MUHAMMAD IKMAL BIN NADZERI

B. ENG. (HONS) PETROLEUM ENGINEERING

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APPLICABILITY STUDY OF ROTATIONAL METHOD BASED FROM ASTM D5985 FOR CRUDE OIL POUR POINT MEASUREMENT

MUHAMMAD IKMAL BIN NADZERI

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Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan.

CERTIFICATION OF APPROVAL

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Muhammad Ikmal Bin Nadzeri
13236

A project dissertation submitted to the
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(PETROLEUM ENGINEERING)

Approved by,

_____

(Mazuin bt Jasamai)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

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 IKMAL BIN NADZERI

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ABSTRACT

Accurate measurement of crude oil physical properties is important in ensuring the parameters are defined clearly before the result could be used for further field implementation. One of the important parameter in flow assurance of crude oil is pour point, defined as the lowest temperature at which movement of the specimen is observed under specific condition. Up until the time this report is written, only one standard method available to measure the pour point of crude oils published by American Society for Testing and Material (ASTM) designated ASTM D5853. However, physical action upon the crude by tilting during measurement is believed to affect the pour point measured, hence giving different measured values from the actual. In this project, alternative method is proposed, which is ASTM D5985 – Standard Test Method for Pour Point of Petroleum Products (Rotational Method). It is understood that this standard is designed to measure the pour point of petroleum products only and it is not intended for use with crude oil. Therefore, study on the pour point obtained using the tilt method and rotational method with respect to the type of sample is conducted and compared to find out if this rotational method is applicable to be used with crude oils or not.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1. BACKGROUND OF STUDY

The continuous increasing demand of energy source nowadays has leave many oil and gas companies choices of either to continuously producing hydrocarbon using conventional method – where majority of it constituted by high gravity high wax content crude – or finding solution for producing unconventional energy source using unconventional method. Problems with producing waxy crude with high paraffin content are mainly related to flow problems especially during its transportation as many important parameters of the crude must be specified before any related facilities can be built.

One of the important parameter is pour point, described as the lowest temperature of the crude before it ceases to flow. In ASTM standard, crude oil pour point is defined specifically as *the lowest temperature at which movement of the test specimen is observed under the prescribed conditions*. Pour point determination is important as to ensure that the facilities being built can guarantees the continuous flow of the crude before it can reach certain destination or additives being used can ensure successful pumpability throughout the whole distribution pipelines and transportation stages. Generally much of the pour point of crude oil is affected by its paraffinic content, and crude that has high paraffin content will usually have high pour point.

Pour point concept is important for flow assurance of crude in long distance pipeline distribution and transportation through tanker. The flow of crude must be ensured to continuous at all time, especially when platforms face unscheduled shut down or pump failures. This is because to resume the flow when the crude has solidified is impossible and the externally applied pressure to restart the flow could exceeds the burst pressure of the pipeline and once the pipe is burst, the remedial effort needed is tremendous. Pour point is also one major parameter for petroleum products. Lubricants for machine and mechanical equipment must ensure it exhibit

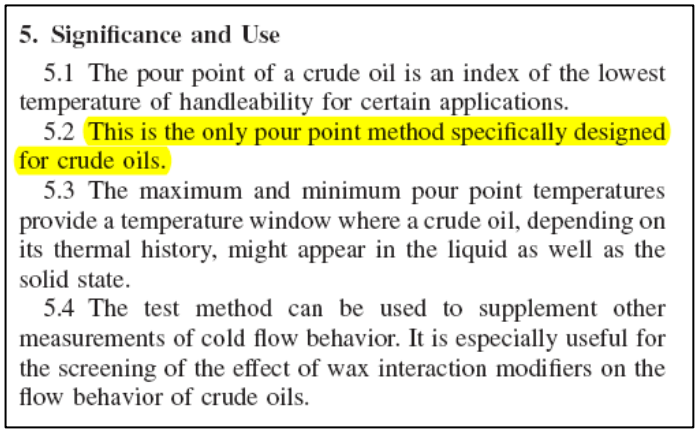
flow characteristics at specific temperature range, especially in countries that are experiencing seasonal climates.

2. PROBLEM STATEMENT

There are several standards and technique published to measure pour point, commonly using physical observation such as cloud point, viscometric measurement or indirect technique by measuring thermodynamic profile of wax in the crude. American Society for Testing and Material (ASTM) has published several standards in which they are divided into 2 type of test specimens; petroleum products and crude oil. The designation and name of the standards are as follow:

- ASTM D97 – Tilt method (Petroleum Products)
- **ASTM D5853 – Tilt method (Crude Oils)**
- ASTM D5949 – Automatic Pressure Pulsing Method (Petroleum Products)
- ASTM D5950 – Automatic Tilt Method (Petroleum Products)
- ASTM D5985 – Rotational Method (Petroleum Products)
- ASTM D6749 – Automatic Air Pressure Method (Petroleum Products)
- ASTM D6892 – Robotic Tilt Method (Petroleum Products)

However, for crude oils, the conventional way of determining pour point for crude is based from ASTM D5853 and it is the only pour point method specifically designed for crude oils although previously ASTM D97 was widely accepted by researches as the standards before ASTM D5853 was published.



5. Significance and Use

5.1 The pour point of a crude oil is an index of the lowest temperature of handleability for certain applications.

5.2 This is the only pour point method specifically designed for crude oils.

5.3 The maximum and minimum pour point temperatures provide a temperature window where a crude oil, depending on its thermal history, might appear in the liquid as well as the solid state.

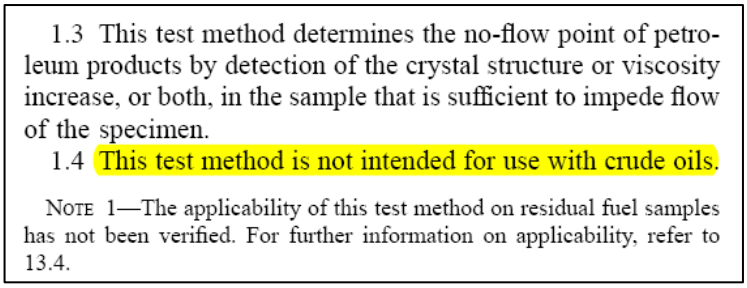
5.4 The test method can be used to supplement other measurements of cold flow behavior. It is especially useful for the screening of the effect of wax interaction modifiers on the flow behavior of crude oils.

Figure 1: Screenshot ASTMD5853 standard showing the availability of it as the only standard for the measurement of crude oil pour point

According to the standard, the test specimen will undergo pretreatment, which it will be heated up to maximum temperature of 60°C, and left for at least 24 hours for cool down. Later, prior to the measurement, the specimen will be heated again minimally and cooled at specified rate and observed for any flow characteristics by tilting the test jar. The process of cooling and tilting is repeated several times and the point at which the oil ceases to flow for at least 5 seconds, added up with 3°C is specified as the pour point.

This method however, although have been practiced world widely, is prone for error, especially from human part when conducting the experiment. This is mainly because the act of tilting the test jar contained with crude to observe for flow characteristics will disturbs the crystallization process inside the crude hence affecting the pour point obtained which will reduce the repeatability of the measurement. Karan et al (2000) who conducted research on novel laboratory technique of measuring waxy crude properties also described that the ASTM D5853 is cumbersome, requiring the crude oil to be 'preheated to a certain prescribed temperature and allowed to be cooled at a prescribed cooling rate, tested in defined dimension of specific type of vessel'.

Therefore, this project is proposing an alternative method, which is based from ASTM D5985 - Standard Test Method for Pour Point of Petroleum Products (Rotational Method) to measure crude oil pour point, except that it was originally designed for petroleum products' pour point measurement. In the standard, it has specifically mentioned that this method is not intended to be used with crude oils. However, it is the purpose of this project to find out if this standard method is applicable to be used with crude oils or not, provided with some modifications and recommendations to be included, if any. The standard mentioned about the unintentional of this method to be used with crudes does not really specify the inapplicability of it to be used with crude oils.



1.3 This test method determines the no-flow point of petroleum products by detection of the crystal structure or viscosity increase, or both, in the sample that is sufficient to impede flow of the specimen.

1.4 This test method is not intended for use with crude oils.

NOTE 1—The applicability of this test method on residual fuel samples has not been verified. For further information on applicability, refer to 13.4.

Figure 2: Screenshot from ASTM D5985-02 showing the Point 1.4 explicitly mentions the unintentional of this method to be used with crude oils

Different with ASTM D5853 tilt method, all of the measurement of D5985 rotational method is conducted using automatically set pour point tester machine. The mechanism is that the test cup filled with test specimen will undergo a very slow rotation approximately at 0.1 RPM while a coaxial, tilt-able temperature sensor is dipped inside the specimen. The continuous gradual decline in temperature will cause the specimen to form a crystal structure or/and increase its viscosity, hence causing the temperature sensor to move out of its position which later on will triggers the light barrier, indicating it has reached the no-flow point.

The reason why crude oil pour point determination using alternative D5985 rotational method is proposed is because it is believed to have less error compared to tilt method due to reason that the mechanism of the rotational and data collection was done completely by computer program and mechanical lever. Compared with D5853 tilt method, all the tilt mechanism was done manually using human hand and observation. The temperature control is also done by externally attached water bath, hence giving better gradual in incremental or decline in temperature to the test cup. This pour point tester machine also has temperature sensor dipped into the specimen during measurement, hence any cooling history and thermal behavior of the crude can be recorded and analyzed.

Other than that, during the temperature measurement and rotating of the specimen, the sample is only left to be rotated in the machine, compared to tilt method – regardless whether it is manually or automatically done – where the sample will be brought out and tilted physically, are prone to the distortions on the crystallization of the wax crystal, hence error on the pour point obtained.

3. PROJECT OBJECTIVES

The objectives of this research are as follow:

- To find out if the rotational method according to ASTM D5985 standard is applicable to be used to measure crude oil pour point
- To find the best pre-treatment technique for crude oil that will give the most accurate pour point reading
- To understand the effect of difference in properties of the test specimen might cause, in this case specifically between crude oils and petroleum products, with regards to its pour point measurement technique

4. SCOPE OF WORK

The scope of this project is mainly about crude oil rheology and flow assurance as the pour point is categorized under the cold flow behavior of the crude. Other than that, understanding on waxy crude handling and wax content measurement are also involved as wax content in crude concept are very much related to pour point. The crude viscosity, API gravity, gel strength, and maybe even wax content and Wax Appearance Temperature (WAT) of the crude will be analyzed to understand the trending of the results better. Furthermore, to enhance more detail understanding, crude oil wax properties and crystallization mechanism will be studied in detail.

5. RELEVANCY AND FEASIBILITY OF THE STUDY

Pour point, although it is only branches of flow characteristics in the upstream part of crude production, it plays an important role in describing the crude properties. Outcomes from this project are hoped could enhance future subsequent researches, hence increase the acceptability and reliability, especially for the facilities construction and decision making processes.

From this project, it hoped that this method could be proved applicable and acceptable as it would ease researches to conduct the pour point measurement in simpler and convenient way. The 25 weeks timespan given is enough to complete

this project in specified time, provided that it is conducted in organized manner and all the specimens and equipment are available

CHAPTER 2

LITERATURE REVIEW

1. RELEVANCY OF POUR POINT DETERMINATION IN CRUDE HANDLING

Determination of pour point is important and it is really much affected by wax content inside the crude. Nowadays, the increasing global demand on new supplies of hydrocarbon has made this high-waxy crude to become increasingly interesting and demanded, in addition that they often have low sulfur content, desirable from environmental point of view. However, understanding the flow properties of crude does not necess considering pour point only but also several other important related parameters such as viscosity and gel strength. It has been a common practice for many pipelines to specify pour point as the sole criterion for determining acceptability of a crude oil (Sifferman, 1979).

Uba, Ikeji and Onyekonwu (2004) described that the economic viability of projects may depend on realistic estimates of flow problems and associated preventive technique. Although the cost of designing and implementing additional flow assurance equipment can be substantial, it would be better rather than to remedy flow problems when insufficient program was set up as the cost incur can be tremendous. Therefore initial planning program with long-term scope of view is crucial before any decision making related to facilities can be made.

Once crude is produced, its journey until reaching the target destination could be varied. Most commonly crude will be travelling in long distance pipelines throughout low-temperature seabed to reach the terminal. It could also be that the crude undergoes long static condition inside a storage tank after being produced from production platform before it can be transported to another place. Another most common situation is during the loading of crude from tanker after it has undergo static cooling inside a tanker and the pipelines, as what was described by Irani and Zajac (1982) for the waxy West African crude oil.

During the transportation of crude, especially from static condition of low temperature i.e from tanker to loading line, the crude has ample time to develop 3-

dimensional gel. Depending on the final temperature, the externally applied pressure required to break the gel structure to initiate flow in the pipeline could exceed the burst pressure of the pipeline. Therefore, modifying the crude pour point property by dampening the gel formation with additives is important to ensure flow and pumpability.

2. COMMON WAXY CRUDE OIL HANDLING TECHNIQUE

Many researches had described various methods of transporting waxy crude oil as it can be mechanically, thermally of chemically means from various authors. For example, Irani and Zajac (1982) from Uhde and Kopp (1971), they described that the most common practiced all around the world of ensuring crude flow below pour point is by heating the crude and insulate the pipelines.

This is because, by heating the crude, it ensures the pumpability of the crude, regardless of the factor of the pour point, the wax content and the intricacy of the interaction among the high molecular weight species responsible for final gelling phenomenon. However, increasing cost of energy needed for heating and the impracticality of it in certain environments has forced researchers to develop alternate schemes.

Other method is by mixing of water together with the crude to create emulsion during its transportation. However, problem arises from this method as the presence of water itself has been shown to assist the wax crystallization and hence, reduce the practicality of this method.

Another is by mixing the high wax content crude with lighter crude or crude with lower pour point. It was understood that only 2% wax in hydrocarbon stream can give rise to high pour point. However, due to lack of the availability of diluting solvents in most circumstances, has limited the practicality of this technique (Holder & Winkler, 1965).

From chemical perspective, the use of polymeric additives to modify crystal structure of the precipitating waxes is beginning to receive considerable attention. Different distinction exists of the use of additive in crude transportation whether to depress the pour point, or treating the waxy crudes. Halim et al (2011) has published

a research on the usage of different type of pour point depressants on Malaysian crude oil, which differentiated by the methyl group branching in the backbone of the polymer. However, the minor differences from the polymer has made a tremendous differences on the crude as some of the polymer reduced the pour point up to 12°C and some even increased it.

The scenario is supported by Irani and Zajac (1982) as they described that the complex nature between wide ranges of high molecular weight species and carbon numbers in raw crude has resulted in specific additives being effective only with very specific types of crudes. Since no additive has proved universally effective, the selection of an efficient additive becomes critical and better understanding of the mechanism of crude oil pour point is crucial. (Tung et al, 2001)

The ways these additives work are different. For example, Sifferman (1979) has conducted a research on 3 types of flow properties; viscosity, pour point and gel strength, on several types of crude samples using emulsion and wax crystal modifier (or noted as flow improver).

In the test using wax crystal modifier for flow improver, it was observed that the flow improver will only effective near and at the pour point of the crude as the waxes have not started to cause flow problems until that time (although some of the wax crystals were already created) and therefore it should not be expected to be effective at temperature higher than this point. Different with additive, it will usually efficient at temperatures higher than the pour point, and it might be the cloud point. The emulsifiers will form low-viscosity, oil-in-water emulsions along the crude.

3. WAX PRECIPITATION MECHANISM THAT LEADS TO CRUDE NO-FLOW POINT

Essentially, the hydrocarbons present in crude petroleum are classified in three (3) general types which are paraffin, naphthenic, and aromatics. The focus of this project is paraffin in crude as generally crude oil with high paraffinic content is classified as waxy crude. Waxes are essentially mixtures of long-chain hydrocarbons with carbon chain lengths ranging from C15 to C75. Generally, paraffin are crystalline in nature, and they tend to crystallize/precipitate from crude at and below

their cloud point, which later on led to solidification of crude, temperature at which it is called pour point (Srwastava et al, 1993)

Uba et al (2004) from Wunderlich (1976) has described the process on which crystallization of wax in crude occurs which led to pour point. Crystallization is the process whereby a disordered phase is aligning among them to form an ordered solid structure, and in this case is wax molecule. It usually involves 2 distinct stages:

- Nucleation

As the temperature of the specimen is lowered to its Wax Appearance Temperature (WAT), the energy of molecular motion becomes increasingly hindered and the randomly tangled molecules in the solution tend to move closer together and form clusters of adjacently aligned chains. The paraffinic molecules continue to attach and detach and forming these ordered structure until the clusters reach a critical size and become stable. These clusters are called nuclei and they are only stable below the melting/dissolution temperature of the wax, as above this temperature their formation is hindered by thermal motion.

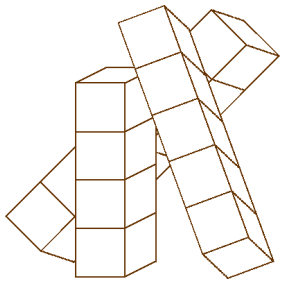


Figure 3: Macro-crystalline wax formed from paraffin

- Growth

Once the nuclei are formed, additional molecules are laid down successively on the nucleation sites and become part of the growing lamella structure or called as crystals, provided that the temperature is kept at or below the wax appearance temperature (WAT). Therefore, it is understood that pour point is extremely affected by the wax crystal size, structure and number. Thus, disturbance on crystallization process and crystal morphology will affect the measurement of pour point as

achieving equilibrium between crystallized wax and dissolved wax is a slow process in crude.

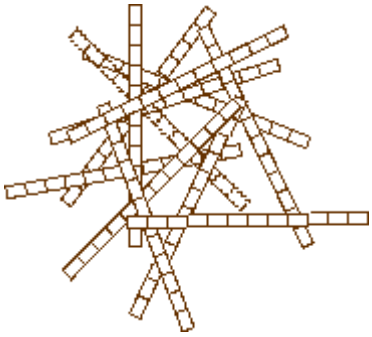


Figure 4: Microcrystalline wax formed from napthenes.

In their study that was conducted by Karan et al (2000) upon 3 types of stock tank oil, increasing the pre-heat temperature by only 20°C from 60°C to 80°C gives significant different in pour point measured as it depressed the pour point of up to 19°C. Thus, it can be deduced that at higher preheating temperature, the crude will have better homogeneity among its wax components and provides longer timespan for the crude to achieve equilibrium and hence making it to have a lower pour point.

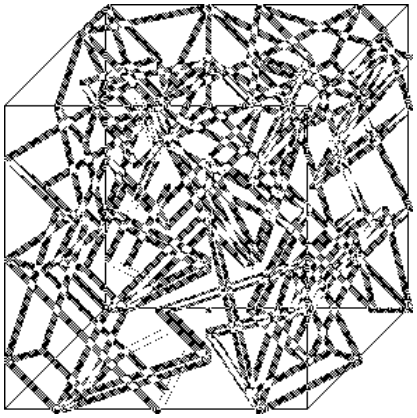


Figure 5: Crystal deposit network of wax

Waxy crude usually consists of a variety of light and intermediate hydrocarbons which is paraffin, aromatics and naphthenic. When wax freezes it forms crystals and the crystals formed from paraffin wax are known as macro-crystalline wax and those formed from naphthenes are known as microcrystalline wax.

Several factors affecting the rate and amount of wax deposition consist of:

- Composition of the hydrocarbon component in crude
- Cooling rate
- Pressure
- Paraffin concentration and their molecular mass
- Nucleating materials (asphaltenes, formation fines and corrosion products)
- Water oil ratio and
- Shear environment

However, not all of the components in the hydrocarbon contributed fairly to the formation of wax crystals. For example, Os'kin (1973) described that the n-paraffins and iso-paraffins are flexible hydrocarbon molecules so they tend to cluster together and precipitate from crude oil as wax solids. However, iso-paraffins, being branched molecules, they tend to delay the formation of wax and usually form unstable wax solids. On the other hand, Napthenes (cyclo-paraffin) are stiff and bulky in nature, hence they tend to disrupt the nucleation and growth process. Finally, impurities/amorphous solid such as asphaltene is believed to induce wax nucleation process by lower the energy barrier (activation energy) on forming the critical wax nucleus.

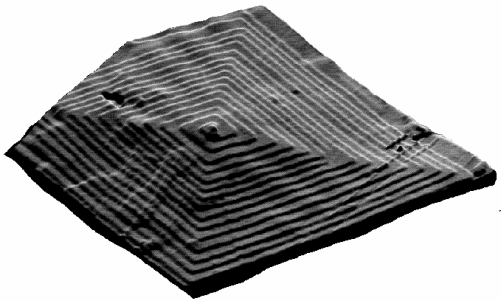


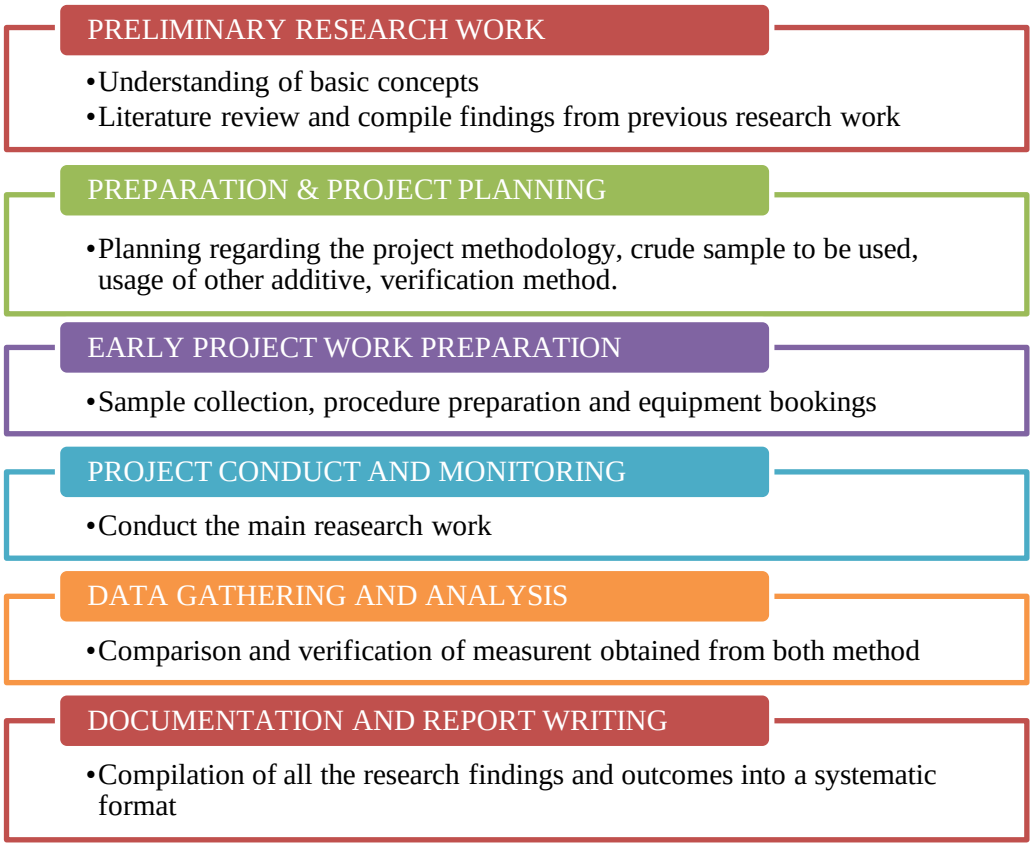
Figure 6: An atomic force microscope image of the spiral growth of paraffin crystal

CHAPTER 3

METHODOLOGY

1. RESEARCH METHODOLOGY

This research generally consists of 6 parts of methodology, beginning from the preliminary research work, up to data gathering and report writing. The description of each stage is presented as follow:



The preliminary research work mainly is selection of the project topic, conducting previous research review and references. Journals, conference papers, books and internet articles are referred. From the data and analysis gathered, author can gain insight and understanding of that the topic is all about.

Project planning and preparation is the stage where necessary test specimens are obtained and equipment is being booked. The crude that will be used in this project mainly the one that has high wax content. Once the test crude is obtained,

several necessary identification, preparation and treatment of the crude will be conducted.

Prior to the measurement, the test crude undergo specific pre-heating and cooling as to find the best pre-treatment technique during the early project work. Since pour point is dependent on the state of thermal pre-treatment and wax crystal formation process as discussed before, prior to the pour point measurement, the crude will undergo varying pre-treatment process, at which it will be heated at different temperature and cooled at different period. In ASTM D-5853, the recommended cooling period after pre-heating before conducting the measurement is 24 hours, and in this project, the period will be varied in order to investigate the optimum pre-treatment heating that gives the lowest pour point.

After the crude has been identified its basic parameters, then it comes the primary project work. The pour point of the crude will be measured using rotational method according to ASTM D5985 standard method and tilt method of ASTM D5853. Equipment that will be used to measure the pour point is Pour Point Tester (PPT) 45150 by PSL System-Technik. Tilt method will be done manually, or with mechanical machine, if available. 3 cycles of the measurement are being set to get the average value.

Once all the experiment project has done, all the data and results will be documented and analyzed for further interpretation in the form of document and report writing.

2. KEY MILESTONE

WEEK	ACTIVITIES
FYP I	
3	Topic Selection and Supervisor Assigning
4	Preliminary Research Work and Literature Review
7	Submission of Extended Proposal
10	Proposal Defense
12	Interim Report Submission

Table 1: Key Milestone planned for the FYP1 Period

WEEK	ACTIVITIES
FYP II	
8	Submission of Progress Report
12	Pre-SEDEX and Submission of Draft Report
13	Submission of Technical Paper and Oral Presentation
14	Submission of Project Dissertation

Table 2: Key Milestone planned for the FYPII Period

3. GANTT CHART

In order to achieve timely and organized project progress, Gantt chart is used as reference to when certain submission and presentation has to be made. Tables below show the Gantt chart for FYPI and FYPII respectively.

FYP I														
ITEM	WEEK													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Project title selection														
Preliminary research work and literature review														
Extended proposal submission														
Proposal defense														
Project planning														
Preliminary project work														
Interim Report submission														

Table 3 Gantt Chart for FYP I

FYP II														
ITEM	WEEK													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Continuation of project work														
Literature review and research referencing														
Progress report submission														
Finalizing project work														
Data gathering, analysis, verification, justification and discussion														
Pre-EDX														
Draft Report submission														
Dissertation (soft bound) submission														
Technical paper submission														
Oral Presentation														
Dissertation submission														

Table 4 Gantt Chart for FYP II

CHAPTER 4

EXPERIMENTAL DESIGN

1. REVIEW ON THE ASTM D5853 – STANDARD TEST METHOD FOR POUR POINT OF CRUDE OILS

This is the only standard specifically designed for crude oil pour point method and it recognizes the potentially strong effect of the crude thermal history on the gelling temperature (Bai, Y. & Bai, Q., 2012), as there is no pretreatment method being specified for the ASTM D5985 rotational method. In tilt method, it employs 2 separate heating and cooling to see the effect of 2 substantially different thermal histories. The pour point measurement is divided into 2 types: maximum (upper) and minimum (lower) pour point. The difference between these two is that for the **maximum** pour point the test specimen has been subjected to a prescribed treatment designed to **enhance** gelation of wax crystals and solidification whereas for the **minimum** it is designed to **delay** the gelation.

The procedure in summary consist the process of 1st preheating in the original container, transferring specimen into test jar, cooling for approximately a day, 2nd preheating and finally the measurement. In length, the specimen will undergo first preliminary heating when the specimen is still inside the container to ensure the homogeneity of the crude before being transferred into small volume of the test jar.

After 24 hours cool down period at room condition, the specimen will be heated for the 2nd time to approximate 45°C and let cooled inside a bath containing specific cooling medium cooled at a specified temperature stages. The specimen is examined at intervals of 3°C for flow characteristic by tilting it. The temperature at which no movement of the specimen is observed and being rounded up to the nearest upper multiple of 3°C temperature is regarded as the pour point. For example, if the specimen observed not moving after being tilted for at least 5 seconds at 14°C (the no-flow point), then the pour point is recorded as 15°C, as according to multiple of 3°C.

Additional information is that, for the minimum pour point, the test specimen will be heated inside a pressure vessel immersed in an oil bath of temperature 105 ±

2°C for 30 minutes and let cooled at room temperature for at least 30 minutes before being transferred into small test jar. Then, it is proceed with the same procedure to measure the pour point, and so it is understood that the specimen does not undergo the 24 hours cool down period as how it is done for the maximum pour point.

By now, one can understood that what is meant by maximum is that the method raises the measured point by allowing a long time for wax seed crystals to form at room temperature during the cooling period which in turn reduce the time for gel formation. On the other hand, minimum protocol lowers the pour point by ensuring that all wax is in solution before cooling is started, and the cooling process is relatively quick, so it is highly possible that the wax crystallization process is out-run hence lower temperature precedes first before the wax gel can be completely formed (Bai & Bai, 2012).

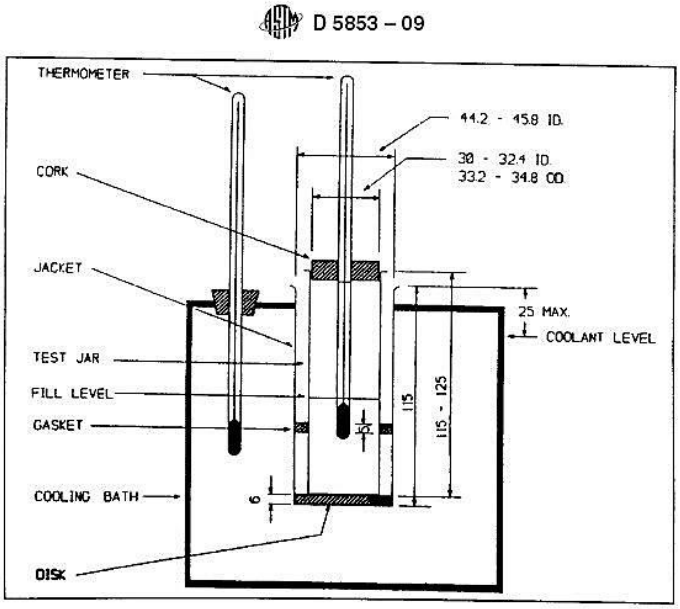


Figure 7: Diagram of experimental setup for tilt method ASTM D5853

Figure above shows the setup of the pour point measurement. For the material being used, the standard specifies that the test jar to be made up of clear glass with the wall thickness shall be no greater than 1.6 mm. This is to ensure that the heat transfer between the specimen inside the test jar and the cooling medium is uninterrupted. Surrounding the test jar is the jacket that made up of metal since metal as a good heat conductor can transfer the cool medium from the bath to the air layer gap that surrounds the test jar in a maximum manner.

2. REVIEW ON THE ASTM D5985 – STANDARD TEST METHOD FOR POUR POINT OF PETROLEUM PRODUCTS (ROTATIONAL METHOD)

This standard is designated to be used on petroleum products, in which rotational force is applied to the specimen cup at a very low speed, which is 0.1 RPM. Upon the cooling of the specimen, the resultant wax crystal formation or viscosity increase in the specimen exerts force on the temperature sensor dipped inside it, offsetting the stationary position at the light barrier on top of it causing detection of the no-flow point.

Much of the procedures in this method are done automatically by machine, in which every temperature controlled are done using a external cooling water bath and since it is done in closed environment, not much of the heat can loss to the surroundings. With the electronic temperature sensor dipped into the specimen, this method can determine the specimen temperature with resolution of 0.1°C at which wax crystals have formed.

As summary, before the measurement, if the sample is very viscous, it can be warmed until all the small wax formed on the wall of the container has dissolved and reasonably fluid to be transferred into the test cup, however, no sample shall be heated more than necessary as the machine will conduct the preheating automatically approximately at 45°C, or depending on the starting temperature value set by the user.

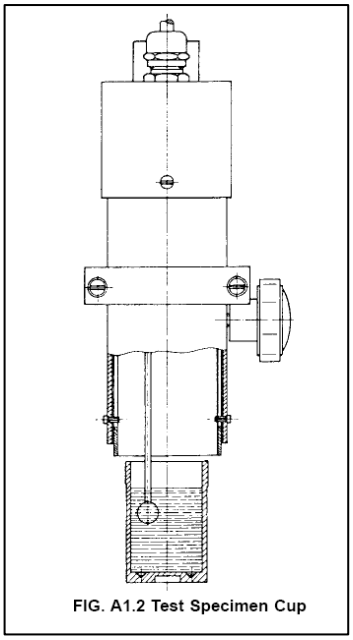


Figure 8: Diagram of experimental setup for pour point measurement based from rotational method ASTM D5985

Then, the test specimen is continuously rotated at 0.1 RPM and flow of the cooling fluid from the chill water bath will maintain the test cup at temperature approximately 8°C lower than the specimen temperature. At the detection of the last flow point, the temperature attained is held on the digital display until reset by the user. The specimen is the heated back to 45°C and the procedure is repeated, depending on the number of cycle set by the user.

One might wonder how severe is the viscosity of the fluid would give effect to the no-flow point obtained if the specimen to be used consists of a very high viscous crude oil sample. This is the clear difference between ASTM D5853 and ASTM D5985 as the no-flow point of this rotational method is dependent on the crystal structure and viscosity increase of the test specimen of the crude. Different with ASTM D5853, the tilt method is conducted since the tilt action only recognizes the wax crystal structure only and not the crude oil viscosity effect.

3. SAMPLE PREPARATION

Correct sample preparation before any testing plays a very important role in ensuring that every specimen allocated for each run is homogenous in terms of component available in it so that the result comparison can be run and

reproducibility of the test is high, especially when it comes to the testing of crude oils. As for private and confidential issue, in the next mention, the crudes that are used in this test will only be written as Crude X.

Initially, those crudes are being heated up in its bulk volume of less than 700 mL and stirred inside water bath temperature of 65°C at least 30 minutes to ensure the entire wax component inside the crude is homogenously uniform throughout the crude before transferring into smaller volume of sample glass cup with approximately 125 mL capacity.

From the sample cup, the specimen can then be heated up to desired pre-heating temperature before transferred into small tube for manual tilt and automatic rotational method.

Figure 9a: Sample originally in large bottle being heated up and stirred

Figure 9b: Sample being transferred into small volume of sample cup and being heated up to desired preheat temperature

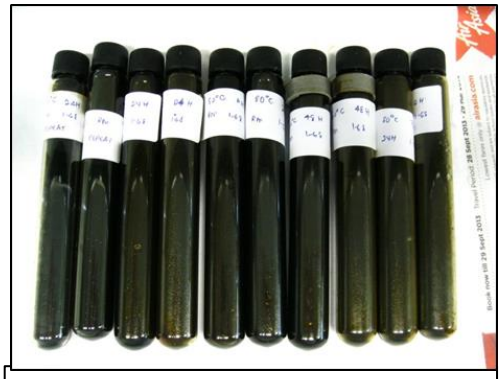


Figure 9c: Test specimen being transferred into small volume of its respective run

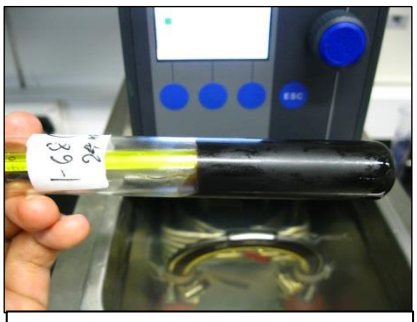


Figure 9d: Test specimen undergo tilt measurement

Figure 9e: Test Specimen being transferred into test cup for automatic rotational method

Figure 9: Sequence for the sample preparation and pretreatment

4. ASTM D5853 TILT METHOD MEASUREMENT TECHNIQUE

Temperature range will be used as pre-heating technique and cooling period that will be used upon the crude for pre-treatment for tilt method measurement is as follow. Note that this is only applicable for crude only and not petroleum products:

- Heating temperature range: 60°C to 80°C
- Cool down period range: 6 hours to 48 days.

		Cooling Period (Hours)				
	-	0	6	12	24	48
Preheat temperatures (°C)	50				50/24	
	60	60/0	60/6	60/12	60/24	60/48
	70				70/24	
	80	80/0	80/6	80/12	80/24	80/48

Table 5: Pretreatment matrix for tilt method

Certain parameters from the standards are being highlighted below to resemble the actual scenario of what was proposed by D5853 standard, as if these parameters are not done accordingly during the measurement of the pour point, it is afraid that different readings from the actual will be obtained.

4.1 Tilt interval of 3°C

As mentioned before, the crude oil pour point is dependent on the state of the formation of the wax crystal growth inside the crude. During the measurement of the pour point, the method requires the test jar to be removed from the jacket and tilted the jar enough to ascertain whether there is movement of the specimen. If there is movement noted, then the test jar is replaced back immediately in the jacket. The act of tilting are advised to be done once the specimen temperature has reached 9°C above the expected pour point. Once there specimen has ceased to flow, the recorded temperature rounded up with the nearest upper multiple of 3°C is the pour point.

First of all, the rounding up act is already giving a hint that the result from this method is largely inaccurate because of having resolution as high as 3°C. This is presumably done that way as to prohibit the researcher from conducting the tilt every

1°C that might disturb the crystallization process and thus giving different whole lot readings. However, it is proposed that during the experiment conduct, there is no much harm if once the expected pour point is almost reaching 3°C, the tilt act is done at every 1 or 0.5°C interval as to observe the actual no-flow point of the specimen as in actual scenario, the temperature drop once the specimen almost reaching the no-flow point is relatively slow.

It is aware that doing such technique is not advisable but since this project involves different preliminary heating and cooling period upon the specimen, one might anticipate the difference in readings from those variables, although it is only small. Even to reduce much movement, a hole of exact 6.5 mm as the thermometer diameter is being drilled on the tube cover to fit the thermometer to ensure that there is not much movement that may disturb the crystallization process during the measurement.

4.2 Presence of air gap between test jar and cooling bath

As the experiment setup shown previous, there is a minimal air gap with maximum thickness of 5.5 mm available between the jacket of the water batch and the test jar. Therefore, one can interpret that the medium of heat transfer between the cooling medium and the test specimen is merely conduction by air. The heat from the specimen will flow into bath and let cooled gradually. The standard prevents the test jar to be inserted or immersed directly into the cooling medium. This is because, direct contact between the test specimen and cooling medium will trigger rapid cooling of the wax crystal and hence will make the crystallization process become incomplete and the pour point obtained could be lower than the actual. This effect will be much severe if temperature difference between the test specimen and the cooling medium is bigger.

As in this project, the way to resemble the procedures as the standard proposed is by using temperature-controlled water bath machines. The water bath machine consists of two types; the 1st one as for preheating of the specimen and 2nd one as cooling. After the specimen has been heated up to 45°C, the specimen is let cooled naturally until the temperature reaches ± 30°C. Then, the sample is immersed in water bath of temperature set to cool from +29°C to +5°C (or any values 10°C below the expected no-flow point). Since the cooling of the water bath from +30°C

to +5°C is rather a slowly process, one can assume the effect of cooling as such way is almost the same as how the standard setup proposed. This is because, to find such cooling medium and construct the exact experiment setup could be time consuming and even cost ineffective.

Figure 10a: 2nd preheat process at approximately 45°C inside the hot water bath

Figure 10b: The specimen is let to cool naturally until temperature reaches 30°C

Figure 10c: The Specimen is immersed in water bath set to cool from 30°C to 10°C

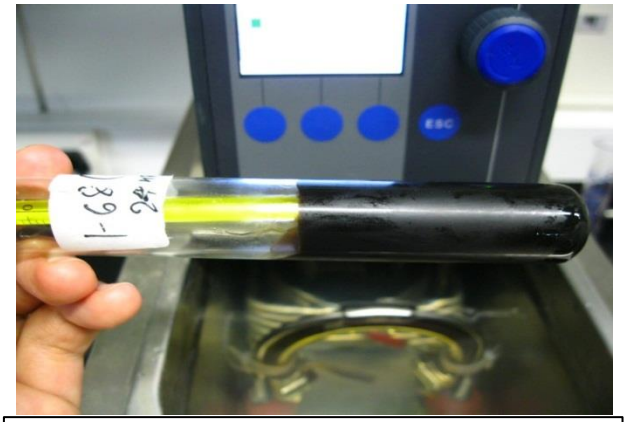


Figure 10d: Final tilt act showing the specimen has ceased to flow for at least 5 seconds.

Figure 10: Sequence of photos showing the measurement technique for tilt method

5. ASTM D5985 ROTATIONAL METHOD TECHNIQUE

After the specimen has been separated during the sample preparation into small tube, it will be measured its pour point using Pour Point Tester PSL Systemtechnik 45150 once the pretreatment process has completed. Temperature range for pre-heating technique and cooling period that will be used upon the crude for pre-treatment for the rotational method will also be the same as tilt method, as follow. Note that this is only applicable for crude oil only and not to be used on petroleum products:

- Heating temperature range: 60°C to 80°C
- Cool down period range: 6 hours to 48 days.

		Cooling Period (Hours)				
	-	0	6	12	24	48
Preheat temperatures (°C)	50				50/24	
	60	60/0	60/6	60/12	60/24	60/48
	70				70/24	
	80	80/0	80/6	80/12	80/24	80/48

Table 6: Pretreatment matrix for rotational method

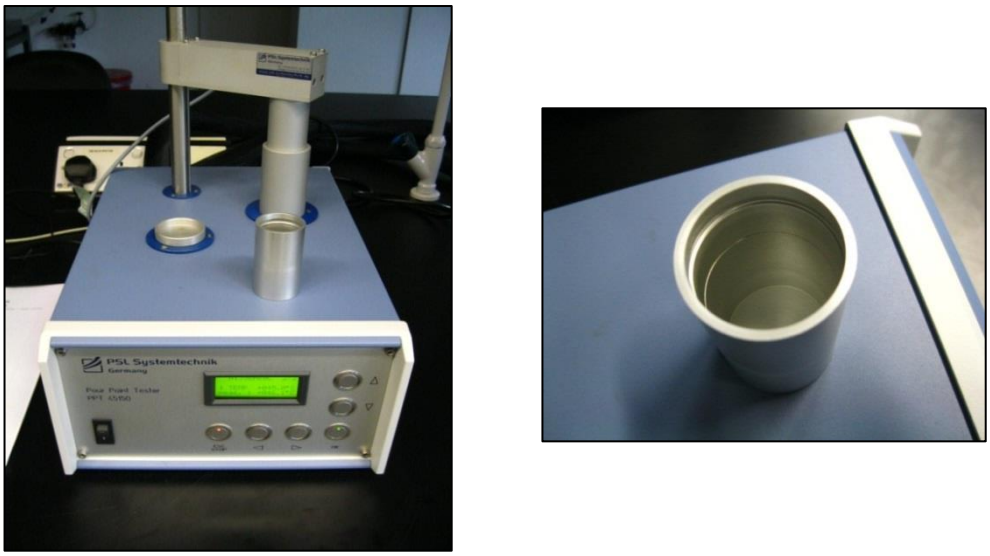


Figure 11: PSL Systemtechnik Pour Point Tester 45150 (left) and the test specimen cup (right).

CHAPTER 5

RESULTS

1. BASIC PROPERTIES OF CRUDE OIL SPECIMEN USED

In this test, one type of crudes was used. Denoted by Crude X, The basic properties of the crude are as follows:

Test	Unit	Results
Density @ 20C	kg/L	0.8065
API Gravity	API	43.95
Asphaltenes	Mass %	0.04
Wax Content	Mass %	10.7
Kinematic Viscosity	mm^2/s 40°C 50°C 100°C 119°C	 2.946 2.463 1.296 1.078

Table 7: Basic Properties of Crude Oil X

Component	Unit	Test Results
Volatiles	mass %	57.07
Asphaltenes & Inorganics (n-Pentane Insolubles)		0.42
Saturates		31.32
Aromatics		9.52
Resins		0.50
Total Recovery		**98.83**

Table 8: The composition of Crude Oil X

2. POUR POINT MEASURED – CRUDE X

Below summarized the no-flow points and pour points measured for Crude X, using both tilt and rotational method. Temperature and cool down period were used as their varying parameter.

Preheat temperature of 60°C						
Cooling period (Hours)		**0**	**6**	**15**	**24**	**48**
Tilt Method	**No-flow point (°C)**	20	20	19	17	18
	Pour Point (°C)	23	23	22	20	21
Rotational Method	**No-flow point (°C)**	21	21	19.6	19.1	19.5
	Pour Point (°C)	24	24	22.6	22.1	22.5

Table 9: Values of no-flow point and pour point at preheat temperature of 60°C

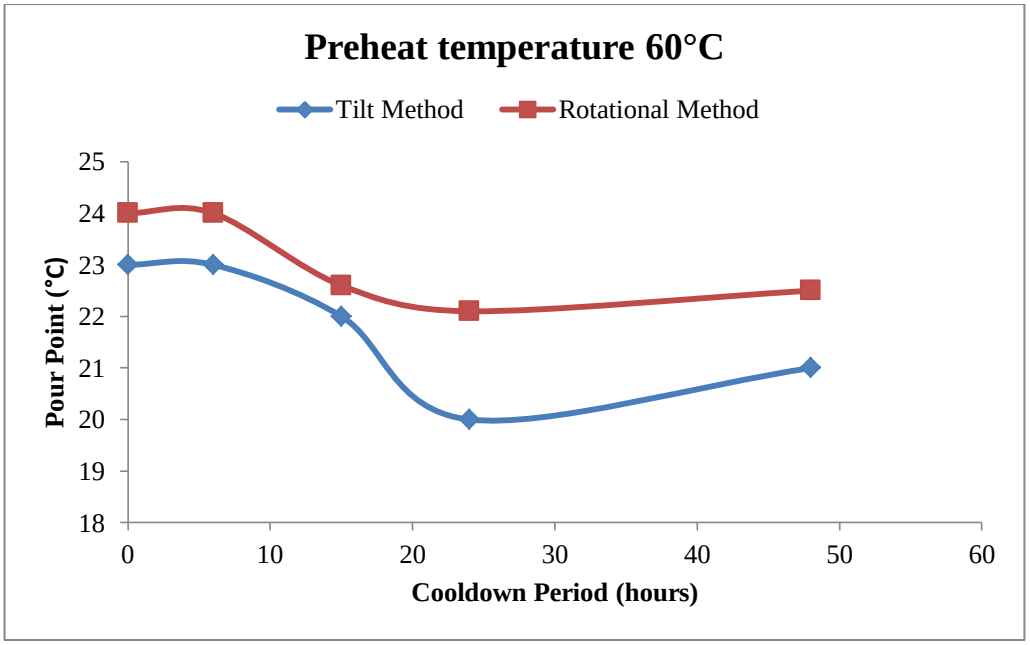


Figure 12: Plot of pour point against cooldown period at preheat temperature of 60°C

Preheat temperature of 80°C						
Cooling period (Hours)		**0**	**6**	**15**	**24**	**48**
Tilt Method	**No-flow point (°C)**	21	21	20.5	19	18.5
	Pour Point (°C)	24	24	23.5	22	21.5
Rotational Method	**No-flow point (°C)**	21.4	21	19.5	19.4	20
	Pour Point (°C)	24.4	24	22.5	22.4	23

Table 10: Values of no-flow point and pour point at preheat temperature of 80°C

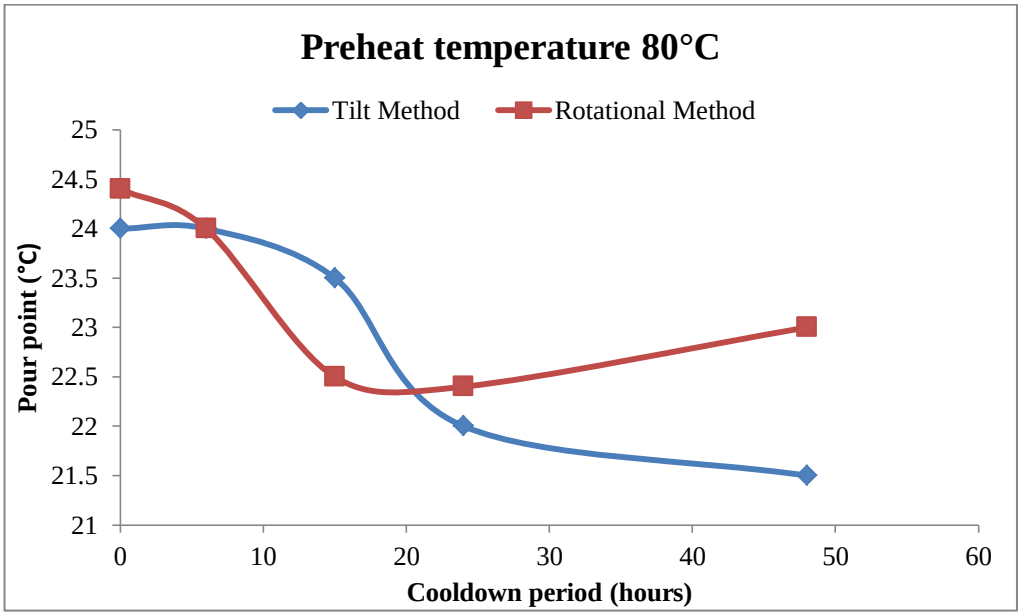


Figure 13: Plot of pour point against cooldown period at preheat temperature of 80°C

Constant cool down period of 24 hours					
Preheat Temperature (°C)		**50**	**60**	**70**	**80**
Tilt Method	**No-flow point (°C)**	18	17	18	19
	Pour Point (°C)	21	20	21	22
Rotational Method	**No-flow point (°C)**	19.3	19.1	19.2	19.4
	Pour Point (°C)	22.3	22.1	22.2	22.4

Table 11: Values of pour point at cool down period of 24 hours

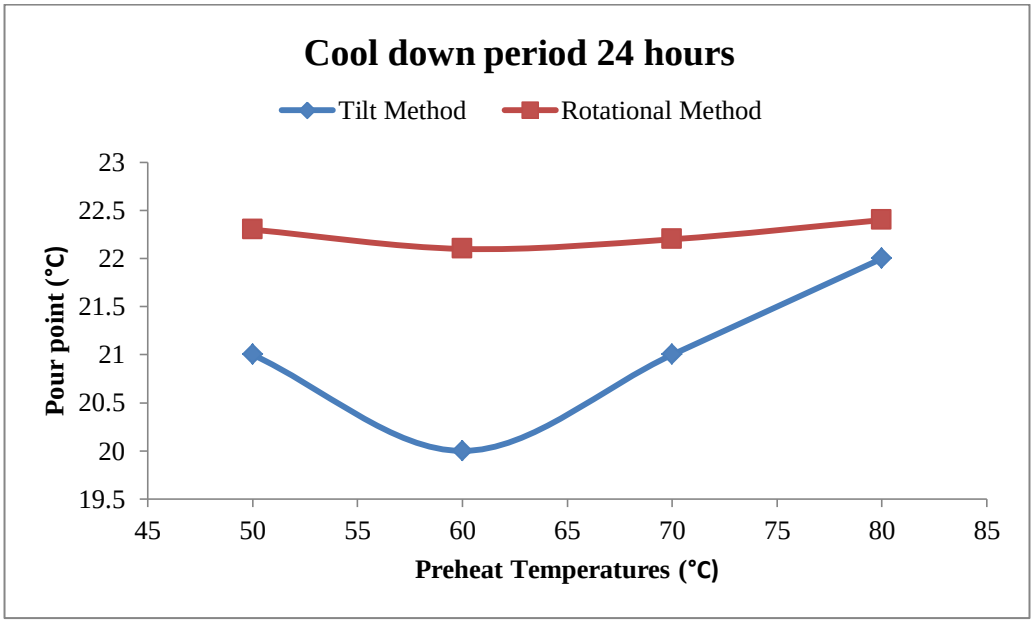


Figure 14: Plot of pour point against preheat temperature at cooldown period of 24 hours

CHAPTER 6

DISCUSSION

1. PRETREATMENT VARIATION EFFECT

From the results, we can see that varying the pretreatment of the crude specimen does give effect to the pour point of the crude oil measured, both from rotational method and tilt method. This indicates that the thermal history effect on the wax formation in crude should be recognized as different thermal history could give different pour point readings.

It can be seen that with increasing cool down period, the pour point of the crude is decreasing. Meaning that, the specimen has to reach a lower temperature to enable the wax crystal to solidify. This scenario is somehow contradict with the original purpose of the maximum pour point as the method should supposedly raises the measured point by a means allowing a long time for wax crystals to form at room temperature which in turn reduce the time for gel formation. So when measurement is conducted, longer cool down time sample should exhibits higher pour point than those of shorter one.

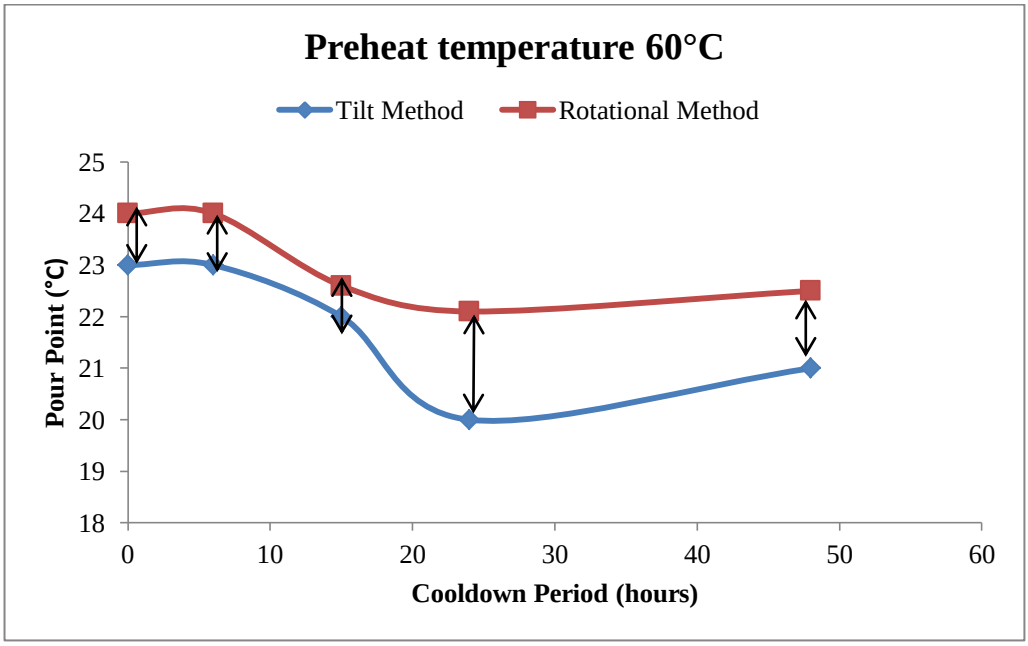
But in this case, the trend is the other way around. What can be assumed is that once the specimen has been heated up to 60°C and let cool down according to its period, the wax in the specimen of the shorter cool down period undergone incomplete formation and rapid solidification as the temperature drops during the measurement hence resulted in higher temperature of no-flow point. Differ from those specimens of longer cool down period, it is assumed that the crystallized wax and dissolved wax has already (or almost) achieve equilibrium which in turn when being heated up again before the testing, causes their wax interaction to break down and the process is repeated again as the temperature dropping during the measurement, which result in lower pour point.

Increase in the pour point readings for the rotational method at preheat temperature of 80°C after 24 hours is because as the crude is being heated up at higher temperature, it causes the vapor pressure of the crude to be very high, usually exceeds 100 kPa at temperature greater than 60°C and make the light end

components of the crude to loss to surroundings. As a result, the majority components left is the heavy components in which what causes for the pour point to become higher. The same trending is also observed in the plot of constant cool down 24 hours in which the tilt method pour point is increasing with increasing preheat temperature.

2. DIFFERENCE IN READINGS BETWEEN TILT AND ROTATIONAL METHOD

One thing that can be noted from those results of manual tilt method and automatic rotational method is that the pour points of the tilt point is higher than those by the rotational method as observed from the 60°C preheat temperature below:

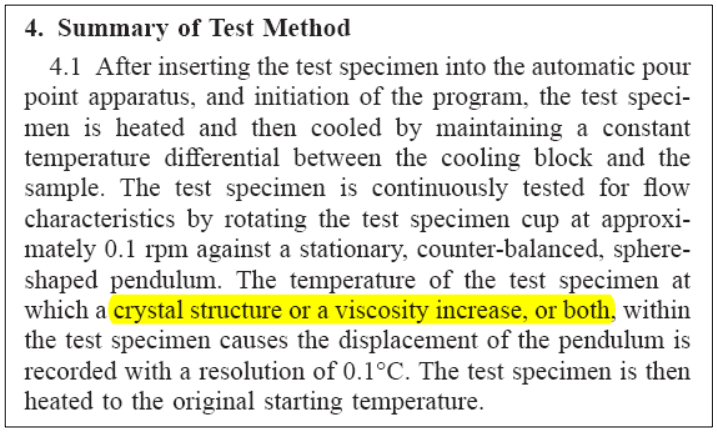


The reason could somehow are interpreted caused by 2 factors:

- **Stability from the rotary motion of the test specimen over the tilt motion**

This is acceptable and expected since the specimen during the rotational method, it undergo a more stable and less rapid movement, and more gradual temperature dropping during the measurement compared to tilt method hence causes the formation of wax is less interrupted and result in higher pour point point.

- **The experimental design of the rotational method that recognize the viscosity effect, as clearly mentioned by the standard**



4. Summary of Test Method

4.1 After inserting the test specimen into the automatic pour point apparatus, and initiation of the program, the test specimen is heated and then cooled by maintaining a constant temperature differential between the cooling block and the sample. The test specimen is continuously tested for flow characteristics by rotating the test specimen cup at approximately 0.1 rpm against a stationary, counter-balanced, sphere-shaped pendulum. The temperature of the test specimen at which a crystal structure or a viscosity increase, or both, within the test specimen causes the displacement of the pendulum is recorded with a resolution of 0.1°C. The test specimen is then heated to the original starting temperature.

Figure 15: Highlight of point in ASTM D5985 mentioned the cause of pendulum displacement by crystal structure and/or viscosity increment of the petroleum products

The no-flow point readings from the crude specimen using this rotational method could be interpreted originated from both of the crystal structure formation, and also viscosity increment of the specimen. Compared to tilt method, the tilt action only recognizes the complete crystal structure formation in which ceases the specimen from pouring, and not the viscosity increment, because even at very high viscosity, provided that the wax crystal formation has not completely formed inside the crude, the tilt action will still make the crude specimen pour, but at very slow movement. Hence, it could be interpreted that the pour point measured in the crude from rotational method is the result from viscosity increment, as with decreasing temperature, the light barrier was triggered 'earlier' than it should.

However, it is only assumption and uncertain how severe the effect of viscosity increament upon the gap between the tilt and rotational method readings. 2 ways can be done in order to identify if there is viscosity effect contributed to the no-flow point readings:

- **Comparison with measurement using higher viscosity oil**

Initial assumption is that by using higher viscosity of oil, the gap between tilt and rotational should be higher. However, after comparison with colleague using crude with greater viscosity, it was reported that the gap between rotational and tilt method

is similar with this project, in which minimal only. By that, it can be assumed that the gap was not severely contributed by viscosity increment, but more by the stability of the rotational method measurement technique.

- **Comparison with measurement using any petroleum products**

Since for petroleum products pour point measurement, there are 2 methods have been assigned, in which tilt method based from ASTM D97 and rotational method D5985, it is presumed if same specimen is to be measured its pour point using those 2 techniques, the result from both tests should be similar. This result then can be compared with the one we have from this project.

However, since most petroleum products have been treated and most of them such as lubricants, diesel and gasoline are having pour point of below -20°C, acquiring cooling medium for the tilt method measurements was very difficult, such as solid carbon dioxide as what was suggested in the standard. Therefore, this kind of comparison cannot be conducted.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATION

This project was initially hoped to achieve its objectives by proving that the method of using rotational using pour point tester is applicable to measure crude oil pour point. Although pour point is just only branches from other major crude oil parameters with numerous other techniques to measure it, it still plays an important role to ensure continuous production and avoiding flow problems.

To conclude, this point measurement using rotational method of ASTM D5985 is applicable to be used to with crude oil as it provides higher consistency and repeatability readings compared to tilt method. Recommendation is that, before any rotational measurement, pre-treatment technique as what was initially suggested by ASTM D5853 should being done upon the crude specimen. No sample should be heated above 60°C as to avoid the loss of light components, unless it is necessarily needed for very waxy crude sample. For cool down period, 12 hours is used as the minimum period after the crude has been heated up initially to dissolve the precipitated wax.

It is recommended that this rotational method of measuring pour point should include the addition of additives in the future as technique of varying it. With that, the effect of additives with the crude using this technique compared to others can be observed the differences.

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