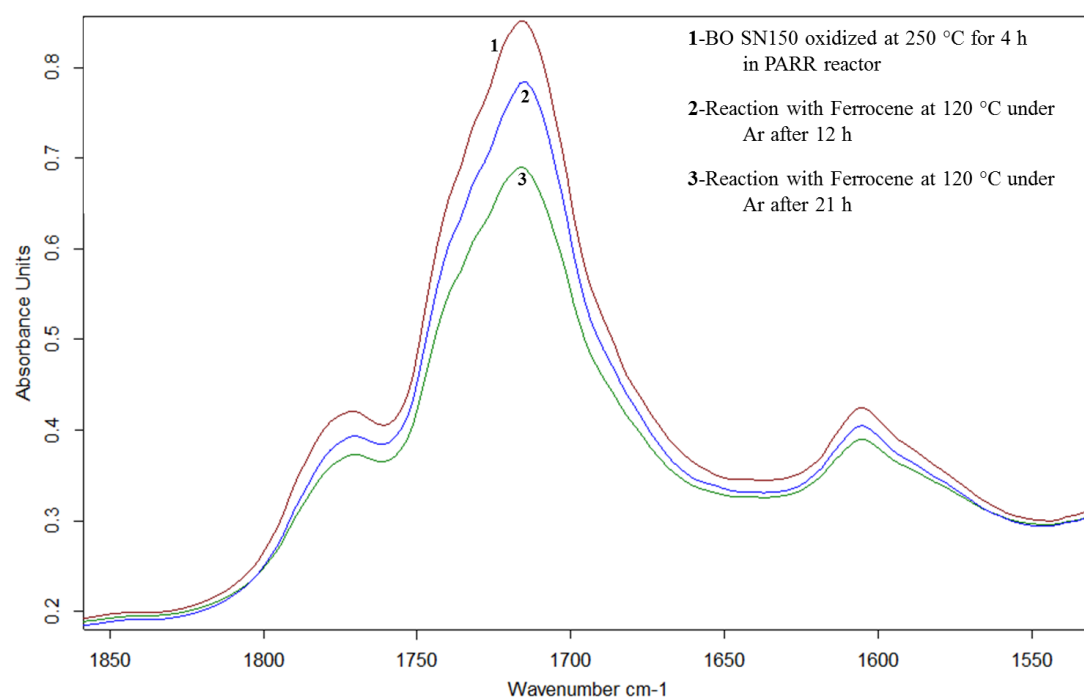


Figure 5.4 IR spectra of reaction of oxidized SN150 base oil (BO) with ferrocene.

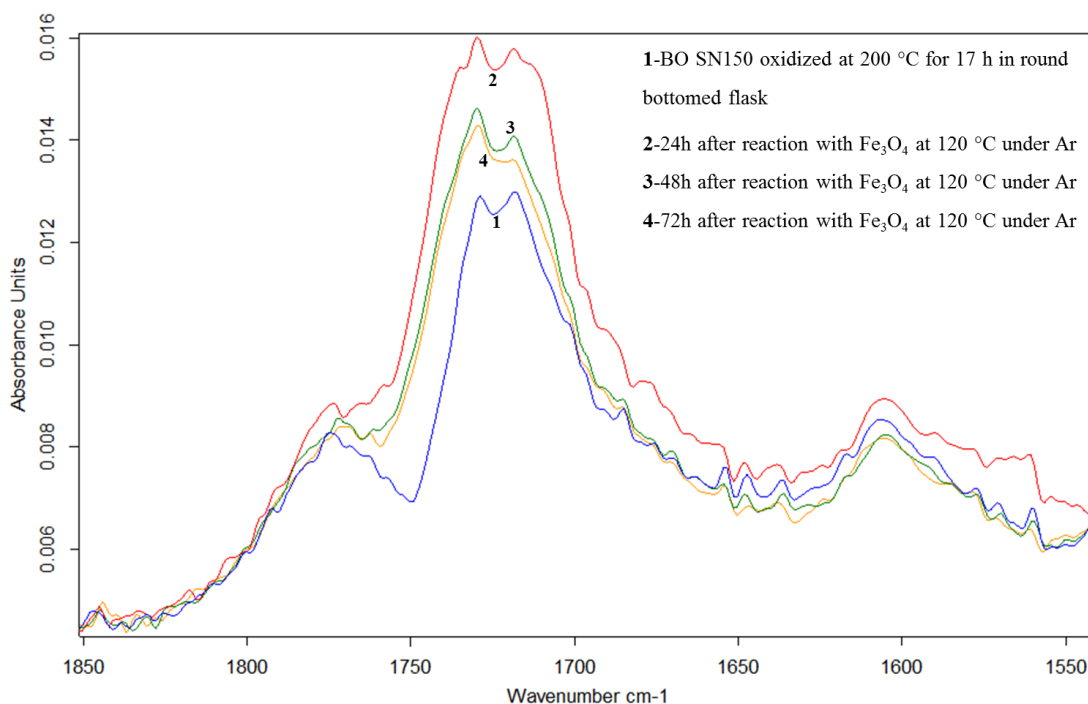
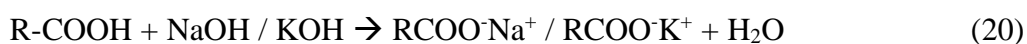


Figure 5.5 IR spectra of reaction of oxidized SN150 BO with Fe<sub>3</sub>O<sub>4</sub> in presence of AIBN as a radical initiator.

## 5.2 Experiments in combination with caustic soda

### 5.2.1 Idea of using sodium hydroxide

The idea of using sodium hydroxide with magnetic np came from that oxidized oil are carboxylic acids (**R-COOH**), and they can form possibly water transferrable salts via saponification reaction and that can increase effect of magnetic np in decarboxylation:



According to mechanism and equations given in part 5.1, carboxylic acids bind to magnetic nps as carboxylates by losing its acidic hydrogen, i.e. providing R-COO<sup>-</sup> would easily bind to magnetic iron oxide nps [68, 78]. After addition of sodium hydroxide, we observed a huge shift in peaks (Figure 5.6). This shift indicated salts are forming during heating process. Initially, in BO SN150 oxidized at 200 °C for 17 hours contains two main peaks at 1775 and 1723 cm<sup>-1</sup>, after reaction with NaOH in presence of magnetic np the peak at 1775 cm<sup>-1</sup> disappeared, intensity of peaks at 1723 cm<sup>-1</sup> dropped and new broad peaks started to appear at 1577 cm<sup>-1</sup>. Literature studies indicate that newly formed peaks correspond to carboxylate salts (1550-1610 cm<sup>-1</sup>) [79]. Monitoring these peaks proved the reaction between carboxylic acids and esters with NaOH to form salts. Also, there is intensity decrease in C-S and S-O regions,

indicating reaction with sulfones, sulfates etc. are also taking place. After seeing these results, we decided to check reaction of oxidized oil with NaOH only, without magnetic nanoparticles. There should be the same reaction, we decided to check what changes if using only sodium hydroxide. The results were given in Figure 5.7 and decreasing of oil oxidation peaks were observed. After getting these results, the reaction was carried at 150 °C, both for sodium hydroxide only and in presence of magnetic nanoparticles. IR spectrum of reaction with sodium hydroxide in presence of magnetic np is shown in Figure 5.8. Firstly, to understand effect of magnetic np on oil reclamation, spectra that were obtained after NaOH treatment only and NaOH+Fe nps treatment at 120 °C were compared (Figure 5.9). Importantly, decrease in the intensity of C=O peak was observed in either case. In the presence of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, reaction time was faster, but there was huge difference in the oxidation peak.

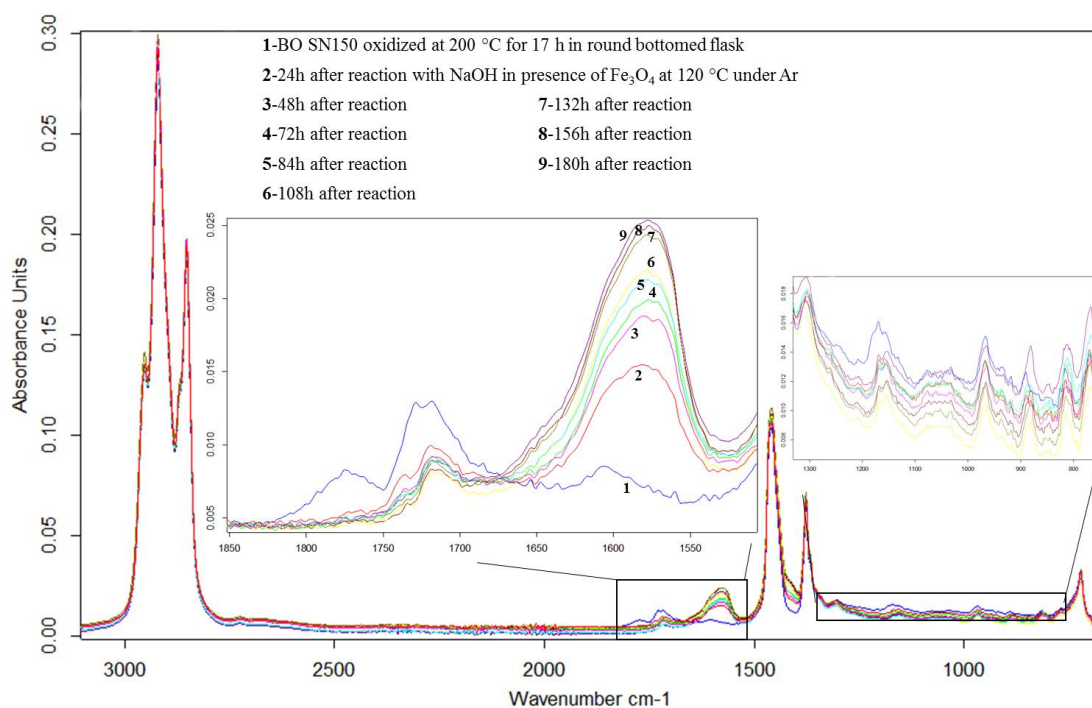


Figure 5.6 IR spectra of reaction of oxidized base oil with NaOH in presence of magnetic nanoparticles at 120 °C.

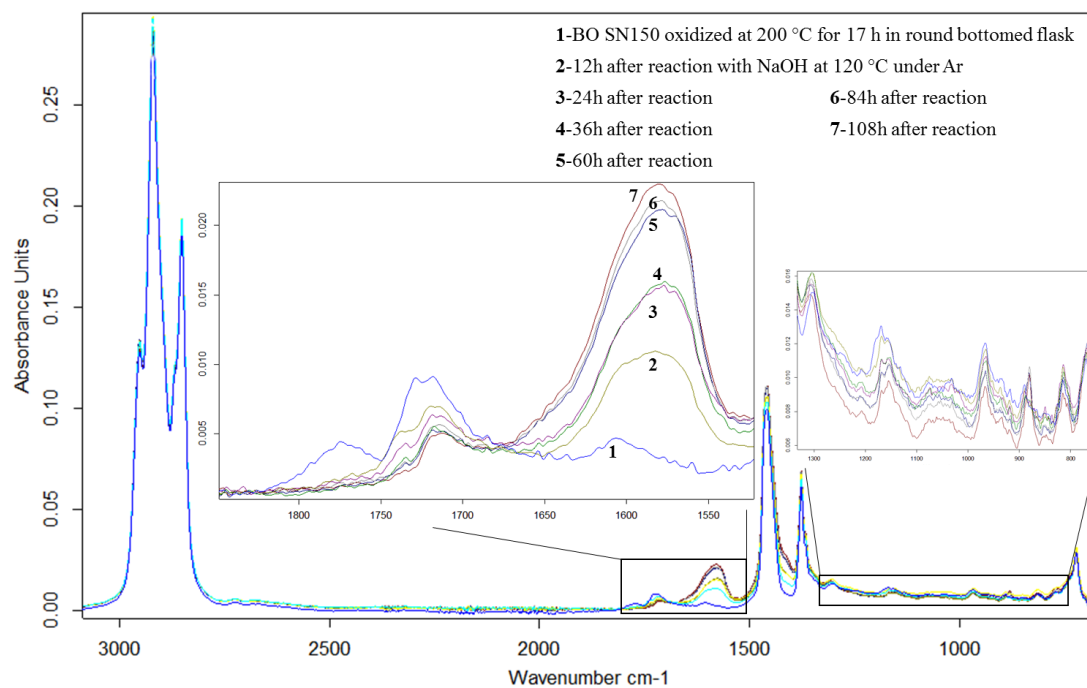


Figure 5.7 IR spectra of reaction of oxidized base oil with NaOH only at 120 °C.

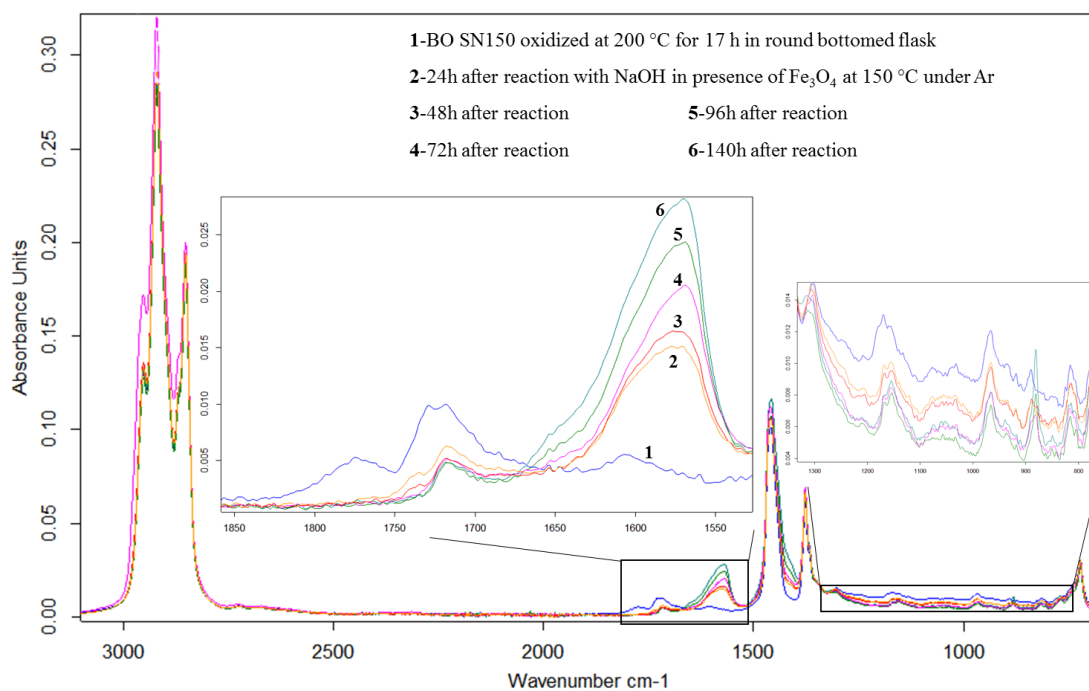


Figure 5.8 IR spectra of reaction of oxidized base oil with NaOH in presence of magnetic np at 150 °C.

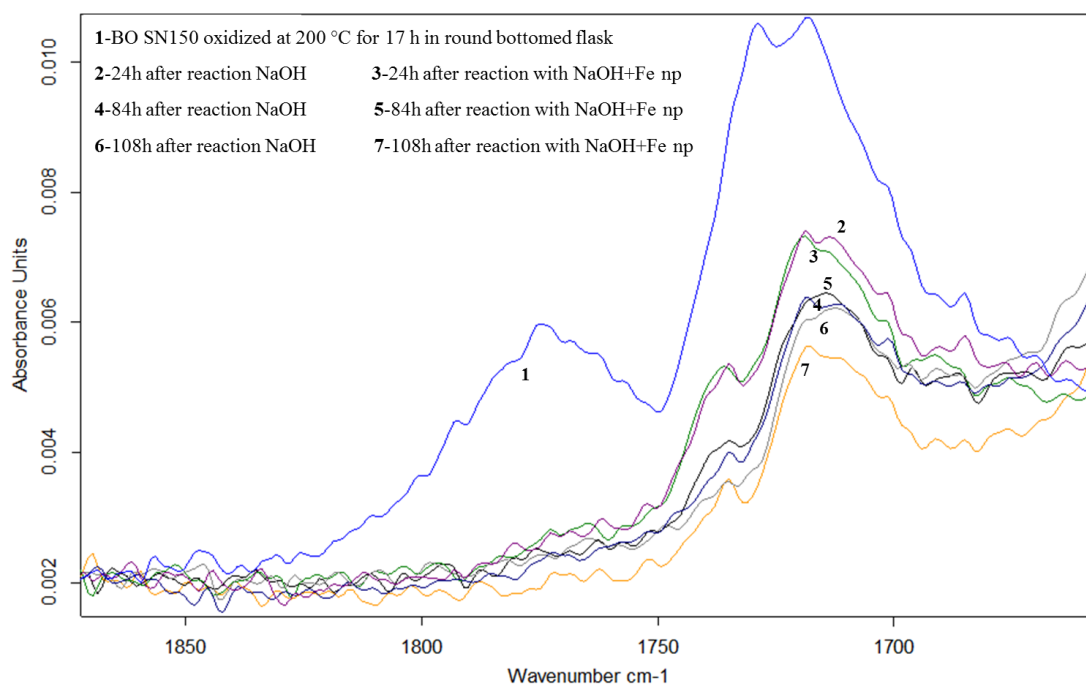


Figure 5.9 IR spectra for comparing effect of magnetic np presence for reclamation process at 120 °C.

Same comparison method was used for comparing effect of temperature. IR spectrums at 120 °C were compared with IR spectrums at 150 °C. Comparison of IR spectra is shown in Figure 5.10. As it is obvious from the figure, that reaction at 150 °C proceed faster, and carbonyl peaks at  $1728\text{ cm}^{-1}$  are decreasing more at 150 °C. Using higher temperature leads to faster and better results. However, controlling reaction at higher temperatures is difficult, due to oxygen leakage to the system.

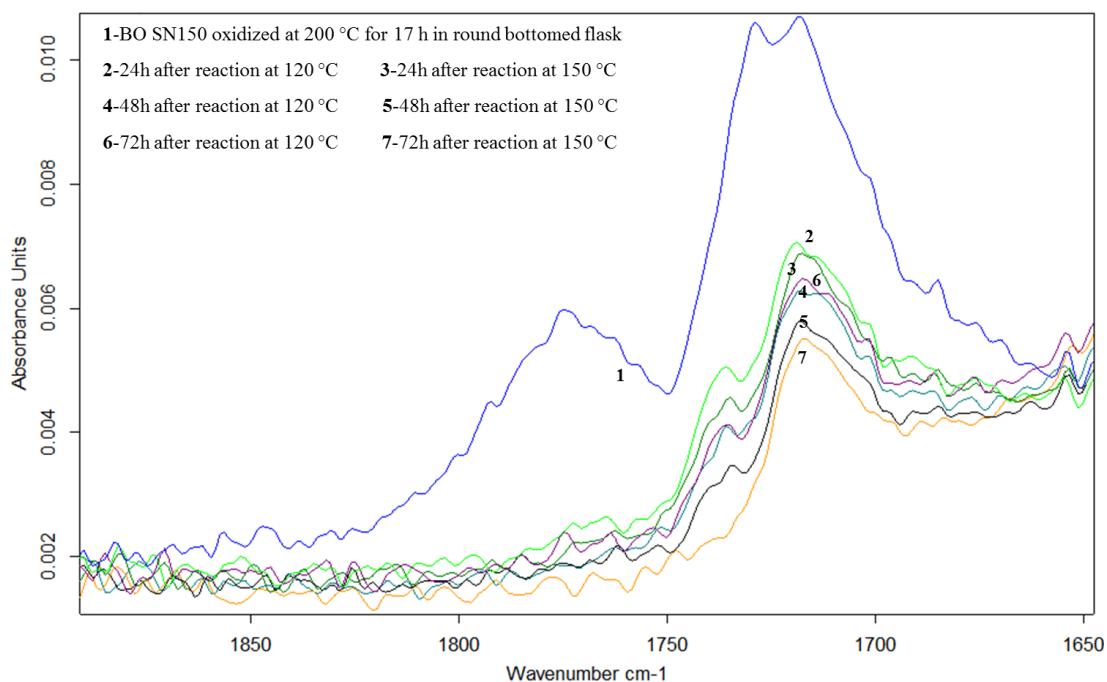
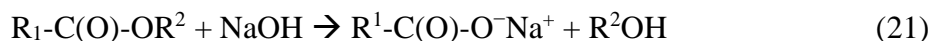


Figure 5.10 IR spectra for comparing reaction with NaOH in presence of  $\text{Fe}_3\text{O}_4$  at 120 °C and 150 °C.

### 5.2.2 After separation of reusable oil

After ending this reaction, a single phase was obtained. We know that we have salts that can be transferred into water phase, and therefore after mixing the treated oil with water two different phases were formed. Reusable clean oil phase is accumulated in the upper part, and salt containing aqueous phase is settled at the bottom of the container. Interestingly, nanoparticles become soluble in water rather than oil. So, both sodium containing and nanoparticle bonded species are transferred to water phase. Photographs of oils recovered at different conditions after separation of top phase are given in Figure 5.11. Initially, color of BO oxidized at 200 °C in a round bottomed flask was black (1). After recovering its color has changed to yellow (3-4) and brown (5-6), become closer to untreated SN150 base oil (6). Oil reclaimed at 120 °C have lighter color than 150 °C. The reason for color of oil reclaimed at 150 °C is the higher temperature, where reclaimed oil also can oxidize if oxygen is present in the system. 150 °C is the limit temperature for oil oxidation. Main reason for increasing temperature is to decrease reaction times. But maintaining very rigid system without leakage helps to increase reaction temperature, thus; reducing reaction time.

During separation of phases, trace amount of water can remain in oil phase, it can be observed in FTIR spectrum (Figure 5.12). Another suggestion; this peak can belong to alcohols, that is formed during the process:



During water treatment stage alcohols may stay in upper phase, due to high non-polarity of R groups. When we look at IR spectrum in Figure 5.12 we can see a broad peak due to stretching of O-H groups that originate from alcohols and water at 3100-3700  $cm^{-1}$ . Presence of water peaks can be easily understood from the peak around 1600  $cm^{-1}$ . This weak peak is also observed in IR spectrum. Oil samples were treated with desiccant material  $MgSO_4$  and filtered from filter paper for removing O-H containing species. In the IR spectrum of top phase after desiccant treatment is given in Figure 5.13. O-H stretching peaks appeared between 3100-3700  $cm^{-1}$  disappeared after the treatment. A study about the removal of an alcohol using  $MgSO_4$  desiccant and the IR spectra that is obtained before and after the treatment were given in Appendix F.) For further separation and to get better results, oil samples can be re-extracted with cheap extraction solvents, like hexane. Water and hexane are immiscible, they do not mix with each other and only hexane dissolves reclaimed oil.

Also, we noticed, that the oxidation peaks at around 1770  $cm^{-1}$  disappeared completely (see Figure 5.13). What remains behind is only small amount of ketone that did not react during reclamation process (This was understood by  $^1H$  NMR spectroscopy, see Figure 5.18). Beyond this, there is also noticeable decrease in sulfur stretching region (800-1400  $cm^{-1}$ ), see Figure 5.13. This decrease in sulfur stretching region explains the color change after reclamation, as oxidized sulfur containing groups are also removed by NaOH treatment.

Bottom phase was also analyzed and IR spectra of this phase shows the presence of carbonyl containing compounds since signals around 1500-1800  $cm^{-1}$  due to  $C=O$  were observed (Figure 5.14). At these region, different molecules show peaks (carbonyl, nitril and water) and they are seen as a huge single peak. Also, there is a strong O-H peak between 3000-3700  $cm^{-1}$ . Presence of  $C=O$  peaks clearly indicate transferring of carboxylate salts to bottom aqueous phase. Presence of C-H peaks in



the aqueous phase between 2750-3000  $\text{cm}^{-1}$  and 1250-1500  $\text{cm}^{-1}$  indicate the transfer of organic material to this phase.

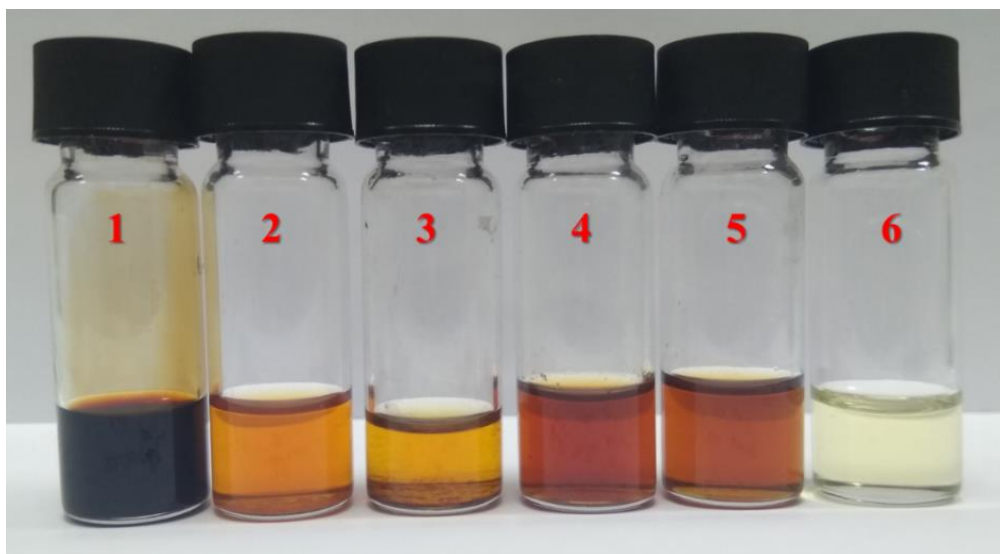


Figure 5.11 Colors observed for reclaimed oil: 1-BO oxidized at 200 °C for 17 hours, 2-Reclaimed oil (treated with NaOH in the presence of  $\text{Fe}_3\text{O}_4$  at 120 °C), 3-Reclaimed oil (treated with NaOH only at 120 °C), 4- Reclaimed oil (treated with NaOH in presence of  $\text{Fe}_3\text{O}_4$  at 150 °C), 5- Reclaimed oil (treated with NaOH only at 150 °C), 6-Untreated N150 base oil.

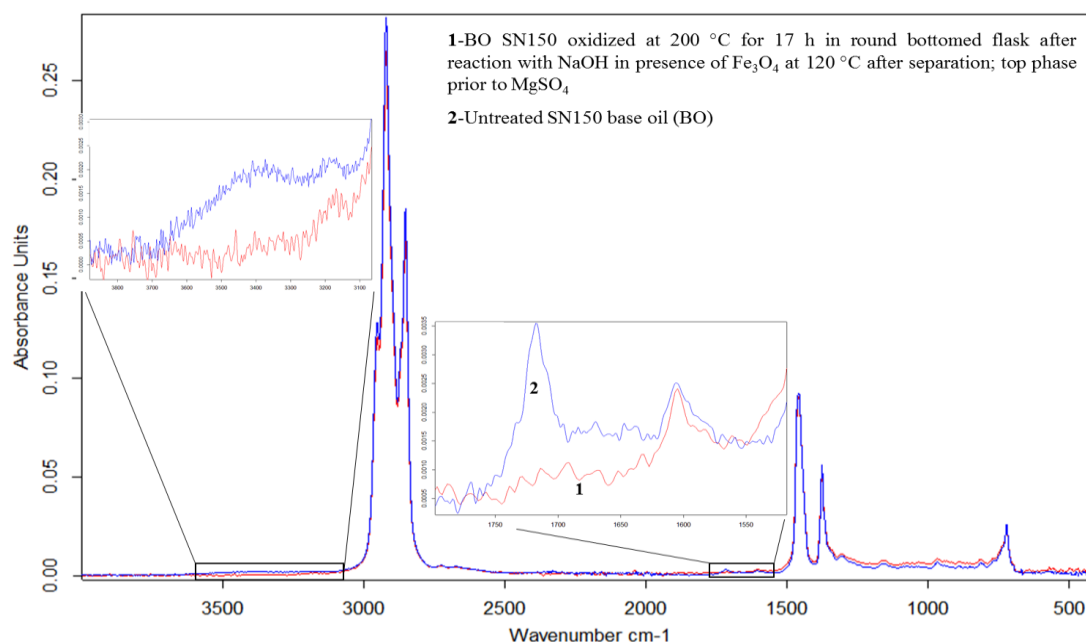


Figure 5.12 IR spectra of separated oil (2), that is treated with NaOH in presence of  $\text{Fe}_3\text{O}_4$  nps at 120 °C (top phase), **prior** to treatment with  $\text{MgSO}_4$  and untreated SN1150 base oil (3).

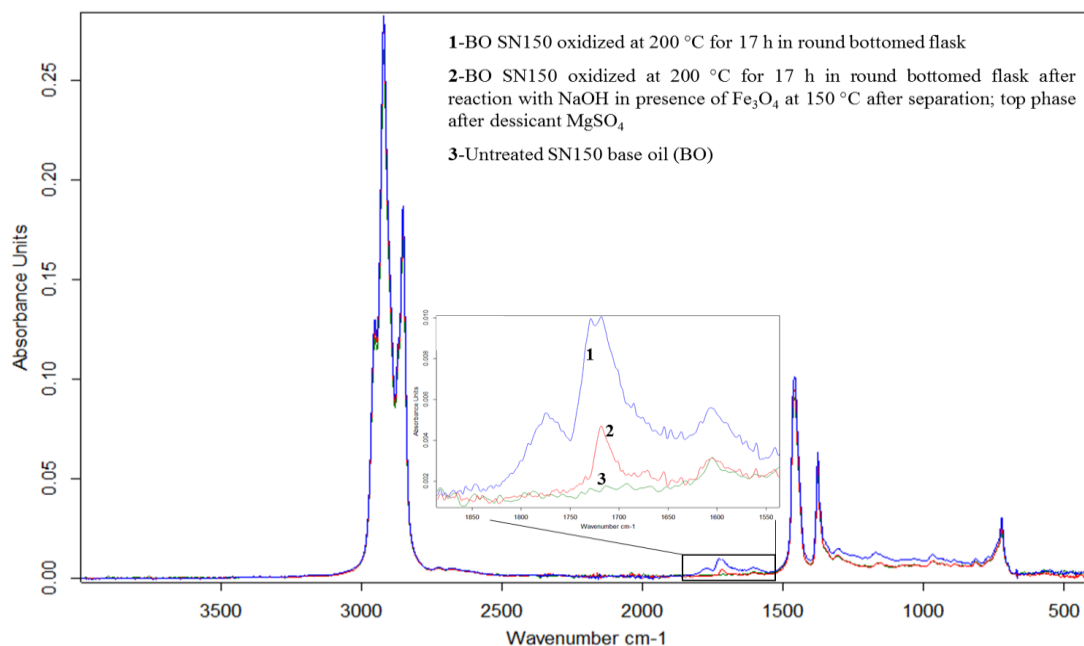


Figure 5.13 IR spectra of separated oil (2), that is treated with NaOH in presence of  $\text{Fe}_3\text{O}_4$  np at 150 °C (top phase), **after** treatment with  $\text{MgSO}_4$  and untreated SN1150 base oil (3).

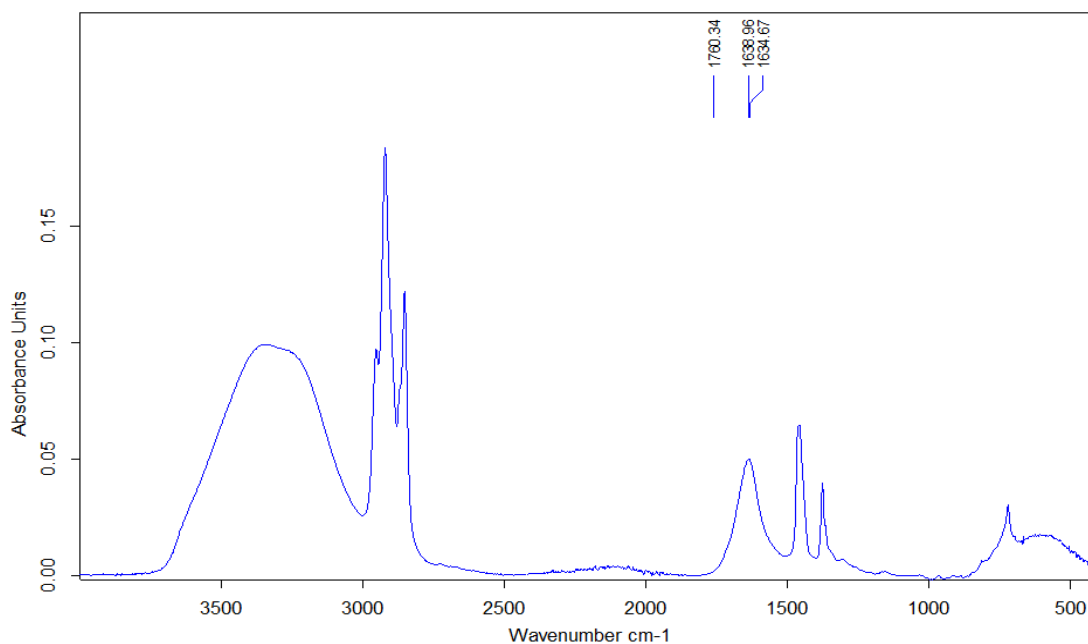


Figure 5.14 IR spectrum of bottom aqueous phase after reaction with NaOH in presence of  $\text{Fe}_3\text{O}_4$  np at 120 °C, after separation.

After separation of phases and treating them with  $\text{MgSO}_4$ , IR spectra oil samples reclaimed using different conditions are compared and given in Figure 5.15. From these spectra, it is clearly seen that reclamation become successful; peaks at 1650-1850  $\text{cm}^{-1}$  that belong to ketones, aldehydes, esters and carboxylic acids almost

disappeared. For understanding difference and effect of reclamation process relative peak areas were compared (Table 5.1 Relative peak areas of IR carbonyl region of oil samples given in Figure 5.15.). It is obvious that oxidized oil samples have highest area among all. All of these IR absorption peaks are close to each other, but, peaks of reclamation at 120 °C (#4&5) is slightly lower than the others. The areas of under the peaks between 1650-1815  $\text{cm}^{-1}$  for reclaimed oil samples are close to each other. When they are compared with oxidized oil sample area, there is almost tenfold decrease. Slight change between areas is due to starting temperature of oxidation (150 °C) of oil as we mentioned before, there is an oxygen leakage to the system. Table 5.1 shows that carbonyl peak areas of all samples are close to each other. Some small conclusions can be derived from C-H stretching region (between 2700-3100  $\text{cm}^{-1}$  and 1400-1500  $\text{cm}^{-1}$ ) peak, during oxidation process C-H stretching peaks decrease slightly. Figure 5.15 shows that lowest intensity C-H peak correspond to oxidized oil spectrum (1) and same peaks of reclaimed oil samples have higher intensities. The intensity change in this peak can serve as a minor indicator for success of reclamation process. We can see similar results in the sulfur region, peaks of reclamation at 120 °C (#4&5) were found to be lower. This also proves color difference of oil reclaimed at different conditions. As the color change occurs due to the oxidation of sulfur containing peaks.

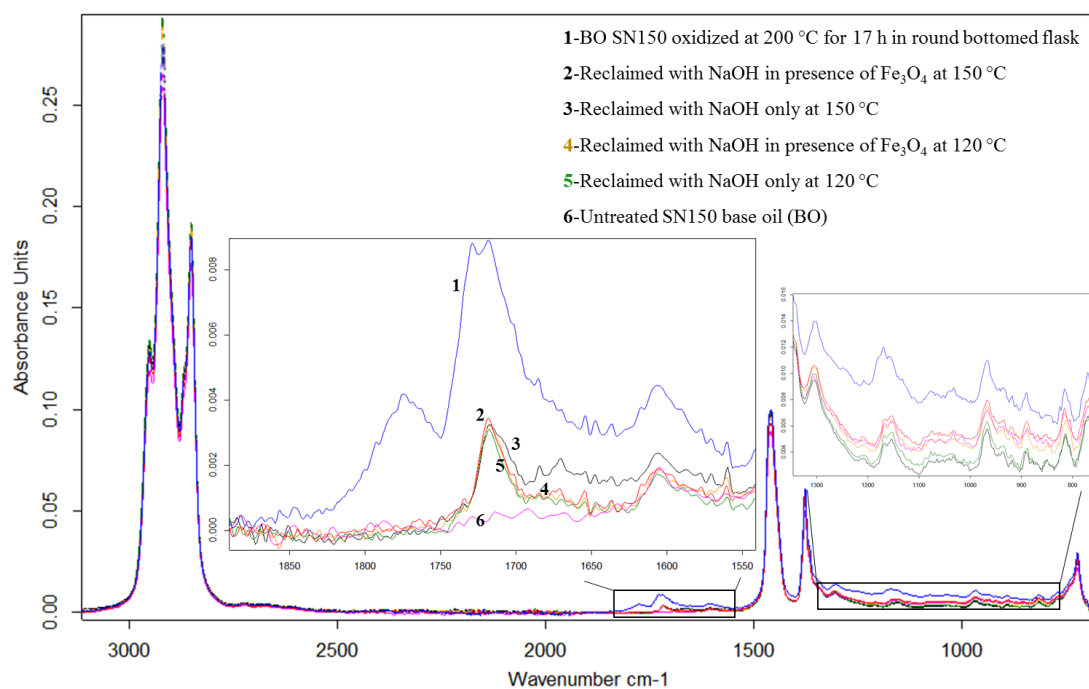


Figure 5.15 IR spectra of oil samples after reclamation at different conditions.

Spectrum of the sample	Integrated region (cm <sup>-1</sup> )	Relative peak area
1-BO SN150 oxidized at 200 °C for 17 h in round bottomed flask	1650-1815	0.523
2-Reclaimed with NaOH in presence of Fe <sub>3</sub> O <sub>4</sub> at 150 °C	1694-1750	0.064
3-Reclaimed with NaOH only at 150 °C	1693-1756	0.053
4-Reclaimed with NaOH in presence of Fe <sub>3</sub> O <sub>4</sub> at 120 °C	1694-1751	0.050
5-Reclaimed with NaOH only at 120 °C	1692-1746	0.050

Table 5.1 Relative peak areas of IR carbonyl region of oil samples given in Figure 5.15.

### 5.2.3 Reaction times

Reaction time are long in order of days. Reaction time mainly depends on reaction temperature and of course the design of the reactor. As expected, at higher temperatures reaction proceed faster than in lower temperatures. Reaction time is an important parameter as it affects both yield and separation. If reaction is finished earlier than full separation may not occur, due to small amount of water-soluble components, also oil can form one phase with water. In same way, keeping too long reaction times will lead to formation of water insoluble clays. According to patent (ref. 69), at high temperatures oil produce clay, which are not water-soluble. Reaction should be finished within certain time window. Ideal reaction time was determined by IR spectroscopic study and we found that ideal reaction time is longer than 5 days for 150 °C and longer than 7 days for 120 °C in our experiments. After certain amount of time passed carboxylate salts peak do not alter much (see Figure 5.3-5.10). Keeping very long reaction time can be also seen with IR spectroscopy, sulfur containing clays start to form at 800-1400 cm<sup>-1</sup>. Clays mainly form due to reaction hydroxide bases with sulfur containing molecules [69]. After increased time of reaction these molecules transform to bigger by attaching other groups and from water insoluble clays. Reaction time should be monitored according to these parameters and increasing the temperature can reduce it. Maintaining system without oxygen leakage gains noticeable importance. Performing these processes in specially designed

reactors can reduce reaction time seriously. Changing temperature from 120 °C to 150 °C reduced the reaction time by 2 days.

### 5.3 NMR studies of oil

#### 5.3.1 NMR spectrum of SN150

SN150 base oil prior to treatment, after treatment, after reclamation were analyzed using both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. During the thermal oxidation process, chemical modifications occur in C-H and C-C bonds, so both carbon and hydrogen NMR spectroscopic techniques can conveniently be used for the analysis of oil samples. Proton NMR is more suitable for research, but it needs to be supported with  $^{13}\text{C}$  NMR for correct peak assignment. Typical  $^1\text{H}$  NMR spectrum of untreated SN150 base oil is given in Figure 5.16. We can divide proton NMR spectrum basically 5 different regions. These regions correspond to different hydrogens, assignment of peaks can be seen in Table 5.2 [80]. There is a huge content of alkane CH bonds, noticeable amount of aromatics present, and small amount of allylic and alkene hydrocarbons present in **untreated** SN150 base oil. This oil is mineral based and thus does not contain natural esters, which expectedly appear between 3.5-5.5 ppm.

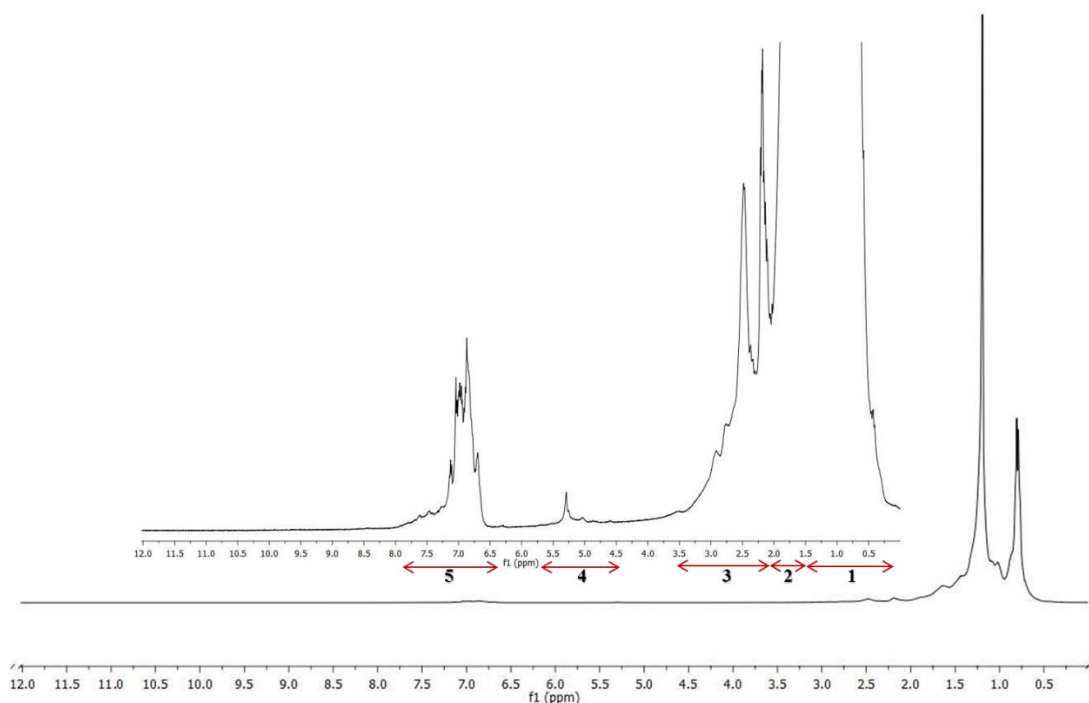


Figure 5.16 Typical  $^1\text{H}$  NMR spectrum of untreated SN150 Base oil. Inset: magnified region for observing other regions.

Region	Spectral region (ppm)	Functional groups
1	0.4-1.6	Alkane CH-CR <sub>3</sub>
2	1.5-2.2	Allylic, Benzylic, Ph-CH
3	2.2-3.5	Alkyne C≡C-H, aromatic
4	4.5-5.5	Alkene C=C-H
5	6.5-8.0	Aromatic Ph-H, PAH

Table 5.2 Assignment of <sup>1</sup>H NMR peaks of untreated SN150.

### 5.3.2 Changes after oxidation of oil

During chemical oxidation of lubricating oil aldehydes, alcohols, carboxylic acids, ester can form (Section 3.4). These changes can be seen in <sup>1</sup>H NMR spectrum given in Figure 5.17. When we look at NMR spectra there are noticeable changes in 3 of the regions. Correlation of these regions is given in Table 5.3. When we look to region 1 in this spectrum we can see oxygen containing aliphatic and aromatic groups started to form; esters, alcohols, ethers, phenols etc. [76]. Also, there is a small peak at ~9.7 ppm, which corresponds to aldehyde groups. Interestingly, there is no corresponding peak for carboxylic acids, references in the literature [1, 33, 49, 74-76, 81]. Obtained results are very interesting, during the oxidation of oils no carboxylic acids are formed. However, C=O stretching peaks seen in IR spectrum (Figure 5.1 IR spectra of untreated and oxidized SN150 base oil in a flask, in a vial and in the PARR model 4838 reactor. correspond to ketones, aldehydes and esters but not to carboxylic acids, as it was misinterpreted in the literature (in order to show that peaks in region 3 of Figure 5.17 belong to aldehydes not carboxylic acids, oleic acid was used as a test acid, seen Appendix H). This also explains failure of Fe<sub>3</sub>O<sub>4</sub> np, during decarboxylation of carboxylic acids. Peak decrease can be justified by adsorption of oxygenated species to magnetic iron oxide np surface [82, 83]. We think that these results and findings will change the fundamental way of thinking and looking at the problem of oxidation of lubricating oils.

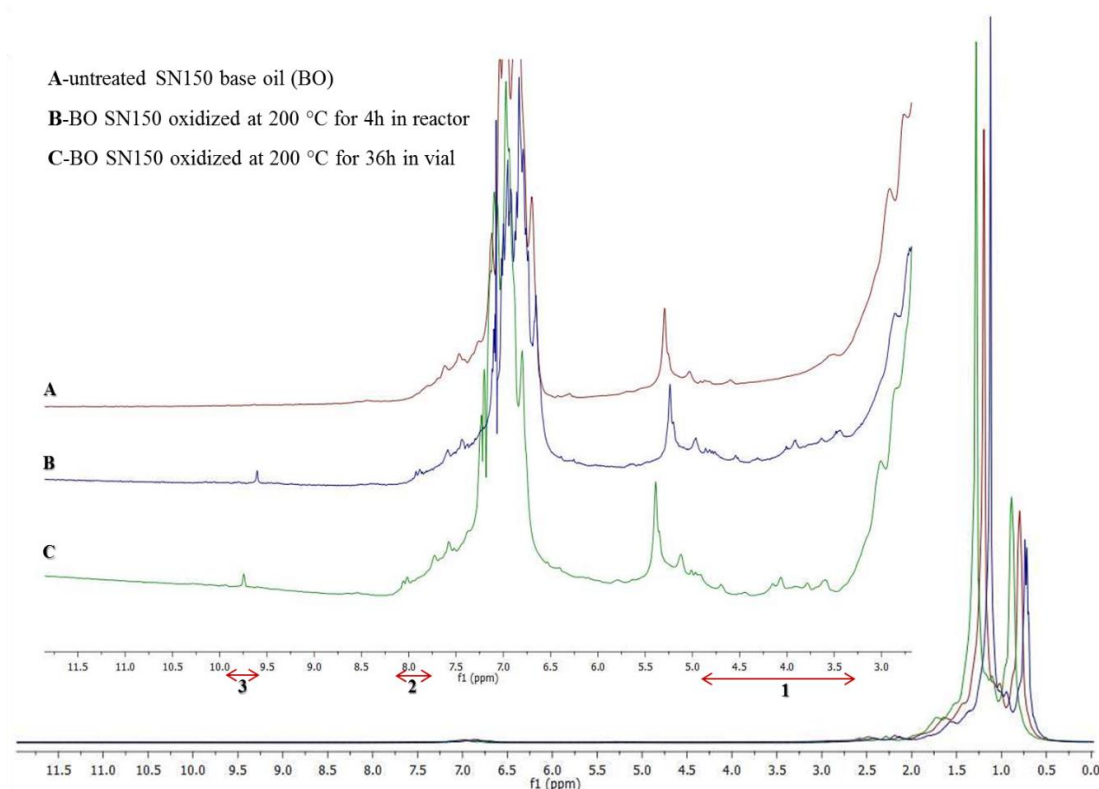


Figure 5.17 Stacked  $^1\text{H}$  NMR spectra of untreated and oxidized base oil.

Region	Spectral region (ppm)	Functional groups
1	3.2-4.8	Oxygenated aliphatic species: esters, alcohols, ethers
2	7.7-8.2	Aromatic groups Ph-H
3	9.5-10.0	Aldehydes

Table 5.3 Assignment of  $^1\text{H}$  NMR regions changed after oxidation of SN150 BO.

### 5.3.3 Changes after caustic treatment

Oil samples that were treated with sodium hydroxide were investigated with  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. As it was mentioned earlier, we get two phases after mixing oily reaction product with water. One phase contains reusable oil and the other phase consist of water mixed carboxylate and sulfonate salts. Initially, top phase was analyzed (Figure 5.18), and this phase was to be same composition as untreated base oil. Spectrum **A** belongs to untreated oil sample, spectrum **C** belongs to oxidized base oil, and spectrum **B** belongs to reclaimed oil with NaOH at 120 °C. When we compare spectrum **B** and **C**, we see that that some very important changes in the NMR spectra

took place: i) the peaks (between 3.5-4.5 ppm) that belong to ester groups were disappeared, ii) aromatic species (~8.0 ppm) and aldehyde (9.7 ppm) peaks disappeared, too. Spectrum of reclaimed oil almost identical with the spectrum of untreated SN150 base oil. This spectral analysis clearly proves effectiveness of reclamation process. What remains in the oil after the treatment is only ketones, that didn't react with sodium hydroxide and they can't be identified from spectrum here.

We said before that after reaction with caustic soda, reusable oil was separated from carboxylate salts with water. After the addition of water two phases form top one is reusable oil, analyses of this phase were done as described above. Next, we analyzed the water containing bottom aqueous phase. The aim of this analysis was to test our hypothesis; during oxidation of lubricating oil, esters are formed and no carboxylic acids produced. According to our results, reclamation process works according to the reaction 25 given below:

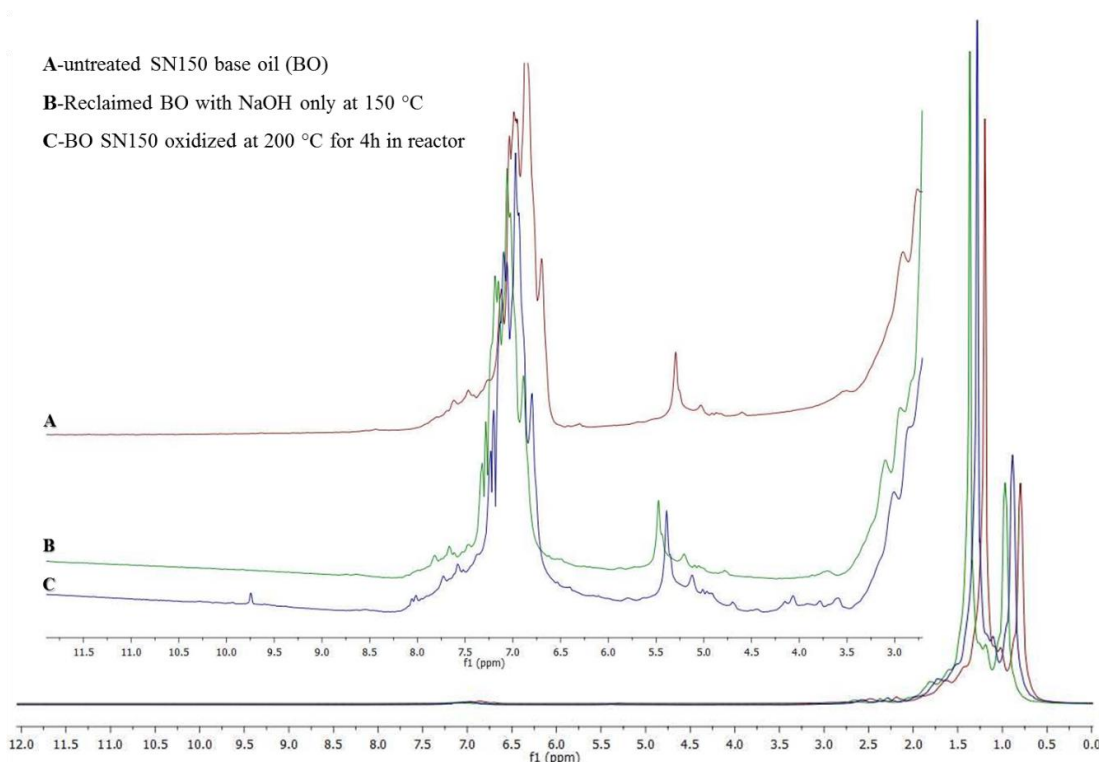


Figure 5.18  $^1H$  NMR spectra of oil reclaimed using NaOH at 150 °C.

So, in fact in top phase we anticipate to observe alcohol moieties. Indeed, they were present in the IR spectra (Figure 5.12). These alcohols were removed with  $MgSO_4$ .



Bottom aqueous phase should contain carboxylate salts, which is not seen with  $^1\text{H}$  NMR prior to the saponification during NaOH treatment.  $^1\text{H}$  NMR spectrum of untreated bottom phase is given in Figure 5.19. Assignment of peaks in spectrum shown in Figure 5.19 is made in Table 5.4 [80]. Noticeable intense peak is seen at  $\sim 4.5$  ppm which belongs to protons in  $\text{H}_2\text{O}$ .

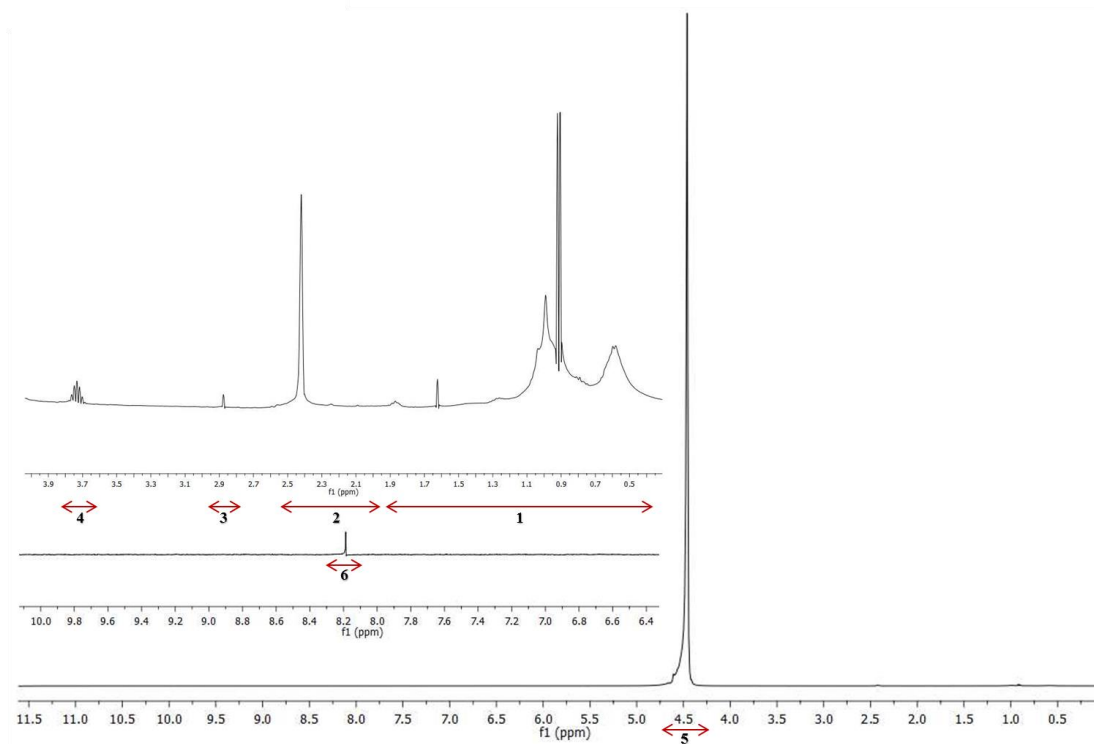


Figure 5.19  $^1\text{H}$  NMR spectrum of untreated bottom phase.

Region	Spectral region (ppm)	Functional groups
1	0.4-1.9	Methyl ( $-\text{CH}_3$ ), $-\text{CH}_2-$ , allylic ( $\text{C}=\text{C}-\text{C}-\text{H}$ ),
2	2.0-2.5	Benzylic ( $\text{Ph}-\text{C}-\text{H}$ ), ketones ( $\text{CH}-\text{C}=\text{O}$ ), Carbonyl $\alpha$ hydrogen ( $\text{CH}-\text{C}=\text{O}$ )
3	2.8-3.0	Alkyl ( $\text{C}\equiv\text{C}-\text{H}$ )
4	3.6-3.8	Alcohols ( $\text{C}-\text{O}-\text{H}$ ), esters ( $\text{CH}-\text{O}$ )
5	4.2-4.8	Water ( $\text{H}-\text{O}$ )
6	8.2	Aldehyde ( $\text{CH}=\text{O}$ )

Table 5.4 Assignment of peaks for  $^1\text{H}$  NMR spectrum of untreated bottom phase that was obtained after the reclamation process where the used oil was treated with only NaOH at  $150^\circ\text{C}$ .

Aldehydes and ketones undergo condensation reaction with strong bases  $\beta$ -unsaturated carbonyl compounds are formed, some of them are water soluble and thus they transferred into aqueous phase in the bottom [77].

From the spectrum given in Figure 5.18, we can say that there is noticeable amount of carboxylate salts transferred into bottom aqueous phase. When these carboxylate salts in aqueous phase are neutralized we should see C(O)-OH peak in the  $^1\text{H}$  NMR spectrum. We think that if we detect an acidic peak after the neutralization reaction, it will indicate the formation of esters, not the carboxylic acids which are very commonly believed to be formed during thermal oxidation of oils. We have neutralized bottom phase using strong 4M hydrochloric acid. Acid was added dropwise and single phase started to separate by formation of two phases: one is clear water phase and the other is dark and sludgy phase. Clear aqueous phase was separated and heated at 109 °C, for water removal. Finally, trace of water was removed using  $\text{MgSO}_4$ . Residue was dissolved in chloroform- $d$   $\text{CDCl}_3$  and transferred into NMR tube for analysis.  $^1\text{H}$  NMR spectrum of this phase shows presence of C(O)-OH broad peak at 9-11 ppm (Figure 5.20). Since acidic protons of HCl dissociate and exchange very rapidly with other acidic protons. Due to this exchange effect, it is used for NMR study of COOH and N-H groups. The IR spectrum of aqueous phase is given in Figure 5.14. There are strong C-H coupling peaks (between 2800-3100  $\text{cm}^{-1}$  and 1400-1500  $\text{cm}^{-1}$ ) that belong to oil hydrocarbons.

The spectrum given in Figure 5.20 very much resembles spectrum of oxidized oil, and only there is a broad signal arises from carboxylic acid. There are other signals due to the presence of different species such as esters, ketones and alcohols during water evaporation step which can cause the formation of new esters, nevertheless unreacted carboxylic acids are clearly seen in spectrum (Figure 5.20). These results prove that during oxidation of lubricating oil no carboxylic acids are formed, rather ester formation takes place. Formation of esters can be possible by the direct oxidation mechanism (part 3.4). According to oxidation mechanism  $\cdot\text{OH}$  free radicals that forms carboxylic acids are produced in small amounts. However, small amount of  $\cdot\text{OH}$  radicals are not enough to produce sufficient carboxylic acids that can still be excess enough for detection after reaction with alcohols etc.

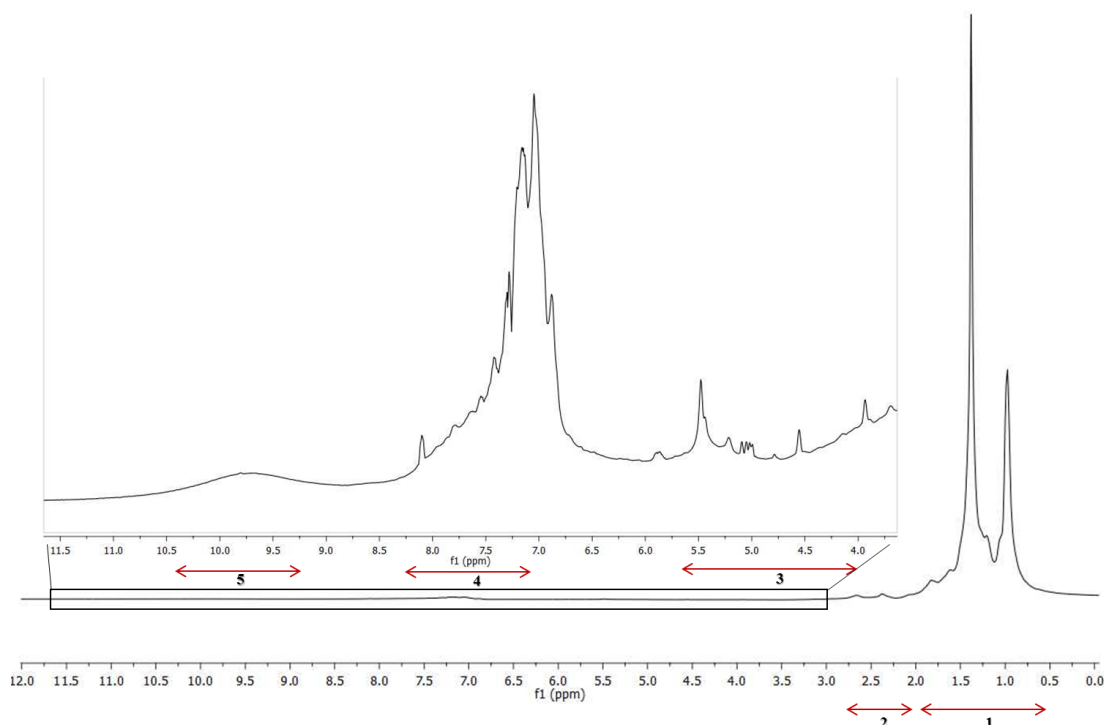


Figure 5.20  $^1\text{H}$  NMR of bottom aqueous phase after neutralization with HCl.

Region	Spectral region (ppm)	Functional groups
1	0.5-1.9	Methyl ( $-\text{CH}_3$ ), $-\text{CH}_2-$ , allylic ( $\text{C}=\text{C}-\text{C}-\text{H}$ ),
2	2.0-3.5	Benzylic ( $\text{Ph}-\text{C}-\text{H}$ ), ketones ( $\text{CH}-\text{CR}=\text{O}$ ), Carbonyl $\alpha$ hydrogen ( $\text{CH}-\text{CH}=\text{O}$ )
3	3.5-5.5	Ethers, alcohols, esters $\text{CH}-\text{O}$
4	6.8-8.2	Aromatic $\text{Ph}-\text{H}$
5	9.0-11.0	Carboxylic $\text{C}(\text{O})-\text{O}-\text{H}$

Table 5.5 Assignment of peaks for  $^1\text{H}$  NMR spectrum of bottom phase of reclamation process with NaOH only at  $150^\circ\text{C}$  after neutralization with hydrochloric acid, HCl.

### 5.3.4 Comparison with Real Used Engine Oil

In our studies, we have used base oil that is oxidized in laboratory conditions. BO was stressed by heating at high temperatures. In real life applications lubricating oil are not used up to this point. Oils are changed according to schedules and do not oxidized up to the extent as the case in our samples. For testing this idea, we obtained used oil sample from the local Shell Gas Station. This used oil has unknown composition.

Oxidized samples prepared in the laboratory and used engine oil from the local source were compared both using IR and NMR spectroscopic techniques. (Figure 5.21- 5.22):

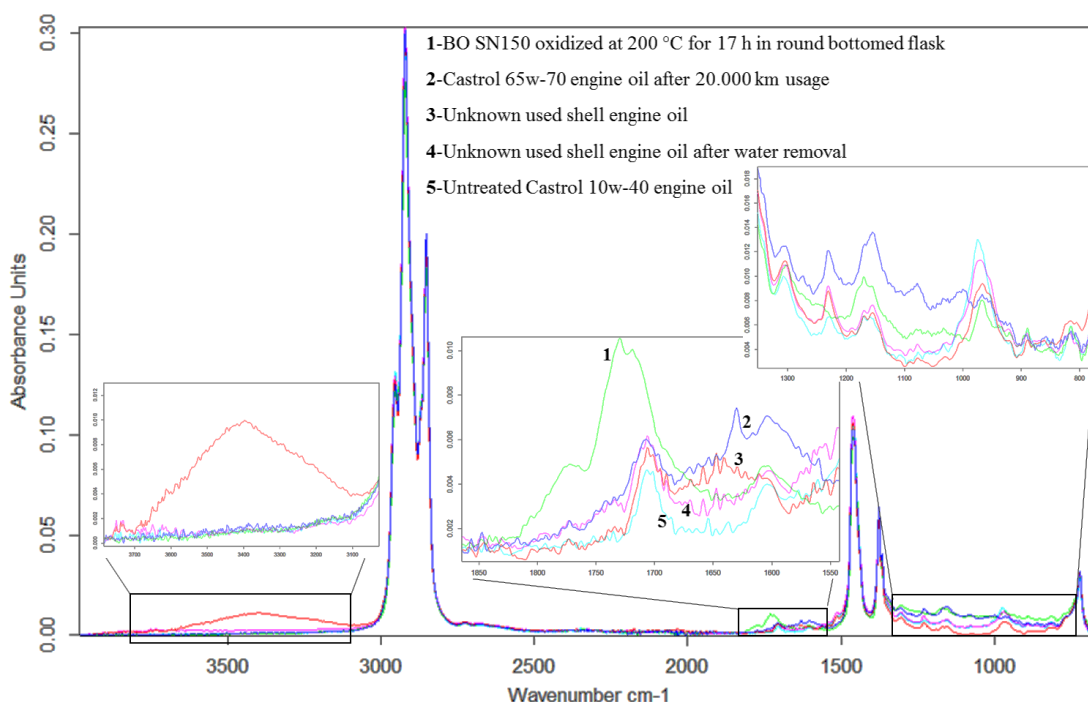


Figure 5.21 IR spectra of untreated Castrol Power 1 4T 10w-40 engine oil, used engine oil and oxidized base oil. Insets show magnified regions of: O-H stretching region (left), C=O stretching region (middle), S=O IR absorption region (right).

Unknown used oil obtained from Shell gas station has some amount of water in it, it is seen from the IR spectrum at region of  $3000\text{--}4000\text{ cm}^{-1}$ . After heating this oil sample for several hours water evaporates totally, which is evident from IR spectrum (Figure 5.21). Changes in the oxidation are mainly seen in C=O and in S=O IR absorption region. Untreated engine oil contains polyacrylic based (PMA-see part 3.1.2) viscosity modifier additive [1]. After some time of oil usage, this additive depletes and oxidation peaks start to appear. But none of these peaks are intense as in our oxidized sample. This indicates that we had been working in quite extreme conditions, in which lubricating oils degrade substantially due to thermal oxidation. Similarly, IR analysis indicated that the used lubricating engine oils also should not contain carboxylic acids. Also, from ZDDP peak region ( $\sim 970\text{ cm}^{-1}$ ) it is seen that used oil still contains some amount of antiwear and antioxidant agent, ZDDP. Many used oils contain still ZDDP when they are changed, due to oil changes are done with respect to mileage [57, 58]. Castrol 65w-70 engine oil used for 20.000 km do not contain ZDDP and S=O region peaks increased a lot more than others. That's presumably why even after very long

working times no acids do form. NMR analysis was done to see effects of oxidation (Figure 5.22).

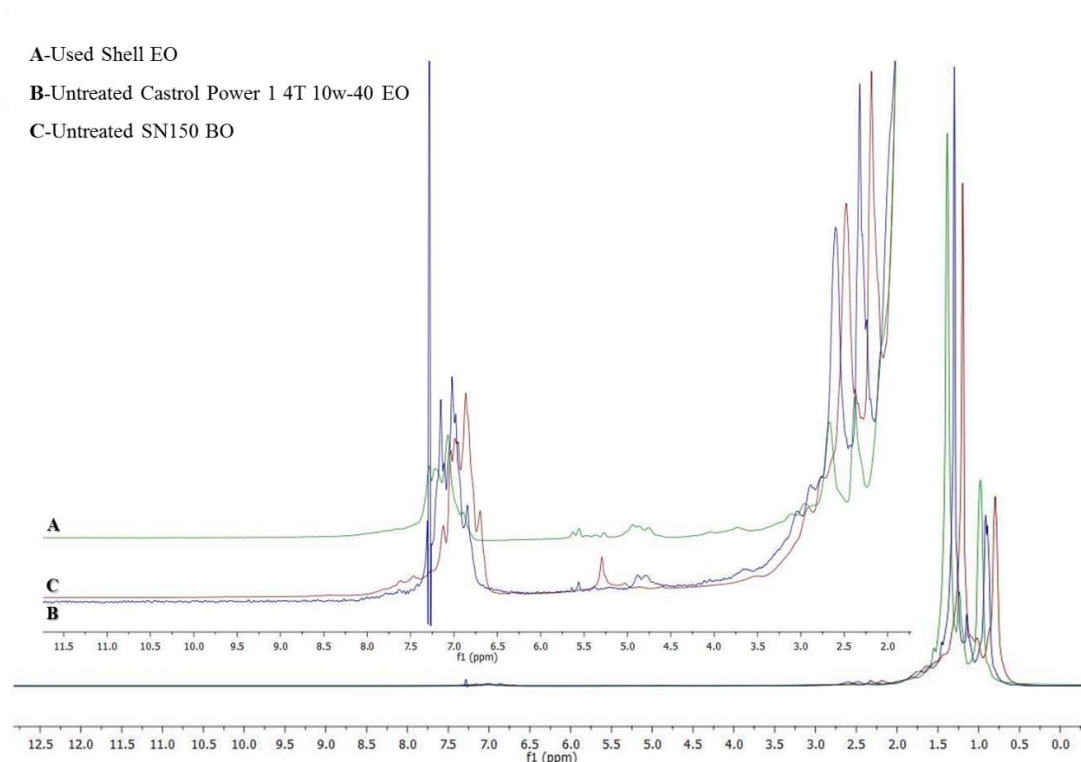


Figure 5.22  $^1\text{H}$  NMR spectra of unknown used oil, untreated Castrol Power 1 4T 10w-40 EO and untreated SN150 BO.

As it also seen from the spectra, there is no any obvious change in ester region (between 3.5-5.5 ppm). The different peaks between 3.5-5.5 ppm correspond to PMA based viscosity modified additive. PMA based viscosity improver is a polymeric material, it contains polymethacrylate esters (Figure 5.23) [31]. These peaks between 3.5-5.5 ppm correspond to PMA, and they are not seen in the NMR spectrum of untreated SN150 BO (**B**). After enough long time of usage, this additive depletes due to thermal process and ester peaks disappear, too. After enough long-time of operation and after disappearing of these peaks, esters start to form due to oxidation process. But, engine oils are changed even before additive depletion. In our studies, we realized that even if their composition changes significantly, carboxylic acids may not start to form.

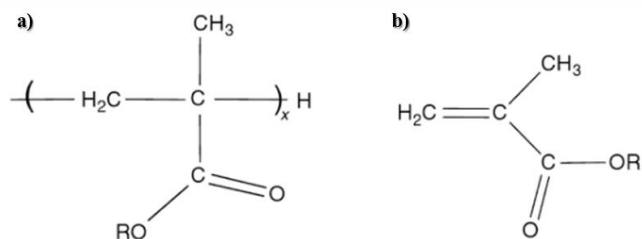


Figure 5.23 Chemical structure of PMA based additive; a) polymer, b) monomer [31].

## 5.4 Titration results

Samples were titrated with accordance to procedure ASTM D974. It is used to measure Total acid number (TAN) and total base number (TBN) of both used and unused oil were determined. Firstly, KOH solution was titrated with freshly prepared 0.1M HCl solution. Molarity of KOH was calculated to be 0.072 M. KOH solution can absorb carbon dioxide from atmosphere and form carbonate salts. This changes concentration of standard solution. It needs to be recalibrated each time before use. With respect to procedure solution were prepared (HCl in IPA and KOH in IPA) (part 4.2.4). Concentration of HCl acid solution was calculated to be 0.1M.

Untreated BO SN150 is basic ( $\text{pH} \geq 7$ ). So, it was titrated with previously prepared 0.1M HCl solution. Titration was repeated twice and results are given in Table 5.6. According to ASTM D974 test method;  $2.0 \pm 0.2$  grams of oil should be mixed with 100 mL of titration solvent [70]. We have used  $1.0 \pm 0.1$  grams of base oil with 50 mL of titrant solvent. All other samples are prepared according to this ratio. For oil samples that were not enough to make  $1.0 \pm 0.1$  grams weight, it was used in smaller amount and titrant solvent was added accordingly. Neutralized oils have long preparation procedure due to water removal and drying steps. Both oxidized oil (200 °C 17 hours), and neutralized acidic oil was also titrated. To be sure, those acidic protons did not remain in oily phase during neutralization step samples were rewashed with DI water. Titration was repeated after water washing step. The unknown composition used oil that was obtained from Shell Gas Station oil change service, was also titrated with standard KOH solution and TAN was calculated. Every titration experiment was repeated twice;

Sample	Weight (g)	Volume of KOH (mL)
BO 200 °C 17h	1.01	1.0
	1.00	0.9
BO neutralized	0.73	1.2
	0.65	1.2
BO neutralized and rewashed	0.51	0.9
	0.27	0.6
Unknown used EO	1.01	0.5
	1.01	0.5
Blank	-	0.3
	Weight (g)	Volume of HCl (mL)
BO SN150 untreated	1.02	2.8
	1.00	2.7

Table 5.6 Titration results of untreated, oxidized, used, neutralized and rewashed oil.

It is obviously seen that acidic fraction of neutralized oil is higher. After neutralization, acidic groups form, which increase acidity of oxidized oil. TAN and TBN were calculated according equations provided in ASTM D974 method [70]. As titrations were repeated twice with different masses, different acid and base numbers were calculated. Both values were within range indicated in ASTM D974 acid/base number determination method. Results are given below in Table 5.7. Base oils are highly basic, and after addition of additives their TBN values decrease. Normally, engine oils are formulated between TBN of 5-16 [84]. Literature study indicates that after 15000 kilometers (km) of engine operation TBN decreases to 0-1 [84]. Some engine oils are formulated to be acidic in the beginning. TAN values of acidic engine oils are around 0-1 and after again according to literature study, after 15000 km of engine operation TAN values become higher than 5 [84]. Generally, both TBN and TAN values change around 5 after 15000-20000 km of operation [84]. After neutralization of aqueous phase obtained after treatment of oxidized oil with NaOH TAN value increases two folds, indicating increasing of acidic groups.

Sample	TAN (mg KOH)/g	
BO 200 °C 17h	2.8	2.4
BO neutralized	5	5.6
BO neutralized and rewashed	4.8	4.5
Unknown used EO	0.8	0.8
TBN (mg KOH)/g		
BO SN150 untreated	16.6	16.4

Table 5.7 TAN of oxidized base oil and neutralized base oil samples.

Initially, untreated SN150 BO is basic and it was titrated used HCl solution to find TBN. TBN value is calculated by adding the amount of KOH solution used for titration HCl amount that used for titration of base oil. After several hours of thermal oxidation process SN150 BO becomes acidic, due to formation of sulfur based and carbonyl group containing acidic moieties but not carboxylic acids.

Initially, BO oxidized at 200 °C for 17 hours contains small amount of sulfur based acidic groups that only can react with KOH during titration [85-87]. But after breaking of ester bonds inside oxidized oil, carboxylic acids form which react with KOH during titration reaction. Even after several runs of washing neutralized oil, TAN value did not decrease much. TAN numbers do not have direct relation with carbonyl region of IR spectrum, TAN number are determined by investigating sulfonyl compounds [85].

## 5.5 Yields of reclamation

According to ref. 20, at least 60% of reusable oil can be recovered from used oil. This is the limit for reusable oil reclamation. In US Patent given in ref. 69, the yield of reusable oil reclamation was ~60% using caustic extraction. Their reclamation process in that patent is based on the use of NaOH/KOH mixture, no spectroscopic data was provided in their study. In our studies, we calculated yield that were obtained from two separate processes. Firstly, we calculated yield directly after treating them with water. Next, samples were dried with desiccant and yield was recalculated. The yields obtained for differently reclaimed oil samples are summarized in Table 5.8.



Sample		Top phase		After desiccant	
Process	Initial weight (g)	weight yield (g)	% yield	weight yield (g)	% yield
NaOH only at 120 °C	6.263	4.563	72.9	3.508	56.0
NaOH + Fe <sub>3</sub> O <sub>4</sub> at 120 °C	5.491	4.174	76.0	3.354	61.1
NaOH only at 150 °C	10.881	7.174	65.9	5.768	53.0
NaOH + Fe <sub>3</sub> O <sub>4</sub> at 150 °C	10.602	7.583	71.5	6.096	57.5

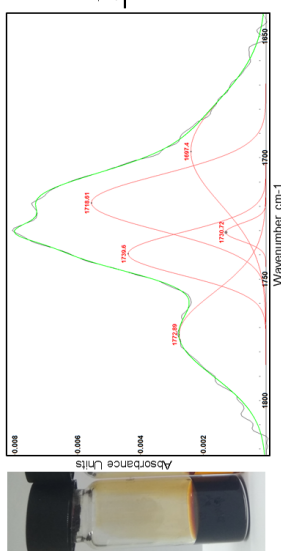
Table 5.8 Weight and percentage yields of reclamation processes at different conditions.

The highest yield obtained at 120 °C by using magnetic np as. Mass loss after desiccant usage is about 12-16%. Yield loss after desiccant treatment can be explained by filtration process due to absorption of oil by the filter paper. Employment of the nanoparticles in the process increased the yield by a few percent. At higher temperatures yield is higher due to higher reaction rate. Working under inert atmosphere conditions gives higher reclamation yields and better results by considering the composition of oils.

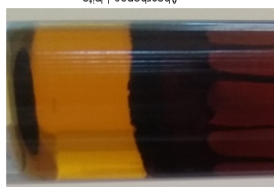
## 5.6 Summary of this work

The whole work can be summarized in one figure (Figure 5.24). Figure summarizes all procedures used, corresponding spectra and images of samples are given.

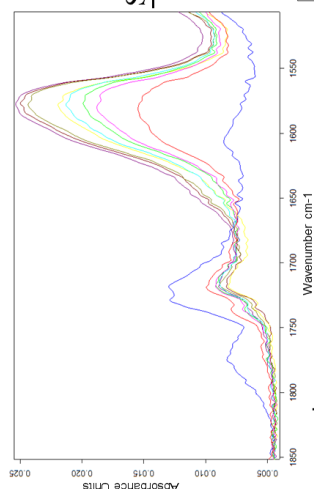
## Esters, Ketones, Aldehydes



NaOH+Fe np

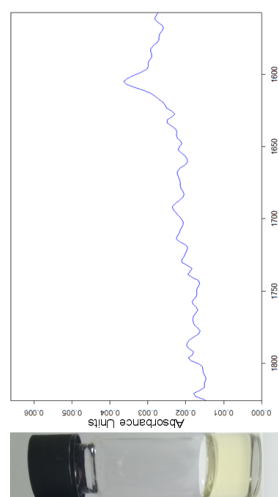


## Carboxylate salts

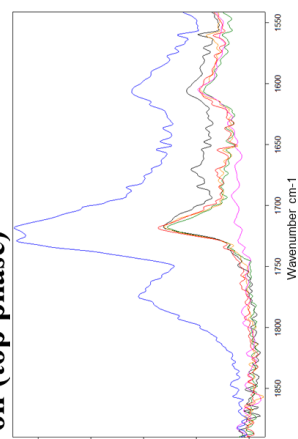


Separation with water  
After desiccant treatment

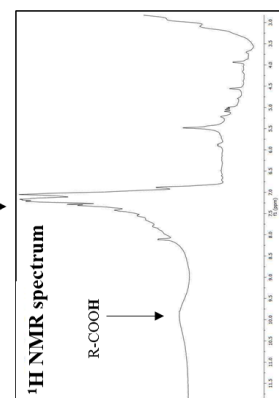
## Base Oil



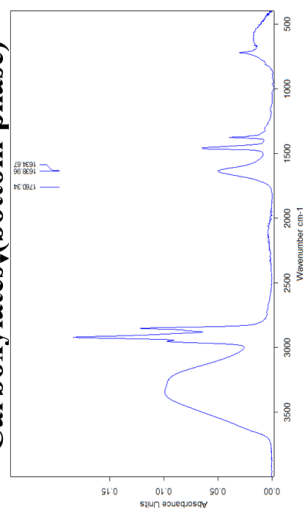
## Reclaimed oil (top phase)



HCl



## Carboxylates (bottom phase)



Separation with water  
Bottom phase

Figure 5.24 Summary of work presented in this thesis

## 6 Conclusion

Literature survey indicates that many reclamation processes are designed for used oils due to the economic and environmental importance of this topic. However, methods for reprocessing or reusing oxidized oils should be based on reaction pathways, products and processes occurring during degradation. Surprisingly, analysis of oxidized oils showed no carboxylic acids, which was commonly believed so. One reason for this misinterpretation of the analysis of used oil is that: infrared spectroscopy itself is not enough to specify full chemistry of oxidized oil in detail. Research done based on such single analysis technique and with theoretical mechanism do not fully explain degradation process of oils. Suggesting a refining method without identifying or misassigning the molecules formed during oxidation process, will lead to lack of understanding the actual mechanism and therefore waste of materials and time will still continue to be a big problem in this field.

### 6.1 Advantages of our method

We have showed that more than 60% of used oil can be reclaimed from used oil. Oil are used almost in every part of our daily life from household materials to industrial applications. Retreating of used oil has gained high importance, especially last few decades. Both depletion of petroleum sources and environmental issues, oil reclamation and re-refining has become a must process. Due to these problems, we have aimed to make an improvement to reclamation methods that are being used. Our method of reclamation has high yield and cost effective. Used chemicals are cheap and can be produced and utilized easily. No need for special equipment or apparatus is required. Beyond this, lubricating properties of reclaimed oils are very comparable with petroleum and ester based lubricating oil. They can be conveniently used in combination with fresh unused oil.

Reclamation process that we followed in this study is based on using commercially available and used caustic soda. Iron oxide nanoparticles are also one of the mostly used nanoparticles as a catalyst in hydrolysis, decarboxylation and in many other

reactions [73, 78, 82]. They can be synthesized in high yields and amounts, from cheap iron salts. Also, amount of nanoparticles in our reactions is too low (~1%) and they can be reused many times. Beyond this it is well known effect that nanoparticles in oil reduce friction [88-90]. Also, small amount of nanoparticles remaining in the reclaimed oil improve friction [88-90]. Moving surfaces are not flat and they are rough in microscopic level, nanoparticles fill the gaps and increase flatness of surface, thus decrease friction and wear [88-90]. Magnetic nanoparticles get attached to steel surfaces, and provide long time friction reduction, even if after oil change these remain and keep doing their job [91].

Ester based oil are being known to be more effective than petroleum base oil. As these oils contain esters, carboxylic groups that naturally tend to bind metal surface. By binding to metal surface ester based oil provide better lubrication and decrease friction more [81]. Esters based oil contain small amount of carboxylic groups, which has tendency to bind metal surfaces. Our reclaimed oils contain desired amount of ketones, which have polar carbonyl groups. Lubrication properties of base oil increase when reclaimed oil are mixed with. Small amount of polar group containing reagents are added in order to keep moving parts cleaner [1]. Reclaimed oils already contain polar groups and reusing these oils also can reduce usage amount of detergents, dispersants etc.

Yield of our reclamation process was calculated in two steps, it is possible to use oil without removing alcoholic groups. They are polar, and contain polar heads it is possible to improve lubrication and dissolve sludge formed on surfaces. Small amount of alcohols will not affect friction negatively. Instead they can act as dispersants and bind oxidized oil molecules. When this is considered, yield increases up to 20% and making total yield higher than 70%.

Beyond this, our method can be coupled with other refining processes, like distillation, hydrotreating etc. Distillation can lead to separation of pure base oil without any sulfur containing groups. In this way, it is also possible to reduce ketone amount for applications that polar groups can cause trouble. Hydrotreating can increase oil lubricating properties, by diversifying oil composition. Also, it can reduce sulfur containing groups, thus can color can be modified. Applying refining process to reclaimed oil will increase possible applications and utilization of reclaimed oil.

## 6.2 Oil oxidation: Carboxylic acids or Esters

Lubricating oil oxidation mechanism is given above and according to mechanisms there a lot of different oxygenated groups can form. Generally, without any analysis or just by simple analysis method claim that oxidized groups compose of carboxylic acids, ketones, aldehydes and esters [1, 33, 49, 74-76, 81, 90]. Most commonly used method of analysis is FTIR spectroscopy [45-49] and it gives different types of C=O peaks between 1650-1850  $\text{cm}^{-1}$ . Simply, by looking to these peaks they claim the formation of carboxylic acids. However, understanding fundamentals of oil oxidation process can improve many reclamation, regeneration, re-refining and re-usage processes. Properties of carboxylic acids and esters are totally differing from each other. We have combined FTIR spectroscopic studies with NMR spectroscopic data. These results indicate that esters are forming during the oxidation, but not carboxylic acids are formed at all. Also by using simple experiments like saponification, neutralization of carboxylic salts and acid-base titration we have proven this phenomenon. Reclamation and re-usage processes are thought and designed according to carboxylic acids that are thought to be formed in oxidized oil.

## 6.3 Other reclamation methods

There are other lubricant reclamation and re-refining methods. Many of them are based on using high amount sulfuric acid [20] or other strong acids. The general idea is based on breaking ester bonds from which people are not aware. But they produce untreatable wastes highly toxic wastes. Others along with acids utilize high extraction solvents [92]. We think that many reclamation processes are designed without knowing the chemistry of oxidized oil in detail. We have shown that oxidized base oils do not have large amount of carboxylic acids, which was generally believed to. Infrared spectroscopy itself is not enough to give full chemistry of oxidized oil. Research done based on single analysis technique and with theoretical mechanism do not fully explain degradation process of oil.

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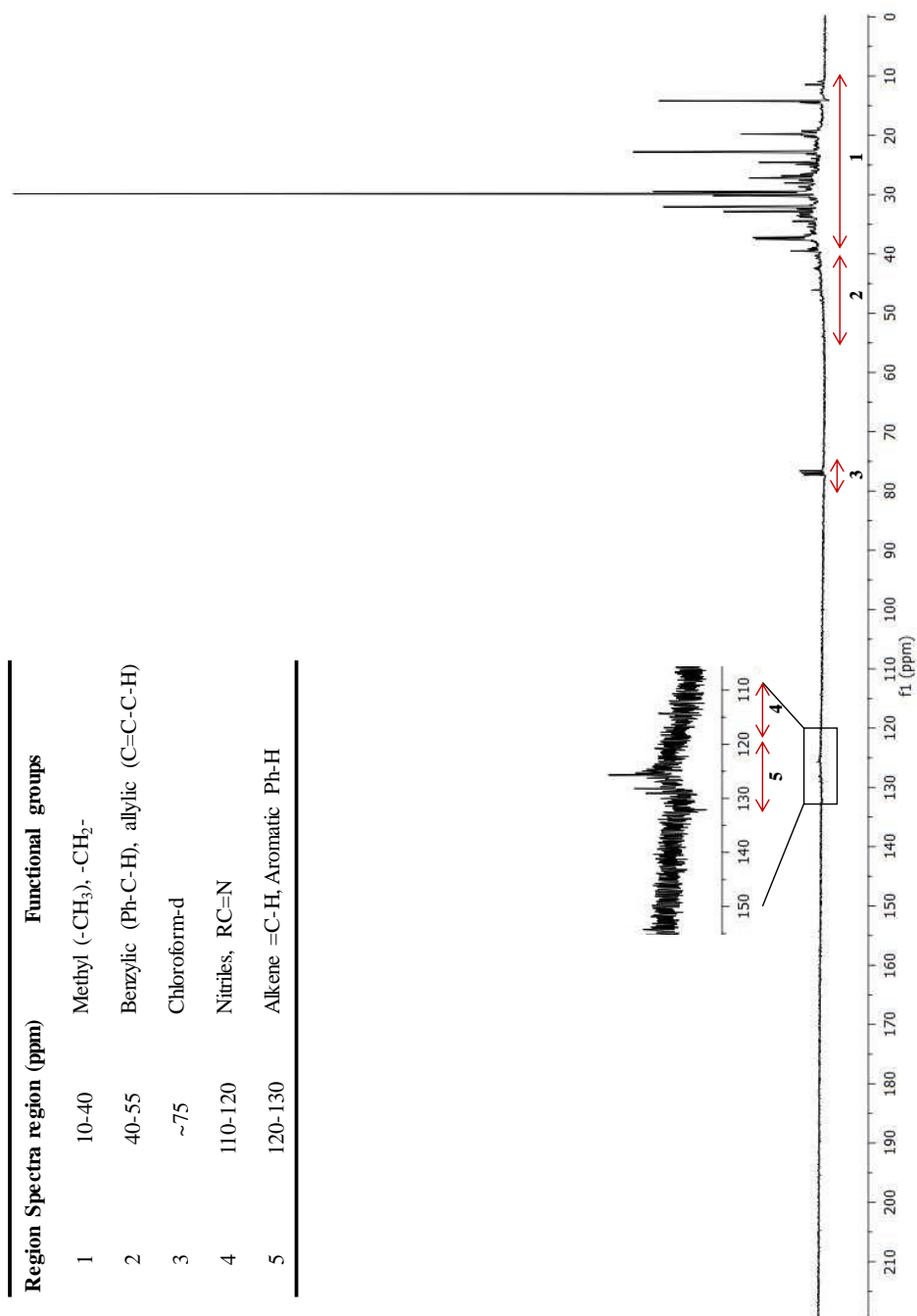
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# APPENDICES

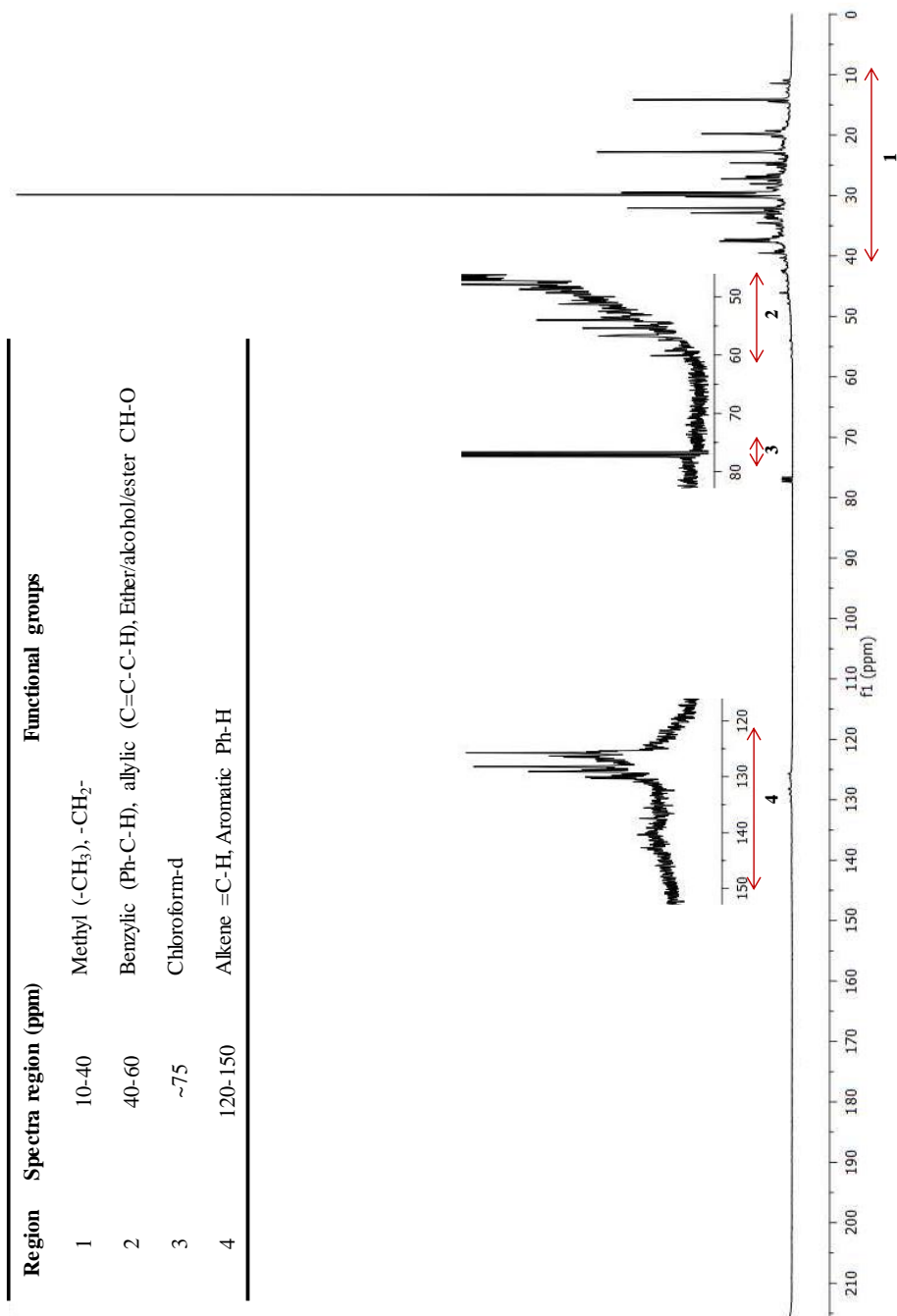
## Appendix A

$^{13}\text{C}$  NMR spectrum of untreated SN150 base oil (in Chloroform- $\text{d}_1$ ).



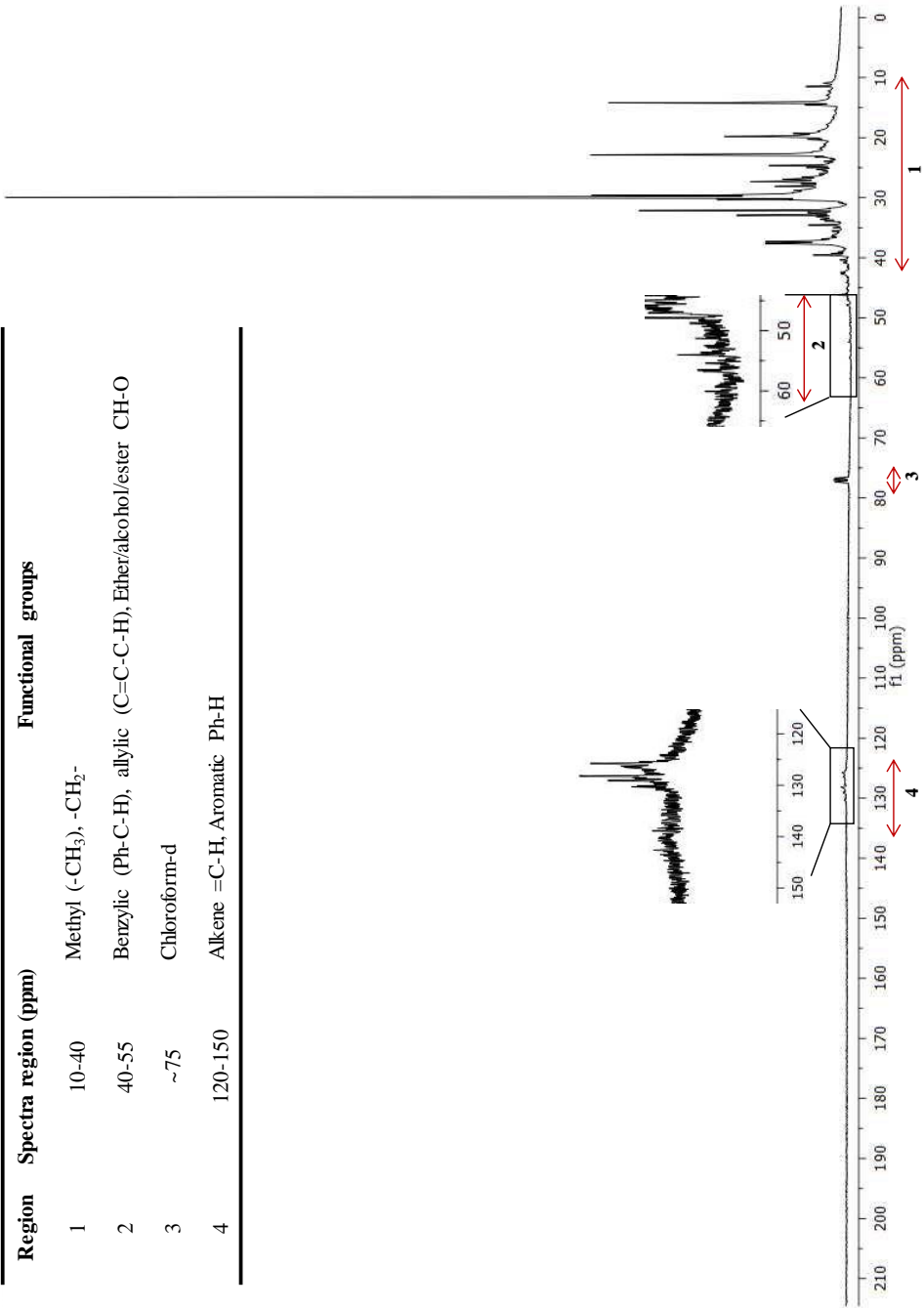
## Appendix B

$^{13}\text{C}$  NMR spectrum of oxidized SN150 base oil at 200 °C for 4 hours in a reactor (in Chloroform-d)



Appendix C

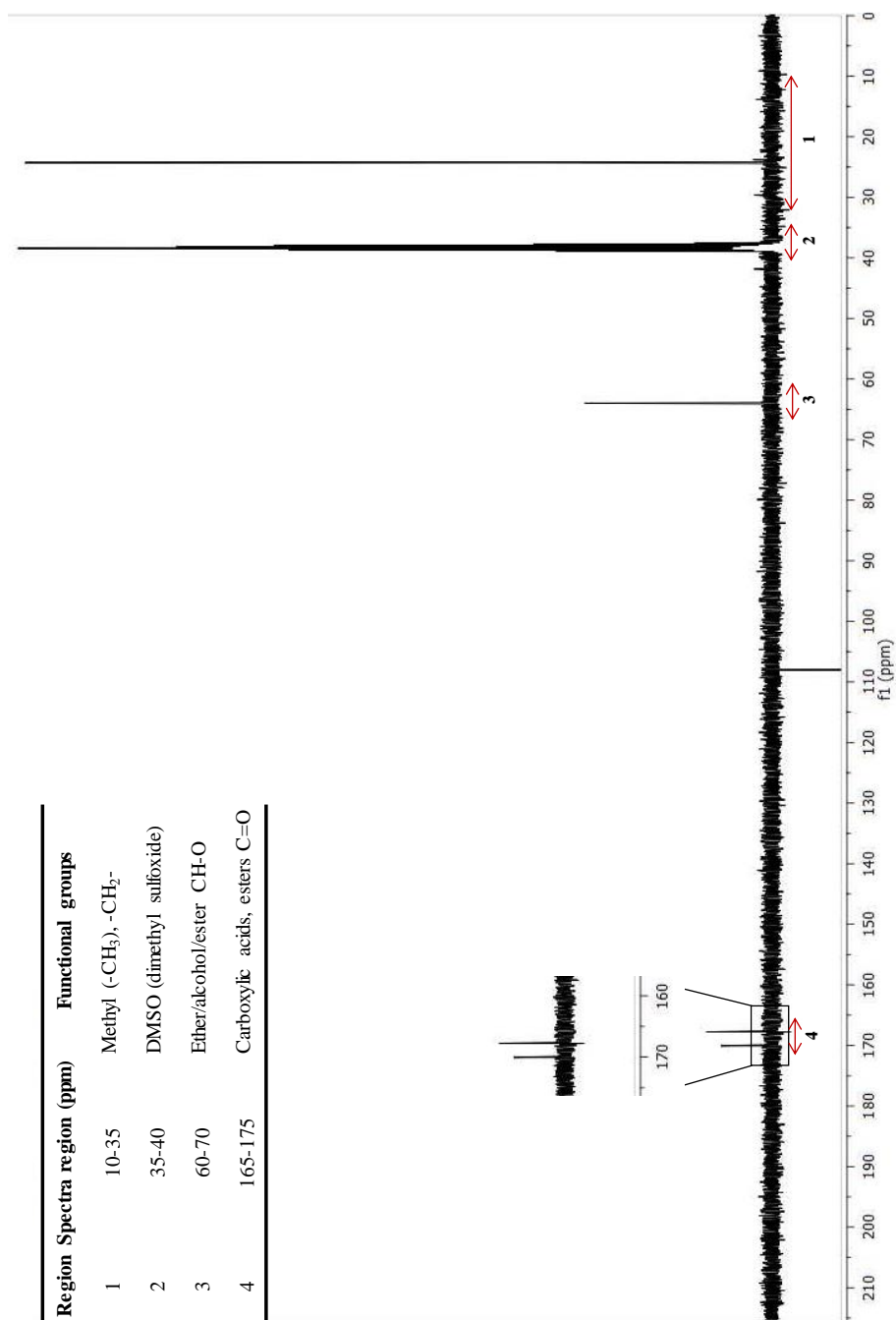
<sup>13</sup>C NMR spectrum of oxidized SN150 base oil at 200 °C for 36 hours in a vial (in Chloroform-d)





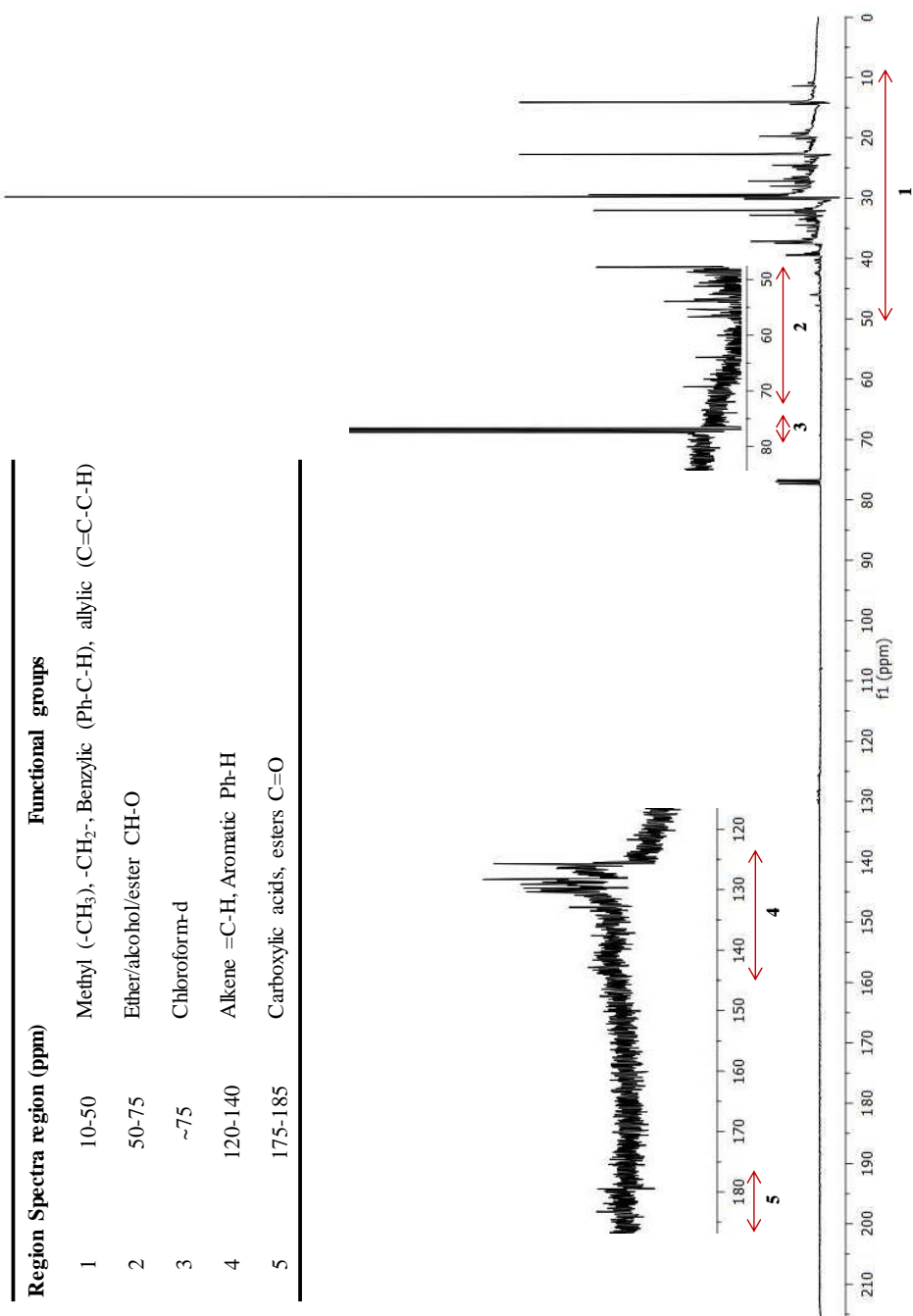
## Appendix D

$^{13}\text{C}$  NMR spectrum of bottom phase of BO oxidized at 200 °C for 4 hours in reactor after reaction with NaOH at 150 °C under Ar for 160h after separation with water (in DMSO- $d_6$ ).



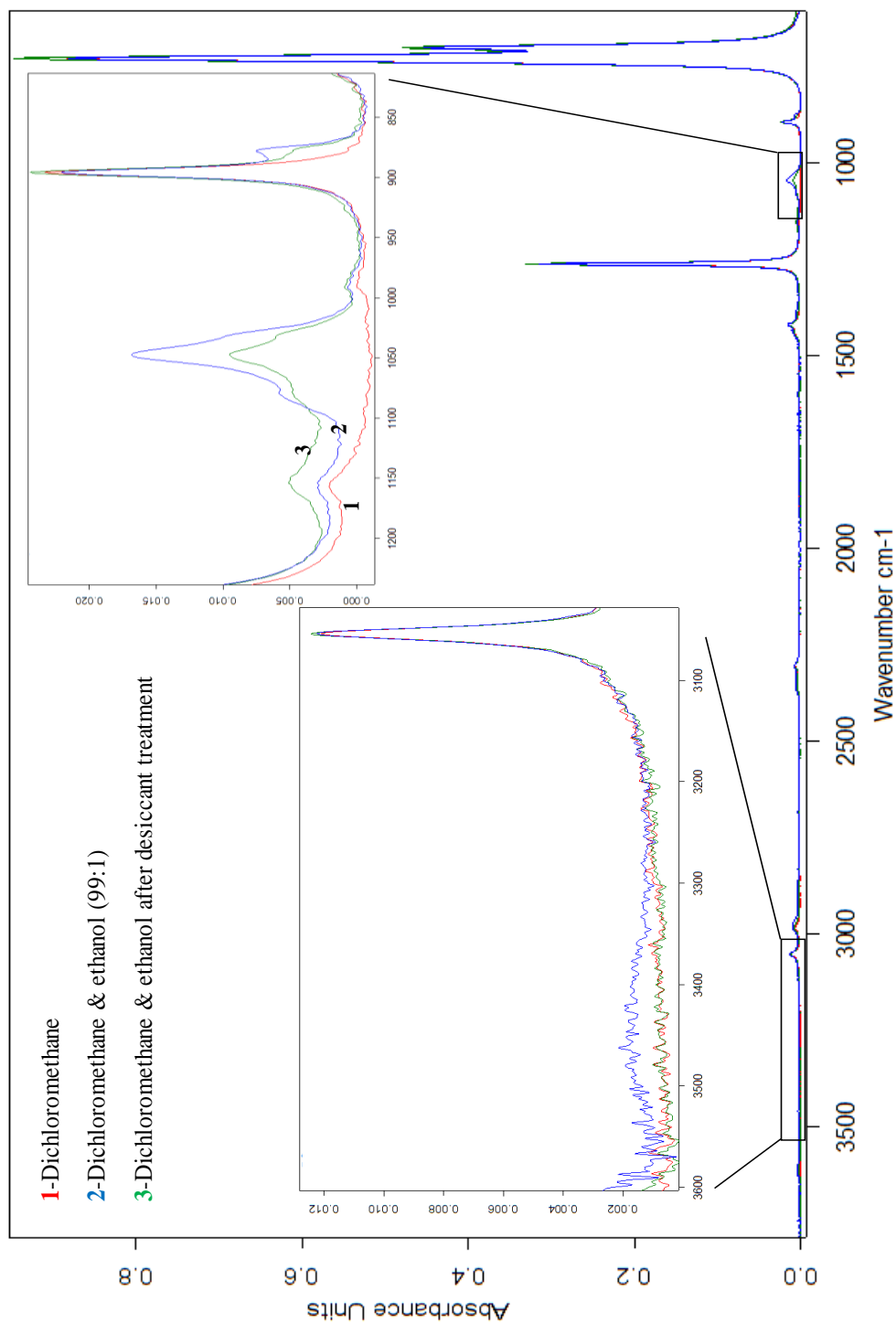
## Appendix E

$^{13}\text{C}$  NMR spectrum of bottom phase of BO oxidized at 200 °C for 4 hours in reactor after reaction with NaOH at 150 °C under Ar for 160h after neutralization with concentrated HCl (in Chloroform-d).



## Appendix F

IR spectrums of testing removal of alcohol from dichloromethane using  $\text{MgSO}_4$  desiccant. Sharp peaks at  $1050\text{ cm}^{-1}$  belong to  $\text{MgSO}_4$  compound.



## Appendix G

$^1\text{H}$  NMR spectra of oleic acid (top) in  $\text{CDCl}_3$  and  $^1\text{H}$  NMR spectrum of oleic acid mixed in base oil in 1:20 ratio (bottom). In both cases broad acid peaks are observed.

