EVALUATION OF THE PERFORMANCE OF WAX INHIBITORS ON WAX DEPOSITION

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EVALUATION OF THE PERFORMANCE OF WAX INHIBITORS ON WAX DEPOSITION

LIEW SHI YAN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

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JANUARY 2014

SUPERVISOR’S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Gas Technology).

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STUDENT’S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
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Date : JANUARY 2014

Dedication

8812

To my late-sister, Shi May for teaching me the spirit of not giving up

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For all the challenges I have faced receiving this title and the research work required to make this study possible, I would like to thank Almighty God for his blessings. It was not an easy road dealing with unstable equipment, guilt, learning how to use the laboratory equipments, trial and error on new methodologies, balancing between two final year projects and facing endless troubles trying to get the result I deem desirable. It is still with God's blessing that I was able to do this much.

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ABSTRACT

Chemical methods were implemented in the crude oil industry to reduce wax deposition in transportation of crude oil via pipeline in subsea conditions. Poly (ethylene-co-vinyl acetate) (EVA) and diethanolamine (DEA) were used in this study to evaluate the performance as an effective wax inhibitor pair at different blend volume ratios in crude oil using cold finger method equipped with an agitator. Aside from that, the study on the rheology behaviour was carried out to validate the effects temperature and shear on the viscosity of the untreated crude oil. 10 mL volume of the wax inhibitor was injected into the cold finger equipment operating at 200 rpm, cold finger temperature at 10 ˚C, and water bath temperature surrounding the vessel at 50 ˚C. It was found that at ratio 1:1 of EVA at 400 ppm concentration to DEA was proven to be the most effective ratio blend at this operating condition with paraffinic inhibition efficiency (PIE) of 50.26%. It was also shown that EVA alone performs far better than DEA with a PIE of 17.28%. However, blend of wax inhibitors outperforms pure wax inhibitors in reducing wax deposition by a significant margin of greater PIE. The wax deposited from the inhibition of pure EVA gives a relatively hard wax texture in comparison to inhibition of pure DEA which gives a relatively softer wax texture. Wax inhibitor blends between EVA and DEA on the other hand give the softest gel texture which implicates the wax to contain lower hydrocarbons. The rheology behaviour of the crude oil behaves close to a pseudo plastic fluid where the viscosity decreases with increasing shear rate and increasing temperature. The result here will be useful to understand the effectiveness of EVA in the presence of wax dispersant, DEA to prevent severe pipeline blockage and losses of crude oil production by controlling wax deposition. It is recommended for future researches to evaluate the performance of wax inhibitor blends by varying the parameters of the cold finger equipment with respect to factors attributing to wax deposition such as molecular diffusion, shear dispersion, and effects of aging.

ABSTRAK

Kaedah kimia telah diamalkan dalam industri petroleum untuk mengurangkan pemendapan wax dalam activity pengangkutan petroleum melalui saluran paip di dasar laut. Poly (ethylene-co-vinyl acetate) (EVA) dan diethanolamine (DEA) telah digunakan dalam kajian ini untuk menilai prestasi sebagai campuran perencat wax pada nisbah gabungan yang berbeza untuk mengawal isu pemendapan wax menggunakan alat '*cold finger'*. Selain daripada itu, kajian reologi dijalankan untuk mengesahkan kesan suhu dan ricih pada kelikatan minyak batu. 10 mL perencat wax telah disuntik ke dalam '*cold finger'* yang beroperasi pada 200 rpm, suhu jari sejuk pada 10 ˚C, dan air suhu mandi sekitar bekas minyak batu pada 50 ˚C. Daripada keputusan eksperimen ini, didapati bahawa pada nisbah 1:1 EVA-DEA merupakan gabungan nisbah yang paling berkesan dengan wax perencatan kecekapan (PIE) sebanyak 50.26%. Ia juga menunjukkan bahawa EVA berfungsi lebih berkesan sebagai perenncat wax daripada DEA dengan PIE daripada 17.28%. Walau bagaimanapun, campuran perencat wax didapati lebih berkesan daripada menggunakan perencat wax tanpa campuran dalam mengurangkan pemendapan wax. Wax daripada perencatan tulen EVA memberikan tekstur wax yang keras berbanding dengan perencatan tulen DEA yang memberikan tekstur wax yang lembut. Pergabungan perencat wax antara EVA dan DEA sebaliknya memberi gel tekstur paling lembut dalam eksperimen ini. Tekstur tersebut mengimplikasi wax tersebut mengandungi molekul hidrokarbon yang rendah. Reologi minyak batu didapati bersifat hampir cecair plastik pseudo di mana kelikatan berkurangan dengan peningkatan kadar ricih dan suhu. Hasil eskperimen ini adalah untuk penambahan latar belakang keberkesanan perencat wax hasil perganbungan EVA dan DEA. Ilmu ini akan digunakan untuk mengelakkan pemendapan saluran paip daripada tersumbat di dasar laut sehingga mengakibatkan kerugian produksi. Ia adalah dicadangkan untuk menyelidik pretasi perencat wax dengan mengubah parameter alat '*cold finger'* untuk mengaitkan faktor-faktor penyebab pemendapan wax seperti resapan molekul, pebaran ricih, dan kesan-kesan penuaan.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

m_m	mass of deposited wax
ρ_d	density of the solid wax
D_m	diffusion coefficient of liquid wax in oil
A	surface area over which deposition occurs
C	concentration of wax in solution
r	radial coordinate
T	temperature of the bulk fluid
W_f	reference amount of wax deposition without chemical treatment
W_t	amount of paraffin deposition with chemical treatment

LIST OF ABBREVIATIONS

API	American Petroleum Institute
ASTM	American Standard Testing Method
CCN	Carbon critical number
DEA	Diethanolamine
DSC	Differential scanning calorimeter
EVA	Poly (ethylene-co-vinyl acetate)
HMWH	High molecular weight hydrocarbons
LMWH	Low molecular weight hydrocarbons
PIE	Paraffinic inhibition efficiency
PPD	Pour point depressant
PPT	Pour point temperature
SARA	Saturates, asphaltenes, resins, and aromatics
UOP	Universal Oil Products
WAT	Wax appearance temperature
WDT	Wax disappearance temperature

1 INTRODUCTION

1.1 Background and motivation of study

Wax deposition in subsea pipelines is a complex phenomenon that has brought many challenges in the production, transportation and refining of crude oil in the petroleum industry. Wax deposition occurs due to the decrease in temperature and pressure during oil production operations which induces the precipitation wax crystals to form from crude oil and deposit onto pipeline walls. Crude oil is mainly composed of saturates, asphaltenes, resins, and aromatics (SARA). It was found that saturates also known as n-paraffins are the main culprit that contributes to wax deposition (Nanthan, 1955). The solubility of n-paraffins decreases with decreasing temperature and pressure leading to the formation of wax precipitates that has the potential to create crystalline net capable of entrapping liquid crude oil (Jorda, 1966). The temperature gradient between pipeline walls and the bulk fluid temperature driven by molecular diffusion mechanism will then cause wax deposition to occur on the surface of pipeline walls. Waxes that manage to deposit onto pipeline walls offer available nucleation sites that attracts other non-polar n-paraffins to bond layer upon layer of wax deposits. The built up wax deposits on pipeline walls would hinder transportation via pipeline operations by causing drastic increase of pressure drop in pipelines, reduction in diameter of the pipe or pipeline blockage resulting to major losses in profit and time to restart the production line (Wu *et al.*, 2012).

Chemical additives also known as wax inhibitors are one of the known wax controlling strategy being implemented by petroleum production industries to reduce the frequency of pigging. Wax inhibitors such as pour point depressants (PPD) and wax dispersants were used to chemically modify the wax solid structure thus reducing the tendency of the wax crystals to interlock and form three dimensional networks growth (Pederson & Rønningsen, 2003). These wax inhibitors are highly responsible in retarding the growth of the wax paraffin to form smaller crystals with higher volume-to-surface ratio. Wax inhibitors do not however, stop the precipitation from happening but creates a temporary kinetic barrier to precipitation that delays the precipitation mechanism from forming harden wax, allowing these wax aggregates to be swept away in the oil production stream flow in time (Tinsley *et al.*, 2009).

Although under the class of chemical additives, the role of PPD and wax dispersants differs widely from one another. PPD also known as wax crystal modifiers functions by co-crystalizing into the paraffin structure through van der Waals interactions leaving the polar moiety end tail to create a steric hindrance to interfere with alignment of new incoming wax molecules. Meanwhile wax dispersants functions by absorbing itself onto the wax crystals, preventing crystal nucleation phenomenon thereby reducing the tendency of the wax molecules to stick together. Frequently, wax dispersants are blended with wax inhibitors to enhance their performance in reducing wax deposition (Malcom, 2009; Marie *et al.*, 2004).

The motivation behind this research is to evaluate the performance of PPD blended with wax dispersant on wax deposition quantitatively and qualitatively. The wax inhibitor and wax dispersant selected for this study are poly (ethylene-co-vinyl acetate) (EVA) and diethanolamine (DEA) respectively. It is desired through the outcome of this research to expand the literature on the role wax inhibitor play in reducing wax deposition in terms of the amount of mass of the wax deposited and the effects it has on the hydrocarbons.

1.2 Problem statement

Wax deposition only requires the presence of wax precipitation as little as 2 wt. % (Létoffé *et al.*, 1995) and the driving force of molecular diffusion mechanism to occur. Malaysia oil wells were literately reported to contain as high as 20.2 wt. % of wax content and pour point temperature (PPT) as high as 36 ˚C (Kelechukwu & Yassin, 2008). With the world oil demand expecting to increase by 50% in 2025 (U.S. Department of Energy, 2004), offshore productions are expected to experience even colder subsea conditions of at least 5 ˚C with increasing offshore oil rigs distance (Azevedo & Teixeira, 2003). The transportation of crude oil via subsea pipelines will severely experience pipeline blockage due to heavy wax formation on pipeline walls leaving petroleum companies with an alarming economical viable issue due to frequent downtime and risk of damaged equipment forced to be abandoned. The percentage of offshore wells built in water depths greater than 500 m are expected to increase from 55% in 2007 to 67% in 2012 with the deepest well forecasted to be as deep as 3000 m below sea level (Wright, 2007). Currently, South China Sea, the Gulf of Mexico, North

Sea, off the coast of West Africa and off the coast of Brazil are amongst the most active offshore well productions to date (Azevedo & Teixeira, 2003).

Chemical methods typically used to address wax deposition issues are widely being studied due to their efficient role in reducing the frequency of costly pigging. Extensive studies were carried out on the role of PPD such as ethylene co-polymers, maleic anhydride co-polymers, and α-olefins co-polymers on the viscosity, pour point and efficiency of paraffin wax inhibition using laboratory methods such as cold finger method, flow loop method and rheometer to simulate the environment as similar as sub-sea pipeline (Machado & Lucas, 1999). The role of wax dispersants were typically studied by introducing novel chemicals created to control wax deposition. However, not much literature documentation was done on the effects on wax deposition through association of PPD with wax dispersants as most researchers are primarily focus on introducing novel chemicals primarily in the area of wax inhibitors. Even so, it is still generally understood that wax dispersants enhance the performance of wax inhibitors by reducing wax deposition by adhering pipeline wall and onto wax precipitates preventing aggregation between wax molecules.

1.3 Objective

The following is the objective of this research:

- To evaluate the effects of combined blend wax inhibitors EVA and DEA on the wax deposition in crude oil using cold finger method.

1.4 Scopes of this research

This experimental study is conducted using the cold finger method equipped with a stirrer to agitate the crude oil inside the vessel. The following are the scopes of this research:

i. Untreated crude oil samples will be characterised with respect to (i) wax appearance temperature (WAT) using Differential Scanning Calorimeter (DSC) (ii) determination of PPT using American Standard Testing Method (ASTM) D-97 (iii) viscosity temperature and rotational speed of spindle dependence using Brookfield viscometer (iv) amount of wax content using modified UOP46-64 method (Burger *et al.*, 1981).

ii. Using cold finger method to determine the optimum ratio blend between a selected pair of wax dispersant with pour point depressant by evaluating the paraffinic inhibition efficiency (PIE) (Bello *et al.*, 2006) from the mass deposited onto the cold finger.

1.5 Significance of study

Wax deposition is an alarming phenomenon that has economically burden the transportation of crude oil in the oil and gas industry. The significance of this study is to expand the literature background on the influences of PPD enhanced by the presence of wax dispersants to resolve wax deposition in subsea pipelines in hopes that this knowledge would aid in lowering down the production cost of crude oil from offshore productions. Chemical methods are relatively economical to study and also apply in the oil production industry in comparison to other wax controlling strategies. Other viable methods are also possible but they can be costly such as hot oiling which consumes a lot of energy resulting to high cost of utilities.

As a result, the effect of the selected wax inhibitor pair on wax deposition is being evaluated using cold finger method to determine the optimum ratio blend with the highest PIE. From the result obtained, it is desired to expand the understanding on the role of wax dispersants and wax inhibitors. It is also desired to recommend wax deposition using cold finger method as a relatively cheaper alternative than the flow loop method to screen for potential PPD experimentally.

1.6 Organisation of this thesis

The structure of the remainder of the thesis is outlined as follow:

Chapter 2 provides a description of the mechanisms involved in wax deposition and the chemical methods studied in modern literature to resolve wax deposition issues. A general discussion of various laboratory methods other than the cold finger method was also presented. A summary of various cold finger method studies was also provided.

Chapter 3 gives a review on the cold finger methodology and the wax characterization of the crude oil. The wax characterization considered in this study involves determination of WAT using DSC, PPT using ASTM D-97 and amount of wax content using modified UOP 46-64 method. The methodology of rheology behaviour of crude oil was also discussed.

Chapter 4 is devoted to the result and discussion obtained from the experimental study carried out. The wax characterization was done on untreated crude oil to obtain its physiochemical properties; WAT, PPT and amount of wax content. A brief discussion was done on the rheology behaviour of the untreated crude oil based on the viscosity readings collected from the rheology experiment. Aside from that, the results on the optimum ratio of the combined PPD and its effects on the wax deposited were discussed.

Chapter 5 concludes the results obtained from this research and provides future recommendations to improvise this study and provide suggestion on potential further studies that could carried out by other researchers interested in addressing wax deposition using chemical methods by performing experimental studies using cold finger method.

2 LITERATURE REVIEW

2.1 Overview

This chapter presents the past studies that have been performed on wax deposition from the thermodynamic and hydrodynamic view points and the efforts to experimentally predict wax deposition. The molecular diffusion, shear dispersion and aging effect are of the many significant factors that lead to wax deposition. The roles of these factors on wax deposition were also discussed in detailed such as the effect of a large differential temperature, shear stripping effect and the effects of flow regime on wax aging (Jessen & Howell, 1958; Jorda, 1966; Azevedo & Teixeira, 2003; Singh *et al*., 2001). Aside from that, this paper also covers on the development of EVA as a commercial PPD and DEA as a wax dispersant and their aspects as part of the waxy crude oil treatment. In addition, the cold finger method is also explained as an introductory literature and also other possible methods of performing laboratory scale wax deposition related experiments.

2.2 Introduction

Wax deposition is amongst the several critical operational challenges faced by the production and transportation pipelines in deepwater oil and gas industries. The pipeline acts as an intermediate form of transportation between the reservoir field to oil rig platform and oil rig platform to onshore upstream refinery plants. In order to prevent major loss of crude oil production due to blockage of these pipelines, strong pumping power and frequent pigging; a mechanical treatment to remove deposited wax on pipeline walls is required. However the increase in distance and depth of subsea transportation via pipeline has increase the frequency of pigging and risk of clogged pipes, which in turn creates an economical issue to the crude oil production team.

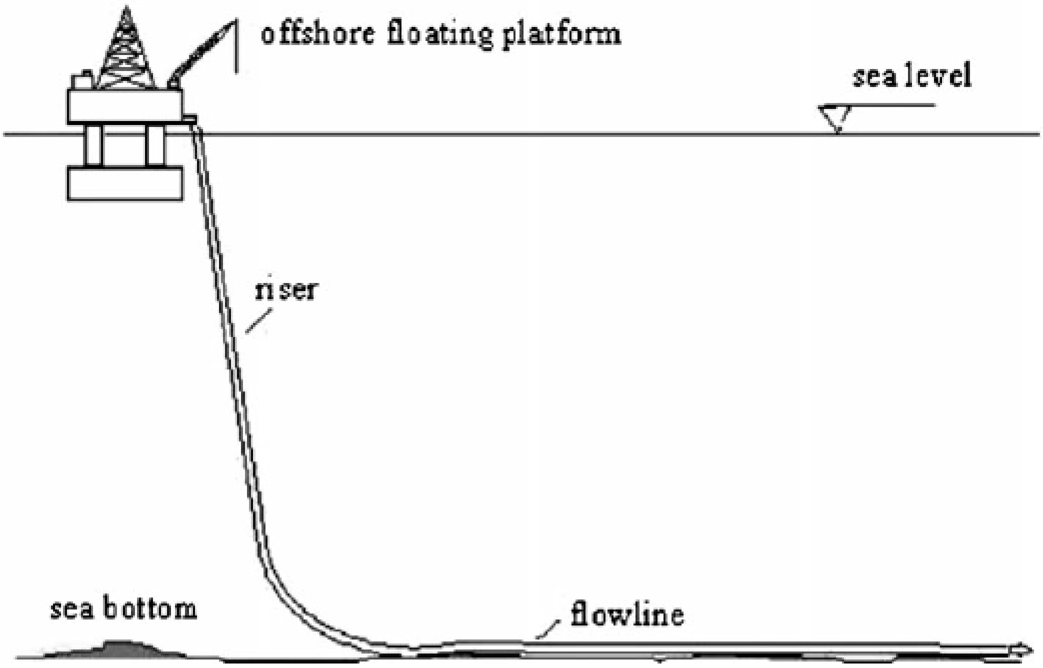


Figure 2- 1: Illustration of a subsea flow line from oil rig platform to upstream refinery plant by Gooya *et al.*, (2013).

The solubility of paraffin in crude oil is highly dependent on the decreasing function of temperature, pressure and the molecular weight of its constituents. As the crude oil leaves the reservoir, the pressure and the temperature of the bulk fluid tends to decrease in the process of its production and transportation. When crude oil at reservoir temperature is loss to surrounding pipeline walls in subsea climate, it tends to form wax precipitates that interlocks into a three dimensional network. Oil is entrapped in this network and forms gel-like structure below WAT. Further cooling subjects to the gel to harden and clog pipelines (Hemant *et al.*, 2008).

Crude oil constituents consist of n-alkanes, asphaltenes, resins, lighter distillates methane hydrates, polar aromatics, nitrogen, and sulphur etc. It is believed that long, straight n-paraffin chains are pre-dominantly responsible for the formation of wax deposits; even in most of Malaysian crude oil fields (Kelechukwu & Yassin, 2008). Nevertheless, not all long-chain aliphatic alkane compounds (C_nH_{2n+2}) exhibit the tendency to form wax deposits.

Table 2-1: Past studies regarding the nature of the deposited wax from crude oil.

Description	Reference
High molecular weight hydrocarbons (HMWH) that predominantly fall in the range of C_{18} to C_{65}.	Srivastava *et al.* (1993)
Present of aromatics, paraffin (C_{18} to C_{36}) and naphthalene components (C_{30} to C_{60}).	Bai and Bai (2010)
Paraffin exist in three forms: 1. Macrocrystalline: Dominated by straight chained n-alkanes found in subsea and export pipelines 2. Semi-microcrystalline: Intermediate between macro- and microcrystalline paraffin. 3. Microcrystalline: Often cycloalkanes and branched alkanes often associated with asphaltenes and other solid deposits found in tank bottoms as sludge-like deposit.	Wylde (2012)
Wax structures depends on the wax concentration, crystallization habit of wax, and the shear stability	Holder and Winkler (1965)

2.2.1 The differences between wax precipitation and wax deposition

Crude oil typically flows out of the reservoir at 70-150 °C and 55-103 MPa into subsea pipelines (Singh *et al.*, 2001). At elevated water depths, the relative constant ambient sea bed temperatures can range from 4 to 8 °C (Rønningsen, 2012). Below WAT, crude oil may separate into a solid-liquid wax phase where wax precipitation is first observed. Wax precipitation has the ability to form three dimensional structures due to the agglomeration of orthorhombic wax crystals nucleation sites (Paso & Folger, 2004). It is thermodynamically driven by variables such as temperature, pressure and composition; hydrodynamically influenced by flow regime; heat and mass transfer; solid-solid and surface solid interactions (Hammami *et al.*, 2003). These wax crystals tend to increase the viscosity of crude oil resulting to higher drag force.

However, the difference between wax precipitation and wax deposition lies here. It is necessary for wax precipitation to occur first before wax deposition can happen. Thus, it is also possible for wax precipitation to happen without leading to wax deposition. Though, it only requires at least 2 wt. % of precipitated wax to cause gelling of virgin waxy crudes (Li *et al.*, 2005; Holder & Winkler, 1965; Létoffé *et al.*, 1995). With the aid of the surface roughness on the pipeline walls at a certain flow regime and lower pipe wall temperature, these precipitates would get entrapped onto the pipeline walls as wax deposits and slowly thicken with time (Patton *et al*., 1970).

2.3 Wax appearance temperature and wax disappearance temperature

WAT is the temperature at which the wax crystals begins to form and precipitate gradually from the solution. The method of WAT determination is influenced by the supercooling involved in the crystallization process. A crude oil with higher composition of light end hydrocarbons tends to have lower WAT. This is due to the presence of light ends acting as a solvent to stabilize the higher end of the hydrocarbons in the crude oil. Reducing pressure further however would cause the lighter molecule weight hydrocarbons to dissipate as gas phase from the crude oil. This effect reduces the solubility of HMWH, thus increasing the WAT of the bulk fluid. Higher WAT would result to wax precipitation at elevated temperatures. This is problematic to subsea pipeline as even relatively warm climates water temperature tends to be around 5 °C (Azevedo & Teixeia, 2003).

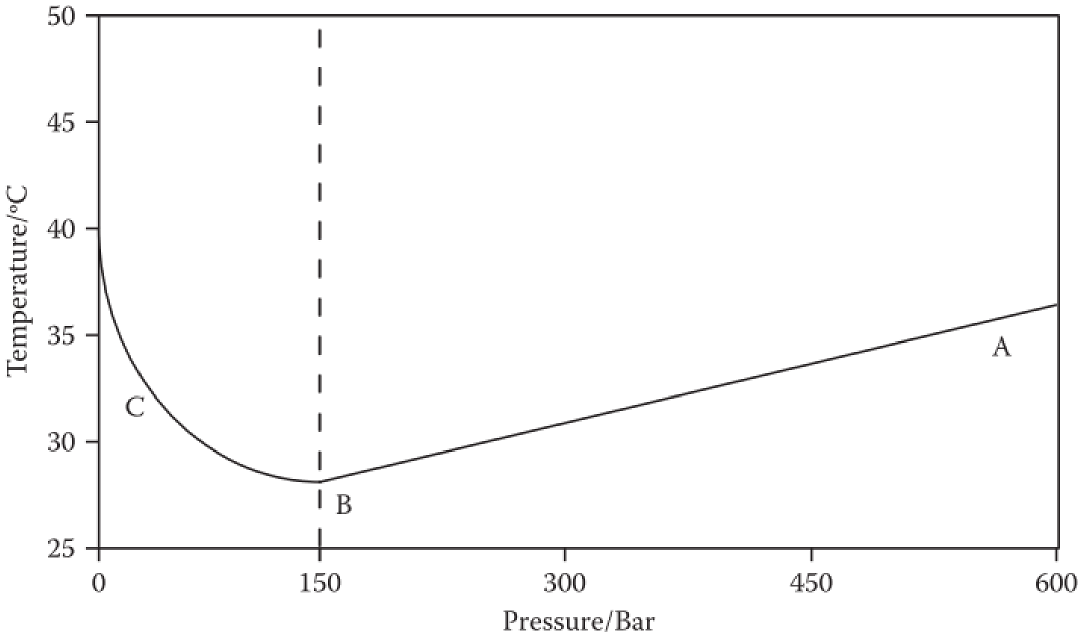


Figure 2- 2: Illustration of a typical phase diagram for wax precipitation by Malcolm (2009, p. 262).

According to Malcolm (2009), in Figure 2-2 point A represents the point at which the crude oil is undersaturated at reservoir pressure. As fluid is produced, the pressure falls and the lighter molecular weight hydrocarbons expand in greater proportion to the dissolved waxes. At point B, the ratio the volume of the light ends to heavy ends is at its greatest. However further reduction of pressure would result to increase in WAT. The curve in point C, reflects the effect of further decreasing pressure which disintegrates the lighter ends of the hydrocarbons thus increasing the WAT of the crude oil.

When the crude oil temperature starts to precipitate in descending rank order according to molecular weight due to super saturation, a single liquid phase of the oil changes into solid-liquid dispersion system at which small amount of wax crystals becomes present in liquid phase. If this system were to be heated at WAT, these wax crystals will still remain present and requires a higher temperature to dissolve them. This temperature is termed as wax disappearance temperature (WDT). WDT which Bhat and Mehrotra (2004) found to be close to the thermodynamic liquidus temperature is believed to be the true solid-liquid phase boundary. It is found WDT to be on an average of 3 °C higher than WAT for prepared wax-solvent mixture consisting C_{20}-C_{40} (Bhat & Mehrotra, 2004).

The difference in WAT and WDT is crucial when trying to determine the cloud point, pour point, and rheology behaviour of the crude oil. Shear and thermal history is normally eliminated by heating the crude oil for a few hours. This is further discussed under Chapter 3 as it concerns the determination method cloud point, pour point, cold finger experiment and determination of the rheology behaviour carried out.

2.3.1 Cloud point and pour point correlation

Cloud point represents the solubility limit of crude oil where solid wax crystals first precipitate. It is also known as WAT. On other hand, PPT is the lowest temperature at which crude oil will flow or pour. It is also greatly affected by oil flow properties. It results to dramatic changes in the viscosity and flow properties of crystallization of paraffin crystals. It can be modified using chemical inhibition method which lowers its pour point.

2.3.2 Rheology behaviour of crude oil

Crude oil at high temperature behaves as a Newtonian fluid showing viscosity-temperature dependence. As the temperature of the crude oil falls below the WAT, precipitation of the wax crystals will suddenly rapidly increase the viscosity entering into the non-Newtonian fluid region. The yield stress of a wax-solvent mixture is believed to be a function of wax composition, and thermal and shear histories. A typical waxy crude oil would normally exhibit a pseudo-plastic with thixotropic properties (Matveeko *et al.*, 1995).

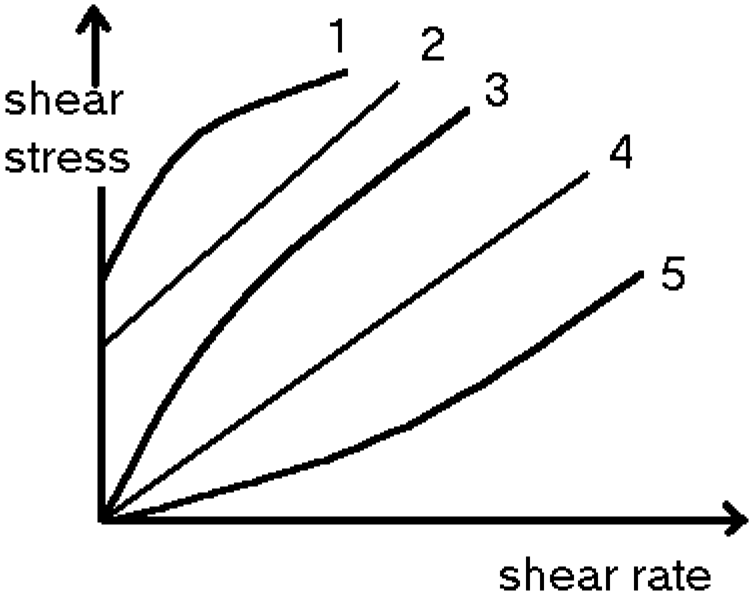


Figure 2- 3: Summary of non-Newtonian fluids (1) Viscoplastic fluid (2) Bingham fluid (3) Pseudo plastic fluid (4) Newtonian fluid (5) Dilatant fluid

The untreated crude oil is found to behave similarly to pseudo plastic fluid. Where with increasing shear rate, the viscosity tends to decrease. This behaviour is termed as shear-thinning.

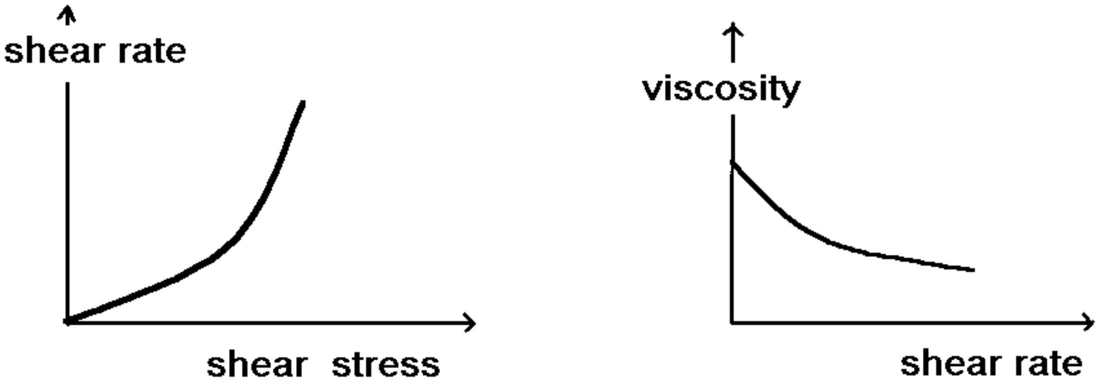


Figure 2- 4: The nature of a pseudo plastic fluid

According to Cheng *et al*. (2000) the nature that untreated crude oil exhibits a non-Newtonian behaviour can described in Bingham style equation. The deviation of the peak from linearity shows an elastic response, followed by creep and the final fracture.

2.4 Wax deposition mechanism

Various investigations have been carried out for the past decades on wax deposition mechanism by several researchers (Burger *et al.*, 1981; Leiroz & Azevedo, 2005). Different methods have been suggested by different researchers and found to play a significant role in wax deposition. The molecular diffusion and shear dispersion mechanism are found to likely be the primary driving force of wax deposition amongst the mechanisms that have been proposed (Malcolm, 2009).

2.4.1 Molecular diffusion mechanism

Simply said, molecular diffusion occurs if the pipe wall is colder than the WAT, wax can form and deposit onto the wall due to the temperature gradient existing between the pipe walls and the bulk fluid which is driven by Fick's law.

$$\frac{dm_m}{dt} = \rho_d D_m A \frac{dC}{dr} = \rho_w D_m A \left(\frac{dC}{dT} \right) \left(\frac{dT}{dr} \right) \tag{2.1}$$

In equation 2.1, m_m is mass of deposited wax, ρ_d is the density of the solid wax, D_m is the diffusion coefficient of liquid wax in oil, A is surface area over which deposition occurs, C is the concentration of wax in solution, T is the temperature of the bulk fluid, and r is the radial coordinate

Large temperature differential will lead to greater wax deposition with a weak porous structure (Jessen & Howell, 1958; Jorda, 1966). The initial wax deposition will increase rapidly and then the rate of deposition will decrease again due to the insulating effect of the wax layer (Towler *et al.*, 2011).

2.4.2 Shear dispersion mechanism

Shear dispersion occurs when already precipitated wax close to the wall moves to a region of lower velocity in the pipe wall and deposits (Malcolm, 2009). This mechanism is shown to have no effect to deposition in the absence of heat flux despite the bulk fluid temperature being under cloud point conditions (Burger *et al.*, 1981; Azevedo & Teixeira, 2003). Despite this, the drag force exerted on the solid waxy crystals from the fluid contributes to the removal of wax and aging of wax deposits which is known as the shear stripping effect. Thus, flow regime within the subsea pipeline also plays a major role in wax deposition. Laminar flow and turbulent flow are currently the two main most fully understood flows that play an influential role on wax deposition.

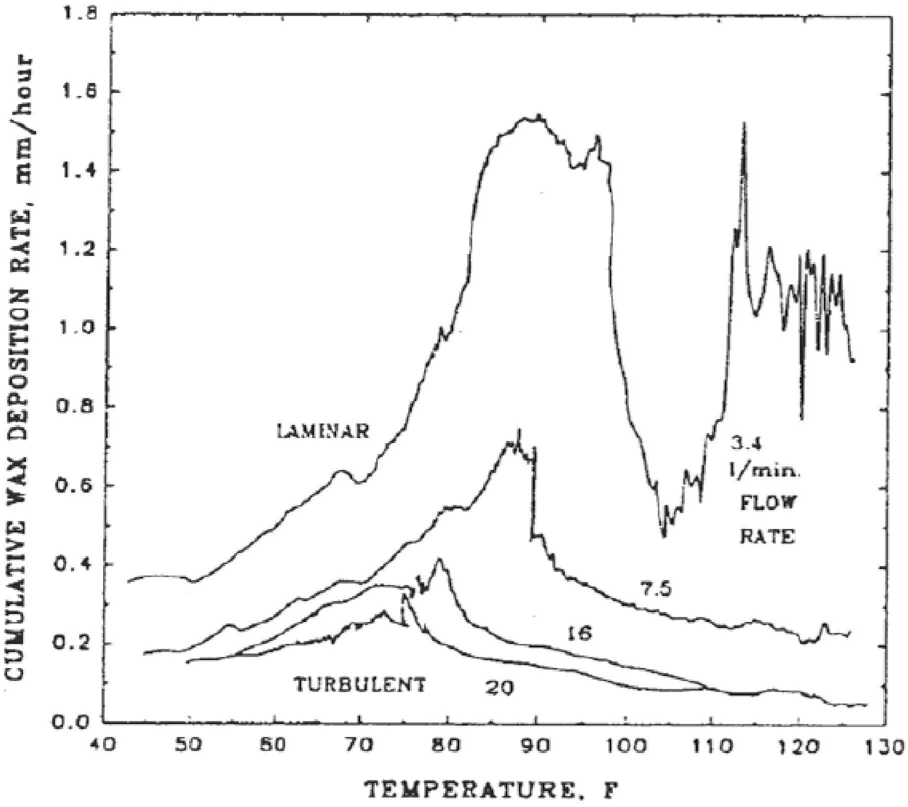


Figure 2- 5: Effect of flow rate on wax deposition rate by Hsu *et al*. (1994).

The laminar flow of the bulk fluid allows longer residence time of the crude oil to lose heat to surrounding colder pipeline walls (Towler *et al.*, 2011). This allows the wax molecules to easily stick onto pipe walls and cluster together. Turbulent flow regime, on the other hand tends to reduce the wax deposition from occurring as it disrupts the adhering and growing of wax deposits. However, mostly wax crystals in this flow regime tend to be hard in nature and capable of depositing on pipeline walls (Towler *et al.*, 2011).

2.4.4 Other proposed mechanisms

Other deposition mechanisms have been proposed as well but are not found to have a major significant effect on wax deposition. Such is the Brownian diffusion mechanism. It also encompasses the Fick's Law where by, the precipitated wax crystals would collide with other thermally agitated oil molecules. Another mechanism called the gravity settling where gravity influences wax deposition due to the density difference between precipitated waxy crystals and oil phase. However, Burger *et al*. (1981) have showed that settling velocities of wax crystals under typical conditions do not contribute significantly to deposition. This was supported with experimental evidence which shows that deposition under horizontal and vertical flow is identical within the limits of experimental error. The contribution of gravity deposition and Brownian diffusion is typically negligible for most research cases at the moment (Correra *et al.*, 2006; Kjøraas, 2012, p. 7)

2.4.5 Wax aging

The gel hardening phenomenon is known as aging. A gel behaves as a porous medium in which wax molecules continue to diffuse through due to radial variation in temperature. This effect is due to the counter diffusion of n-paraffin molecules having a carbon number lower than the critical carbon number (CCN) outer gel layer. Thus, light n-paraffin components diffuse from liquid phase of the gel deposit to the bulk oil, while the heavy n-paraffin components diffusion from the bulk oil into the gel deposit. The wax content of the deposited gel increases with time (Paso & Folger, 2003; Singh *et al.*, 2000).

It was found that wax content to be a strong function of aging time and temperature difference across it. This was validated through a flow loop experimental data (Singh *et al.*, 2000). Oddly it was also found that an increase in the wall temperature or flow rate results in a decrease in the gel thickness and consequently an increase in the rate of wax content aging of the gel.

2.5 Chemical methods

It is understood that wax inhibitors have certain combination of mechanisms involving nucleation, co-crystallization and adsorption which contributes to the process of wax crystallization (Behbahani *et al.,* 2011). Though, the deviations from expected crystallization can be easily influence the presence of other components such as aromatics, asphaltenes, resins, water, additives, modifiers, PPDs and shorter-chained n-paraffins. This deviation particularly interests us as the change in wax morphology affects the cloud point, pour point, fluid viscosity, fluid rheology behaviour, and gel strength of the wax crystals. Over the years, extensively used wax modifiers that were studied can be summarized as the following: highly branched poly-α-olefins, ethylene-vinyl copolymers, alkyl esters of unsaturated carboxylic acid-α-olefin copolymers, ethylene-vinyl fatty acid ester copolymers, long-chain fatty acid amides and poly n-alkyl acrylates and methacrylate copolymers (Machado & Lucas, 2002).

Basically, there are three groups of chemicals used to resolve wax deposition issues which are wax crystal modifier, detergents and dispersants. A molecular structure of a wax crystal modifier consists of a hydrophobic chain that interacts with the paraffin molecules and a polar moiety which is responsible for modifying the wax crystals morphology (Machado *et al.*, 2001). They are capable of altering the growth and surface characteristics of the crystals thereby reducing the tendency of the crystals to stick to metal surfaces such as pipe walls and lowering pour point and viscosity (Pederson and Rønningsen, 2003). There are many different observations reported on the performance of these wax inhibitors such as large or small crystals form, aggregate structures, and the presence of asphaltenes hindering the ability of the PPD to perform its aggregation (Tinsley *et al*., 2009). Malcolm (2009) classified PPDs into ethylene polymers and copolymers, comb polymers, and miscellaneous branched polymers with long alkyl groups. These classes of polymer have slightly different characteristics of inhibiting the wax but they similarly function to aggregate and modify the crystal structure. It is important to keep in mind that PPDs are formulated into products with active polymers contained in a solvent. The amount of polymer that can dissolve in a solution is still dependent on the thermodynamic phase behaviour of the polymer solution such as the temperature and pressure effect. Wax modifiers do not however, stop the precipitation from happening but creates a temporary kinetic barrier to precipitation that delays the precipitation mechanism from forming irreversible harden wax, allowing these wax aggregates to be swept away in the oil production stream flow in time (Tinsley *et al.*, 2009).

Detergents and dispersants on the other hand, are surface-active agents known as surfactants that keep the wax crystals dispersed to reduce the interaction between the solid surfaces. Surfactants also known as wetting agents can be classified into cationic, anionic and non-ionic surfactants. Despite having similarity in chemical structure with PPD, wax dispersants are known to have higher polar functional group that defines its surfactant character (El-Gamal, Khidr & Ghuiba, 1998). Not much studies has been carried out to define the role of wax dispersants on wax crystals but it is generally known that they function by coating wax crystals structure to prevent wax crystal growth by altering the wetting characteristics of the paraffin wax to minimize the wax adhesion onto pipeline walls or other wax crystals (Bai & Bai, 2005).

2.5.1 Past studies using wax crystal modifier EVA

In this research, the EVA copolymer is used to inhibit the crude oil. An EVA polymer typically aggregates wax precipitate from a solution at low temperature. They are able to reduce the cloud point, viscosity and pour point of Brazilian crude oils by modifying crystals and forming weak aggregates with the wax. It was also tested on five different Iranian crude oils of varying densities, viscosities, asphaltenes content and wax content and it was proven to be effective an effective PPD. This ability is aided by the presence of the vinyl acetate functional group contained in the copolymer (Machado *et al*., 2001). EVAs containing between 20 wt. % to 30 wt. % of vinyl acetate is an optimum range in reducing viscosity. On the other hand, the concentration of the additive will also affect the viscosity and pour point of crude oil (Machado *et al*., 2001). Their study reveals adding too many EVA additives will also potential negate its effect to modify wax crystals by providing additional nucleation sites for the wax caused by the precipitation of copolymer especially EVAs with low vinyl acetate content. On contrary, EVA is proven ineffective on crude oil containing aromatic compounds and asphaltenes (Machado *et al*., 2001).

It is also important to keep in mind that PPDs are formulated into products with active polymers contained in a solvent to prevent the gelation of the wax inhibitor in cold climate. Amongst the solvents that are found to be soluble with EVA are cyclohexane, chloroform, and toluene.

Table 2-2: Intrinsic viscosity for several systems EVA/solvent by Brandrup and Immergut (1999).

Solvent	Solubility parameter of the solvent $(cal/cm^3)^{½}$	EVA 20	EVA 30
Cyclohexane	8.2	0.83	0.61
Toluene	8.9	1.31	0.67
Chloroform	9.3	1.09	0.86

Although the solubility profile (Brandrup & Immergut, 1999) shows that chloroform has the best solubility parameter with EVA, Behbahani *et al*. (2011) have proven that cyclohexane despite its lower solubility with EVA, has proven to improve the rheological behaviour in Iranian crude oil compared to toluene-EVA and chloroform-EVA.

2.5.2 Past studies of wax crystal modifier enhances by the presence of wax dispersant

In this study, DEA a water-soluble additive is used as a wax dispersant. Studies have shown that the efficiency of wax dispersants blended together with EVA was more significant than EVA or wax dispersant alone (Marie *et al.* 2004). Wax crystal modifier were used to aggregate and improve the flow of the crude oil whereas the wax dispersant functions by reducing the crystals size and improve that stability of the suspensions of wax crystals within the bulk fluid. It was found that EVA alone was capable of reducing the crystal size as small as 20 μm depositing harder deposits. Further addition of wax dispersant reduces the size to as low as 5 μm (El-Gamal, Khidr & Ghuiba, 1998). The mechanism of the EVA is to inhibit into the wax crystals while the wax dispersant were absorbed at the surface of the crystals (Marie *et al.* 2004).

2.6 Methods experimental analysis

In the wax deposition studies, chemical inhibition is still one of the most sought after strategy currently being researched. In order to test the effectiveness of new PPD, studies are being done on a laboratory scale first. Pour point, viscosity and cloud point were being used to validate the effectiveness of PPD (Tinsley *et al.*, 2009; Behbahani *et al.*, 2011).

Aside from that, another method called the cold finger method is one of the still most commonly used methods of determining wax deposition tendency. Although there are many variation configuration of this device, the most often used versions involve a stationary cold finger. Cross-references between heat and diffusion models were made to correlate the relationship between cold finger testing and deposition in flow lines (Weispfennig, 2001). With minimized errors, there is an advantage of using cold finger to accurately predict the extent and type of deposit likely to occur in a system (Becker, 2001).

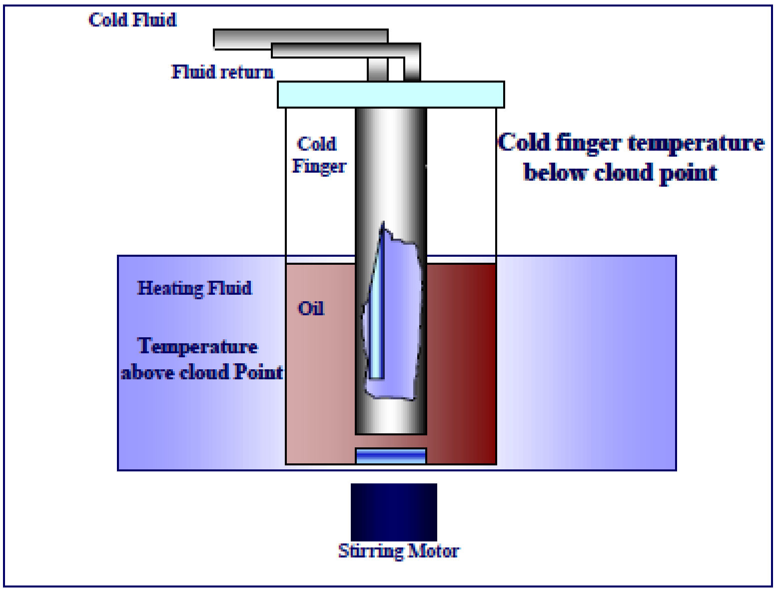


Figure 2- 6: Illustration of cold finger device by Becker (2001).

However, oilfield engineers much prefer real-world experience to reflect the actual situation happening within the pipelines through the flow loop method. The flow loop can analyse the drag reduction and bulk flow properties. However the cost also escalates with the complexity of the flow loop and the raw material needed to run the experiment (Becker, 2001). In this research, the cold finger method is chosen to screen for the effect of wax inhibitor blend has on wax deposition.

2.6.1 Past studies using cold finger method

Studies using cold finger method have been performed on Brazilian, Nigerian and Mexican crude oils to screen potential PPDs. Successful studies has been carried out on evaluating wax inhibitors and even further in depth thermodynamic studies was performed in order to obtain wax diffusivity from experimental cold finger method (Correra *et al.*, 2003).

Table 2-3: Summary on past studies using the cold finger method.

Description	Crude oil	Reference
Increasing shear rates increases wax concentration and decreases amount of wax. Shear rate also has an effect on enhancing the performance of wax inhibitors.	Mexican crude oil	Jennings and Weispfennig (2006)
Measures the critical difference temperature and critical time deposition occurs on crude oil with different API. The critical difference temperature is important as wax deposits will not form on the pipe walls below critical temperature.	Brazilian crude oil	Santos *et al*. (2004)
Optimize the use of solvent to dissolve polymer and methods of injection	Mexican crude oil	Jennings and Weispfennig (2010)
Constructing a procedure to experimentally predict the overall diffusivity coefficient of waxes into oil	Unmentioned	Correra *et al.*, (2006)

It is still a common technique applied in laboratory scale that has an economical advantage compared to the flow loop analysis in PPD screening, and also evaluation of wax deposition mechanisms.

2.7 Summary

This chapter presents the mechanisms that influences wax deposition and also the past studies carried out to overcome the challenges of transportation of crude oil. Several mechanisms were being discussed and found that the molecular diffusion and shear dispersion to be one of the main contributing factors that leads to wax deposition. However, Singh *et al.* (2001) has pointed out that there seem to be aging phenomena that is driven by counter diffusion happening between the LMWH with HMWH. This phenomenon is responsible for altering the strength of the gel which can be a bothersome issue to wax deposition within pipelines. Aside from that, the knowledge imparted by these past researches have been sufficiently useful to aid in understanding the complexity behind the thermodynamic and hydrodynamics of crude oil. Various studies were also carried out on wax inhibitors to understand their mechanism of inhibition. It was found that, wax crystal modifiers general play the role of inhibiting the wax structure leaving the polar moiety end to create steric hindrance. The presence of wax dispersant on the other hand is absorbed onto the surface of the wax crystal creating a barrier that prevents the interaction between wax crystals.

3 MATERIALS AND METHODS

3.1 *Overview*

This chapter presents the experimental methodologies conducted using cold finger method. The crude oil was characterized to determine the pour point, WAT, and rheology behaviour. The performance of the wax inhibitor blends were evaluated using cold finger method equipped with an agitator.

3.2 *Introduction*

In this research, the cold finger experiment was used to evaluate the performance of the wax inhibitor blends on wax deposition. EVA and DEA were used as wax crystal modifier and wax dispersant respectively. Although the cold finger experiment is not a direct representation of the actual situation happening inside the pipeline, it however reflects the qualitative effects that crude oil inhibits within the pipeline as earlier discuss under Chapter 2.

The cold finger temperature represents the pipeline walls exposed to subsea temperatures. The rotational speed of the stirrer reflects the flow regime in terms of shear rate. Both of these studies have been performed by Azevedo and Teixeira (2003). Their study has provided valuable information to the effects of wax deposition. In their study, they highlighted that shear does not lead to wax deposition without the effect of molecular diffusion but it contributes to the amount of wax deposited on pipeline walls. Singh *et al*. (2001) believe that aging to have significant effect on the gelation strength of wax deposits. Aging is found to be affected by the residence time and also the shear forces applied on the hydrocarbon distribution. In this study, the experiment was conducted to evaluate the performances wax inhibitor blend EVA and DEA to obtain the optimum blend ratio. The response variable of this study will be the mass and the nature of the gelation of the wax on the cold finger.

3.3 *Chemicals*

Poly (ethylene-co-vinyl acetate) (vinyl acetate 25 wt. %, melt index 19g/10 min), diethanolamine (DEA) (purity 98%), cyclohexane (purity 99.5%), toluene (purity 99.8%), acetone (purity 99.5%), and petroleum ether were obtained from Sigma Aldrich. Raw crude oil was kindly supplied by Petronas Refinery in Kertih.

3.4 Equipment

The following are the equipment used during the duration this study was conducted.

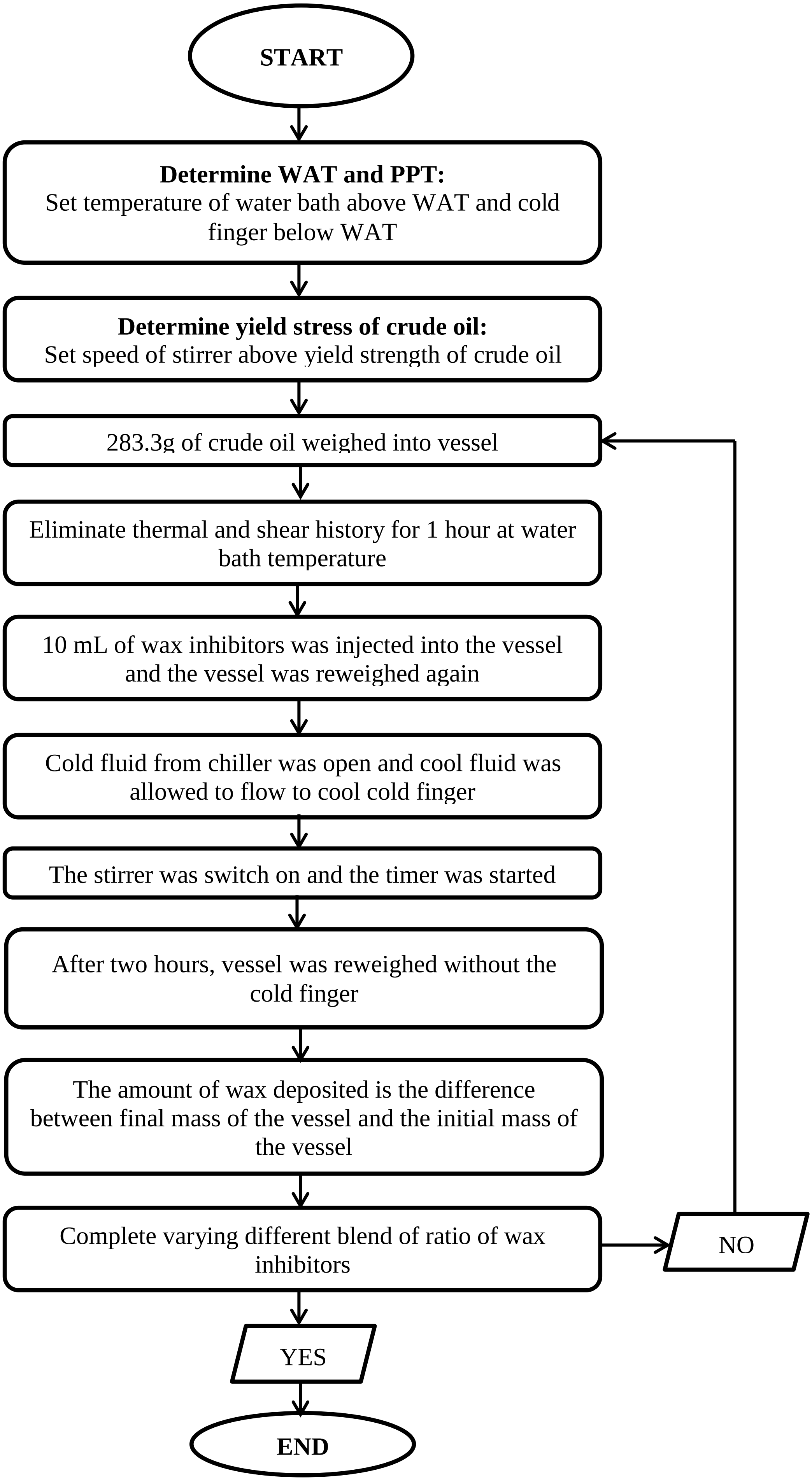
Table 3-1 Summary of a list of equipments used in this research.

Equipment	Usage
Differential Scanning Calorimeter (DSC)	To determine the WAT of the crude oil sample.
K46100 Cloud Point and Pour Point Apparatus	To determine the pour point of the crude oil sample.
Brookfield Rotational Digital Rheometer Model LV/DV-III	To determine the rheology behaviour of crude oil sample.
Cold finger deposition test	To evaluate the performances of wax inhibitors on wax deposition

3.5 Experimental preparation and procedure

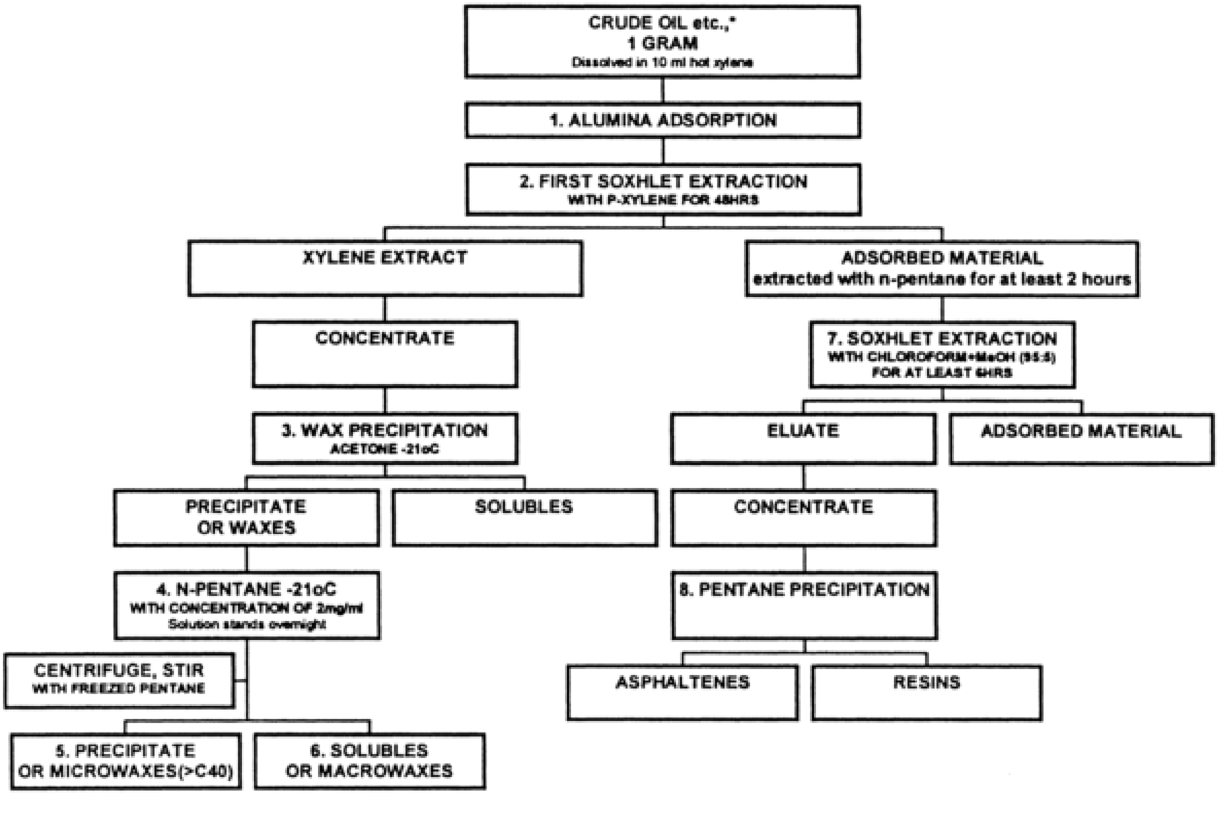
Laboratory testing with crude oil requires some preliminary preparation of the oil sample in order to ensure accuracy of the experimental data. This preparation includes producing a homogenous oil sample used for testing. Generally, most crude oil tests requires oil to be heated to a high temperature and stirred during the heating period in order to eliminate shear and thermal stress to product a homogenous fluid. This can be accomplished by heating the crude oil at 80 °C for an hour prior to testing time. The sample can be heated using an oven or a heating water bath.

A pour point test requires the test sample to be heated to eliminate thermal and shear stress before being allowed to sit at room temperature for a minimum 24 hours as part of the preliminary preparation for ASTM D-97 standard for pour point determination. The following illustrates the process flow diagram of the methodology to be conducted in this study.


START
Determine WAT and PPT:
Set temperature of water bath above WAT and cold finger below WAT
Determine yield stress of crude oil:
Set speed of stirrer above yield strength of crude oil
283.3g of crude oil weighed into vessel
Eliminate thermal and shear history for 1 hour at water bath temperature
10 mL of wax inhibitors was injected into the vessel and the vessel was reweighed again
Cold fluid from chiller was open and cool fluid was allowed to flow to cool cold finger
The stirrer was switch on and the timer was started
After two hours, vessel was reweighed without the cold finger
The amount of wax deposited is the difference between final mass of the vessel and the initial mass of the vessel
Complete varying different blend of ratio of wax inhibitors
NO
YES
END

3.5.1 *Wax content analysis*

Wax content analysis was used to evaluate the amount of wax content contain inside the crude oil sample. In order to separate the paraffin waxes from the crude oil, UOP Method 46-64 was used. However, this method is not suited as the procedure of using fuller’s earth clarification step tends to removes certain portions of the waxy materials that are potentially deposited a pipeline. Thus a modified UOP Method 46-64 done by Burger *et al*. (1981) was adopted to determine wax crystals content for this research. Figure 3-1 shows a general idea how crude oil is separated generally.



* Crude oil, n-pentane asphaltenes, extracts, etc.

Figure 3- 1: Proposed scheme for the qualitative and quantitative separation of asphaltenes, micro- and macrocrystalline waxes by Thanh *et al*. (1999).

In modified UOP 46-64, acetone precipitation technique is used to characterise the wax content in crude oil samples instead. 5 g of sample was weighed into a tared bottle. About 35 cm³ of petroleum ether was added into the tared bottle and stirred with a rod until the sample is dissolved. 110 cm³ of acetone was then added into the tared bottle and stirred again. The sample was then stored at a cool place at -20 °C and allowed to stay for 2 hours. A Buchner porcelain filtering funnel, Whatman No. 934 glass fibre filters, vacuum flask, and a mixture of 3:1 acetone-ether solution were also pre-cooled to -20 °C. A filter was wetted with a cold solvent mixture to allow to sit in the filter funnel. The sample was filtered by pouring slowly into the funnel, using the stirring rod as a guide. The stirring rod, bottle, and filter cake was washed with cold solvent mixture. The vacuum was disconnected, and the filter was removed using forceps and place in the original tared bottle. The wax crystals on the filter funnel and the stirring rod were washed into the bottle with toluene. The toluene was then evaporated to dryness at 100 ˚C. The bottle was reweighed. The difference between the initial tared bottle and the final tared bottle is the weight of the wax crystals contained in the original 5 g sample.

3.5.2 Determination of cloud point and pour point temperature

DSC is used to determine the cloud point of the crude oil sample. The temperature at which heat is released by the phase change from liquid to solid can be reflected as the WAT of the crude oil. Calibration and heat flow is carried out using the melting high purity metal indium. Dry N_2 gas is purged through the DSC cell, and the cooling is accomplished with a liquid-nitrogen cooling accessory. The crude oil is pre-heated at 80 °C for an hour to eliminate any shear or thermal history. About 3-5 mg of crude oil is put into an aluminium crucible, which is then sealed and weighed. The crucible is then heated to 80 °C and kept at that temperature for about 1 minute to ensure the temperature in the system is at equilibrium. The DSC is then set to start at 80 °C to -30 °C with a cooling rate of 5 °C/min.

The pour point of the crude oil is determined using ASTM D-97 standard method. The crude oil is place inside a pour point test jar, equipped with a thermometer and a cork. The test jar is allowed to stand vertically and cooled using K46100 Cloud Point & Pour Point Apparatus.

Figure 3- 2: K46100 Cloud Point & Pour Point Apparatus.

The test jar was tilted 90 ° from its vertical stand for 5 seconds every time the bulk fluid temperature drops by 3 °C to determine if the sample is capable of moving (pouring). The pour point is determined as the lowest temperature the crude oil sample does no flow when cooled statically.

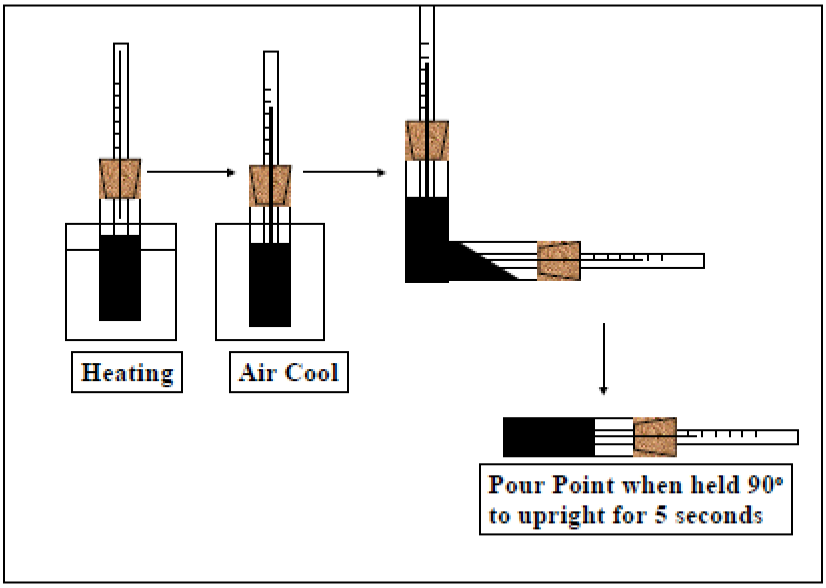


Figure 3- 3: Illustration of a pour point test procedure by Becker (2001).

3.5.3 Rheology measurements

The rheology behaviour of the crude oil is determined using Brookfield Rotational Digital Rheometer Model LV/DV-III. The machine is attached to a water bath thermostat. Spindle 31 is selected and 9 mL of sample crude oil is used to obtain the viscosity readings from the crude oil sample.

The sample was first preheated in an oven for an hour to eliminate thermal and shear history before running inside the Rheometer. The reading is taken from the highest temperature at 80 °C to 30 °C at different rotation speeds at 50 rpm, 100 rpm, 150 rpm, 200 rpm, and 250 rpm.

3.5.4 Preparation of EVA-Solvent

Polymeric inhibitors normally requires the present of solvent to enhance its ability to inhibit and thermodynamically retain its soluble nature. In this study, cyclohexane was used as EVA's solvent. The cyclohexane solvent is heated up to 60 °C using direct heating. EVA is then dissolved inside the solvent. A glass rod is used to stir the solution until it is mixed homogeneously (Qian *et al*., 1997). The solution was heated for at least one hour to ensure complete dissociation of EVA.

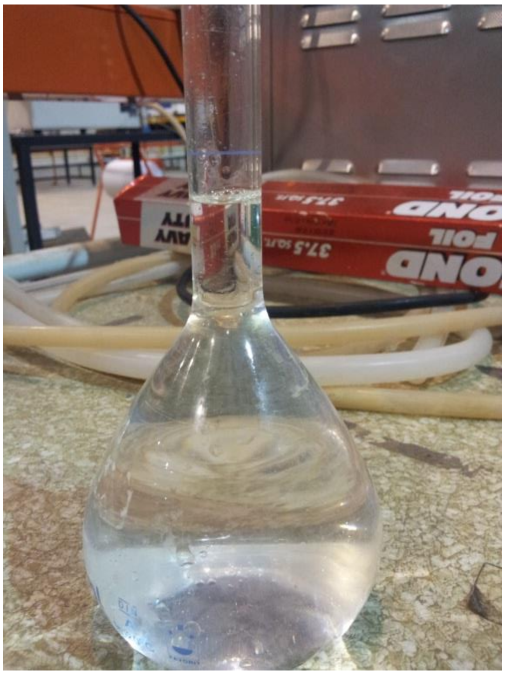


Figure 3- 4: EVA-cyclohexane feedstock solution.

3.5.5 *Cold finger deposition test*

Cold finger method experiments are conducted by immersing vessels containing crude oil samples into a hot water bath of a pre-defined fixed temperature above WAT. Cool water is allowed to flow inside the cold finger at a set temperature to replicate the condition in subsea pipeline walls. Due to the differential temperature in the bulk fluid, wax deposition would occur on the cold finger. About 283.3g equivalent to 300 mL of crude oil was used for each experiment.

Figure 3- 5: Cold finger equipment.

The crude oil samples stored in vessels are weighed to obtain initial weight and are conditioned inside the heating bath and heated up above WAT for an hour in order to eliminate the influence of thermal history. While waiting for the sample vessel to reach up to the water bath temperature, the rotational speed of the stirrer is adjusted to a fixed speed and 10 mL of wax inhibitor blend was injected into the vessel. Cold fluid valves were opened to allow cold fluid to flow and cool the cold finger. The cold finger is then immersed into the sample vessel. The time is taken from the moment the cold fluid valves were left to open until the set residence time (Jennings & Weispfennig, 2005).

The cold finger temperature was allowed to remain at 10 ˚C. The rotational speed of the stirrer was set at 200 rpm. The residence time the experiment was set to run for two hours.

3.5.6 Wax deposition measurement

The responding data measured in this study is the mass of the wax deposited on the cold finger. The remaining deposited wax will then be remove by heating the cold finger in a beaker and then washed with hot cyclohexane to clean the cold finger for the next experiment.

The sample vessels that had already cause wax deposition will be weighed again with a final mass. The difference between the initial and final mass of the vessel represents the amount of wax deposited on the cold finger (Zhang *et al*., 2010).

3.6 Summary

This chapter presents the methodologies carried out to perform this research. The cold finger method is used to evaluate the performance of wax inhibitor blend on wax deposition. The wax is first hence characterized to determine the WAT, PPT and amount of wax content before running the cold finger experiment. The responding data is the mass of wax deposited on cold finger.

4 RESULT AND DISCUSSION

4.1 Overview

This chapter presents the results and discussion on the experiment carried out for this research. Wax characterization to determine the WAT, PPT and amount of wax content through DSC, ASTM D 97 and modified UOP 46-64 standard method was carried out respectively. In addition, the viscosity of the crude oil was measured using Brookfield Rotational Digital Rheometer Model LV/DV-III. The performance of wax inhibitor blend was evaluated using cold finger method. The result show that a blend between EVA and DEA has the best performance in paraffinic inhibition efficiency compared to each of the wax inhibitors EVA and DEA alone.

4.2 Introduction

The WAT, PPT and amount of wax content were determined using standard methods mentioned in Chapter 3. The procedure was followed closely and ensured that thermal and shear history does not affect the accuracy of the data collected. Each run was repeated at least twice and the average value is obtained.

4.3 Wax characterisation

The amount of wax content was determined by precipitating the wax crystals from the untreated crude oil sample using modified UOP Method 46-64 (Burger *et al.,* 1981). The initial weight of the sample was measured at 5 g of untreated crude oil sample. When measured, about 0.69 g of solid precipitated from the crude oil sample. Thus, the untreated crude oil sample consists of 13.4 wt. % of wax content.

$$\frac{Initial\ mass - Final\ mass}{Initial\ mass} x\ 100\% = Amount\ of\ wax\ content\ (wt.\%) \qquad (4.1)$$

Table 4-1: Physico-chemical properties of untreated crude oil sample.

Physiochemical properties	Standard Test Method	Value
WAT	DSC	33 °C
Pour point	ASTM D-97	2 °C
Wax content (wt. %)	Modified UOP 46-64	13.4

Table 4-1 shows the summary result of the wax characterization carried out. It was found that the WAT of untreated crude oil is at 33 ºC and the PPT of the crude oil is at 2 ºC. The untreated crude oil sample was found to contain 13.5 wt. % amount of wax content.

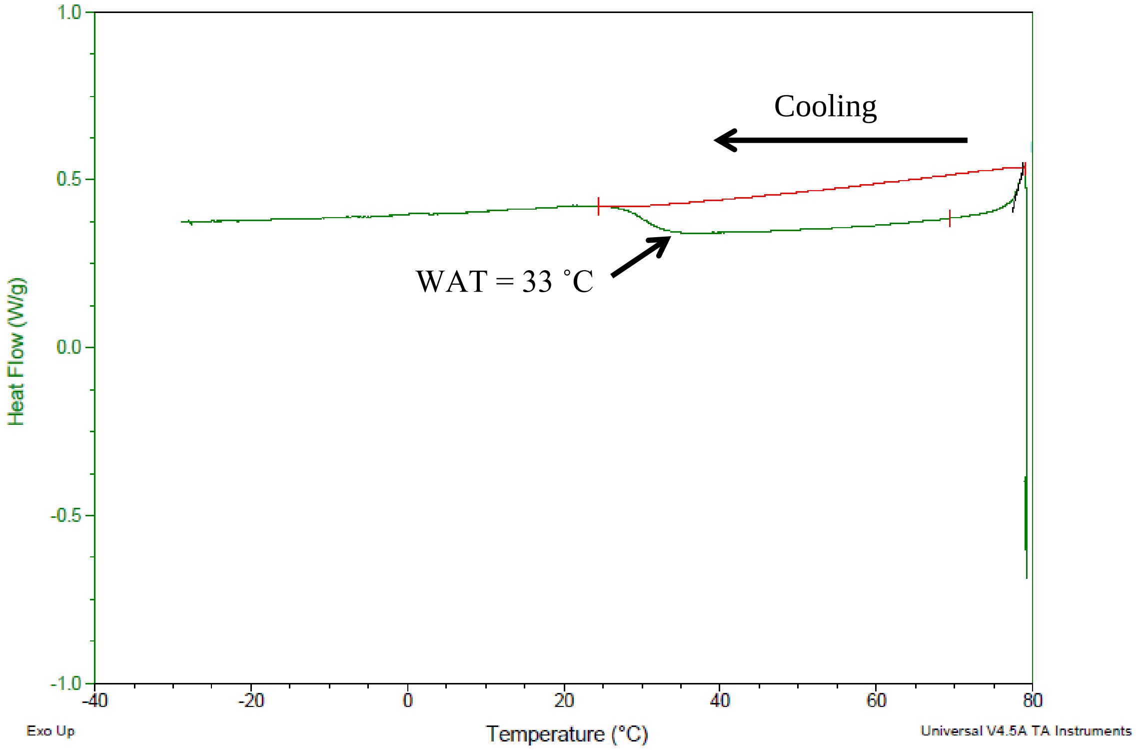


Figure 4- 1: Result obtained from DSC on untreated crude oil.

In Figure 4-1, shows the DSC result when the crude oil sample is being cooled from 80 ºC to -30 ºC. The WAT is determined by observing the slope at which the formation of solid expels out heat or known as exothermic energy. The highest temperature where the precipitate starts to form was chosen. In our case, the WAT happens to fall at 33 ºC. The PPT of the untreated crude oil on the other hand, using ASTM D-97 method is at 2 ºC.

4.4 Rheology behaviour of untreated crude oil

The rheology of the untreated crude oil was studied using Brookfield Rotational Digital Rheometer Model LV/DV-III. Figure 4-2 and 4-3 show the shear stress versus shear rate and apparent viscosity versus shear rate of the crude oil sample respectively. It was generally found that the untreated crude oil behaves as a non-Newtonian pseudo plastic fluid at all temperatures. A faint curve can be observed at shear rate above 51 s^{-1} for all temperature ranging between 30 ˚C to 80 ˚C in figure 4-2 and 4-3. The curve indicates the decreasing resistance to shear stress of the bulk fluid with increasing shear rate. This effect is known as shear thinning which is the property commonly describe in all crude oils. It is observed that the yield stress of the untreated crude oil decreases with increasing temperature in figure 4-3. Yield stress is the transition point between elastic solid-like and viscous liquid-like behaviour (Chang & Boger, 1998). According to the result the yield stress is affected by the shear rate. Figure 4-3 shows that the yield stress of the untreated crude oil sample is at shear rate 34 s^{-1} (100 rpm) for all range of temperatures.

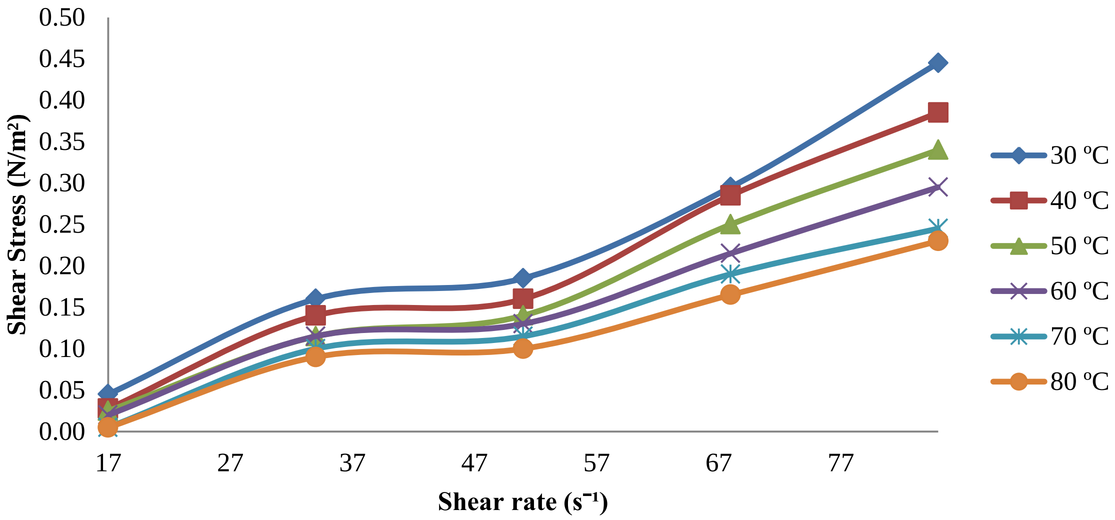


Figure 4- 2: The shear stress of untreated crude oil at different shear rate (17 s^{-1} , 34 s^{-1}, 51 s^{-1}, 68 s^{-1}, 85 s^{-1}) and temperature (30 ºC, 40 ºC, 50 ºC, 60 ºC, 70 ºC, 80 ºC).

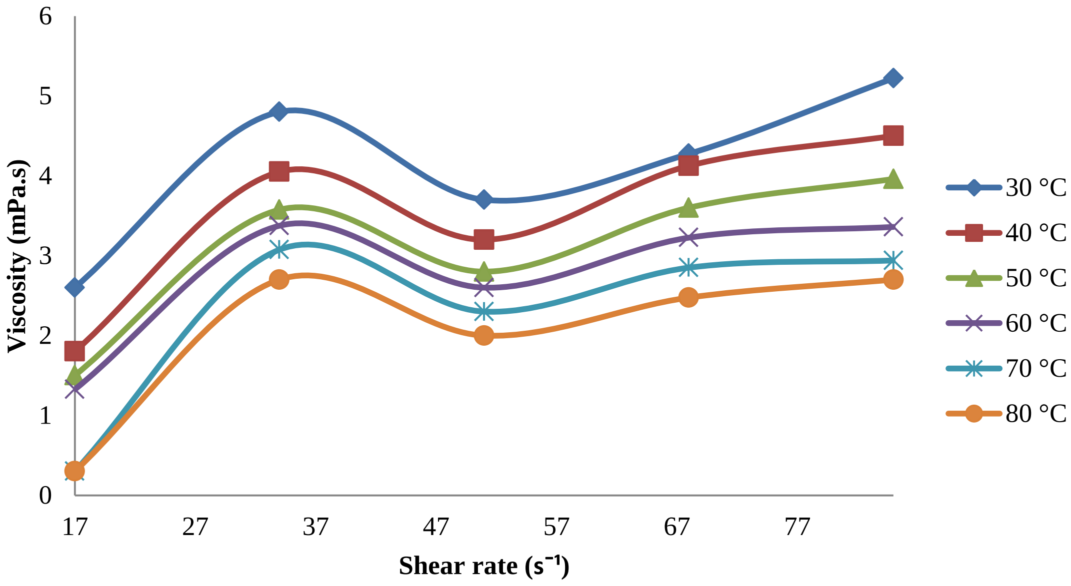


Figure 4- 3: The relative viscosity of untreated crude oil at different temperature (30 ºC, 40 ºC, 50 ºC, 60 ºC, 70 ºC, 80 ºC) and shear rate (17 s⁻¹ , 34 s⁻¹, 51 s⁻¹, 68 s⁻¹, 85 s⁻¹).

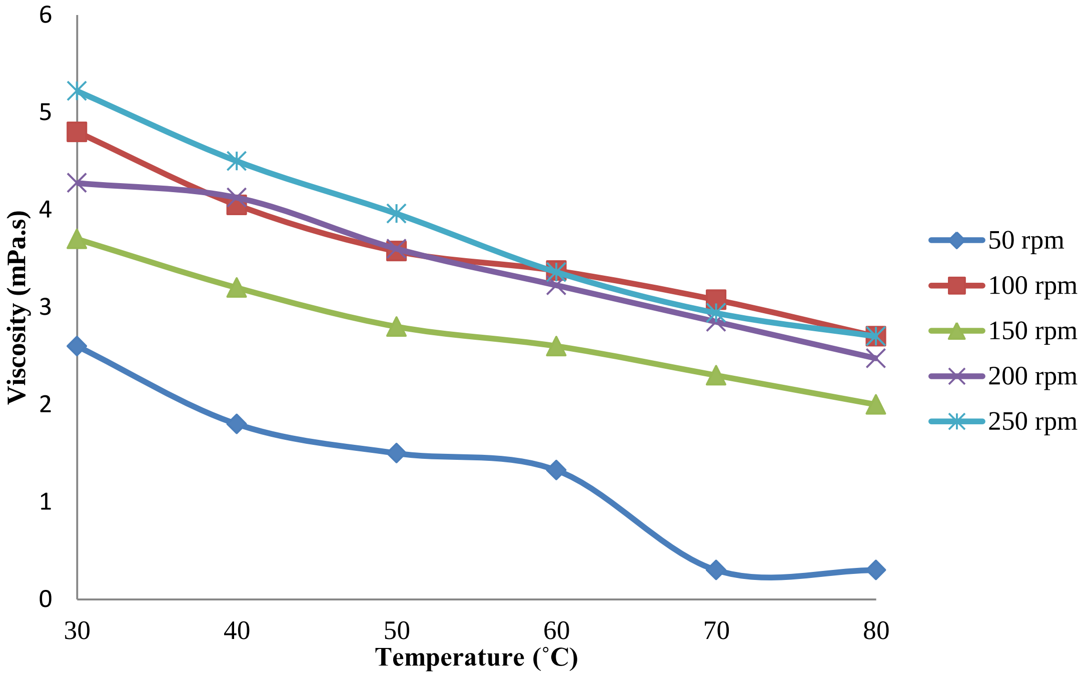


Figure 4- 4: The relative viscosity of untreated crude oil at different temperature (30 ºC, 40 ºC, 50 ºC, 60 ºC, 70 ºC, 80 ºC) and shear rate (17 s⁻¹ , 34 s⁻¹, 51 s⁻¹, 68 s⁻¹, 85 s⁻¹).

Figure 4-4 on the other hand shows the viscosity of the untreated crude oil depressed with increasing temperature. Temperature has a severe effect on the viscosity of the fluid.

4.5 Paraffin Inhibition Efficiency

The effect of combined wax inhibitor blend on wax deposition is being evaluated using cold finger method. The evaluation is being performed by determining the optimum blend ratio that gives the highest paraffinic inhibition performance. The blend prepared was done using 400 ppm of EVA-cyclohexane solution with pure DEA (98% purity). 10 mL of these wax inhibitors blend was prepared and injected at the beginning of the experiment into the cold finger equipment. The mass of both the crude oil and wax inhibitors inside the vessel were initially measured. The cold finger equipment was equipped with a stirrer running at 200 rpm to replicate the shear effect of crude oil pipeline transportation. The temperature of the cold finger and the water bath were set at 10 ˚C and 50 ˚C respectively to replicate the temperature gradient between the pipeline wall and the bulk fluid. The experiment was carried out for duration of two hours to presume the aging effect upon the wax deposited onto the cold finger. After two hours, the final mass of the remaining crude oil sample and wax inhibitors inside the vessel was measured. The difference between the initial and final mass represents the amount of wax deposited onto the cold finger. The nature of the wax deposited onto the cold finger was also observed. The wax on the cold finger was then scrapped onto a petri dish for future analysis and the remaining traces were washed off with hot cyclohexane.

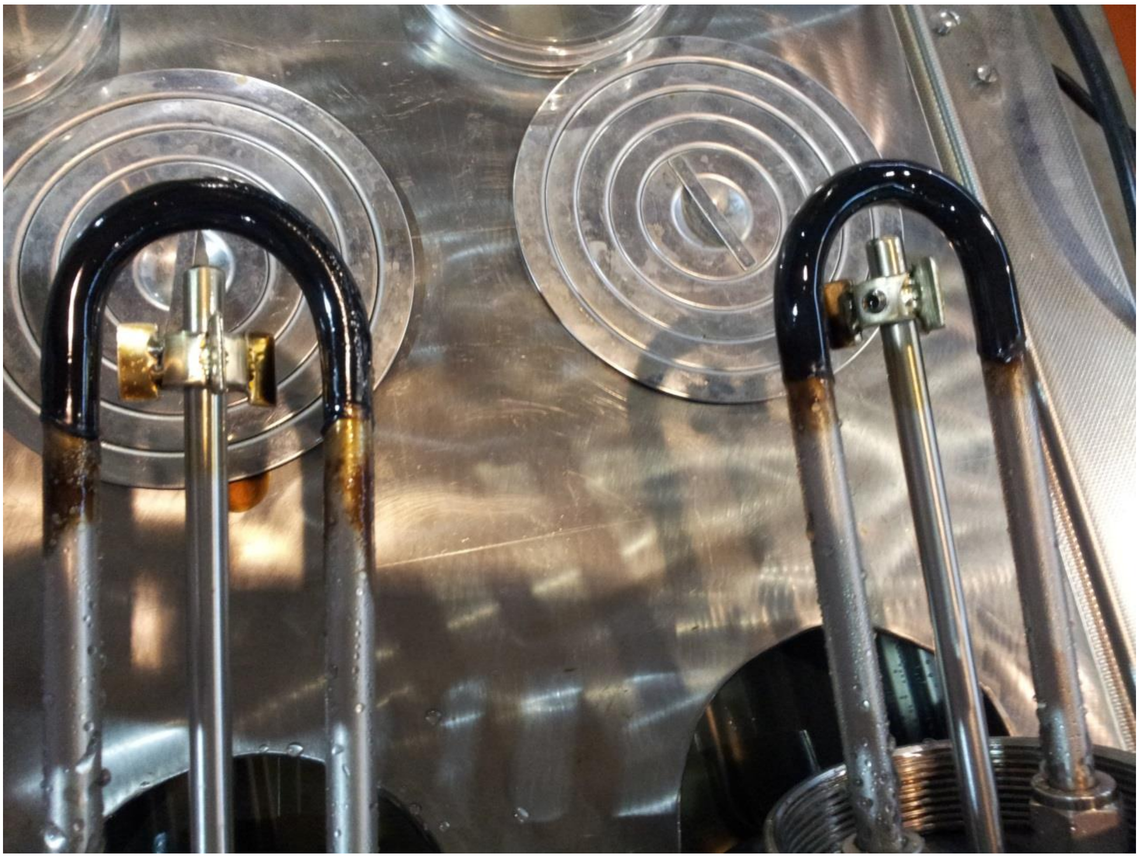


Figure 4- 5: Wax deposited onto the cold finger.

Figure 4-5 summarizes the result obtained from the paraffinic inhibition screening carried out using cold finger method. Paraffin inhibition efficiency (PIE) was calculated according to the following formula:

$$PIE(\%)=\frac{W_f - W_t}{W_f}x100 \tag{4.2}$$

where W_f is the reference amount of wax deposition without chemical treatment (g) and W_t is the amount of paraffin deposition with chemical treatment (g) (Bello *et al.*, 2006).

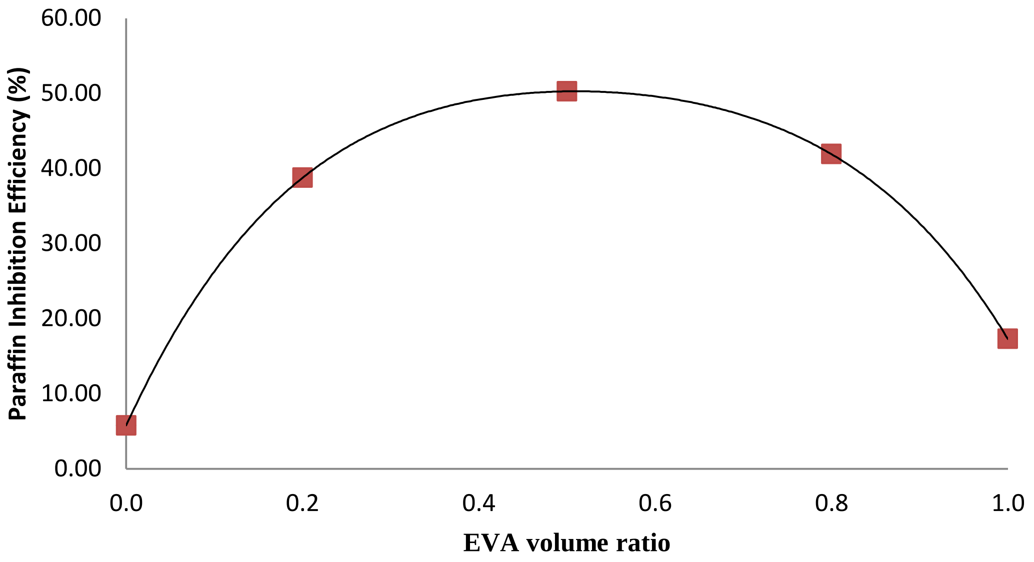


Figure 4- 6: Paraffin inhibition efficiency of EVA-DEA blend.

The result shows that wax inhibitor blend with 5 mL EVA and 5 mL DEA (1:1) volume ratio has the best performance in reducing mass of wax deposited on the cold finger with PIE value of 50.26%. The physical state of the deposited wax was soft gel like. Wax inhibitor with only pure EVA alone (10 mL EVA) has a PIE value of 17.28%. The physical state of the deposited wax was found to be hardened gel. Wax inhibitor with only pure DEA alone (10 mL DEA) on the other hand, gives a PIE value of 5.76%. The physical state of the deposited wax was found to be slightly softer than the wax deposited from pure EVA.

The mechanism of EVA copolymers although widely studied was found to be rather complex as it acts as both a nucleating agent and as a wax inhibitor depending on the solvent and paraffin solubility (Marie *et al.*, 2004). EVA is known to aggregate the structure of the paraffin wax by burying itself inside the wax crystals. Wax dispersant on the other hand is known to complement the performances of EVA by reducing the paraffinic crystal size. The role of wax dispersant is to prevent crystal aggregation by preventing the crystal nucleation phenomenon between crystal surfaces by absorbing itself on the surface of the wax crystals. From the results above, it shows that comparatively PPD are the best class amongst wax inhibitors to reduce the deposition of wax pure EVA has a higher PIE value than DEA but results to harder gelation of wax. Pure DEA although has the low PIE performance, results to softer gel structure than pure EVA. By blending EVA with DEA, the PIE of all blends shows far better result than pure wax inhibitors alone. The soft gel structure from all blend ratios implicates lower hydrocarbons that deposit onto the cold finger. This was also observed by Ahn, Wang and Shuler (2005), whereby wax that deposits from an emulsion is softer than wax deposited in the absence of any chemical. The result of their study shows that surfactants tend to form tighter emulsions that lowers interfacial tension reduces the amount of wax deposited. In the pipeline field where aging can severely result to harden gel on pipeline walls, it is desirable to have softer wax structure deposition so that high shear stress could easily break the structure and be carried away by the flow.

The test performed on the evaluation of PIE using cold finger method were found to be within p-value < 0.5 for all replicated data. Thus, cold finger method with careful handling shows promising features to carry out experimental wax inhibitor screening that is able to replicate the effects of temperature gradient, shear effect and aging on wax deposition in pipelines. It also uses lesser resources and utilities than flow loop method.

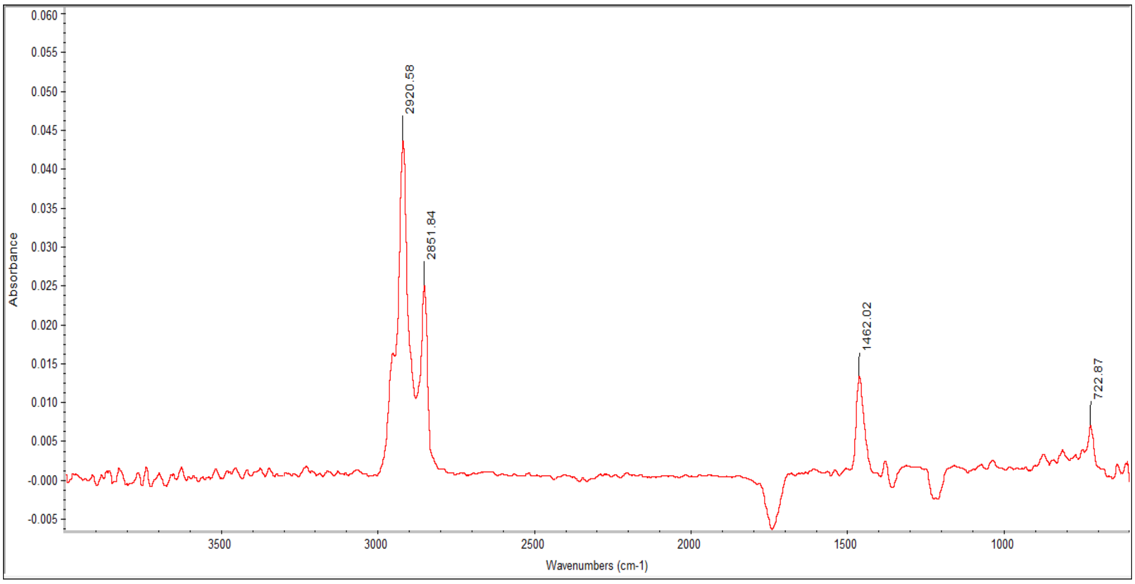


Figure 4- 7: FTIR result from wax deposited on the cold finger from untreated crude oil samples.

FTIR result of the wax deposited on the cold finger mainly consist alkanes and traces of alkenes. Wavelengths 2920.58 cm^{-1} and 2851.84 cm^{-1} indicate C-H stretches from alkane groups. Wavelength at 722.87 cm^{-1} on the other hand indicates four or more CH_2 bends detected within the alkane groups. Meanwhile wavelength at 1462.02 cm^{-1} shows the molecular motion exhibited by C-H in plane bends by the alkene groups also known as olefins. FTIR analysis for all samples of inhibited crude oil also show the same result of wavelengths implying that wax inhibition is a matter of nucleation and absorption of the wax inhibitors on the paraffin structure by modifying the interlocking capabilities rather than forming new bonds (Pederson and Rønningsen, 2003).

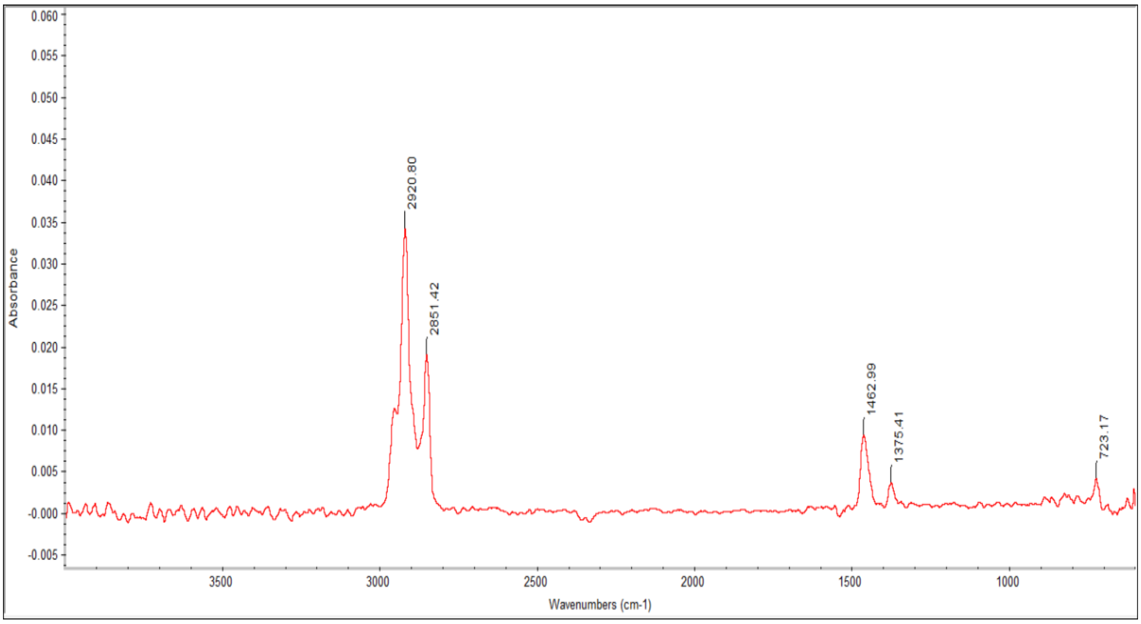


Figure 4- 8: FTIR analysis of wax inhibitor 10 mL EVA

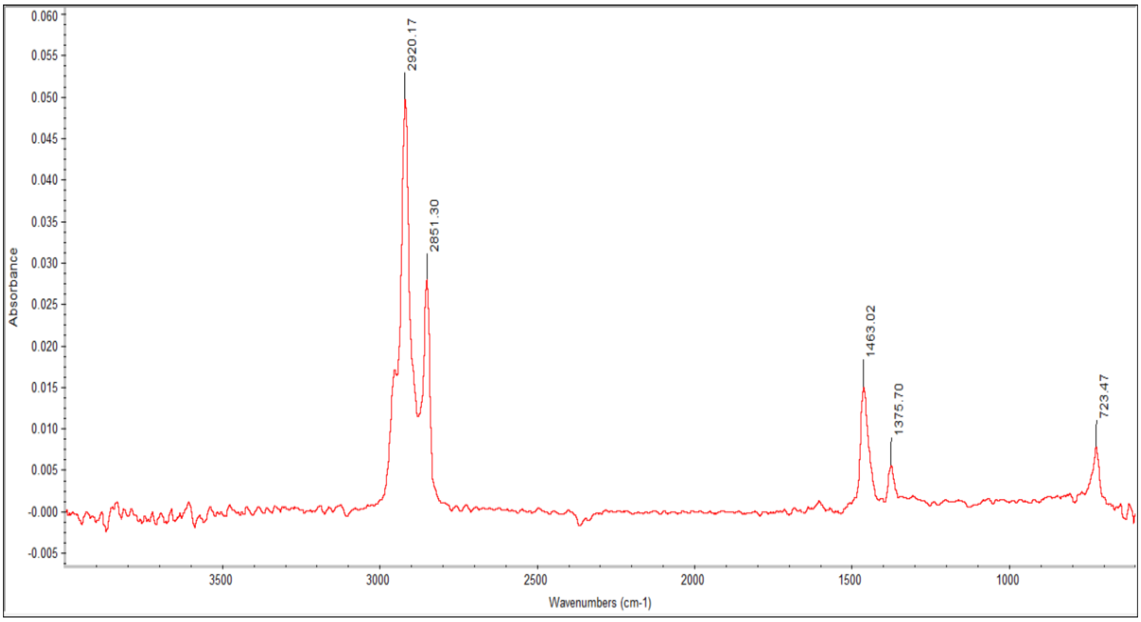


Figure 4- 9: FTIR analysis of wax inhibitor blend at EVA 8 mL and DEA 2 mL.

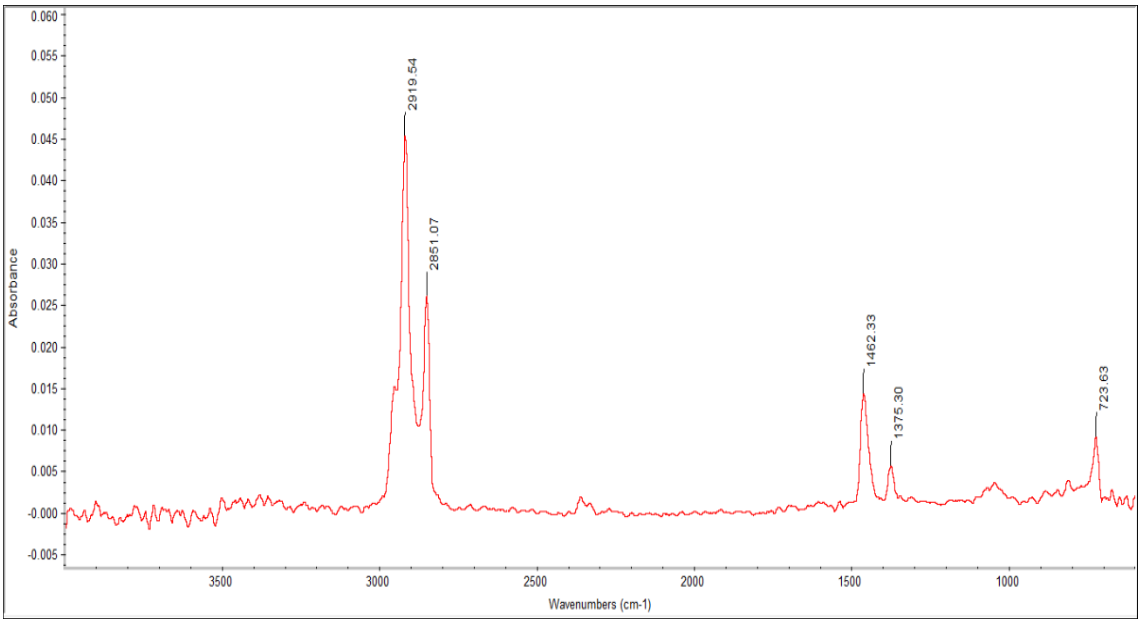


Figure 4- 10: FTIR analysis of wax inhibitor blend at EVA 5 mL and DEA 5 mL.

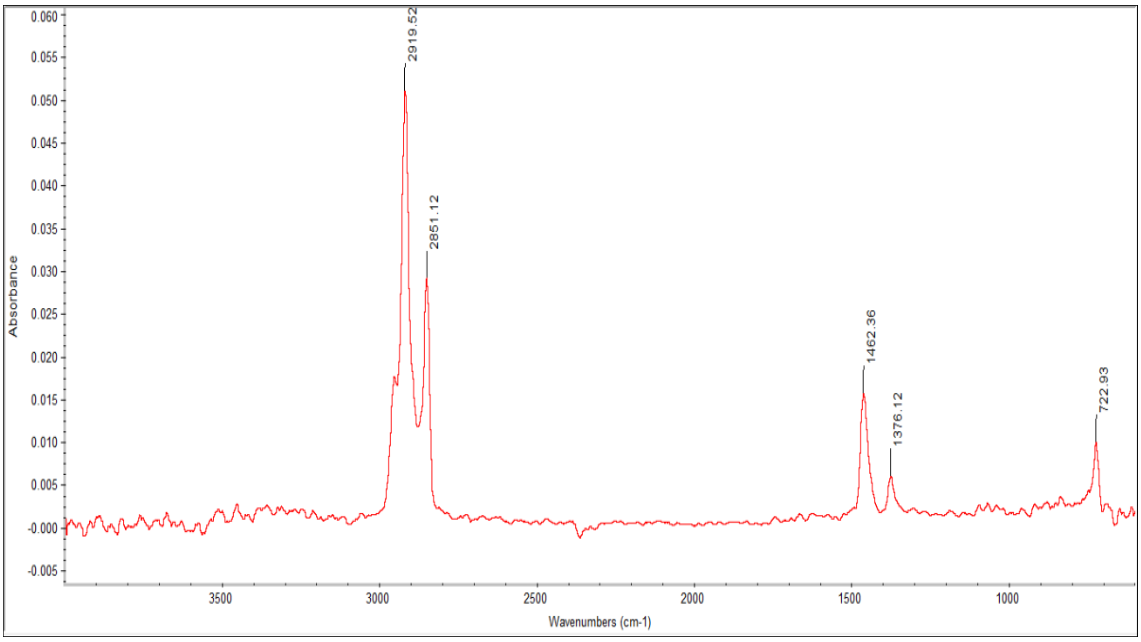


Figure 4- 11: FTIR analysis of wax inhibitor blend at EVA 2 mL and DEA 8 mL.

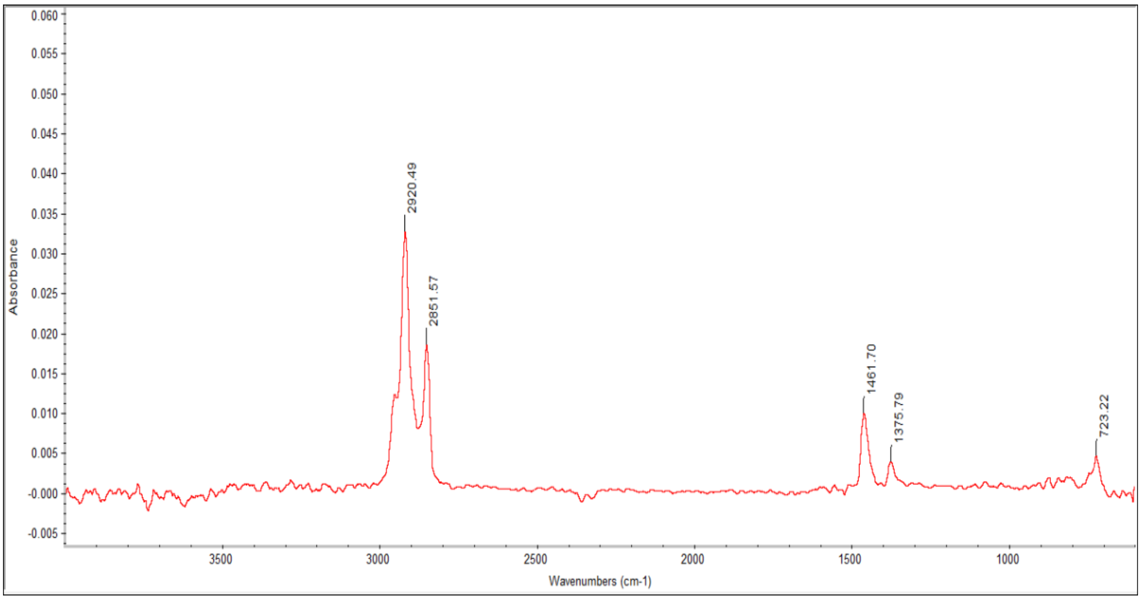


Figure 4- 12: FTIR analysis of wax inhibitor DEA 10 mL.

4.6 Summary

This chapter presents the results from the experiment carried out and the discussion done on the results obtained. The WAT, pour point, and amount of wax content were found to be at 33 ° C, 2 ° C and 13.4 wt. % respectively. The rheological behaviour of the untreated crude oil shows shear thinning properties that behaves close to pseudo plastic fluids found generally in most crude oils. Pure EVA has higher value of PIE than pure DEA. However, the blend between the two wax inhibitors shows far better results than each of wax inhibitor alone.

5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From experiment conducted on the evaluation of the performance of the wax inhibitor blends, one can conclude the EVA and DEA blend has a far better effect on reducing wax deposition than EVA or DEA alone. At volume ratio (1:1) of 10 mL wax inhibitors (EVA: DEA), the PIE is at its highest with a value of 50.26%. The wax deposited out from the inhibition of wax inhibitor of pure EVA gives a relatively hard wax texture whereas pure DEA gives a relatively soft wax texture. The EVA and DEA blend gives the softest gel structure especially at volume ratio (1:1). The soft structure suggests the wax deposited to consist of lower hydrocarbons.

Aside from that, the rheology behaviour of the crude oil shows that it behaves as a pseudo plastic fluid commonly found in most crude oil studies. This effect refers to shear thinning properties where by the resistance of the bulk fluid decreases with increasing shear rate. The viscosity of flow behaviour is influenced by the temperature and shear effect upon the crude oil sample.

The cold finger method has the ability to screen for potential wax inhibitors by evaluating the performance of the chemical additives in replicable pipeline condition. The cold finger allows the evaluation of the wax inhibitors under molecular diffusion conditions, shear dispersion conditions and aging effect on wax deposition. It also consumes lesser resources in comparison to the test flow loop.

5.2 Recommendations

Some recommendations were made for future wax deposition studies to expand the literature background on the performance of wax inhibitor blend between PPD and wax dispersant:

a. The evaluation of the performances of wax inhibitor blend by varying the parameters of the cold finger equipment in terms of differential temperature, shear rate and duration of the experiment carried out.
b. Evaluate the effects of the wax inhibitor blend on the rheology behaviour of crude oil.

c. Observe the morphology of wax crystal structure using crossed polarized microscopy (CPM) of crude oil inhibited with wax inhibitor of varying blends between PPD and wax dispersant.
d. Qualitative and quantitative analysis of the carbon distribution in the wax deposited.

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APPENDICES

A.1 Raw data from experimental runs

Table A- 1: Raw data collected from Brookfield Rheometer for first run

Temperature (°C)	**RPM**	**Viscosity (mPas)**	**Shear Stress (N/m²)**	**Shear Rate (s⁻¹)**	**Torque (%)**
30	50	2.20	0.04	17.00	0.35
30	100	4.50	0.15	34.00	1.50
30	150	3.40	0.17	51.00	1.70
30	200	4.05	0.28	68.00	2.70
30	250	4.92	0.42	85.00	4.10
40	50	1.20	0.02	17.00	0.30
40	100	3.90	0.13	34.00	1.30
40	150	3.00	0.15	51.00	1.50
40	200	3.90	0.27	68.00	2.60
40	250	4.32	0.37	85.00	3.60
50	50	1.20	0.02	17.00	0.20
50	100	3.45	0.11	34.00	1.10
50	150	2.80	0.14	51.00	1.40
50	200	3.30	0.23	68.00	2.20
50	250	3.84	0.33	85.00	3.20
60	50	0.85	0.01	17.00	0.10
60	100	3.45	0.12	34.00	1.10
60	150	2.60	0.13	51.00	1.30
60	200	3.00	0.20	68.00	1.80
60	250	3.12	0.28	85.00	2.80
70	50	0.00	0.00	17.00	0.00
70	100	3.15	0.10	34.00	1.10
70	150	2.20	0.11	51.00	1.00
70	200	2.55	0.17	68.00	1.60
70	250	2.64	0.21	85.00	2.10
80	50	0.00	0.00	17.00	0.00
80	100	2.70	0.09	34.00	0.90
80	150	2.00	0.10	51.00	1.00
80	200	2.25	0.15	68.00	1.50
80	250	2.40	0.21	85.00	2.10

Table A- 2: Raw data collected from Brookfield Rheometer for second run

Temperature (°C)	**RPM**	**Viscosity (mPas)**	**ShearStress (N/m2)**	**Shear Rate (1/s)**	**Torque (%)**
20	150	162.80	8.29	51.00	81.30
30	50	3.00	0.05	17.00	0.50
30	100	5.10	0.17	34.00	1.70
30	150	4.00	0.20	51.00	2.00
30	200	4.50	0.31	68.00	3.00
30	250	5.52	0.47	85.00	4.50
40	50	2.40	0.04	17.00	0.30
40	100	4.20	0.15	34.00	1.50
40	150	3.40	0.17	51.00	1.70
40	200	4.35	0.30	68.00	2.90
40	250	4.68	0.40	85.00	3.90
50	50	1.80	0.03	17.00	0.30
50	100	3.70	0.12	34.00	1.30
50	150	2.80	0.14	51.00	1.40
50	200	3.90	0.27	68.00	2.60
50	250	4.08	0.35	85.00	3.40
60	50	1.80	0.03	17.00	0.30
60	100	3.30	0.11	34.00	1.10
60	150	2.60	0.13	51.00	1.30
60	200	3.45	0.23	68.00	2.30
60	250	3.60	0.31	85.00	3.00
70	50	0.60	0.01	17.00	0.10
70	100	3.00	0.10	34.00	1.00
70	150	2.40	0.12	51.00	1.20
70	200	3.15	0.21	68.00	2.10
70	250	3.24	0.28	85.00	2.70
80	50	0.60	0.01	17.00	0.10
80	100	2.70	0.09	34.00	0.95
80	150	2.00	0.10	51.00	1.00
80	200	2.70	0.18	68.00	1.80
80	250	3.00	0.25	85.00	2.50

Table A- 3: Raw data on the evaluation of paraffin-inhibition efficiency

Inhibitor ratio		**Experimental runs for weight of wax deposited from crude (g)**				
EVA	**DEA**	**1**	**2**	**3**	**Average**	**PIE (wt. %)**
Untreated		6.5	6.2	6.4	6.4	0.00
0.0	1.0	6.2	6.0	5.8	6.0	5.76
0.2	0.8	3.9	3.6	4.2	3.9	38.74
0.5	0.5	3.2	3.0	3.3	3.2	50.26
0.8	0.2	3.9	3.7	3.5	3.7	41.88
1.0	0.0	5.6	5.3	4.9	5.3	17.28

A.2 Statistical analysis

A.2.1 ANOVA Two-Factor with Replication on the raw data on the rheology behaviour of untreated crude oil

SUMMARY	**Temp**	**RPM**	**Viscosity**	**Shear Stress**	**Shear Rate**	**Torque**	**Total**
1st Run							
Count	30	30	30	30	30	30	180
Sum	1650.000	4500.000	82.890	4.710	1530.000	46.150	7813.750
Average	55.000	150.000	2.763	0.157	51.000	1.538	43.410
Variance	301.724	5172.414	1.484	0.012	597.931	1.105	3804.768
2nd Run							
Count	30	30	30	30	30	30	180
Sum	1650.000	4500.000	95.570	5.330	1530.000	52.450	7833.350
Average	55.000	150.000	3.186	0.178	51.000	1.748	43.519
Variance	301.724	5172.414	1.342	0.014	597.931	1.325	3795.801
Total							
Count	60	60	60	60	60	60	
Sum	3300.000	9000.000	178.460	10.040	3060.000	98.600	
Average	55.000	150.000	2.974	0.167	51.000	1.643	
Variance	296.610	5084.746	1.435	0.013	587.797	1.206	

ANOVA

Source of Variation	***SS***	***df***	***MS***	***F***	***P-value***	***F crit***
Sample	1.067	1	1.067	0.0011	0.9741	3.8683
Columns	1008166.000	5	201633.300	199.1535	9E-100	2.2399
Interaction	2.281	5	0.456	0.0005	1	2.2399
Within	352333.2	348	1012.452			
Total	1360503.000	359				

A.2.2 ANOVA Single Factor on the raw data on the evaluation of paraffin-inhibition efficiency

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Untreated crude oil	3	19.1	6.37	0.023
EVA:DEA (0 mL: 10 mL)	3	18.0	6.00	0.040
EVA:DEA (2 mL: 8 mL)	3	11.7	3.90	0.090
EVA:DEA (5 mL: 5 mL)	3	9.5	3.17	0.023
EVA:DEA (8 mL: 2 mL)	3	11.1	3.70	0.040
EVA:DEA (10 mL: 0 mL)	3	15.8	5.27	0.123

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	26.320	5	5.264	92.890	3.62E-09	3.106
Within Groups	0.680	12	0.057			
Total	27	17				