Abstract

Five commercial pour point depressant have been tested for their structure and effectiveness in remediating paraffin (wax) depositions from neem crude oil. All PPDS were characterized by FTIR the results showed that all sample contain aromatic compound, aliphatic compound but some of them contain ester and olfien .The samples were also surveyed by GC ,The results show follows all PPDS Contain mainly different type of solvents such as ethyl benzene ,O-xylene,p-xylene,toluene in high concentration ,naphthalene ,cyclopentylcyclopentene,1,2,3,4tetramethyl benzene,1,2,3trimethyl benzene and eicosadiene in small concentration

PPDS evaluated as pour point depressant and flow improver on neem crude oil. the pour point and viscosity at different temperature for different doses (500,750,1000,1250ppm) were studied by measuring viscosity and pour point, result showed that the best viscosity was improved when adding epri2 at doses1250 ppm then epri 1 then china PPDS but epri25j1 did not have any effect in these type of crude oil . the result of pour point showed that the best results were epri2 PPDS giving a reduction in pour point of 9 C^0 ,followed by epri1 PPDS , china PPDS ,but epri25j1 did not have any effect

Also kerosene and diesel have been tested for their effectiveness in remediating paraffin wax depositions from neem crude oil and compare it with PPDS ,it is found that need high doses of solvent(5%,10%,15%,20%,25%,30%,35%) to make change in the pour point and viscosity this compares with PPDS .

But in term of cost, it is found that these large doses are not a problem because they are retrieved when distilling crude oil into product.

When comparing kerosene with diesel, it is found that the rate of reduction in pour point and viscosity of neem crude oil in kerosene bigger than diesel

GC and FTIR were used to study the chemical composition of wax extracted from two type of Sudanese crude oil (neem,hadida),the result showed that it consists of only normal paraffins ,the carbon number distribution in neem crude oil fromC11-C29 and the critical carbon numberC17,For hadida crude oil the carbon number distribution C11-C30 and the critical carbon number C15.

Also the DSC-1 was used to measure melting point and crystallization point of wax the results showed that the melting point from wax exctracted from neem52$C^0$and crystallization is46C^0,and for hadida crude oil the melting point is68$C^0$and the crystallization point is63C^0.

Chapter One

Introduction

Chapter One

Introduction

1.1-Petroleum -background

from Latin: *petra*: "rock" + *oleum*: "oil".is a naturally occurring, yellow-to-black liquid found in geological formations beneath the Earth's surface, which is commonly refined into various types of fuels.

It consists of hydrocarbons of various molecular weights and otherorganiccompounds.The name *petroleum* covers both naturally occurring unprocessed **crude oil** and petroleum products that are made up of refined crude oil.petroleum is formed when large quantities of dead organisms, usually zooplankton and algae, are buried underneath sedimentary rock and subjected to intense heat and pressure.

Petroleum is recovered mostly through oil drilling (natural petroleum springs are rare). This comes after the studies of structural geology (at the reservoir scale), sedimentary basin analysis, reservoir characterization (mainly in terms of the porosity and permeability of geologic reservoir structures)(Guerriero et al.,2011).It is refined and separated, most easily by distillation, into a large number of consumer products, from gasoline (petrol) and kerosene to asphalt and chemical reagents used to make plastics and pharmaceuticals.Petroleum is used in manufacturing a wide variety of materials,and it is estimated that the world consumes about 90 million barrels each day.

1.1.1-Composition

In its strictest sense, petroleum includes only crude oil, but in common usage it includes all liquid, gaseous, and solid hydrocarbons. Under surface pressure and temperature conditions, lighter hydrocarbons methane, ethane, propane and butane occur as gases, while pentane and heavier ones are in the form of liquids or solids. However, in an underground oil reservoir the proportions of gas, liquid, and solid depend on subsurface conditions and on the phase diagram of the petroleum mixture(Hyne,2001)

An oil well produces predominantly crude oil, with some natural gas dissolved in it. Because the pressure is lower at the surface than underground, some of the gas will come out of solution and be recovered (or burned) as *associated gas* or *solution gas*. A gas well produces predominantly natural gas. However, because the underground temperature and pressure are higher than at the surface, the gas may contain heavier hydrocarbons such as pentane, hexane, and heptane in the gaseous state. At surface conditions these will condense out of the gas to form natural gas condensate, often shortened to *condensate*. Condensate resembles gasoline in appearance and is similar in composition to some volatilelight crude oils.

The proportion of light hydrocarbons in the petroleum mixture varies greatly among different oil fields, ranging from as much as 97 percent by weight in the lighter oils to as little as 50 percent in the heavier oils and bitumens.

The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium. Many oil reservoirs contain live bacteria(Ollivier and Magot,2005)..The exact molecular composition varies widely from formation to formation but the proportion of chemical elements vary over fairly narrow limits as follows:(Sleight,1999)

Most of the world's oils are non-conventional

Table(1.1)chemical elements composition of crude oil by weight

Element	**Percent range**
Carbon	83 to 85%
Hydrogen	10 to 14%
Nitrogen	0.1 to 2%
Oxygen	0.05 to 1.5%
Sulfur	0.05 to 6.0%
Metals	< 0.1%

Four different types of hydrocarbon molecules appear in crude oil. The relative percentage of each varies from oil to oil, determining the properties of each oil.

Table(1.2)typesof hydrocarbon molecules appear in crude oil by weight

Hydrocarbon	**Average**	**Range**
Alkanes (paraffins)	30%	15 to 60%
Naphthenes	49%	30 to 60%
Aromatics	15%	3 to 30%
Asphaltics	6%	remainder

Crude oil varies greatly in appearance depending on its composition. It is usually black or dark brown (although it may be yellowish, reddish, or even greenish).

1.1.2-Chemistry

Petroleum is a mixture of a very large number of different hydrocarbons; the most commonly found molecules are alkanes (paraffins), cycloalkanes (naphthenes), aromatic hydrocarbons, or more complicated chemicals like asphaltenes. Each petroleum variety has a unique mix of molecules, which define its physical and chemical properties, like color and viscosity.

The *alkanes*, also known as *paraffins*, are saturated hydrocarbons with straight or branched chains which contain only carbon and hydrogen and have the general formula C_nH_{2n+2}. They generally have from 5 to 40 carbon atoms per molecule, although trace amounts of shorter or longer molecules may be present in the mixture.

The alkanes from pentane (C_5H_{12}) to octane (C_8H_{18}) are refined into gasoline, the ones from nonane (C_9H_{20}) to hexadecane ($C_{16}H_{34}$) into diesel fuel, kerosene and jet fuel. Alkanes with more than 16 carbon atoms can be refined into fuel oil and lubricating oil. At the heavier end of the range, paraffin wax is an alkane with approximately 25 carbon atoms, while asphalt has 35 and up, although these are usually cracked by modern refineries into more valuable products. The *cycloalkanes*, also known as *naphthenes*, are saturated hydrocarbons which have one or more carbon rings to which hydrogen atoms are attached according to the formula C_nH_{2n}. Cycloalkanes have similar properties to alkanes but have higher boiling points.

The *aromatic hydrocarbons* are unsaturated hydrocarbons which have one or more planar six-carbon rings called benzene rings, to which hydrogen atoms are attached with the formula C_nH_n. They tend to burn with a sooty flame, and many have a sweet aroma. Some are carcinogenic.

1.1.3-Classification

The petroleum industry generally classifies crude oil by the geographic location it is produced in (e.g. West Texas Intermediate, Brent, or Oman), its API gravity (an oil industry measure of density), its sulfur content,and it's composition. Crude oil may be considered *light* if it has low density or *heavy* if it has high density; and it may be referred to as sweet if it contains relatively little sulfur or *sour* if it contains substantial amounts of sulfur.

The geographic location is important because it affects transportation costs to the refinery. *Light* crude oil is more desirable than *heavy* oil since it produces a higher yield of gasoline, while *sweet* oil commands a higher price than *sour* oil

Also It's classified due to composition to paraffinic base ,Naphthenic base and Mixture base

Classification formula

$KW=TB/G$……………(1.1)

$CI=(87.552/TB)+473.7G-456.8$……….(1.2)

TB=mean averageboiling poin,0R

G=specific gravity at 60F

Equation(1) shows the Watson characterization factor ranges from less than 10 for highly aromatic materials to almost 15for highly paraffinic compounds .crude oils show a narrower range of KWand vary from 10.5 for highly Naphthenic crude to12.9for paraffinic base crude.

Equation(2) shows the correlation index is useful in evaluating individual fractions from crude oils the CI scale is based upon straight-chain paraffin having a CI value of 0 and benzene having CI value of 100 .theCI values are not quantitative,but the lower the CI valueThe greater the concentrations of paraffin hydrocarbons in the fraction ,and the higher theCIvalue,the greater the concentration of naphthenes and aromatics

1.2-Wax and wax deposition problem

The continuous flow of crude oil is a vital factor for the economy of countries. A new term of the so called flow assurance is added to the oil and gas industry to ensure successful and economical flow of hydrocarbon stream from reservoir to the point of sale.

Flow assurance is the engineering and science of predicting and managing production behavior as it moves from a reservoir to market through the changing environment of the production system.

The main challenges in flow assurance are solid depositions in the pipelines which can lead to reduction in the production or in worst case completely block the pipelines.

Wax deposition is a common problem in the oil industry ,when the oil temperature is lower to its trouble point ,paraffin crystals begin to precipitate, this deposits took place at any level of the production facilities(tubing ,production lines ,separators ,storage tank ,pipeline)wax deposition on the pipe walls limits the pumping of waxy crude oil . The deposits may vary from soft to hard, from yellow to black and consist of a mixture of wax, oil, asphaltenes and inorganic material.

The petroleum wax is long hydrocarbon chains found naturally in crude oils and condensate and contains at least 15 or more carbon atoms. The wax is classified to two types these two types of wax are commonly encountered in crude oil.

The first is the macro crystalline wax composed of mainly straight chain paraffin (n-alkanes with varying chain paraffin length (about C_{20} to C_{50}).

The second is microcrystalline or amorphous waxes containing high portion of iso-paraffins (cyclo-alkanes) and naphthenic with a molecular weight ranges from C_{30} to C_{60} which can begin to precipitate and form deposits in the pipe line when the temperature decrease during production. (Al-Yaari, 2011)(Dobbs, 1999)

There are applied different methods for preventing and removing wax deposition such as mechanical removing, heating application, solvent techniques, and wax treatment chemicals.

In this study we concentrate on wax treatment technique and it’s divided into two types:

1-Wax Removing Chemicals

2-wax Prevention chemicals

1.3-objectives

1. To study the characterization of pour point depressant by GC and FTIR
2. To study the characterization of different type of wax by GC and FTIR
3. To Measure pour point and rheological properties of neem crude oils at different temperatures
4. To investigate the effectiveness of adding wax prevention chemicals(pour point depressant) on the flow properties of neem crude oil.
5. To Investigate the effectiveness of adding wax removing chemicals (kerosene and diesel) on the flow properties of neem crude oil.
6. To determine the minimum amounts of chemicals that are needed to improve the flow properties at different flow conditions.

Chapter Two

Literature Review

Chapter Two

Literature Review

2.1-wax and wax deposition

The petroleum wax/paraffin are long hydrocarbon chains found naturally in crude oil and condensate and contain at least 15 or more carbon atoms.these molecules can be either straight or branched hydrocarbon chains and can contain some cyclic and /or aromatic hydrocarbon

The severity of the wax deposition problems are related to the crude oil and the molecular compostion of the wax molecules.the waxes in crude oil are often more difficult to control compared to those found in condensate ,because the Alkane chains are often longer in the crude oil than in the condensate,which consists of lighter hence shorter hydrocarbons

It is generally the long straight hydrocarbon chains(n-paraffin)in the crude oil that causes deposition problems in the production pipelines.these are wax moleculeswith 25-50 or even longer carbon chains,which forms clearly defined and needle-shaped macrocrystalline waxes when precipitated.these hard crystalline waxes are difficult to remove,and are the main components responsible for blocking of the pipelines.

When the crude oil contains wax molecules with 16-25 carbon atoms or branched wax molecules,it will generallyform a microcrystalline structure.this will result in a more soft mushy wax,which is the major contributing factor to tank bottom sludge .

The structure of the wax molecules ,straight or branched, and the presence of cyclic and aromatichydrocarbonrings,will have a significant effect on melting point , boiling point and solubility of the waxes in the crude oil. However in general the melting point of the waxes is normally increasing as the molecular size of the waxes increases.thus as higher melting point a wax have , the more difficult it is to keep the wax from depositing .

Wax is a component of crude oil that remains in solution until operating conditions are favorableto its precipitation, a condition caused by changes in the temperature–pressure equilibrium of the crude. Upon precipitation (crystallization), wax is deposited on the components of the production system by various mechanisms including molecular diffusion, shear dispersion, Brownian diffusion, and gravity settling. Brownian diffusion and gravity settling are not very significant in the dynamic condition obtainable in crude oil production.

Wax deposition has been reported in all facets of the production system including the reservoir, wellbore, tubing, flow lines, and surface facilities. Wax deposition causes loss of production, reduced pipe diameter, and increased horsepower requirements, and negatively impacts production economics. The available remedial measures include mechanical, chemical, and thermal techniques

Temperature reduction/heat loss is a dominant factor in wax problems, as wax begins to precipitate from crude when the temperature falls to or below the cloud point (wax appearance temperature [WAT]).

However, other factors such as pressure, oil composition, gas-oil ratio, water-oil ratio, flow rate, well completion, and pipe-surface roughness also contribute to the problem of wax deposition. Laboratory experimental work using stock tank oil (STO) under static condition predominated wax deposition research in the past.

Recent investigations have centered on the use of live oil at reservoir temperature and pressure, which is more representative of the reservoir oil in experimental work under dynamic conditions. Thermodynamic modeling of wax deposition and validation with experimental data is gaining wide acceptance.

The onset of wax deposition (true cloud point) is yet to be achieved because all the available techniques require some crystals to be formed for detection, thus giving a value that is less than the true cloud point.

The improvement of existing techniques or the development of new ones, to detect the onset of wax crystallization is a major challenge to research in this area.

2.2-problem of Wax Deposition

The problem of wax deposition has plagued the petroleum industry for decades, arousing two main concerns—technical and economic—upon its occurrence. Wax deposition can be mild, or it can be severe enough that it is unmanageable (Figure 2.1). The earlier the problem is diagnosed in the life of a reservoir (or well), the easier it will be to design a preventive or control management plan that will reduce or eliminate some of the technical and economic problems associated with wax deposition. Technical issues associated with wax deposition include:

- Permeability reduction and formation damage when it occurs around the wellbore and its vicinity.
- Reduction in the interior diameter and eventual plugging of production strings and flow channels (see Figure 2).
- Changes in the reservoir fluid composition and fluid Rheology due to phase separation as wax solid precipitates.
- Additional strain on pumping equipment owing to increased pressure drop along flow channel consequent to rheological changes as wax begins to crystallize.
- Limiting influence on the operating capacity of the entire production system.

Figure (2.1) Severity of Wax Deposition

The critical role of economics in crude oil production makes wax deposition a significant economic concern to the industry due to the following:

- Capital investment and operating costs are increased when developing paraffinic crude oil fields. This could cause serious financial strain on the operator of such a field or even lead to abandonment when it becomes uneconomical due to blockage of facilities by wax deposits.
- Lost production.
- Risk element in development, a problem that could jeopardize the development of marginal fields given the prevailing economic situation. The additional cost of controlling and managing wax puts a greater risk of abandonment on such fields.

Hence, control of wax deposition is essential. To address the issue of wax deposition, three important phenomena have to be considered: wax precipitation, dynamic wax deposition, and heat transfer from the wellbore. Wax plug, which is obtained from wax deposition, is a gel that contains solid wax crystals and trapped liquid (Venkatesan et al., 2007). Wax precipitation is a thermodynamic phenomenon that will lead to deposition of solid wax crystals. Dynamic wax deposition is the phenomenon in which a gel is formed with wax crystals and liquid. Wax precipitation should be described accurately in order to develop the solutions to control wax deposition in wellbores.

2.3-Wax Crystallization

Crystallization generally is the process of separation of solid phase from a homogenous solution, the separated solid phase appearing as crystals. Paraffins (waxes) remain in solution as natural components of crude oil until temperature gets to or below their solubility limit. The separation of wax (solid phase) out of the oil (liquid phase) at favorable prevailing conditions (Hammami et al., 2003) is referred to as wax precipitation or crystallization. Crystallization and precipitation have been used interchangeably in wax deposition studies and will be used to mean the same process in this work. Two types of wax crystals have been distinguished (Elsharkawy et al., 1999): macro-crystalline wax composed mainly of normal paraffin and micro-crystalline wax from iso-paraffins and naphthenes (cyclo-paraffins).

Wax crystal formation involves two stages—nucleation and growth—with nucleation preceding growth stage. As the solubility limit is approached, the kinetic energy of the paraffin molecules is reduced as a result of temperature reduction. Consequent to this reduced kinetic energy, the motion of the wax molecules is hindered, leading to continuous reduction and closure of the space between the molecules. As this process continues, the wax molecules get tangled, forming clusters which grow larger and become stable upon reaching a certain critical size. The critical size is dependent upon the prevailing condition. However, the clusters re-dissolve when critical size is not attained and become unstable.

These clusters are referred to as nuclei. Nuclei that achieve critical cluster size will have an increasing number of molecules clinging to them as the prevailing condition remains favorable to crystal formation, leading to an increase in size of formed wax crystals. This process of increase in size is known as wax crystal growth stage. Nucleation and growth occur simultaneously in the oil system, with one or the other predominating at a time.

2.4-Wax Deposition

Sometimes in the literature, deposition is used interchangeably with precipitation, but they are different concepts. Wax deposition is the formation of a layer of the separated solid phase, and the eventual growth of this layer, on a surface in contact with the crude oil.

Wax deposition can be formed from an already precipitated solid phase (wax) through mechanisms of shear dispersion, gravity settling, and Brownian motion, or from dissolved wax molecules through a molecular diffusion mechanism. Precipitation does not necessarily lead to deposition, as precipitated wax may not deposit due to other prevailing operating conditions. Thus, precipitation, though an important condition for deposition, is not necessarily sufficient for wax deposition. Singh et al. (2001) reported that there are two stages or steps that are involved in wax deposition: wax gel formation followed by aging of deposited wax gel.

Petroleum wax deposits contain some crude oil, water, gums, resins, sand, and asphaltenes, depending on the nature of the particular crude oil, which are entrapped during the crystallization and deposition process. The trapped oil causes diffusion of wax molecules into the gel deposit and counter-diffusion of oil out of the gel deposit, a process that depends on the critical carbon number of the oil. The critical carbon number is unique for different waxy crude oils and depends on the prevailing operating conditions also (Singh et al., 2000).

In the gel deposit, the fraction of molecules with carbon numbers greater than the critical carbon number increases, while that of molecules with carbon numbers lower than the critical carbon number decreases. The process of diffusion and counter-diffusion leading to hardening of the gel deposit, increase in size of deposit, and increase in the amount of wax in gel deposit, is called aging, the second stage of wax deposition. Molecular diffusion, therefore, is critical to aging and hardening of wax gel deposits. Singh et al. (2000) reported that the deposition of wax gel on the pipe/tubing wall follows a process that can be described by the following five steps:

1. Gelation of the waxy oil (or formation of incipient gel layer) on the cold surface.
2. Diffusion of waxes (hydrocarbons with carbon numbers greater than the critical

carbon number) towards the gel layer from the bulk oil.

3. Internal diffusion of these molecules through the trapped oil.
4. Precipitation of these molecules through the trapped oil.
5. Counter diffusion of de-waxed oil (hydrocarbons with carbon numbers lower than the critical carbon number) out of the gel deposit layer.

Steps 3, 4, and 5 are reported to be responsible for the increase in solid wax content of the wax gel deposit (aging of the wax deposit).

2.4.1-Mechanism of Wax Deposition

The mechanism of wax deposition is considered here with respect to the lateral transport of waxy residue. Wax deposition is believed to occur as a result of lateral transport by diffusion, shear dispersion, and Brownian diffusion. Gravity settling is believed to be a possible transport mechanism also.

2.4.1.1-Molecular Diffusion For all flow conditions, oil will be in laminar flow either throughout the pipe or at leastin a thin laminar sublayer adjacent to the pipe wall. When the oil is being cooled, there will be a temperature gradient across the laminar sublayer. If temperatures are below the level where solid waxy crystals can be precipitated, then the flowing elements of oil will contain precipitated solid particles, and the liquid phase will be in equilibrium with the solid phase; that is, the liquid will be saturated with dissolved wax crystals. The temperature profile near the wall will lead to a concentration gradient of dissolved wax, and this dissolved material will be transported toward the wall by molecular diffusion. When this diffusing material reaches the solid/liquid interface, it will be precipitated out of solution.

2.4.1.2-Brownian Diffusion Small, solid waxy crystals, when suspended in oil, will be bombarded continually by thermally agitated oil molecules. These collisions will lead to small random Brownian movements of the suspended particles. If there is a concentration gradient of these particles, Brownian motion will lead to a net transport, which in nature and mathematical description is similar to diffusion. The possible contribution of Brownian diffusion to wax transport and deposition has been mentioned prominently in USSR literature.

2.4.1.3-Shear Dispersion When small particles are suspended in a fluid that is in laminar motion, the particles tend to move at the mean speed and in the direction of surrounding fluid.

The particle speed is that of streamline at its center, and the particle rotates with an angular velocity which is half the fluid shear rate.

If the particles approach a solid boundary, both linear and angular velocities will be reduced. Because of fluid viscosity, rotating particles will impart a circulatory motion to a layer of fluid adjacent to the particle. This rotating fluid region exerts a drag force on neighboring particles.

In a shear field, each particle passes and interacts with nearby particles in slower or faster moving streamlines. When only two particles are present, far from a wall and at a very low Reynolds number, these passing encounters result in large temporary displacements.

As the particles pass, their trajectories are such that the particles curve around one another and return to their original streamline. Thus, there is no net lateral displacement. If the particle concentration is high, however, then a significant number of multiparticle interactions will occur. These multiparticle collisions result in net lateral transport and a dispersing of particles.

2.4.1.4-Gravity Settling Precipitated waxy crystals are denser than the surrounding liquid oil phase. Hence, if particles were noninteracting, they would settle in a gravity field and could be deposited on the bottom of pipes or tanks. For an initially uniform mixture in a vessel, there would be a beginning rate of settling followed by a diminishing rate of deposition, which asymptotically would approach zero at complete settling.

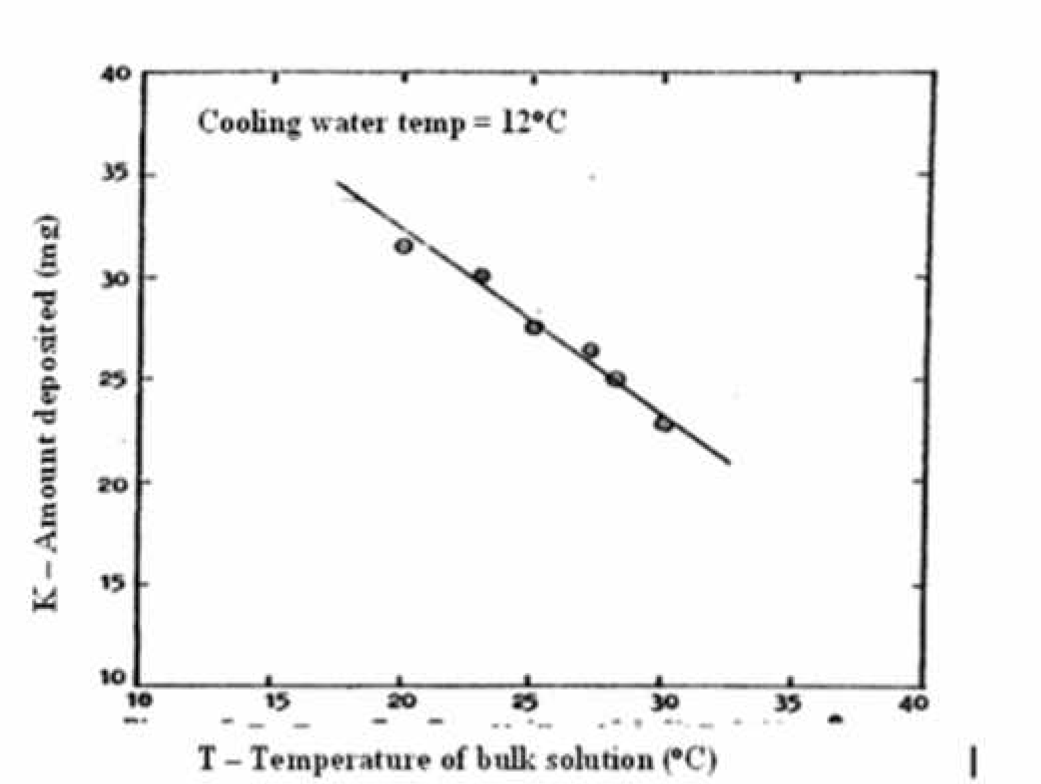
2.4.2-Factors Leading To Wax Precipitation and Deposition

Wax precipitation occurs when the wax molecules contained in the crude oil reach their solubility limit due to change in equilibrium conditions in the crude, resulting in loss of paraffin solubility. The solubility limit is directly dependent on temperature and, as such, is defined by temperature, given other specified conditions. There are other factors that affect the precipitation of wax and thus wax deposition. While some of these factors influence wax precipitation by shifting the solubility limit in terms of temperature upwards/downwards, others provide a favorable environment for deposition to occur. Such factors include oil composition plus available solution gas, and pressure of the oil which affects the amount of gas in solution. Others are flow rate, completion, and pipe or deposition surface roughness.

2.4.2.1-Temperature seems to be the predominant and most critical factor in wax precipitation and deposition due to its direct relationship with the solubility of paraffin. Sadeghazad et al. (1998) reported that temperature and the amount of light constituent are the two most important factors affecting wax precipitation and deposition. Paraffin solubility increases with increasing temperature and decreases with decreasing temperature.

In working with food-grade wax in a model oil solvent consisting of mineral oil and kerosene mixed at a ratio of 3:1, Singh et al. (2000) showed the relationship between wax solubility and temperature. Wax precipitates from crude oil when the operating temperature is at or below the WAT (cloud point temperature). It has been reported that wax deposition will not occur until the operating temperature falls to or below the WAT (Erickson et al., 1993). All other factors actually lead to wax deposition when the temperature is already at or below the cloud point. The ambient temperature around the pipe is generally less than the oil temperature in the pipe. Thus, there is loss of heat through the pipe wall to the surroundings because a temperature gradient exists between the bulk oil and the colder pipe wall. This temperature gradient leads to wax deposition when the pipe wall temperature falls below the cloud point. The rate of wax deposition is in direct proportion to the temperature difference between the bulk oil and the pipe wall (Eaton et al., 1976) when bulk oil temperature is fixed. However, Haq (1981) showed that keeping the pipe wall temperature constant at a value below the cloud point of the oil and varying the bulk oil temperature reduce the amount of wax deposited as the temperature difference between the bulk oil and pipe wall increases (Figure 2.2)

The temperature gradient between the cold tubing/pipe wall and the bulk oil initiates a concentration gradient in the paraffin molecule distribution. Paraffin molecules near the pipe wall crystallize out of the oil as wall temperature falls below cloud point, leading to a reduction in the number of dissolved paraffin molecules around the wall inducing a radial concentration gradient. The simple law of diffusion is obeyed then as dissolved paraffin molecules in the oil diffuse towards the wall, causing additional precipitation and further deposition. This leads to increasing wax deposit thickness with time. Cole and Jessen (1960) opined that it is the difference between the cloud point temperature and the temperature of the pipe wall that most importantly determines the rate of wax deposition.



Figure(2.2)Effect of temperature gradient on wax deposition (Haq, 1981).

2.4.2.2-Crude Oil Composition

Crude oil is composed of saturates aromatics, resins, and asphaltenes (SARA), the distribution of which in a particular crude oil system is shown by the SARA analysis. SARA determines the susceptibility of the crude to deposition of wax solids, and thus the stability of the crude oil. Saturates are flexible in nature, the flexibility being highest in normal paraffins because they are straight chain compounds. The very high flexibility of normal paraffins makes it possible for them to easily cluster and crystallize. The iso-paraffins equally enjoy a high level of flexibility, but form a more unstable wax. Cyclo-paraffins (naphthenes) are least flexible due to their cyclic nature and do not contribute much to wax deposition.

These components are in thermodynamic equilibrium at initial reservoir conditions. It is known that aromatics serve as solvents for high molecular weight saturates, which are the sources of paraffin waxes in crude oil while the polar components, especially asphaltenes, induce wax nucleation (Hammami et al., 1999). Singh et al. (2001) reported, however, that the solubility of paraffins in aromatic, naphthenic, and other organic solvents becomes low at room temperature (low temperatures). Light ends of saturates equally help to keep the high molecular weight heavy ends in solution. The onset of production results in the loss of these light ends, as they are first to leave the reservoir. This alters the original composition of the oil system, resulting in decreased solubility of the paraffin waxes. This loss of solubility could lead to precipitation and deposition of wax.

In a model study, Huanquan et al. (1997) reported that increasing the percentage of light end (C5) in a synthetic oil system decreased the cloud point temperature, reducing the chance of wax deposition.

Generally, the weight percent of the saturates in the crude oil, the structural distribution of the paraffin components, and the occurrence of other solids like formation fines, corrosion materials, and presence of asphaltenes which could form nucleating sites—all contribute to wax precipitation and deposition.

Oils containing high C30+ (especially normal paraffin C30+) concentrations exhibit high cloud point temperatures (Ferworn et al., 1997).

Therefore, knowledge of the oil composition (SARA) gives a fair idea of the wax deposit potential of the crude and, hence, the oil stability.

Oil stability has been reported to depend on its solids content and the balance between aromatics and saturates. By SARA analysis, the distribution by weight percent of saturates, aromatics, resins, and asphaltene components, for stable and unstable crude oils, is as follows:

Unstable crude: Saturates > Aromatics > Resins >Asphaltenes

Stable crude: Aromatics > Saturates > Resins >Asphaltenes

This distribution is to be expected since the aromatics keep the heavy paraffin wax in solution, while a crude oil system that displays a large amount of saturates (paraffin) is likely to be unstable (Carbognani et al., 1999) and thus precipitate and deposit wax.

2.4.2.3-Pressure

as an important parameter in the exploitation of reservoir fluids, plays a significant role in wax precipitation and deposition.

The pressure profile during oil production is such that the reservoir pressure declines with production, and the pressure of the flow stream drops all the way from the reservoir to the surface.

The lighter components of the reservoir fluid tend to be the first to leave the reservoir as pressure depletes.

This causes an increase in the solute solvent ratio, since the light ends serve as solvent to the wax components. Hence, the solubility of wax is reduced with the loss of these light ends.

Brown et al. (1994) studied the effect of pressure on the cloud point of dead oil as well as live oil by measuring cloud point at atmospheric pressure and higher pressures.

The wax appearance temperature increases with increase in pressure above the bubble point, at constant composition.

This phenomenon implies that increase in pressure in the one-phase liquid region (above bubble point pressure) will favor wax deposition.

The situation is different below the bubble point where there is two-phase existence. Here wax appearance temperature decreases with increase in pressure up to bubble point pressure (Brown et al., 1994) due to dissolution of light ends back into the liquid phase.

The WAT increases with increase in pressure for STO, commonly referred to as dead oil (Brown et al., 1994; Karan et al., 2000). Huanquan et al. (1997) reported that the WAT increases with increase in pressure for a fixed component liquid mixture

2.4.2.4-Other Contributing Factors

Though temperature, composition, and pressure of oil play the most significant role in wax deposition, other factors that have been identified as contributing to wax deposition include flow rate, gas-oil ratio, and pipe/tubing wall roughness.

Laboratory investigations have revealed that wax deposition is influenced more by laminar flow than when flow is in the turbulent regime.

Increasing flow rate from laminar to turbulent reduces maximum deposition rate and at the same time lowers the temperature at which maximum deposition rate occurs (Hsu et al., 1994), a scenario that is expressed in Figure(2.3)

Low flow rates offer the moving oil stream longer residence time in the flow channel. This increased residence time allows more heat loss to the surroundings, leading to a higher chance of the bulk oil temperature falling below the WAT and enough time for wax precipitation and final deposition.

Jessen and Howell (1958) believed that when flow is in the laminar regime, wax deposition increases with increase in flow rate. Increase in flow rate in the laminar regime makes more fluid available for wax deposition.

However, wax deposition decreases as flow moves to the turbulent regime. Turbulent flow stream exerts a kind of viscous force, which tends to drag or slough the wax deposits from the pipe wall. When this viscous drag exceeds the resistance to shear in the deposits, the wax then sloughs and is lodged back into the liquid.

This removal mechanism has a significant impact on the wax deposition rate (Hsu et al., 1994).

There is a difference in texture between wax deposited at high flow rates and wax deposited at low flow rates (Jessen and Howell, 1958; Tronov, 1969; Haq, 1981).

Paraffin wax deposited at high flow rates appears harder, being more compact and more firmly attached to the deposition surface, the molecules having good cohesion among them. In his study of the effect of deposition surface roughness on paraffin deposition, Hunt (1962) concluded that deposits do not adhere to metals themselves, but are held in place by surface roughness which acts as wax nucleating sites.

Jorda (1966) observed that paraffin deposition increases with greater surface roughness.

In their wax deposition study with pipes of different materials, Jessen and Howell (1958) concluded that the amount of wax deposited on a smooth surface is less than that deposited on steel.

However, (Patton and Casad ,1970) could not see any correlation between wax deposition and surface roughness, but opined that adhesion bond at a surface should be proportional to the total contact area and therefore related to surface roughness.

Gas/oil ratio influences wax deposition in a manner that depends on the pressure regime.

Above the bubblepoint, where all gases remain in solution, solution gas helps to keep wax in solution. Luo et al. (2001) reported that wax appearance temperature will be high with low GOR (gas oil ratio), while Singh et al. (2004) observed that injection of lift gas in a closed loop reduced wax deposition by causing a depression in wax appearance temperature as a function of pressure.

High GOR would result in more expansion and subsequent cooling as pressure of the oil system depletes a situation that can aggravate the wax deposition problem.

In a study to reduce wax-appearance temperature by injection of diluents lift gas, Singh et al. (2004) noted that good results were not obtained in high GOR wells.

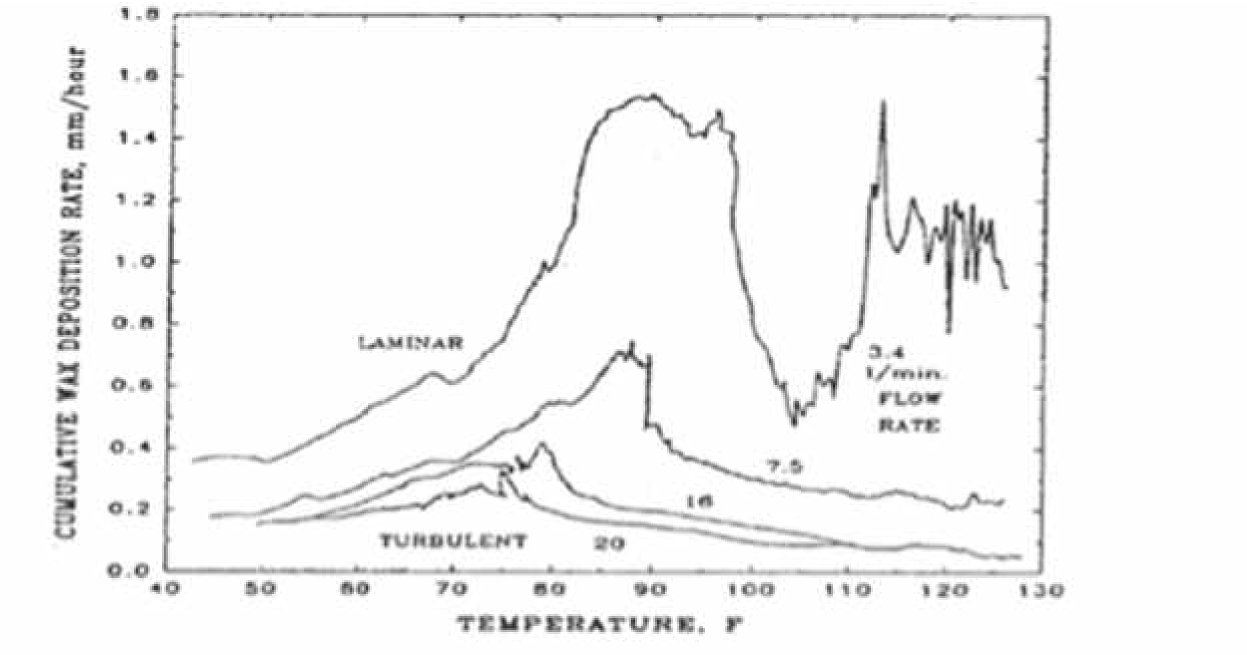


Figure (2.3): Effect of flow rate on wax deposition rate (Hsu et al., 1994)

2.5-Wax treatment techniques

In flow assurance the most important task is to maintain the well stream flow, and prevent any blockage from occurring that can stop the production.

In order to sustain an optimal production at all time, thoroughly analysis and research have to be implemented in the planning phase of a field, to achieve better understanding and predict any possible challenges that can occur.

This include important knowledge about pressures, temperatures, flows, fluid samplings, solid samplings and laboratory testing, which will all be helpful in determining the processes that can take place in the flow lines, and be able to come up with solutions to the challenges that may arise.

In most cases the flow assurance solutions would add a substantial amount of cost for the project, however these costs would be small compared to loss caused by reduction or shutdown of the production due to pipeline blockage (Abney et al,2003).

The problems related to wax deposition are often associated with deepwater flow lines, and tend to involve more difficult flow assurance challenges.

However there have been evolved numerous techniques to remove and reduce the build-up of wax deposition downhole and in the flow lines.

Many of the methods have achieved great results when applied, however their success rate is dependent on the wax composition and crude oil found in the specific reservoir, and therefore will vary for the different fields.

In many cases a combination of two or more treatment methods have been used to more efficiently remove and reduce the wax depositions.

The wax treatments techniques are divided into two categories, the wax removal techniques andthe wav prevention techniques(Mokhatab,2009)

2.5.1-Wax removal techniques

The most common methods used for removing already deposit wax are by mechanical removal, heat application and chemical removal. However some of these techniques are also regarded as wax preventive techniques, such as with heat application.

2.5.1.1-Mechanical removal

Pigging is the first widely used mechanical removal technique used to remove wax deposits formed at the pipeline walls, and is a good and cost effective method.

The pigging operations are performed by using a scraper or cutter, which will scrape the wax deposition of the walls inside the pipelines.

There are developed different types of pigs with different shapes and materials, which will have profound effect on the wax removal performance.

The most conventional used pigs are disc, cup and polly, which all have different wax removal performance depending on the wax hardness and thickness.

2.5.1.2-Heat application

Different thermal solutions for removing or reducing wax deposition have shown to be successful for flow lines.

Active heating has especially been regarded as an efficient flow assurance solution against wax, due to the advantages to control the temperature above the formation region (Esaklulet al,2003)

The thermal management system is normally broken down to passive insulation and active heating.

Passive insulation is mainly techniques used to prevent the warm well stream fluid to lose it heat by using different insulation methods.

Active heating use external sources to heat the flow lines to keep the temperature of the well stream fluid above the wax deposition temperature, with the use of electrical heating or hot fluid. Active heating makes it possible to maintain the temperature through the production, however in long flow lines the operational cost can become very high (Thant et al,2011).

2.5.1.3-Wax removing chemicals

There are many different types of chemicals that can be used to remove wax depositions, and several methods on how to apply them.

The most common chemical methods used in the oil and gas industry as a removal technique are hot oiling and wax solvents.

The application of thermochemical packages are a more controversial wax removal technique.

2.5.1.4-Hot oiling

The hot oiling is a technique that has been used a lot in the early days in the oil and gas industry for removing wax depositions downhole and in the flow lines.

In the process hot oil is heated to a temperature above the melting point for wax and then pumped into the well, normally through the annulus space.

The heated oil will circulate around the tubing and melt the wax deposits inside the tubing, and then be brought back to the surface via a heating system in the production tubing.

As a result of the process the melted wax inside the tubing will be transported with the well stream fluids through the flow lines to the production facilities.

During the hot-oil process a wax dispersant is usually added to the crude oil, to enhance the dispersion of the melted wax with the crude oil.

The hot-oil technique is a fast and simple method, which will effectively remove the wax deposition. However this method can be dangerous, especially when applied to wells that have crude with low flash point.

There have been operations where the hot-oil has been replaced with steam or hot water to melt the wax, but is rarely used due to risk of corrosion and emulsion problems.

2.5.1.5-Wax Solvent

The adding of solvent downhole and to the flow lines have shown to be effective to remove wax depositions, as it will help to resolve the precipitated wax and make it easier to transport the crude oil to the surface (Ferworn et al,1997)

The different solvents have different abilities to dissolve wax deposits, which depends on the wax, the location in the system and the temperature. Normally the solvents are applied in frequent batch treatments or continuously. Aliphatic and aromatic solvents are the two main groups of solvent used on the oilfields. The aliphatic solvents are straight or ring formed hydrocarbons, and the most common aliphatic solvent used are diesel, kerosene and condensate

The aromatic solvents are chemical containing a carbon ring with delocalized electron double bonding, such as xylene and toluene, which are the most popular solvents used today(Barker et al,2001). A mixture of xylene or toluene together with an aliphatic solvent has shown to increasethe wax removal. Adding a surfactant can also enhance the performance of the solvent by helping it to disperse the waxes (Thierheimer,1990)

More faster and effective wax removal has been achieved by heating the xylene and toluene solvent when employed(Straub et al,1989)

Other solvent that have been applied with good success are benzene, chlorinated hydrocarbons, and carbon disulfide. However many of the solvents used are not environmental friendly and some highly toxic. Many also possess dangerous risks related to low flash points, such as the aromatic solvents, and corrosion problems, as seen with chlorinated hydrocarbons (Woo et al,1984)

2.5.1.6-Thermochemical packages

Thermochemical packages are wax removal methods that utilizes the heat of an exothermic reaction to melt the wax deposits downhole or in flow lines. A common reaction used is the acid-catalyzed decomposition of ammonium nitrate. The reaction starts by mixing a sodium nitrate and ammonium nitrate or chloride in an aqueous solution, in the presence of HCl as catalyst. There will be developed huge amount of heat as the reaction rate increases, which will be transported upwards the pipelines and melt the waxes. The reaction is controlled by keeping the pH in range between 5.0 and 8.0. However keeping the reaction under control is very important, as the reaction can cause great risks to the pipelines and materials, or worst case damage the pipeline system (Ashton et al,1989)

2.5.2- Wax preventive techniques

The wax preventive techniques are different solutions intended to prevent the wax from precipitate and deposit in the flow lines. The preventive solutions can be as simples as (Mokhatab,2009)

- Increasing the pipeline pressure, which will lead to an increase in the shear rate, thereby making it harder for the wax to deposit inside the pipeline walls.
- Insulate or bury the flow lines, so that no heat will be lost from the well stream fluid, thereby keeping the temperature above the WAT. Different insulation materials used are polypropylene foam, rubber, glass and plastic, which have all low heat transfer coefficients, assuring less heat lost to the surroundings. Burying the flow lines will be effective due to the high heat capacity of the soil, which will absorbed and store the heat from the flow lines (Thant et al,2011)
- Coating the inside of the flow lines with a material that will keep the wax from

adhering on the pipeline wall. Types of coating material that have been proposed are plastic pipes or plastic-coated pipes. These have shown to decrease the deposition rate on the pipeline walls. However when a layer of wax deposition have covered the pipe, the growing rate will be the same as for steel pipelines (Al-Yaari,2011)

Besides from the preventive techniques mention above there are also other preventive techniques which are more controversial methods, such as cold flow, magnetic fluid conditioning and microbial prevention. Some of these methods have given varied results when applied, therefore more research is needed. However these methods are more environmental friendly as there are no chemicals released.

• Cold flow

Cold flow is a new technology that is being exploited as a method for removing wax deposition in deepwater and cold oilfields. The method approach is to decrease the temperature of the bulk fluid, to prevent the temperature gradient in the flow lines, and thereby stop the wax precipitate from depositing on the pipeline walls. The whole well stream fluid will be cooled down to the temperature of the surrounding seawater, thereby making the wax precipitate inside the bulk fluid and be transported as solid dispersion within the well stream fluid (Aiyejina et al,2011).However further investigation needs to be done to work out how to effectively cool down the well stream fluid, and how to transport the cold well stream fluid to the surface without causing severe gelling in the flow lines (Argo et al,2007)

• Magnetic fluid conditioning (MFC)

The MFC technology uses magnets and electromagnets to prevent wax depositions, usually downhole. The techniques utilizes a magnetic field to alter the kinetics of the precipitated wax, which disturbs the wax crystal agglomeration process, making it harder for wax to precipitated and grow into larger crystals (Tung et al,2001) Studies have shown that the WAT have not been change by the MFC technique, but it had an effect on the viscosity of the crude oil. There is still little information about the mechanisms for this technique, and there have been a variety of claims about the success rate for the method(Chow et al,2000)

• Microbial prevention

The use of selectively isolated bacteria have shown to be an effective and environmental friendly method to both remove and prevent wax deposition in flow lines (Sadeghazad and Ghaemi,2003)The selected microbes used are called paraffin degrading bacterial (PDB). These are tough bacteria that can survive the extreme conditions found in the reservoir, well tubular, and surface flow lines, with the varying temperatures, pressures and anaerobic environment (no oxygen present). The microorganisms mechanism are to biodegrade the long wax molecules into smaller components, which thereby prevents wax precipitation or deposition in the flow lines. The mechanism will cause a decrease in the WAT as a result of the breakdown of the wax molecules, which will decrease of the wax content in the crude oil. The breakdown into smaller hydrocarbons will also reduce the viscosity of the crude oil, and increase the API of the oil. The API is a measurement of how light or heavy oil is compared to water. The bacteria can also form a bio-film layer inside the pipeline wall, which will avoid wax from adhering to the pipeline wall (Rana et al,2010)

2.5.2.1-Chemical wax prevention

In the recent years there has been more focus on using chemical prevention against wax deposition to minimize transportation problems with waxy crude oils. These wax reducing chemicals are added early to the well stream fluid, normally by injection at the wellhead or downhole. Here their present will affect the wax crystallization and growth process of the crude oils, which will occur as the temperature of the well stream fluid decreases during the transportation in flow lines.

In many cases the application of wax preventive chemicals alone will not fully manage to prevent wax depositions in the whole flow lines, however they can reduce the frequency of other wax removing techniques, such as mechanical removal (Kelland,2009)

There are mainly three different preventive chemicals used against wax deposition:

- Wax dispersants
- Inhibitors or wax crystal modifiers
- Pour-point depressants (PPDs) or flow improvers

Wax dispersants are surface active chemicals, which prevent wax deposition by reducing their tendency to adhere to the pipeline walls, and by keeping the precipitated wax dispersed as separated particles (Pedersen and Ronningsen,2003). The preventive mechanisms for wax dispersants are quite different compared to the mechanisms for the wax inhibitors and PDDs.

The wax inhibitors are chemicals referred to as wax crystals modifiers, and will affect the WAT for the crude oil. While the PPDs are chemical that affects the pour-point, which will reduce the gelling of the crude oil as the temperature decreases, and thereby improve the flow. However for both of these classes to be able to reduce the wax deposition they have to be applied before the temperatures are below the WAT, so that they can interfere with the crystallization process of the waxes. There are a lot of similarity between the two chemical classes in both the chemistry and mechanisms, and in most cases the wax inhibitors will also function as PPDs (Kelland,2009).The wax inhibitors and PPDs chemicals will therefore be summarized together further on.

2.5.2.2- Wax dispersants

Wax dispersants as a preventive technique alone are rarely used in the oilfields, however in combination with other wax inhibitors, such as PPDs, their present have given better results in preventing wax depositions.

Wax dispersants are surfactants, which are amphiphilic chemicals that possess both a hydrophobic part, which is water repelling, and a hydrophilic part, which is water attractive. Usually the dispersant molecules consist of a long hydrocarbon chain, the hydrophobic part, with a hydrophilic head. Figure (2.4) below shows an example of a common wax dispersant group called alkyl sulphonates.

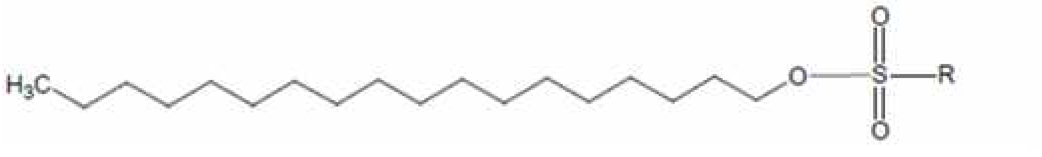


Figure (2.4)An example of a wax dispersant, alkyl sulphonate. The R-group is usually an alkyl or aryl group.

The wax dispersants ability to reduce wax depositions are mainly by adhering into the pipeline wall and creating a surface film, which make it difficult for the precipitated wax to stick to the wall. Some wax dispersants can also create a surface film which will let the precipitated wax bind weakly to the wall, but this bond will easily break off with the turbulent fluid flow, thereby preventing wax deposition build-up inside the pipelines.

Wax dispersant will also absorb to growing wax crystal, and prevent them to agglomerate together, which will make it easier to transport the precipitated wax with the well stream flow (Ahn et al,2005).

Other common wax dispersants are alkyl aryl sulphonates, fatty amine ethoxylates, other alkoxylated products, and imidazolines. Imidazolines dispersants are good surface coating chemicals, which can also prevent gelling of the crude oil in cold climates and acts as a good corrosion inhibitor (Martin et al,2010)

2.5.2.3-Wax inhibitors and pour-point depressants (PPDs)

The chemicals used as wax inhibitors and PPDs are normally polymers with long alkyl chains, which are intended to interfere with the wax crystallization and growth process. However the mechanisms for the wax inhibitors and PPDs are not fully understood and different mechanisms have been proposed. The general mechanism is that wax inhibitor polymers contain a structure similar to the wax structure, which will allow the polymer to be incorporated into the wax crystal growth. Beside the similar structure the polymer can also contain a structural part, which will cover the wax site, and thereby prevent new wax molecules to attach to the wax and continuing further growth (Jennings et al,2008) The effect of this alternation causes a reduction in the three dimensional network the wax deposition can form, and promote the formation of smaller wax aggregates. The overall effect will give a lower pour-point and a reduction in the viscosity of the crude oil, which makes it easier to transport the crude oil (Pedersen and Ronningsen,2003).

The wax inhibitor chemicals are often waxy materials and solid at room temperature, and therefore must be dissolved before they are applied in the field (Manka et al,2001) The wax inhibitors are usually dissolved in aromatic solvents. The use of a good solvent in cold climates can also avoid gelling of the wax inhibitor, such as toluene, xylene and cyclopentane.

In general good wax inhibitors, with concentration of 50-200 ppm, have shown to prevent wax deposition at temperatures from 10-15 °C below the WAT. While the PPDs, with relatively high dosage, have shown to reduce the pour point temperature with up to 30 °C (Pedersen and Ronningsen,2003)

The main chemical groups used as wax inhibitors and PPDs are:

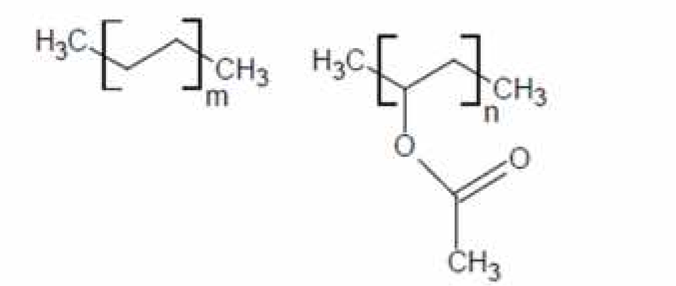
- Ethylene copolymers
- Miscellaneous polymers
- Comb polymers

2.5.2.3.1-Ethylene copolymers

Different types of polyethylene polymers copolymerized with larger monomers are common and effective wax inhibitors. These copolymers will consist of monomers of ethylene, and another larger monomer, which will contain branches or side chain that can interfere with the wax molecules in the crude oil, thereby preventing them from aligning together and form larger wax deposits. Polyethylene polymers alone can crystallize together with the wax molecules of similar structure, and therefore have limited success preventing wax deposition (Kelland,2009)

The most successful copolymer are ethylene/vinyl acetate (EVA), shown in the figure(2.5)below. It is the percentage of vinyl acetate in EVA, which determines how effective the polymer will inhibit the wax crystallization growth. Increasing the vinyl acetate content will interrupt the crystallization process and lower the WAT, and also make the polymer more polar, which will enhance the solubility. However to much vinyl acetate will limit the co-crystallization with the wax, and cause a negative effect on the wax inhibition (Lindeman et al,2005).The optimum vinyl acetate in EVA polymers are around 25-30 percent (Machado et al,2001).

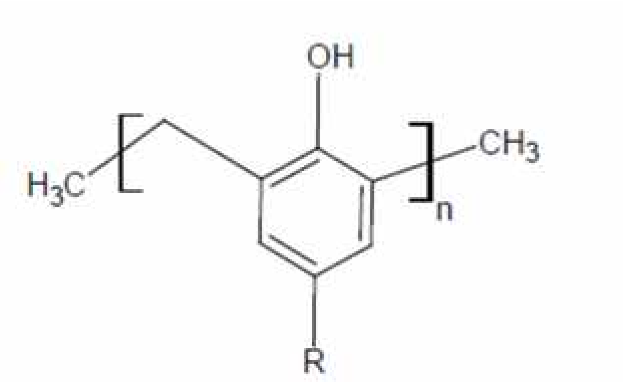
Other ethylene copolymers used as wax inhibitors are ethylene/small alkene copolymers, such as poly(ethylene butene) and poly(ethylene-*b*-propylene), and ethylene/acrylonitrile copolymers (Tinsleyet al,2007)



Figure(2.5) Ethylene/vinyl acetate (EVA).

2.5.2.3.2-Miscellaneous polymers

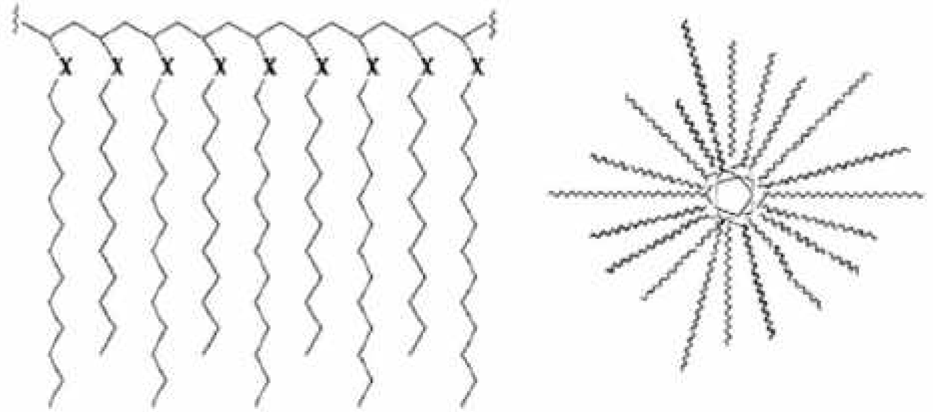
The miscellaneous polymers are chemicals that have shown to be good wax inhibitors or have synergetic effective with PPDs against wax deposition, which means their present will enhance the wax deposition removal. Some chemicals that have been used against wax deposition are alkyl phenol-formaldehyde resins figure(2.6), long chain phosphoric ester surfactants with sodium aluminate, and branched polymer, such as polyethyleneimine with pendant carbon 18 groups and dendrimerichyperbranchedpolyesteramides with long alkyl chains (Martella et al,1993)



Figure(2.6) Alkyl phenol-formaldehyde resins.

2.5.2.3.3-Comb polymers

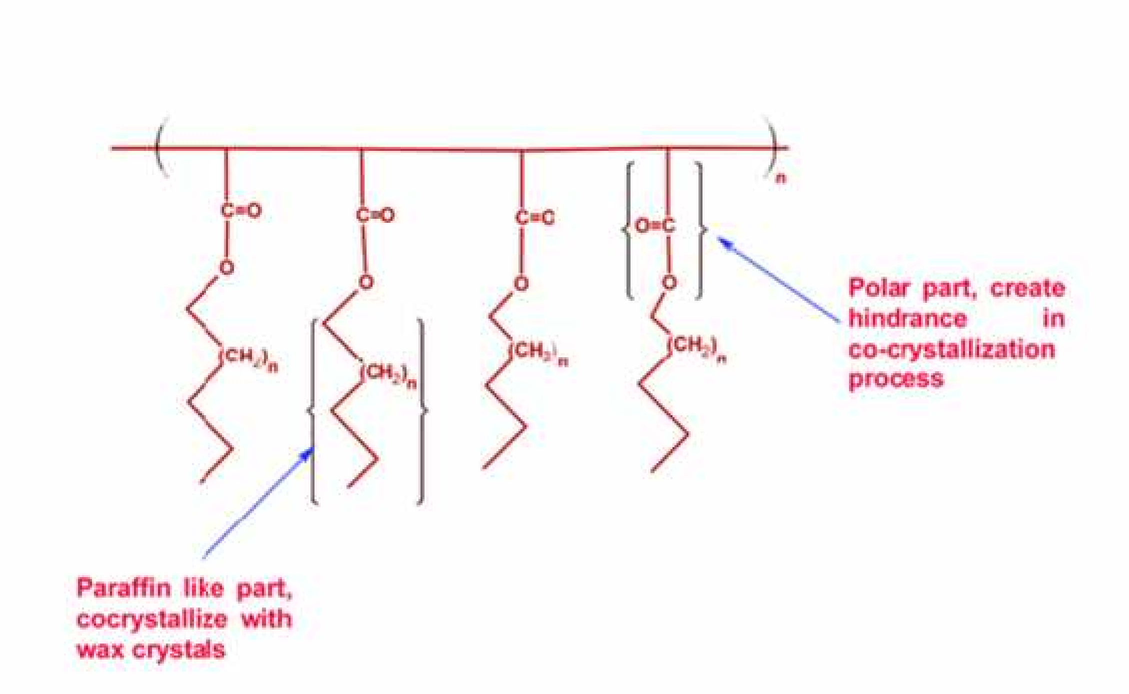
The comb polymers are regarded as the most effective wax inhibitor class used today. These polymers have got their name as a result of their chemical structure, because they look like a comb, as the figure (2.7) shows below. The comb polymer consists of a polyvinyl backbone with different pendant chains, which are normally long alkyl chains.



Figure(2.7)A general structure of comb polymers .

The structural designs of the PPDs normally contain three variable characteristic, which can influence their performance, and should be chosen in relation to the wax structures in the specific crude (figure 2.8) (Soni et al,2008)

- The length on the polymers pendent chains is the most important variable, since the interaction between the wax in the crude oil and the PPD should be of similar length to get the best wax inhibition.
- The polymer backbone have shown little affect on the performance of the wax PPDs, but provides a structure for where the pendant chains are suspended from.
- A polar part on the backbone will prevent the whole polymer to be co-crystallized with the wax alkane chains. This part on the polymer will prevent further agglomerating, and thereby prevent the wax growth.



Polar part, create hindrance in co-crystallization process

Paraffin like part, cocrystallize with wax crystals

Figure (2.8) The general structural characteristics for the comb polymers (Soni et al,2008)

The polymer molecular weight may also influence the PPDs performance in the way the polymer interacts with the wax. A short and low molecular weight polymer may cause to little disruption to wax crystallization, while a very long and high molecular weight polymer can interact with itself instead of with the wax.

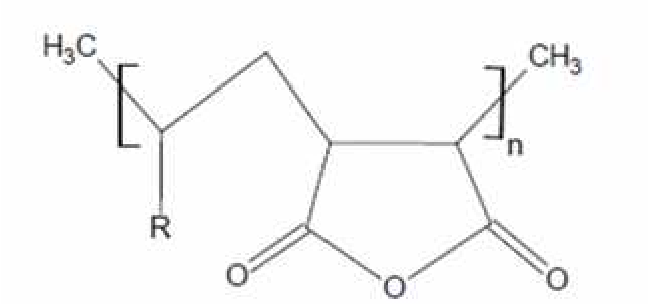
The inhibition mechanism for the PPDs involves having a long alkyl side chain that can be embedded into the wax crystal by binding to the waxes of similar size. This interaction will thereby decrease the rate of wax formation, leading to a more soft wax that can be easier transported (Jang et al,2007)The high specificity of crude oils makes it difficult to develop universal PPDs that can be used in the different fields. The PPDs have to be developed to interact with wax alkane chains length and portions for the specific crude treated. It can therefore be wise to have a range of comb polymers available for wax treatment in case of changes in the crude oil composition. Comb polymers containing a range of alkyl chains have been proposed to get a better cover of the different wax alkane chains and improved performance (Wirtz et al,1994)

The comb polymers are usually divided into two different polymer classes, which are the maleic copolymers and (meth)acrylate ester polymers.

2.5.2.3.4-Maleic copolymers

Maleic anhydride monomers are often used to make effective comb polymers. The maleic anhydride monomers can be polymerized together with other vinyl comonomers, and then added a long alkyl side chain by reacting the anhydride with various alcohols of different length, alkyl mercaptans or alkylamines to from monoester, diester, thioester or imides (Son et al,1993)

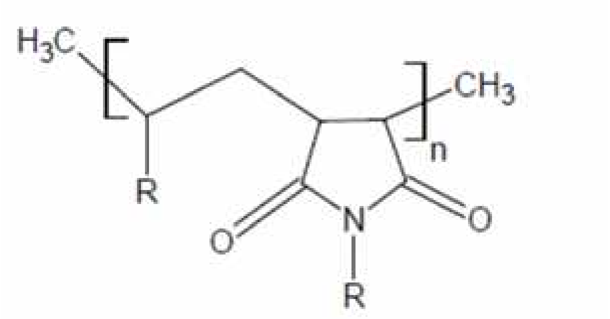
The chemical structure in figure (2.9)shows a copolymer of long chain α-olefin and maleic anhydride, where the maleic anhydride can be further derivatized to get another long side chain group (Soni et al,2008)



Figure(2.9) Chemical structure of α-olefin maleic anhydride copolymer.

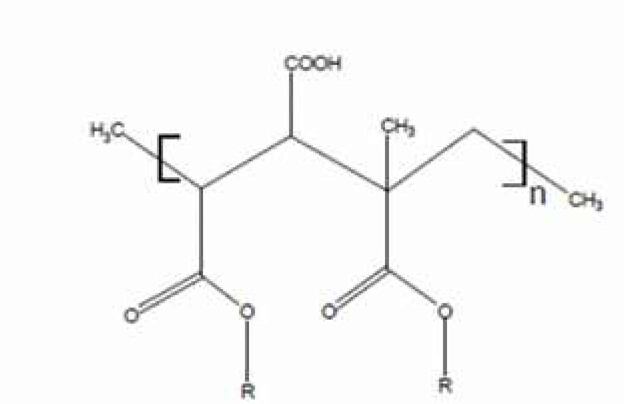
The α-olefin maleic anhydride copolymer structure will then have an alternating structure of the two monomers, which can improve the polymer as a wax inhibitor.

The side chain groups on the maleic anhydride copolymer should be of long alkyl chains, preferably of similar size as the wax molecules. A maleic anhydride/α-olefin copolymer reacted with carbon 18 alkylamines to make a maleimide have been used as PPDs figure (2.10)(Kelland,2009)



Figure(2.10) Alkyl maleimide/α-olefin copolymers.

Other chemicals claimed as good flow improvers as copolymers of maleic anhydride are methacrylate and styrene (Han et al,2009) Figure (2.11) below shows a monoester of maleic anhydride/(meth)acrylate ester copolymer.



Figure(2.11)Monoester of maleic/(meth)acrylate ester copolymers.

2.5.2.3.5-(Meth)acrylate ester polymers

Polymers of acrylate or methacrylate ester are the other class of comb polymers commonly been used as wax inhibitors or PPDs. These polymers are made up by (meth)acrylic acid monomers, where the ester groups are made from long-chain alcohols. The length on the alkyl side chain should be longer than 18 carbons length, to get the best interaction with the waxes in the crude and inhibit further wax growth. The optimum alkyl ester chain have been found to be between 20-24 carbons length, except the cost of alcohols over 18 carbons are high (Gateau et al,2004)The difference between methacrylate polymers and acrylate polymers are a methyl group or a hydrogen atom on thePolymers of acrylate or methacrylate ester are the other class of comb polymers commonly been used as wax inhibitors or PPDs. These polymers are made up by (meth)acrylic acid monomers, where the ester groups are made from long-chain alcohols. The length on the alkyl side chain should be longer than 18 carbons length, to get the best interaction with the waxes in the crude and inhibit further wax growth. The optimum alkyl ester chain have been found to be between 20-24 carbons length, except the cost of alcohols over 18 carbons are high(Gateau et al,2004).The difference between methacrylate polymers and acrylate polymers are a methyl group or a hydrogen atom on the 23backbone of the polymer (figure 2.12). The methacrylate polymers have shown to give the best wax inhibition (Mcdougall,1972)

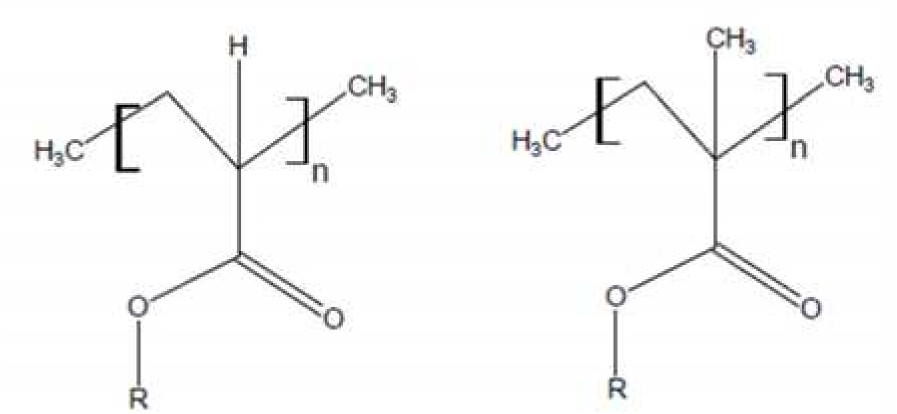


Figure (2.12) Structure of acrylate ester and methacrylate ester polymers, the R-group is normally a long alkyl chain.

The frequency of the alkyl side chains on the polyacrylate ester polymers is also important for the wax inhibition performance, but this will be dependent on the wax composition in that specific crude. One study for a specific crude oil showed the optimum performance with 60% of 18 carbons length side chains, where the rest of the acrylate ester groups where methyl side chains (D et al,2003)

A blend of two polyalkyl(meth)acrylate have shown to give a better performance as PPDs (Wirtz et al,1994).This can be two poly(meth)acrylate polymers with different length in their side chains (Duncum et al,2000).There is comerciallyavalaible a poly(meth)acrylate polymer with a mix of 7% C18, 58% C20, 30% C22 and 6% C24 alkanols. A polymer with a mixture of different alkyl side chains will cover a broader range of wax molecule lengths, and thereby give a better chance to interact with the wax and prevent further wax growth.

Other wax inhibition improvments on the polyalkylmethacrylate ester polymer class have been discovered by using different copolymers, such as copolymers of (meth)acrylic acid ester of 16 carbons alcohols with a small percentage of hydrophilic (meth)acrylic acid, vinyl pyridine, or N-vinyl pyrrolodone (Wirtz et al,1994).

2.6Neem field background

The NEEM facility is situated at a distance of about 140 kms from Heglig Base office, and was commissioned on May 15 2005; Well fluid from 117 wells is being received at Neem FPF. The present rate of production from the Facility is about 9,000 barrels of liquid per day with 75% w/c. Along with Neem FPF.

The fluid from each of the wells is produced using the ESP and is brought to FPF through flow lines originating from individual wells. At FPF, individual flow lines feed into a common production header. The Fluid from production header enters to 3 Crude processing trains through crude / crude exchangers. Separated gas is sent to the flare header and processed crude oil is sent to the storage tank. From storage tank it is pumped to Heglig CPF through 16" Neem-CPF pipeline. Online BS&W analyzer is provided for continuous monitoring the quality of exported oil. Apart from this auto sampler is used to grab the sample and make lab test. Pour point and API gravity are also tested in the lab regularly.

The separated water enters in to the produced water Treatment system. Here it passes through skim tanks, CPI separators, retention pond, evaporation pond#1 & 2 before being discharged to the environment.

The Oil ppm before being disposed to environment is maintained less than 5 as per the Environmental legislation of Sudan. The Area around water disposal point is observed to be having good grass growth and number of birds of different species is observed around thearea.

Oil from produced water tank, CPI and Retention pond is transferred to Drain sump and from drain sump it is put back to the FWKO. Water from the produced water tank flows to CPI , retention pond and then flows through 2 Nos. of ponds in series, where left over oil further gets separated and is skimmed using vacuum trucks. The recovered oil at each stage is put back into process system.

General characteristics of Neem Crude oil

The general characteristics of neem crude oil as detailed below :

- low sulphur content ,the sulphur content is 0.0855m%
- density at 15°C is 0.8655 g/cm^3,API Gravity 31.85
- low acid number,it is 0.45 mgKOH/kg
- high wax content 38 Wt%
- high pour point 36°C
- low asphaltenecontent,it is 0.21 Wt%
- low viscose crude in high temperature but in low temperature the viscosity increase due to appear of paraffin in crude,the kinematics viscosity in different temperatures ,mm^2/sec

Kinematic Viscosity @40°C	46.30
Kinematic Viscosity @50°C	23.19
Kinematic Viscosity @80 °C	11.06
Kinematic Viscosity @100°C	7.546

Micro Carbon Residue Wt%	4.05
Water vol.%	0.6
Salt Content mgNaCl/kg	1.15
Compositional Analysis by ppm	
As	<0.0281
Fe	0.2006
K	0.2350
Na	18.20
Ni	9.722
V	0.2692
Mg	1.382
Ca	18.33
Pb	<0.0150

Chapter Three

Materials andMethods

Chapter Three

Materials andMethods

3.1-Materials:

Neem crude oil has been received from FPF OUTLET STORAGE TANK in the field ,five type of commercial pour point depressant , one gallon of kerosene , one gallon of diesel were taken from Khartoum refinery company.

3.2- Viscosity Measurement

3.2.1-Equipment:

Viscosity is fluid’s internal resistance to flow and may be taken as ameasure of fluids friction

A Brookfield viscometer (model DV 111 ULTRA)(LV) with programmable RHEOLOADER software was used .it is composed of a small sample adapter connected with a water bath –(TC502) and SC4-34 concentric cylinder spindle .

This Brookfield viscometer is designed to have the following specification :

- speed range (0.01-250 revolution per minute)
- Torque Accuracy (±1.0%of full scale range)

Photograph 3.1 Brookfield viscometer(model DV-111 Ultra) with Rheocalc Software

3.2.2-Viscosity test Procedure

A sample of eight mills was measured and added to sampler of 20 mills capacity .the spindle was selected according to viscosity range , speed was run at 18 revolutions per minute, shear rate 5 (1/sec)and time interval at 00:20 mm:ss

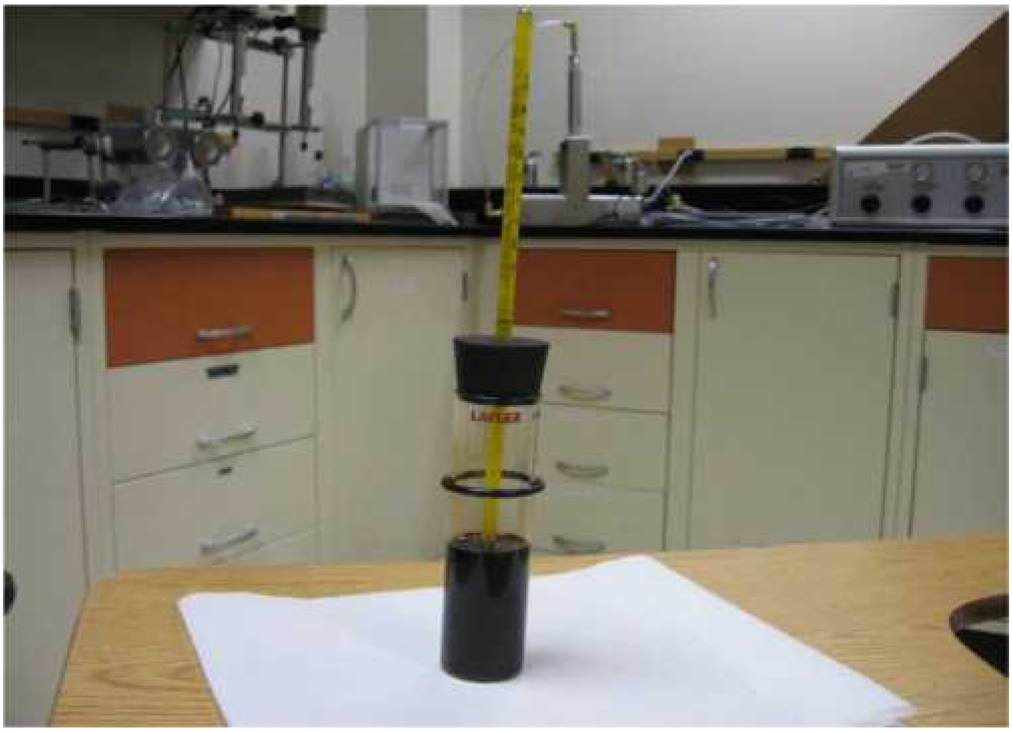
3.3- Pour point measurement

3.3.1- POUR POINT equipment:

Pour point is the lowest temperature at which a liquid remains pourable

Pour point cabinet is composed of four baths temperatures (-51 ^{0}C,-34^{0}C,-17^{0}Cand 0 ^{0}C),Thermometer holders, test tube ,denaturized ethylic alcohol and defrosting heater. The equipment is shown on photograph(3.2)and(3.3)

Photograph (3.2) pour point cabinet.



Photograph (3.3) pour point test jar

3.3.2- Pour point procedure:

Seventy –five mills were added into pour point jar .the sample was reheated to a temperature 20 ^{0}C above the expected pour point. The sample of neem crude oil was heated to 45^{o}C.the sample crude oil was cooled at a specified rate 9 ^{0}C. and then examined at intervals of 3 ^{0}C for flow characteristics.pour point was the lowest temperature at which movement of the sample was observed(ASTM 58553-95)

3.4- Wax Content Measurement

3.4.1 -Wax Content Equipment:

The wax content equipment is made –up of three main units:Evaporator ,Rotavapor cryostat and Gooch crucible .

3.4.2 Determination of paraffin wax content of crude oil test procedure:

About two grams of sample were weighted in 500 mills Erlenmeyer flask .three hundred mills of petroleum naphtha (boiling range 40-60 ^{0}C)were added as a solvent then 15 grams of dry fuller’s earth were added to the flask with agitation for 15 minutes using stirrer device. The solution was filtered under vacuum suction through asbestos material in Gooch crucibles. the filtrate was transferred into a 500 mills round bottom flask and the petroleum naphtha was evaporated using rotavapor . the temperature of the water-bath was increased slowly to 95 ^{0}C .Two hundred mills of a solvent mixture (75% of acetone and 25% of petroleum naphtha)was added to the warm sample,and the content was transferred into Erlenmeyer flask (500 mills) and swired the resulted solution was chilled to -17 ^{0}C

And maintained at that temperature for 20 minutes,the sample was filtered under vacuum suction through asbestos materials in Gooch crucible maintained at -20 ^{0}C. The remained wax particles were rinsed in the flask by the acetone-petroleum naphtha mixture ,which was chilled before at -17 ^{0}C. The Gooch crucible was removed and the wax on the asbestos wool was washed with hot petroleum naphtha using a dropper and vacuum suction .the filtrate was transferred into a weighted 100-mill liters round bottom flask . the solvent –wax was evaporated under vacuum by using rotvapor to remove petroleum naphtha .the round bottom flask was placed in a dissector for 15 minutes and was re-weighed

3.5- Whole - Oil Gas Chromatography measurement

3.5.1Whole - Oil Gas Chromatography Analysis equipment

Varian CP 3800 Gas Chromatograph, Flame Ionization Detector, silica capillary columns The equipment is shown on photograph 3.4

Photograph (3.4) Gas Chromatography

3.5.2Whole - Oil Gas Chromatography Analysis procedure

Crude oil samples,were subjected to whole oil- Gas chromatographic analysis. This was achieved by using Varian CP 3800 Gas Chromatograph, equipped with Flame Ionization Detector; 50m × 0.2 mm film thickness 0.5µm fused silica capillary columns, coated with methyl silicone (PONA). The sample (1µL) was injected. Detector (FID) and injector temperatures were kept at 280°C. The oven temperature was programmed as follow:

Table (3.1) oven temperature program:

Temperature(C^o)	**Rate(C^o/min)**	**Hold(min)**	**Total time(min)**
60	-	5	5
150	10	0	14
300	20	60	81
310	20	15	97

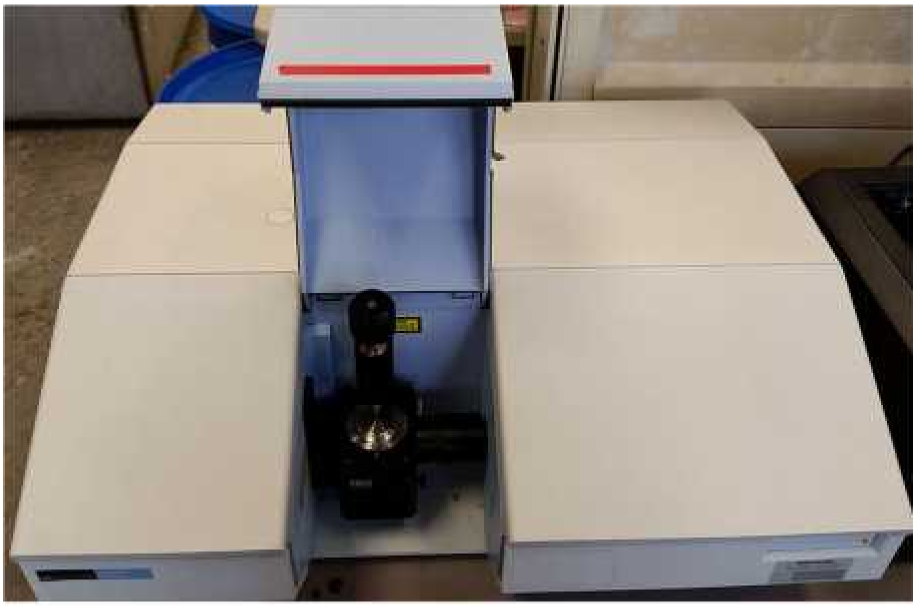
Helium was used as carrier gas. The data were collected from retention time: 0-97minutes.

3.6 FTIR Measurement

3.6.1 FTIR equipment

IR sources, Detectors, Beam splitter, Fourier transform, KBr Windows

The equipment is shown on photograph 3.5



Photograph (3.5) Fourier transform Infra Red spectroscopy

3.6.2 FTIR procedure

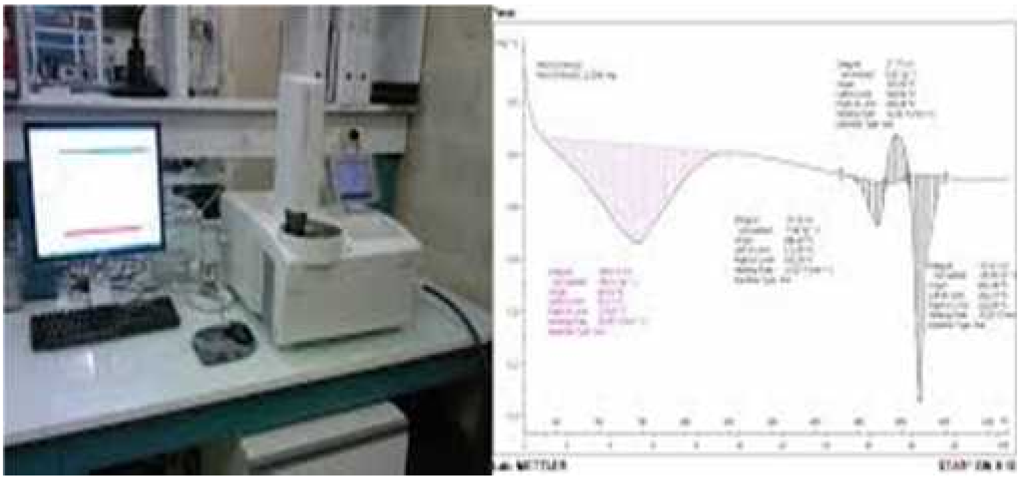
Sample was loaded directly in the KBr Windows,introduced into the FTIR and scanned at 4000-400 cm^{-1}at resolution intervals of 4.000cm^{-1}using NICOLET(370 DTGS).A description of the spectrum is attached.

3.7 Differential scanning calorimeter measurement

3.7.1- DSC equipment

Gas controller,infra cooler, furnace (in the temperature range RT to700 ^{0}Cand with a max.heating rate 100 k/min(at700 ^{0}C) ,aluminum pans, indium and zinc standards,sample.

The equipment is shown on photograph 3.6.



Photograph (3.6) Differential scanning calorimeter

3.7.2- DSC procedure

Extracted wax of two sample of crude oil were performed using DSC-1 differential scanning calorimeter.the temperature scale was calibrated using a two –point calibration, measuring the onset temperature of indium and zinc standards. The enthalpy scale is calibrated using the observed ΔH from an accurately known amount of indium. Crude oil samples were transferred in aluminum pans ,typically between 0.5and 30 mg :to obtain a good signal –to-noise ratio , almost 10mg of sample was employed for each measurement. A blank pan was used on the reference side .the cooling rate used was 1 ^{0}C/min data acquisition and processing was carried out using DSC-1 Software

Chapter Four

Results and Discussion

Chapter Four
Results and Discussion

4.1-introduction

The wax treatments chemicals are divided into two categories, the wax removal chemicals and the wax prevention chemicals.

4.1.1 Wax removal chemicals

The most common chemical methods used in the oil and gas industry as a removal technique are hot oiling and wax solvents. The application of thermochemical packages are a more controversial wax removal technique

The adding of solvent downhole and to the flow lines have shown to be effective to remove wax depositions, as it will help to resolve the precipitated wax and make it easier to transport the crude oil to the surface

The different solvents have different abilities to dissolve wax deposits, which depends on the wax, the location in the system and the temperature. Normally the solvents are applied in frequent batch treatments or continuously. Aliphatic and aromatic solvents are the two main groups of solvent used on the oilfields. The aliphatic solvents are straight or ring formed hydrocarbons, and the most common aliphatic solvent used are diesel, kerosene and condensate. The aromatic solvents are chemical containing a carbon ring with delocalized electron double bonding, such as xylene and toluene .A mixture of xylene or toluene together with an aliphatic solvent has shown to increase the wax removal.

Other solvent that have been applied with good success are benzene, chlorinated hydrocarbons, and carbon disulfide. However many of the solvents used are not environmental friendly and some highly toxic. Many also possess dangerous risks related to low flash points, such as the aromatic solvents, and corrosion problems, as seen with chlorinated hydrocarbons

4.1.2 Wax Prevention Chemicals

In the recent years there has been more focus on using chemical prevention against wax deposition to minimize transportation problems with waxy crude oils. These wax reducing chemicals are added early to the well stream fluid, normally by injection at the wellhead or downhole. Here their present will affect the wax crystallization and growth process of the crude oils, which will occur as the temperature of the well stream fluid decreases during the transportation in flow lines.

There are mainly three different preventive chemicals used against wax deposition:

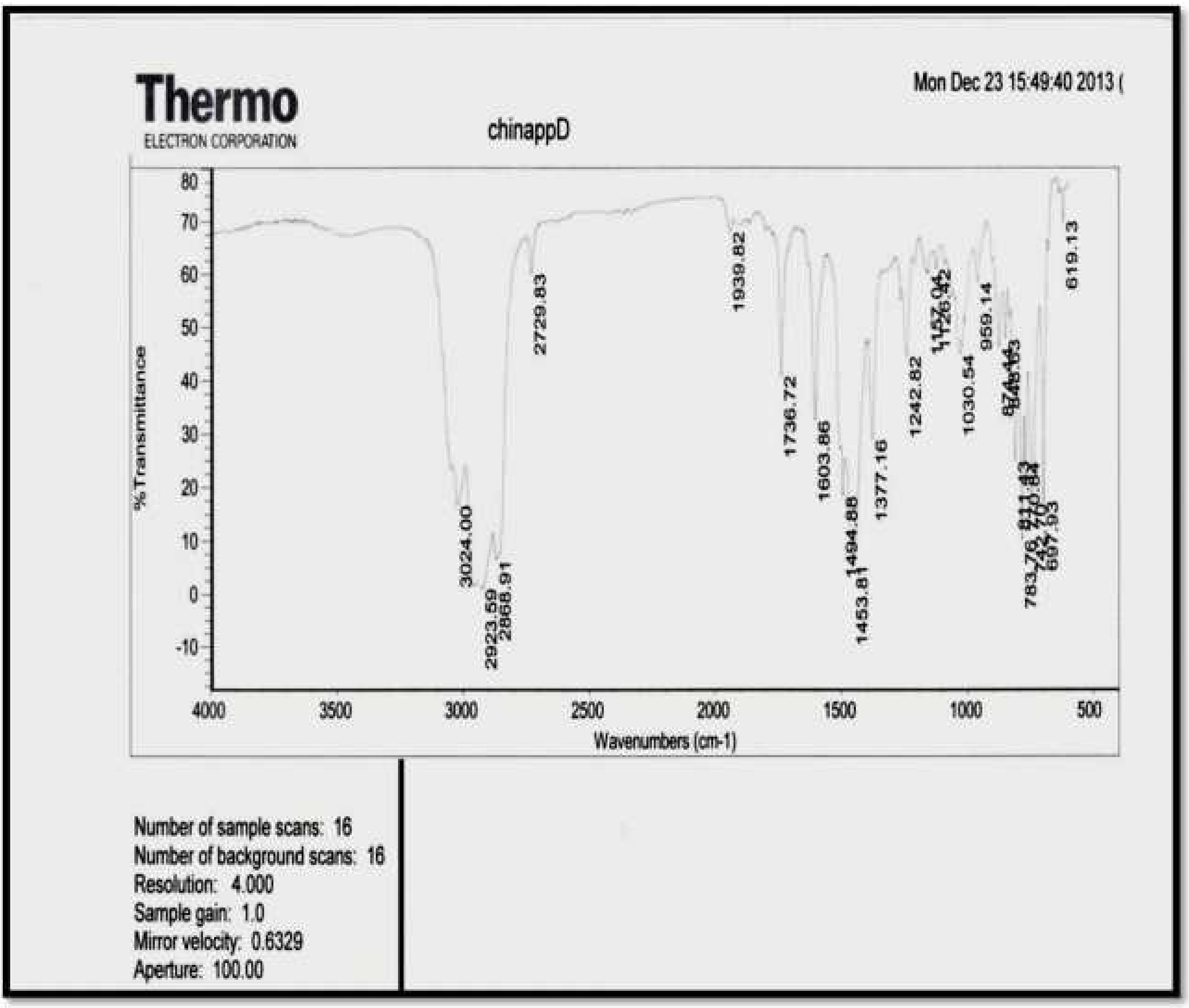
- Wax dispersants
- Inhibitors or wax crystal modifiers
- Pour-point depressants (PPDs) or flow improvers

In this research five commercial pour point depressant have been tested for their structure and effectiveness in remediating paraffin (wax) depositions from neem crude oil. All PPDS were characterized their structure by FTIR and Gas chromatography, and also compression their effectiveness withalphatic solvents(kerosene and diesel).Also wax was extracted from two different types of Sudanese crude oil(neem,hadida crude oil ,it have been tested their composition and melting point.

4.2Characterization of wax treatment chemicals by FTIR

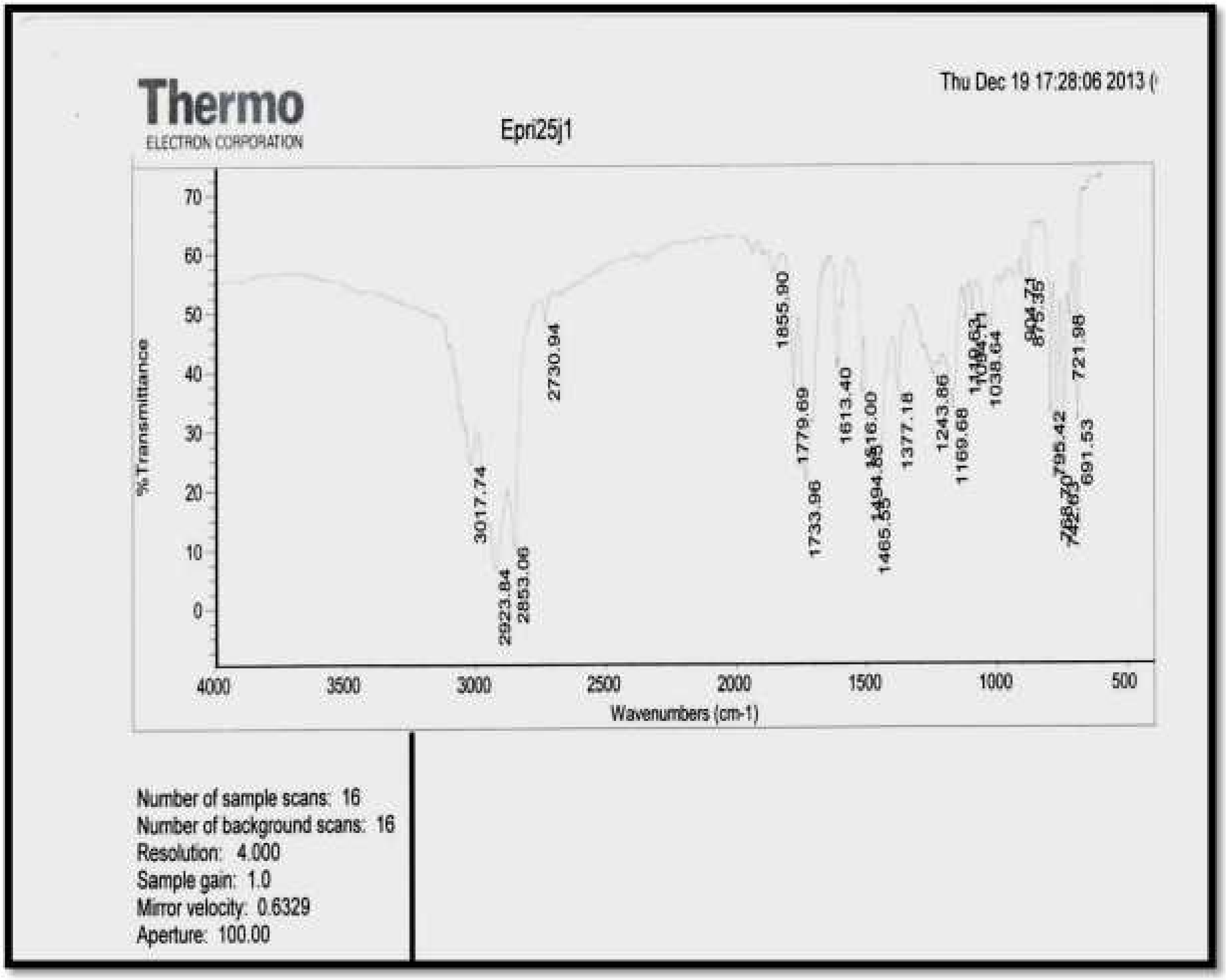
The chemical structure of PPDS were studied by FTIR SPECTROSCOPY in this respect,FTIR spectrum of all types of PPDSwere represented in table (4.1).The all FTIRspectrumfig(4.1)(4.2)(4.3)(4.4)(4.5) shows increasing ofpeak intensity at 3100 cm^{-1}and decreasing of peak intensity at3000cm^{-1}which represent C-H stretching of alkene or aromatic, furthermore the appearance of strong peak at 1500 and 1600 cm^{-1}(indicating the presence of aromatic ring) and alsobe confirmed from the pattern of the weak overtoneand combination tone bands found from 2000 to 1600cm^{-1},also show a strong absorption band between 3000cm^{-1}and 2850cm^{-1}which is attributed to the presence of aliphatic hydrocarbon.

Also fromfig(4.2)(4.3)(4.4)(4.5)FTIR Spectrums shows increasing of peak intensity at1735cm^{-1}and decreasing of peak intensity at 1700cm^{-1},this strong band indicates either carboxylic acid,ester,aldehyde and amide,also the appearance of strong peak at 1150 cm^{-1} and 1240 cm^{-1} co-vibration indicating formation of ester group.



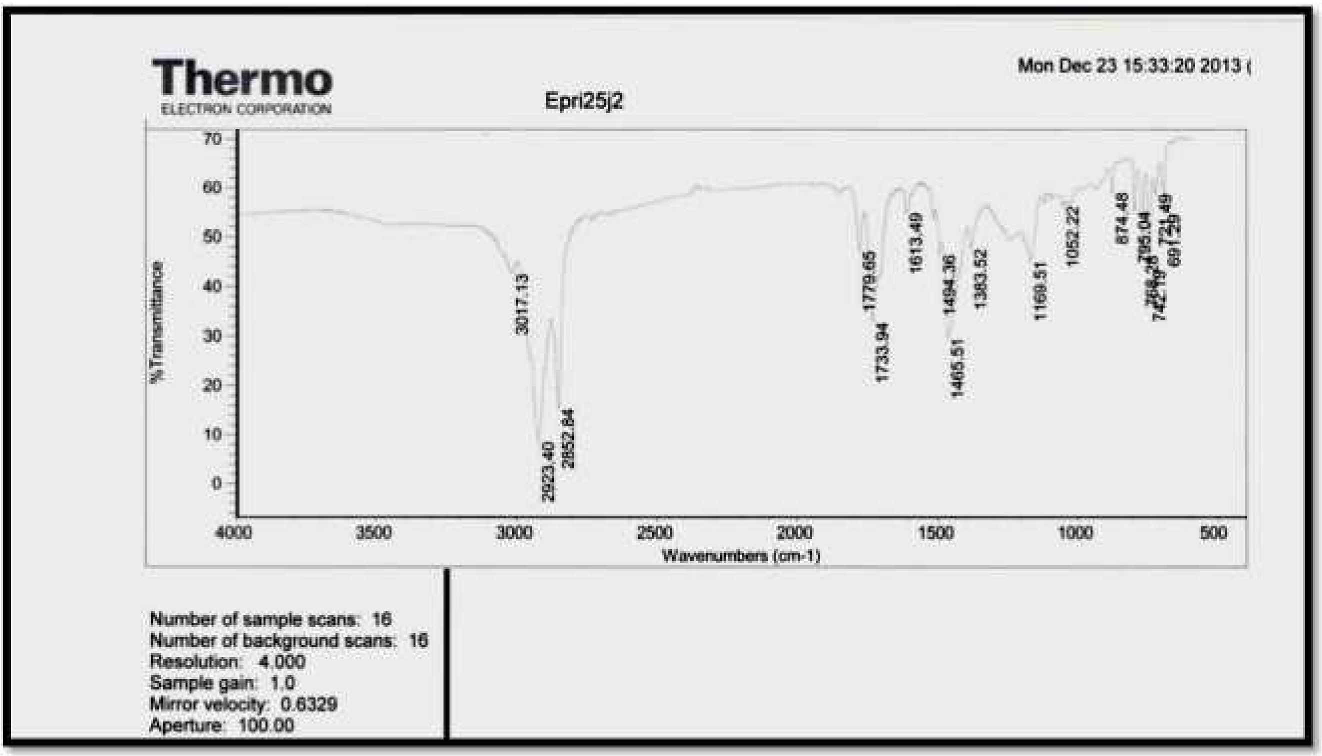
Number of sample scans: 16
Number of background scans: 16
Resolution: 4.000
Sample gain: 1.0
Mirror velocity: 0.6329
Aperture: 100.00

FIGURE (4.1): FTIR spectra ofPPD OF Chinese Origin



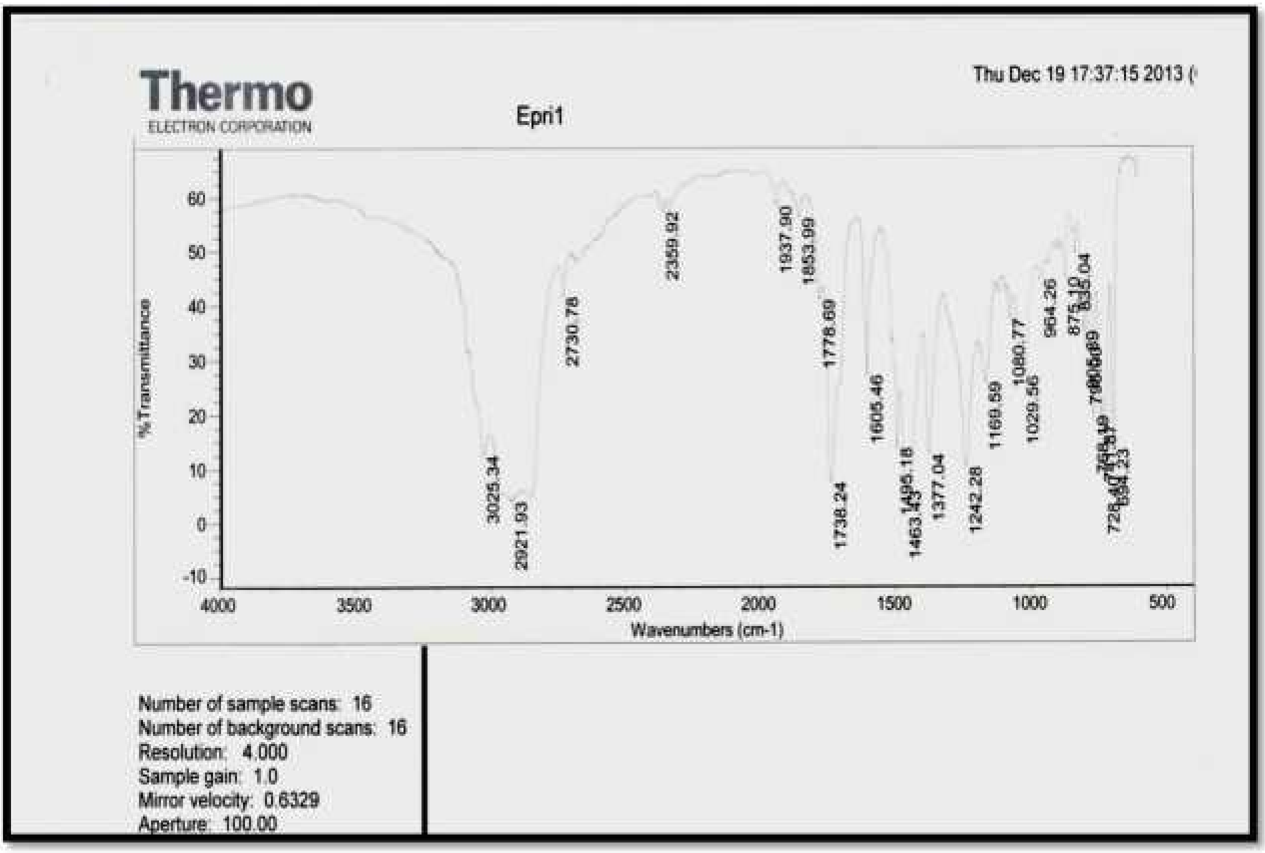
Number of sample scans: 16
Number of background scans: 16
Resolution: 4.000
Sample gain: 1.0
Mirror velocity: 0.6329
Aperture: 100.00

FIGURE (4.2):FTIR spectra of Epri25j1 PPDS



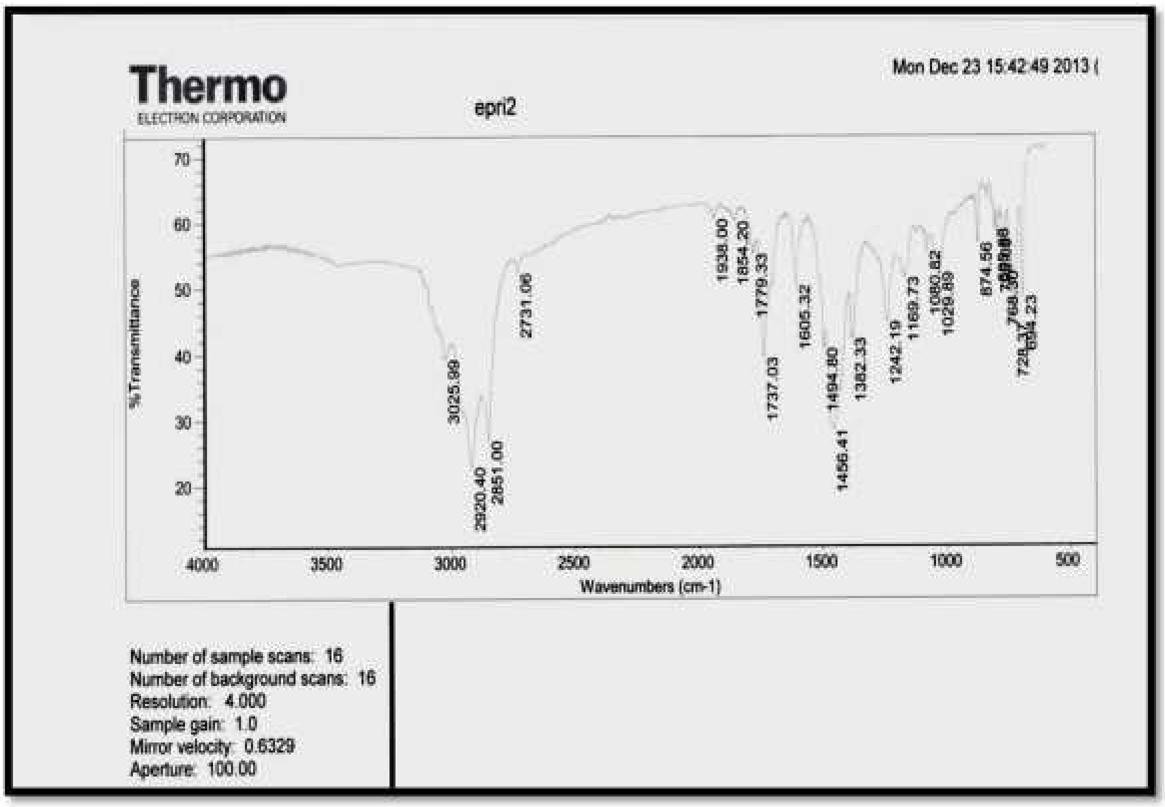
Number of sample scans: 16
Number of background scans: 16
Resolution: 4.000
Sample gain: 1.0
Mirror velocity: 0.6329
Aperture: 100.00

FIGURE 4.3: FTIR spectra of Epri25j2 PPDS



Number of sample scans: 16
Number of background scans: 16
Resolution: 4.000
Sample gain: 1.0
Mirror velocity: 0.6329
Aperture: 100.00

FIGURE 4.4FTIR spectra of Epri1 PPDS



Number of sample scans: 16
Number of background scans: 16
Resolution: 4.000
Sample gain: 1.0
Mirror velocity: 0.6329
Aperture: 100.00

FIGURE 4.5: FTIR spectra of Epri2 PPDS

Table(4.1) FTIR Spectral interpretation

China PPD	EPRI25J1 PPD	EPRI25J2 PPD	EPRI 1 PPD	EPRI 2 PPD
Mono substituted aromatic hydrocarbons Aliphatic hydrocarbons	Meta substituted aromatic hydrocarbons Ester (general) Aliphatic hydrocarbons	Meta substituted aromatic hydrocarbons Ester (general) Aliphatic hydrocarbons	Mono substituted aromatic hydrocarbons Aliphatic hydrocarbons Ester (general) Trans olefins	Mono substituted aromatic hydrocarbons Aliphatic hydrocarbons Ester (general)

4.3-Characterization of wax treatment chemicals by GC

Its observed from the below results table(4.2,4.3,4.4,4,5and4.6) most of PPDs contain mixtures of aromatic solvents and other compound such as polymer, ester, olefins, etc. while some of PPDs mainly contain strong solvents (china PPDs)(table(4.2)and this means that the presence of solvents is very important

From table (4.5)(4.6) it is observed that the PPDS Contain mainly different types of benzene compounds such as ethyl benzene,toluene,O-xylene ,m-xylene ,p-xylene in high concentration 1,2,4trimethyl benzene,1,2,3trimethyl benzene, and other in small concentration.

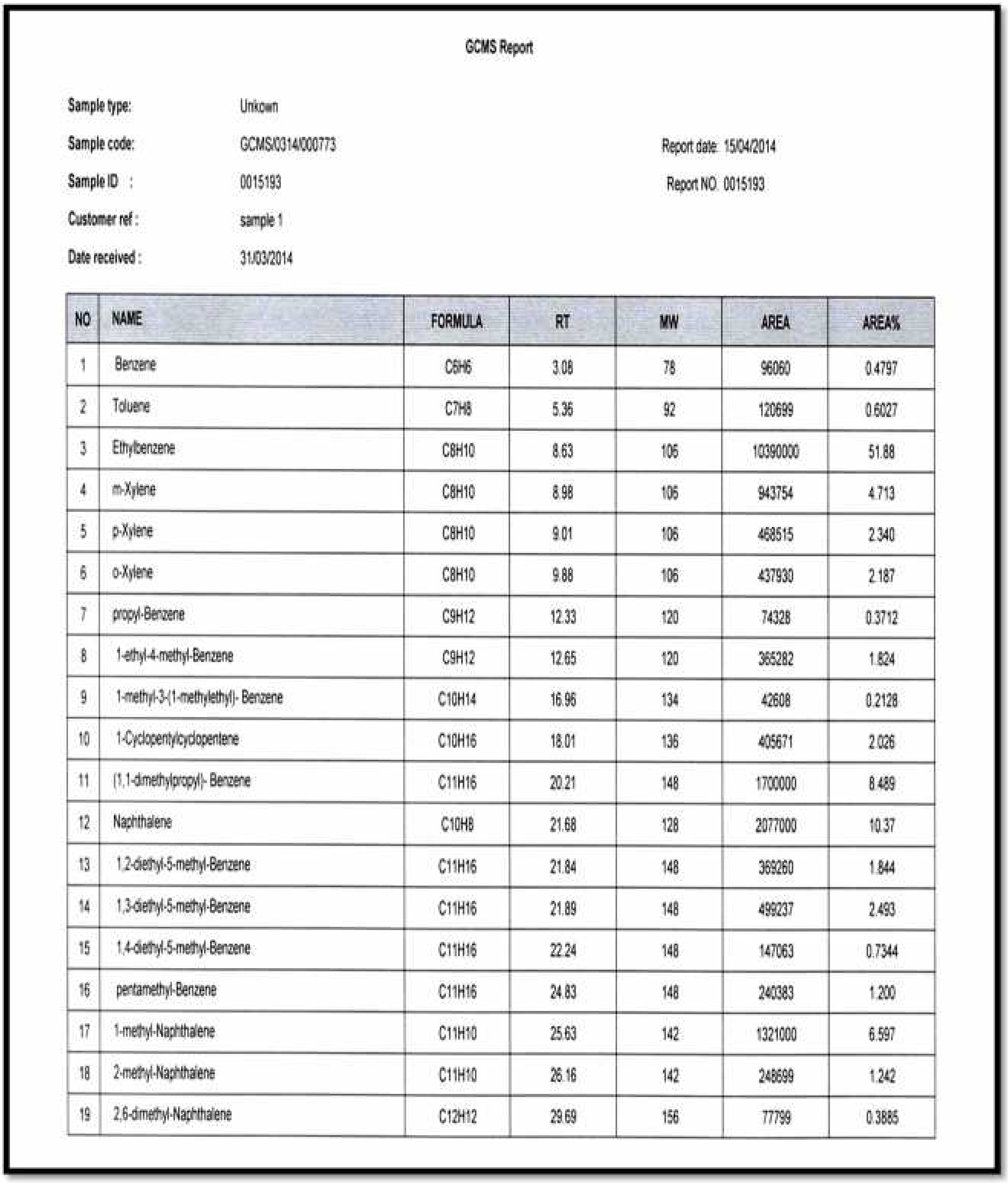
From table (4.2) it can be seen that the presence of other solvent such as 1-cyclopentylcyclopentene ,1-methyl-naphthalene.

Wax deposition not only contains wax, but also contains other compound such as resin, asphaltenes these need dissolve by solvent.

From table (4.3) and (4.4) it can be seen that the presence of long olefins such as1,19eicosadiene, 9-nonadecene, 5-eicosadiene is due to the fact that(the general mechanism is the wax inhibitor polymer contains a structure similar to the wax structure , which will allow the polymer to be in corporate into the wax crystal growth ,beside the similar structure the polymer can also contain a structural part ,which will cover the wax site ,and thereby prevent new wax molecules to attach to the wax and continuing further growth

From FTIR and GC Results it observed that the presence of ester in the instullation of some of them such Epri25j1,Epri25j2, Epri1,Epri2 the structure and composition of flow improvers should posses high polar functional groups such as amide ,ester,amine and hydroxyl groups, when additives contains both long chain hydrocarbon and polar moieties it may be efficient as was wax dispersants and flow improver become this polar functional groups increase the solubility of PPDS in crude oil

Table(4.2)characterization of china PPD by GC



GCMS Report

Sample type: Unkown

Sample code: GCMS/0314/000773

Report date: 15/04/2014

Sample ID : 0015193

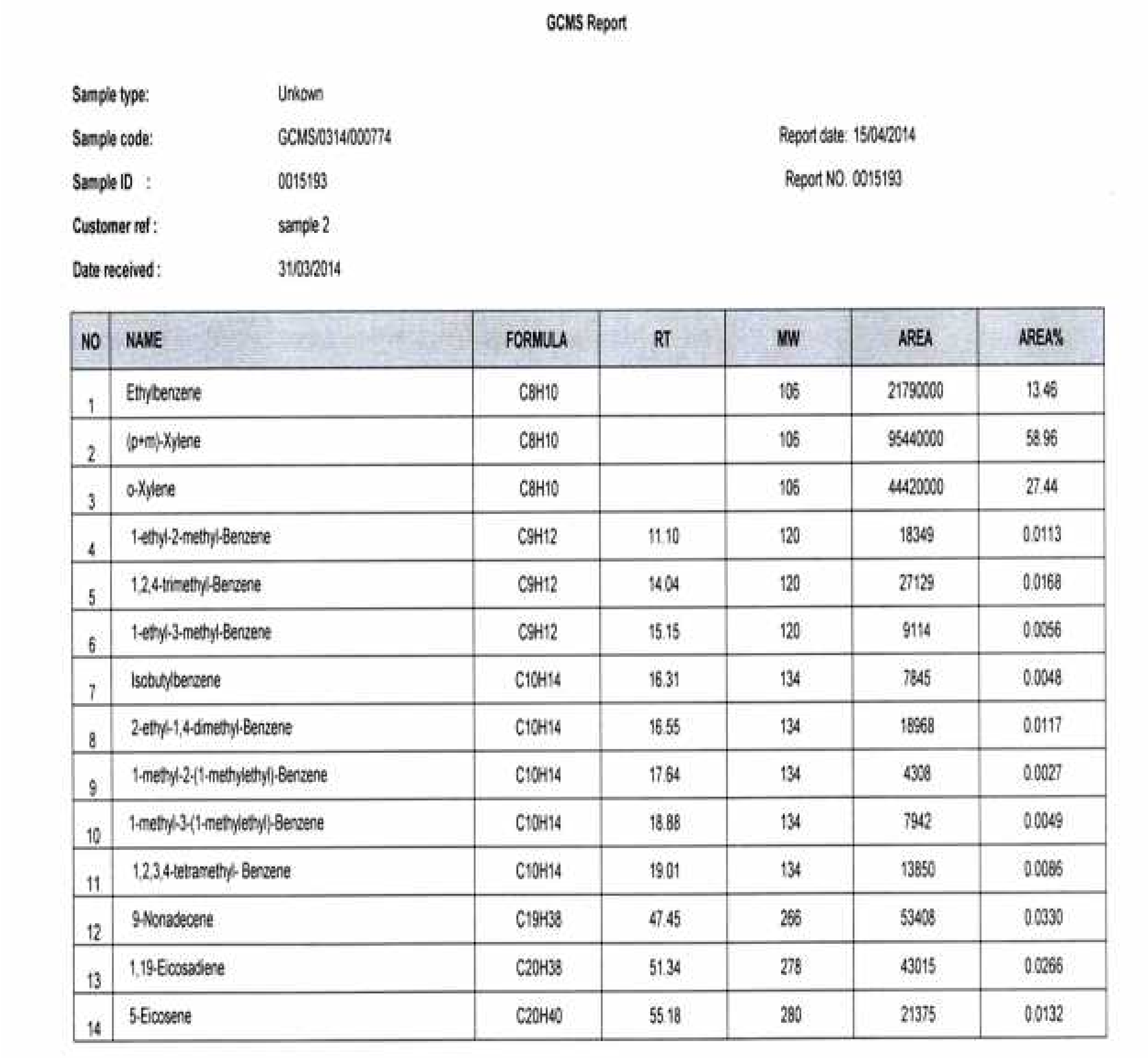
Report NO. 0015193

Customer ref : sample 1

Date received : 31/03/2014

NO	NAME	FORMULA	RT	MW	AREA	AREA%
1	Benzene	C6H6	3.08	78	96060	0.4797
2	Toluene	C7H8	5.36	92	120699	0.6027
3	Ethylbenzene	C8H10	8.63	106	10390000	51.88
4	m-Xylene	C8H10	8.98	106	943754	4.713
5	p-Xylene	C8H10	9.01	106	468515	2.340
6	o-Xylene	C8H10	9.88	106	437930	2.187
7	propyl-Benzene	C9H12	12.33	120	74328	0.3712
8	1-ethyl-4-methyl-Benzene	C9H12	12.65	120	365282	1.824
9	1-methyl-3-(1-methylethyl)- Benzene	C10H14	16.96	134	42608	0.2128
10	1-Cyclopentylcyclopentene	C10H16	18.01	136	405671	2.026
11	(1,1-dimethylpropyl)- Benzene	C11H16	20.21	148	1700000	8.489
12	Naphthalene	C10H8	21.68	128	2077000	10.37
13	1,2-diethyl-5-methyl-Benzene	C11H16	21.84	148	369260	1.844
14	1,3-diethyl-5-methyl-Benzene	C11H16	21.89	148	499237	2.493
15	1,4-diethyl-5-methyl-Benzene	C11H16	22.24	148	147063	0.7344
16	pentamethyl-Benzene	C11H16	24.83	148	240383	1.200
17	1-methyl-Naphthalene	C11H10	25.63	142	1321000	6.597
18	2-methyl-Naphthalene	C11H10	26.16	142	248699	1.242
19	2,6-dimethyl-Naphthalene	C12H12	29.69	156	77799	0.3885

Table(4.3)characterization of Epri25j1 PPD by GC



GCMS Report

Sample type: Unkown

Sample code: GCMS/0314/000774

Sample ID : 0015193

Customer ref : sample 2

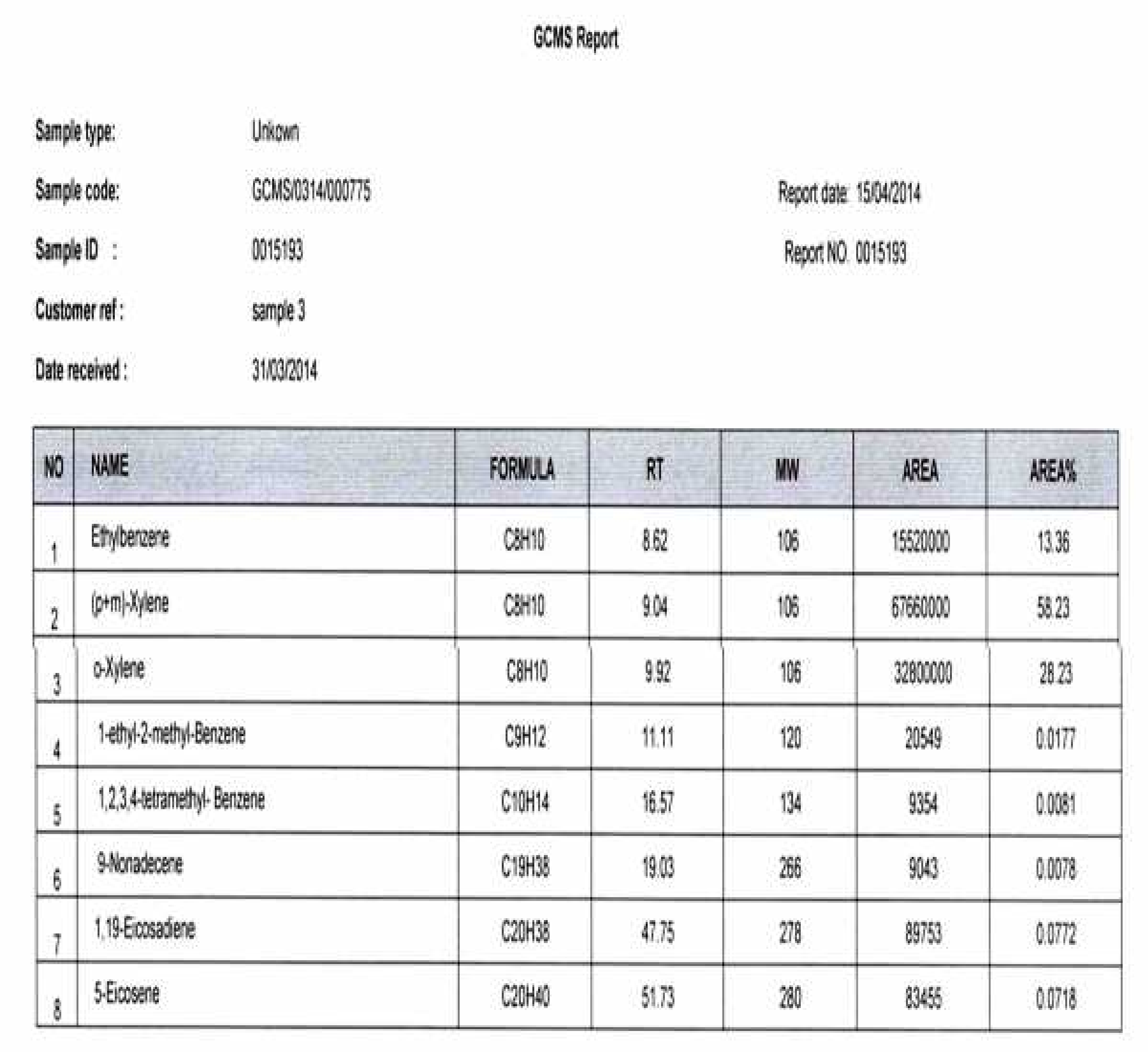
Date received : 31/03/2014

Report date: 15/04/2014

Report NO. 0015193

NO	NAME	FORMULA	RT	MW	AREA	AREA%
1	Ethylbenzene	C_8H_{10}		106	21790000	13.46
2	(p+m)-Xylene	C_8H_{10}		106	95440000	58.96
3	o-Xylene	C_8H_{10}		106	44420000	27.44
4	1-ethyl-2-methyl-Benzene	C_9H_{12}	11.10	120	18349	0.0113
5	1,2,4-trimethyl-Benzene	C_9H_{12}	14.04	120	27129	0.0168
6	1-ethyl-3-methyl-Benzene	C_9H_{12}	15.15	120	9114	0.0056
7	Isobutylbenzene	$C_{10}H_{14}$	16.31	134	7845	0.0048
8	2-ethyl-1,4-dimethyl-Benzene	$C_{10}H_{14}$	16.55	134	18968	0.0117
9	1-methyl-2-(1-methylethyl)-Benzene	$C_{10}H_{14}$	17.64	134	4308	0.0027
10	1-methyl-3-(1-methylethyl)-Benzene	$C_{10}H_{14}$	18.88	134	7942	0.0049
11	1,2,3,4-tetramethyl- Benzene	$C_{10}H_{14}$	19.01	134	13850	0.0086
12	9-Nonadecene	$C_{19}H_{38}$	47.45	266	53408	0.0330
13	1,19-Eicosadiene	$C_{20}H_{38}$	51.34	278	43015	0.0266
14	5-Eicosene	$C_{20}H_{40}$	55.18	280	21375	0.0132

Table(4.4) characterization of Epri25j2 PPD by GC



GCMS Report

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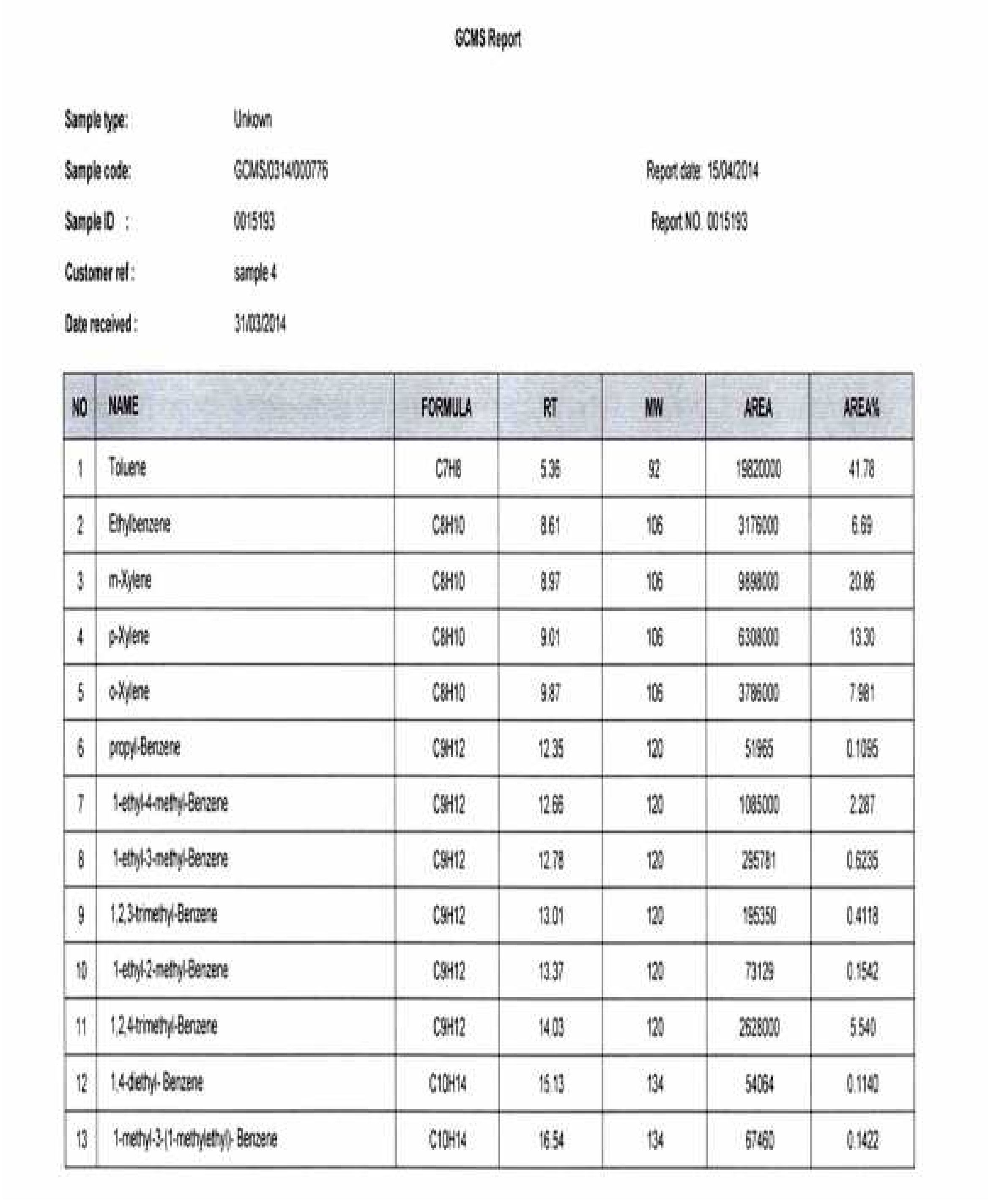
Sample code:	GCMS/0314/000775	Report date: 15/04/2014
Sample ID :	0015193	Report NO. 0015193
Customer ref :	sample 3	
Date received :	31/03/2014	

NO	NAME	FORMULA	RT	MW	AREA	AREA%
1	Ethylbenzene	C_8H_{10}	8.62	106	15520000	13.36
2	(p+m)-Xylene	C_8H_{10}	9.04	106	67660000	58.23
3	o-Xylene	C_8H_{10}	9.92	106	32800000	28.23
4	1-ethyl-2-methyl-Benzene	C_9H_{12}	11.11	120	20549	0.0177
5	1,2,3,4-tetramethyl- Benzene	$C_{10}H_{14}$	16.57	134	9354	0.0081
6	9-Nonadecene	$C_{19}H_{38}$	19.03	266	9043	0.0078
7	1,19-Eicosadiene	$C_{20}H_{38}$	47.75	278	89753	0.0772
8	5-Eicosene	$C_{20}H_{40}$	51.73	280	83455	0.0718

Table(4.5)characterization of Epri 1 by GC



GCMS Report

Sample type: Unkown

Sample code: GCMS/0314/000776

Report date: 15/04/2014

Sample ID : 0015193

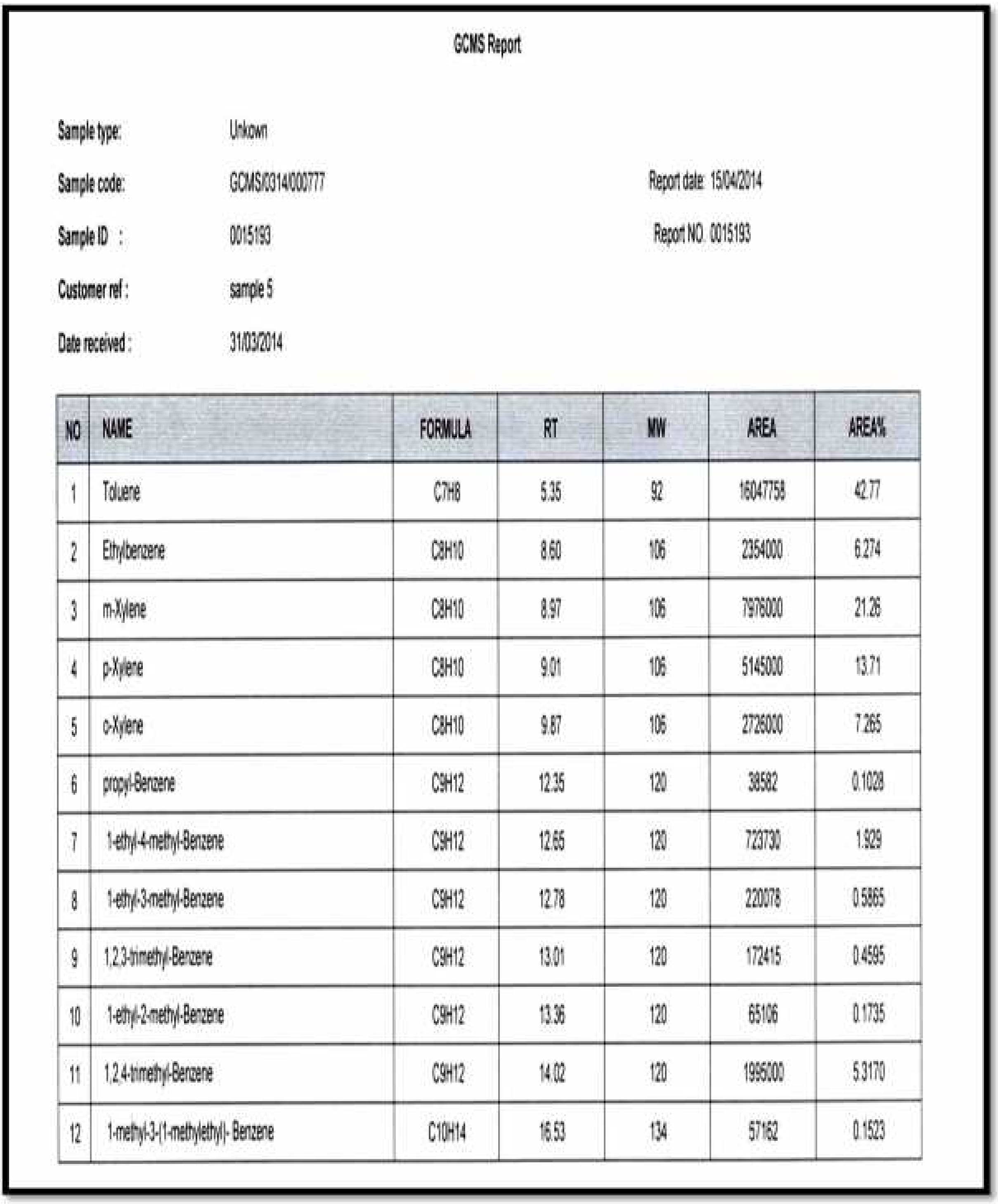
Report NO. 0015193

Customer ref : sample 4

Date received : 31/03/2014

NO	NAME	FORMULA	RT	MW	AREA	AREA%
1	Toluene	C_7H_8	5.36	92	19820000	41.78
2	Ethylbenzene	C_8H_{10}	8.61	106	3176000	6.69
3	m-Xylene	C_8H_{10}	8.97	106	9898000	20.86
4	p-Xylene	C_8H_{10}	9.01	106	6308000	13.30
5	o-Xylene	C_8H_{10}	9.87	106	3786000	7.981
6	propyl-Benzene	C_9H_{12}	12.35	120	51965	0.1095
7	1-ethyl-4-methyl-Benzene	C_9H_{12}	12.66	120	1085000	2.287
8	1-ethyl-3-methyl-Benzene	C_9H_{12}	12.78	120	295781	0.6235
9	1,2,3-trimethyl-Benzene	C_9H_{12}	13.01	120	195350	0.4118
10	1-ethyl-2-methyl-Benzene	C_9H_{12}	13.37	120	73129	0.1542
11	1,2,4-trimethyl-Benzene	C_9H_{12}	14.03	120	2628000	5.540
12	1,4-diethyl- Benzene	$C_{10}H_{14}$	15.13	134	54064	0.1140
13	1-methyl-3-(1-methylethyl)- Benzene	$C_{10}H_{14}$	16.54	134	67460	0.1422

Table(4.6)characterization of Epri2 by GC



GCMS Report

Sample type: Unkown

Sample code: GCMS/0314/000777

Report date: 15/04/2014

Sample ID : 0015193

Report NO. 0015193

Customer ref : sample 5

Date received : 31/03/2014

NO	NAME	FORMULA	RT	MW	AREA	AREA%
1	Toluene	C_7H_8	5.35	92	16047758	42.77
2	Ethylbenzene	C_8H_{10}	8.60	106	2354000	6.274
3	m-Xylene	C_8H_{10}	8.97	106	7976000	21.26
4	p-Xylene	C_8H_{10}	9.01	106	5145000	13.71
5	o-Xylene	C_8H_{10}	9.87	106	2726000	7.265
6	propyl-Benzene	C_9H_{12}	12.35	120	38582	0.1028
7	1-ethyl-4-methyl-Benzene	C_9H_{12}	12.65	120	723730	1.929
8	1-ethyl-3-methyl-Benzene	C_9H_{12}	12.78	120	220078	0.5865
9	1,2,3-trimethyl-Benzene	C_9H_{12}	13.01	120	172415	0.4595
10	1-ethyl-2-methyl-Benzene	C_9H_{12}	13.36	120	65106	0.1735
11	1,2,4-trimethyl-Benzene	C_9H_{12}	14.02	120	1995000	5.3170
12	1-methyl-3-(1-methylethyl)- Benzene	$C_{10}H_{14}$	16.53	134	57162	0.1523

4-4-characterization of wax extracted from two types of sudanese crude oil

The performance of PPDS depends on the characteristics of crude oil itself including total wax content, the chain length and shape(linear or branched),and quantity and type of wax present in crude oil

In this respect, UOP method is used to isolate wax from crude oil to be analyzed with Gc

Further analysis of n-paraffins by Gc for neem crude oil and Hadida crude oil was carried out to determine the carbon numbers as shown in figure (4.7)(4.11)from data represented in table(4.7) (4.8)the total carbon average of paraffin in Neem crude oil is $C_{17}$with broad molecular weight distribution and for Hadida crude oil the total carbon average of paraffin is $C_{15}$with broad molecular weight distribution.

This means that the n-paraffin with C_{17} for Neemand C_{15} for Hadida tends to form precipitate and block the crude oil flow by forming interlocking networks.

From fig (4.6) and(4.10) it is found that the wax containing normal paraffin chains only.

Wax melting point and crystallization point was been measured by DSC1(fig8)(fig9)(fig12)(fig13),the results show that melting point of wax from neem crude oil $52C^{O}$fig(4.8)and the crystallization point $46C^{o}$fig (4.9),But for hadida crude oil $68C^{o}$(4.13) and the crystallization point $63C^{O}$(4.12).

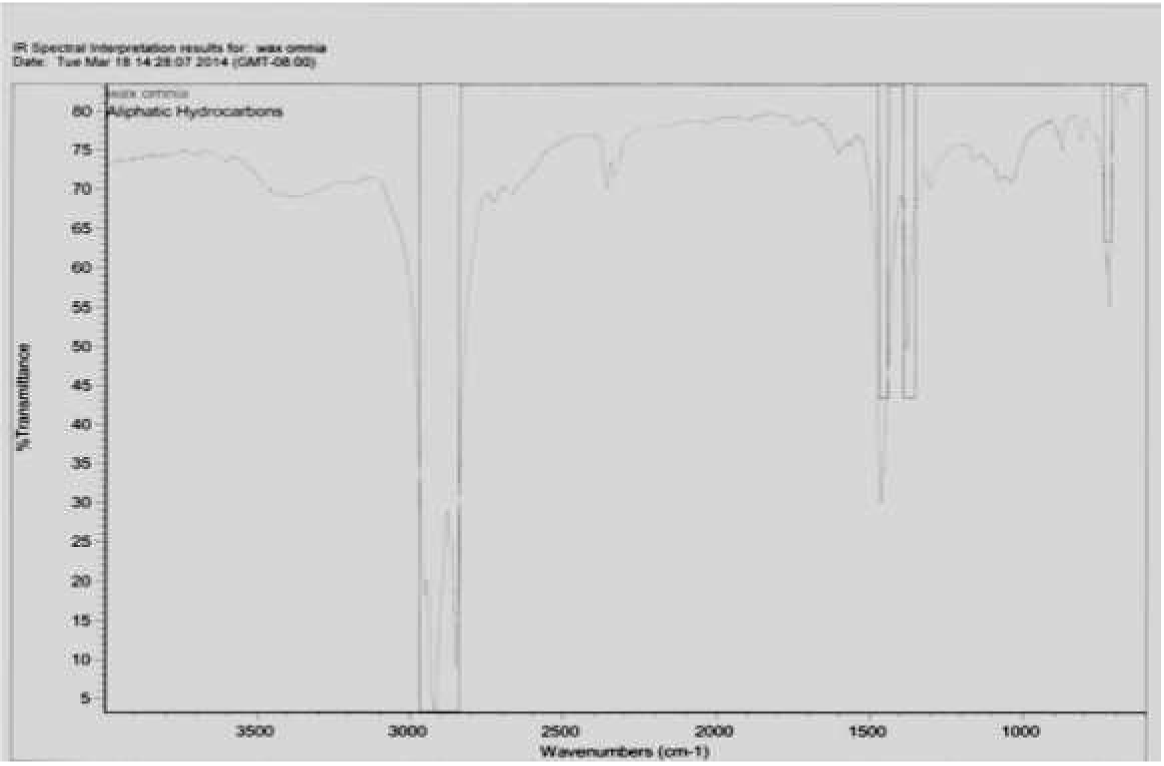
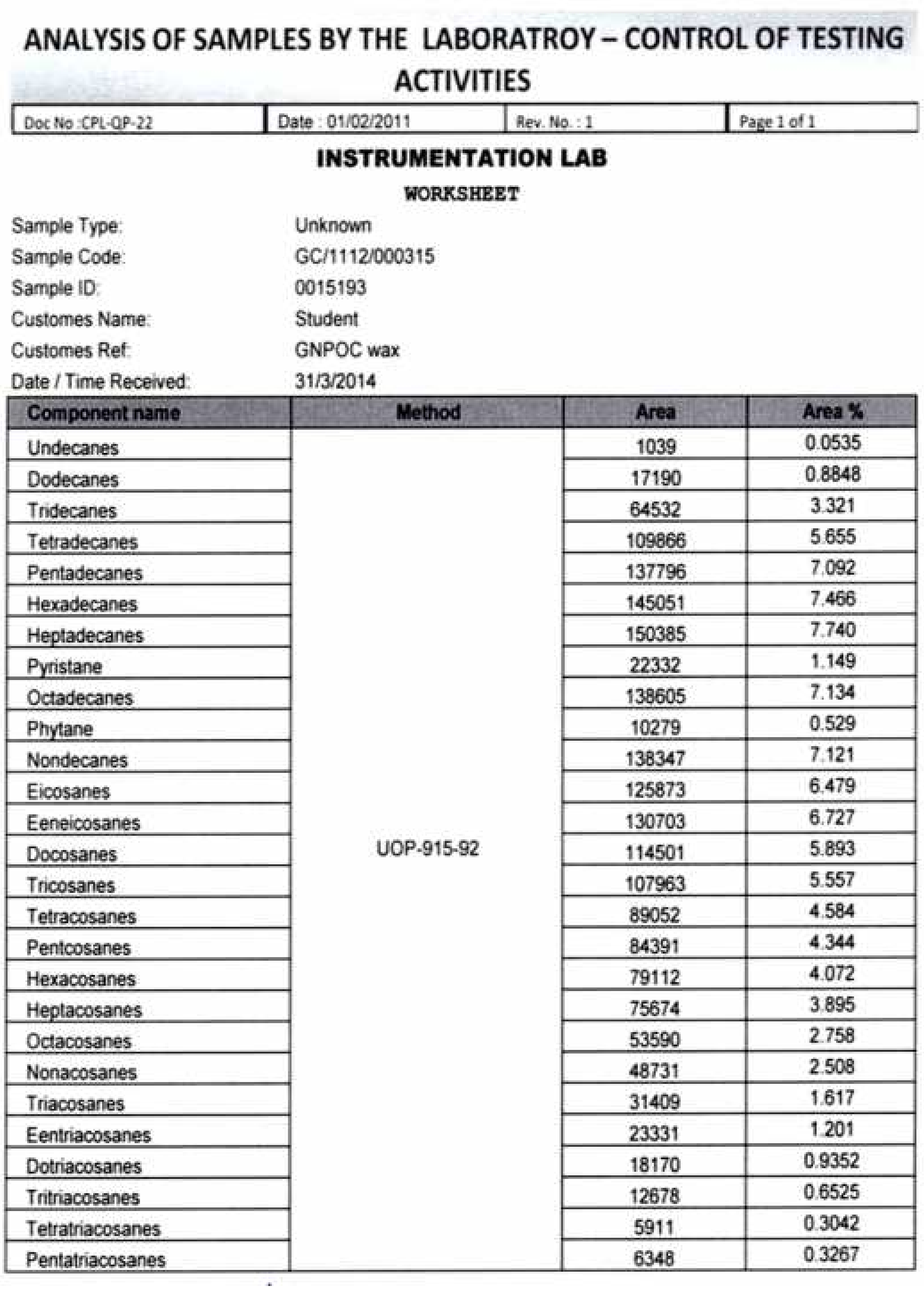


FIGURE 4.6FTIR spectra of wax extracted from Neem crude oil

Table(4.7)Characterization ofwax extracted from neem crude oilbyGC



ANALYSIS OF SAMPLES BY THE LABORATROY – CONTROL OF TESTING ACTIVITIES

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INSTRUMENTATION LAB

WORKSHEET

Sample Type:	Unknown
Sample Code:	GC/1112/000315
Sample ID:	0015193
Customes Name:	Student
Customes Ref:	GNPOC wax
Date / Time Received:	31/3/2014

Component name	Method	Area	Area %
Undecanes	UOP-915-92	1039	0.0535
Dodecanes		17190	0.8848
Tridecanes		64532	3.321
Tetradecanes		109866	5.655
Pentadecanes		137796	7.092
Hexadecanes		145051	7.466
Heptadecanes		150385	7.740
Pyristane		22332	1.149
Octadecanes		138605	7.134
Phytane		10279	0.529
Nondecanes		138347	7.121
Eicosanes		125873	6.479
Eeneicosanes		130703	6.727
Docosanes		114501	5.893
Tricosanes		107963	5.557
Tetracosanes		89052	4.584
Pentcosanes		84391	4.344
Hexacosanes		79112	4.072
Heptacosanes		75674	3.895
Octacosanes		53590	2.758
Nonacosanes		48731	2.508
Triacosanes		31409	1.617
Eentriacosanes		23331	1.201
Dotriacosanes		18170	0.9352
Tritriacosanes		12678	0.6525
Tetratriacosanes		5911	0.3042
Pentatriacosanes		6348	0.3267

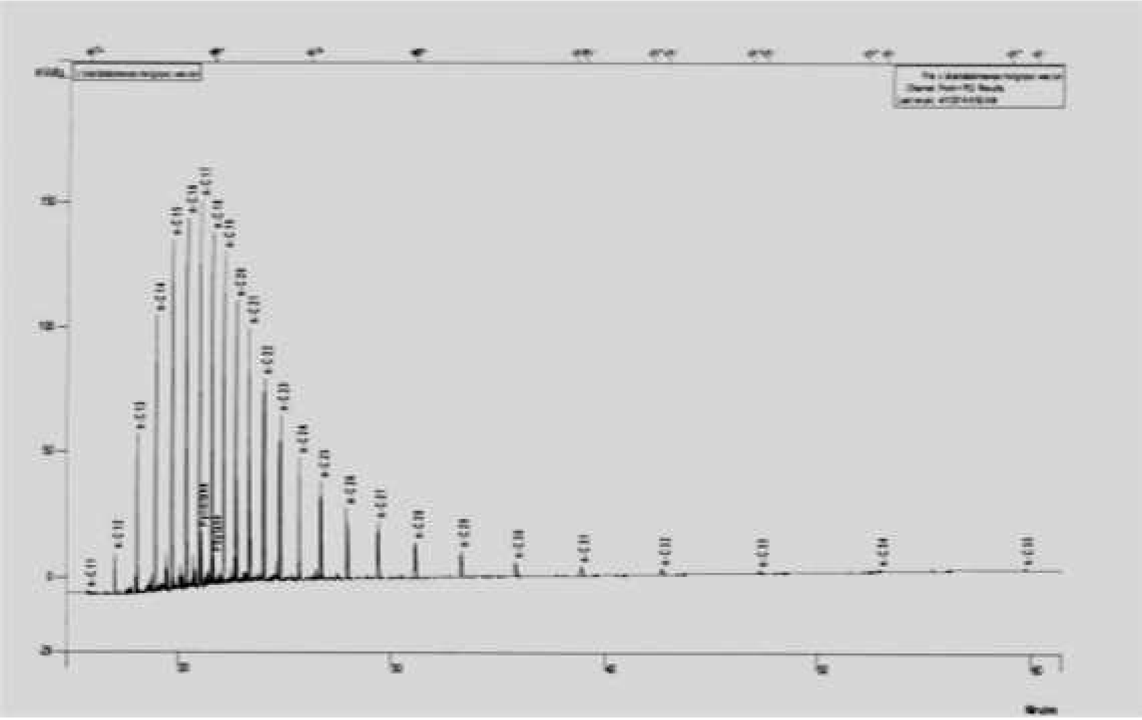


FIGURE 4.7:chromatogram of wax extracted from neem crude oil

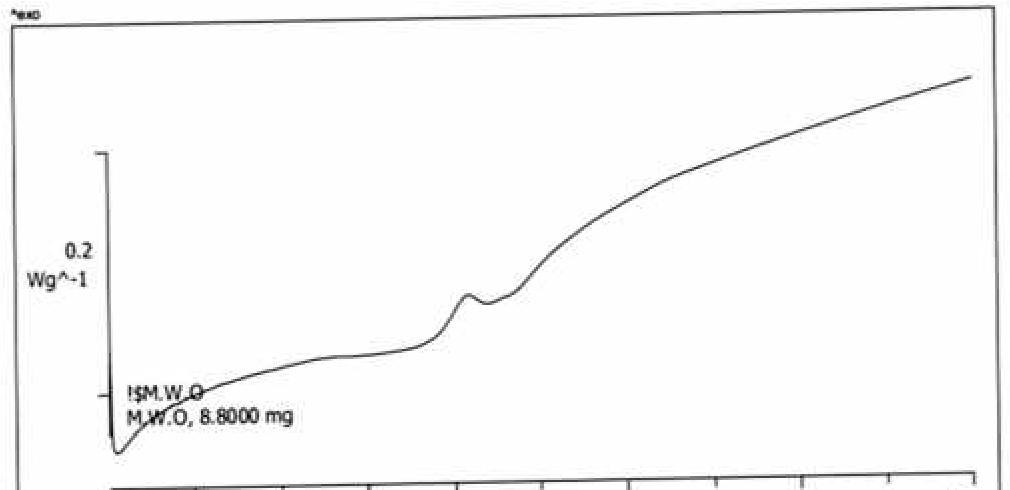


FIGURE 4.8: melting pointofwax extracted from neem crude oil

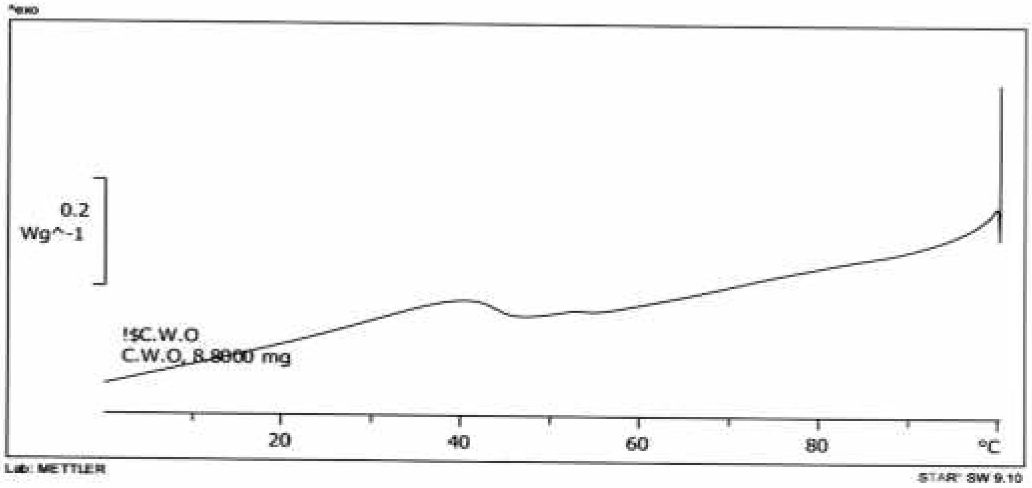


FIGURE 4.9:crystlization point of wax extracted from neem crude oil

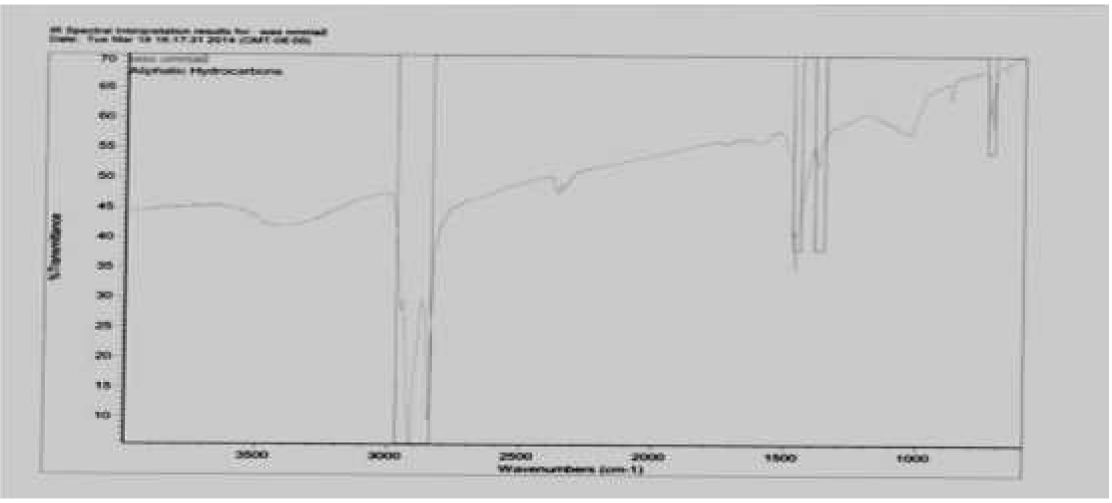
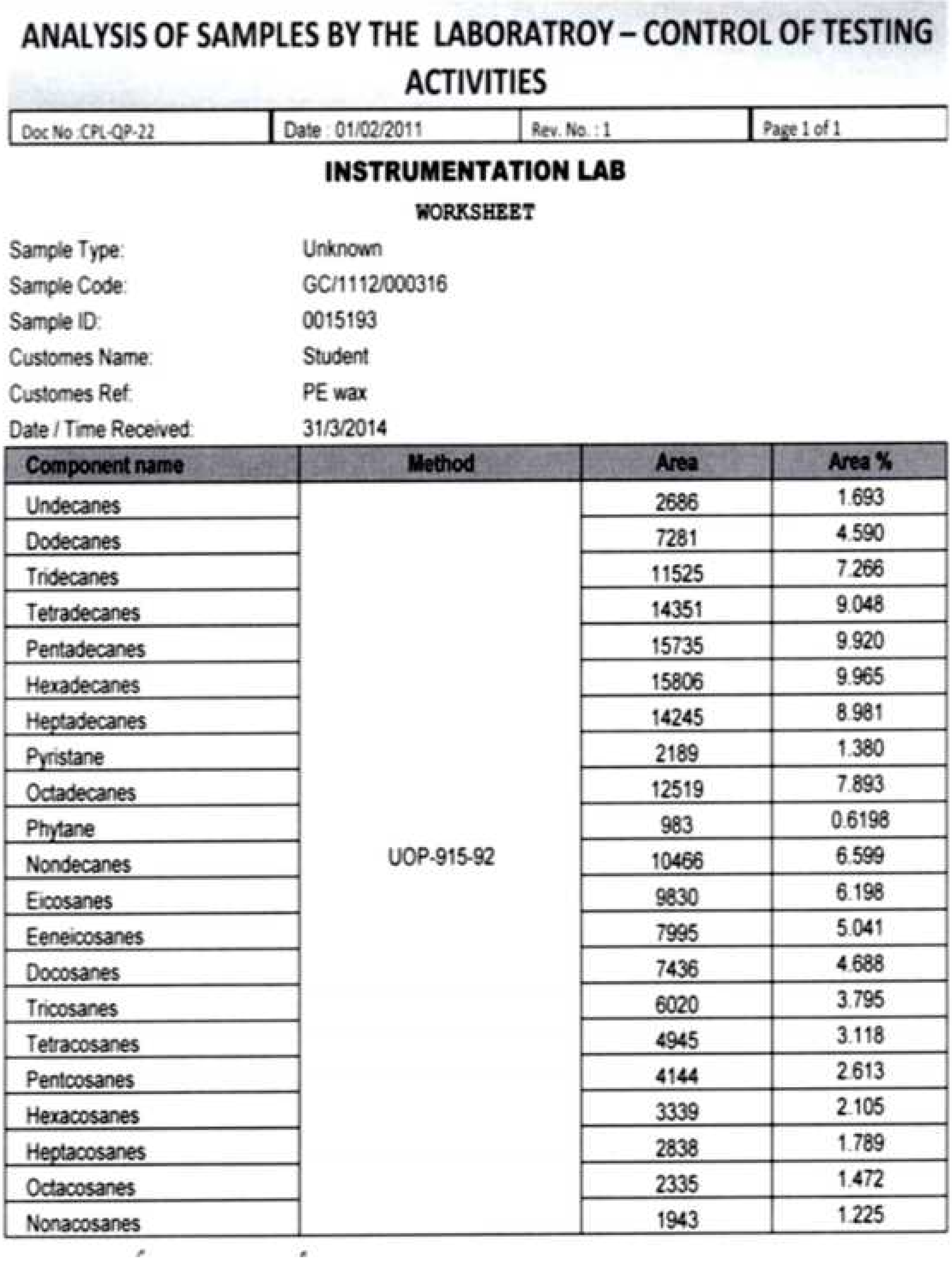


FIGURE 4.10FTIR spectra of wax extracted from hadida crude oil

Table(4.8)Characterization of wax extracted from hadida crude oil byGC



ANALYSIS OF SAMPLES BY THE LABORATROY – CONTROL OF TESTING ACTIVITIES

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INSTRUMENTATION LAB

WORKSHEET

Sample Type:	Unknown
Sample Code:	GC/1112/000316
Sample ID:	0015193
Customes Name:	Student
Customes Ref:	PE wax
Date / Time Received:	31/3/2014

Component name	Method	Area	Area %
Undecanes	UOP-915-92	2686	1.693
Dodecanes		7281	4.590
Tridecanes		11525	7.266
Tetradecanes		14351	9.048
Pentadecanes		15735	9.920
Hexadecanes		15806	9.965
Heptadecanes		14245	8.981
Pyristane		2189	1.380
Octadecanes		12519	7.893
Phytane		983	0.6198
Nondecanes		10466	6.599
Eicosanes		9830	6.198
Eeneicosanes		7995	5.041
Docosanes		7436	4.688
Tricosanes		6020	3.795
Tetracosanes		4945	3.118
Pentcosanes		4144	2.613
Hexacosanes		3339	2.105
Heptacosanes		2838	1.789
Octacosanes		2335	1.472
Nonacosanes		1943	1.225

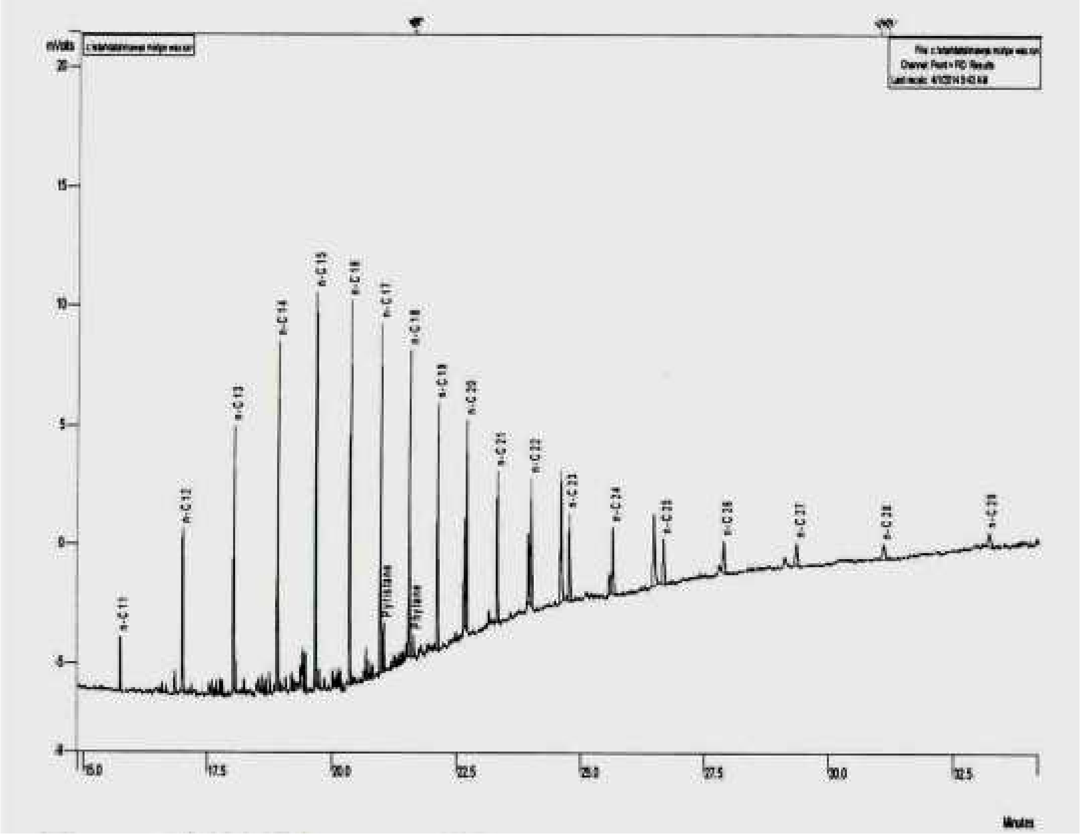


FIGURE 4.11:chromatogram of wax extracted from hadida crude oil

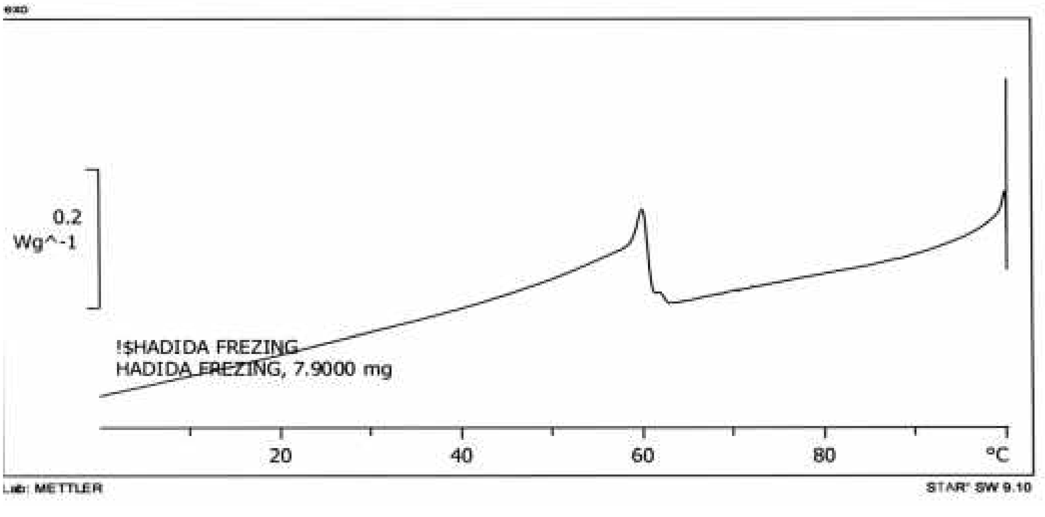


FIGURE 4.12:crystlization point of wax extracted from hadida crude oil

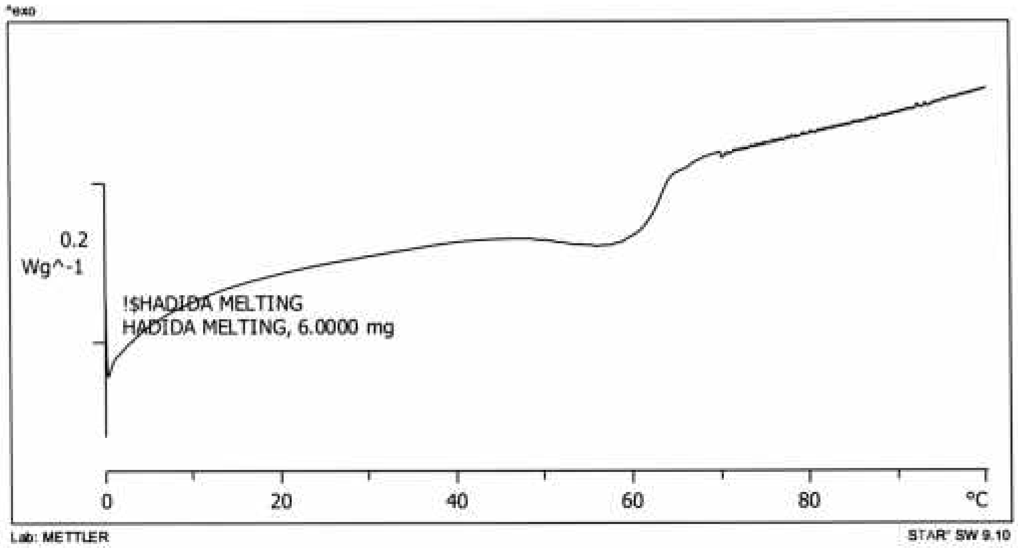


FIGURE 4.13: melting point ofwax extracted from Hadida crude oil

4-5 Evaluation of wax treatment chemical in improving flow characteristic of Neem crude oil and comparison with kerosene and diesel

4.5.1-Theeffect of PPDS on pour point reduction ofNeem crude oil

The effectively of any PPDS depends upon its ability to keep the paraffin wax compound in solution or dispersed .It is observed that crude oil responses differently with the same additives at different doses these responses may be interms of change in pour point or change in rheological properties or both

The high wax crude oils are characterized by high pour point, highviscosity, high gel strength, and abundant wax deposits

It is well known that, as the paraffin wax content increases in crude oil, this leads to difficult solubility of wax in oil, in some cases forming a separate solid phase

The relation between Δp and additive concentration for crude oils without and with additives are shown in figure (4.14) the pour point reduction was calculated by the following equation

Pour point reduction (Δp)=PPpure-PPadd

Where, PPpure is the pour point of the pure crude oil and PPadd is the pour point of the crude oil containing additives .

From fig(4.14) was showed that the Δp value of all concentration for Epri25j1 PPD is zero this means there is no effect of PPDS in the reduction of pour point ,as for china PPDS note also the Δp value is equal to zero for all concentration except 1250 ppm the value is 3, but for Epri 1 PPD the value is 3 for all concentration except 1250 ppm is 6 and for Epri 2 the Δp value for concentration 500, 750ppm is 3 and 1000,1250ppm is 9,this means the best PPDS of all type is Epri2 and most suitable one with this type of crude oil

Table(4.9) effect of different doses of China ppdon pour point reduction of neem crude oil

doses	pour point	pour pointreduction
blank	36	0
500 ppm	36	0
750 ppm	36	0
1000 ppm	36	0
1250 ppm	33	3

Table(4.10) effect of different doses of Epri 25j1 ppd on pour point reduction of neem crude oil

doses	pour point	Pour point reduction
blank	36	0
500 ppm	36	0
750 ppm	36	0
1000 ppm	36	0
1250 ppm	36	0

Table(4.11) effect of different doses of Epri 1ppds on pour point reduction of neem crude oil

doses	pour point	Pour point reduction
blank	36	0
500 ppm	33	3
750 ppm	33	3
1000 ppm	33	3

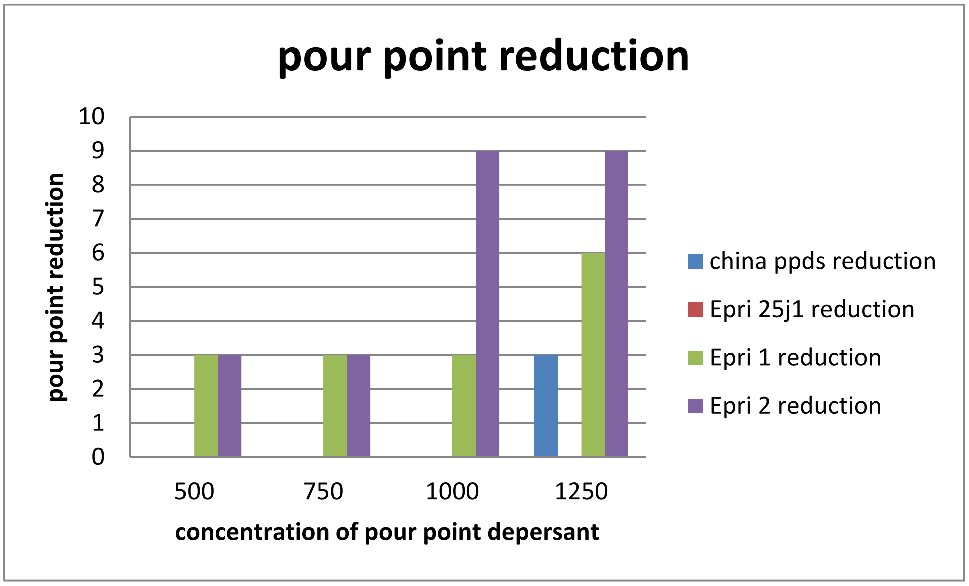
1250 ppm	30	6

Table(4.12) effect of different doses of Epri 2 ppdon pour point reduction of neem crude oil

doses	pour point	Pour point reduction
blank	36	0
500 ppm	33	3
750 ppm	33	3
1000 ppm	27	9
1250 ppm	27	9

Table(4.13) effect of different type of PPDS on pour point reduction of neem crude oil

doses	China ppds reduction	Epri 25j1 reduction	Epri 1 reduction	Epri 2 redution
500 ppm	0	0	3	3
750 ppm	0	0	3	3
1000 ppm	0	0	3	9
1250 ppm	3	0	6	9



Fig(4.14)The effect of PPDS at different concentration on pour point reduction ofNeem crude oil.

4.5.2-Theeffect ofkerosene and diesel on pour point reduction of Neemcrude oil

It has been added two types of aliphatic solvent (kerosene, diesel) with concentration 5%, 10%, 15%, 20%, 25%, 30%, 35%

From fig (4.15) when diesel and kerosene addedtoNeem crude oil at the same concentration ,a reduction in pour point found in adding kerosene greater than adding diesel.

Experimental result showed that relatively high volume of aliphatic(up to 30%) solvent was needed to depress the pour point of neem crude oil by 12^{o}C table(4.13)(4.14),this is when compared with the pour point depressant

The ineffectiveness of aliphatic solvents (kerosene and diesel) in depressing the crude oil pour point by appreciable range is due to the fact that the alphatic solvent are straight or ring form of hydrocarbonsthat modify the thermodynamic properties of the crudes by shifting the wax precipitation equilibrium curve in order to depress the pour point. Highdosages of aliphatic solvents are needed to achieve this equilibrium curve shift.

From fig(4.15)indicate that the reduction of pour point in kerosene is greater than adding diesel at the same concentration this is due to the fact that theLight ends of saturates equally help to keep the high molecular weight heavy ends in solution. The onset of production results in the loss of these light ends, as they are first to leave the reservoir. This alters the original composition of the oil system, resulting in decreased solubility of the paraffin waxes. This loss of solubility could lead to precipitation and deposition of wax.

It was found that it is on the cost estimation side the best use of the diesel and kerosene than use pour point depressant because it can be retrieved when distilling crude oil into products.

Table(4.14) effect of different doses of kerosene on pour point reduction of neem crude oil

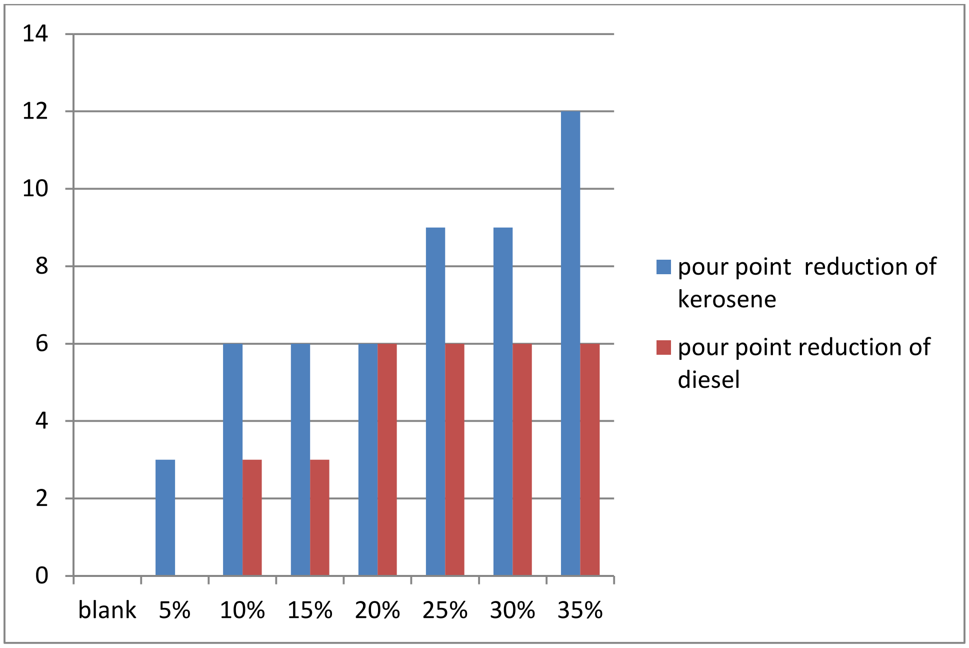
doses	pour point	Pour point reduction
blank	36	0
5%	33	3
10%	30	6
15%	30	6
20%	30	6
25%	27	9
30%	27	9
35%	24	12

Table(4.15) effect of different doses of diesel on pour point reduction of neem crude oil

doses	pour point	Pour point reduction
blank	36	0
5%	36	0
10%	33	3
15%	33	3
20%	30	6
25%	30	6
30%	30	6
35%	30	6

Table(4.16) The effect of kerosene and diesel at different concentration on pour point reduction ofneem crude oil

doses	Pour point reduction of kerosene	Pour point reduction of diesel
blank	0	0
5%	3	0
10%	6	3
15%	6	3
20%	6	6
25%	9	6
30%	9	6
35%	12	6



Fig(4.15)The effect of kerosene and diesel at different concentration on pour point reduction ofneem crude oil

4.5.3-The impact of PPDS on viscosity of NEEM crude oil at different temperature

The viscosity is used to evaluate the crude oil flow ability in the absence and presence of the pour point depressant additives the viscosity at different temperature (75-28^{o}C)for untreated and treated crude oil with different doses (500-1250ppm)were determined .it was observed that the viscosity of crude oil was increased with cooling therefore. The high wax content leads to the formation of gelled crude oil at low temperatures due to crystallization of wax which in turn affects the viscosity of crude oil.

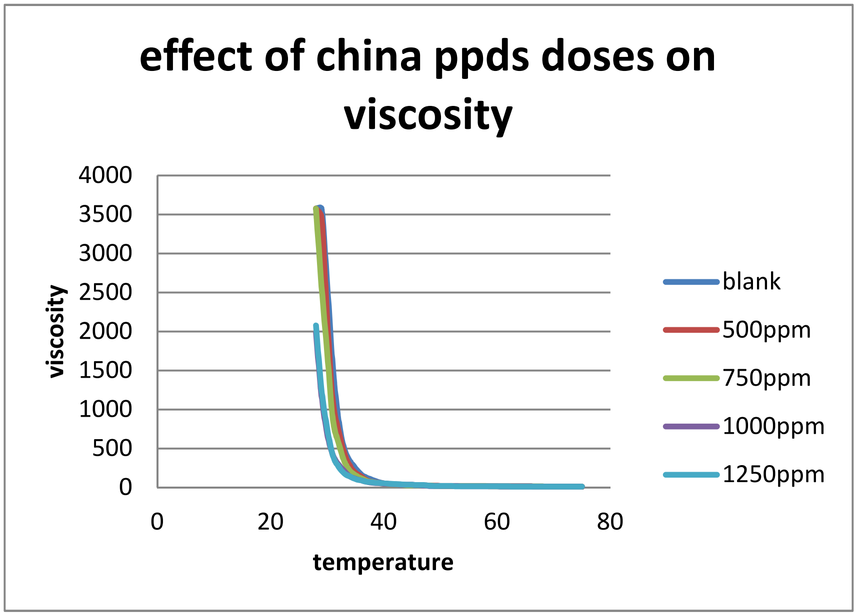
The apparent viscosities (CP)of the untreated and treated crude oils with five commercial pour point depressant .china PPD(table(4.16),fig(4.16))was determined at different temperatures to evaluate the effect of PPD on viscosity and what is the best one

The value of the viscosity (cp) decreased by addition china PPD at high concentration (1250ppm) but in other concentration (500,750,1000ppm)no decrease in viscosity .either in epri25j1(table(4.17),fig(4.17)) does not have any decrease in viscosity at all concentration ,on the other hand it was observed that the viscosity of crude oils was decrease with adding Epri 1(table(4.18),fig(4.18)) at all concentration (500,750,1000,1250ppm)but the largest decrease in viscosity appear when adding Epri2(table(4.19),fig(4.19)) at all concentration ,especially in the 1250ppm viscosity reduce from 3572.571cp to303.2686 at 28^{0}C this means epri 2is the pest one and suitable with this type of crude oil.

Table(4.17) Effect off china ppds on viscosity of neem crude oil

Temperature	Blank	500ppm	750ppm	1000ppm	1250ppm
75	6.66524	6.66524	9.997867	9.997867	9.997867
74	6.66524	9.99787	9.997867	9.997867	9.997867
73	6.66524	9.99787	9.997867	9.997867	9.997867
72	6.66524	9.99787	9.997867	9.997867	9.997867
71	6.66524	9.99787	9.997867	9.997867	9.997867
70	6.66524	9.99787	9.997867	9.997867	9.997867
69	9.99787	9.99787	9.997867	9.997867	9.997867
68	9.99787	9.99787	13.33049	9.997867	9.997867
67	9.99787	9.99787	13.33049	9.997867	9.997867
66	9.99787	13.3305	13.33049	13.33049	9.997867
65	9.99787	13.3305	13.33049	13.33049	9.997867
64	9.99787	13.3305	13.33049	13.33049	9.997867
63	9.99787	13.3305	13.33049	13.33049	9.997867
62	9.99787	13.3305	13.33049	13.33049	13.33049
61	9.99787	13.3305	13.33049	13.33049	13.33049
60	13.3305	13.3305	13.33049	13.33049	13.33049
59	13.3305	13.3305	13.33049	13.33049	13.33049
58	13.3305	16.6631	16.66311	13.33049	13.33049
57	13.3305	16.6631	16.66311	13.33049	13.33049
56	13.3305	16.6631	16.66311	13.33049	13.33049
55	13.3305	16.6631	16.66311	13.33049	13.33049
54	13.3305	16.6631	16.66311	13.33049	13.33049
53	13.3305	16.6631	16.66311	16.66311	13.33049
52	16.6631	19.9957	16.66311	16.66311	16.66311
51	16.6631	19.9957	19.99573	16.66311	19.99573
50	19.9957	19.9957	19.99573	16.66311	19.99573
49	19.9957	23.3284	19.99573	19.99573	19.99573
48	19.9957	23.3284	23.32836	19.99573	23.32836
47	23.3284	26.661	23.32836	23.32836	29.9936
46	23.3284	26.661	23.32836	26.66098	29.9936
45	26.661	29.9936	26.66098	33.32622	33.32622
44	29.9936	29.9936	26.66098	33.32622	36.65884
43	33.3262	33.3262	33.32622	36.65884	39.99147
42	36.6588	36.6588	36.65884	39.99147	43.32409
41	43.3241	43.3241	39.99147	43.32409	46.65671
40	53.322	49.9893	46.65671	46.65671	53.32196

39	69.9851	59.9872	53.32196	53.32196	59.9872
38	96.646	69.9851	66.65244	59.9872	63.31982
37	123.307	89.9808	83.31556	69.98507	73.31769
36	166.631	139.97	116.6418	89.9808	89.9808
35	246.614	186.627	156.6332	109.9765	106.6439
34	339.927	276.608	216.6204	139.9701	139.9701
33	496.561	439.906	336.5948	209.9552	179.9616
32	863.149	726.512	569.8784	293.2708	266.6098
31	1533.01	1096.43	863.1492	416.5778	406.5799
30	2592.78	2139.54	1722.966	686.5202	749.84
29	3572.57	3455.93	2576.117	1173.083	1246.401
28	3572.57	3575.9	3575.904	1982.91	2076.224

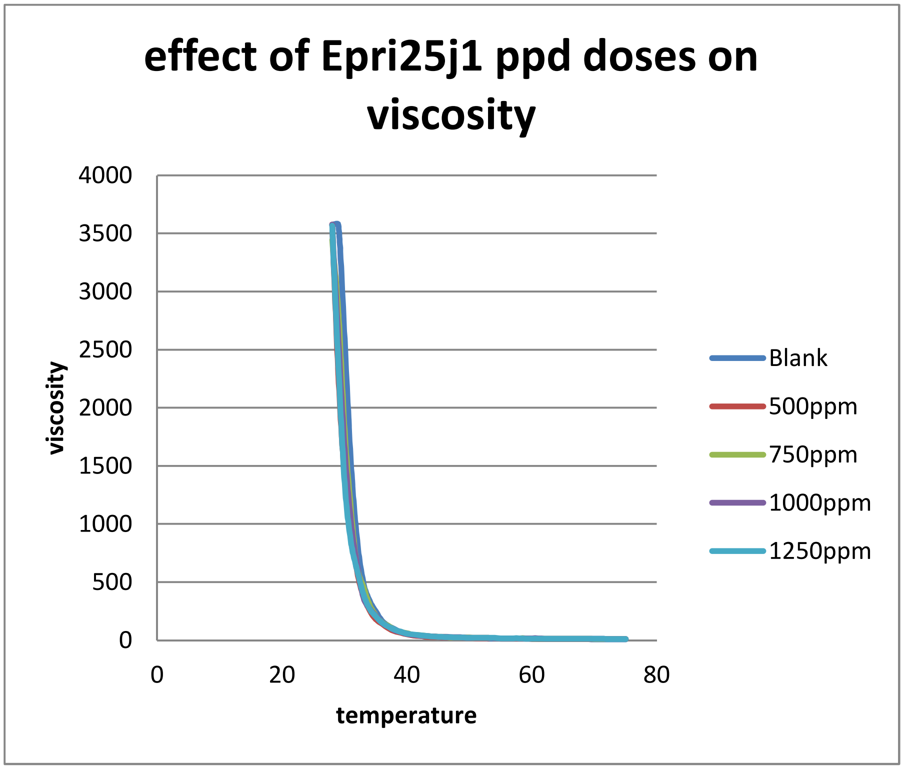


Fig(4.16)Effect of china ppds at different concentration on viscosity

Table(4.18) Effect of Epri25j1 ppds on viscosity of neem crude oil

Temperature	Blank	500ppm	750ppm	1000ppm	1250ppm
75	6.665244	9.997867	9.997867	9.997867	9.997867
74	6.665244	9.997867	9.997867	9.997867	9.997867
73	6.665244	9.997867	9.997867	9.997867	9.997867
72	6.665244	9.997867	9.997867	9.997867	9.997867
71	6.665244	9.997867	9.997867	13.33049	13.33049
70	6.665244	9.997867	9.997867	13.33049	13.33049
69	9.997867	9.997867	13.33049	13.33049	13.33049
68	9.997867	9.997867	13.33049	13.33049	13.33049
67	9.997867	9.997867	13.33049	13.33049	13.33049
66	9.997867	9.997867	13.33049	13.33049	13.33049
65	9.997867	9.997867	13.33049	13.33049	13.33049
64	9.997867	9.997867	13.33049	13.33049	13.33049
63	9.997867	9.997867	13.33049	13.33049	13.33049
62	9.997867	9.997867	13.33049	13.33049	13.33049
61	9.997867	9.997867	13.33049	16.66311	13.33049
60	13.33049	9.997867	13.33049	16.66311	13.33049
59	13.33049	13.33049	16.66311	16.66311	13.33049
58	13.33049	13.33049	16.66311	16.66311	16.66311
57	13.33049	13.33049	16.66311	16.66311	16.66311
56	13.33049	13.33049	16.66311	16.66311	16.66311
55	13.33049	13.33049	16.66311	16.66311	16.66311
54	13.33049	16.66311	16.66311	16.66311	19.99573
53	13.33049	16.66311	19.99573	19.99573	19.99573
52	16.66311	16.66311	19.99573	19.99573	19.99573
51	16.66311	16.66311	19.99573	19.99573	19.99573
50	19.99573	19.99573	23.32836	19.99573	19.99573
49	19.99573	19.99573	23.32836	23.32836	23.32836
48	19.99573	19.99573	23.32836	26.66098	23.32836
47	23.32836	23.32836	23.32836	26.66098	26.66098
46	23.32836	23.32836	29.9936	29.9936	26.66098
45	26.66098	26.66098	29.9936	29.9936	29.9936
44	29.9936	26.66098	33.32622	33.32622	33.32622
43	33.32622	29.9936	36.65884	36.65884	36.65884
42	36.65884	36.65884	43.32409	39.99147	43.32409
41	43.32409	39.99147	46.65671	46.65671	49.98933
40	53.32196	49.98933	59.9872	53.32196	56.65458
39	69.98507	63.31982	69.98507	69.98507	73.31769

38	96.64604	76.65031	89.9808	86.64818	89.9808
37	123.307	103.3113	123.307	116.6418	116.6418
36	166.6311	139.9701	153.3006	149.968	149.968
35	246.614	179.9616	213.2878	209.9552	203.29
34	339.9275	256.6119	303.2686	273.275	269.9424
33	496.5607	379.9189	459.9019	366.5884	396.582
32	863.1492	589.8741	633.1982	639.8635	603.2046
31	1533.006	966.4604	1133.092	1023.115	849.8187
30	2592.78	1396.369	1809.614	1646.315	1353.045
29	3572.571	2279.514	2819.398	2579.45	2352.831
28	3572.571	3575.904	3442.599	3575.904	3565.906

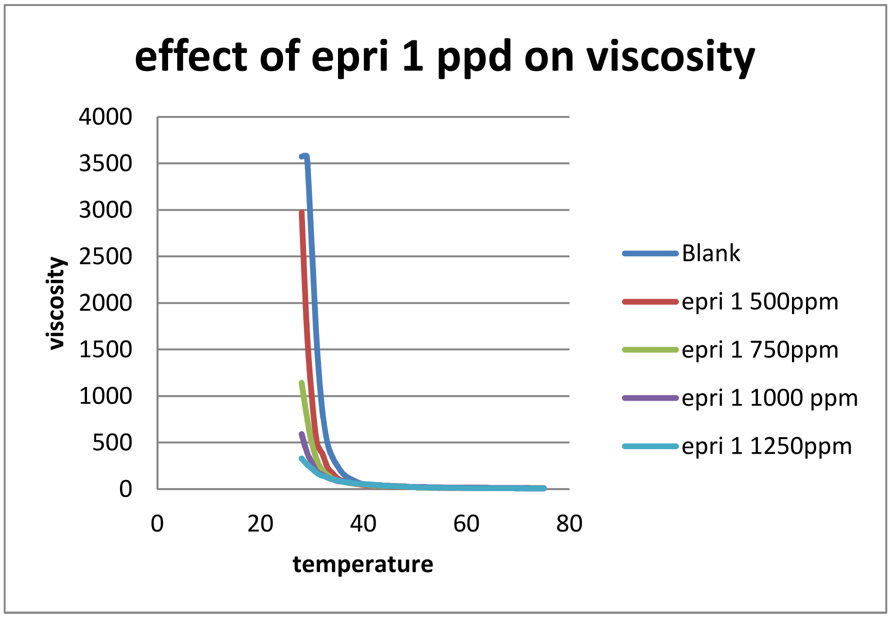


Fig(4.17)Effect ofEpri25j1 ppds at different concentration on viscosity

Table(4.19) Effect of Epri 1 ppd on viscosity of neem crude oil

Temperature	Blank	500ppm	750ppm	1000ppm	1250ppm
75	6.6652444	9.99787	9.997867	9.997867	6.665244
74	6.6652444	9.99787	9.997867	9.997867	6.665244
73	6.6652444	9.99787	9.997867	9.997867	6.665244
72	6.6652444	9.99787	9.997867	13.33049	6.665244
71	6.6652444	9.99787	9.997867	13.33049	9.997867
70	6.6652444	9.99787	9.997867	13.33049	9.997867
69	9.9978667	9.99787	9.997867	13.33049	9.997867
68	9.9978667	9.99787	9.997867	13.33049	9.997867
67	9.9978667	9.99787	9.997867	13.33049	9.997867
66	9.9978667	9.99787	9.997867	13.33049	9.997867
65	9.9978667	9.99787	9.997867	13.33049	9.997867
64	9.9978667	9.99787	9.997867	16.66311	9.997867
63	9.9978667	9.99787	9.997867	16.66311	9.997867
62	9.9978667	13.3305	9.997867	16.66311	9.997867
61	9.9978667	13.3305	13.33049	16.66311	9.997867
60	13.330489	13.3305	13.33049	16.66311	9.997867
59	13.330489	13.3305	13.33049	16.66311	13.33049
58	13.330489	13.3305	13.33049	16.66311	13.33049
57	13.330489	13.3305	13.33049	16.66311	13.33049
56	13.330489	13.3305	13.33049	16.66311	13.33049
55	13.330489	13.3305	16.66311	19.99573	16.66311
54	13.330489	16.6631	16.66311	19.99573	16.66311
53	13.330489	16.6631	16.66311	19.99573	16.66311
52	16.663111	16.6631	16.66311	23.32836	16.66311
51	16.663111	16.6631	16.66311	23.32836	19.99573
50	19.995733	19.9957	19.99573	23.32836	19.99573
49	19.995733	19.9957	23.32836	23.32836	23.32836
48	19.995733	19.9957	23.32836	29.9936	26.66098
47	23.328356	23.3284	26.66098	29.9936	29.9936
46	23.328356	23.3284	29.9936	33.32622	29.9936
45	26.660978	26.661	33.32622	36.65884	33.32622
44	29.9936	33.3262	33.32622	36.65884	36.65884
43	33.326222	33.3262	36.65884	43.32409	43.32409
42	36.658844	36.6588	36.65884	43.32409	46.65671
41	43.324089	39.9915	43.32409	49.98933	49.98933
40	53.321956	43.3241	49.98933	53.32196	53.32196

39	69.985067	49.9893	53.32196	63.31982	59.9872
38	96.646044	59.9872	59.9872	66.65244	63.31982
37	123.30702	69.9851	66.65244	73.31769	73.31769
36	166.63111	86.6482	76.65031	79.98293	79.98293
35	246.61404	113.309	93.31342	86.64818	93.31342
34	339.92747	169.964	113.3092	103.3113	106.6439
33	496.56071	236.616	153.3006	123.307	126.6396
32	863.14916	383.252	203.29	156.6332	143.3028
31	1533.0062	493.228	306.6012	183.2942	169.9637
30	2592.7801	983.124	486.5628	286.6055	219.9531
29	3572.571	1736.3	783.1662	399.9147	266.6098
28	3572.571	2972.7	1143.089	593.2068	329.9296

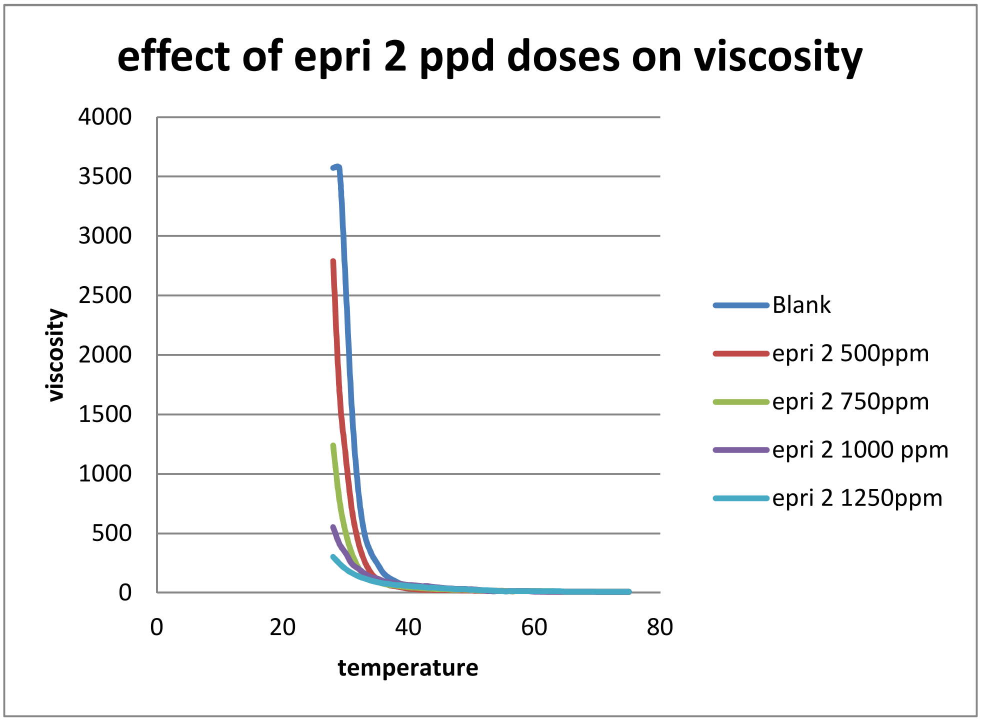


Fig(4.18)Effect ofEpri1 ppds at different concentration on viscosity

Table(4.20)Effect of Epri2 ppds on viscosity of neem crude oil

Temperature	Blank	500ppm	750ppm	1000ppm	1250ppm
75	6.665244	9.997867	9.997867	9.997867	9.997867
74	6.665244	9.997867	9.997867	9.997867	9.997867
73	6.665244	9.997867	9.997867	9.997867	9.997867
72	6.665244	9.997867	9.997867	9.997867	9.997867
71	6.665244	9.997867	9.997867	9.997867	9.997867
70	6.665244	9.997867	9.997867	9.997867	9.997867
69	9.997867	9.997867	9.997867	9.997867	9.997867
68	9.997867	9.997867	9.997867	9.997867	9.997867
67	9.997867	9.997867	9.997867	9.997867	9.997867
66	9.997867	9.997867	9.997867	9.997867	9.997867
65	9.997867	9.997867	9.997867	9.997867	9.997867
64	9.997867	9.997867	9.997867	9.997867	13.33049
63	9.997867	9.997867	13.33049	9.997867	13.33049
62	9.997867	9.997867	13.33049	9.997867	13.33049
61	9.997867	13.33049	13.33049	9.997867	13.33049
60	13.33049	13.33049	13.33049	9.997867	13.33049
59	13.33049	13.33049	13.33049	13.33049	13.33049
58	13.33049	13.33049	13.33049	13.33049	13.33049
57	13.33049	13.33049	13.33049	13.33049	13.33049
56	13.33049	13.33049	13.33049	13.33049	13.33049
55	13.33049	16.66311	16.66311	13.33049	13.33049
54	13.33049	16.66311	16.66311	16.66311	16.66311
53	13.33049	16.66311	19.99573	16.66311	19.99573
52	16.66311	16.66311	19.99573	19.99573	23.32836
51	16.66311	16.66311	19.99573	26.66098	23.32836
50	19.99573	19.99573	23.32836	29.9936	26.66098
49	19.99573	19.99573	26.66098	33.32622	29.9936
48	19.99573	19.99573	26.66098	33.32622	29.9936
47	23.32836	23.32836	26.66098	36.65884	33.32622
46	23.32836	23.32836	29.9936	39.99147	36.65884
45	26.66098	23.32836	29.9936	43.32409	39.99147
44	29.9936	23.32836	33.32622	49.98933	43.32409
43	33.32622	26.66098	36.65884	56.65458	43.32409
42	36.65884	26.66098	39.99147	56.65458	49.98933
41	43.32409	29.9936	43.32409	63.31982	53.32196
40	53.32196	36.65884	46.65671	66.65244	56.65458

39	69.98507	43.32409	53.32196	73.31769	63.31982
38	96.64604	53.32196	59.9872	79.98293	66.65244
37	123.307	63.31982	66.65244	89.9808	73.31769
36	166.6311	86.64818	76.65031	99.97867	79.98293
35	246.614	113.3092	93.31342	119.9744	89.9808
34	339.9275	169.9637	119.9744	133.3049	103.3113
33	496.5607	266.6098	149.968	163.2985	119.9744
32	863.1492	426.5756	213.2878	203.29	139.9701
31	1533.006	696.518	329.9296	243.2814	166.6311
30	2592.78	1153.087	506.5586	333.2622	199.9573
29	3572.571	1699.637	783.1662	413.2452	246.614
28	3572.571	2789.405	1239.735	553.2153	303.2686



Fig(4.19)Effect ofEpri2 ppds at different concentrationon viscosity

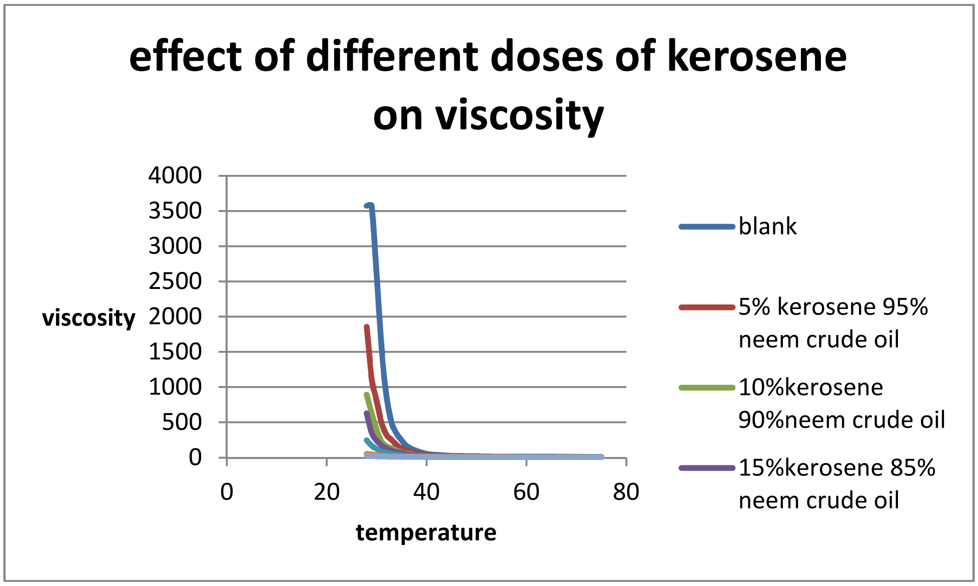
4.5.4-The impact of kerosene and diesel on viscosity ofneemcrude oil at different temperature

The apparent viscosities (CP)of the untreated and treated crude oils with kerosene and diesel was determined at different temperatures and concentrations(5%,10%,15%,20%,30%,35%).The value of the viscosity (cp) decreased by addition kerosene at all concentration fig(4.20).,on the other hand from fig(4.20) it was observed that the viscosity of crude oils was decrease with increase concentration from fig (4.21) it observed thatThe value of the viscosity (cp) decreased by addition diesel at all concentration except5%concentration no decrease in viscosity.

Table(4.21) Effect of kerosene on viscosityof neemcrude oil

Temerature	**blank**	**5% kerosene**	**10% kerosene**	**15% kerosene**	**20% kerosene**	**30% kerosene**	**35% kerosene**
75	6.6652444	6.6652444	6.66524444	6.665244444	6.6652444	3.332622222	3.332622222
74	6.6652444	6.6652444	6.66524444	6.665244444	6.6652444	3.332622222	3.332622222
73	6.6652444	6.6652444	6.66524444	6.665244444	6.6652444	3.332622222	3.332622222
72	6.6652444	6.6652444	6.66524444	6.665244444	6.6652444	3.332622222	3.332622222
71	6.6652444	9.9978667	6.66524444	6.665244444	6.6652444	3.332622222	3.332622222
70	6.6652444	9.9978667	6.66524444	6.665244444	6.6652444	3.332622222	3.332622222
69	9.9978667	9.9978667	6.66524444	6.665244444	6.6652444	3.332622222	3.332622222
68	9.9978667	9.9978667	6.66524444	6.665244444	6.6652444	3.332622222	3.332622222
67	9.9978667	9.9978667	6.66524444	6.665244444	6.6652444	3.332622222	3.332622222
66	9.9978667	9.9978667	9.99786667	9.997866667	6.6652444	3.332622222	3.332622222
65	9.9978667	9.9978667	9.99786667	9.997866667	6.6652444	3.332622222	3.332622222
64	9.9978667	9.9978667	9.99786667	9.997866667	6.6652444	3.332622222	3.332622222
63	9.9978667	9.9978667	9.99786667	9.997866667	6.6652444	3.332622222	3.332622222
62	9.9978667	9.9978667	9.99786667	9.997866667	9.9978667	3.332622222	3.332622222
61	9.9978667	9.9978667	9.99786667	9.997866667	9.9978667	3.332622222	3.332622222
60	13.330489	9.9978667	9.99786667	9.997866667	9.9978667	3.332622222	3.332622222
59	13.330489	9.9978667	9.99786667	9.997866667	9.9978667	3.332622222	3.332622222
58	13.330489	9.9978667	9.99786667	9.997866667	9.9978667	3.332622222	3.332622222
57	13.330489	9.9978667	9.99786667	9.997866667	9.9978667	6.665244444	3.332622222
56	13.330489	13.330489	9.99786667	9.997866667	9.9978667	6.665244444	3.332622222
55	13.330489	13.330489	9.99786667	9.997866667	9.9978667	6.665244444	3.332622222
54	13.330489	13.330489	9.99786667	9.997866667	9.9978667	6.665244444	3.332622222
53	13.330489	13.330489	9.99786667	9.997866667	9.9978667	6.665244444	3.332622222
52	16.663111	13.330489	13.3304889	9.997866667	9.9978667	6.665244444	3.332622222
51	16.663111	13.330489	13.3304889	9.997866667	9.9978667	6.665244444	3.332622222
50	19.995733	16.663111	13.3304889	13.33048889	9.9978667	6.665244444	3.332622222
49	19.995733	16.663111	13.3304889	13.33048889	9.9978667	6.665244444	3.332622222
48	19.995733	16.663111	13.3304889	13.33048889	9.9978667	6.665244444	6.665244444
47	23.328356	19.995733	13.3304889	13.33048889	9.9978667	6.665244444	6.665244444
46	23.328356	19.995733	16.6631111	13.33048889	9.9978667	6.665244444	6.665244444
45	26.660978	19.995733	16.6631111	13.33048889	9.9978667	6.665244444	6.665244444
44	29.9936	23.328356	16.6631111	13.33048889	9.9978667	9.997866667	6.665244444
43	33.326222	23.328356	19.9957333	16.66311111	13.330489	9.997866667	6.665244444
42	36.658844	26.660978	19.9957333	16.66311111	13.330489	9.997866667	6.665244444
41	43.324089	29.9936	19.9957333	19.99573333	13.330489	9.997866667	6.665244444
40	53.321956	36.658844	26.6609778	19.99573333	16.663111	9.997866667	9.997866667
39	69.985067	46.656711	29.9936	23.32835556	16.663111	9.997866667	9.997866667
38	96.646044	63.319822	33.3262222	29.9936	16.663111	9.997866667	9.997866667
37	123.30702	76.650311	46.6567111	36.65884444	23.328356	13.33048889	9.997866667
36	166.63111	106.64391	56.6545778	46.65671111	26.660978	13.33048889	9.997866667
35	246.61404	129.97227	73.3176889	63.31982222	36.658844	13.33048889	9.997866667

34	339.92747	179.9616	96.6460444	76.65031111	43.324089	16.66311111	9.997866667
33	496.56071	253.27929	133.304889	99.97866667	53.321956	19.99573333	13.33048889
32	863.14916	319.93173	159.965867	129.9722667	73.317689	23.32835556	13.33048889
31	1533.0062	489.89547	226.618311	173.2963556	86.648178	29.9936	16.66311111
30	2592.7801	803.16196	393.249422	243.2814222	123.30702	33.32622222	16.66311111
29	3572.571	1129.7589	633.198222	353.2579556	169.96373	46.65671111	23.32835556
28	3572.571	1856.2706	893.142756	629.8656	246.61404	53.32195556	26.66097778

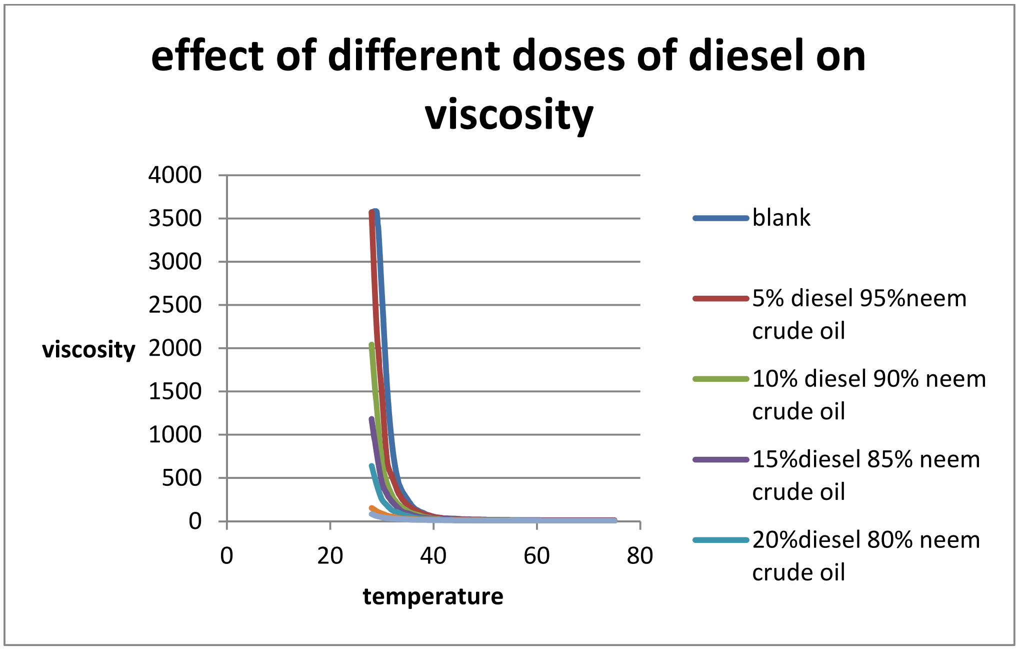


Fig(4.20)Effect ofdifferent concentration of kerosene on viscosity of neem crude oil

Table(4.22) Effect of diesel on viscosity of neemcrude oil

temperature	blank	5% diesel	10% diesel	15%diesel	20%diesel	30% diesel	35% diesel
75	6.665244	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
74	6.665244	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
73	6.665244	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
72	6.665244	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
71	6.665244	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
70	6.665244	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
69	9.997867	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
68	9.997867	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
67	9.997867	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
66	9.997867	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
65	9.997867	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
64	9.997867	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
63	9.997867	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
62	9.997867	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
61	9.997867	13.33049	6.665244444	9.99786667	6.6652444	6.665244444	6.66524444
60	13.33049	13.33049	9.997866667	13.3304889	6.6652444	6.665244444	9.99786667
59	13.33049	13.33049	9.997866667	13.3304889	6.6652444	6.665244444	9.99786667
58	13.33049	13.33049	9.997866667	13.3304889	6.6652444	6.665244444	9.99786667
57	13.33049	13.33049	9.997866667	13.3304889	6.6652444	6.665244444	9.99786667
56	13.33049	13.33049	9.997866667	13.3304889	13.330489	6.665244444	9.99786667
55	13.33049	13.33049	9.997866667	13.3304889	13.330489	9.997866667	9.99786667
54	13.33049	16.66311	9.997866667	13.3304889	13.330489	9.997866667	9.99786667
53	13.33049	16.66311	9.997866667	13.3304889	13.330489	9.997866667	9.99786667
52	16.66311	16.66311	9.997866667	16.6631111	13.330489	9.997866667	9.99786667
51	16.66311	16.66311	13.33048889	16.6631111	13.330489	9.997866667	9.99786667
50	19.99573	16.66311	13.33048889	16.6631111	13.330489	9.997866667	9.99786667
49	19.99573	19.99573	13.33048889	16.6631111	13.330489	13.33048889	9.99786667
48	19.99573	19.99573	13.33048889	16.6631111	13.330489	13.33048889	9.99786667
47	23.32836	19.99573	16.66311111	19.9957333	13.330489	13.33048889	9.99786667
46	23.32836	23.32836	16.66311111	19.9957333	16.663111	13.33048889	9.99786667
45	26.66098	23.32836	16.66311111	19.9957333	16.663111	13.33048889	9.99786667
44	29.9936	26.66098	19.99573333	19.9957333	16.663111	13.33048889	9.99786667
43	33.32622	29.9936	19.99573333	23.3283556	16.663111	13.33048889	13.3304889
42	36.65884	33.32622	23.32835556	23.3283556	16.663111	13.33048889	13.3304889
41	43.32409	43.32409	26.66097778	23.3283556	23.328356	19.99573333	13.3304889
40	53.32196	49.98933	33.32622222	29.9936	26.660978	19.99573333	13.3304889
39	69.98507	69.98507	43.32408889	36.6588444	26.660978	19.99573333	13.3304889

38	96.64604	83.31556	53.32195556	43.3240889	29.9936	19.99573333	16.6631111
37	123.307	109.9765	73.31768889	53.3219556	36.658844	19.99573333	16.6631111
36	166.6311	143.3028	89.9808	69.9850667	46.656711	26.66097778	16.6631111
35	246.614	186.6268	116.6417778	93.3134222	63.319822	29.9936	19.9957333
34	339.9275	249.9467	156.6332444	109.976533	76.650311	33.32622222	23.3283556
33	496.5607	349.9253	206.6225778	163.298489	106.64391	39.99146667	26.6609778
32	863.1492	513.2238	293.2707556	223.285689	126.63964	53.32195556	29.9936
31	1533.006	683.1876	439.9061333	309.933867	183.29422	66.65244444	36.6588444
30	2592.78	1443.025	686.5201778	446.571378	253.27929	89.9808	46.6567111
29	3572.571	2229.524	1299.722667	773.168356	419.9104	116.6417778	59.9872
28	3572.571	3572.571	2042.897422	1183.08089	639.86347	153.3006222	83.3155556



Fig(4.21) Effect ofdifferent concentration of diesel on viscosity of neem crude oil

Chapter Five

Conclusion and Recommendation

Chapter Five

Conclusion and Recommendation

5.1: Conclusion

In this research the flow properties of neem crude oil were identified and investigate .five chemicals were characterized and evaluated with their effect on pour point .it was found that the most effective compound for pour point depressant was epri2 with an effective concentration of 1250ppm

It was also found that all PPDS contains aromatic compound, Aliphatic compound with different type of solvent including ethyl benzene ,o,p Xylene ,and toluene in high concentration.

5.2: Recommendation:

The following are recommended:

- The establishment of avis breaking unit at the central processing facilities and use the light components to improve the flow properties and prevent wax deposion
- Thermal treatment maybe used and its affect on the rheological properties of the crude
- The cost comparison is to be made between pour point depressant chemical (PPDS),Thevisbreaking product and the thermal treatment method .
- Trials of the above mentioned methods are to be compared coastwise when coupled with the thermal treatment.

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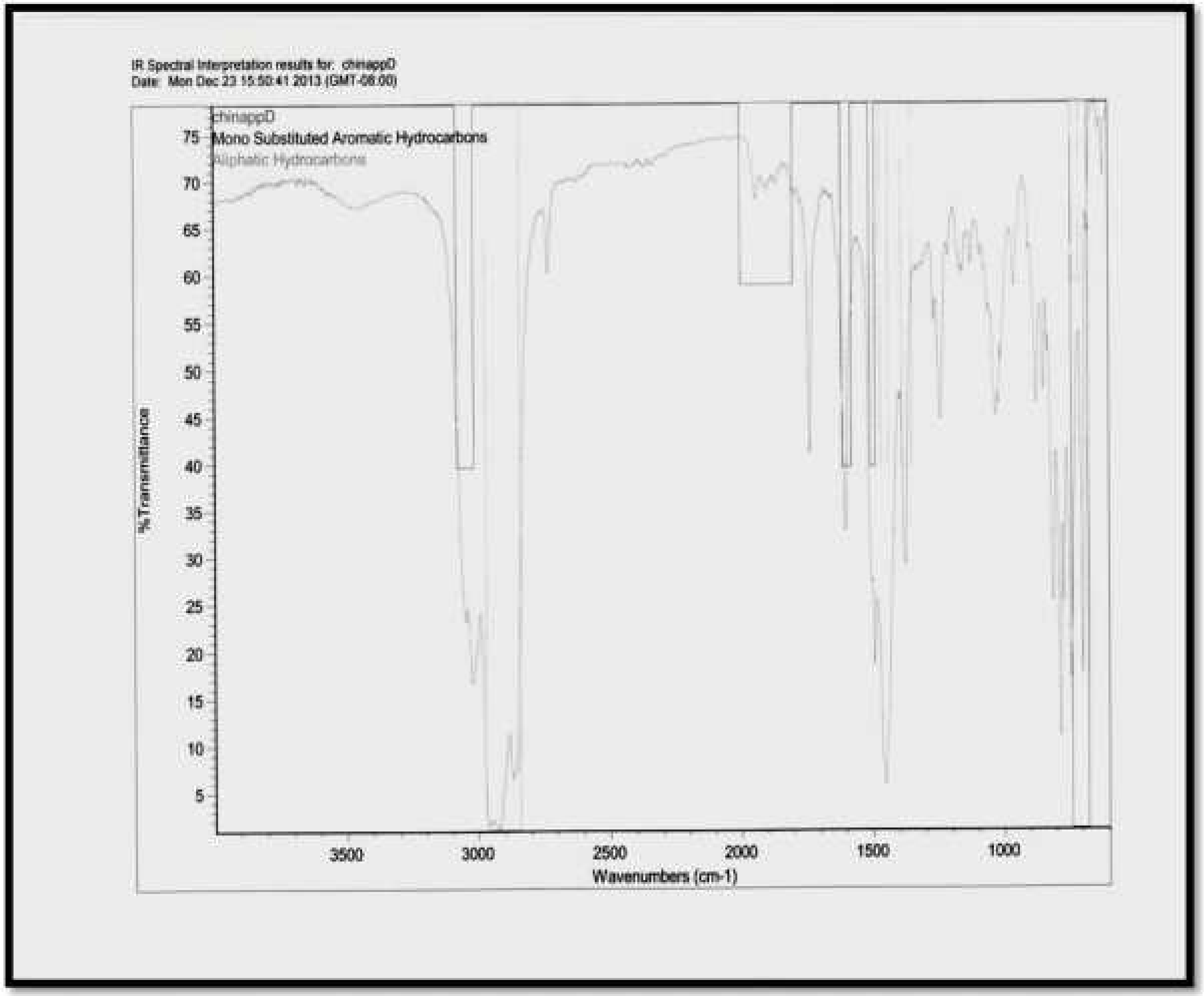
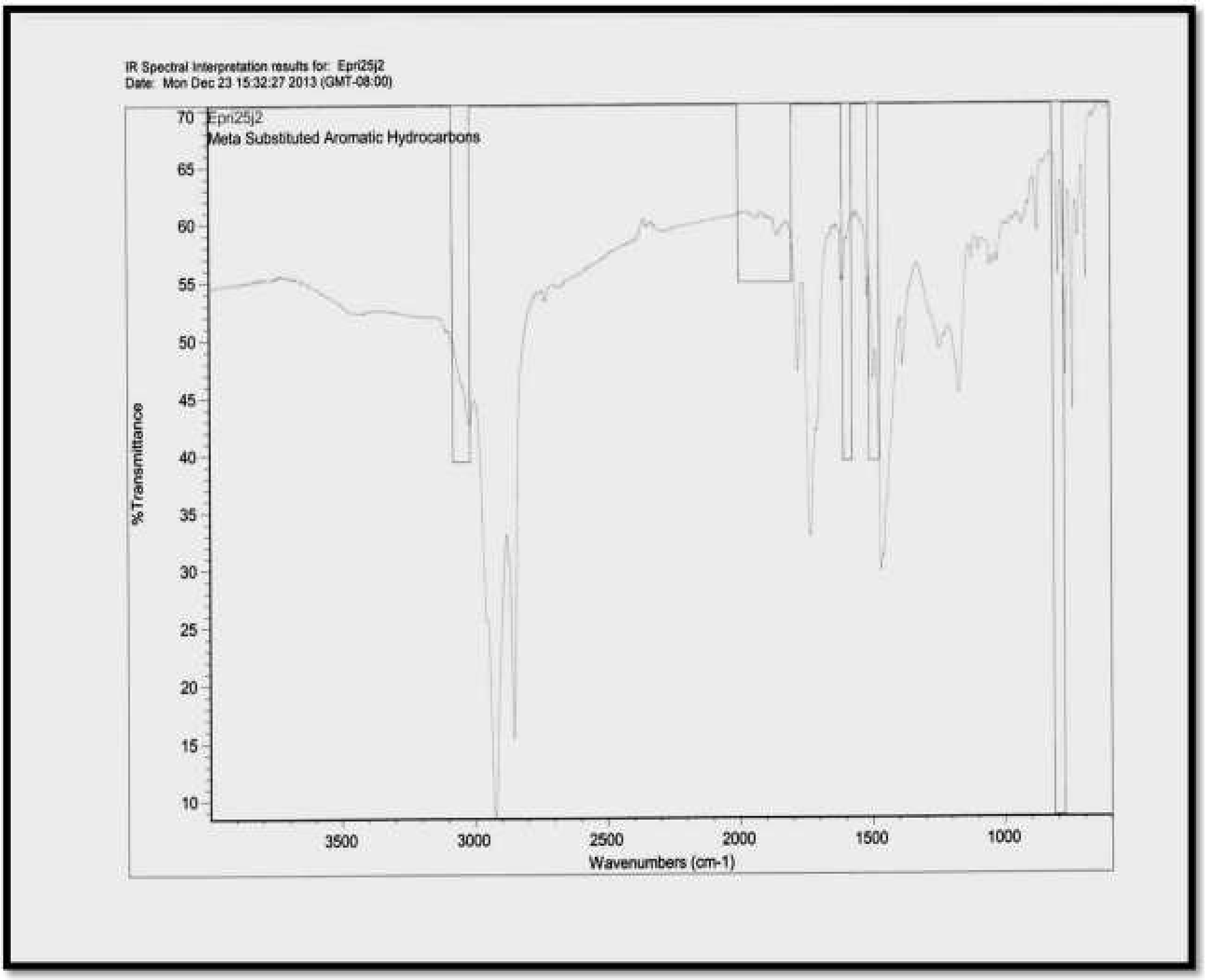
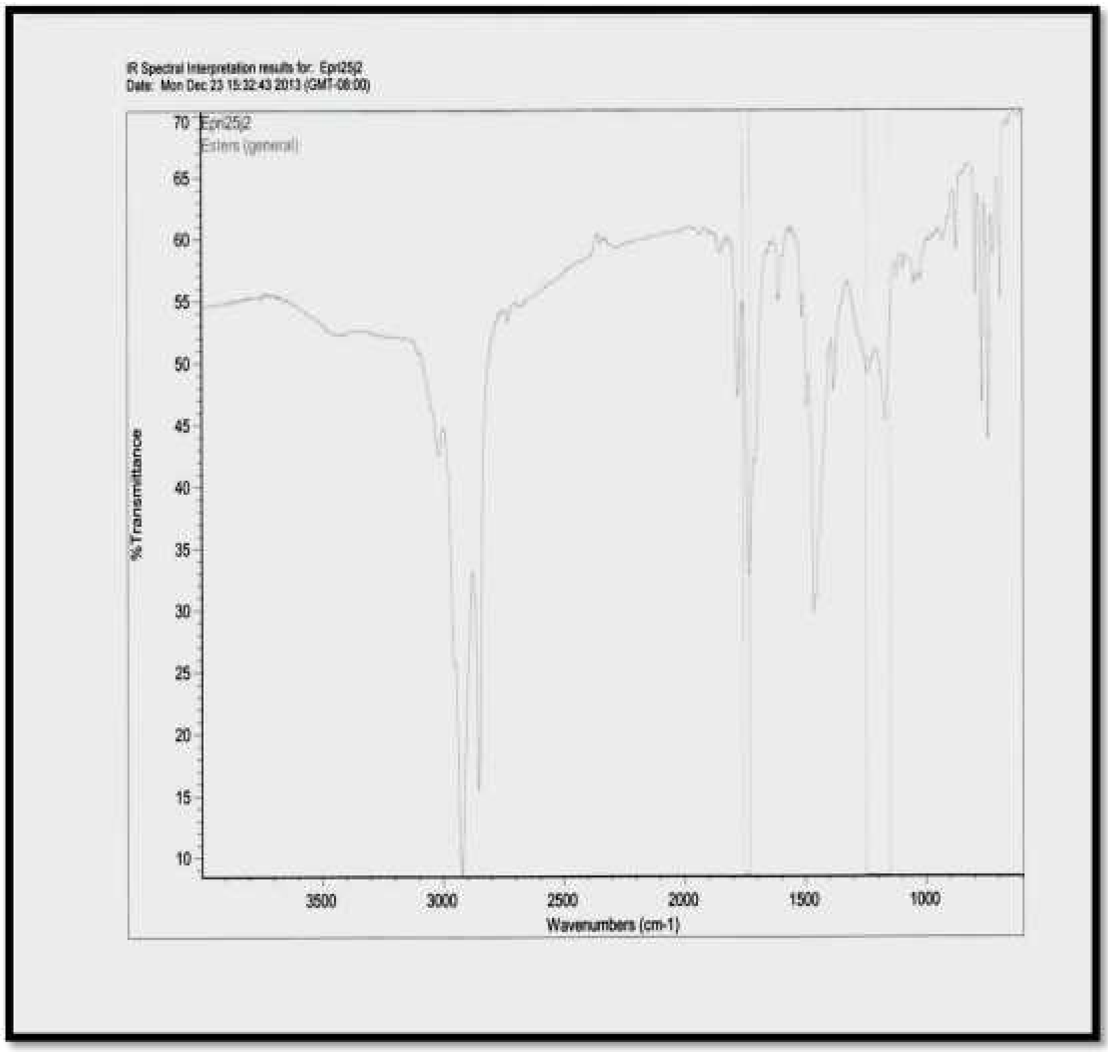
Appendix



FTIR spectra of PPD OF Chinese Origin



FTIR spectra of Epri25j2 PPDS



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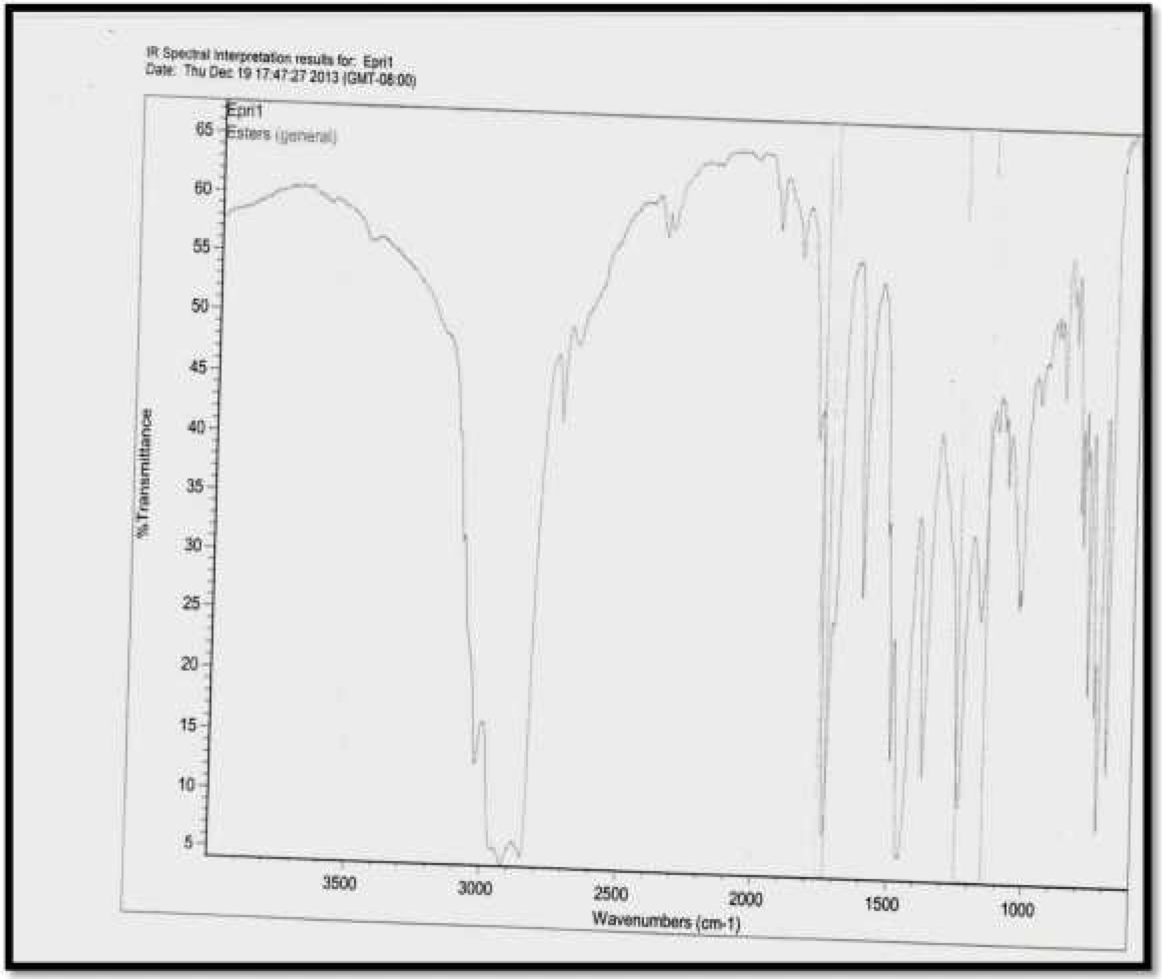

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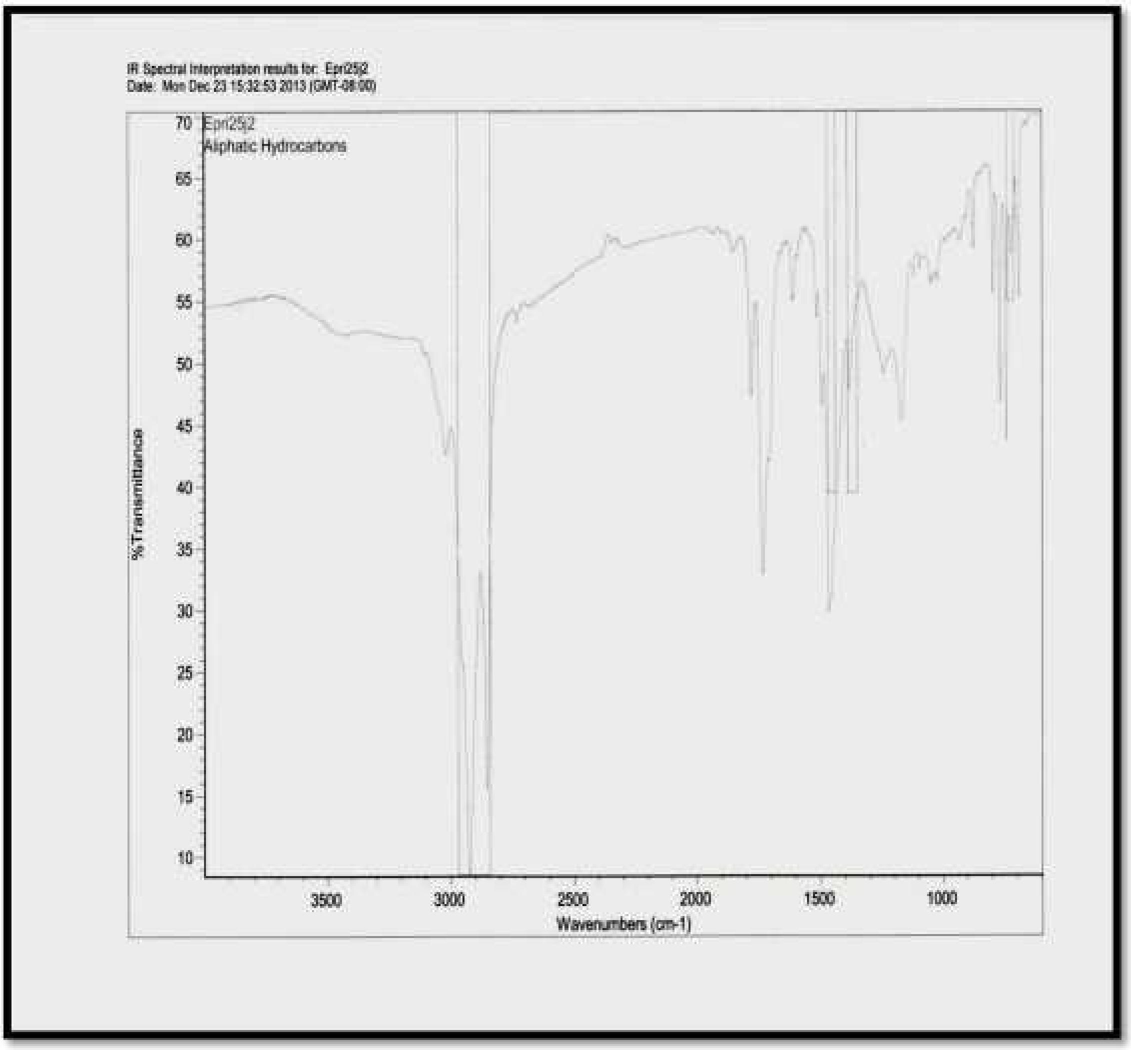

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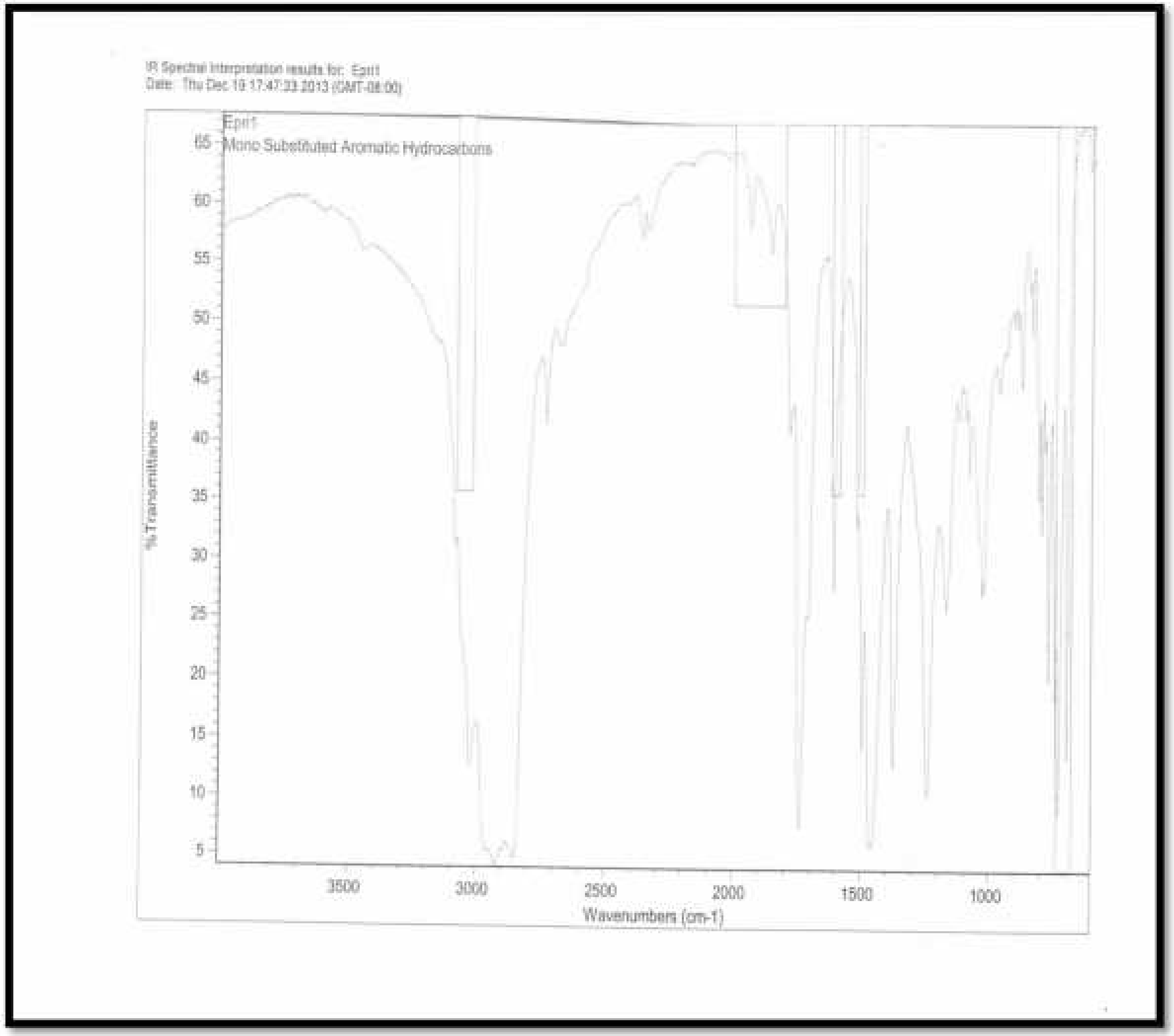

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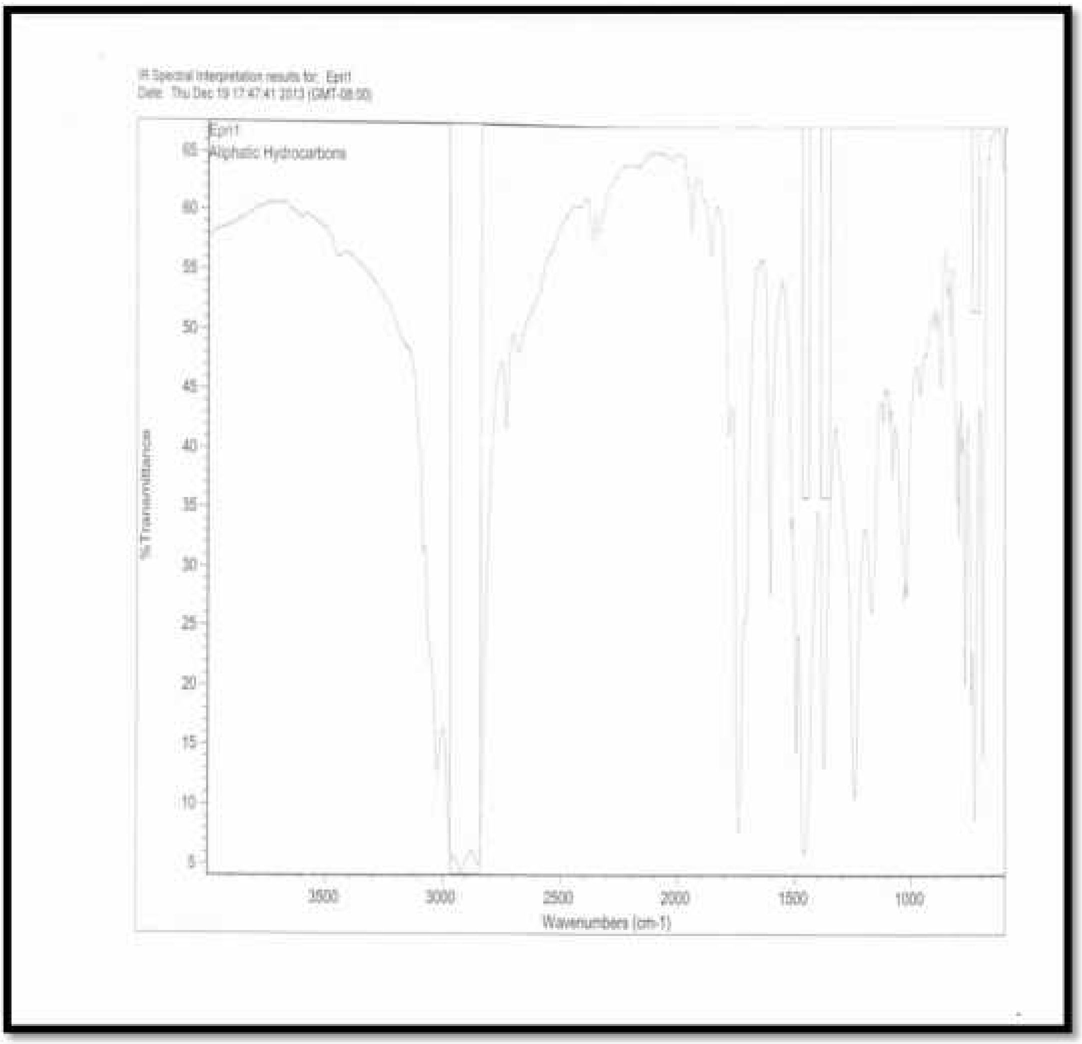

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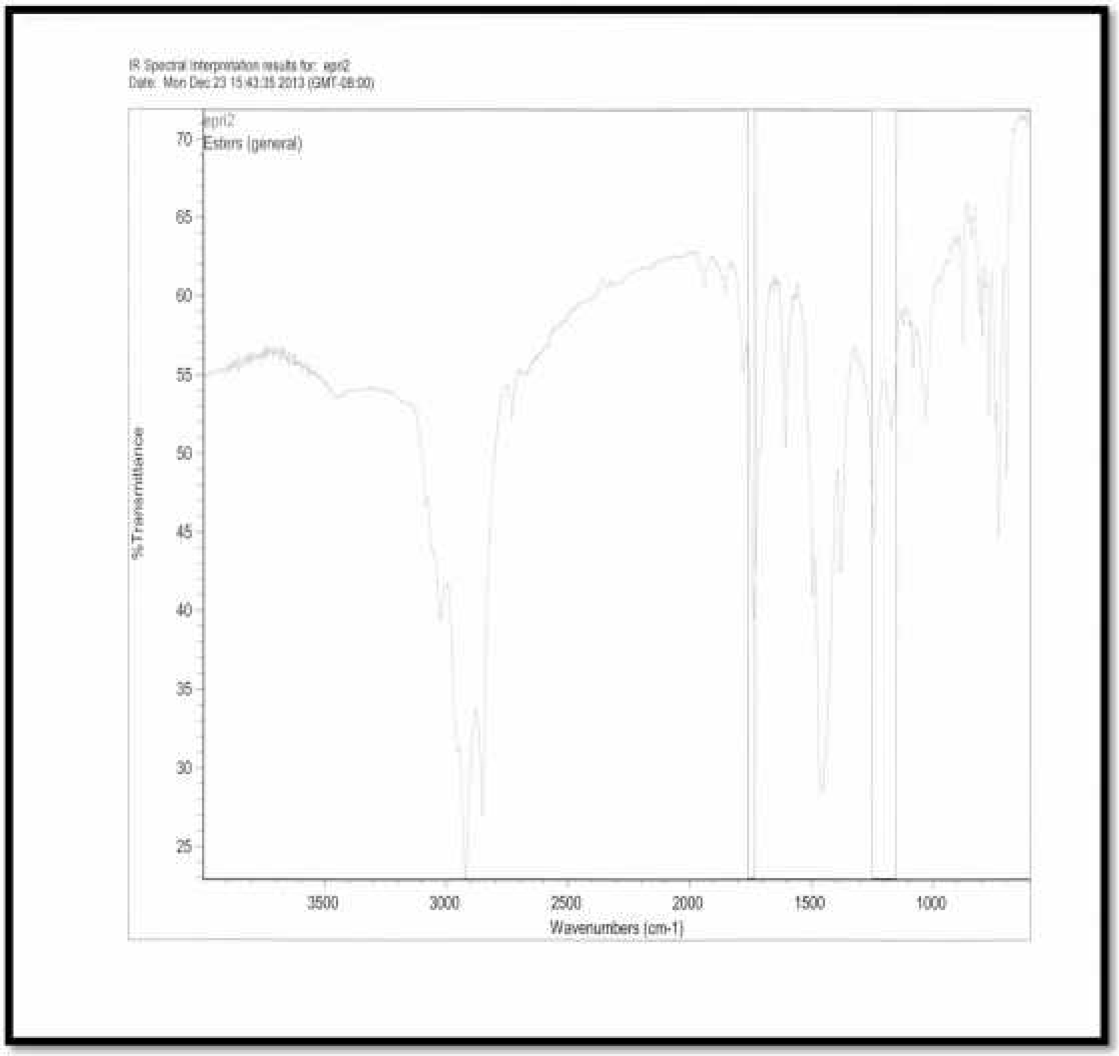

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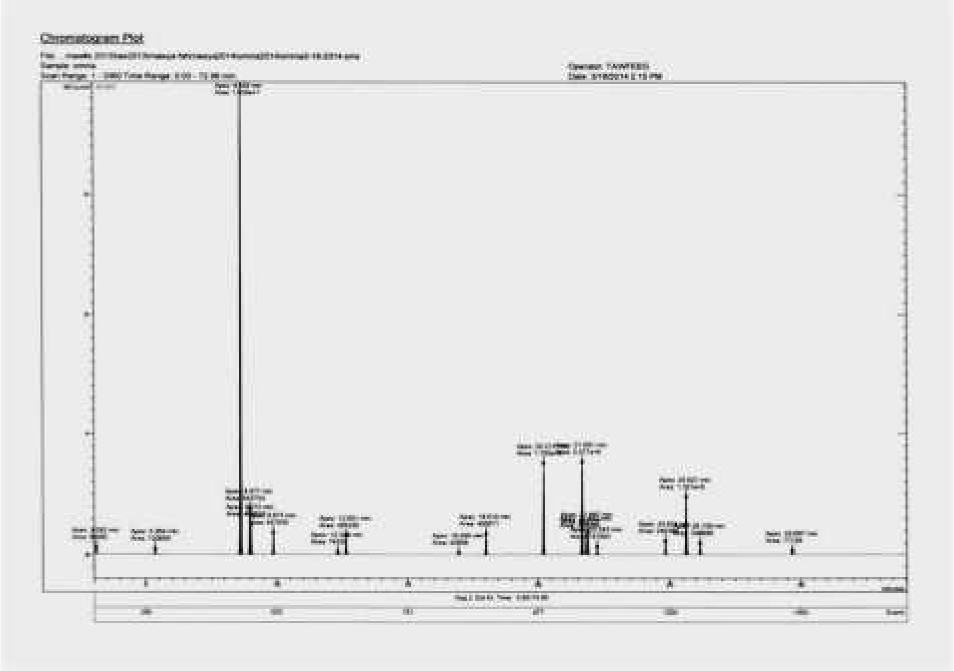
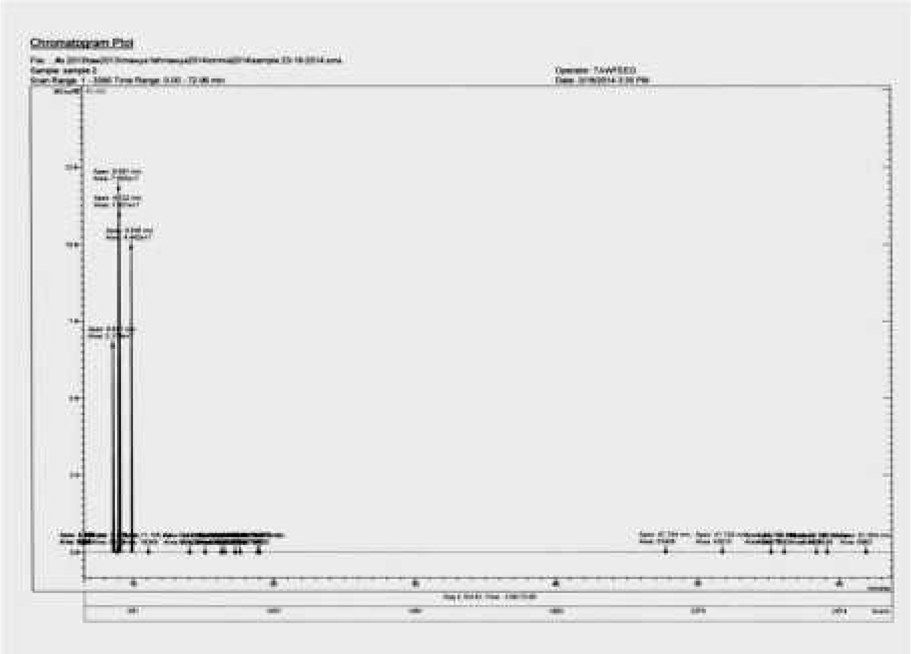


Chromatogram of China PPD



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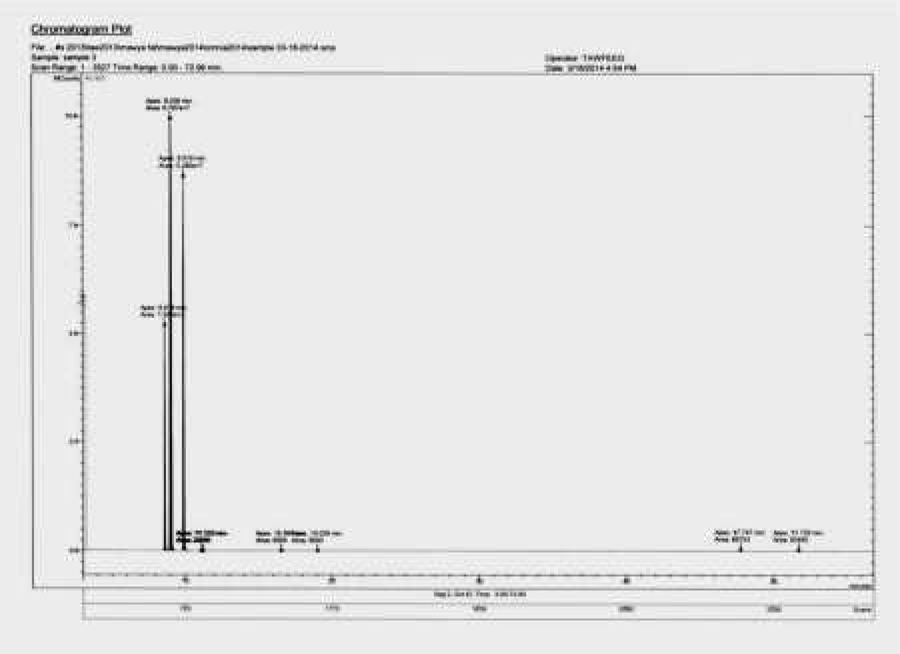

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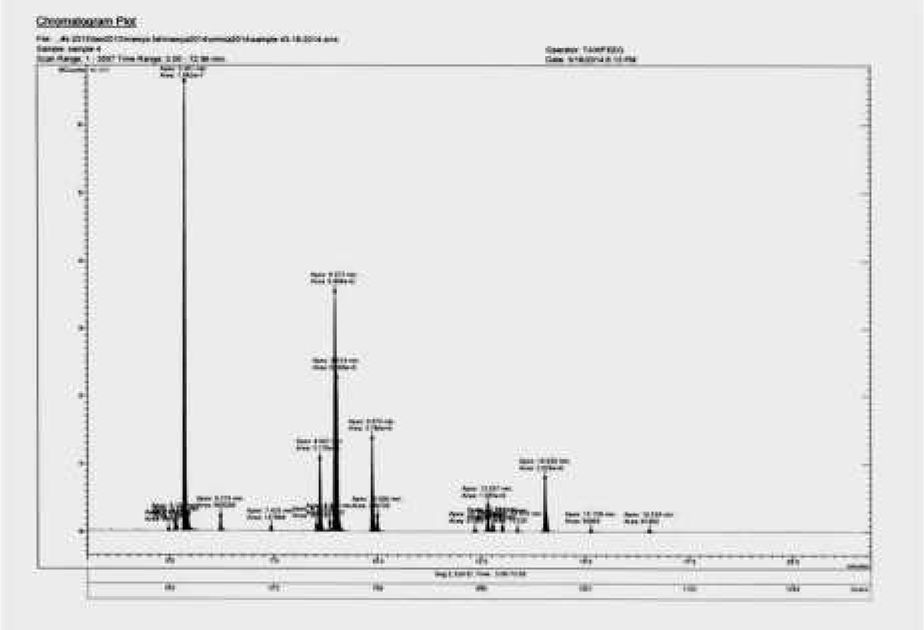

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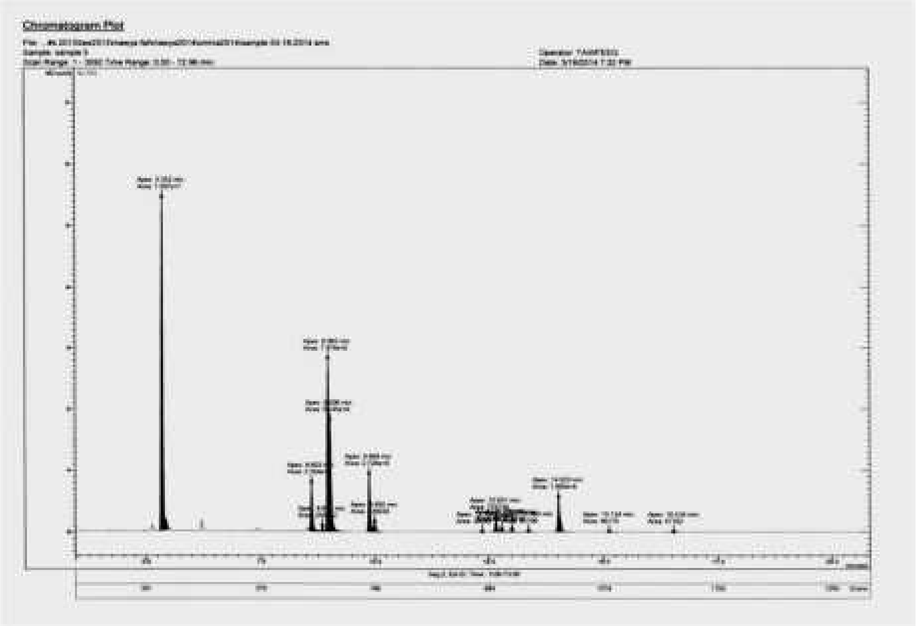

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