CRUDE OIL POUR POINT MEASUREMENT BY USING ROTATIONAL METHOD

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by

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Dissertation submitted in partial fulfillment of
The requirements for the
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CERTIFICATION OF APPROVAL

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Approved by,

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JANUARY 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.

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MUHAMMAD FARID AFIQ BIN ZOLKIFLI

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ABSTRACT

The petroleum industry has facing great challenges in all aspects such as wax deposition. Transportation and production of waxy crude oil has becomes major operational problem that is needed to be solved. The wax deposition along the surface facilities occurred due to the ambient temperature of the crude oil drop below the crude oil pour point. Therefore, determining crude oil pour point is very significant and important in solving this problem. Tilt method is a conventional method in measuring crude oil pour point in petroleum industry. However, rotational method is an alternative developed in obtaining the crude oil pour point. Pre-treatment is a crucial process subjected to crude oil in ensuring the pour point of the crude oil that obtained is reliable and accurate before measurement of pour point is conducted. In this project, the pre-treatment is varied in term of settling time and pre-heating temperature which will be resulted in the crystallization process of wax. As the samples have undergone pre-treatment, the pour point of crude oil is measured by using rotational method and tilt method in comparing the value of pour point obtained from varied pre-heating temperature, settling time and different measurement methods.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Waxy crude oil is defined as the crude oil contains high amount of paraffin wax that made up the component of the crude oil which is exhibited by high pour point of the crude oil. The pour point of the crude oil is the lowest temperature of the crude to flow. The crude oil is ceased to flow as the ambient temperature of the crude oil is drop below the pour point due to the precipitation of wax. The wax deposition can also be influenced by the changes in pressure and composition of crude oil. Wax can be existed in gas, liquid and solid state depending on the temperature and pressure of the surrounding.

Paraffin molecules are constituents of crude oil which are soluble under reservoir temperature and pressure. As the equilibrium of the composition is being disturbed due to the reduction of temperature and pressure of the flowing stream, the wax tends to precipitate. The wax molecule is an extended discrete entity when the temperature of the oil is above the pour point, once the temperature declines; it has been proposed that the wax molecules join either with similar molecules or with other surfaces.

The high pour point of crude oil will caused the deposition of wax inproduction tubing, flowlines, pipelines and storage tank. The deposition of wax in the pipelines can have greater impact on the production of the crude oil, transportation of crude oil especially in pipeline and in the storage tank. Waxy crude oil is difficult to be transported from the offshore to the onshore terminal via subsea pipeline, especially in cold weather due to the temperature of seabed falls below the pour point of the crude oil. Therefore, measuring the pour point of crude oil is significant in preventing such problems in production, transportation and storage of oil.

In petroleum industry, there are several standards that have been used to measure the pour point. The most common standards by American Society for Testing and Materials (ASTM) International are ASTM D97 (for petroleum products) and ASTM D5853 (for crude oils) which both of these standards use the tilt method. The establish methods that available are ASTM D5950 (automatic tilt method), ASTM D5985 (rotational method) and ASTM D7346 (no flow point, air pressure method). These different methods differ mainly in their accuracy, amount of time needed and sample amount of crude oil. It is well known that the rotational method is not being intended to be used to measure the pour point of crude oil. Thus, one of the purposes of conducting this project is to find out on how the rotational method works on measuring crude oil pour point.

Crude oil that is stored at temperature below the pour pointwill cause wax deposition on the walls of the container.Hence, proper pre-treatment is needed to be carried out for obtaining reliable result of the crude oil pour point. The pre-treatment is conducted by heating the crude sample to a temperature above the expected pour point. The crude oil is then let to cool for certain period of time in order for the crystallization of wax to equilibrate. By taking this step, the complete solubility of the wax can be achieved and thus, the pour point that obtained is reliable and more accurate.

On the whole, this project is conducted to find the suitable pre-treatment by modifying the conventional pre-treatment in term of settling time of crude oil and the temperature of pre-heating crude oil. The crude oil pour point obtained from different pre-treatment will be compared and analyze at the end of the experiment. The pour point is then measured through rotational method and the results of the method will be compared with the tilt method.

1.2 Problem Statement

The conventional standard test in determining crude oil pour point is tilt method (ASTM D5853) which according to the method, the crude oil isstrongly disturbed due to the physical handling of the crude oil sample during the measurement. Thus, the tilting action might affect the wax crystallization process and causing the pour point measurement inaccurate.

Varying the pre-treatment condition such as pre-heating temperature and settling time are significant in investigating the effects of pre-treatment towards the crude oil pour point. By referring to the standard method, the pre-treatment is consuming time as the settling time taken is quite long.

1.3 Objective & Scope of Study

In this project, the crude oil is tested with modified pre-treatment process before the pour point of the crude oil is determined. As the pre-treatment process has been done, the pour point of the crude oil will be measured by using rotational method according to ASTM D5985. The results of modified pre-treatment will be analyzed and the performance shown by the rotational method will be evaluated and compared to the tilt method.

The objectives of this project are as the following:

a) To study the effect of modified pre-treatment process towards the pour point of crude oil in term of pre-heating temperature and settling time.
b) To find out the accuracy of rotational method in measuring crude oil pour point.
c) To compare the effectiveness of rotational method with tilt method.

1.4 Relevancy of the Project

This project is approached as it is significant to the oil production industry. The measurement of the crude oil pour point is considered as the first step beforefurther treatment towards the crude oil is conducted. Therefore, it is very important to determine the pour point of the crude oil accurately. The pre-treatment that are conducted and the crude oil pour point obtained via rotational method could enhance the subsequent researches in the future in preventing the wax deposition.Hence, the deposition of wax in the tubing, pipeline, flowline, production facilities and in the storage tank could be prevented and thereby increase the integrity and reliability of the facilities.

1.5 Feasibility of the Study within the Scope and Time Frame

All of the objectives stated above are achievable and feasible within scope and time frame. This project comprises of laboratory work. The project will be conducted within 4 months which will be executed on September 2013 to December 2013. The crude oil sample will be obtained from the oil field. All of the tools that are required for this project will be prepared before this project started.

CHAPTER 2

LITERATURE REVIEW

2.1 Crude Oil with Wax Content

Crude oil that is constituent by light and intermediate hydrocarbons such as paraffin, naphthenic, wax, aromatics and heavy organic components is defined as waxy crude oil. The waxy crude oil also contained low amount of asphaltenes, resins and organo-metallics(Chin, 2001). The most components of wax are paraffin which is C_{18}-C_{36} and naphthenic which is C_{30}-C_{60}. Based on Hyne, all crude oils contain paraffin molecules and it is considered as waxes if the paraffin molecules are 18 carbon atoms or longer in length. The wax could be existed in various states which are gas, liquid and solid depending on the temperature and pressure. According to Chin, the formation of paraffin wax is referred as macrocrystalline wax meanwhile naphthenic is defined as microcrystalline wax.

Deposition of wax occurs as the ambient temperature of the wax is decreased below the cloud point or Wax Appearance Temperature (WAT). The cloud point is defined as the temperature below the point which the oil is saturated with wax (Rand, 2010). In addition, the tendency of wax to deposits is higher as the wax content in the oil is at least 2%. According to Kulkarni and Iyer, the waxy crude will form crystallization of the crude's paraffin molecules if it is allowed to be cooled below the pour point temperature. Based on the research done by Singhal, Sahai, Pundeer and Chandra, the wax crystallization is occurred by three successive stages which are nucleation, crystal growth and agglomeration. The crystallization is started as the temperature decreases, causing the interaction of the paraffin molecules to increase. As the forces among the molecules are greater than the solvent-paraffin interactions, the paraffin molecules attracted to each other and combine to form crystal nuclei. The growth of the paraffin becomes faster as the free paraffin and nuclei at the site where the cohesion energy is greater. The rheological properties of the crude oil is modified when the temperature decrease below the crystallization temperature and hence leading to the deposition of the paraffin wax and leading to the pour point (Singhal et al., 1991).

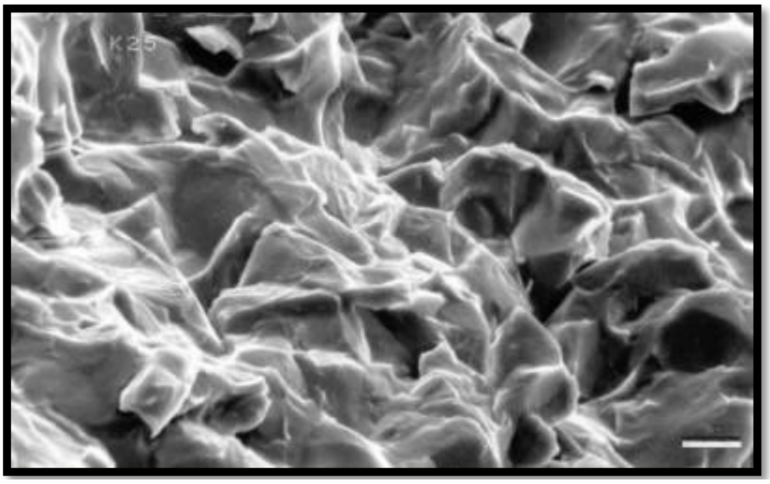

Figure 1: Wax Crystallization
Retrieved fromhttp://www.quorumtech.com/image-gallery/cryo-sem-images/materials-general

2.2 Effects of Deposition of Wax

The deposition of wax can give huge impact towards production, transportation and storage of the crude oil and consuming lots of time, money and workforce.According toAdesina, Churchill, Anthony and Olawale,some of the effects are reducing the crude oil production, hindering the flow of the crude oil, deposition of wax in the surface facilities and as well as increasing the service cost and loss of production during shutdown. The deposition of wax may take place along the pipelines, in the production tubing, and production facilities until the oil goes into the storage tank (Thanh, Hsieh and Philp, 1999).

The wax deposition in the tubing may cause the internal diameter of the tubing to be reduced and thus, reducing the production rate of crude oil. The wax is also able to settle down inside the surface facilities such as choke and separator which will cause the integrity of the equipment in doubt. As the wax deposits in the pipeline, it will cause the pumping problems and reducing the pumpability of the pipe to flow the crude oil. As consequence, high pressure will be needed to transport the crude oil through the pipeline. At certain point, the deposition of wax will be critical and therefore, maintenance and services should be conducted which will consume high cost. In order to maintain and fix the facilities, the production of crude oil will be shut down and therefore, causing loss of profit.

On the whole, the presence of the solid waxes will causes several major problems which are, its accumulation on the walls reduces the flowline section, causing the blockage of filters, valves and pipelines, and reducing or even stopping oil production or transport(Coto, Pena, Espada, Robustillo and Martos, 2008).

Figure 2: Wax Deposition in Pipeline
Retrieved from http://www.worldoil.com/uploadedimages/Issues/Articles/Nov2009/09-11_Wax_Mokhatab_Fig1.jpg

2.3 Pour Point of Crude Oil

Pour point is defined as the lowest temperature at which the liquid will continue to flow, when cooling takes place under certain condition (Cerić, 2012). It is also referred as the lowest temperature at which the oil is still flowing and operating (Harnoy, 2002). According to Hyne, waxy crude oil contains significant amount of paraffin wax in the crude oil which is indicated by pour point of the crude oil. The pour point of crude oil is the temperature level which indicated the crude oil is flowing unsatisfactorily. Morrison and Murphy stated that the pour point of crude oil may be varies from -60^{o}C to 30^{o}C. However, Hyne stated that the crude oil pour point is in between -60^{o}C to 52^{o}C. The crude oil will be ceased to flow as it is cooled down below the pour point which is caused by the formation of paraffin wax in the crude oil.

By referring to Cerić, the relationship of pour point and paraffin's content is proportional. Harnoy stated that, the high pour point of crude oil is the resulted of high paraffin content that composed part of crude oil composition. As the paraffin's content in the crude oil is higher, the pour point will be higher or vice versa. However, temperature is an important parameter that determines the pour point. For example, if the crude oil pour point is 10^{o}C in a reservoir, meanwhile the temperature of the reservoir is 30^{o}C and thus, the crude oil will be in liquid state in the reservoir condition. Therefore, the crude oil is mobile and flow under the condition. On the other hand, if the pour point of the crude oil is 30^{o}C and the reservoir temperature is 20^{o}C, thus the crude oil will be immobile (Speight, 2013).

Generally, heavy oil has high molecular weight of hydrocarbons, in the range of C_{40} to C_{120} which problems related to the deposition of paraffin waxes (Thanh et al., 1999)[8]. Therefore, the high pour point of crude oil is originally referred to heavy oil that has high wax content. According to Speight, heavy oil exhibited high pour point and high melting point which resulted to the poor of fluid properties of the oil and therefore, causing the low mobility of the heavy oil. However, the high pour point also could be exhibited by light crude oil with high amount of paraffin content.

The pour point generally measured on stock tank oil (STO) samples and the crude sample is considered as dead oil. According to Karan and Ratulowski, the operational decision with respect to wax deposition and pipeline restartability is easy to take when the temperatures encountered are above the measured dead oil pour point. However, the seabed temperature is much lower than the dead oil pour point at the offshore fields and subsea transportation. Under these circumstances, the crude oil is not only exhibited high pressure but also contained solution gas and is referred as live oil. It is a common practice to measure the pour point on the STO due to the expensive downhole tool and lack of laboratory apparatus and techniques that able to handle the high pressure of live oil. It is also known that the properties of live oil and dead oil are different from each other.

2.4 Pour Point Measurement

According to Nadkarni, there are several standard tests are in use in determining the crude oil pour point which are tilt method (ASTM D97 - applied for petroleum product and ASTM D5853 – applied for crude oil), automatic tilt method (ASTM D5950) and rotational method (ASTM D5985). There are also another pour point test which is automatic air pressure method (ASTM D6749) and pressure differential method (ASTM D7346).

By referring to manual tilt method, ASTM D97/ASTM D5853 and automatic tilt method (ASTM D5950), the crude oil sample is tilted in every 1^{o}Cor 3^{o}C and therefore causing the disturbed to the sample which influencing the crystallization process of the crude sample. The cooling rate of these methods is quite slow as it depends on the ASTM specification. The thermal behavior experienced by crude sample cannot be observed by this method. The automatic air pressure method is conducted by applying pressurized air towards the surface of the sample in every 1^oC or 3^oC. This will disturbed the crystallization process and also the accuracy is depending of the tests limits at 1^oC or 3^oC. According to pressure differential method, the pressure change of a closed area of the test specimen is measured. However, the real flow of the crude sample sometimes cannot be obtained due to the density change during crystallization.

The pour point of crude oil will be measured as the oil that have been produced from reservoir and transporting the crude oil through the pipeline, particularly the pipeline beneath the sea bed. According to McAleese, the pour point is determined during the crude oil sample is obtained from the logging activities which it will be tested if there is pour point problem of the crude oil viaASTM – D97-96A. To conduct pour point test in order to determine the pour point is below or above certain critical value, a temporary ice bath is designed to obtain data whether the crude oil is pourable at a specific temperature and ASTM procedure will not be followed. If the critical temperature obtained is near the critical temperature of sea bed temperature, then the ASTM procedure will be followed. McAleese suggested that the crude oil should be pre-heated to the reservoir temperature before the pour point is carried out.

2.5 Tilt Method

In the early days, the tilt method is done in measuring the pour point. The procedure is started asthe crude oil is placed inside a thin-walled Pyrex tube and the crude oil is heated approximately 30 minutes in ensuring the waxes is in liquid state. After the crude oil sample is heated, the thermometer is placed inside the tube and immersed in the crude oil sample by fitting it with a cork. The next step is the tube containing the crude oil sample is turned and held at 90^o angle to the upright for 5 seconds. The movement of the fluid is observed and recorded. The process is repeated by decreasing the temperature by 5^oF as the temperature drops. As the crude oil sample has equilibrated at room temperature, the sample is cooled by placing it in a refrigerated system to a critical temperature at which the crude oil sample will be no longer flow as the tube is held at 90^o to the upright for 5 seconds. The temperature which the crude oil sample is no longer flow is recorded as the pour point of the crude oil sample (Becker, 1997).

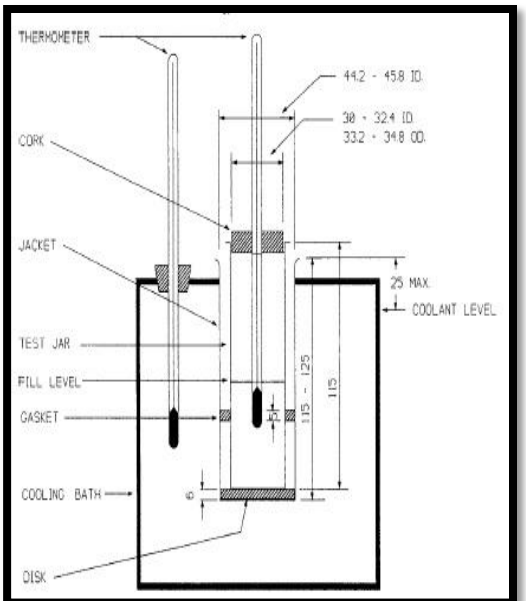

Figure 3: Tilt Method

Retrieved from http://www.scribd.com/doc/64221650/D5853-2009; Accessed date:2nd July 2013

2.6 Rotational Method

By using rotational method, the pour point of the crude oil can be determined with an accuracy of 0.1^{o}C.The determination of crude oil sample pour point by an automatic instrument and continuously rotates the test specimen against a suspended detection device during cooling of the crude oil sample. According to Nadkarni, this test method includes the range of temperatures from -57^{o}C to 51^{o}C.The test precision of rotational method has shown repeatability of 2.3^{o}C and reproducibility of 8.7^{o}C. The temperature measurement will be conducted inside the crude oil sample and hence, the thermal behavior of the crude oil sample can be observed during cooling down process through the temperature/time graph. With the assist of graphical data, the cooling curve will be able to represent the appearance of cloud point and therefore, the pour point can be determined. By using this method, the crude oil sample will not be disturbed mechanically and thus, increase the reproducibility of the measurement.

The US Patent 3498104 has stated that, the rotational method is a method when a body of cylindrical block with temperature sensor is partly immersed into the test sample and the cup sample is capable to move at least one direction. In addition, the liquid and the body is able to be moved relatively to each other in such a way that a force generated which partly determines the deflection of the body. As the temperature of the liquid has drops to temperature near the pour point, the liquid will exert larger force due to normal rise in viscosity at decreasing temperature.

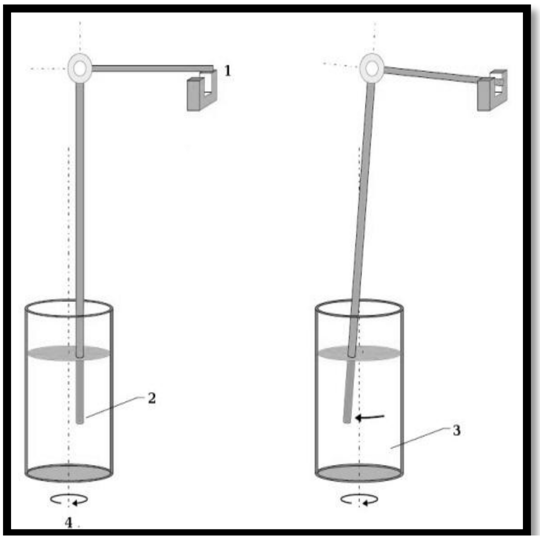

Figure 4: Rotational Method
Retrieved from http://www.psl-systemtechnik.de/pour_point_tester_knowledge.html?&L=1&print=1

2.7 Pre-Treatment

According to ASTM D5853, the crude oil cannot be heated more than 60^{o}C as the temperature higher than that will cause the vapor pressure to exceed 100kPa. Under this condition, the sample container may rupture and might cause possible injury to the personnel. Opening of the container will cause the foaming with resultant loss of the crude sample. The standard procedure also stated that the pour point of a crude oil is depends on the crystallization state of the wax. In order to achieve equilibrium between crystallized wax and dissolved wax, the process may consume lot of time as it is a very slow process. By experience, the equilibrium is achieved when the crude oil sample is hold for settling process for 24 hours.

In order to achieve complete wax solubility, the crude oil should be heated to a temperature above the expected cloud point and expected pour point. Based on the

ASTM guide, the temperature of 20^{o}C above the expected pour point will usually satisfy the cloud point requirement.

As Wauquier stated, the pre-heating temperature of crude oil at 45^{o}C to 65^{o}C will obtain result of lower temperature of crude oil pour point. This is due to the crude oil which contains seeds of paraffinic crystals that have been destroyed during the pre-heating process conducted. On the other hand, as the crude oil is pre-heated to a higher temperature (about 100^{o}C), an increase in pour point will be obtained which is due to the vaporization of light component of wax and thus causing the heavy component of wax to settled in the crude oil. The condition will cause the crude oil become heavier.

CHAPTER 3

METHODOLOGY

3.1 Project Methodology

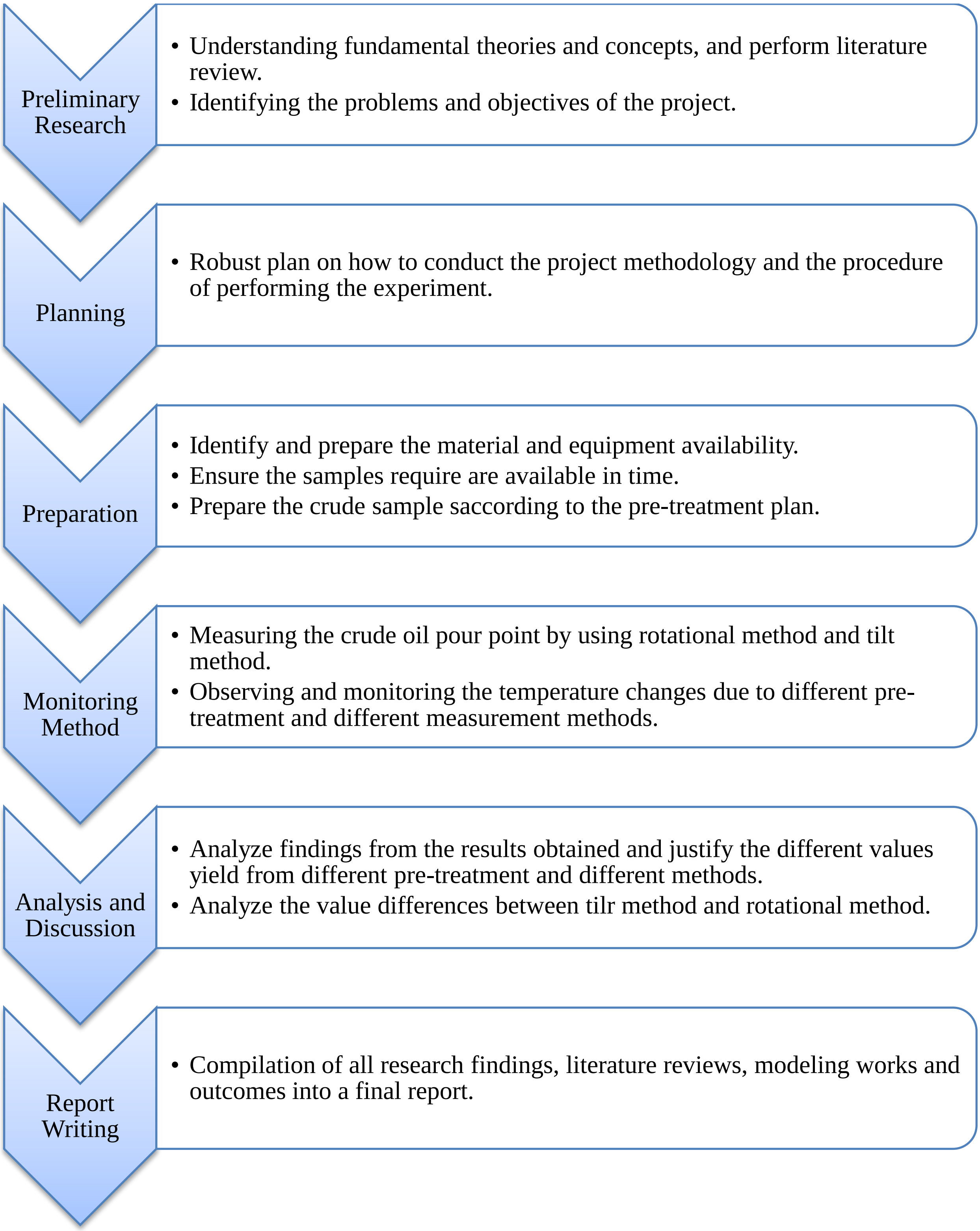

Figure 5: Process Flow Chart

3.2Procedure

3.2.1 Pre-Treatment

- **Preparation of Samples at 60^{o}C**

1. The crude oilsample is poured into the test tube with fixed volume which is 20mL.
2. Water bath is boiled to 65^{o}C for heating process of crude sample.
3. The test tubecontained crude oil sample is closed with the cork carrying thermometer.
4. The thermometer and test tube is adjusted to be coaxial and the thermometer bulb is immersed to a depth which is 3 mm below the surface of the crude oil sample.
5. The crude oil sample is heated in water bath to a temperature higher than the expected pour point which is approximately 60^{o}C.
6. After the temperature reached specified temperature, the crude oil sample is continuously heated for 30 minutes but not exceed 60^{o}C in ensuring wax bonding are completely broken.
7. As the heating process completed, the crude oil sample is kept at room temperature (between 18 and 24^{o}C) for 24 hours before measurement conducted.

Note: The steps are repeated with the sample is kept at room temperature for 6, 12, and 18 hours.

- **Preparation of Samples at 80^{o}C**

1. The crude oil sample is poured into the test tube with fixed volume which is 20mL.
2. Water bath is boiled to 65^{o}C for heating process of crude sample.
3. The test tubecontained crude oil sampleis closed with the cork carrying thermometer.
4. The thermometer and test tube is adjusted to be coaxial and the thermometer bulb is immersed to a depth which is 3 mm below the surface of the crude oil sample.
5. The crude oil sample is heated in water bath to a temperature higher than the expected pour point which is approximately 60^{o}C.
6. After the temperature reached specified temperature, the crude oil sample is continuously heated for 30 minutes but not exceed 60^{o}C in ensuring wax bonding are completely broken.
7. As the heating process completed, the crude oil sample is kept at room temperature (between 18 and 24^{o}C) for 24 hours before measurement conducted.

Note: The steps are repeated with the sample is kept at room temperature for 6, 12, and 18 hours.

3.2.2Pour Point Measurement

3.2.2.1 Rotational Method

The pour point measurement is conducted by the following steps;

1. The crude oil sample is inserted into test sample cup gently.
2. The crude oil sample cup is inserted into the PPT while the coaxial, tiltable bedded temperature sensor is dipped into the crude oil sample and the crude oil sample cup is set to a slow rotation of about 0.1 r/ min.
3. The program is initiated as the heating temperature of the crude oil sample is set to 45^{o}C and the frequency of measurement is set to 3 cycles.
4. As the temperature of the crude oil sample has reached 45^{o}C, the crude oil sample is cooled with constant temperature differential between the cooling block and the crude oil sample by the flowing and circulating water inside the PPT.
5. The temperature gradient that is displayed in temperature/time-graph is observed which shown the thermal behavior of the sample via *WinPPT software*.
6. As the pour point of the crude oilsample has reached (with increasing of viscosity), the temperature sensor is moved out of its position and the light barrier is triggered.
7. The temperature of the crude oil sample at the condition is recorded as the pour point of the crude oil sample with resolution of 0.1^{o}C.

3.2.2.1 Tilt Method

The pour point measurement is conducted by the following steps;

1. Water bath is boiled to 50^{o}C for heating processof the crude oil sample.
2. The crude oil sample is heated to 45^{o}C shortly in the water bathin order to melt down the wax deposition inside test tube. .
3. As the temperature of the crude oil sample has reached 45^{o}C, the crude oil sample is left to be cooled till 9^{o}C from the expected pour point at the room temperature.
4. The crude oil sample is immersed into the water bath with temperature of 24^{o}Cfor cooling process of the crude oil sample to take place.
5. Every 3^{o}C drop in temperature of the crude oil sample, the test tubeis tilted 90^{o}for 5 seconds until the crude oil sample is no longer flowing.
6. The temperature of crude oil sample at which the crude oil freeze due to wax deposition is reported as freezing point and pour point reading is recorded at the nearest interval 3^{o}C of the freezing point.

Note: The steps are repeated 3 times in obtaining 3 pour point reading of the crude sample.

3.3 Gantt Chart

	FYP I														FYP II													
Activities / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Selection of Project Topic																												
Project Planning																												
Research/ Literature Review																												
Extended Proposal Submission																												
Proposal Defense Presentation																												
Laboratory Work & Data Collection																												
Submission of Draft of Interim Report/ Draft of Project Dissertation																												
Submission of Interim Report / Project Dissertation																												

Table 1: Gantt Chart

3.4 Key Milestone

Week	Activities
5	Completion of preliminary research work
7	Submission of Extended Proposal
9	Completion of Proposal Defense
12	Confirmation of sample and procedure of project
13	Submission of Interim Draft Report
14	Submission of Interim Report

Table 2: Key Milestone of Final Year Project I

Week	Activities
5	Finalized simulation procedure
7	Conducting simulation, result analysis and discussion
8	Submission of Progress Report
10	Preparation for Pre-SEDEX
12	Pre-SEDEX
13	Submission of Technical Paper, Draft Project Dissertation and VIVA
14	Submission of Project Dissertation

Table 3: Key Milestone of Final Year Project II

3.5 Tools & Equipment

The materials required for this project as below;

- Crude oil
- Water

Experiments method is conducted as the following lab equipment:

- Test jar
- Test tube
- Measuring cylinder
- Thermometer
- Cork
- Water bath
- PSL Systemtechnik GmbH; Pour Point Tester (PPT)

Figure 6: PSL Systemtechnik GmbH; Pour Point Tester (PPT)
Retrieved from http://www.psl-systemtechnik.de/pour_point_tester_knowledge.html?&L=1&print=1

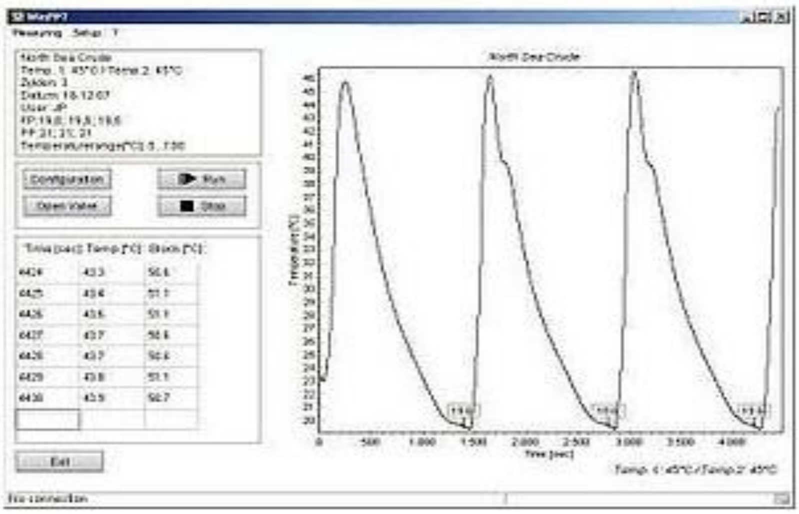

Figure 7: WinPPT Software
Retrieved from http://www.psl-systemtechnik.de/pour_point_tester_knowledge.html?&L=1&print=1

CHAPTER 4
RESULT & DISCUSSION

4.1 Experimental Result

The result of this project is presented in the tables below. Table 5 below shows the result of tilt method meanwhile Table 6 recorded the result of rotational method in measuring crude oil pour point. In both methods, the pour point of the crude oil are reported in 6 hours interval of settling time as mentioned in the procedure and each of settling time is divided into 2 pre-heating temperature which are 60^{o}C and 80^{o}C. Both of the methods measured 3 cycles of crude oil pour point in order to obtain average freezing point (FP) and average pour point (PP) reading in reducing errors.Since the standard pour point measurement is read at interval 3^{o}C, the results below consist the reading of freezing point which represent the temperature of crude oil when it's no longer flowing. Therefore, the freezing point of the crude oil is more significant to use in order to compare the result of different settling time, different pre-heating temperature and different measurement methods.

- **Tilt Method**

Temp. (^{o}C) /Time (sec)		24			18			12			6		
60	FP	27	26	26	27	27	26	27	27	27	27	28	28
	PP	27	27	27	30	30	30	30	30	30	30	30	30
80	FP	26	27	27	27	27	27	28	27	28	28	28	28
	PP	27	30	30	30	30	30	30	30	30	30	30	30

Table 4: Tilt Method Measurement

- **Rotational Method**

Temp. (^{o}C) /Time (sec)		24			18			12			6		
60	FP	26.8	27.3	27.3	27.4	27.4	27.6	27.6	27.9	27.7	27.9	28.3	28.1
	PP	27	30	30	30	30	30	30	30	30	30	30	30
80	FP	27.1	27.7	27.8	27.4	27.7	28.0	28.2	28.3	28.3	28.5	28.7	28.4
	PP	30	30	30	30	30	30	30	30	30	30	30	30

Table 5: Rotational Method Measurement

4.1.1Average Freezing Point

- **Tilt Method**

Temp. (^oC) /Time (sec)		24	18	12	6
60	FP	26.3	26.7	27.0	27.7
	PP	27	27	30	30
80	FP	26.7	27.0	27.3	28.0
	PP	27	30	30	30

Table 6: Average Freezing Point of Tilt Method

- **Rotational Method**

Temp. (^oC) /Time (sec)		24	18	12	6
60	FP	27.1	27.5	27.7	28.1
	PP	30	30	30	30
80	FP	27.5	27.7	28.3	28.5
	PP	30	30	30	30

Table 7: Average Freezing Point of Rotational Method

4.1.2 Results of Rotational Method

The graphs below are correlated to the result of rotational method in Table 5. The graphs are temperature/time graph displayed in *WinPPT Software* as the time is represent time taken for crude oil to achieve pour point.

- 60^{o}C pre-heating temperature / 24 hours settling time

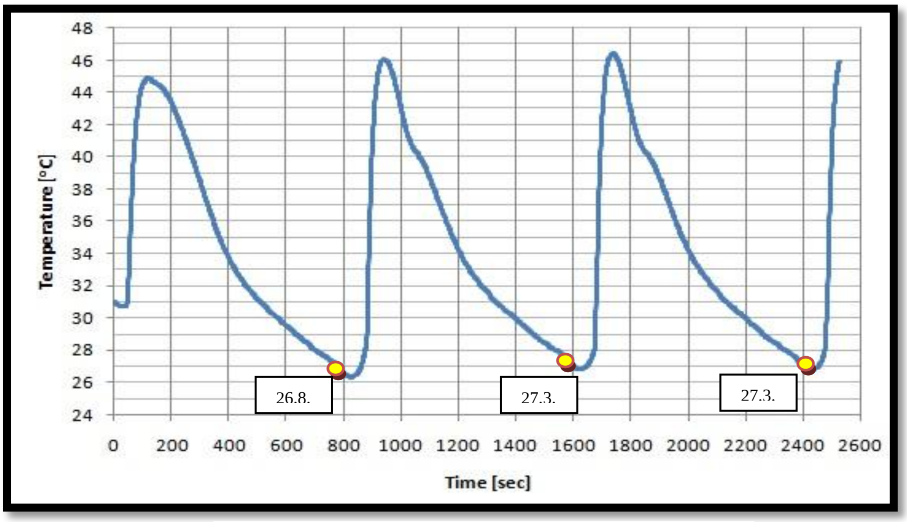

Figure 8: 60^{o}C / 24 hours Sample

- 60^oC pre-heating temperature / 18 hours settling time

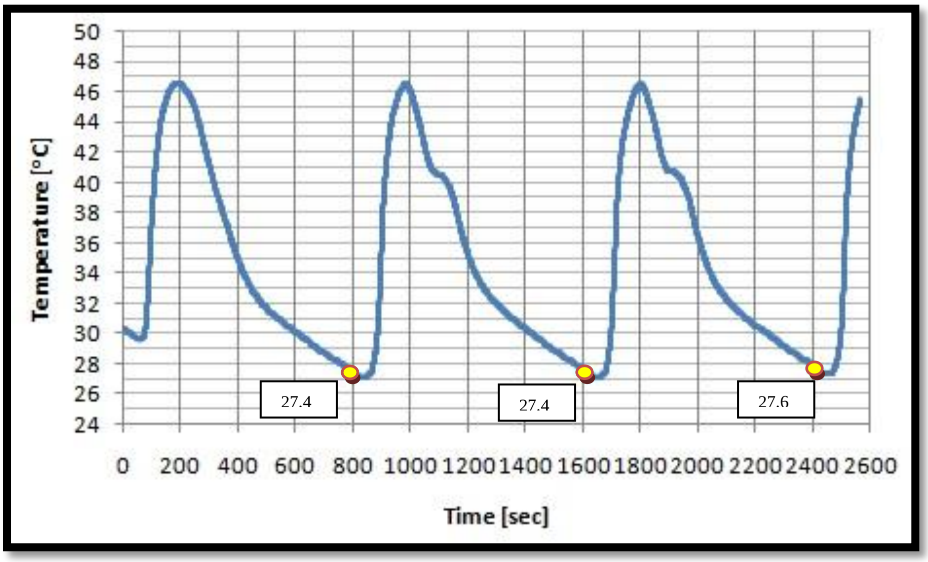

Figure 9: 60^oC / 18 hours Sample

- 60^oC pre-heating temperature / 12 hours settling time

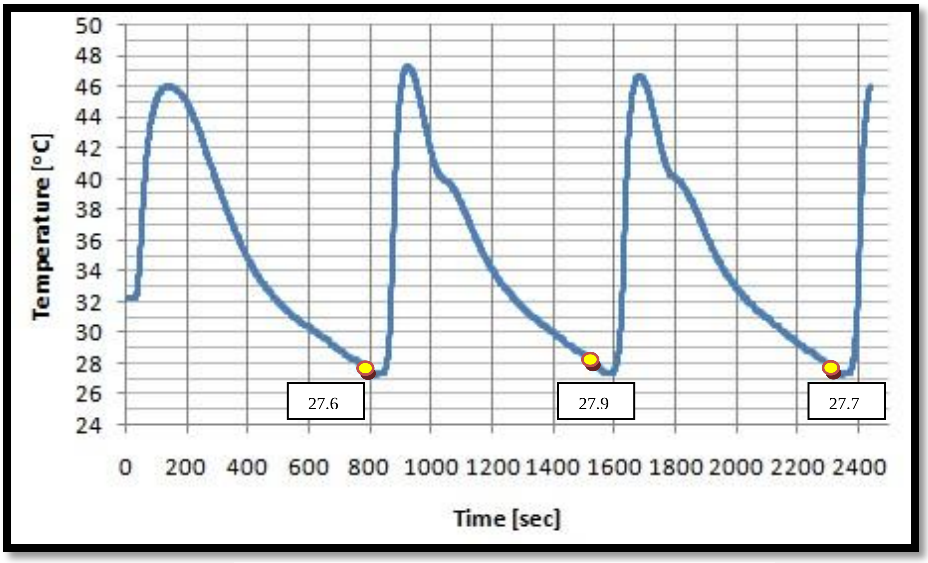

Figure 10: 60^oC / 12 hours Sample

- 60^oC pre-heating temperature / 6 hours settling time

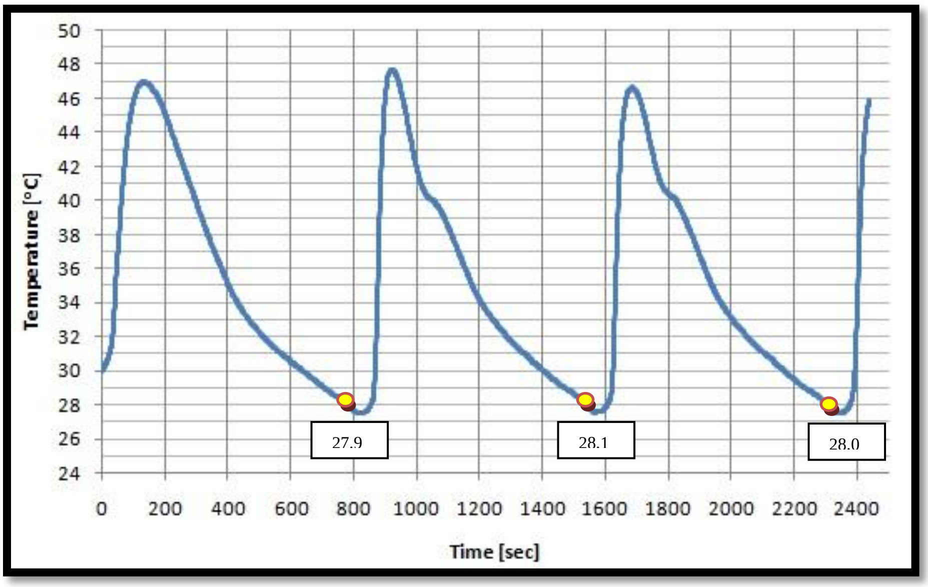

Figure 11: 60^oC / 6 hours Sample

- 80^oC pre-heating temperature / 24 hours settling time

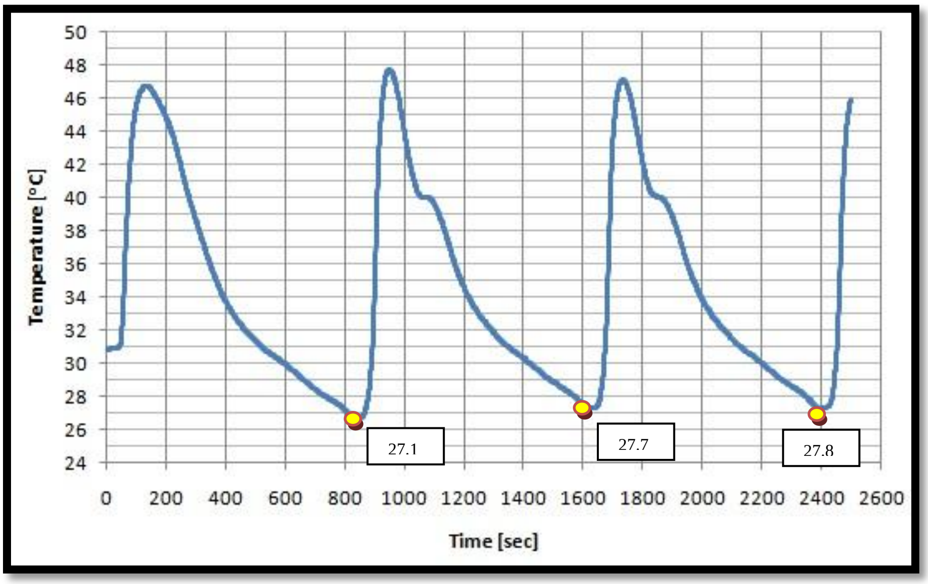

Figure 12: 80^oC / 24 hours Sample

- 80^{o}C pre-heating temperature / 18 hours settling time

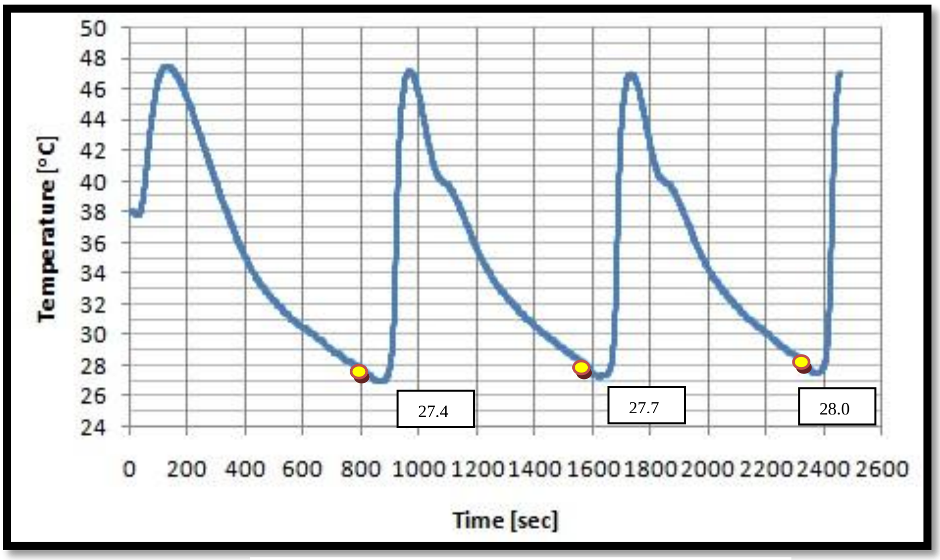

Figure 13: 80^{o}C / 18 hours Sample

- 80^{o}C pre-heating temperature / 12 hours settling time

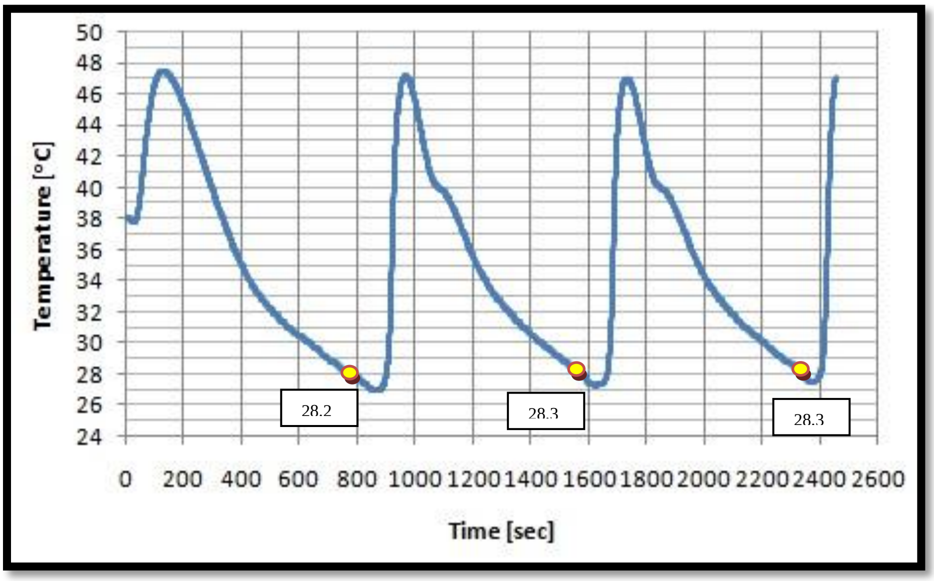

Figure 14: 80^{o}C / 12 hours Sample

- 80°C pre-heating temperature / 6 hours settling time

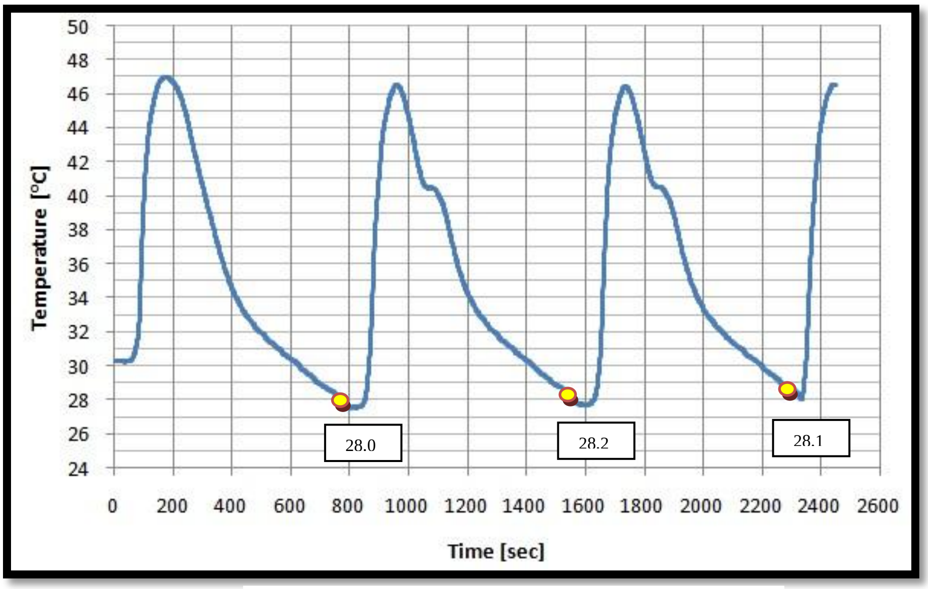

Figure 15: 80°C / 6 hours Sample

4.2 Analysis& Discussion

4.2.1 Pre-Heating Temperature

Based on Table 4 and 5, the average freezing point of each sample is calculated and the graphs are plotted by using the average freezing point. The graphs below show the pre-heating temperature which are 60^{o}C and 80^{o}C before the measurement is carried out.

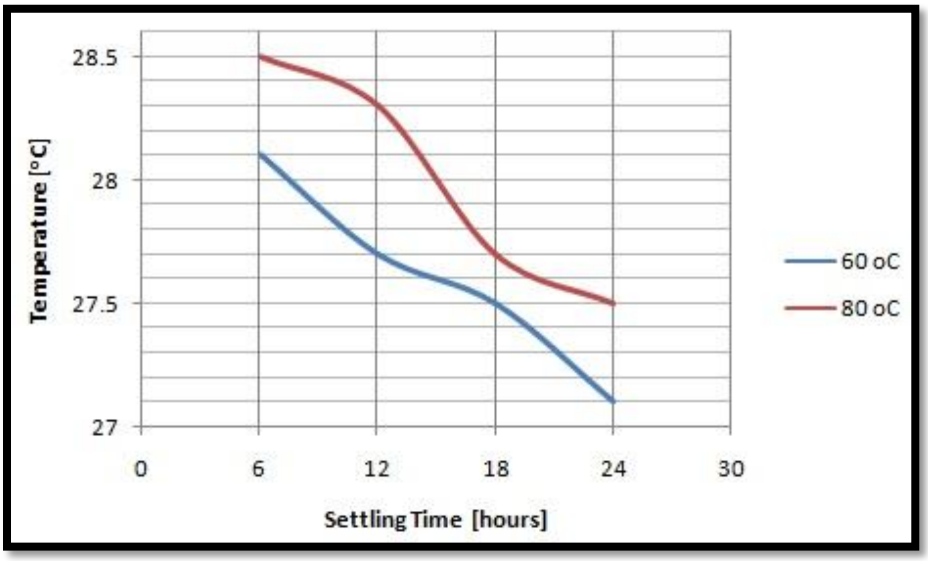

Figure 16: Comparison of 60^{o}C and 80^{o}C of Rotational Method

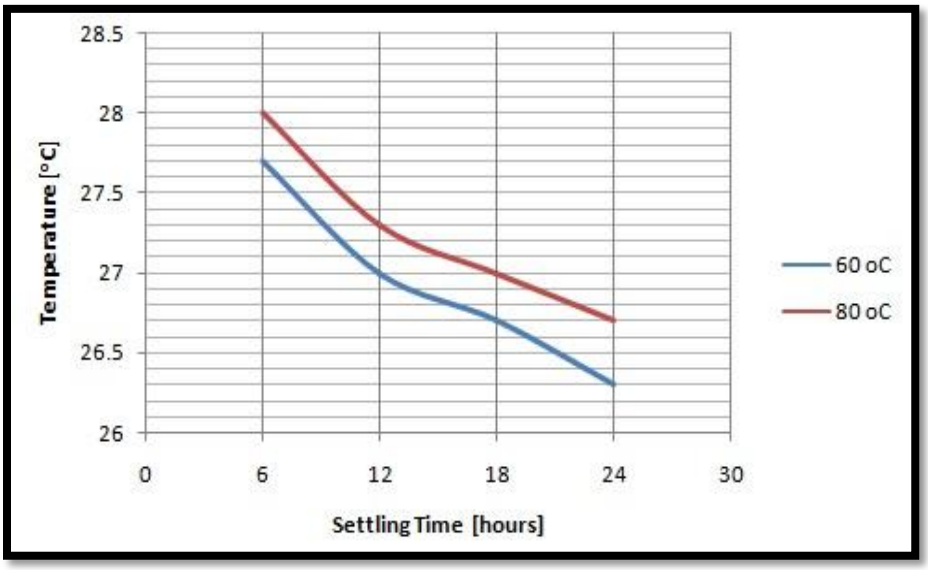

Figure 17: Comparison of 60^{o}C and 80^{o}C of Tilt Method

From the graphs, it shows that the 80^{o}C has recorded higher freezing point compared to 60^{o}C. Since the settling time has been varied to 6 hours interval, all of the 60^{o}C samples exhibited lower average freezing point compared to the 80^{o}C samples.Therefore, it could be pre-concluded that the higher the pre-heating temperature, the higher the freezing point of the crude oil. In order to prove the theory, the samples that are measured by tilt method also exhibited the same result as the rotational method.

The thermal behavior presented by both pre-heating temperature is discussed as the crude oil is heated to a higher temperature, the crude oil tends to evaporate the light molecular component of the wax inside the crude oil (Wauquier, 1995). This will caused the heavy molecular components of the wax to settle and causing the crude oil to become heavier. Therefore, the viscosity of the crude oil will be increased and thus, shorter time is taken to measure the pour point as the crude oil freeze faster due to the deposition of wax. As the time taken is faster, the pour point of the crude oil is higher. Pre-heating the crude oil below 60^{o}Ctends to yield lower pour point since the pre-heating will destroy the seeds of paraffinic crystals that consist in the crude oil and therefore, longer times needed for wax to deposit when cooling take place.

4.2.2 Settling Time

The graphs below are plotted from the values in Table 5 and Table 6, showing the value of average freezing point of every crude oil samples that have been undergone different settling time which are 24 hours, 18 hours, 12 hours and 24 hours.

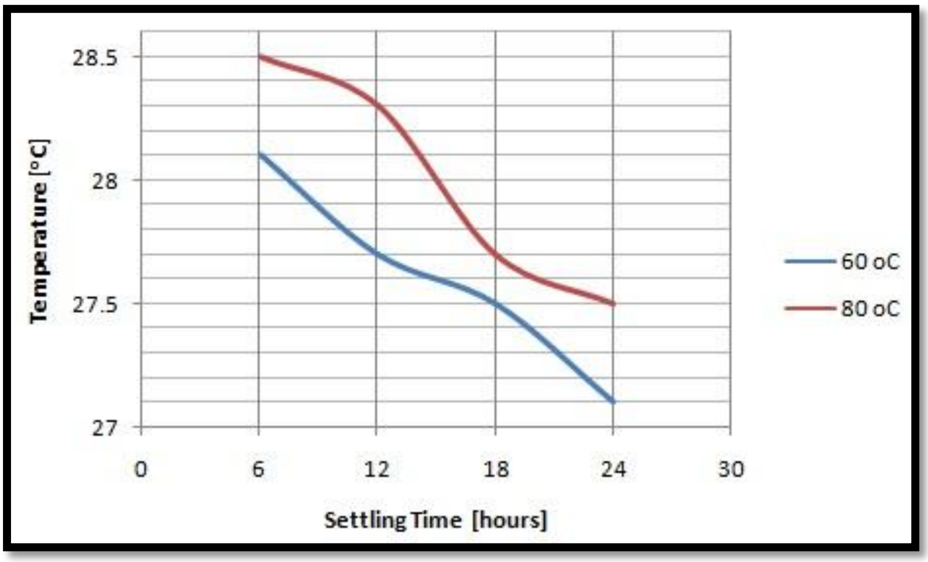

Figure 18: Pour Point Value for Different Settling Time (Rotational Method)

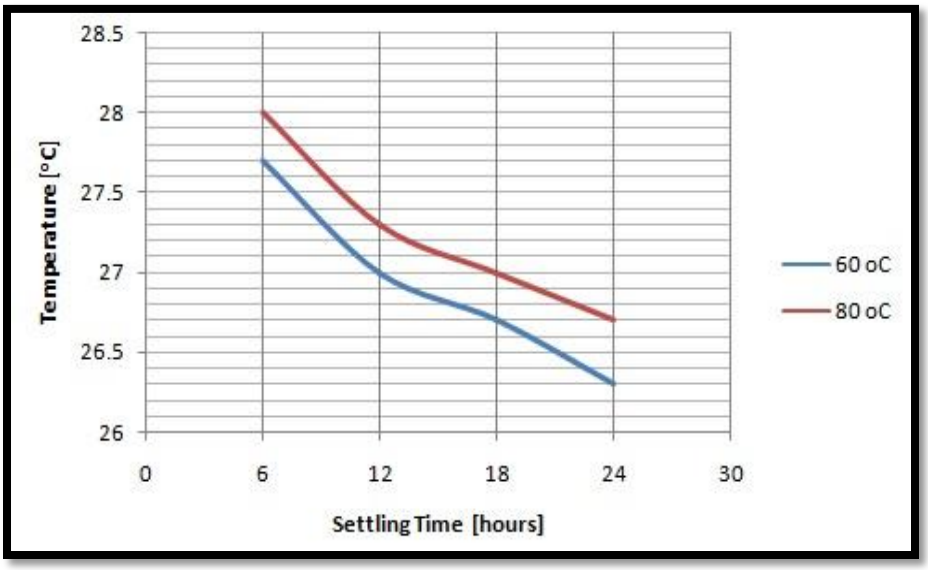

Figure 19: Pour Point Value for Different Settling Time (Tilt Method)

Based on the graphs above, it shows that the result for 24 hours samples is the lowest compare to other samples. The 24 hours is considered as the standard settling time for the equilibrium of the wax to achieve. As the settling time has been decreased to 6 hours, the pour point of the crude oil has increased. Therefore, settling time has given significant effect to the pour point of the crude oil. This is proven as both of pre-heating temperature (60^{o}C and 80^{o}C) has shown same trending when the settling time of the crude oil has been reduced to 6 hours. Besides, tilt method and rotational have recorded the same results which shown the increment of the pour point as the settling decreased.

This phenomenon occurred due to the crystallized wax and dissolved wax which is not equilibrium as the settling time has become shorter. As the cooling process take place, the 6 hours samples tend to precipitate the wax faster compared to 24 hours and thus, the time taken for the crude oil to achieve pour point is lower. This will lead to the increase in viscosity of the crude oil and therefore, higher pour point. In discussing the standard settling time which is 24 hours, the amount of time taken is long enough for the crude oil sample to achieve equilibrium between crystallized wax and dissolved wax as the cooling process take place. The equilibrium condition will delay the increase in viscosity and therefore, the time taken to achieve pour point is longer. This will result in lower pour point.

4.2.3 Measurement Methods

The conventional method which is tilt method is used in order to compare the results yield by rotational in order to determine its accuracy and effectiveness. From the results obtained, the following graphs are plotted:

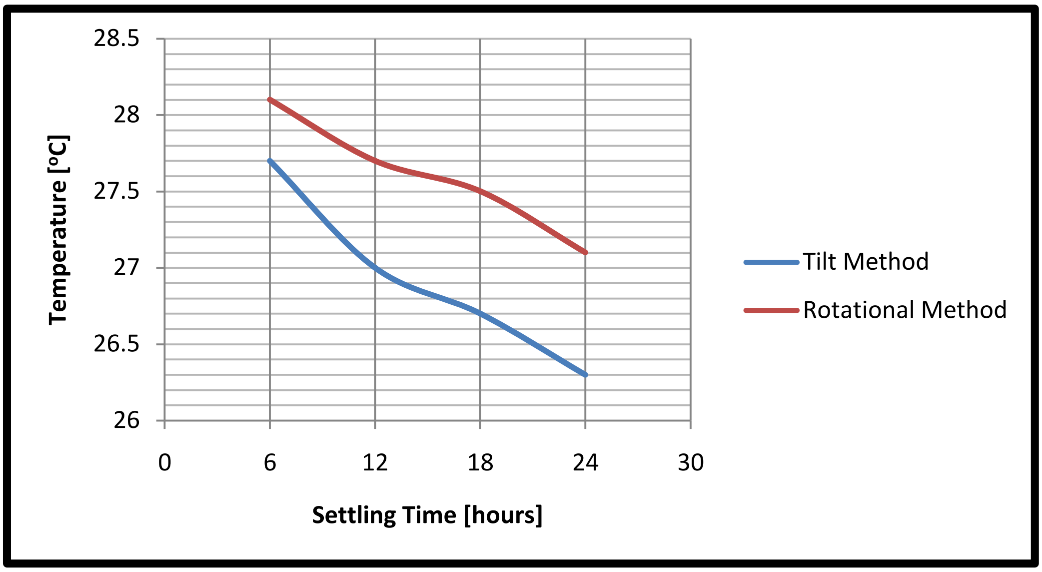

Figure 20: Comparison of Rotational Method and Tilt Method for 60^oC

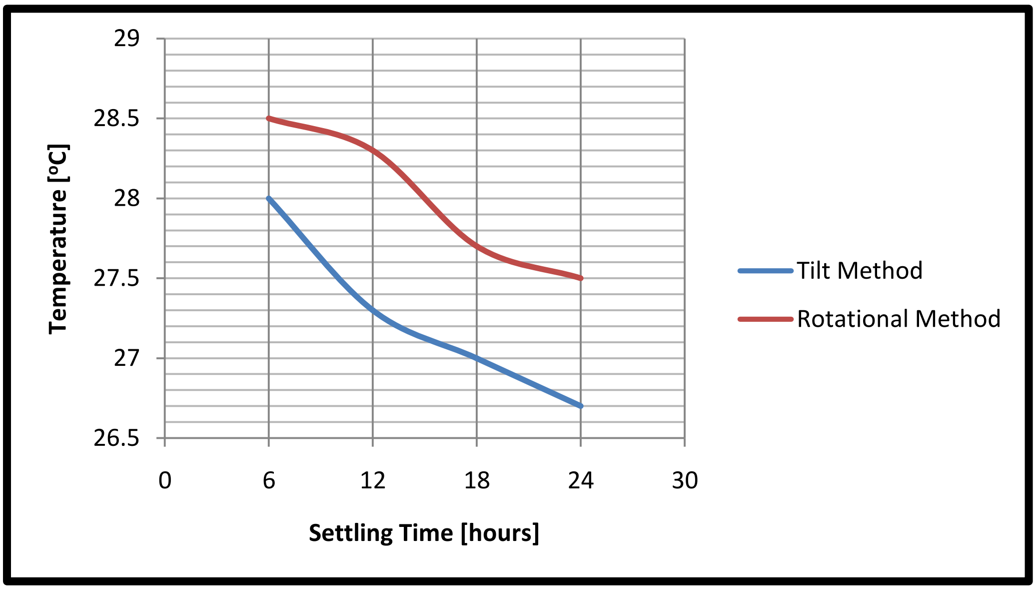

Figure 21: Comparison of Rotational Method and Tilt Method for 80^oC

According to the graphs shown above, the rotational method has presented slightly higher average freezing point reading compare to tilt method. One of the reasons that causing the differential is the resolution of rotational method is 0.1^oCmeanwhile the tilt method is 1^oC. Therefore, the rotational method is more accurate in term of resolution. The way of handling the tilt method is also affecting the results of the freezing point. During the experiment conducted, the crude samples might be mechanically disturbed which affect the wax deposition and crystallization process of wax. The tilt action might cause the freezing point of tilt method slightly incorrect as the crude sample is tilt $90^o$for a few times before the crude sample freezes.

Meanwhile, the rotational method measures the pour point inside the cup container and tested with cylinder shaped sensor. The way of measuring is able to avoid the mechanical action like the tilt method as the crude sample is not tilted for 90^o. The cup container will be rotated against the cylinder shaped sensor during the measuring process and stop once the freezing point achieved. The rotations of the cup container might have less effect towards the crude oil pour point compared to the tilt action.

The rotational method is applicable to measure the pour point crude oil as the differential of the freezing point temperature is very small which is about 1^oC at maximum. By referring to both of the graphs above, the tilt method and rotational method have same pattern of decreasing and the gap of temperature between the two lines at every point is constant and not overlapping with each other.

4.3 Percentage Error

4.3.1 Settling Time

In order to estimate the length of settling time that is acceptable to be applied to hold the crude oil before measurement conducted without affecting the pour point of crude oil, percentage error for each of settling time is calculated for both methods. The freezing point of each settling time is compared with the standard settling time which is 24 hours by using rotational method samples. The calculation is as below;

Percentage error (%) = $\frac{|Value\ \ of\ 24\ hours\ \ Sample\ \ -Value\ \ of\ 18\ /\ 12\ /\ 6\ hours\ \ Sample\ \ |}{Value\ \ of\ 24\ hours\ \ Samp\ le}$x 100

Rotational Method

- 60^{o}C pre-heating temperature / 18 hours settling time

  Percentage error (%) = $\frac{|27.1-27.5|}{27.1}$x 100

  = 1.45%

- 60^{o}C pre-heating temperature / 12 hours settling time

  Percentage error (%) = $\frac{|27.1-27.7|}{27.1}$x 100

  = 1.48%

- 60^{o}C pre-heating temperature / 6 hours settling time

  Percentage error (%) = $\frac{|27.1-28.1|}{27.1}$x 100

  = 3.69%

Tilt Method

- 60^{o}C pre-heating temperature / 18 hours settling time

Percentage error (%) = $\frac{|2.63-26.7|}{26.3}$x 100

= 1.52%

- 60^{o}C pre-heating temperature / 12 hours settling time

Percentage error (%) = $\frac{|26.3-27.0|}{26.3}$x 100

= 2.43%

- 60^{o}C pre-heating temperature / 6 hours settling time

Percentage error (%) = $\frac{|26.3-27.7|}{26.3}$x 100

= 3.80%

From the observation, the 6 hours settling time of the crude oil has shown the biggest percentage different among the other 2 samples. The 12 hours and 18 hours crude sample has shown the percentage error less than 3% which are 1.45%, 1.48%, 1.52% and 2.43%. The percentage of different for 12 hours sample that is measured by tilt method is quite big compared to 12 hours sample that is measured by rotational. The possible reason is the resolution of rotational method is smaller compared to tilt method which gives the different value and thus, high percentage of different.

4.3.2 Measurement Methods

In comparing the rotational method with tilt method, the percentage error is calculated to show the percentage of different between the two methods. All of the samples will be calculated by subtracting the value of freezing point at specified pre-heating temperature and specified settling time of tilt method with rotational method. The calculation is as below;

$$\text{Percentage error (\%)} = \frac{|Value\ \ of\ Tilt\ \ Method\ - Value\ \ of\ Rotational\ \ \ Method|}{Value\ \ of\ Tit\ Method} \text{x } 100$$

Calculation:

<u>60°C Samples</u>

- 60°C pre-heating temperature / 24 hours settling time

$$\text{Percentage error (\%)} = \frac{|26.3-27.1|}{25.7} \text{x } 100$$

$= 5.22\%$

- 60°C pre-heating temperature / 18 hours settling time

$$\text{Percentage error (\%)} = \frac{|26.7-27.5|}{26.7} \text{x } 100$$

$= 3.00\%$

- 60°C pre-heating temperature / 12 hours settling time

$$\text{Percentage error (\%)} = \frac{|27.0-27.7|}{27.0} \text{ x } 100$$

$= 2.59\%$

- 60°C pre-heating temperature / 6 hours settling time

$$\text{Percentage error (\%)} = \frac{|27.3-28.1|}{27.1} \text{ x } 100$$

$= 2.93\%$

80^{o}C Samples

- 80^{o}C pre-heating temperature / 24 hours settling time

Percentage error (%) = $\frac{|26.3-27.1|}{25.7}$ x 100

= 3.0%

- 80^{o}C pre-heating temperature / 18 hours settling time

Percentage error (%) = $\frac{|26.7-27.5|}{26.7}$ x 100

= 2.59%

- 80^{o}C pre-heating temperature / 12 hours settling time

Percentage error (%) = $\frac{|27.0-27.7|}{27.0}$ x 100

= 2.66%

- 80^{o}C pre-heating temperature / 6 hours settling time

Percentage error (%) = $\frac{|27.3-28.1|}{27.1}$ x 100

= 3.26%

As the percentage of different has been calculated, it shows that the percentage of different for all of the samples is less than 5%. It is also correlated that the pour point obtained between the rotational method and tilt method does not exhibited big gap. The maximum different of value between both methods is 1^{o}C. Therefore, it is still acceptable and practical to apply rotational method in order to measure the crude oil pour point.

CONCLUSION

In conclusion, the main idea of this project is to study the effect of pre-treatment towards the crude oil pour point. The pre-treatment is a process that is required to be conducted based on the standard of using tilt method (ASTM D5853) that involved pre-heating the crude sample and hold the crude sample before the pour point is measured for crude oil to settle. Thus, this project is conducted to study the thermal behavior by varying the pre-heating temperature to 80^{o}C and the settling time to 6 hours interval. Besides, rotational method is used in this project in order to compare the effectiveness of the method in measuring the crude oil pour point.

From the data obtained, it can be concluded that the best pre-heating temperature is at 60^{o}C at maximum. As discussion mentioned above, the 60^{o}C is set as the maximum pre-heating temperature in order to prevent the light molecular component of wax to evaporate which will caused inaccuracy towards the pour point reading. The results show that the increment of the pre-heating temperature will increase the pour point of the crude oil. Thus, increasing of pour point will increase the percentage error and therefore, the pour point reading will be incorrect.

Throughout the experiment, the settling time is varied to 6 hours, 12 hours and 18 hours. From the graph of results, the shorter the settling time, the higher the crude oil pour point. By calculating the percentage error, it shows that the 6 hours has highest error compared to 12 hours and 18 hours. Therefore, it can be concluded that the settling time of pre-treatment could be decrease but not exceed 12 hours since the shorter of the settling time, the percentage of error will be increased. The 12 hours is chosen since the percentage error of 12 hours is still acceptable. Hence, by reducing the settling time, the shorter the time consumed to measure pour point.

Finally, the rotational method is compared with the conventional method. The rotational method has shown the accuracy as the resolution of temperature is smaller (0.1^{o}C). Besides, the method of handling the measurement is better compare to tilt method as the crude sample is not mechanically disturbed. The result of rotational method might be more accurate compare to tilt method. However, as the percentage error has been calculated, most of the crude samples show small percentage error. Therefore, the rotational method is applicable and is a better way to measure the crude oil pour point.

RECOMMENDATIONS

There are several recommendations that could be made in order to improve this project in the future. The crude oil sample could be examined the wax content, asphaltenes, resins and the components of the crude oil by using liquid chromatography. Several crude oil properties and rheology could be identify and correlate to the pour point of the crude oil such as viscosity, gel strength, and Saturate, Aromatic, Resin and Asphaltene (SARA) analysis.By doing this experiment, the thermal behavior exert by crude oil could be studied and understand and the components of crude oil could be known. This analysis could enhance the crude oil pour point research in order to observe the effect of pre-treatment towards the pour point of crude oil.

Besides, advanced laboratory apparatus and surrounding condition could be setup in the future to reduce the error while handling the crude oil during the pre-treatment process and pour point measurement process. Since the tilt method involved manual tilting action, there is huge possibility that errors are committed during the measurement taken. Therefore, advanced laboratory apparatus could be used to assist the measurement process. In addition, during the pre-treatment process take place, there is possibility that the crude oil not homogenous even slightest. Several processes should be designed before the pre-treatment conducted in order to ensure the crude oil is homogenous.

In studying the crude oil pour point, it is involved the crude oil that recovered from the reservoir. Therefore, the crude oil produced might also contained high amount of light gas such as methane and known as live oil. Study need to be made in measuring the pour point of live oil since the presence of gas might lower the pour point of the crude oil. Thus, in the future, the crude oil sample is needed to be pressurized with light gas in preparing the live oil before the pour point is conducted.

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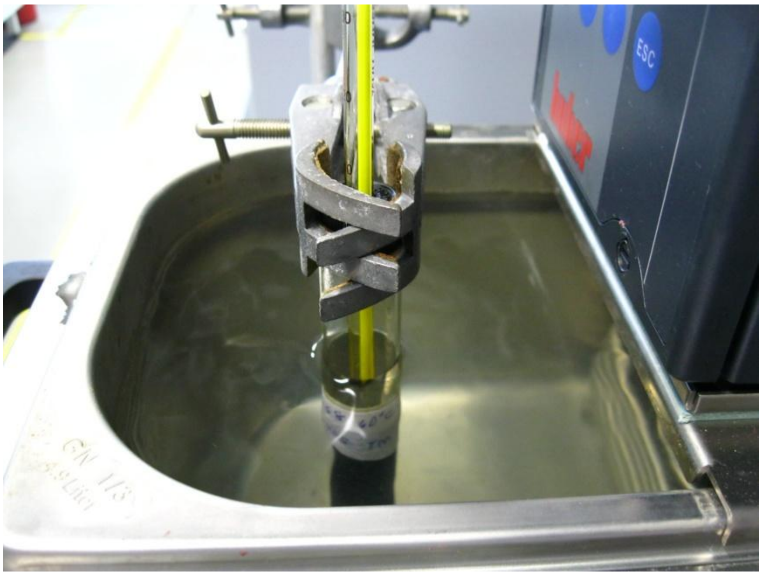
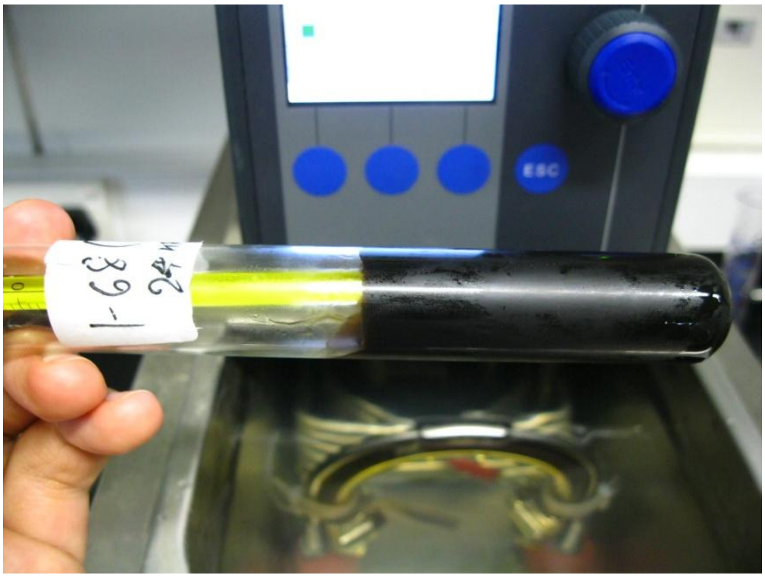
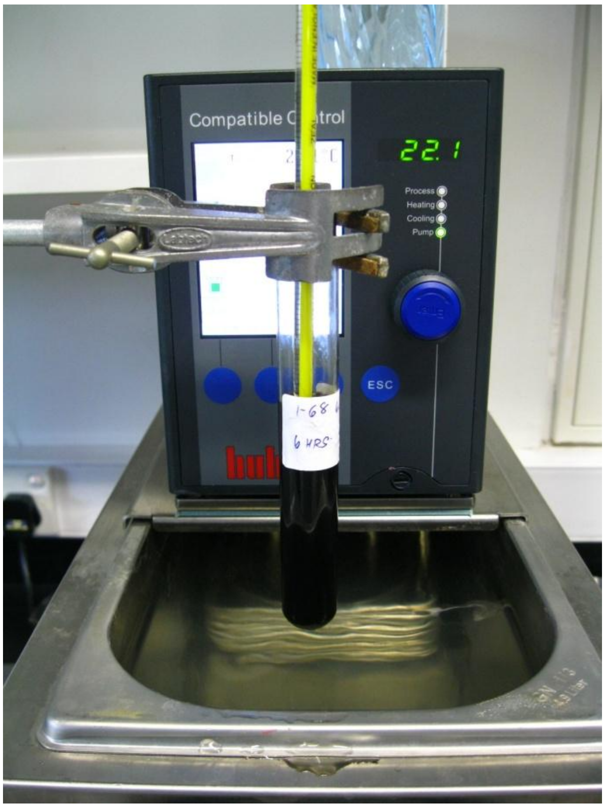
APPENDIX



Crude Oil Sample is heated inside Water Bath



Tilting Action



Crude Oil Sample is cooled at Room Temperature