SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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IMPACT OF POUR POINT DEPRESSANT ENHANCED WITH GRAPHENE OXIDE ON THERMAL AND MICROSTRUCTURE PROPERTIES OF SIMULATED CRUDE OIL MODEL

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation **" Impact of pour point depressant enhanced with graphene oxide on thermal and microstructure properties of simulated crude oil model"**. I also declared that it has not been previously for the award for any degree or diploma or other similar title of this for any other examining body or university.

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TABLE OF CONTENTS

Contents

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS

^{o}C	Degree Celcius
g	Gram
μm	Micrometer
%	Percentage
mV	Millivolt
r_c	Radius of critical nucleus
ΔH	Enthalpy change
T_g	Glass Transition Temperature
T_m	Melting Temperature

LIST OF ABBREVIATIONS

PPD	Pour Point Depressants
WAT	Wax Appearance Temperature
EJN	Emulsified Jaypol Normal
EJGO	Emulsified Jaypol Graphene Oxide
EJGO1	Emulsified Jaypol Graphene Oxide 1
EJGO2	Emulsified Jaypol Graphene Oxide 2
EJGO3	Emulsified Jaypol Graphene Oxide 3
EJGO4	Emulsified Jaypol Graphene Oxide 4
EJGO5	Emulsified Jaypol Graphene Oxide 5
GO	Graphene Oxide
DSC	Differential Scanning Calorimetry
POM	Polarized Optical Microscope
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
JAYPOL 658G	Acrylate Polymer
DEA	Diethylamine
MWV	Meadwestvaco
MSZW	Meta-stable zone width

KESAN AGEN TEKAN TITIK TUANG (PPD) DENGAN GALAKKAN GRAPHENE OKSIDA TERHADAP CIRI-CIRI HABA DAN MIKROSTRUKTUR KEPADA MODEL SIMULASI MINYAK MENTAH

ABSTRAK

Perbezaan saiz sisi Graphene Oksida (GO) yang direndahkan mengunakan alat sonik telah dikaji keterbandingan dengan penambahan agen tekan titik tuang (PPD) akan menambah baik kemampuan mengalir bagi model simulasi minyak mentah, GO terbahagi kepada 5 kategori, dimana berbezanya masa sonik. GO1, GO2, GO3, GO4, dan GO5 di sonikkan dengan masa yang berbeza masing-masing 0 min,10 min,30 min,60 min and 100 min. GO1 adalah sebagai sampel rujukan, sebagai penanda aras terhadap hasil kajian. Penyediaan emulsi PPD bermula dengan menyediakan larutan berasaskan air termasuk GO dan larutan berasaskan minyak, bersama kedua-dua larutan dikacau di dalam mandian air. Tambahan pula, sifat morfologi tersonik dikaji mengunakan scanning electron microscopy (SEM),dan Fourier-transform infrared (FTIR).Daripada imej SEM memaparkan pengurangan saiz sisi GO seiring dengan peningkatan masa sonik. GO yang telah disonik dikenalpasti dengan mengunakan FTIR, keputusan hasil kajian menunjukkan corak puncak adalah sama dengan sampel rujukan. Ujian kestabilan telah dijalankan salama 4 minggu, saiz zarah sampel meningkat dengan aktiviti beku cair, tetapi tidak menjejaskan kestabilan emulsi. Keupayaan zeta adalah dalam lingkungan (-50mV - -60 mV) ini menunjukkan emulsi berada dalam lingkungan yang stabil. Imej pembentukkan kristal telah dikaji. mekanisme heterogen nukleasi, keseragaman, dan bentuk batang kristal telah dilihat mengunakan Polarizing Optical Microscopy (POM),imej menunjukkan dengan kehadiran GO akan melambatkan pembentukkan lilin kristal dan kecenderungan membentuk kelihatan batang daripada bentuk mengelupas pada suhu rendah. Lebih kecil saiz GO akan mempamerkan menyebaran yang baik di

dalam simulasi minyak mentah. Untuk kajian yang lebih mendalam terhadap pembentukkan kristal, perubahan dinamik rangkaian struktur kristal telah dikaji. Kajian terma telah dijalankan mengunakan Differential Scanning Calorimetry (DSC), ianya menunjukkan corak menaik terhadap suhu kemunculan lilin (WAT) apabila hadirnya saiz sisi GO yang kecil walau bagaimanapun ianya lebih tinggi daripada sampel kosong (lilin asli) Permukaan simulasi minyak mentah telah dikaji mengunakan Scanning Electron Microscopy (SEM).Permukaan sampel kosong menunjukkan corak berombak ,ini kerana terhasilnya rangkaian struktur 3 dimensi, Bagi Emulsified Jaypol Graphene Oxide 5 (EJGO5) menunjukkan permukaan seperti kulit manusia ,dimana GO bertindak sebagai tapak nukleasi yang teredar dengan baik. Prestasi titik tuang bagi Nano-hibrid PPD telah ditambah baik jika dibandingkan dengan emulsi biasa PPD (EJN). Peningkatan corak prestasi dengan pengurangan saiz sisi GO menunjukkan saiz sisi GO adalah faktor yang mempengaruhi peningkatan prestasi titik tuang dan keupayaan mengalir bagi emulsi PPD.

IMPACT OF POUR POINT DEPRESSANT ENHANCE WITH GRAPHENE OXIDE ON THERMAL AND MICROSTRUCTURE PROPERTIES OF SIMULATED CRUDE OIL MODEL

ABSTRACT

Different lateral size of Graphene oxide (GO) reduce by sonication were comparatively investigated as additive for PPD to improve the flow ability of crude oil simulated crude oil model. The GO was divided into 5 categories ,which is different in sonication time. The GO1, GO2, GO3, GO4, GO5 were sonicated at different time which is 0 min,10 min,30 min,60 min and 100 min respectively. The GO1 will be the control sample , as a bench mark of the result. The preparation of the emulsified PPD begin with the preparation of water-based solution which include the GO and oil-based solution ,together both of the solution stirrer in the water bath. Furthermore, the morphology properties of sonicated GO were investigated using scanning electron microscopy (SEM) and, Fourier-transform infrared (FTIR) .From SEM image it seems as reduction lateral size of GO as increase the sonication time. Sonicated GO surface properties was confirmed by the FTIR results that show the same peak pattern from control sample. The stability test are conducted about 4 weeks ,the particle size of the sample increased by freeze thawed activities, but does not affect the stability of the emulsion. The zeta potential is about (-50mV - -60 mV) showing that the emulsion is in the stable range. The image of the crystal formation was studied. The heterogeneous nucleation mechanism, uniform and rod-like shape crystals were observed by polarizing optical microscopy ,the POM image showing that ,when present of GO it will delay the formation of wax crystal and tendency to form rod like instead of flake like at low temperature ,the smaller size of GO will exhibit good dispersion in the simulated crude oil. For further study on crystal formation, the dynamic changes of crystal structure network were taken apart in this

study. The thermal study was conducted using Differential Scanning Calorimetry (DSC),that shows the improving the Wax Appearance Temperature (WAT) when adding the smaller lateral size of GO but higher from the blank sample (pure paraffin wax).The surface of the simulated crude oil was study using Scanning Electron Microscopy (SEM) ,The surface of the blank sample show wavy pattern ,this due to the formation of the 3D structure network, for Emulsified Jaypol Graphene Oxide 5 (EJGO5) show the surface like a human skin ,which is GO act as well distributed nucleation site .The pour point performance of Nano-hybrid PPD was improved compared with Emulsified Normal PPD (EJN) The increasing trends of performance by reducing lateral size of GO showing that the GO lateral size is the most influenced factor that increased pour point and flow ability performance of Emulsified PPD.

Chapter 1

INTRODUCTION

1.1 Research Background

The Pour Point Depressant (PPD) is the best other alternative way have been given to the wax solidification in the oil and gas production industry stated by (Manka and Ziegler, 2001) .The precipitation of wax crystal from crude oil can cause significant issues during production, transportation and storage. The solidification of paraffin wax will form solid deposits, which reduce the cross-section of flow lines (Hassan Ali, 2012).The content of the crude oil is the other reason ,precipitation of wax , the crude oil often contains substantial amounts of paraffin wax ,which constitutes the saturated aliphatic fluid fraction .When the crude oil temperature falls beneath the wax appearance temperature (WAT) also known as cloud point ,the paraffin wax precipitate in an orthorhombic unit cell as needle or plate-like crystal (Jafari Ansaroudi *et al.*, 2013). Untreated crude oil can imparting high pour point ,high viscosity ,high yield stress ,and non-Newtonian flow behaviour to waxy crude oil .

The precipitation of paraffin waxes brings immense difficulties to the production and pipeline transportation on waxy crude oil .The paraffin wax begin to precipitate from the oil due to super-saturation ,when the temperature of waxy crude oil is below its wax appearance temperature (WAT) (Pedersen and Rønningsen, 2003). Nowadays, several methods have been develop to minimise the problems caused by wax crystal deposition

and aggregation. The prevention technique is mechanical remediation (pigging), applying heat or using hot solvent flush and the chemical inhibitor treatment such as poly(acrylate) base as pour point depressants (PPD),thermodynamic (TWI) and crystal modifiers (Yang *et al.*, 2015). Nevertheless, the chemical prevention of the wax to precipitate is more convenient . Chemical treatment is chosen to inhibit of the wax deposited since chemical treatment is more economical and more efficient compared to other methods.

Generally, pour point depressant selected in treatment the wax deposited via chemical inhibitor treatment . (Manka and Ziegler, 2001) found that , pour point depressant (PPD) are polymeric material with long hydrocarbon chains that interact with the paraffin in the crude oil and inhibit the formation of large wax crystal matrices . The co-crystallization occur between wax molecule and PPD will retards the wax crystal formation and growth, alters the paraffin's heat of crystallization and depressant the crude's pour point while affecting the size and shape of the crystal. The addition of GO will form a nucleation site and prevent it to form a large 3-dimensional structure crystal network that make improve in flow ability. The observation can clearly seen in Polarizing optical microscopy (POM) to look deep into the kinetic growth of wax crystal at certain temperature .According to (Yang *et al.*, 2015), most polymeric additives is categorized as crystalline-amorphous copolymer, ethylene-vinyl acetate copolymers and comb polymers. Hence, pour point depressant consist of polymers, which has comb structure that avoid the wax crystal growth on pipeline wall .

Acrylate polymer such as ethylene vinyl acetate (EVA) and poly methacrylate (PMA) become preferred choice in treating wax deposition. It is because EVA is a block olefin copolymer with rubber like properties and has excellent viscosity properties

(Totten, 2003). Meanwhile, PMA is known as comb polymer family due to their comb-like structure. Comb polymer has excellent ability to act as pour point depressant since it can withstand low temperature condition, which is below 0^0C (Totten, 2003).

Most of the conventional polymeric PPDs are in solution form. This limits the PPD application in at cold climates for example during winter season. This is because PPD solutions are easily solidified at low temperature. The solidification problem of PPD will ruin the treatment itself as it cannot be injected into the pipeline in solid form, other things is about mobility or the movement of the solid ,it is quite heavy to homogenous spread in the pipeline compared to solution which the PPD in emulsion system ,it is more convenient to get efficient spread of the PPD in the turbulent flow in the transportation pipeline (Becker, 1999). The costing for preheating and dilution is a prerequisite to be considered for its utilization in a crude oil industry. So, it is impractical to use the PPD solution in the cold environments.

Emulsion technology has been viewed to solve the PPD solidification at room temperature. According to (Admiral, Abdullah and Ariffin, 2016), they successfully established the emulsion PPD which could flow at room temperature. At the same time, the behaviour of emulsion such as freezing point, viscosity at room temperature, particle size and zeta potential still improved. Nevertheless, there is some issue on PPD performance during emulsion even it possesses a good thermal stability emulsion. Introduction of nano-size filler into a polymer become a well-known method to enhance the existing polymer properties (Boccaccini et.al, 2010). This polymer classification is known as polymer nanocomposites. This polymer nanocomposites concept can be employed to boost the PPD emulsion in treating the paraffin wax.

In recent year, graphene and graphene oxide become the current attention in research world. It gives positive impact toward the polymer nano composites properties. Graphene is the strongest material because of π–π stacking in chemical structure .The π–π bond is described as the non-covalent interactions, which involves in the stacking of aromatic molecules. Aromatic network of sp^2 carbon atoms makes this interaction important in graphene functionalisation.

Graphene and graphene oxide were applied in biomedical field. Graphene was used as a substrate for addition or adsorption of molecules and the functional groups in a controlled manner (Mao et.al, 2013). Covalent and non-covalent surface modifications have been performed to improve biocompatibility and colloidal stability.

In this work, graphene oxide was used to study the behaviour of nanocomposite in the PPD emulsion and improve the PPD performance. In addition, the research work on sonication graphene oxide for different lateral size of GO-PPD on wax crystal still limited. So, it is importance to gain a new generation of nano hybrid pour point depressant used in oil and gas technology application. The work study more on the wax apparent temperature (WAT),which the temperature start to form , and morphology of the crystal formation arrangement of wax using SEM .The kinetic behaviour of wax crystal formation also studied using polarized optical microscopy (POM) .

1.2 Problem Statement

Huge numbers of the world's oil endure when paraffin wax precipitates out and solidifies in formation pores and fluid flow channels, at the wellbore ,on the side walls of wells ,in the tubing ,casings ,perforations, pump strings ,rods, and the complete oil transfer system of flow lines and pipelines (Mahmoudkhani *et al.*, 2017) .Paraffin wax deposition is expensive, causing diminished of the production ,equipment failure ,bottlenecks ,loss of storage ,clogging of refinery pipework ,and loss of efficiency .It is one of the oil industry's most expensive problematic nuisances. Paraffin wax is the initial glue that causes asphaltenes ,corrosion and debris to stick ,collect and build up ,due to paraffin wax deposition ,currently there are thousands of well shut-in with no production ,numerous pipelines blocked ,transport vessels taken out of service ,tanks locked-in and refinery equipment shut down , also the expanded plausibility of failures and catastrophic event caused by build-up The alteration of crude oil is very significant to avoid or delay the deposition of paraffin wax. The PPD was applied to overcome the problem above by chemical treatment ,which is more convenient for low cost of operation.

The conventional PPD faces the solidification issue, due to the solidification at room temperature. In addition, it is difficult to deliver the high active content of polymer at low viscosity value. According to (Becker, 1999), some PPD is less efficient especially for pour point reduction. If PPD dissolve, it is quite hard to achieve high active content, hence higher dosage of PPD must be used. The imprecation is that high dosage contributes to high treatment cost. The conventional PPD consist of active content in the high range of 5-10 wt.%.

Admiral, Abdullah et al. 2016 suggested that the emulsion method can be used on PPD to solve the solidification issue. However, it still has limitations on PPD performance. It is ideal to get a PPD which can be utilized at any range of temperature. The advantage for proposing nano hybrid pour point depressant where the active content in range of 30-50 wt. % can be achieved and high molecular weight and environment friendly (reduce solvent usage) PPD can be produced. However, PPD emulsion still lacks in term of application performance even possess a good flow-ability at low temperature. Since the performance of PPD is merely dependable on the existing of polymer properties.

The performance issue can be solved by incorporating of nano size graphene oxide with emulsified PPD. It is interesting alternative when smaller lateral size of graphene oxide can boost the PPD performance subjected to inhibit the wax crystal in paraffin wax. Addition of graphene oxide in the PPD emulsion is very promising route to solve the above problem as it can produce an immense improvement in polymer properties. Graphene oxide consist of π-π interaction which is non-covalent interaction involve in the stacking of aromatic ring molecules. This interaction prevent graphene oxide aggregation through steric or electrostatic repulsion. Therefore, in this study, it is hypothesized that the lateral size of Graphene oxide (GO) will improve the PPD performance through steric or electrostatic repulsion. This repulsion force will prevent the crystal growth formation on the pipeline wall

The suitable method to achieve the smaller lateral nano-size of Graphene oxide is by sonication. The sonication promote the energy to break of the sheet of graphene oxide ,which creates shear stresses and cavitation in the solvent. This has the effect of breaking

apart graphene oxide and exfoliating the sheets into individual graphene oxide flakes .Shi et.al (2007) proved that, the nanocomposites have an intercalated and flocculated structure.

The integration of graphene oxide in the PPD emulsion give a new alternative for the manufacturer petroleum industry to improve their performance of current PPD product. Moreover, graphene oxide more economical that it can reduced the costing.

1.3 Objectives

1. To study the impact of lateral size of nano graphene oxide to inhibit the wax crystal .
2. To study the kinetic crystal formation of paraffin wax after applied the nano hybrid PPD
3. To study the wax apparent temperature (WAT) of paraffin wax with addition different lateral size of graphene oxide as nano-hybrid PPD

1.4 Thesis outline

In this thesis, there are five chapters discusses on poly (acrylate) base of Nano graphene oxide as Nano-hybrid pour point depressants. A brief description on each chapter are elaborated as follows:

- **Chapter 1** briefly introduced the research project. This chapter cover the introduction about the research background, problem statement, objectives and outline of the thesis
- **Chapter 2** is the literature review part. In this chapter, it covers brief introduction on graphene oxide. This chapter also covers the overview of background pour point depressants, development of pour point depressants, mechanism of pour point depressants, and general intro of PPD-emulsion. Application of Nano-hybrid polymeric material in advancement of polymer nanocomposites and graphene oxide in polymeric pour point depressant and emulsion product discussed. Moreover, several physical blending methods has been reviewed in this chapter such as in situ intercalative polymerization, solution intercalation and melt intercalation method. The best method has been chosen to be applied in physical blending of graphene oxide in emulsified PPDs.
- **Chapter 3** covers the methodology used in this works including materials, experimental method that is physical blending process, sample characterization, applied test and evaluation of emulsion
- **Chapter 4** consist of result and discussion of the research project
    - **4.1** focuses on the results characterization of different system (GO1/GO2/GO3, GO4/GO5). The testing conducted including Fourier

Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM)

- **4.2** focuses on the results characterization of Graphene Oxide loading. The testing was conducted such as Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), Particle Size and Zeta Potential.
- **4.3** focuses on application of Nano-hybrid pour point depressants. In the application of Nano-hybrid PPDs section, Pour Point Measurement Based on ASTM D97, Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), effect of Different lateral size of Graphene oxide and Impact microstructure of paraffin wax using Polarized Optical Microscopy (POM) are discussed.

- **Chapter 5** concludes the findings from the research project with few recommendations for future work.

Chapter 2
LITERATURE REVIEW

2.1 Crude oil

2.1.1 Overview

The crude oil industry are suffering during the transportation and storage of the crude oil ,because of the solidification occur on the crude oil give trouble in the pipeline .A number of variables contribute to the possibility that a well or flowline will experience flow assurance problems in its lifetime. Particularly critical in deep-water field development, flow assurance has been addressed using a conservative approach in the past. Millions of dollars have been invested in preventive and mitigation techniques ranging from chemical inhibitors to electrically heated seabed flowlines. Most of these techniques have met with success, and they have become part of the conventional wisdom.

To prevent the occurring of solidification of crude oil shown in Figure 2.1 ,the study of the crude oil content itself need to focus more on that .Which is the new technologies of improving the PPD using nano GO can play the main role in this study to inhibit the formation of the wax precipitation in the crude oil.

The main component of natural gas is methane but other hydrocarbons, such as ethane, propane, butane and also present of sulphur, oxygen, and nitrogen contents in crude oils. Crude oils contain different hydrocarbon and heteroatom containing molecules and the comprehensive review of the composition and the chemistry of crude oils was published (Speight, 2006) .Table 1.2 shows that the hydrocarbon found in crude oil

Figure 2. 1 Wax deposition on wall (left) and gelation (right) of waxy crudes in pipeline (Yang et al., 2015)

Table 2. 1 Hydrocarbon found in the crude oil (Speight, 2006)

Hydrocarbon	**Chemical**	**Name**
Saturated	Straight chain	n-Paraffin
	Branched chain	iso-Paraffin
	Alicyclic	Naphthanes
Aromatic	1-Ring	Benzenes
	2-Ring	Naphthalene
	3-Ring	Phenanthrenes

Petroleum or the equivalent term ‘‘ crude oil ’’ is a mixture of gaseous , liquid, and solid molecules that occur in rock deposits found in different parts of the world. The oil recovery from porous sedimentary rocks depends on the efficiency with which oil is

displaced by some other fluids (Morrow, 1991). The flow behaviour of crude oil, gas, and brine in the porous rock medium of petroleum reservoirs is controlled largely by the interactions occurring at the interfaces within the various fluid (Group, 2007).The composition and properties of crude oils, such as viscosity, vary with the age of the oil field. As an increase in viscosity of crude oils, their density increases. The density of crude oils, expressed in terms of API gravity, relates to specific gravity.

(Kok *et al.*, 1996) state that in their study the API density is varied depend on the weather of country, the paraffin contents of the crude oils were determined by DSC, analysis as previously described . The pour points were determined by the ASTM procedure (ASTM D97-87). According to some estimates from the International Energy Agency (IEA), heavy oil represents at least half of the recoverable oil resources of the world. Heavy oil is defined as petroleum which has a density equal or lower than 20 API, but if petroleum has 10 API or less it is considered as extra heavy oil or bitumen, which is denser than water. The difference between bitumen and extra heavy oil is ambiguous and usually refers to the production technology, so we will include both under the term extra-heavy oil. As a framework, conventional oil such as Brent or West Texas Intermediate has a density ranging between 38 and 40 API.(Martínez-Palou *et al.*, 2011)

In fact ,the demand for heavy and extra-heavy crude oil has been marginal ,this is because of their high viscosity and composition complexity that make them more difficult and expensive to produce ,transport and refine .Referring to Table 2.1 above shows that Orinoco Belt in Venezuela and Libya are good example of region producing extra heavy

oil.(Martínez-Palou *et al.*, 2011) state that to replace the declining production of conventional middle and light oil it takes over next two decades .

2.1.2 Type of wax

Paraffin waxes consist of straight chain saturated hydrocarbons with carbons atoms ranging fromC_{18} to C_{36}. Paraffin wax consists mostly with normal paraffin content (80–90%), while, the rest consists of branched paraffin (iso-paraffins) and cycloparaffin. The petroleum waxes are generally categorized into two groups, paraffin wax and microcrystalline wax ,present in petroleum distillates and residues. Paraffin waxes consist of straight chain saturated hydro- carbons with carbon atoms ranging fromC_{18} to C_{36}.(Rehan *et al.*, 2016) .

Microcrystalline waxes are composed of branched and cyclic hydrocarbons with carbon atoms ranging from C30 to C60 (Speight, 1991). The reasons for high molecular weight or larger carbon number waxes in oils are still under exploration. One possible explanation is that the larger carbon number waxes are composed of shorter carbon number molecules produced at lower temperature reactions. For instance, C_{50} wax consists of two C_{25} and C_{70} consist of two C_{35}s . According to (Pu,H., *et al.*, 2014) fossilized organic matter shows waxes of C_{25} toC_{45} are produced from land plant sand bacteria. This is one of the reasons that why non-marine oils contain more waxes than marine oils. Figure 2.2 shows main paraffin structures. Normal paraffin is a saturated hydrocarbon with molecules containing carbon atoms linked in a straight (unbranched) chain.

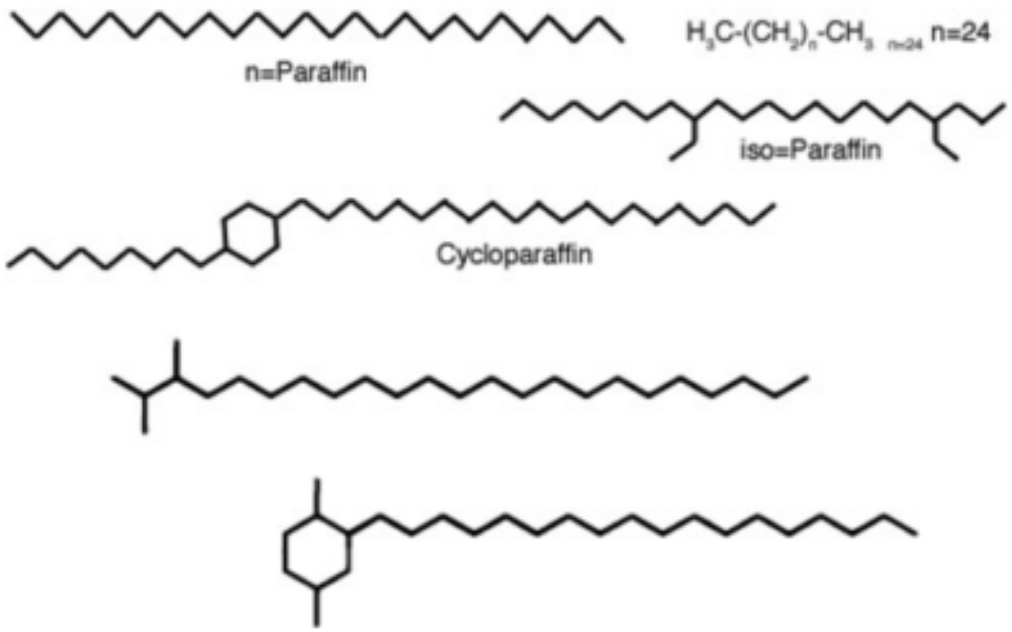

Figure 2. 2 Main paraffinic wax structures

2.1.3 Wax deposition treatment

Many of the researcher straggling to improve the treatment become more sustainable and low-cost of the maintenance .If the crude oil are not treated well ,the catastrophic failure will occur to the transportation pipeline towards the end ,and it will disturbing the production continuity. Nowadays, two type of treatment are being applied to the crude oil industry, which is more practical to apply.

2.1.3.1 Physical treatment

In the scope of the physical treatment of wax deposition ,divided into thermal, magnetic, and pigging . But they provide only temporary relief and often cause problem of their own. Most importantly, they stop the production ,sometimes for several days at a time dependent on the severity of the precipitation and deposition.

2.1.3.1.1 Pigging

Pigging is widely used in pipelines for wax removal. However, pigging operation relies heavily on “rules of thumb.” Because of its complexity, rather-limited pigging models were presented to predict the wax-removal mechanics in past decades. This work aims to develop a pigging model for wax removal in pipelines. In field operation, the mechanical pig is widely used for removing the wax build-up from the internal pipeline wall (Davidson, 2002).

In short, most of the findings for wax removal in pipes in the past were refined from laboratory experiments with waxy gels or mixtures of commercial wax and mineral oil. So far, the pigging model development is still not mature. . In response, this paper (Huang *et al.*, 2017) aims to develop a pigging model to predict the wax-breaking force . which reveals that the wax-failure stress always exceeds the yield stress of the same wax deposit during pipeline pigging. In this paper, a laboratory setup is used to conduct pigging experiments to investigate the effect of the hardness of the scraping element in the pig on wax removal. Furthermore, a pigging model is developed to describe the wax removal from the pipe wall. This model could be a practical tool in designing the optimal pigging programs.

2.1.3.1.2 Thermal

The latest technology successfully integrated state-of-the-art in a heat management system to offer safe, reliable and cost-effective crude oil transfer. The pipeline is a versatile heat management system designed to deliver heat for pipelines that can be hundreds of kilometres long. When the heat are supply ,the temperature of the

crude oil are always above the WAT the followability of the crude oil much more easier . The paraffin wax are not crystallize above the WAT . It is good for transporting the crude oil . Consequently, a huge amount of energy is consumed to heat the crude oil by hot water or electrical power every year

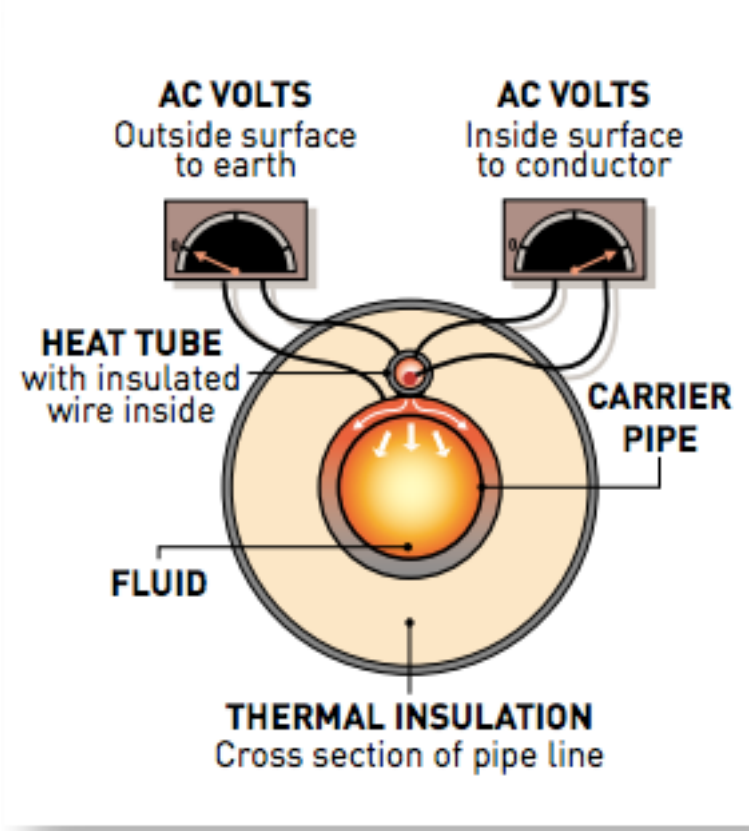

Figure 2. 3 : Cross section for typical single tube welded system (PENTAIR Raychem Tracer, 2010)

2.1.3.1.3 Magnetic Radiation

In order to save the energy cost, the magnetic paraffin control technology is presented and evaluated with the hot oiling method, and accordingly the effect of the magnetic radiation on the oil transportation is detailed. According to (Zhang, Zhang and Dong, 2010) the magnetic treatment can compensate for the resistance rising of the pipeline caused by the hot water reduction. Especially, the transportation of crude oil (at the surrounding temperature of -10°C~-30°C) without any heating has been observed in the Daqing oil field under the radiation of a magnetic field of 120 mT. In addition, the effect of the length of pipelines on the performance of magnetic treatment was also investigated.

In recent years, magnetic paraffin control (MPC) technology has been utilized as an assistance of conventional paraffin control methods (Tung *et al.*, 2003) . Magnetic field treatment can aggregate paraffin particles inside the crude oil into large ones by reorienting paraffin molecules of magnetic anisotropy (Zhang *et al.*, 2015)(Takahashi *et al.*, 2004) . The aggregation will increase the particle size and lead to the viscosity reduction of crude oil, which lowers the pressure drop and decreases the resistance of pipeline transportation. The magnetic treatment is performed with magnetic field activators installed on oil pipelines, which is safe and easy to adopt for practical applications. It is meaningful for transporting high-viscosity and paraffin-rich oils, especially for transportation of offshore oil via deep-water pipelines.

2.1.3.2 Chemical treatment

A lot of the crude oil industry ,preferred to applied the chemical treatment, because of the cost is much lower than physical treatment in term of maintenance. The

usage of the chemical is minimum for the transportation of crude oil ,this is because the chemical in liquid state, which easily to distribute after injected into pipeline. The turbulent flow in the pipeline help the chemical to well disperse to all the crude oil.

To overcome the problem in the pipeline of crude oil , ten years investigation has resulted in substantial progress in identification and chemical treatment of these problem areas. The chemical treatment inhibit the formation of the factor that make the flow ability of the crude oil in pipeline affected. The paraffin inhibitors or known as pour point depressant are polymers capable of crystal distortion or modification during the deposition process. Because of this co-crystallization mechanism, it is necessary to have the chemical in solution above the cloud-point temperature. This prevents or interferes with the molecular diffusion mechanism of deposition. It also modifies the crystal structure of waxes precipitated into small, highly branched structures with low cohesive properties. Three popular crystal modifiers are copolymers in these groups: (1) Group A-copolymer of ethylene vinyl acetate, (2) Group B-copolymer of C18 through C22 methacrylate, and (3) Group C-copolymer of olefin/maleic anhydride esters.

2.2 Polymer as Pour Point Depressant (PPD)

2.2.1 Overview Background of Pour Point Depressant (PPD)

Nowadays, the alternatives for managing cold flow issues were extremely restricted. Heat was a conspicuous arrangement, stories of flames being worked under the sumps of vehicles are for sure authentic. A more sensible option, in any event in a few cases, was to build the solvency power of the fluid portion of the oil by the addition of kerosene to the lubricant, however this additionally diminished the viscosity of the oil at

high temperature. There was likewise the option of including one of a few normally happening materials, for example, asphaltenic resins or microcrystalline waxes, which were evacuated at different phases of the refining process. Unfortunately, while such materials were now and again sensibly powerful, they were not broadly applicable.

These materials depress the pour point of oil, they were designated pour point depressants. The presence of these naturally occurring pour point depressants proposed that there could well be synthetic materials that could function at low temperature and presumably better. The structures of natural hydrocarbon pour point depressants, is the greater part of the waxy materials themselves, if clear clues to the early synthetic efforts. The alkylated naphthalenes, wherein the alkyl groups contained linear waxy paraffinic structures. This improvement empowered the trial of other waxy materials.

Throughout the years, a wide assortment of synthetic materials has been presented industrially as pour point depressants. Chlorinated wax is the most outstanding case of small-molecule chemistry, however most business items are direct to high molecular weight polymers, for example, polymethacrylate, polyacrylate, acrylate-styrene copolymers, esterified olefin-or styrene maleic anhydride copolymers, alkylated polystyrene, and vinyl acetate-fumarate copolymers.

Dispersants are often blended with polymeric inhibitors to improve the additive performance. Low cost wax dispersants include alkyl sulfonates, fatty amine ethylates and other alkylated product. These products function well only when blended with polymeric inhibitor, (Hassan Ali, 2012) . Normal method to controlling the wax deposition for subsea pipelines is by regular pigging. According to Figure 2.4, this method improved the flow due to the passing the pipe is probably caused by a combination of smoothing of the rough wax layer and removal of the wax back into the

flowing oil. The smoothing of the pipeline deposits can significantly reduce the friction factor in turbulent flow (Zhang Fusheng, 1995) .

According to (Souchik, 2009), they found that the treated PPD will change the structure of the paraffin wax mixture by partially transformed from orthorhombic into hexagonal form. This is important in wax plays the role of lowering the melting point of wax.

Polymeric materials have been advanced adequately to function for a wide temperature range by modify the flow properties of lubricants. There are few types of polymer commonly used, as wax inhibitor chemical, which are, olefin-based polymer and ester polymer. Ethylene vinyl acetate (EVA) and poly methacrylate (PMA) are the most common types of olefin and ester polymer used nowadays. Both types of the polymer have their own advantage and disadvantage. EVA is a block olefin copolymer with rubber like properties and has excellent viscosity modified properties. However, it has the lower pour point ability compare to the PMA.

The pour point is the lowest temperature which oil or fuel will pour under low temperature condition while the pour point depressant (PPD) is the chemical used to enhance the pour point of the fuel. PMA is belonging to acrylate family or commonly known as comb polymer family due to their comb-like structure. Comb polymer has excellent ability to act as pour point depressant since it can withstand low temperature condition, which is below 0^{o}C.The high molecular weight PMA can act as both PPD and viscosity modifier. High molecular weight PMA can act as both PPD and viscosity modifier.

2.2.2 Mechanism of Pour Point Depressant (PPD)

The mechanism of the paraffin wax dispersant is to penetrate the into waxy oil gel, be adsorbed on individual particle, and reduce the tendency of wax particles to stick together. Moreover, the dispersants may adsorb on the inner surface of the pipeline and reduce the ability of wax to adhere to pipe wall.

Figure 2.4 and Figure 2.5 show, the prevention mechanism of interlocking wax crystal by polymer additive. Figure 2.5 show the mechanism to modify the wax growth crystal ,it prevent agglomeration primarily involves the structure of the PPD to disrupt the crystal habit of wax crystal. The structure involved in this mechanism process which is the pendant chains, which use to co-crystallize with the wax and the polar end group. These groups are responsible for disrupting the orthorhombic crystal structure into a compact pyramidal form . This process prevents the crystal from agglomerating and forming a gel like structure to deposit in the pipeline surface.

When the paraffin wax are not treated with PPD the crystal structure easy to grow ,the lateral growth forms needles or plates like .The crystal structure continues to grow below the cloud point temperature ,so the large structure 3D crystal network formatting ,crystal size >100um ,the oil ceases to flow

The treated paraffin wax with PPD ,the co-crystallization occurs between wax molecules and PPD crystal units , the crystal confine to form a structured crystal due to present of polymer that modified the wax crystal growth .The interlocking of wax crystal is prevented ,leading to smaller and more random structure , hence creating fault in wax crystal which change the shape and size of wax crystal and prevent the interlocking of

crystal into different shape . The end good of paraffin wax is no aggregation of gel-like wax network. The oil continues to flow without yield stress .

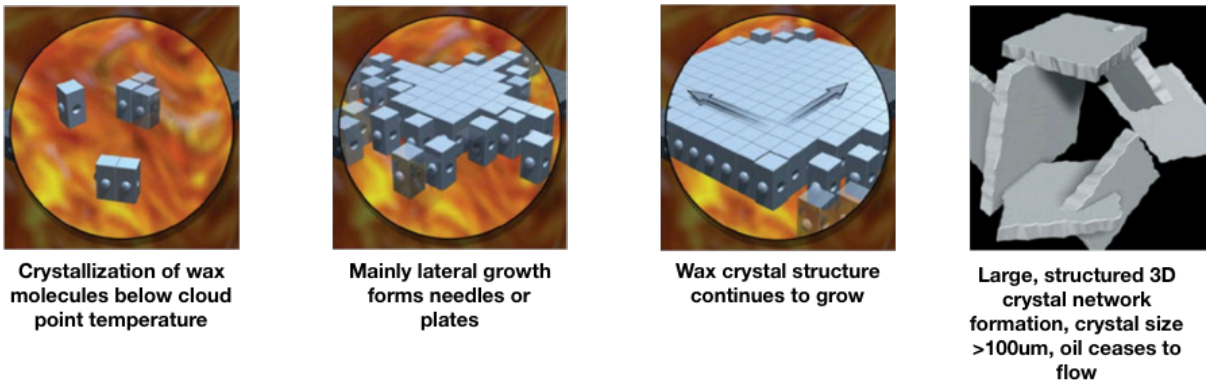

Figure 2. 4 Wax molecule formation without present of PPD (Souchik, 2009)

2.2.2.1 Adsorption and Co-crystallization theory

The polymer either being adsorbed into the face of the wax crystal if the PPD is comb polymer shown in Figure 2.5. Thus, the wax like components of the additive are incorporated into the wax crystal lattice and thus modify the morphology of the growing crystal (DeYoreo and Vekilov, 2003)

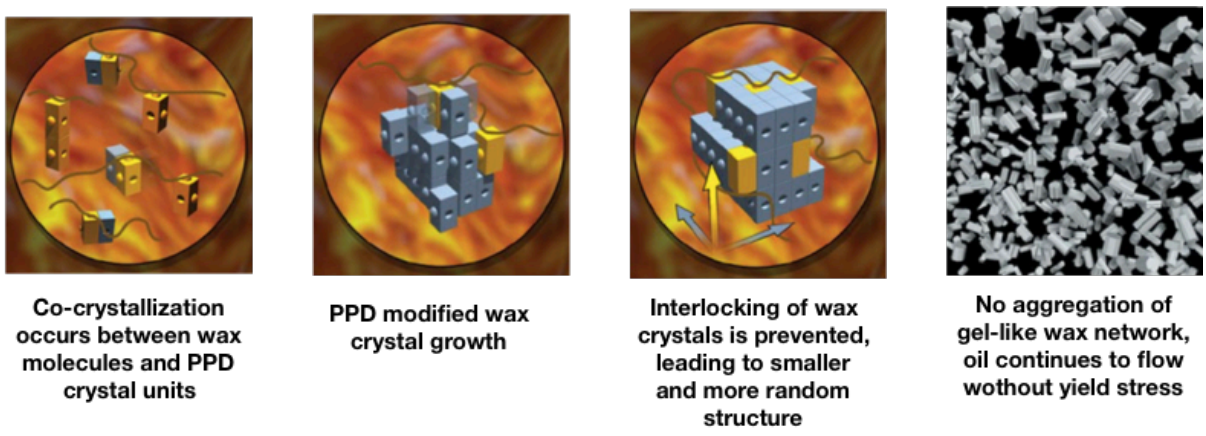

Figure 2. 5 Wax molecule formation with present of PPD (Souchik, 2009)

According to (Yang *et al.*, 2015), at temperature near or below the WAT, many polymeric wax inhibitors and PPDs co-crystallize with wax molecules or adsorb on growing surface of precipitated wax crystal. Incorporation of polymeric wax inhibitor and PPDs into wax crystal disrupts growth, inhibiting wax deposition, and improving flow ability. Molecular dynamic (MD) simulation has been used to investigate the effect of polymeric Wax Inhibitors and PPDs on the growth of wax crystals (Yang *et al.*, 2015).

2.2.2.2 Nucleation theory

The additive heterogeneously nucleates the wax crystal and this result in crystal of relatively smaller size (DeYoreo and Vekilov, 2003) . According to (Yang *et al.*, 2015) , at temperature well above the WAT, certain polymeric WIs and PPDs self-assemble into micelle-like aggregate exhibition a crystalline core and soluble hairy brushes surrounding the core, creating a larger number of subcritical size wax nuclei (so-called poly nucleation) shown at Figure 2.6. Partially shielded nuclei reduce super saturation, reduce crystal growth rates, and facilitate of more abundant smaller wax crystals. Wax crystal size reduction facilities inhibition and rheological beneficiation.

Figure 2. 6 Image of POM treated crude oil and non-treated crude oil

2.3 Graphene oxide as Nano-material

2.3.1 Introduction to Graphene oxide

Graphene oxide has been study in the context of many application such as polymer nanocomposite , energy related materials, sensors, paper like materials, field effect transistor, and biomedical applications due to its excellent electrical, mechanical and thermal properties.(Potts *et al.*, 2011) Graphene oxide is a strongly oxygenated and highly hydrophilic layered material that can be readily exfoliated in water to yield stable dispersion consisting mostly of single-layer sheets which referred to as Graphene oxide sheets.