Thermal Shrinkage and Gas Void Formation of Waxy Crude Oil with Additive

By

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Dissertation submitted in partial fulfillment of

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CERTIFICATION OF APPROVAL

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Approved by,

_____

(Dr. Azuraien Jaafar)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK.

May 2012

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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MOHD SYUAIB BIN JAMALUDIN

ABSTRACT

The presence of paraffin wax in crude oils especially during the extraction and transportation processes causes problems to the producer, transporter and refiner. There are two critical effects result. First, the pressure drops where the drive efficiency will decrease and the other one is the decline in term of the mobility of the crude. This report discussed the thermal shrinkage and gas voids formation of waxy crude oil. The effect of final temperature to the volume, pressure and gas composition of the gelled crude is evaluated. As the gelled crude undergoes cooling process or thermal shrinkage, the effect of chemical additives on the formation of gas voids is also investigated.

During plant shutdown, high pressure pump is required to move the gelled crude. The presence of gas voids during thermal shrinkage or cooling process indicates the opportunity to reduce the restart pressure by considering the compressibility of the gelled crude. The challenge faced by most engineers and plant operators are to accurately predict the restart pressure. The outcome of this project would be beneficial to oil and gas operating companies in managing the platform as well as to enhanced the profit.

Literature reviews on existing studies related to the title of the project have been done prior to the initial phase of the project. The methodologies and results from different studies are compared. The next phase would be the experimental works where the static petroleum crude in the pipeline at seabed level is simulated by the equipments and tools in the laboratory. Besides, an additive is also added to the crude oil which is pour point depressant (PPD). As the crude oil is cooled, formation of gas voids will take place. From here, detailed analysis is done with respect to the three parameters which are gas voids volume, pressure and gas composition.

ACKNOWLEDGEMENT

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CHAPTER I

INTRODUCTION

1.1. Background of Study

The oil and gas industry can be categorized into 'upstream' – the exploration and production sector of the industry and also 'downstream' – the sector which involves with refining and processing of crude oil and gas products, distribution and also marketing. Challenges in the oil and gas industry are continually evolving but that does not stop the effort to improve the operational efficiency and overall performance.

The product, petroleum, is one of the most important energy sources commonly used nowadays. The hydrocarbons of petroleum energy are used in applications ranging from plastics made from alkenes, fuel for vehicles, lubricants such as motor oil, wax which is found in frozen food packaging and others.

Being a non-renewable resource, the petroleum's supply is limited. Therefore, further explorations to find for new reservoir have been done. Petroleum or the crude oil is extracted from the reservoir where an oil platform helps to extract and process oil and natural gas.

The point of interest of this study is during the transportation of the crude oil. During platform shutdown, a phenomenon called thermal shrinkage and gas voids formation occurs due to low seabed temperature.

The major problem in the extraction and transportation of crude oils is the formation and deposition of paraffin wax which occurs at the inner wall of the pipeline, reduces the internal diameter and causes blockage to occur. Crude has a non-Newtonian characteristic, such that if its temperature is below Wax Appearances Temperature, the viscosity will increase drastically and produce a gel-like structure. There will be possibility that the crude oil will be immobilized if the temperature continues to drop below the pour point. Thus, higher restart pressure is needed, which results in high

Capital Expenditure (CAPEX). Therefore it is important to study the thermal shrinkage and gas void formations which will reduce the restart pressure as well as to reduce the CAPEX. Apart from that, the effect of adding chemical additives is observed when conducting the experiments.

1.2. Problem Statement

There are several papers which studies on wax deposition but very few of them discuss on the thermal behavior of the crude itself. The issue of restarting the flow has always been the major problem in the transportation of waxy crude. As the gas voids are formed, there is a possibility of reducing the restart pressure by taking into accounts the compressibility of the gelled crude. Detailed analysis on thermal shrinkage and gas voids formation has to be done to overcome the problems occurred.

1.3. Objectives and Scope of Study

- To study the formation of gas void in the gelled crude.
- To investigate the effects of concentration of PPD on the formation of gas voids.

As for the scope of study, it includes the measurement of volume and pressure of gas void as well as observation on its composition.

1.4. The Relevance of the Project

The main interest of the project is to determine the compressibility of the gas void formed in the gelled crude. The results of this project could be vital in oil and gas industry whereby most companies are burdened with high cost of restart pressure and energy consumption. If the compressibility of the gas void is justified, this will ensure a more cost-efficient operation of the platform and consequently give more profit.

1.5. The Feasibility of the Project

The project requires facilities to simulate the real pipeline. The laboratory equipments that are available include water bath for cooling purposes, crude tank to store the crude oil, gas chromatography machine to analyze the gas voids composition and custom-made bubble line flow rig to simulate the thermal shrinkage of waxy crude oil in the pipeline. The existing studies related to thermal shrinkage are being compared. As for the research activities, all of the tools and equipments are in good condition to be used. In fact the experiments do not require long time to be finished, thus make it feasible.

CHAPTER II

LITERATURE REVIEW

In this research, the effect of the thermal history and chemical additives on the waxy structure of statically cooled waxy crude oils is examined. Quite often the pipelines transporting waxy crude oils may be shut down for normal operational reasons and also for emergency reasons for example like line damage, power failure or even earthquake [1]. As a result, the crude oil which is warm initially may be cooled statically below its pour point, leading to a strong gel-like structure to form.

During cooling process or the thermal shrinkage, it is assumed that the gelled crude has the characteristic of non-Newtonian flow behavior [2]. At the Wax Appearance Temperature (WAT), wax deposition starts to occur in the production pipeline. This is considered as one of the major flow assurance risks that need to be considered while developing new fields or maintaining existing operations. The problems associated with wax deposition are reduced productivity, increased pressure drop and risk pipeline clogging [3].

The restart pressure required after plant shutdown is significantly high to ensure the flowability of the gelled crude, thus increasing the energy usage and cost. In addition, there were gas voids observed during the cooling process in the pipeline [4]. If this research manages to prove the compressibility of the gas voids, this will reduce one of the major concerns as the oil and gas industry continues to expand deepwater operations to greater depths and distances in cold environments. Several methods are recommended for improving transport of heavy crude oils [5], among them are:

- Thermal:
  - Preheat oil and/or transport hot uninsulated line, insulated line
  - Heat oil and insulated line by hot fluid tracing or electrical heating

- Mechanical:
  - Pump oil at temperature below pour point

- Pass a pig or scraper through the line to reduce paraffin deposits

- Chemical:
  - Dilute oil with solvent
  - Inject pour-point depressants (flow improvers)
  - Inject paraffin dispersants

- Rheological:
  - Create oil-in-water emulsion
  - Create core flow

As for chemical, dilution of oil with a light-hydrocarbon solvent lowers the viscosity to an acceptable value and allows pumping at reasonable flow rates. This will result in high viscosity and temperature sensitive oil-condensate blend but essentially pseudoplastic [6]. Besides, paraffin dispersants which work in the presence of water are also used. They are surface-active agents that water-wet paraffin particles and flow lines, preventing the particles from uniting and depositing. Typical dispersants used are nonionic poly-ethers manufactured from ethylene oxide, propylene oxide, or mixtures of both.

Pour-point depressants (PPD) or flow improvers help to alter wax crystallization. They are linear polymers and copolymers with side alkyl chains, alkyl chains in the backbone, or both. There are four basic types of PPD [7], as listed below:

- Ethylene vinyl acetate copolymers
- Methacrylate copolymers
- Olefin/maleic anhydride copolymers
- Polysaccharides

There is a study on the comparisons of wax crystals structures in waxy crude oil beneficiated with and without a PPD. The additive used is Additive A-14 with different concentration ranging from 100 ppm to 1000 ppm. Firstly, the wax crystals in virgin crude oil have a corresponding homogenous size distribution and high degree of dispersity of the particles. This provides sufficient surface energy for the wax crystals to interconnect into a three-dimensional network structure. As for the second case, the wax crystals of oil beneficiated with PPD have the tendency to assemble as clusters and increase the unoccupied zone. As forming a three-dimensional network structure requires more wax precipitated, thus the low-temperature flow property of treated oil is improved [8].

The addition of PPD in wax helps to lower the wax precipitated and lower the melting point of wax. The experimental data shows that the claim is true with the DSC results that indicate the melting point and solid-solid transition temperature of paraffin mixtures are decreased [9]. From the results, it is understandable that PPD does not stop the wax deposition completely but rather shift the precipitation toward a lower temperature.

Appropriate application of crystal modifier chemicals also aid in reducing gelling of crude oil. Temperature is important to both the process of emulsion resolution and crystal modification. Crystal modifier chemicals function efficiently if applied as early in the production stream as possible. Improper addition of chemical under less than optimal conditions usually happen due to lack of capillary injection facilities which complicate the logistics of crystal modifier action. Very often when deposition occurs in the well, chemicals are being added after the wellhead. This may prevent continued deposition in transfer lines and storage vessels, but the source of the problem goes untreated.

One of the major concerns prior to the field application of any treating chemicals involves the formulation of chemistries that treat the problems within the constraints of the system. If a chemical freezes at 50°F, its application in areas where the average ambient temperature is below 30°F is ill-advised, as it would be frozen most of the time [10]. Most chemicals that are added to wells, storage facilities, or transfer lines are

pumped. In this situation, frozen materials will not lend themselves to pumping. So, blending of the active ingredient is necessary to facilitate its injection by pumps.

To mitigate temperature drop, the flowlines and other subsea components have insulation. Pipe-in-pipe flowline is the most effective insulation system used when there is a high potential for constriction or plugging. The space between the pipes is partially evacuated, then filled with insulating material such as syntactic polypropylene. The main purpose of the insulation system is to allow the well fluid to be transported at great distances while maintaining almost all their original temperature, essentially preventing the formation of both hydrates and wax. However, pipe-in-pipe insulation does not prevent flowline cooling indefinitely especially during plant shut down. Below are some suggestions to deal with the long plant shut down [11]:

- Inject slugs of chemicals into the production steam just prior to the shut down, using either umbilical or a separate chemical injection line. Methanol or glycol in amounts of 25-50% of the water content serve as antifreeze by depressing the freezing point below the seabed temperature and prevent the formation of hydrate.
- Inject paraffin inhibitors (chemical additives) into the well stream to keep paraffins and waxes from solidifying or depositing on the pipe wall.

Figure 1 and Figure 2 explain how the gas voids are formed in the pipeline while Figure 3 shows the step by step formation of gas voids with respect to Temperature vs. Distance along pipeline graph.

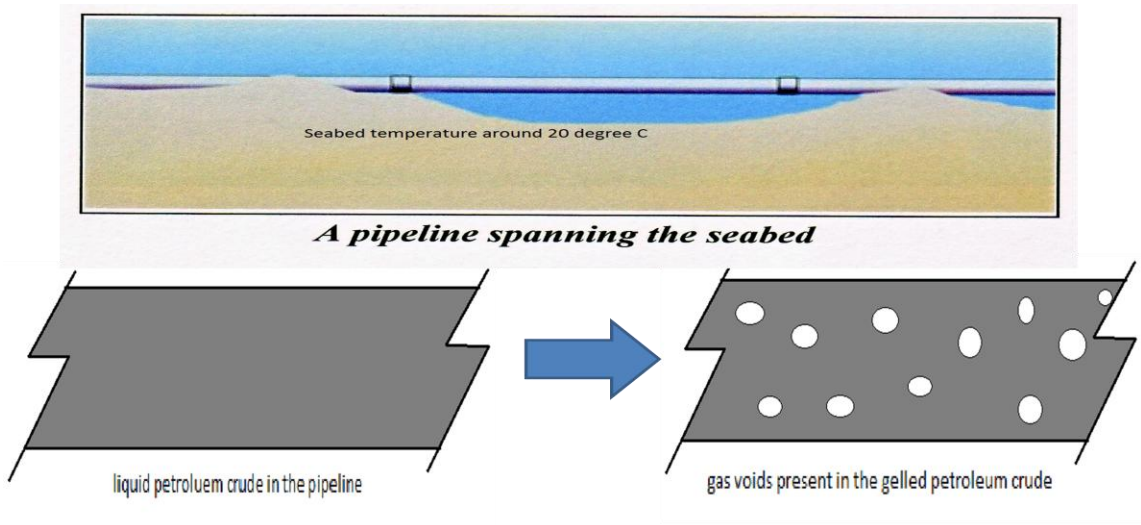


Figure 1: Gas voids formation diagram.

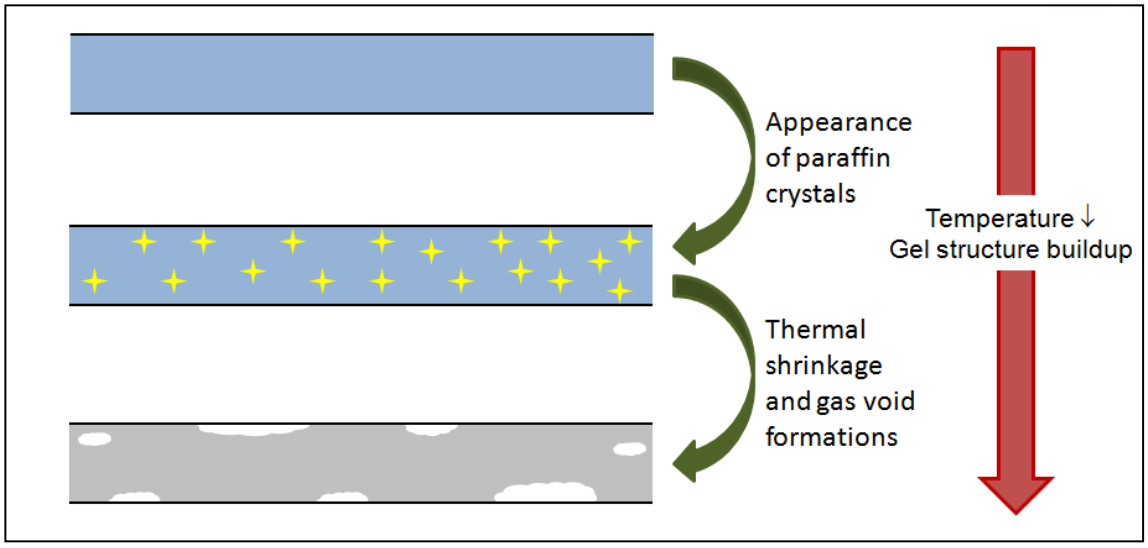
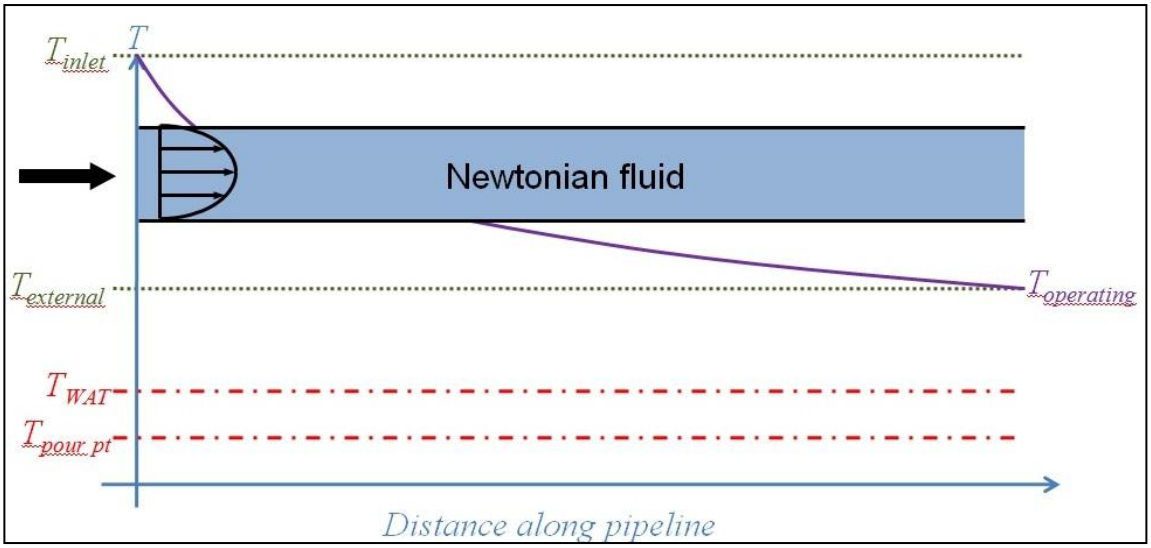
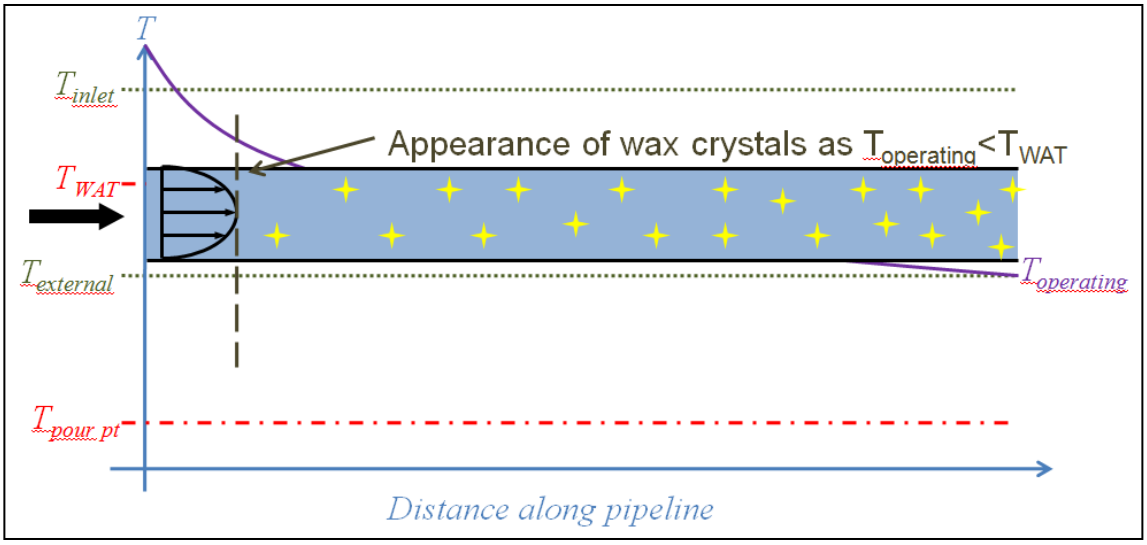


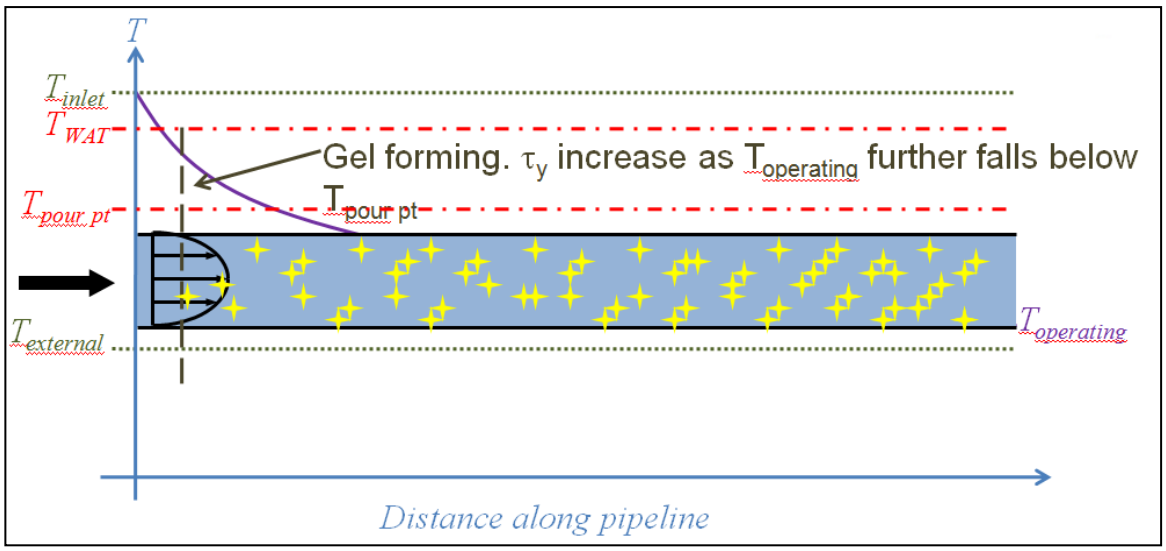
Figure 2: Wax formation stage.


T
T inlet
Newtonian fluid
T external
T operating
T WAT
T pour pt
Distance along pipeline

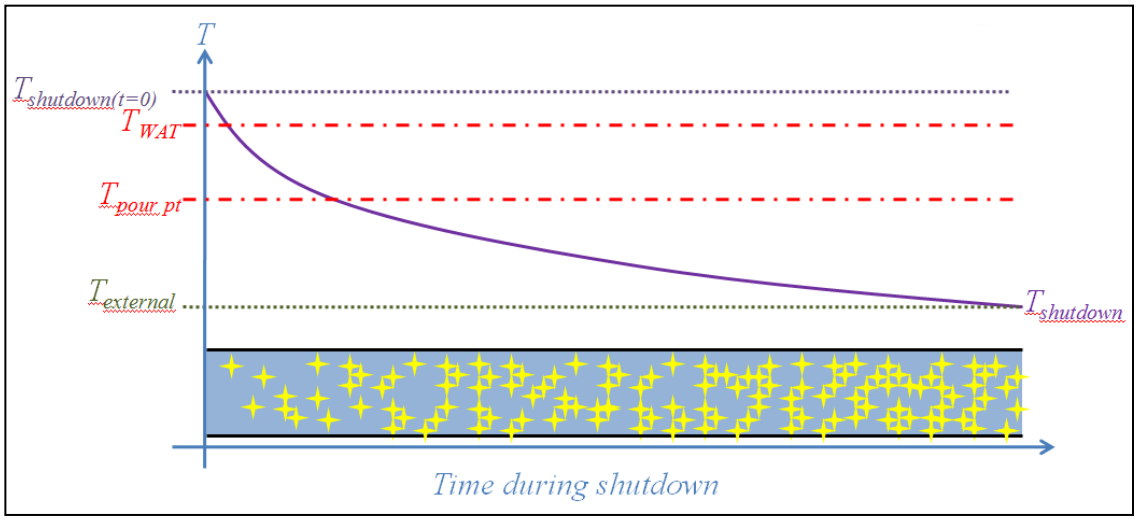
(a)


T
T inlet
Appearance of wax crystals as T operating<T WAT
T WAT
T external
T operating
T pour pt
Distance along pipeline

(b)



(c)



(d)

Figure 3: Formation of gas voids (a) Newtonian crude before thermal shrinkage (b) Wax formation start during thermal shrinkage (c) Wax form solid layer (d) Wax occupy in the pipeline.

Eventhough chemical additives are effective but they are rather expensive. Thus, the challenges faced by operators and engineers are:

- To take extensive adjustment to ensure continuous, problem-free, minimum-cost flow.
- To maximize production while maintaining the life expentancy of the wells.

According to the same project done by previous student, the pressure within the gas voids is below ambient and the gas voids appear at the center of the tank (container). There are two difficulties faced [12]:

i. Gas voids appearance is not consistent such that the repeatability is low.
ii. Problem in taking the gas sample properly due to the pressure being below ambient and the presence of contaminations.

All of the difficulties faced, important findings and results discussed in this section will be the guideline as the author is looking to improve his project outcome and obtain the best result. The next section will be discussing on the methodology of the project.

CHAPTER III

METHODOLOGY

3.1 Research Methodology

The following figure summarizes all of the steps involved during this study:

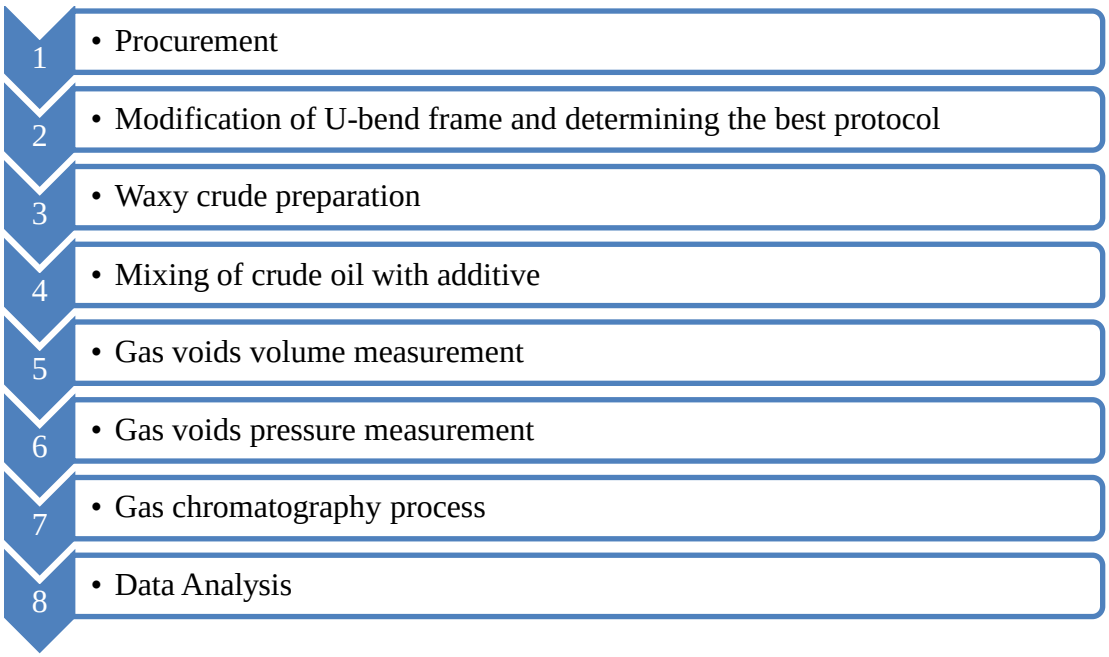


Figure 4: Experimental procedure.

3.2 Experimental Setup

The type of crude and additive used are Sepat and pour point depressant (PPD) respectively. The procedure and experimental setup for this project are different compared to the previous work done by Idris. H where the crude tank is manually fabricated. In this project, the flow line bubble rig is purchased as a ready part which will be discussed in Section 3.2.1

3.2.1 Bubble line flow rig

- It consists of:

- Polyurethane tube with internal diameter of 8mm
- PVC stopcock valve
- High performance glass type syringe 50 micro liter
- U-bend frame made of clear color acrylic sheet

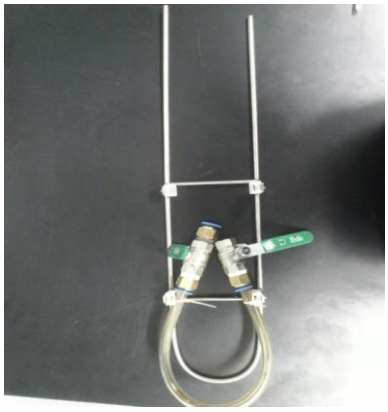


Figure 5: Bubble line flow rig.

3.2.2 Magnetic Stirrer

-To stir both crude and additive to ensure homogeneity while maintaining it at a certain temperature.

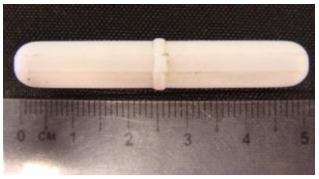


Figure 6: Magnetic stirring bar.

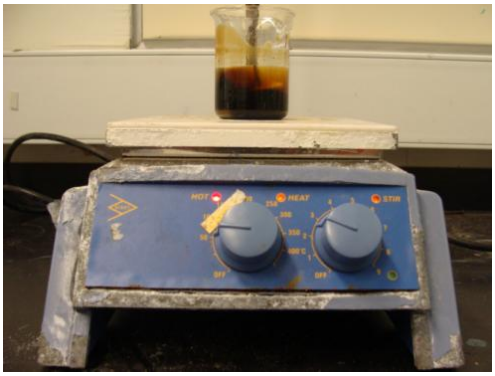


Figure 7: Magnetic stirrer.

3.2.3 Vivo RT2 water bath

- Used for cooling of crude oil.

- Fix cooling rate

Figure 8: Vivo RT2 water bath.

3.2.4 Vernier caliper

- To measure the gas voids volume.

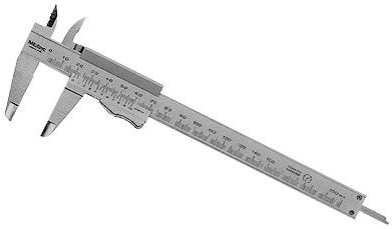


Figure 9: Vernier caliper.

3.2.5 Syringe

-To be tapped at the tube twice; one for pressure measurement and another one for gas composition.

Figure 10: Syringe.

3.2.6 Pressure transmitter

- To measure the gas voids pressure.

Figure 11: Pressure transmitter.

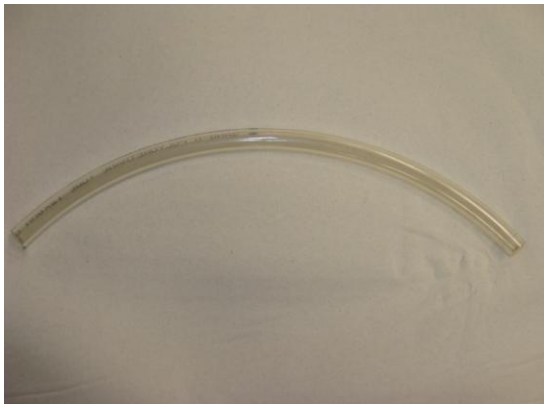
3.2.7 Gas chromatography machine

- To determine the gas voids composition.

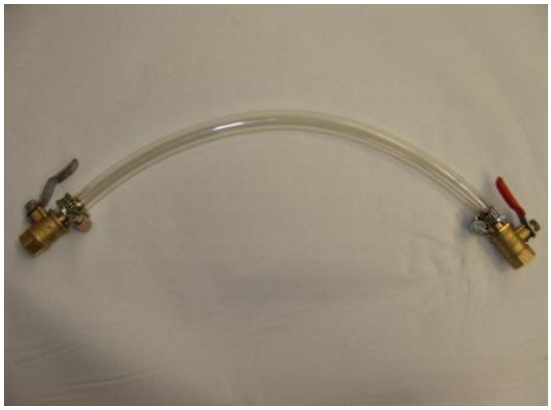
Figure 12: Gas chromatography machine.

3.2.8 Arrangement of the Experimental Setup

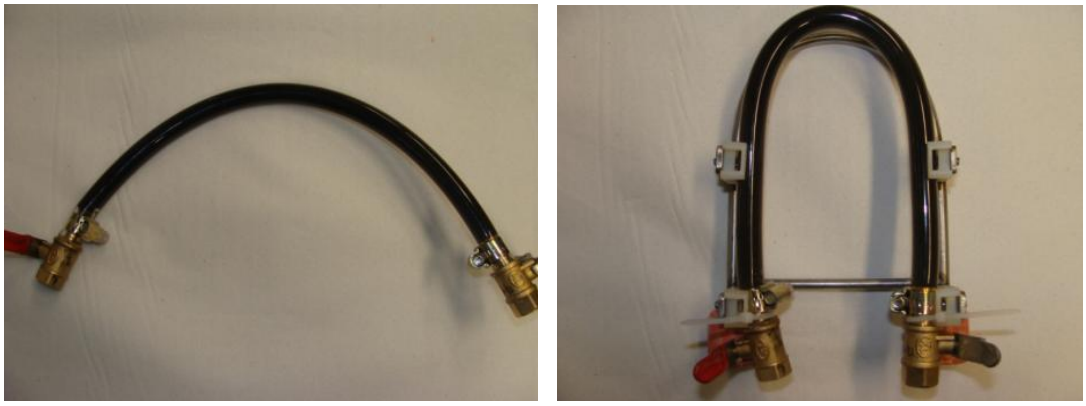
Figure 13 describes the step by step arrangement for the experiment before the tube and U-bend frame are placed inside the water bath:



(a)



(b)



(b) (d)

Figure 13: Arrangement of experimental setup (a) Polyurethane tube (b) Valves connected (c) Crude oil inserted (d) Tube tied to U-bend frame.

3.3 Project Activities

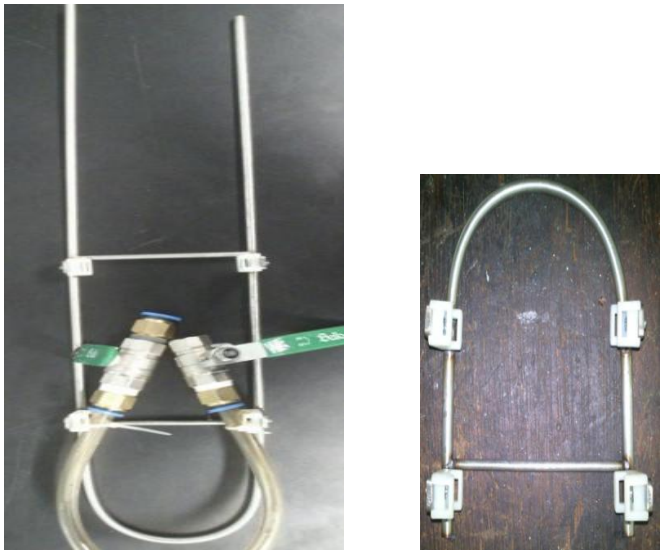
The detailed activities of the project can be described below:

3.3.1 Modification of U-bend Frame and Determining the Best Experimental Protocol

After the first trial of experiment has been done, it is found out that the length of the U-bend frame is too long. It is then modified as to ensure that:

i. The frame is fully immersed inside the water bath.
ii. The frame is positioned as inverted-U rather than U-shape for the voids to occur at the apex.

Therefore, the frame is cut by using abrasive cutter machine so that the length from the top until the other end is 15 cm. In addition, by using gas tungsten arc welding machine (GTAW), the position of tube's support is shifted as indicated in Figure 14. After cutting and welding, usually the affected part will produce sharp edges. Thus, the last step is to smoothen the surface by using rasp, Figure 15.



(a) (b)

Figure 14: Modification of U-bend frame (a) before (b) after cut.

Figure 15: Smoothening of the frame's surface.

Before commencing the real experiments, several test protocols need to be set up in order for the voids to form at the apex. During the first trial (before the frame is cut), the frame is put inside the water bath in U-shape. For the result, the voids are scattered and not gathered in one place.

After modification of the frame, it is positioned as inverted-U to encourage the voids to migrate to the apex by the principle of density difference. At this stage, there are two important observations made:

i. The voids formed at the side of the tube rather than at the apex, Figure 16.

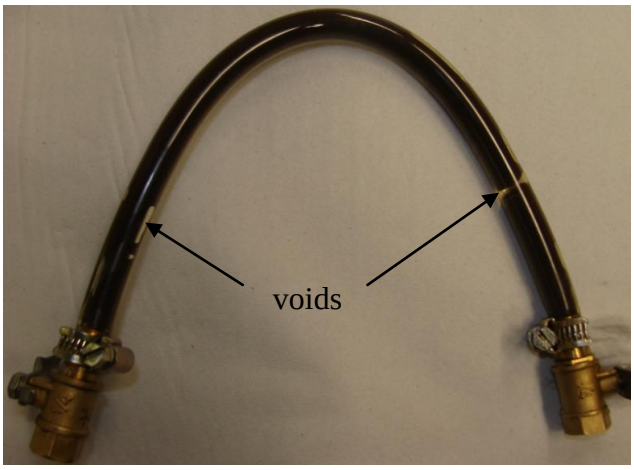


Figure 16: Gas voids formed at the side of the tube.

ii. Water seeped through the connection between valve and tube, Figure 17.

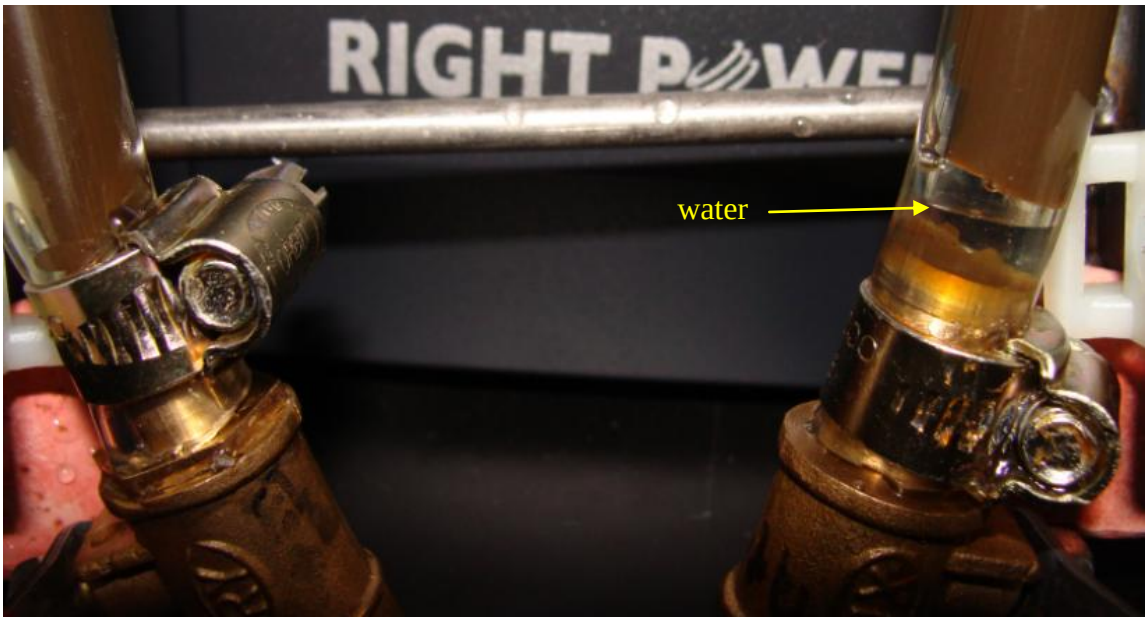


Figure 17: Water present inside the tube.

Due to these two problems, there are two steps that can be implemented to overcome them. First, the original length of tube is reduced from 30 cm to 20 cm. The author's hypothesis is as the crude becomes more solidified at low temperature, shorter tube's length will provide enough time for the voids to migrate to the apex. Otherwise, if the tube is longer, the voids may not have sufficient time to migrate, which explains why they are not formed at the apex. Secondly, cling film is used to seal the connection between the tube and valves to avoid water from seeping through.

After implementing the suggested steps, the results are exactly as predicted from the hypothesis. Reducing the tube's length and sealing it with cling film do solve the problems and gives the desired results, as in Figure 18. The voids formed are at the apex and continuous. After the best protocol has been determined, the real experiments with additive are started.

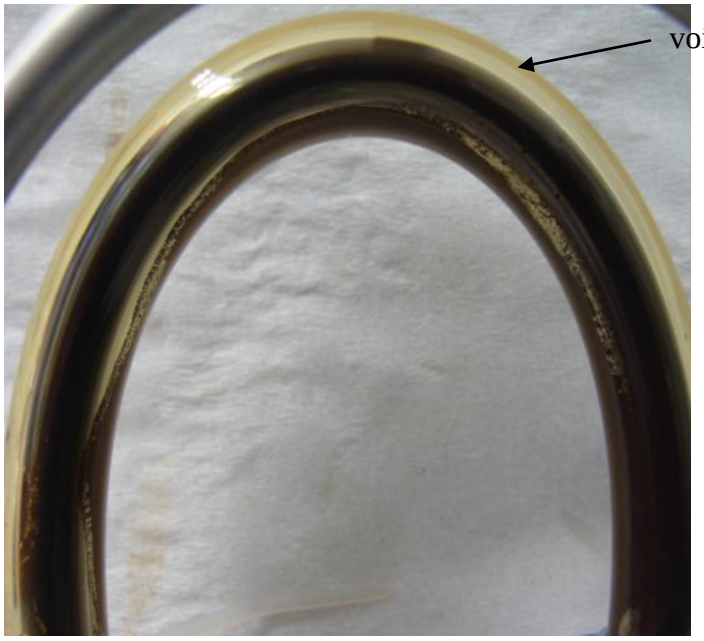


Figure 18: Voids formed at apex.

3.3.2 Preparation of Crude Oil

The crude oil has the tendency to separate into heavy part and light part due to density difference if it is stored for a long period of time. That is why before commencing the experiment, the crude oil is prepared to allow normal mixing process. The crude is heated up to 60°C for two hours of agitation process. This is to make sure that the crude becomes homogeneous and has good mixing between heavy part and light part (at 60°C, the crude will behave as Newtonian fluid). In the same time, while mixing the crude with additive, the tube is immersed inside the water bath at the same temperature to avoid thermal shock, which will cause the crude to solidify once it is in contact with the tube.

3.3.3 Mixing of Crude Oil with Additive

Crude oil and additive will not be homogeneous if they are not mixed properly such that the additive will not fully dissolved with crude oil and consequently yields incorrect result. After the amount of additive required has been calculated (refer to Section 4.2), both crude and additive are placed inside a beaker and stirred by using magnetic stirrer for 30 minutes at the temperature of 60°C. After that, the mixture is transferred inside the tube. Then experiment begins after the tube is immersed inside the water bath and cooled from 60°C to 20°C.

3.3.4 Measurement of Gas Voids Volume

Apart from volume, another important result obtained from this step is the distribution of gas voids. This step will be the first as the volume can be measured directly at the tube without the need to suck the gas voids out by using syringe. The procedure is described as below:

i. The mixture of crude oil and additive is inserted into the polyurethane tube at the inlet valve up to the outlet valve.

ii. The tube is immersed and let cooled from 60°C to 20°C.
iii. During the cooling process, gas voids formation is observed at every decrement of 5°C.
iv. After the temperature has reached 20°C, the tube is taken out from the water bath.
v. The diameter and length of the gas voids are measured directly at the tube by using vernier caliper.
vi. Finally, gas void volume over total crude volume is calculated.

3.3.5 Measurement of Gas Voids Pressure

The purpose of measuring the pressure is to observe the compressibility of the gas voids provided that the gas voids pressure is lower than atmospheric pressure. It is a continuation from Section 3.3.4, which is the gas voids volume measurement. Basically the steps are the same from Step (i) to step (iv), with additional steps as follow:

i. A syringe is connected to a pressure transmitter to record the pressure.
ii. Then the syringe is tapped of the apex of the tube where the gas voids are located due to pressure difference.
iii. The reading is taken three times to calculate the average value.

3.3.6 Measurement of Gas Voids Composition

Gas voids composition is determined by using gas chromatography. In gas chromatography, the moving phase is a carrier gas. Commonly used inert gases are helium, nitrogen and argon. The instrument used to perform gas chromatography is called as a gas chromatograph or also known as gas separator. Similar to the gas voids pressure measurement, this is also a continuation from Section 3.3.4 with additional procedure as below:

i. A syringe is used to suck up the gas from the tube.

ii. The syringe is tapped at the apex of the tube.
iii. Then, the syringe is sealed.
iv. Finally, the gas inside the syringe will be transferred to the gas chromatography machine.
v. The result of the gas composition will be produced and further analysis will be done.

To avoid contamination of gas sample, pressure measurement and gas chromatography are done separately.

3.4 Gantt Chart

Activity	FYP1				FYP2				
	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept
Project study									
Proposal submission									
Proposal defense									
Experimental setup									
Experimental work									
Analysis of result									
Final documentation									

Table 1: Gantt chart.

3.5 Key milestone

Activity	FYP1				FYP2				
	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept
Experimental setup plan		•							
Acquiring flow line bubble rig			•						
Acquiring sample					•				
Experiment commence						•			
Experiment complete								•	
Data analysis									•

Table 2: Key milestone.

CHAPTER IV

RESULTS & DISCUSSIONS

In the previous section, we have discussed about the fabrication process, preparation of crude oil and additive as well as the procedure for volume, pressure and gas composition measurement. Throughout this project, the cooling rate is fixed at 0.4°C/min. The cooling rate is calculated as shown in Eqn. 1:

$$Cooling\ rate = \frac{60℃ - 20℃}{100min} = 0.4\ ℃/min \qquad \textbf{Eqn. 1}$$

In this chapter, the results of the experiments together with the analysis and interpretations will be discussed thoroughly.

4.1 The effects of PPD toward the Formation of Gas Voids

Firstly, the effect of PPD is observed before analyzing the results of the three parameters, namely the volume, pressure and gas composition.

(a)

(b)

Figure 19: Crude at the end of experiment, 20°C (a) with PPD (b) without PPD.

It can be observed that originally the crude will solidify at 20°C, as in Figure 19(b). However, the addition of PPD causes the crude to remain in liquid form even after the experiment finishes as shown in Figure 19(a). This situation is justified as the function of PPD is to reduce the pour point temperature. So, even at 20°C crude with additive will still be in liquid form because the pour point temperature has been lowered from the original value.

4.2 Gas Voids Volume

The purpose of this section is to observe the gas voids volume percentage in a specified crude volume and also the formation of it based on the three concentrations of PPD involved. Firstly, the total crude volume is calculated.

$$V_{crude} = \pi r_{tube}{}^2 L_{tube} \qquad \textbf{Eqn. 2}$$
$$= \pi(0.004^2)(0.2)$$
$$= 1.0053 \times 10^{-5} m^3$$
$$= \mathbf{10.053\ mL}$$

Where,

$r_{tube} = 0.004m$

$L_{tube} = 0.2m$

$1m^3 = 1 \times 10^6 mL$

As this project involves the utilization of additives, the mass of PPD for each concentration also needs to be measured. As it is in a liquid form, the mass cannot be measured directly by using the weight balance, but rather the density of both crude and PPD has to be taken into account. A sample of calculations for 200ppm concentration of PPD is shown below:

i) <u>Mass of crude</u>

$$\%\ concentration\ \left(\frac{w}{w}\right) = \frac{ppm}{10{,}000} = \frac{X_{PPD}}{X_{PPD} + X_{crude}} \qquad \textbf{Eqn. 3}$$

$$0.02\% = \frac{X_{PPD}}{X_{PPD} + X_{crude}}$$

Where,

$X_{crude} = mass\ of\ crude$

$X_{PPD} = mass\ of\ PPD$

$Mass_{bottle}$ = 16.885 g

$Mass_{bottle + crude}$ = 24.9022 g

$Mass_{crude}$ = $Mass_{bottle + crude}$ - $Mass_{bottle}$ = 8.0172 g

$Volume_{crude}$ = 10 mL

$$\rho_{crude\ at\ 10mL} = \frac{m}{V} \qquad \textbf{Eqn. 4}$$

$$= \frac{8.0172\ \text{g}}{10\ \text{mL}}$$

$$= 0.80172\ g/mL$$

$$\rho_{crude\ at\ 10.053mL} = 0.805969\ g/mL$$

$$m_{crude\ at\ 10.053mL} = \rho V$$

$$= 0.805969 g/mL \times 10.053 mL$$

$$= \mathbf{8.1025} \boldsymbol{g}$$

ii) <u>Mass of PPD</u>

$$0.02\% = \frac{X_{PPD}}{X_{PPD} + 8.1025}$$

$$X_{PPD\ at\ 10.053mL} = \mathbf{0.16535} \boldsymbol{g}$$

iii) <u>Density of PPD</u>

$Mass_{bottle}$ = 48.299 g

$Mass_{bottle + PPD}$ = 64.188 g

$Mass_{PPD}$ = $Mass_{bottle + PPD}$ - $Mass_{bottle}$ = 15.8897 g

$Volume_{PPD}$ = 20 mL

$$\rho_{PPD\ at\ 20mL} = \frac{m}{V}$$

$$= \frac{15.8897\ \text{g}}{20\ \text{mL}}$$

$$= 0.79445\ g/mL$$

$$\rho_{PPD\ at\ 10.053mL} = \mathbf{0.39935}\ \boldsymbol{g/mL}$$

iv) Volume of PPD required

$$V_{PPD\ at\ 10.053mL} = \frac{m_{PPD\ at\ 10.053mL}}{\rho_{PPD\ at\ 10.053mL}}$$

$$= \frac{0.16535g}{0.39935\ g/mL}$$

$$= 0.41407mL$$

$$= \mathbf{414.07}\boldsymbol{mg}$$

Where,

$1mL = 1000\ mg$

Basically 414.07 mg of PPD is needed for 200 ppm of PPD. After mixing both crude and PPD, the results at the end of experiment are recorded and can be divided into two parts which are gas voids volume percentage and also gas voids formation.

Gas voids are formed at the apex of the tube. If the tube is stretched out to a straight position, the voids are having cylindrical shape, Figure 20. Thus, for ease of analysis and calculations, the voids volume is assumed to be as follow:

$$V_{void} = \pi {r_{void}}^2 L_{void} \qquad \textbf{Eqn. 5}$$

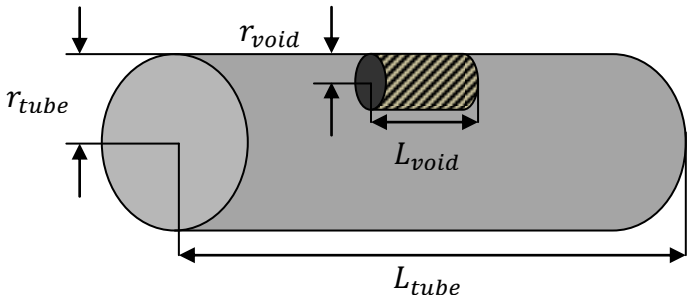


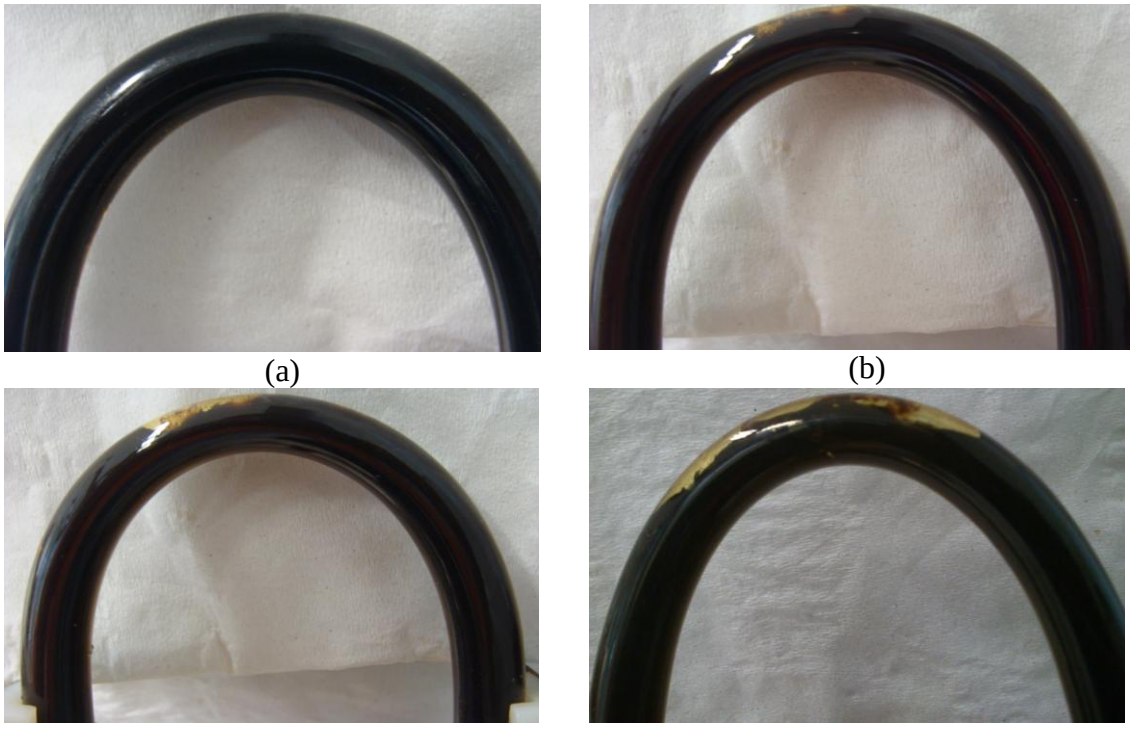
Figure 20: Schematic diagram of the shape of the voids.

For each concentration, the experiment is repeated three times for accuracy and reliability. Then, the average volume and percentage of gas voids volume can be determined by the following formula:

$$V_{average} = \frac{V_1 + V_2 + V_3}{3} \qquad \textbf{Eqn. 6}$$

$$Gas\ void\ \% = \frac{V_{void}}{V_{crude}} \times 100 \qquad \textbf{Eqn. 7}$$

Observation on the formation of gas voids is made periodically. At every decrement of 5°C, the voids volume is measured. However, it is noted that the voids only started to form at temperature below 30°C, which is below its pour point temperature of 35°C. From there, the small voids will begin to migrate to the apex and coalesce to form bigger voids as shown in Figure 21.



(a) (b) (c) (d)

Figure 21: Formation of gas voids for crude with 200ppm of PPD at (a) 35°C (b) 30°C (c) 25°C (d) 20°C.

From Figure 22, as the concentration of PPD increases, the voids volume decreases. The graph plotted in Figure 23 indicates that the highest void volume is recorded at 200 ppm, which is 3.61×10^{-7} m^3 while the lowest volume is 0.0866×10^{-7} m^3, which occurred at 1000 ppm.

(a) (b)

Figure 22: Formation of gas voids for crude with (a) 500ppm (b) 1000ppm of PPD.

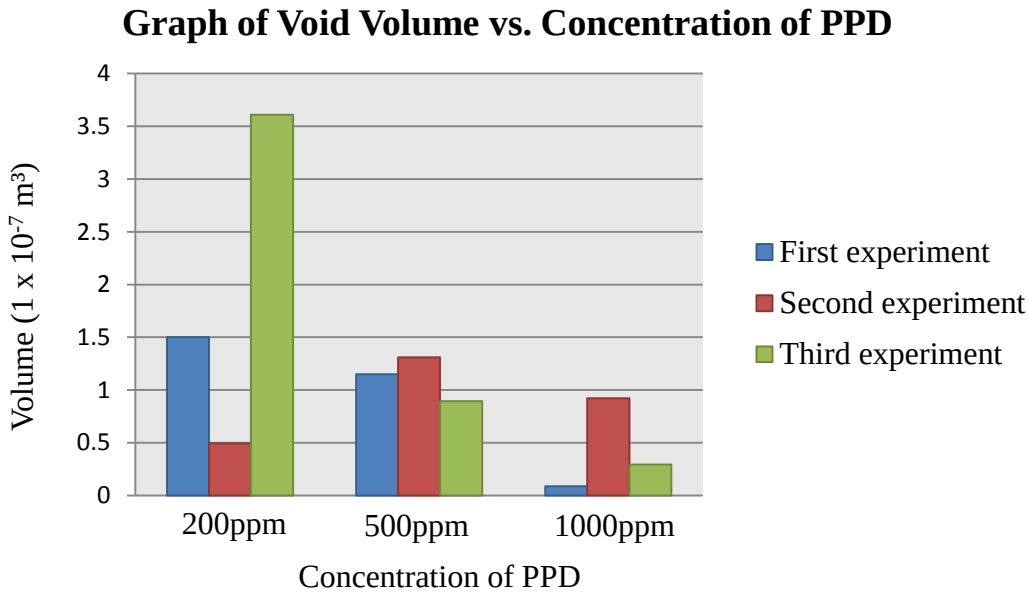


Figure 23: Graph of void volume vs. concentration of PPD.

Then, the average void volume is calculated for each concentration. Gas voids percentage can be determined by using Eqn. 7. The results tabulated in Table 3 prove that gas voids percentage is decreasing as the concentration of PPD increases. This could be due to the function of PPD itself. PPD serves as flow improvers, as it reduces the pour point temperature of crude. Even at 20°C, crude with higher concentration of PPD will still be in liquid form and thus, reducing the voids volume. It can be concluded that the lesser the concentration is, the more the crude will solidify at the end of experiment and vice versa.

	200ppm	**500ppm**	**1000ppm**
Average Length (mm)	27.32	10.95	7.22
Average Diameter (mm)	2.88	3.60	2.44
Average Volume (m^3)	1.867E-07	1.115E-07	4.338E-08
Void Percentage (%)	1.86	1.11	0.43

Table 3: Gas voids volume percentage at different PPD concentration.

4.3 Gas Voids Pressure

The next parameter to be studied is gas voids pressure. Similar to volume measurement, average value of pressure has been taken for each concentration. It is calculated based on the following formula:

$$P_{average} = \frac{P_1 + P_2 + P_3}{3} \qquad \textbf{Eqn. 8}$$

Figure 24 gives us the range of the pressure recorded by pressure transmitter which is between -0.2 and-0.6 mmHg. In addition, the graph shows that the values are uniform, at around the average value of -0.4 mmHg. The pressure values are negative which indicate that the pressure inside the tube is less than the atmospheric pressure.

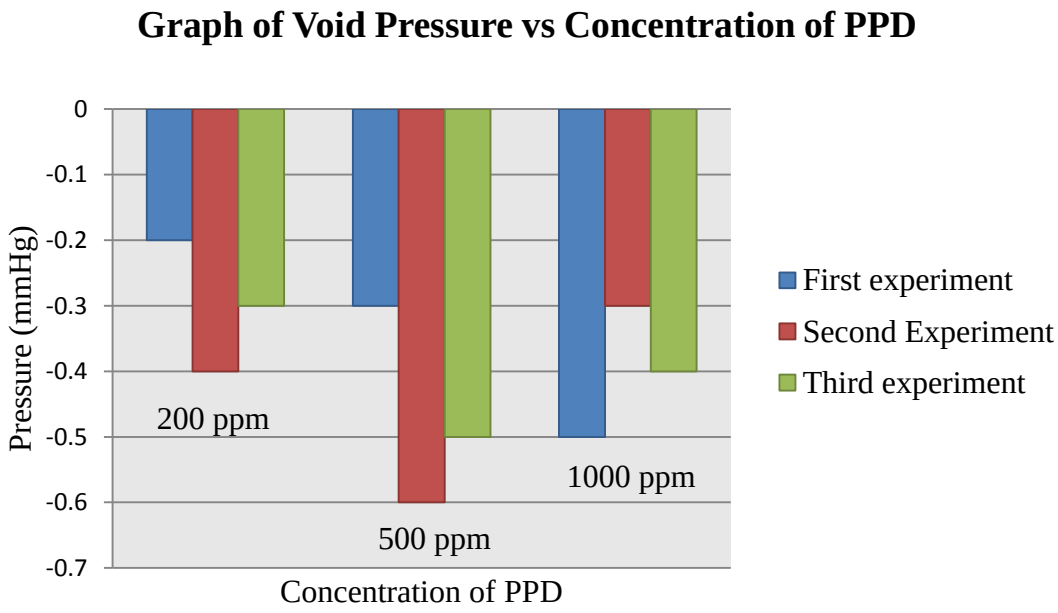


Figure 24: Graph of void pressure vs. concentration of PPD.

Table 4 summarizes the average value of pressure for each concentration. The pressure difference is small which implies that it does not change much regardless of the concentration. So, it can be concluded that addition of PPD, yields negative pressure inside the pipeline and contributes to the compressibility of the crude with respect to gas voids pressure.

	200ppm	**500ppm**	**1000ppm**
Average Pressure (mmHg)	-0.300	-0.467	-0.400
Average Pressure (bar)	-0.0004	-0.000622	-0.000533

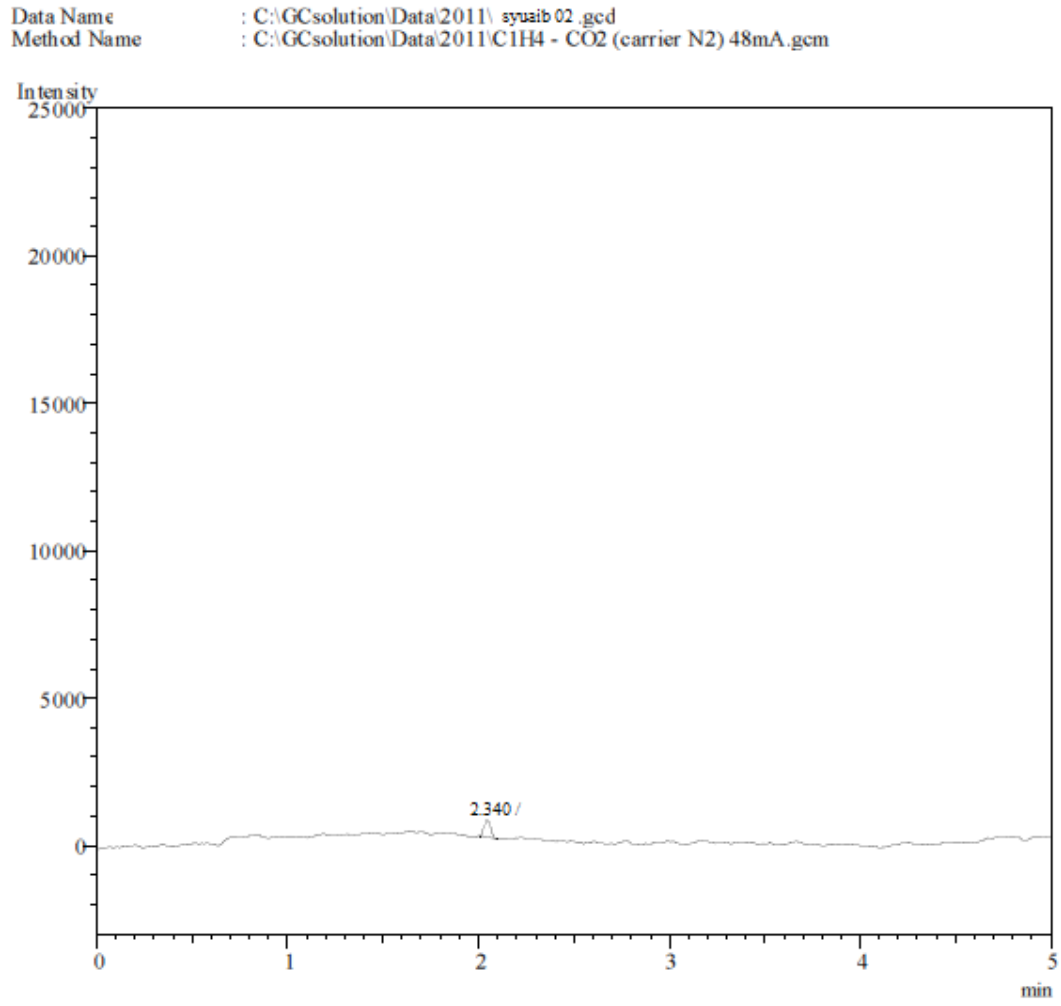
Table 4: Gas voids pressure at different PPD concentration.

Where,

$1mmHg = 0.001333224\ bar$

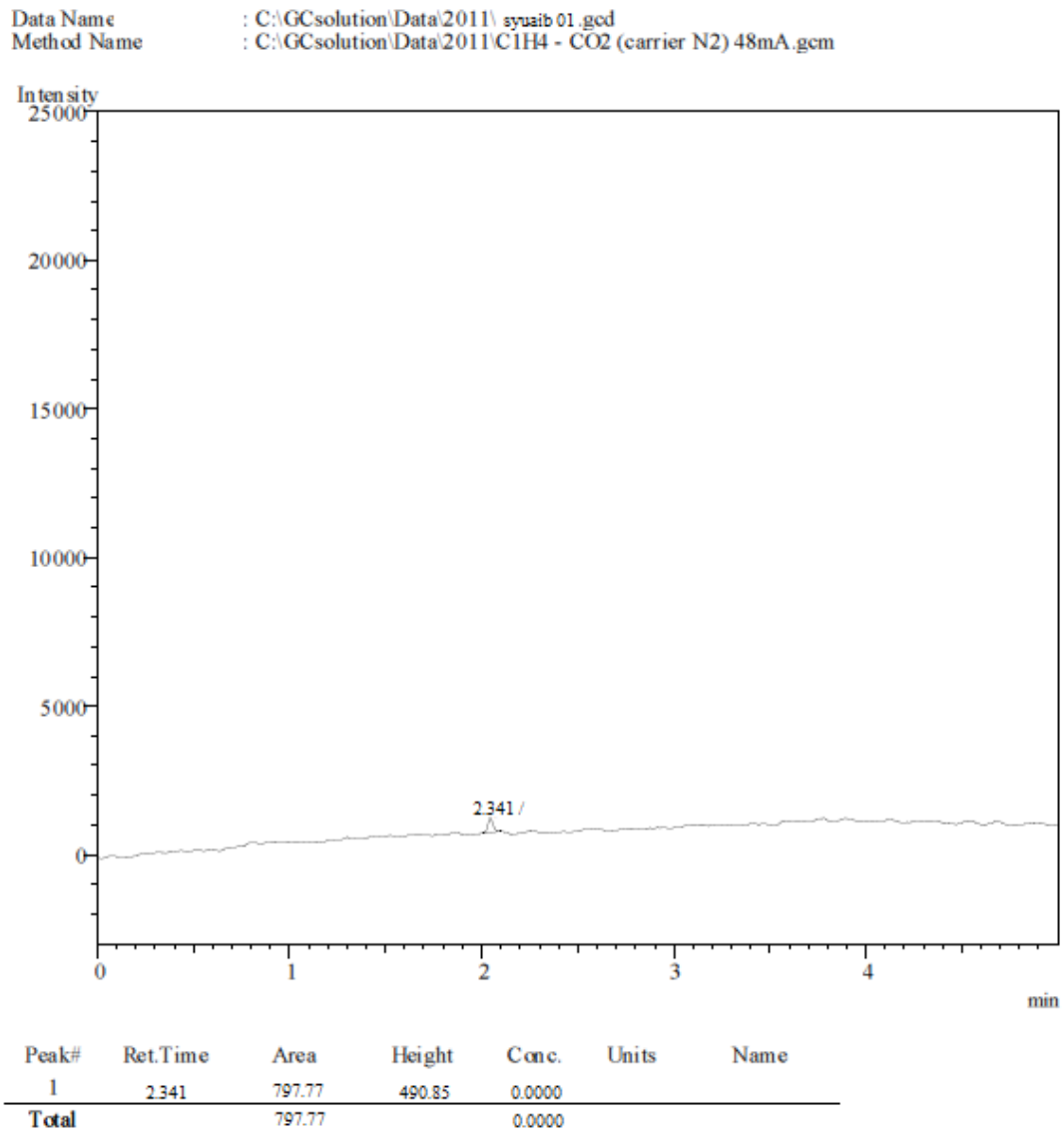
4.4 Gas Voids Composition

According to the previous work by Idris. H, the voids only consist of air, no other gases present. In this project, gas chromatography is done to the gas voids sample for 500 and 1000 ppm concentration of PPD. The results are shown in Figure 25.



Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	2.340	853.55	594.35	0.0000		
Total		853.55		0.0000		

(a)



(b)

Figure 25: Gas chromatography for gas sample of crude with (a) 500ppm (b) 1000ppm of PPD.

The results consist of intensity vs. time graphs. The model of the equipment is GC-2010 Gas Chromatograph that uses flame ionization detector. The intensity or also known as concentration of the sample gas is measured in term of volume. It is obtained by the multiplication of area and height. It has no unit as it is in the form of a ratio.

From Figure 25(a) and Figure 25(b), it can be seen that only one peak occurs at 2.340 and 2.341 min respectively. According to the technician in charge of the equipment, the sample only consists of air as it has only one peak. When thermal shrinkage occurs inside the pipeline, the shrunken crude will produce an empty space or void. In theory, the void will consist of the lighter part of the crude (carbon dioxide, oxygen, nitrogen, methane, ethane and propane) that has the tendency to bubble up in gas form. So, if proper approach to obtain the gas sample is done, without contamination, the results supposed to produce more than one peak. However, due to some human errors, they contribute to the contamination and eventually only produce one peak.

CHAPTER V

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusion

The outcome of this project is to investigate the thermal shrinkage and gas voids formation of waxy crude oil. Three parameters of interest are gas voids volume, pressure and gas compositions.

The best protocol for conducting the experiment was determined by trial and error method in order for the gas voids to occur at the apex for the ease of analysis, such as the length and also sealing of the tube with cling film. In addition, the original U-bend frame was also modified to fit inside the water bath.

Several hypotheses are made before conducting the experiment. Through the volume, the amount of gas voids with respect to the total crude volume as well as gas voids distribution can be determined. The gas voids percentage reduces as the concentration of PPD increases. This happens as a result of crude with high concentration of PPD tends to be in liquid rather than in solid. Thus, crude in liquid form produces fewer voids compared to crude in solid form.

If the compressibility of gas voids is justified, this will help to reduce the restart pressure. This can be achieved if the gas voids pressure is lower than atmospheric pressure. Based on the results, it has been proven that it is indeed lesser than the outside pressure. It remains in the range of the average value regardless of the concentration of PPD. In fact, the presence of voids which consist of air has proven that at the seabed temperature inside the pipeline, there is an opportunity to compress the gelled crude and consequently reduce the restart pressure and operating cost of the platform. However, a more precise approach to obtain the gas sample will improve the accuracy of the results with respect to the gas composition.

5.2 Recommendations

Throughout this project, it has been identified that there are room of improvement by which necessary modifications or changes can be made in order to increase the quality as well as the productivity of the research. Therefore, it is hoped that to those who will be undertaking this work in the future, will consider the recommendations below:

- To vary the cooling rate. Different cooling rate will have different effect on the formation of gas void
- To use lower temperature for cooling process as lower temperature will produce bigger void
- To analyze the void volume by using CATIA drawing, by which the calculations by pixel of the void formed can be made, rather than assuming it as a cylinder
- To use different type of crude. For example, medium severe waxy crude (Pour point ±20°C) that may have more of the light hydrocarbon. This will give higher chance of getting more than one component during gas chromatography
- To implement a more accurate method of obtaining the gas sample. This can be done by having two syringes instead of one where one syringe will be filled with a known composition inert gas (Helium). Then, both syringes are tabbed into the tube simultaneously. The syringe with inert gas will be pushed to displace the gas inside the tube so that the other empty syringe can suck it
- To investigate the structure of the wax formed
- To perform heat transfer analysis in order to predict the cooling rate
- To check the pressure obtained whether it satisfies the Ideal Gas Equation or not

CHAPTER VI

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