ANALYSIS OF WAX APPEARANCE AND DISSOLUTION TEMPERATURES FOR LIGHT AND HEAVY CRUDE OILS

BY

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14569

Dissertation submitted in partial fulfilment of
the requirements for the
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

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(DR Aliyu Adebayor Sulaimon)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHAMMAD SHAHRULL IKHMAL BIN NORDIN

ABSTRACT

Analysis of wax appearance temperature and wax dissolution temperature for light and heavy crude oils is to have an experimental research regarding the properties of light and heavy crude oils depending on some parameter which is wax appearance temperature and wax dissolution temperature. Based on the real industry, the crude oils naturally will be solid in certain temperature due to the circumferences and surrounding factor. The purpose of this research is to analyse the crude oils properties and hysteresis process. Therefore, the research will conducted by using rheometer.

The samples of crude oils been request form PRSB, Bangi and PPM, Melaka. There are two types of light crude oils and three types of heavy crude oils. The equipment been used to complete this research is rheometer. Rheometer been used in laboratory located at block 20 is Discover Hybrid Rheometer (DHR) and been assisted by graduated assistant at block 20. DHR could show the pattern of the curve according to the parameter been setup and the WAT and WDT could be identify at the moment the flow curve change.

The range of the WAT and WDT for light crude oils are 32 ^{o}C to 36 ^{o}C and 36 ^{o}C to 40 ^{o}C while the heavy crude oils are 5 ^{o}C to 24 ^{o}C and 15 ^{o}C to 32 ^{o}C. There was difference range between light and heavy crude oils it might because of composition of wax in the crude oils. It’s also may be affected by the density of the crude oils.

As the conclusion, the objective been achieved. The best crude oils is lower WDT and WAT which is heavy crude oils 2 5.35 ^{o}C and 15.98 ^{o}C based on seabed condition in Malaysia which 15 ^{o}C.

ACKNOWLEDGEMENT

I would like to express my gratitude and great appreciation to those who help me a lot in completing this report. A special thanks to my Supervisor, Dr. Aliyu Adebayor Sulaimon, Senior Lecturer of Department of Petroleum Engineering, who have given his full effort in guiding me in achieving the goal as well as his encouragement to keep up my motivation and performances in completing this Final Year Project.

I also would like to acknowledge with much appreciation to the staffs or laboratory technicians at Block 15 and Block 20 for their cooperation and some guidance to me on how to use and handle equipment.

Besides, I would also like to thank to my lab assistant or GA, Madam Shahaidah, whose guiding me and also help me a lot in completing this project and not to be forgotten Dr Azureain from Mechanical Department who has assist me in this project and give the permission to use her lab. Last but not least, I would like to pledge my gratitude and deep obligation to my parents, who continually convincing the spirit. This dissertation would not have been possible without guidance and persistent help from all those special persons.

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INTRODUCTION

1.1 Background

Most of the crude oil especially in Malaysia contain of wax and the crude oil naturally become waxy when the hydrocarbon chain bundled together. So it show that the crude oil have their specific chemical properties. This research is related to analysis of wax appearance and dissolution temperatures for light and heavy crude oils. The process that related to this research are cooling rate and heating rate or known as endothermic and exothermic condition.

Crude oils and natural gas fluids are composed of nearly 100% hydrocarbons. A series of naturally occurring hydrocarbons with the chemical formula CnH2n+2 are known as paraffin (James Outlaw).The molecular structure for paraffin is long chain molecule of hydrocarbon particles and in certain condition, the molecular structure is cyclic or form branched. The theory is, as the structure more complex, the wax contain is higher and easily to crystallize (Kamaruddin 2013).

Briefly, wax appearance temperature is a condition where the crude oils continues in cooling rate and form the solid crystallization wax structure, hence it also known as cloud point (Peng Ye,2011). However, wax dissolution temperature is a temperature where the wax crystal completely change the phase from solid to liquid.

During the process of WAT and WDT, there undergo the thermal process which are endothermic and exothermic. Endothermic is a process been done by absorbs the energy from surrounding in form of heat. The energy been absorbs is requires to break the bond between the particles. Thus, the exothermic is opposite process of endothermic which release the energy to the surrounding in form of heat and forming the bond. (http://www.kentchemistry.com/links/Matter/EndoExo.htm)

1.2 **Problem Statement**

Most of the crude oils consists of wax substantial fraction which known as most waxy solid deposits from crude oils and according to Bhat and Mehrotra, (2004) paraffin waxes are mixtures which are about 40 to 60 percent of n-alkanes and constitute inside crude oils deposits. The deposition of n-paraffin commonly occur along the pipe walls when the temperature of the crude oils falls below WAT and it may be cause by the wax content, flowrates and fluid viscosity(Thomas 2006).Naim(2013) said standard production environment condition is 15 ^{o}C. So, the researcher need to determinate the WAT and WDT and it will be the good information for industry to prevent or reduce the WAT and WDT by using inhibitor The researcher have to find out that hysteresis occur during the experiment. Currently, industry needs the hysteresis process to reduce the cost and time so that the process can be reversible. Nevertheless, the researcher have to figure out the characteristics by used rheometer which is correlate with wax appearance temperature (WAT) and wax dissolution temperature (WDT).

1.3 **Objective**

The objectives of the project are:

- To measure the WAT and WDT of crude oils using rheometer.
- To investigate the phenomena of hysteresis, if any.

1.4 **Scope of Study**

This research will use rheometer to determine the WAT and WDT for light crude oils and heavy crude oils and to analyze the effect of hysteresis, if any. Below are the parameter to be analyze:

1. Temperature of the crude oils
2. Viscosity of the crude oils
3. Change of physical properties

CHAPTER 2

LITERITURE REVIEW

2.1 Pour Point Depressant

Crude oils and gas condensate contain waxy components that called as paraffin where the concentration, structure and molecular weight vary from one hydrocarbon source to another (Farah, 2013). Both of them present may be constituents of the heavier polar fraction of oil known as asphaltenes. Paraffin have only limited solubility in the crude unless the temperature of the oil above the cloud point or wax appearance temperature (WAT). WAT is the temperature at which paraffin first begins to crystalize. Paraffin is assumed to be in solution under the reservoir conditions however if this condition are altered, the paraffin can precipitate from the crude and adhere to the surfaces of the system.

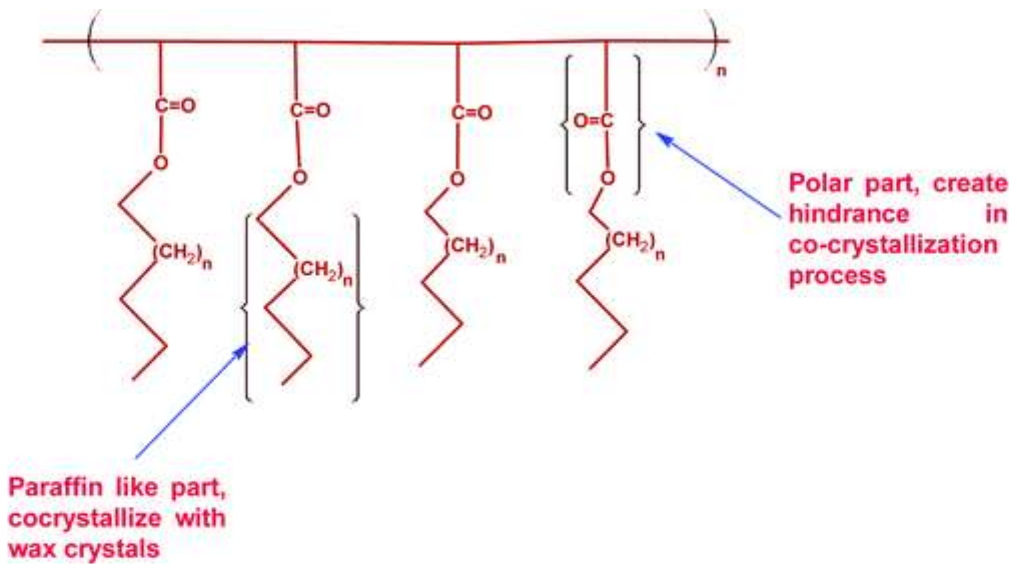

Figure 2.1: Paraffin Crystallization (paraffindepositionandcontrol.wikispaces.com)

There are several factors that influence the precipitation of paraffin from crude oils which are the temperature of the produced fluid falls as it comes up the well bore and into the processing facilities (Elijah 2006). Paraffin may begin to come out of solution and form deposits on the tubing and pipe walls. Moreover, the composition of the hydrocarbon liquid changes either by mixing with other stream and still precipitation could occur.

Furthermore, foreign substances in the crude oils such as silt, salts and corrosion by products which are iron sulphide and iron oxide serve as a nuclei around and it may cause the crystallization of paraffin (Hidayah 2013). When this phenomena continues occur, it may cause the big problem to extract the crude oil. The surface of tubing or flowlines may cause the precipitation.

Thus, paraffin can be restricted production with deposits on the formation face, tubing and flowlines. It can cause pumps and related equipment to stick, resulting in both a loss of production and costly well workers.

2.1.1 **<u>Live Versus Dead Crude Oils</u>**

All crude oil contain paraffin component. Paraffin naturally occurring organic molecules composed of carbon and hydrogen. They have the general formula C_nH_{2n+2} and contain chains of carbon atoms bonded to hydrogen atoms. Crude oils contain three types of paraffin (Wang et al. 1999), which are liquid and not likely to cause deposition problem which are low molecular weight straight chain, branched chain and cyclic paraffin. The melting point will increase when the carbon number increase and the solubility will decrease as the increase number of carbon. Moreover, branched chain can have major influence on the melting point of paraffin.

Above are all the characteristic of live crude oils and supposedly dead crude oils comes after live crude oils and it can be called as the live crude oils have come to the expired period. The different between those two was the timeline of the crude oils which is known as ageing factor. Based on Webb, Lager and Black, (2008) all the crude oil will be face the ageing period within two to three weeks after the crude oils produce from reservoir.

According to Al firdaus (2014), he said that live crude oils will age within a week if the crude oils have been exposed to surrounding without a proper management. Different area of crude oils will give the different properties, so that give crude oils and crude oils might be give different properties or might be slightly same. Based on the research has been conduct by Harnmami and Raine, (1999), it prove the hypothesis.

2.2 <u>**Wax Appearance Temperature and Wax Dissolution Temperature**</u>

Wax appearance temperature (WAT) is known as cloud point (Peng Ye 2011). WAT is the deposition of paraffin will commonly occur along the pipe walls when the temperature falls for the certain temperature Golczynski, (2006). In fact, the solubility of paraffin in crude is limited depend on the temperature of the oils. The solubility of the paraffin will get higher as the temperature is above the "cloud point". WAT can be defined as the temperature at which paraffin begins to crystallize and expend in the crude oils Alfirdaus, (2014). Under the reservoir conditions, paraffin is assumed to be in solution and can change by precipitating from the crude and adhere to the surfaces of the system. The precipitation will form and deposited along the wall of pipes when the fluids or the crude oils reach the WAT (Karen, 2000).

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2.3 **Light Crude Oils and Heavy Crude Oils**

Generally, light crude oil contain of lower characteristic compare to heavy crude oils. Most of crude oils in Malaysia is light or slightly intermediate crude oils and it can be recognised through the physical properties. The table below show the physical properties of crude oils

Table 2.1: Comparison of physical properties of heavy and light crude oils (Exxon)

Physical properties	Type of crude oils	
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2.4 **Mechanism of Wax Deposition**

Paraffin are inert and will not react with other components, they retain their physical properties regardless of the chemicals mixture of the crude in which they occur. As a consequence, the temperature at which paraffin crystalize is not affected by outside chemicals influences.

Furthermore, we can determine whether the paraffin will crystalize or not are physical condition to which it is exposed. The physical condition with the greatest influence on paraffin is temperature. If the crude becomes cool enough to allow the paraffin crystalize, there is nothing which can be done to stop the growth of the crystals. The best that can be hoped for is to modify the form of the crystals so when coming out of the solution from the crude they do not gather and collected and are therefore less likely to deposit on surfaces.

Within under normal conditions, most of the crude oils pipelines operate under a turbulent flow of regime. In this type of flow there is a turbulent core and laminar boundary layer adjacent to the pipe wall. There are two mechanisms that govern the transportation of dissolved or precipitated wax from the crude to the pipe wall that molecular diffusion and shear dispersion. Molecular diffusion is responsible in transportation of the wax dissolved: meanwhile shear dispersion is responsible in transportation of the precipitated wax.

2.4.1 **Molecular Diffusion**

At the site plant, the oil will be cooling down and molecular diffusion will occur as soon as the pipe wall temperature is reaches the WAT. Molecular diffusion can be defined as the thermal motion of all particles at any temperature above zero definitely. Often, the rate of this movement is a function of temperature, viscosity of the fluid and the size of the particles. After the occurring of the molecular diffusion, there is different of wax concentration between a higher level of dissolved wax in the turbulent core of the oil and the lower level of wax that are still in the solution at the pipe wall (Wikipedia Article: Oil Well).

This phenomenon causes the dissolved wax to diffuse towards the pipe wall where it is precipitated (Ring, 1994). In fact, a deposition of wax only occurs when the oil is being cooled. If the temperature of the pipe wall is higher than the temperature of the oil, the molecular diffusion process can be reversed and the waxy residues that precipitated on the pipe wall can be re-dissolved.

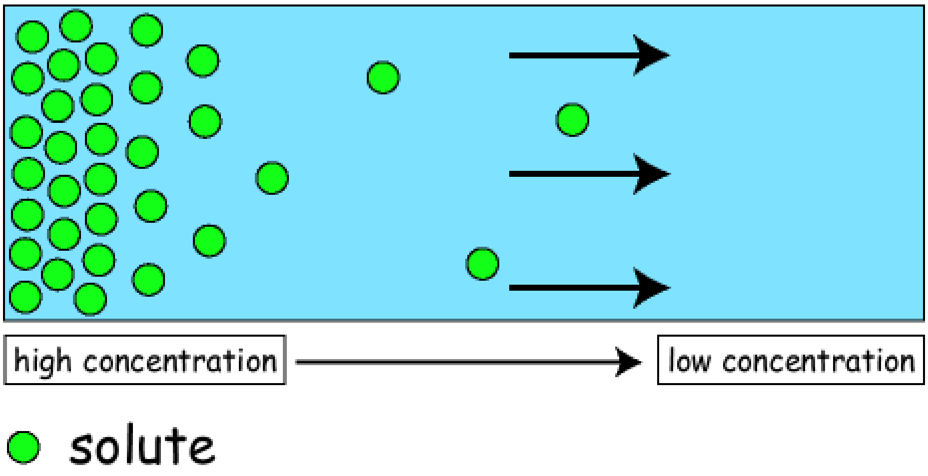


Figure 2.2: The Solute Transportation (forums.studentdoctor.net)

2.4.2 **Shear Dispersion**

Generally, wax crystals already exist in the flowing crude oil and tend to flow together with the crude oil at the average speed of the crude oil. At the region which is close to the pipe wall, lateral movement of the particles of wax that caused by shearing of the liquid occurred and called as shear dispersion. As a result, the precipitated wax will be transported from the turbulent core to the pipe wall surface either deposit directly onto the wall surface or link with wax that already deposited through molecular diffusion process.

There are several factors that affect shear dispersion that are shear rate at the pipe wall, the precipitated wax quantity and also the shape and size of wax crystal. Shear dispersion mechanisms can be significant if the precipitated wax content is high in the turbulent core and when the bulk oil temperatures is below the WAT. Indeed the increasing of the shear rate tends to encourage more lateral movement of wax particles to be deposited at the pipe wall, but a high shear force also would encourage the deposited wax crystals to be deposited on the pipe wall.

Therefore, molecular diffusion process will dominate at higher temperatures, meanwhile shear dispersion process will dominate at lower temperature and these both processes are likely to proceed simultaneously.

2.5 **Treatment Process**

Wax deposition is a common problem that most of the operator would face in the industries. Many cases that caused by this problem had involve a huge amount of money as it is not been treated at the early stages of the problems development. Due to this consideration, there are several options that have been developed in order to overcome this problem that are by pipe insulating, dilution with low wax content crude, pigging, physical removing and also chemical additives. Sometimes, combinations of two or more of the options will be necessary depends on the problems occurred situations.

2.5.1 **Melting the Deposits**

Paraffin deposits can be liquefied through the application of heat that applied continuously to a system that using line or down hole heaters. In this method, heat is most commonly applied using hot oil truck and this process is known as hot oiling where liquids such as hot crude or hot water are pumped down into the well to remove wax deposits (Petrowiki). Based on this application, hot oiling process is not just concentrating in removing of the paraffin depositions in the wellbore solely but also in tubing, flow lines and tanks. This method is relevant as it have some advantages as it is easy to apply, low cost and also able to obtain results immediately.

2.5.2 **Scraping**

The present of pressure is the factor in the scrapping of a we1l. Hot oiling process cannot be used in a high pressure well but it can be a different scenario if a well must be shut in to scrape, a hot oiling process during scraping operations will be preferred in many cases. For the time being, there are two types of scraping operations that are periodic scraping which is conducted according to the schedule planned and also continuous scraping.

In the periodic scraping operations, scraping physically removes paraffin without melting it first and this mechanism is able to avoid re-deposition of wax, but it may cause plugging .Moreover, the costs required in this operations is about same as hot oiling process and it is well established as this technique have been used in many areas.

Meanwhile, continuous scraping is operates while the well is producing, thus keeps production levels high. Besides, continuous scraping can be used for paraffin removal form a high pressure well. In a gas lift well, this process can be applied with the continuous injection of chemicals to keep the wax deposits soft and easier to be removed.

Although scraping method have many advantages, this operation also have several disadvantages that cause it is not been chosen in certain critical conditions as it is not as efficient as hot oiling process. Besides, the minimum charges for periodic scraping can be uneconomical for isolated wells. Scraping can cause deposited paraffin to be removed from the wall of the wellbore or pipeline in scratch form with different sizes. Large particle of paraffin may settle in flow lines and finally can cause blockage. Apart from that, directly and indirectly contact between metal and metal could roughens the tubing wall and this will encourage the deposition of wax.

2.5.3 **Chemical Treatment**

In addition to the mechanical applications that are hot oiling and scraping in order to control the deposition of wax, there are several approaches that involving the application of chemicals that may prove more efficient and beneficial. Paraffin control by using chemicals can be classified as solvents, dispersants and also wax crystal modifiers (WCM) (Ann, nil).

2.5.3.1 **Solvents**

By definition, solvent is the component of a solution that present in the greatest amount and it is act as the substance in which the solute is dissolve. Based on the current mechanism, solvent will remove paraffin deposits by dissolving that paraffin. In fact, there are many types of solvents that have been used in the past include condensate, casing head gasoline, pentane, light gas oil, xylene, toluene, carbon tetrachloride, carbon disulphide and terpenes (Kamaruddin, 2013).

Recently, the most common types of solvent that used were chlorinated hydrocarbons that are carbon tetrachloride, trichloroethylene and also perchloroethylene that are high density, non-flammable and the most important is inexpensive. However, the crude oil that treated with these chlorinated hydrocarbons may cause problems in the refinery stage. Due to these severe problems, the applications of these chemicals type were discontinued.

It should be recognized that the mechanisms used by hot oiling process in order to removes paraffin deposits is totally different from the mechanism of solvent does. In hot oiling process, heat is introduced into the tubular in order to melt the paraffin so that when the paraffin converted into liquids form, it will be carried out with the produced oil. In fact, hot oiling able to remove the lower melting paraffin easier that the high melting paraffin as it is required a great deal of heat to be applied. It will be worst if the high melting paraffin is not completely removed by hot oiling process, it will accumulate and slowly reduce the internal diameter of the pipeline or tubular until it is totally block the path and finally the production is retarded.

Solvent will attacks the wax crystal from the outside in and a good solvent will dissolve paraffin molecules off the surface of the tubular regardless of the size and melting point of the molecules. Thus, this situation will require much less energy than is needed to melt the crystal for hot oiling process. The effectiveness of the solvent is affected by temperature and agitation where the solvent will be more effective as the temperature and agitation is increased.

In the application of solvent, there is not necessary to be coupled with heat application and the extreme agitation, but both heat and agitation able to speed up the process of dissolving. In fact, hot solvents will dissolve paraffin faster than cold solvents and the energy requirement also still lower than energy required for hot oiling.

Consumption volume of solvent is very important in order to ensure the dissolution of the paraffin is complete. Consequently, if the recommended dosage of the chemicals is too high, this may be economically unattractive to the customers or clients. Thus, in order to make solvent usage is economical, the finding of the optimum dosage of the chemicals that is believed as the starting point where the deposition can occur is necessary and then allowed to soak several hours to dissolve the deposit. In addition, solvents may also be effective in removing blockage in flow line depends on the degree of blockage.

If the flow lines are totally blocked, solvent will dissolve paraffin off the face of the deposit. Meanwhile, if the flow lines are partially blocked, solvents are able to penetrate the blockage and eventually dissolve the deposits. Heat application again can be a good catalyst for the solvent to be effective.

2.5.3.2 **Dispersants**

Dispersant can be defined as a liquid or gas that is added to a mixture to promote dispersion or to maintain dispersed particles in suspension. In fact, solvents will lose effectiveness if the water present with the crude is too much. There is different situation with dispersant as it is more effective when more than a 20 % of water cut is present. By mean of application, dispersants perform a different function than solvents as it is act as the carrier fluid that removes the paraffin.

Dispersant will not act to remove paraffin when it is injected on a continuous basis but used to prevent the paraffin deposition in systems that have been cleaned mechanically, thermal or chemical means. Dispersant will work by coating the paraffin crystal and the metal surfaces. Thus, this scenario will cause the paraffin crystals to repel each other. This approach does not prevent the paraffin crystal from forming but it is prevent the solid deposition to occur and make it moving with the crude.

2.5.3.3 **Wax Crystal Modifier (WCM)**

A wax crystal modifier is a substance that used to prevent paraffin deposition by co-crystalizing and modifying the wax crystal (Petrowiki). Wax crystal modifiers are usually polymeric materials. This approach will change the shape of the paraffin crystal so that it does not form needles shape and no network as it comes out of solution and will move with the liquid portion of the crude. In general, the number, size and shape of wax crystals determine the tendency to increase crude viscosity, network into a gel and also form deposit.

There are four common patterns of the paraffin crystal growth:

1. Needles shape - able to form network and trap the crude in it.

2. Malcrystals shape - poorly shaped crystals as it is cannot form network.

3. Plates - possible to curl on the edges to form hollow needles that able to form network.

4. Microcrystalline waxes - can be found in the residues in refinery stills and impossible to be encountered in the crude wax deposits or precipitation.

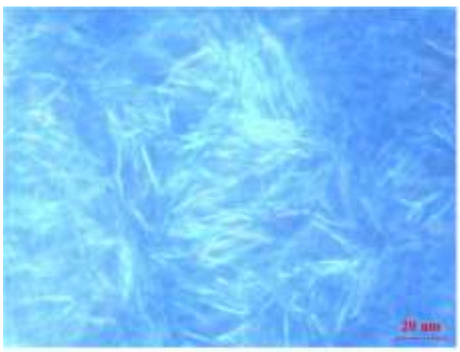


Figure 2.3: Needles Wax Crystal (openi.nlm.nih.gov)

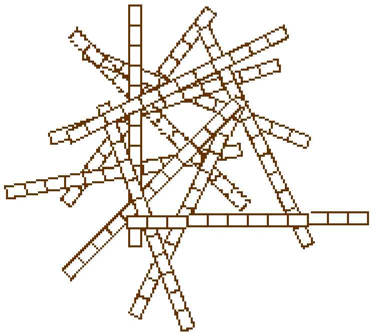


Figure 2.4: Microcrystalline (openi.nlm.nih.gov)

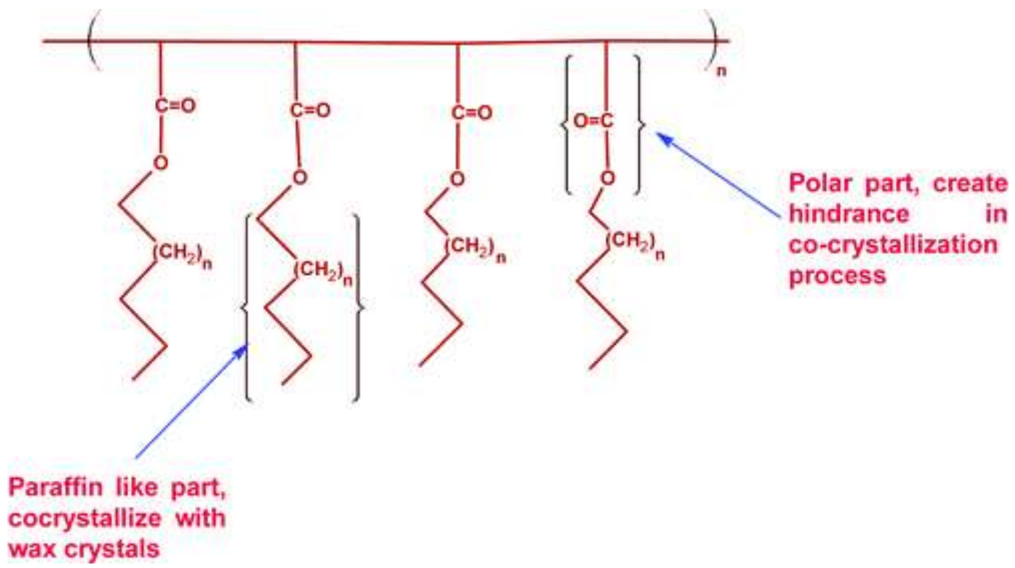
Wax crystals grow by addition of individual paraffin molecules to the edge of the crystal nucleus. Wax crystals modifiers have a structure that in part is similar to that or wax. Therefore, they co-crystalize with the wax by taking the place of a paraffin molecule on the edge of the growing crystal (Al-Firdaus, 2013). The balance of the wax crystals modifier interferes with the proper molecular registration of new paraffin molecule and growth terminates or occurs in a different direction so that a well-formed needle does not grow. Then, the malcrystals which form will remain suspended in the crude and will pump along with the liquid portion of the crude oils.

CHAPTER 2

LITERITURE REVIEW

2.1 Pour Point Depressant

Crude oils and gas condensate contain waxy components that called as paraffin where the concentration, structure and molecular weight vary from one hydrocarbon source to another (Farah, 2013). Both of them present may be constituents of the heavier polar fraction of oil known as asphaltenes. Paraffin have only limited solubility in the crude unless the temperature of the oil above the cloud point or wax appearance temperature (WAT). WAT is the temperature at which paraffin first begins to crystalize. Paraffin is assumed to be in solution under the reservoir conditions however if this condition are altered, the paraffin can precipitate from the crude and adhere to the surfaces of the system.



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2.4 **Mechanism of Wax Deposition**

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At the site plant, the oil will be cooling down and molecular diffusion will occur as soon as the pipe wall temperature is reaches the WAT. Molecular diffusion can be defined as the thermal motion of all particles at any temperature above zero definitely. Often, the rate of this movement is a function of temperature, viscosity of the fluid and the size of the particles. After the occurring of the molecular diffusion, there is different of wax concentration between a higher level of dissolved wax in the turbulent core of the oil and the lower level of wax that are still in the solution at the pipe wall (Wikipedia Article: Oil Well).

This phenomenon causes the dissolved wax to diffuse towards the pipe wall where it is precipitated (Ring, 1994). In fact, a deposition of wax only occurs when the oil is being cooled. If the temperature of the pipe wall is higher than the temperature of the oil, the molecular diffusion process can be reversed and the waxy residues that precipitated on the pipe wall can be re-dissolved.

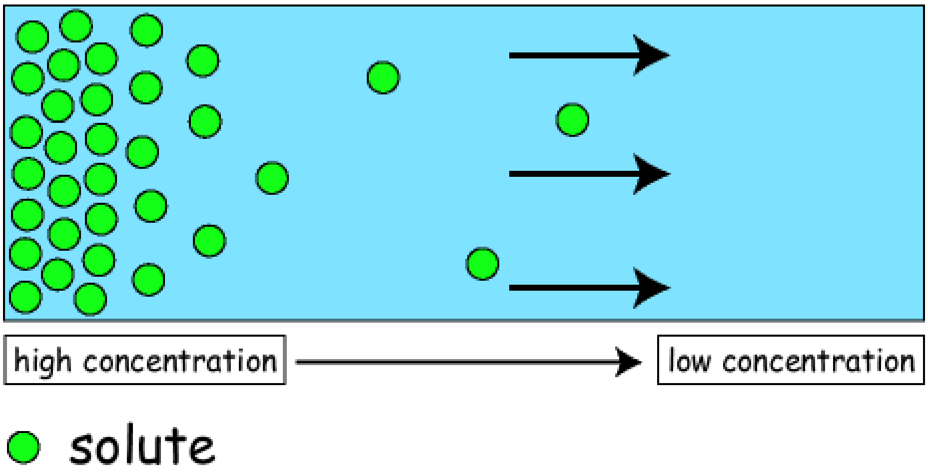

Figure 2.2: The Solute Transportation (forums.studentdoctor.net)

2.4.2 **Shear Dispersion**

Generally, wax crystals already exist in the flowing crude oil and tend to flow together with the crude oil at the average speed of the crude oil. At the region which is close to the pipe wall, lateral movement of the particles of wax that caused by shearing of the liquid occurred and called as shear dispersion. As a result, the precipitated wax will be transported from the turbulent core to the pipe wall surface either deposit directly onto the wall surface or link with wax that already deposited through molecular diffusion process.

There are several factors that affect shear dispersion that are shear rate at the pipe wall, the precipitated wax quantity and also the shape and size of wax crystal. Shear dispersion mechanisms can be significant if the precipitated wax content is high in the turbulent core and when the bulk oil temperatures is below the WAT. Indeed the increasing of the shear rate tends to encourage more lateral movement of wax particles to be deposited at the pipe wall, but a high shear force also would encourage the deposited wax crystals to be deposited on the pipe wall.

Therefore, molecular diffusion process will dominate at higher temperatures, meanwhile shear dispersion process will dominate at lower temperature and these both processes are likely to proceed simultaneously.

2.5 **Treatment Process**

Wax deposition is a common problem that most of the operator would face in the industries. Many cases that caused by this problem had involve a huge amount of money as it is not been treated at the early stages of the problems development. Due to this consideration, there are several options that have been developed in order to overcome this problem that are by pipe insulating, dilution with low wax content crude, pigging, physical removing and also chemical additives. Sometimes, combinations of two or more of the options will be necessary depends on the problems occurred situations.

2.5.1 **Melting the Deposits**

Paraffin deposits can be liquefied through the application of heat that applied continuously to a system that using line or down hole heaters. In this method, heat is most commonly applied using hot oil truck and this process is known as hot oiling where liquids such as hot crude or hot water are pumped down into the well to remove wax deposits (Petrowiki). Based on this application, hot oiling process is not just concentrating in removing of the paraffin depositions in the wellbore solely but also in tubing, flow lines and tanks. This method is relevant as it have some advantages as it is easy to apply, low cost and also able to obtain results immediately.

2.5.2 **Scraping**

The present of pressure is the factor in the scrapping of a we1l. Hot oiling process cannot be used in a high pressure well but it can be a different scenario if a well must be shut in to scrape, a hot oiling process during scraping operations will be preferred in many cases. For the time being, there are two types of scraping operations that are periodic scraping which is conducted according to the schedule planned and also continuous scraping.

In the periodic scraping operations, scraping physically removes paraffin without melting it first and this mechanism is able to avoid re-deposition of wax, but it may cause plugging .Moreover, the costs required in this operations is about same as hot oiling process and it is well established as this technique have been used in many areas.

Meanwhile, continuous scraping is operates while the well is producing, thus keeps production levels high. Besides, continuous scraping can be used for paraffin removal form a high pressure well. In a gas lift well, this process can be applied with the continuous injection of chemicals to keep the wax deposits soft and easier to be removed.

Although scraping method have many advantages, this operation also have several disadvantages that cause it is not been chosen in certain critical conditions as it is not as efficient as hot oiling process. Besides, the minimum charges for periodic scraping can be uneconomical for isolated wells. Scraping can cause deposited paraffin to be removed from the wall of the wellbore or pipeline in scratch form with different sizes. Large particle of paraffin may settle in flow lines and finally can cause blockage. Apart from that, directly and indirectly contact between metal and metal could roughens the tubing wall and this will encourage the deposition of wax.

2.5.3 **Chemical Treatment**

In addition to the mechanical applications that are hot oiling and scraping in order to control the deposition of wax, there are several approaches that involving the application of chemicals that may prove more efficient and beneficial. Paraffin control by using chemicals can be classified as solvents, dispersants and also wax crystal modifiers (WCM) (Ann, nil).

2.5.3.1 **Solvents**

By definition, solvent is the component of a solution that present in the greatest amount and it is act as the substance in which the solute is dissolve. Based on the current mechanism, solvent will remove paraffin deposits by dissolving that paraffin. In fact, there are many types of solvents that have been used in the past include condensate, casing head gasoline, pentane, light gas oil, xylene, toluene, carbon tetrachloride, carbon disulphide and terpenes (Kamaruddin, 2013).

Recently, the most common types of solvent that used were chlorinated hydrocarbons that are carbon tetrachloride, trichloroethylene and also perchloroethylene that are high density, non-flammable and the most important is inexpensive. However, the crude oil that treated with these chlorinated hydrocarbons may cause problems in the refinery stage. Due to these severe problems, the applications of these chemicals type were discontinued.

It should be recognized that the mechanisms used by hot oiling process in order to removes paraffin deposits is totally different from the mechanism of solvent does. In hot oiling process, heat is introduced into the tubular in order to melt the paraffin so that when the paraffin converted into liquids form, it will be carried out with the produced oil. In fact, hot oiling able to remove the lower melting paraffin easier that the high melting paraffin as it is required a great deal of heat to be applied. It will be worst if the high melting paraffin is not completely removed by hot oiling process, it will accumulate and slowly reduce the internal diameter of the pipeline or tubular until it is totally block the path and finally the production is retarded.

Solvent will attacks the wax crystal from the outside in and a good solvent will dissolve paraffin molecules off the surface of the tubular regardless of the size and melting point of the molecules. Thus, this situation will require much less energy than is needed to melt the crystal for hot oiling process. The effectiveness of the solvent is affected by temperature and agitation where the solvent will be more effective as the temperature and agitation is increased.

In the application of solvent, there is not necessary to be coupled with heat application and the extreme agitation, but both heat and agitation able to speed up the process of dissolving. In fact, hot solvents will dissolve paraffin faster than cold solvents and the energy requirement also still lower than energy required for hot oiling.

Consumption volume of solvent is very important in order to ensure the dissolution of the paraffin is complete. Consequently, if the recommended dosage of the chemicals is too high, this may be economically unattractive to the customers or clients. Thus, in order to make solvent usage is economical, the finding of the optimum dosage of the chemicals that is believed as the starting point where the deposition can occur is necessary and then allowed to soak several hours to dissolve the deposit. In addition, solvents may also be effective in removing blockage in flow line depends on the degree of blockage.

If the flow lines are totally blocked, solvent will dissolve paraffin off the face of the deposit. Meanwhile, if the flow lines are partially blocked, solvents are able to penetrate the blockage and eventually dissolve the deposits. Heat application again can be a good catalyst for the solvent to be effective.

2.5.3.2 **Dispersants**

Dispersant can be defined as a liquid or gas that is added to a mixture to promote dispersion or to maintain dispersed particles in suspension. In fact, solvents will lose effectiveness if the water present with the crude is too much. There is different situation with dispersant as it is more effective when more than a 20 % of water cut is present. By mean of application, dispersants perform a different function than solvents as it is act as the carrier fluid that removes the paraffin.

Dispersant will not act to remove paraffin when it is injected on a continuous basis but used to prevent the paraffin deposition in systems that have been cleaned mechanically, thermal or chemical means. Dispersant will work by coating the paraffin crystal and the metal surfaces. Thus, this scenario will cause the paraffin crystals to repel each other. This approach does not prevent the paraffin crystal from forming but it is prevent the solid deposition to occur and make it moving with the crude.

2.5.3.3 **<u>Wax Crystal Modifier (WCM)</u>**

A wax crystal modifier is a substance that used to prevent paraffin deposition by co-crystalizing and modifying the wax crystal (Petrowiki). Wax crystal modifiers are usually polymeric materials. This approach will change the shape of the paraffin crystal so that it does not form needles shape and no network as it comes out of solution and will move with the liquid portion of the crude. In general, the number, size and shape of wax crystals determine the tendency to increase crude viscosity, network into a gel and also form deposit.

There are four common patterns of the paraffin crystal growth:

1. Needles shape - able to form network and trap the crude in it.

2. Malcrystals shape - poorly shaped crystals as it is cannot form network.

3. Plates - possible to curl on the edges to form hollow needles that able to form network.

4. Microcrystalline waxes - can be found in the residues in refinery stills and impossible to be encountered in the crude wax deposits or precipitation.

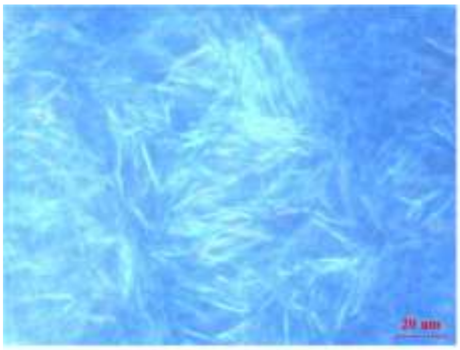

Figure 2.3: Needles Wax Crystal (openi.nlm.nih.gov)

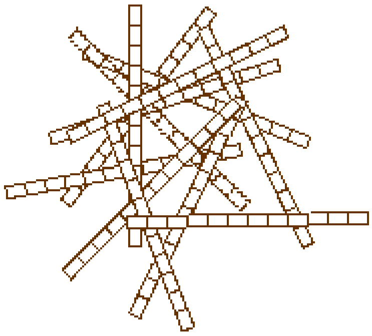

Figure 2.4: Microcrystalline (openi.nlm.nih.gov)

Wax crystals grow by addition of individual paraffin molecules to the edge of the crystal nucleus. Wax crystals modifiers have a structure that in part is similar to that or wax. Therefore, they co-crystalize with the wax by taking the place of a paraffin molecule on the edge of the growing crystal (Al-Firdaus, 2013). The balance of the wax crystals modifier interferes with the proper molecular registration of new paraffin molecule and growth terminates or occurs in a different direction so that a well-formed needle does not grow. Then, the malcrystals which form will remain suspended in the crude and will pump along with the liquid portion of the crude oils.

CHAPTER 4

RESULT AND DISCUSSION

4.1 **Overview**

In this chapter, the researcher would explain regarding the properties of the crude oil such as API^o .Then, the researcher will explained details the analysis of the result and data obtained and the hysteresis phenomena.

4.2 **Properties of Crude Oils**

The properties of crude oils have been provided by the PRSB and PPM been shown at table 4.0. Based on the table, the researcher could distinguish the crude oils either it was light crude oils or heavy crude oils. As Exxon website been reference, heavy crude oils should have 20 API^o and below while light crude oil 35 API^o and above. So the crude oils been divided into their categories either light or heavy crude oils as shown.

By knowing the categories or types of the crude oils, the researcher could predict that the viscosity, density and specific gravity. Theoretically, the properties been mentioned before should be high for heavy crude oils and low for the light crude oils as be wrote in literature review.

In the real case, the viscosity, density and specific gravity of the crude oils might be change due of the environment or surrounding factors. The factors could affect the changes are changes of pressure, lithology, consists of foreign particles such as silt, mud and others.

Table 4.0: API° Properties of Crude Oils

Type of crude oils	**API°**
Light Crude Oil 1	45.00
Light Crude Oil 2	47.00
Heavy Crude Oil 1	19.00
Heavy Crude Oil 2	15.00
Heavy Crude Oil 3	17.00

4.3 **Results**

Below are the tables of temperature and viscosity data for respective crude oils.

Table 4.1: Temperature and Viscosity Data for Light Crude Oil 1

LIGHT CRUDE OIL 1					
Cooling rate Temperature ^{0}C	Viscosity cp x 10^{3}	WAT ^{0}C	Heating rate Temperature ^{0}C	Viscosity cp x 10^{3}	WDT ^{0}C
-16.90	12731.40	36.04	-15.00	31664.80	39.98
-16.85	13856.70		-17.69	28085.90	
-17.14	14836.90		-17.69	21752.80	
-17.44	16355.30		-17.57	19138.81	
-17.85	18787.30		-17.47	18486.82	
-18.15	21248.60		-16.05	17223.08	
-15.99	18772.60		-12.01	14666.94	
-11.95	12469.50		-8.02	10010.00	
-7.99	8119.95		-4.01	6034.23	
-4.00	4999.80		-0.06	2537.63	
0.02	3067.02		4.02	1623.04	
4.02	1784.21		7.98	708.45	
8.01	971.06		11.97	333.24	
12.0	330.23		15.97	145.87	
16.00	70.76		19.97	50.56	
20.01	15.56		24.00	20.55	
24.04	6.33		27.98	7.39	
28.01	3.03		32.07	3.23	
31.99	1.34		36.03	0.865	
36.04	0.02		39.98	0.03	

Table 4.2: Temperature and Viscosity Data for Light Crude Oil 2

LIGHT CRUDE OIL 2					
Cooling rate Temperature ^0C	Viscosity cp x 10^3	WAT ^0C	Heating rate Temperature ^0C	Viscosity cp x 10^3	WDT ^0C
-27.35	1835.42	32.20	-11.63	1623.04	36.97
-24.57	1518.42		-14.02	1607.11	
-21.79	1359.55		-11.04	1551.32	
-19.01	1035.75		-8.06	1333.24	
-16.23	904.75		-5.01	1293.97	
-13.45	912.23		-2.03	1005.96	
-10.67	809.67		1.01	883.54	
-9.12	799.46		4.00	667.24	
-7.57	600.67		6.98	440.12	
-3.12	500.36		9.98	200.34	
1.33	300.34		12.97	146.34	
3.34	170.34		15.98	100.25	
5.35	105.12		19.01	89.13	
9.36	79.57		22.01	66.12	
13.3	35.98		24.95	29.10	
17.24	13.24		27.99	15.93	
21.18	2.88		30.98	10.90	
25.12	0.85		33.28	5.09	
29.06	0.17		34.01	1.20	
32.20	0.03		36.97	0.08	
35.34	0.02		39.97	0.08	

Table 4.3: Temperature and Viscosity Data for Heavy Crude Oil 1

HEAVY CRUDE OIL 1					
Cooling rate Temperature ^{0}C	Viscosity cp x 10^{3}	WAT ^{0}C	Heating rate Temperature ^{0}C	Viscosity cp x 10^{3}	WDT ^{0}C
-16.85	12731.40	24.04	-15.00	21664800	32.07
-16.89	13856.70		-17.69	18085900	
-17.14	14836.90		-17.69	11752800	
-17.44	16355.30		-17.57	9138810	
-17.85	18787.30		-17.47	8486820	
-18.15	21248.60		-16.05	7223080	
-15.99	18772.60		-12.01	4666940	
-11.95	12469.50		-8.02	2746000	
-7.99	8119.95		-4.01	1623040	
-4.00	4999.80		-0.06	1007110	
0.02	3067.02		4.02	551319	
4.02	1784.21		7.98	333244	
8.01	971.06		11.97	193974	
12.04	440.23		15.97	105955	
16.04	135.76		19.97	61646.1	
20.01	8.93		24.00	19756.3	
24.04	0.27		27.98	7200	
28.01	0.42		32.07	252.048	
31.99	0.37		36.03	216.125	
36.04	0.23		39.98	255.791	

Table 4.4: Temperature and Viscosity Data for Heavy Crude Oil 2

HEAVY CRUDE OIL 2					
Cooling rate Temperature ^{0}C	Viscosity cp x 10^3	WAT ^{0}C	Heating rate Temperature ^{0}C	Viscosity cp x 10^3	WDT ^{0}C
-27.35	10035.42	5.35	-11.63	1623.04	15.98
-24.57	70184.23		-14.02	1007.11	
-21.79	4059.55		-11.04	551.32	
-19.01	2035.75		-8.06	333.24	
-16.23	904.75		-5.01	193.97	
-13.45	395.23		-2.03	105.96	
-10.67	203.67		1.01	83.54	
-9.12	130.46		4.00	67.24	
-7.57	80.67		6.98	40.12	
-3.12	50.36		9.98	20.34	
1.33	30.34		12.97	6.34	
3.34	7.34		15.98	0.25	
5.35	0.51		19.01	0.13	
9.36	0.40		22.01	0.12	
13.3	0.36		24.95	0.10	
17.24	0.32		27.99	0.09	
21.18	0.29		30.98	0.09	
25.12	0.25		33.28	0.09	
29.06	0.22		34.01	0.09	
32.2	0.26		36.97	0.08	
35.34	0.23		39.97	0.08	

Table 4.5: Temperature and Viscosity Data for Heavy Crude Oil 3

HEAVY CRUDE OIL 3					
Cooling rate Temperature ^0C	Viscosity cp x 10^3	WAT ^0C	Heating rate Temperature ^0C	Viscosity cp x 10^3	WDT ^0C
-25.45	4999.80	18.99	-10.35	19023.92	21.33
-23.22	3067.02		-8.23	15045.56	
-17.35	1784.21		-6.12	10023.52	
-11.48	971.06		-4.00	8013.54	
-5.61	440.23		-1.89	7324.31	
-3.33	203.67		3.33	5314.45	
-1.05	170.45		5.34	2011.99	
1.23	130.46		7.35	705.31	
3.51	80.67		9.36	303.45	
6.22	50.36		11.37	100.34	
8.93	30.34		14.69	40.45	
11.64	20.00		18.01	6.34	
14.35	7.34		21.33	0.13	
18.99	0.40		24.65	0.12	
19.59	0.40		27.12	0.10	
23.40	0.32		29.59	0.09	
27.80	0.29		31.13	0.09	
29.40	0.25		32.67	0.09	
31.10	0.22		34.21	0.09	
32.20	0.26		35.75	0.08	
33.28	0.23		37.29	0.08	

There are several types of crude oils been test which had been labeled as Heavy Crude Oil 1, Heavy Crude Oil 2 , Heavy Crude Oil 3 , Light Crude Oil 1 and Light Crude Oil 2. The criteria to define the best heavy crude oil and light crude oil are have lower WDT and WAT. Based on the data, the researcher have to find out whether the hysteresis occur or not.

Figure 4.0 was the WAT and WDT profiles for Light Crude Oil 1.The orange graph shown the wax appearance temperature profile while blue graph shown the wax dissolution temperature profile. The orange graph was involve the exothermic phenomena and it also known as a cooling rate. Those phenomena lead the Light Crude Oil 1 to form the crystals. Wax appearance temperature is the temperature where the crude oil start to crystalize which is the moment when the crude oil have the possibility to become solid. So, basically the WAT of Light Crude Oil 1 is 36.04 ^{o}C.

Furthermore, blue graph shown that the wax dissolution temperature been detected at 39.98 ^{o}C. Wax dissolution temperature is the temperature where the crude oil start to decrystallize. This process also undergo the endothermic phenomena and heating rate.

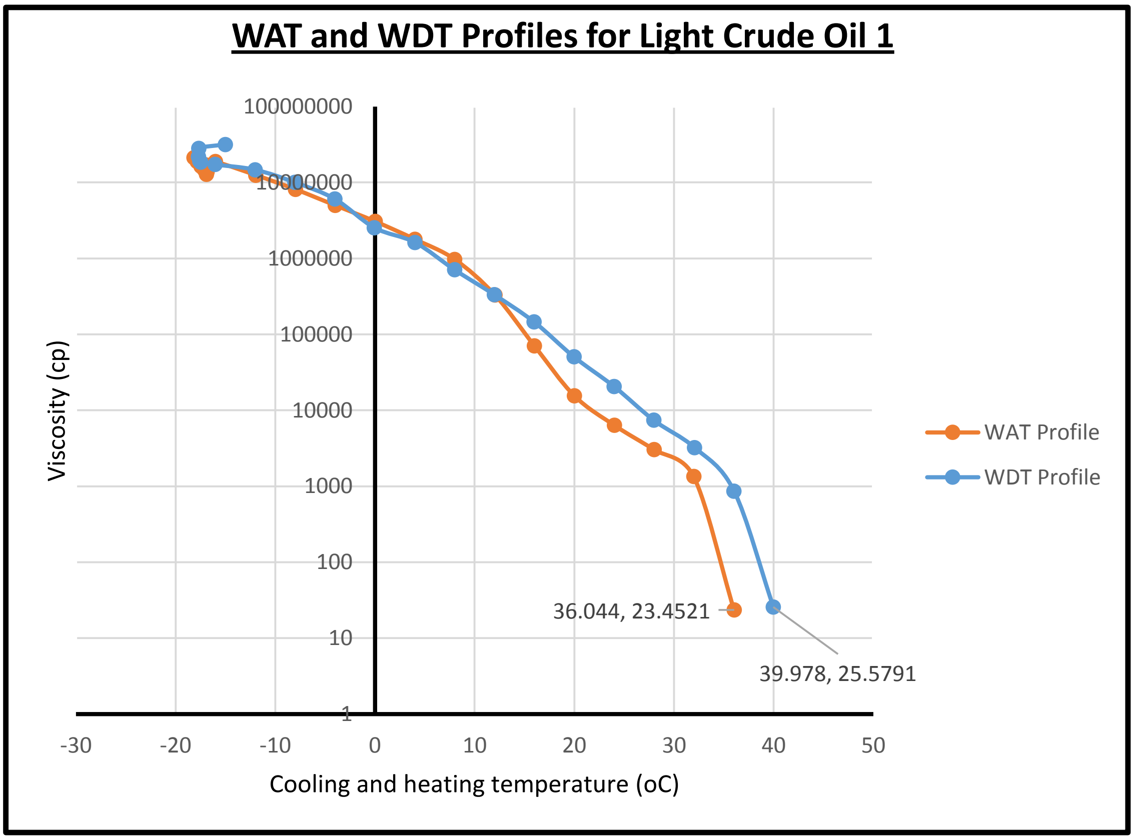

Figure 4.0: WAT and WDT Profiles for Light Crude Oil 1

Graph at figure 4.1 is WAT and WDT profiles for Light Crude Oil 2.The blue graph shown the wax dissolution temperature profile while orange graph shown the wax appearance temperature profile. The blue graph was involve the endothermic phenomena and it also known as a heating rate. Those phenomena lead the Light Crude Oil to decrystallize. Wax dissolution temperature is the temperature where the crude oil start to decrystallize which is the moment when the crude oil have the possibility to become liquid. So, basically the WDT of Light Crude Oil 2 is 36.97°C.

Then, orange graph shown that the wax appearance temperature been detected at 32.20°C. Wax dissolution temperature is the temperature where the crude oil start to crystallize. This process also undergo the exothermic phenomena and cooling rate.

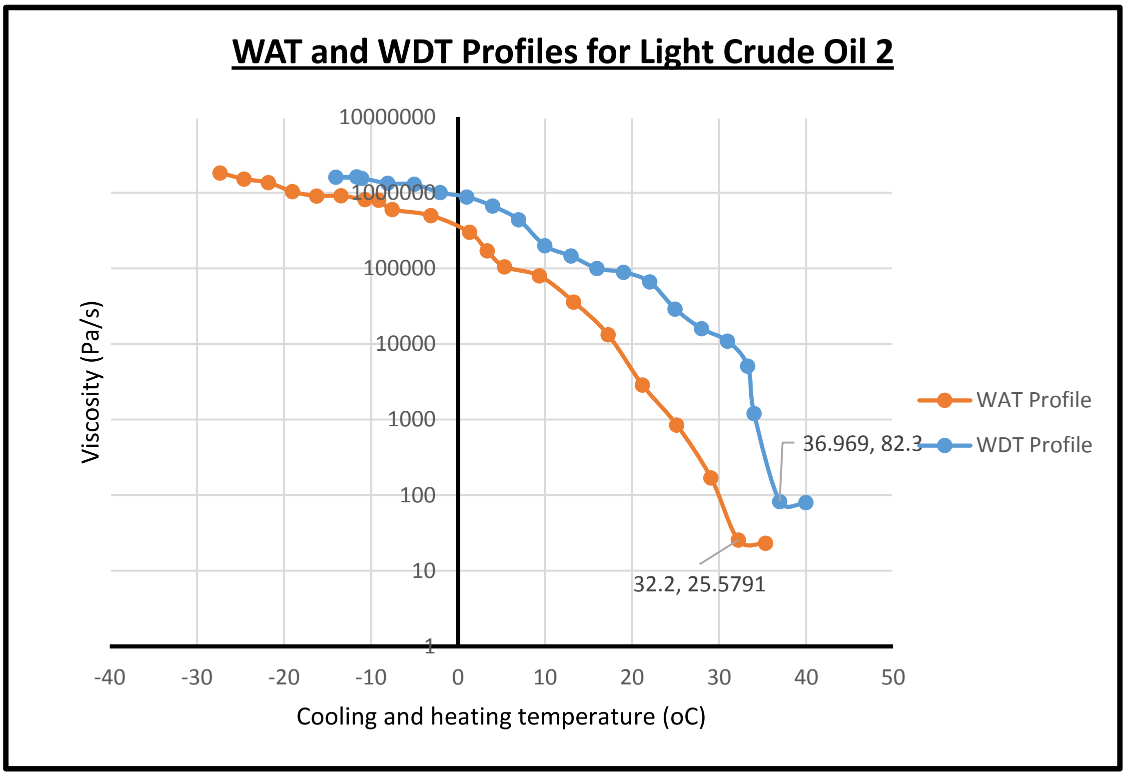

Figure 4.1: WAT and WDT Profiles for Light Crude Oil 2

Figure 4.2 shown that the WAT and WDT profiles for heavy crude oil 1. Based on the graph we could see the pattern of the graph. The starting viscosity is higher for both graph which are 234.52 cp and 255.79 cp for WAT profile and WDT profile compare to the light crude oil 1 and light crude oil 2. This was been effected by the value of API° of the crude oil. The value for heavy crude oil 1 is 19 API° compare to light crude oil 1 and light crude oil 2 which are 45 API° and 47 API°.

The orange graph represent the WAT profile and the profile been undergo the endothermic process which lead the crude oil to become crystals. The increasing of the temperature known as the heating rate and the WAT been detected at 24.04 °C. Furthermore the blue graph represent the WDT profile and the profile been undergo the exothermic process which lead the crude oil to become decrystallize. The decreasing rate of the temperature known as the cooling rate and the WDT been detected at 32.07°C.

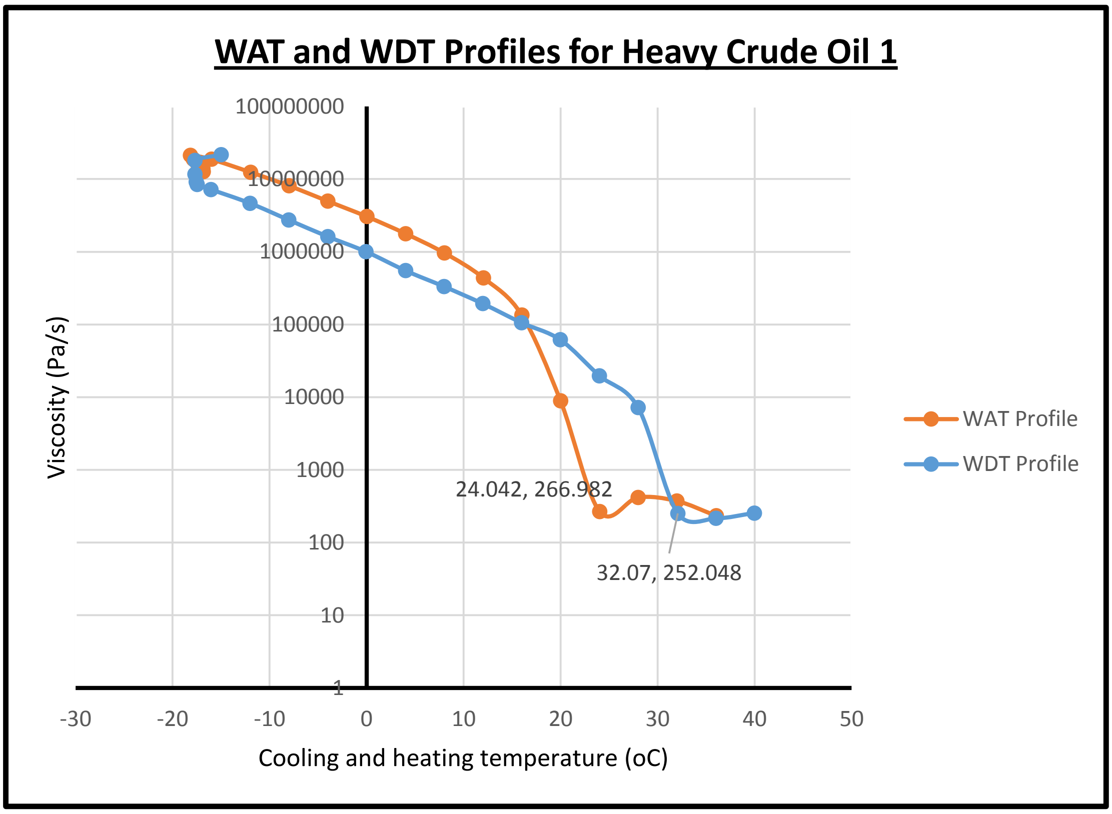

Figure 4.2: WAT and WDT Profiles for Heavy Crude Oil 1

Graph been shown at figure 4.3 was the WAT and WDT profiles for Heavy Crude Oil 2.The blue graph shown the wax dissolution temperature profile while orange graph shown the wax appearance temperature profile. The blue graph was involve the endothermic phenomena and it also known as a heating rate. Those phenomena lead the Heavy Crude Oil 2 to decrystallize. Wax dissolution temperature is the temperature where the crude oil start to decrystallize which is the moment when the crude oil have the possibility to become liquid. So, basically the WDT of Light Crude Oil is 15.98 ^{o}C.

Hence, orange graph shown that the wax appearance temperature been detected at 5.35 ^{o}C. Wax dissolution temperature is the temperature where the crude oil start to crystallize. This process also undergo the exothermic phenomena and cooling rate.

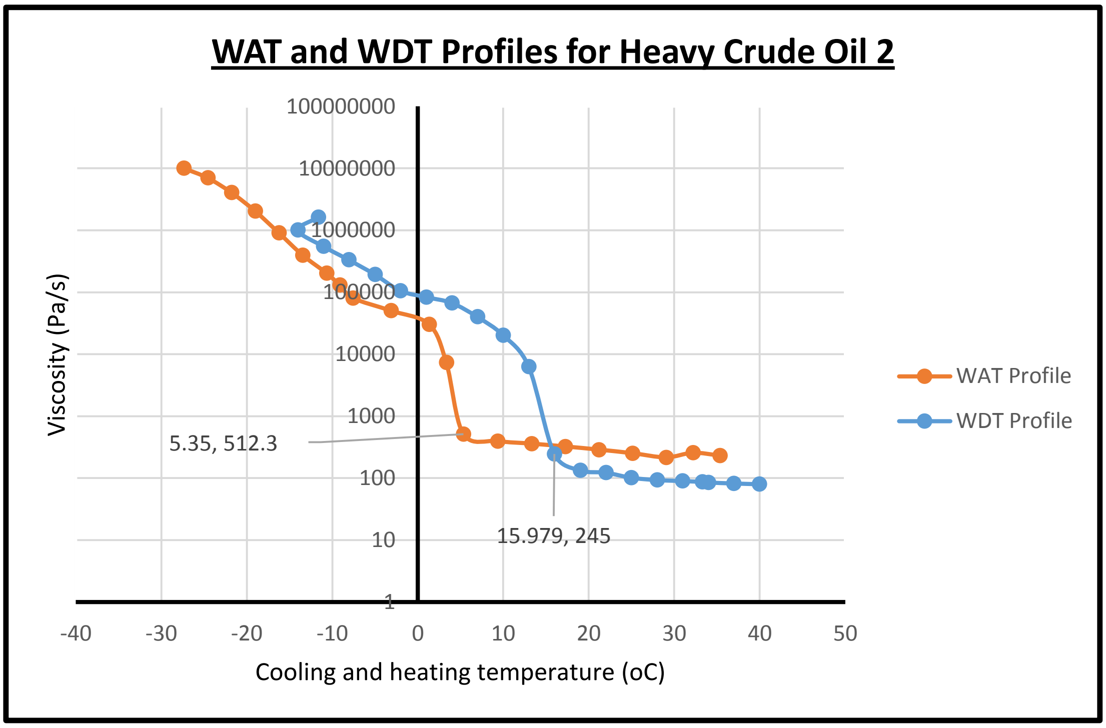

Figure 4.3: WAT and WDT Profiles for Heavy Crude Oil 2

Graph been shown at figure 4.4 was the WAT and WDT profiles for Heavy Crude Oil 3.The blue graph shown the wax dissolution temperature profile while orange graph shown the wax appearance temperature profile. The blue graph was involve the endothermic phenomena and it also known as a heating rate. Those phenomena lead the Heavy Crude Oil 3 to decrystallize. Wax dissolution temperature is the temperature where the crude oil start to decrystallize which is the moment when the crude oil have the possibility to become liquid. So, basically the WDT of Heavy Crude Oil 3 is 21.33 ^{o}C.

In addition, orange graph shown that the wax appearance temperature been detected at 18.99^{o}C. Wax dissolution temperature is the temperature where the crude oil start to crystallize. This process also undergo the exothermic phenomena and cooling rate

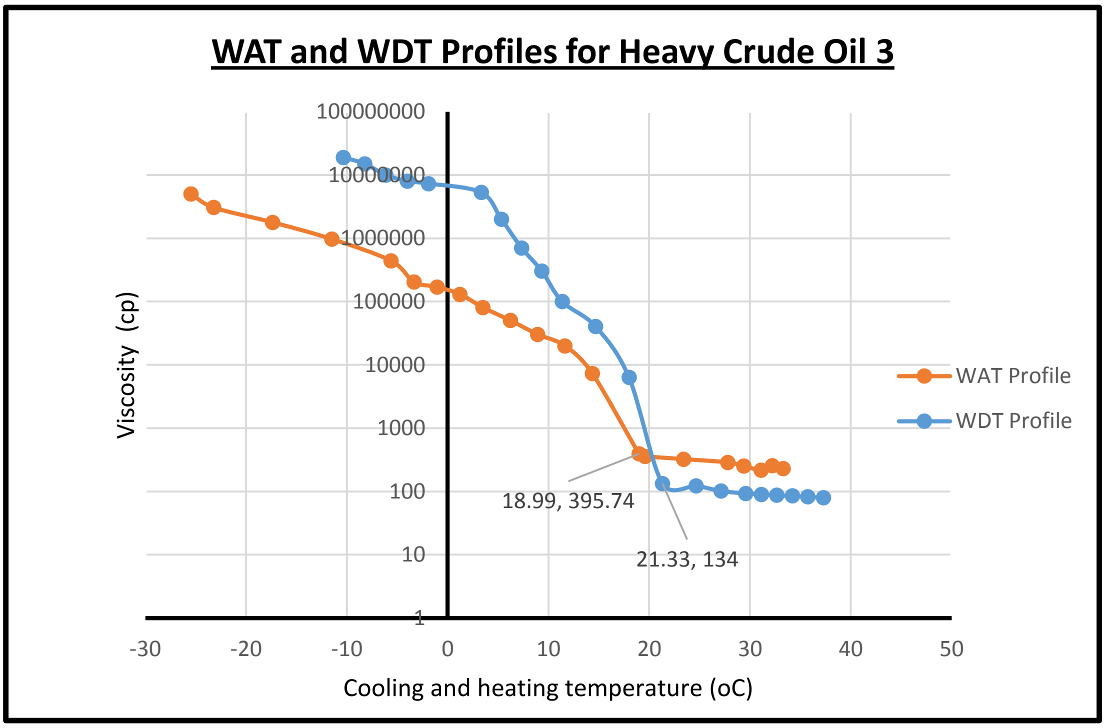

Figure 4.4: WAT and WDT Profiles for Heavy Crude Oil 3

Table 4.6: Summary of Result

Types of Crude oils	Wax appearance temperature ^{o}C.	Wax dissolution temperature ^{o}C.	API^{O} Gravity
Heavy Crude Oil 1	24.042	32.070	19
Heavy Crude Oil 2	5.350	15.979	15
Heavy Crude Oil 3	18.990	21.330	17
Light Crude Oil 1	36.044	39.978	45
Light Crude Oil 2	32.200	36.969	47

Table 4.5 shown that the various temperature of each crude oils for wax appearance temperature and wax dissolution temperature. Refer to figure 2, the WAT and WDT for light crude oil 1 are 36.04 ^{o}C and 39.98 ^{o}C while figure 3 the WAT and WDT are 32.2 ^{o}C and 36.969 ^{o}C.Based on the two differ types of light crude, light crude oil 1 have higher value WAT and WDT compare to light crude oil 2. There are several factor that influence the process which are API gravity and wax contain.

The difference wax appearance temperature and wax dissolution temperature for each heavy crude oil. Figure 4, the WAT and WDT are 24.04 ^{o}C and 32.07 ^{o}C for heavy crude oils 1while figure 5 WAT and WDT for heavy crude oil 2 are 5.35 ^{o}C and 15.98 ^{o}C and the last figure 6 for heavy crude oil 2 18.99 ^{o}C and 21.33 ^{o}C. Those WAT and WDT been affected by the value of API and wax contain.

Based on the table 4.5, the researcher could assume that, every crude oil from different wells did not have the same chemicals properties and physicals properties. The researcher make the assumption if those type of crude oils were in Malaysia, the best crude oil been produced without any paraffin inhibitor or wax inhibitor was heavy crude oil 2 because normally crude oil production at Malaysia undergo the sea bed level temperature at 15 ^{o}C. So, heavy crude oil3 will independently produce through the pipe without worry to become solid.

Theoretically WAT and WDT should be the same value because it was the same method and phenomena. But, in reality the WAT and WDT not same may cause by experiment uncertainty or super cooling.

4.4 **Hysteresis**

Table 4.7: Hysteresis Data

Type of Crude Oils	Temperature (°C)	Viscosity(cp) x 10^3		Differences in viscosity (cp) 10^3
		WAT Profile	WDT Profile	
Light Crude Oil 1	-10.00	10000.00	11000.00	-1000.00
	10.00	800.00	550.00	250.00
Light Crude Oil 2	-10.00	800.00	1400.00	-600.00
	10.00	80.00	200.00	-1200.00
Heavy Crude Oil 1	-10.00	10000.00	3500.00	6500.00
	10.00	800.00	250.00	550.00
Heavy Crude Oil 2	-10.00	180.00	500.00	-320.00
	10.00	0.30	20.00	19.70
Heavy Crude Oil 3	-10.00	900.00	19000.00	-18100.00
	10.00	25.00	300.00	-275.00

Table 4.6 shows the results from a hysteresis experiment. In this test, the sample was cooled from 40°C to -40°C at a cooling rate of 1°C/min and a constant shear rate of 10 s–1.The range to determine the hysteresis is -10°C and 10 °C. There are 3 ways to determine hysteresis, the first is difference between the up and down curve , hysteresis integral and overlapping surfaces between the up and down curve. Based on cased study been research by Julio (2013), difference between up and down cruve been done by set the fixed parameter which is at -10°C and 10 °C. Then, calculate the difference between WDT profile and WAT profile. The differences might be affected by wax contain and the density the crude oils. According to table 4.6, heavy crude oil 3 at -10°C claimed the highest hysteresis which at 18100000 cp.

4.5 **Limitation**

- The equipment is limited and damage
- Time constrain due to the many people queue up for use the same equipment
- Further outcome will be achieved cause need to wait the researcher turn to use the equipment.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The hypothesis of the project about to analysis if wax appearance temperature and wax dissolution temperature for light and heavy crude oils was false. Theoretically the value of WDT and WAT should be the same, but it was not. Based on the experiment, the researcher could find out some of the error which are super cooling and vibration of the equipment have disturbing the viscosity of the crude oil. The researcher also find out that, the gap contact of the crude oil and the equipment.

In addition, the researcher have achieved the respective objective along this research. Those objective would be address below according the objective

1. The WAT and WDT been obtained by using the rheometer. The rheometer show the flow curve of each crude oils in viscosity and temperature curve. The WAT could be determine when beginning of the curve change drastically from high temperature to lower temperature while WDT can be identify by end of changes of curve from lower temperature to high temperature.
2. Hysteresis been detected throughout the pattern and shape of the curve.

5.2 Recommendation

If there any researcher are interested to further findings, you may determine the WAT and WDT by using various of equipment and the researcher suggests to use the cross polarize microscope, and differential scanning calorimeter, This is because, those equipment have their own limitation such as the gap could be use, the range of temperature. So you are fixed the variation so that you could verify which equipment have the least zero error.

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APPENDIX

Figure 7.0: Crude Oils Start To Emit Form the Gaps (Block 20)

Figure 7.1: Power Source of Heat and Cool Condition (Block 20)

Figure 7.2: The Rheometer start to defrost (Block 20)

Figure 7.3: Computer System (Block 20)

Figure 7.4: Computer System (Block 20)