EVALUATING THE EFFECT OF EMULSION ON WAX DEPOSITION PREVENTION OF OIL FROM FANG OIL FIELD

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เนื่องด้วยเหตุการณ์ โควิต 19 ปริมาณการอุปโภคพลังงานลดลง สำนักบริหารสารสนเทศพลังงานของสหรัฐอเมริกาคาดการณ์ว่าจะมีปริมาณอุปโภคพลังงานกลับมาอยู่ในระดับเดียวกับระดับอุปสงค์ก่อนการระบาดของ โควิต 19 ภายในปี 2022 ดังนั้นจึงเป็นความจำเป็นอย่างยิ่งที่จะการรักษาการผลิตให้ไม่ให้เกิดการรบกวนจากปัญหาการไหล นอกจากนี้ การตกตะกอนของไขเป็นหนึ่งในปัญหาหลักของการไหล เพื่อจัดการปัญหาการเกิดไขในอุตสาหกรรม มีวิธีการ 3 วิธี อันได้แก่ การจัดการเชิงกล การจัดการโดยใช้ความร้อน และ การจัดการเชิงเคมี โดย การจัดการเชิงเคมีนั้นมีความง่ายต่อการใช้งาน

สำหรับการศึกษาในครั้งนี้ เป็นการศึกษาการจัดการการเกิดไขโดยวิธีการเชิงเคมี โดยทำการศึกษาผลของอีมัลชั่นต่อการเกิดไขโดยสารเคมีที่นำมาใช้ คือ สารเอ็น-เฮบเทน และสารโพลีมาเลอิกแอนไฮไดรด์อัลวันออกตะเดกเคน หรือ พีเอ็มเอโอ โดยทำการวัดผลของอุณหภูมิที่จุดเท อุณหภูมิปรากฏไข และการเกิดไขของน้ำมันดิบ ซึ่งทำการวัดผลในหลายแง่มุม เช่น อีมัลชั่น อุณหภูมิ หรือ ความเข้มข้นของสารเคมี โดยผลของอีมัลชั่นที่มีต่อการเกิดไข อีมัลชั่นที่มีอยู่โดยที่มีปริมาณน้ำในน้ำมันเพิ่มมากขึ้นที่ 0 เปอร์เซ็นต์ ถึง 40 เปอร์เซ็นต์ ปริมาณน้ำในน้ำมันจะเพิ่มขึ้นส่งผลให้ปริมาณการเกิดไขเพิ่มขึ้น และ ปริมาณการเกิดไขลดลงเมื่อปริมาณน้ำในน้ำมันเพิ่มขึ้นที่ 40 เปอร์เซ็นต์ ถึง 80 เปอร์เซ็นต์ และ ประสิทธิภาพของสารเคมีจะลดลงเมื่อปริมาณน้ำในน้ำมันเพิ่มขึ้น

โดยผลของสารเอ็น-เฮบเทนมีบทบาทสำคัญต่ออุณหภูมิที่จุดเท อุณหภูมิปรากฏไข และการเกิดไขของน้ำมันดิบ โดยสารเอ็น-เฮบเทน มีประสิทธิภาพของสารเคมีต่อ อุณหภูมิที่จุดเท อุณหภูมิปรากฏไข และการเกิดไขของน้ำมันดิบสูง เมื่อเทียบกับน้ำมันดับและ อีมัลชั่นที่ไม่มีสารเคมี โดยประสิทธิภาพของ สารเอ็น-เฮบเทนจะเพิ่มขึ้น เมื่อความเข้มข้นของสารเอ็น-เฮบเทนเพิ่มขึ้น ในขณะที่สารพีเอ็มเอโอจะมีความเข้มข้นที่เหมาะสมโดยแสดงประสิทธิภาพสูงสุดที่ความเข้มข้น 7500 ส่วนในล้านส่วน ซึ่งจะแสดงผลในลักษณะเดียวในแต่ละกรณีของปริมาณน้ำในน้ำมันและอัตราเฉือนสำหรับอุณหภูมิปรากฏไข หากทำการเพิ่มความเข้มข้นมากกว่า จุดที่เหมาะสมสุด จะลดประสิทธิภาพของสารเคมีลง

สำหรับสารผสมระหว่าง 10 เปอร์เซ็นต์ และ 15 เปอร์เซ็นต์ ของ สารเอ็น-เฮบเทน ซึ่งมีประสิทธิภาพสูงและคำนึงถึงด้านเศรษฐกิจ กับ พีเอ็มเอโอ 7500 ส่วนในล้านส่วนซึ่งเป็นความเข้มข้นที่เหมาะสม และผลจากศึกษาพบว่า ประสิทธิภาพของ สารผสม 15 เปอร์เซ็นต์ สารเอ็น-เฮบเทน และ พีเอ็มเอโอ สูงกว่า สารผสม 10 เปอร์เซ็นต์ สารเอ็น-เฮบเทนและพีเอ็มเอโอ

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Due to the COVID-19 situation, the energy consumption demand right now declines. However, the trend predicted by EIA is that the demand will be fully recovered at the end of 2022. Thus, it is important to maintain the production without disruption from flow assurance issue. In addition, wax deposition is one of the important issues for flow assurance. To manage the wax deposition, there are 3 major methods which are mechanical, thermal and chemical methods. The chemical method can easily be utilized.

For this study, wax deposition prevention is studied with chemical method. Also, the study is investigating the effect of emulsion on wax deposition by using two chemicals, n-heptane and poly (maleic anhydride-alt-1-octadecane) or PMAO. Also, pour point, WAT and wax deposition are measured with several aspects such as emulsion, temperature and chemical concentration. For the effect of emulsion on the wax deposition, the presence of emulsion with increasing water cut initially increases amount of wax deposition in the case of water cut from 0% to 40% and the amount of wax deposition decreases by comparing amount of wax deposition from 40 to 80%. Also, for the effect of emulsion on wax inhibitor performance, water cut increases with more diminishing effect of wax inhibitor with all cases of inhibitor performance.

For inhibitor performance, n-heptane plays a major role for pour point, wax appearance temperature and wax deposition measurement illustrated by the higher inhibitor performance comparing to the crude oil and its emulsion without chemical. Also, the performance increases with an increase in concentration. However, PMAO has its own optimum concentration at 7500 ppm which yields the highest effect of inhibitor performance for all cases of water cut and all shear rates for WAT. By adding more concentration for PMAO beyond optimum concentration, the inhibitor performance reduces comparing to optimum concentration.

For the better effect of inhibitor performance, 10% and 15% n-heptane which exhibits the high performance and economical aspect and PMAO at 7500 ppm are mixed to obtain the optimum concentration. It is found that 15% n-heptane with 7500 ppm of PMAO yields higher inhibitor performance than that at 10% n-heptane with PMAO for amount of wax deposition.

Field of Study:	Georesources and Petroleum Engineering	Student's Signature ....
Academic Year:	2020	Advisor's Signature ....

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Chapter 1

INTRODUCTION

1.1 Background

Economic recession caused from covid-19 impact to energy demand and consumption (Peng et al., 2021). However, economic stimulus policy and vaccination have been produced. Thus, the output of world economic in 2021 is anticipated to be bounced back to 6% and also world energy demand is expected to be 4.6% that beyond 2019 demand by 0.5%. Even though, the oil consumption is not expected to be at the level 2019 which yearly demand is below 2019 around 30%. However, the trend of the oil demand is expected to be increased (EIA, 2021).

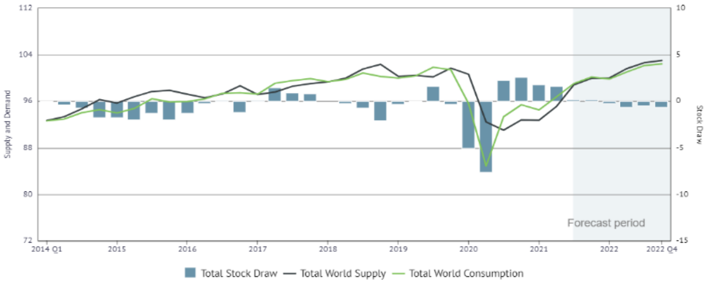


Figure 1.1 Global oil supply and inventory (EIA, 2021)

According to data of 1st quarter of liquid fuel consumption and EIA's assumption that economic continues to recover, the global liquid fuel consumption growth in 2021 is expected to be 5.3 millions barrel per day comparing to 2020 which is declined 8.6 million barrel per day. Moreover, EIA predict global oil consumption will be raised 3.7 barrel per day which results 101.4 million barrel per day for global consumption that is above 0.4 million barrel per day in 2019 (EIA, 2021).

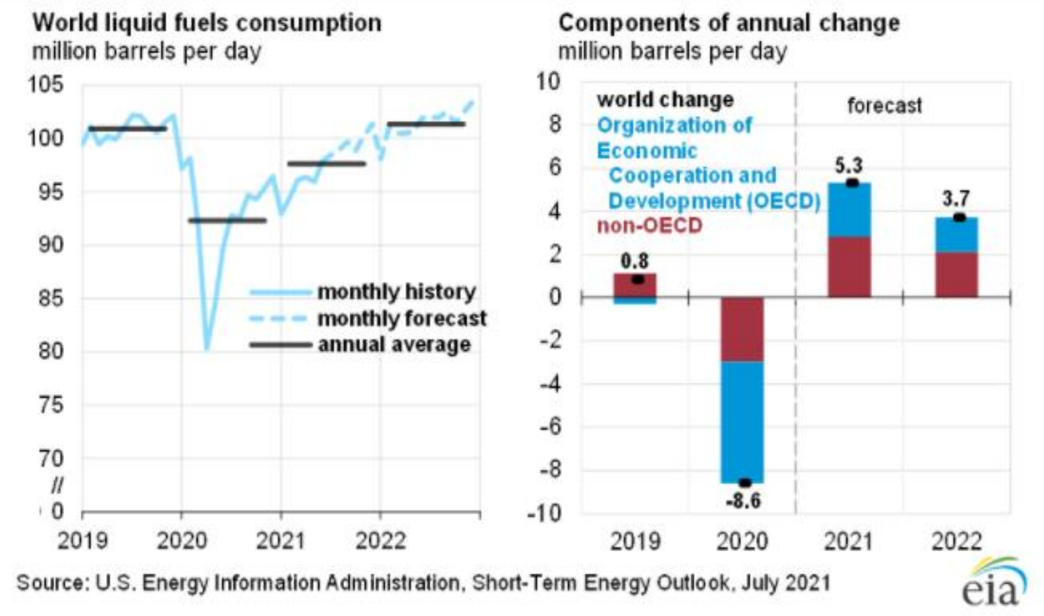


Figure 1.2 Global forecast fuel consumption and annual change (EIA, 2021)

In oil production, hydrocarbon production may encounter unfavorable condition such as low working temperature which may cause flow assurance issue as following and wax deposition is one of the main causes of this issue for petroleum production (Watson et al., 2003; Nura, 2020). The factors leading to wax deposition issue are 1. changing of hydrocarbon composition 2. the alteration of the flow rate which result from declining of pressure (Makwashi 2020) 3. reduction of hydrocarbon temperature (heat loss due to ambient temperature of nearby environment) (Al-Safran and Brill 2017). If there is no treatment related to wax deposition, the result will decrease production tube which also leads to reduce hydrocarbon production. In the extreme case, the available oil production is declined and reached uneconomical level (Theyab, Diaz et al. 2016) and the wells have to be abandoned.

Therefore, it is importance to develop strategy for safety and reliability in hydrocarbon production (Hammami and Ratulowski 2007).

1.2 Classification of Petroleum

The hydrocarbons in crude oil can generally be divided into four categories as follow; paraffins, naphthene, aromatics and resins-asphaltenes. Moreover, paraffins group can be further classified to be 3 group alkanes, alkenes and alkyne (McCain 1990).

Paraffins

The percentage of this hydrocarbon to the overall is normally 15 to 60% of crude and the ratio of hydrogen to carbon atom is 1:2 paraffins are the desired content in crude and what are used to make fuels. The more it is short, the more lighter it will become and alkenes are composed of branched hydrocarbon chain and the basic formula for alkynes is C_nH_{2n} (McCain 1990).

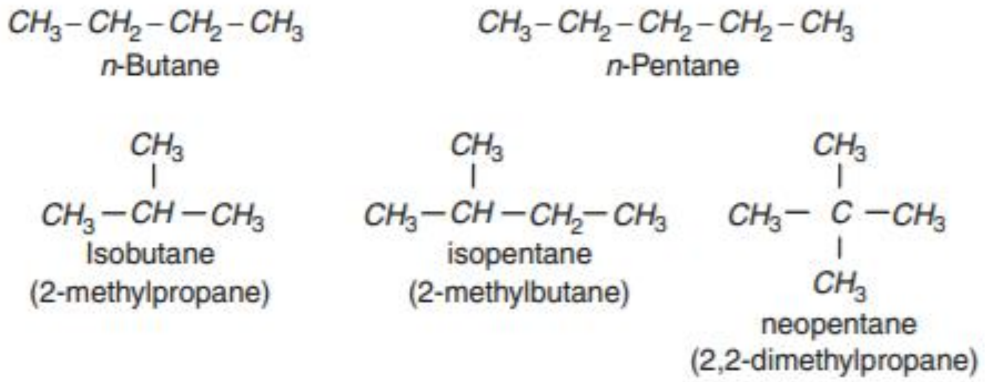
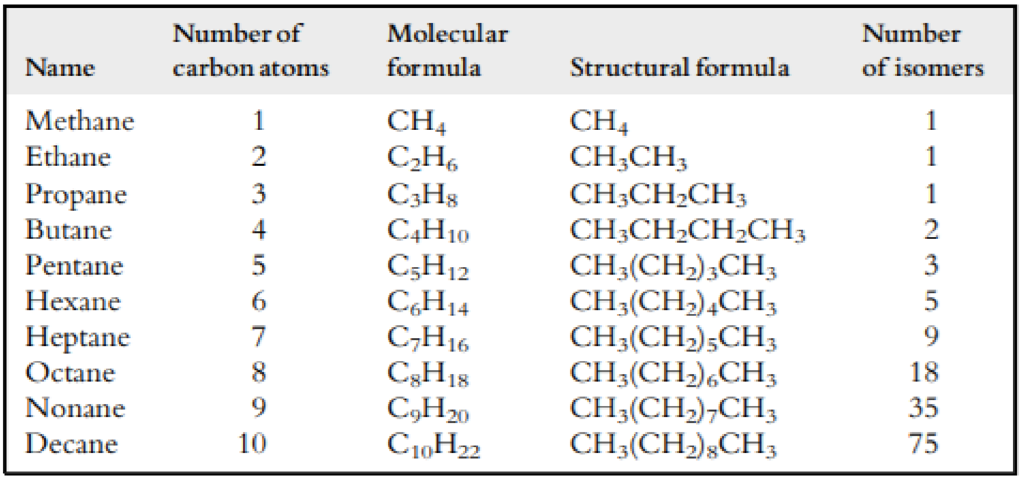


Figure 1.3 Paraffin structure (Mohamed A. et al., 2010)

The simplest form of alkane is methane which have only 1 carbon. Thus, it is denoted as C1. The different of the member of this group from higher or lower member is by -CH2- group which shown in the Figure 1.4. All of them have the similar properties with changing carbon atom in the chain. Another type which has structural isomerization is branch hydrocarbon called isoparaffinic. This structural is from the same two molecule but the bond is different. Thereby, butane and all other alkanes can be in the form of both straight chain and branch chain. The number of isomers depend on the carbon number that the number increases as carbon number increases. There are two isomers for butane and three isomers for pentane and 75 isomers for decane (C10H22). 600 isomers or more are for C5-C12 paraffins and these isomers can be identified in the petroleum component around 200 to 400. Different isomers lead to different structure and also properties (Fahim, Al-Sahhaf et al. 2009).



Name	Number of carbon atoms	Molecular formula	Structural formula	Number of isomers
Methane	1	CH_4	CH_4	1
Ethane	2	C_2H_6	CH_3CH_3	1
Propane	3	C_3H_8	$CH_3CH_2CH_3$	1
Butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
Pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
Hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
Heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
Octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
Nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
Decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

Figure 1.4 Ten paraffin name and formula (Fahim et al., 2010)

Naphthene (Cycloalkanes)

Naphthene is saturated hydrocarbon which composes of one or more carbon atom ring and its formula is CnH2n.

The percentage of this hydrocarbon to the overall is normally 30 to 60% of crude and the ratio of hydrogen to carbon 1:2. Also, Cyclohexane is the simplest form.

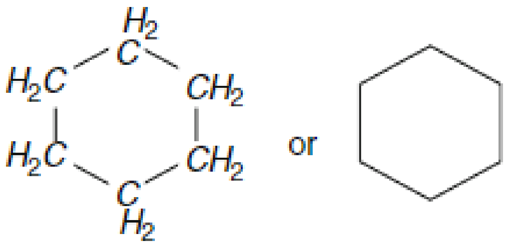


Figure 1.5 Cyclohexane

The boiling point of naphthene is higher than paraffin. 5-6 carbon atom ring is commonly represented for naphthene and the ring is represented the denser fraction of the crude oil and the density and viscosity of this hydrocarbon are more than equivalent paraffin. Also, the example of naphthene figure is illustrated as follows (Fahim, Al-Sahhaf et al. 2009);

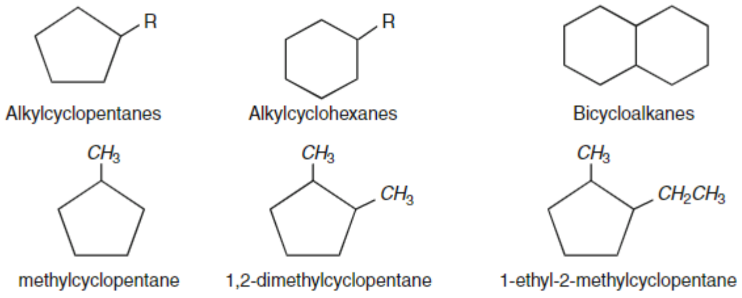


Figure 1.6 Example of naphthene

Aromatics

The component of this hydrocarbon to the overall is normally 3 to 30% of crude. They have a much less hydrogen in comparison to carbon than found in paraffin. They are also more viscous. Under same condition, they are normally found as semi-solid while a paraffin would be a viscous liquid.

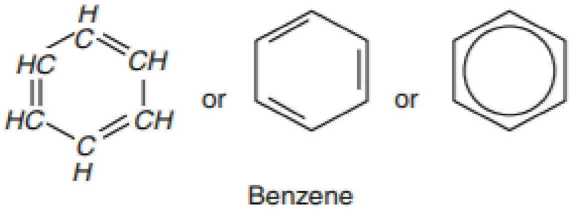


Figure 1.7 Benzene structure

Different sources of benzene crude oil have different concentration that light petroleum fraction contains mono aromatics that have at least one hydrogen atoms which take place by another alkyl groups. In addition, benzene, xylene and toluene are the example of atomic. Also, they increases the octane number (Fahim, Al-Sahhaf et al. 2009).

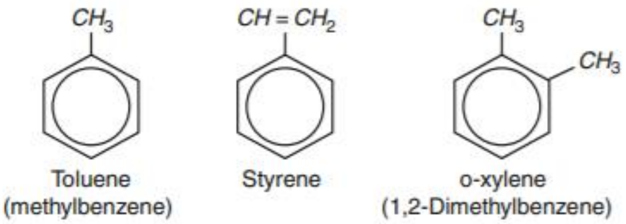


Figure 1.8 Others aromatic structure

Resins and Asphaltenes

The heteroatoms which comprise of nitrogen sulphur and metal fraction which have high boiling compound have governed the physical properties of crude oil which are pour point, viscosity, solubility, specific gravity, flash point and density etc. Thus, it is important to classify the heavy fraction to determine their properties in refinery (Fahim, Al-Sahhaf et al. 2009).

Resin and asphaltenes contain larger molecules, mainly hydrogen and carbon with sulfur, oxygen and carbon ranging of one to three atoms per molecule. The primary structure is comprised of rings, aromatic with three to ten or more rings in each molecule (McCain 1990).

Asphaltene is flammable with dark solid that normally has carbonaceous leftover after it is burnt. Several aromatic layers link together and folded to form a solid structure called micelle. There are wide range which range from 100 to 100000 for their molecular weight and the example of asphaltene is such as pentene and n-heptane (Fahim, Al-Sahhaf et al. 2009).

As high percentage of asphaltene, their characteristic about precipitation within the pore of the formation causes an issue in the production (Fahim, Al-Sahhaf et al. 2009).

The definition for asphaltenes for their solubility is that it cannot soluble in aliphatic hydrocarbon but it have ability for solute in aromatic hydrocarbon which are toluene (Andersen and Speight, 1999; Speight and Long, 1995; Rogel, 2000).

While resin molecular weight is between 500-1000 with polar molecule. Also, resin cannot dissolve in propane but have ability to solute in n-heptane. In addition, the main factor for dissolving and stability of asphaltene in crude oil is resin by surrounding the asphaltene micelles and solute them in the crude oil. Moreover, amount of resin is normally found more than asphaltene fraction (Fahim, Al-Sahhaf et al. 2009).

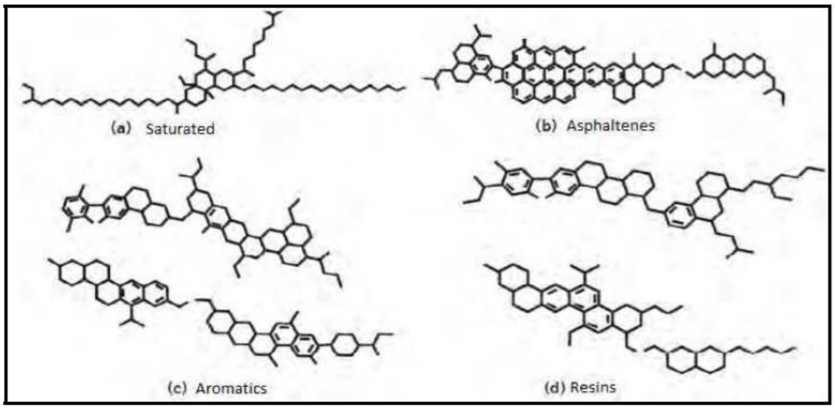


Figure 1.9 Saturated, aromatic, asphaltene and resin structure

1.3 Petroleum wax formation

At the reservoir condition, paraffinic particles dissolve completely in the oil mixture (Singh et al., 2000). Due to the low solubility of paraffinic component in crude oil and condensate at normal condition, it is classified as the source component of wax deposition (Toweler et al, 2011).

The main issue of wax deposition is the gel which comprises of wax crystal and trapped liquid but the solid wax is not the main issue (Theyab 2018). As there is an occurrence of precipitation, the waxy crude oil change is its viscosity and oil gelation

(Tordal, 2006). Paraffinic wax comprises of long chain alkane with 20 to 50 carbon atom (Theyab, 2018).

First of all, wax particle will precipitate out of crude oil as solid particle at the temperature below wax appearance temperature standing for temperature that wax crystal starts forming in oil when cooling process is performed and wax also deposits in the pipe wall (inlet coolant temperature) below this temperature (Theyeb, 2018)

Not only wax deposition creates pressure loss and also causes the reduction in production Moreover, the damage of wax deposition is also caused around wellbore (Theyab, 2018).

At the surrounding temperature below WAT which pipe wall temperature is called inlet coolant temperature, the wax crystal starts to gel which is 3-D structure of wax crystal and trapped oil due to heat loss resulting in heat loss and mass transfer.

Wax deposition continually deposits as time passes. Also, the mechanism that governs the wax deposition is molecular diffusion which dissolved wax particle diffuse toward and deposit on the pipe wall. The temperature near pipe wall is low. Thus, wax crystal can be precipitated out of crude oil. Thereby, dissolved wax near pipe wall is less than the location which is distant from pipe wall. For shear dispersion, wax particle moves lateral direction due to the collision between each particle. Brownian diffusion is motion of wax precipitate with Brownian motion move toward and deposit on the pipe wall and gravity setting that is sedimentation of wax particle toward the bottom of the pipe and this mechanism is valid in the case of shut the well or there is no flow (Huang, 2015).

1.4 Remediation and prevention of wax deposition

Higher concentration of heavy wax content, aging process and deeper reservoirs is the main cause of the problem (Min, 2018). As the time passes, wax deposit thickness increases because wax crystal precipitates from the oil continual deposit. Thus, this will result in increasing pressure drop during the production and promote wax deposition (Theyab, 2018). The lighter hydrocarbon composition comes out of the reservoir first and the result for single phase flow which the temperature is beyond the bubble point is that WAT increases as the pressure decline

The wax deposit on the pipe wall surface and the absorption force on the surface held the deposited wax. This absorption force is dependent free surface energy of both surface and paraffinic wax. Thus, the surface characteristic is one of the factor influence wax deposit (Theyab, 2018). Apart from free energy aspect, wax is deposited due to the surface roughness (Jonathan and Southgate 2004).

On the other hand, wax deposition decreases with increment of flow rate to turbulent flow because this is resulted in increasing of shear rate (Theyab, 2018).

For wax deposition prevention management, there are 3 types which are chemical, mechanical and thermal methods. For thermal method, it comprises of thermal insulation, heat retention, hot oil circulation and stream circulation while mechanical method uses scrapper in the borehole and pigging in the pipeline (Theyab, 2018).

For chemical method, there are 4 types of wax inhibitors which are pour point depressant (PPD), dispersant, solvent and crystal modifier. Moreover, crystal modifier can be divided further into 1. comb polymer 2. branched polymer with long alkyl group 3. ethelene polymers and 4. copolymer. Maleic-Anhydride-alt-1-ocatadecene also called PMAO is comb polymer and it is effective to wax deposition reduction because it has van der Waal interaction with crude oil which weaken the 3-D wax structure (Ridzuan, Adam et al. 2016).

1.5 Petroleum emulsion formation

Petroleum emulsion is normally found in hydrocarbon reservoir with formation of water and oil as shown in Figure 1.10 and Figure 1.11. Figure 1.12 provides the picture of normal reservoir which water formation located lower from hydrocarbon layer (Murtada et al., 2018)

As the light hydrocarbon migrates to the reservoir, some of water from formation also migrate along with. Thus, it is normally found petroleum hydrocarbon along with water or the water comes from stream when injects the fluid with additives. The water in the underground is called connate water or formation water. When it is being produced from the well and reaches to the surface with hydrocarbon fluid, it is called produced water (Jonathan and Southgate 2004).

The produced hydrocarbon reaching to the surface is in the form of fluid mixture and the component of produced hydrocarbon influences the compound of the mixture. The water, hydrocarbon, solid particle and also additive chemical are the example of compound of mixture (Jonathan and Southgate 2004).

Moreover, most of the field is found that there are higher content of water and emulsion is formed when two immiscible fluid which are oil and water contact with emulsifying agent asphaltene and also turbulence with generated stress to mix both oil and water. For type of emulsion, there are 3 types which are 1. water-in-oil (W/O) emulsion 2. oil-in-water (O/W) emulsion 3. multiple emulsion.

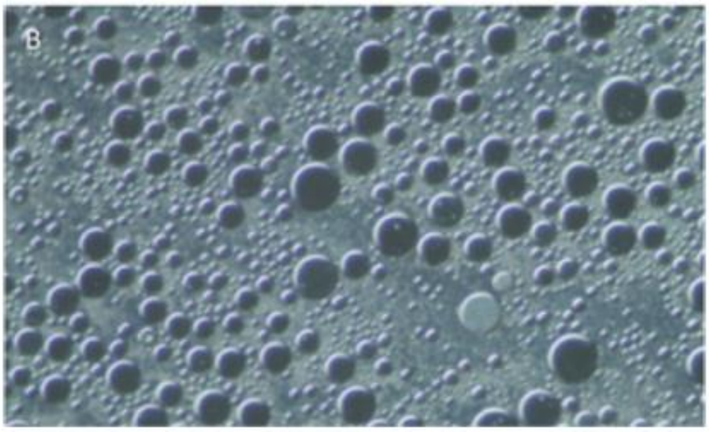


Figure 1.10 Microscopic image of oil in water emulsion (Sousa et al., 2014)

Water in oil emulsion is normally found in the industry (de Oliveira et al., 2018). In addition, the asphaltene is the main parameter for emulsion stability even if there is small amount (Zhang, Tian et al. 2016).

Schubert and Armbruster (1989) summarized that there are three factors causing emulsion which are 1. two immiscible fluid interaction 2. emulsifying agent such as asphaltene and resin and 3. mixing energy to make one liquid diffuse to another

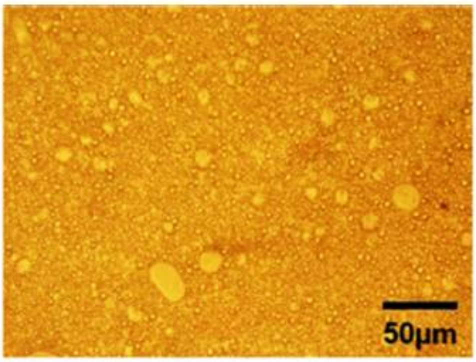


Figure 1.11 Microscopic image of Water in oil emulsion

(Le Follotec, Pezron et al. 2010)

The forming of emulsion results in many water droplets in the oil which causes higher emulsion viscosity and operation cost (Sellman, Sams et al. 2013).

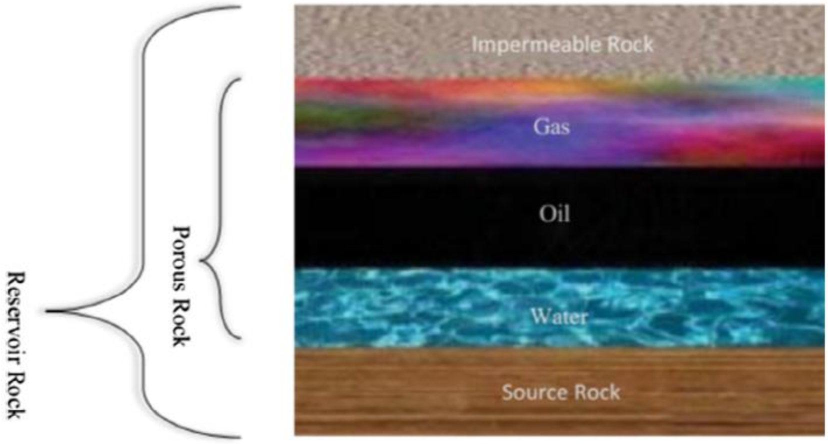


Figure 1.12 Reservoir layers (Igunnu and Chen, 2012).

1.6 Relationship of wax and emulsion

As the cooling process, the needle-like wax crystal precipitates out of bulk oil and forms the compact 3-D structure network and also surrounds the dispersed phase from Figure 1.14.

Their characteristics to rheological properties also depend on the emulsifying agent. The water cut increases with the decrease in viscoelastic and yield of emulsion with GMO, emulsifier of the researcher study. Thus, the most influential impact to the 3D network formation is wax crystal which available amount of wax crystal decreases with an increase in water cut and there is a little influence from water droplet in the oil phase. Thus, more compact 3-D network which generates more gel strength is by reducing water cut.

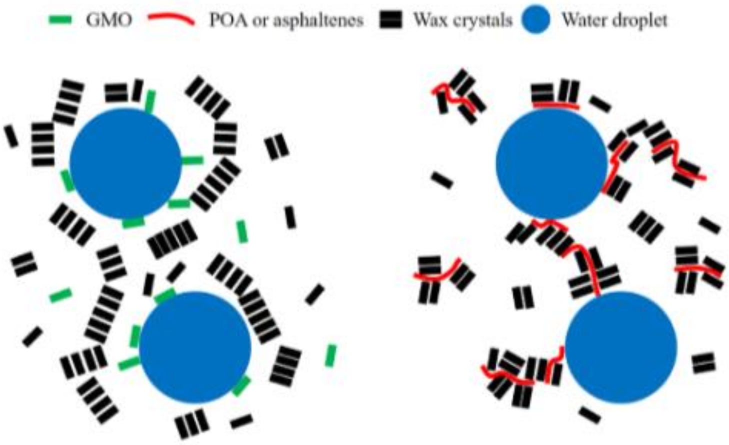


Figure 1.13 Schematic of the gelation mechanisms of the different emulsifier-doped model oil emulsions (Chen et al., 2021)

The evident to support this explanation is from the precipitated wax crystals micrograph in the emulsions. It is clearly seen wax crystal in the emulsion with asphaltene. However, it cannot observe with another emulsion GMO. Thus, this can be concluded that emulsion can promote crystallization of wax molecule on droplet surface only in the case of co-crystallization between wax molecule and wax crystal.

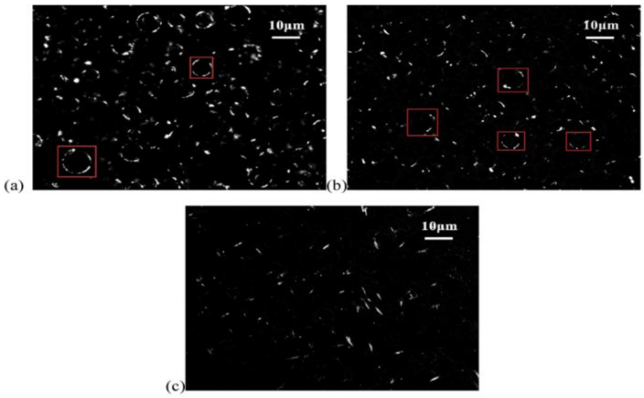


Figure 1.14 Micrographs of the wax crystals precipitated in different model oil emulsions at 15°C under polarized light. (a) POA; (b) asphaltenes; (c) GMO (Chen et al., 2021)

While using another emulsifier which is POA wax crystal is difficult to overlap, it is less influence by 3-D structure network. However, another one which is co-crystallization between wax molecule and droplet plays a major role. Thus, higher POA or asphaltene fraction in the oil results in higher viscoelastic parameter and yield values of the emulsion. All in all, higher water fraction leads to more compact greater gel strength. There are two ways for emulsion stability with the wax crystal of water in oil emulsion by forming 3-D dimensional network at the oil phase and absorbed at the oil-water interface. These behavior is found through emulsifier-doped model of oil emulsion micrograph.

1.7 Objectives of Study

Crude oil with water becomes emulsion and its component vary with different source and time in production. In this study, the chemical method is employed with various chemical concentration to cope with wax deposition problem.

1. To investigate the effect of emulsion on wax deposition of crude oil from Fang oil field
2. To evaluate wax deposition prevention by using wax inhibitors
3. To measure the pour point temperature, wax appearance temperature and wax deposition at various parameters such as amount of water cut, temperature, types of chemicals, chemical concentration and shear rate.

This scope of this study is to explore the wax deposition prevention of crude oil from Fang oilfield using cold finger technique for wax deposition, viscometry method for WAT and ASTM 5949 for pour point. Moreover, the parameter of the research is water cut by using distilled water because there is insignificant difference in pour point measurement between distilled water and produced water.

The contribution of this research work is to study the effect of emulsion on wax deposition issue and also wax deposition prevention by utilizing the chemical with optimum concentration for Fang oil field.

There are 5 chapters in this thesis. Chapter 1 provides the background and basic knowledge related to wax deposition, emulsion and contribution of this study. The literature review and theory of wax deposition prevention, remediation experimentation and also its emulsion are presented in Chapter 2. Chapter 3 represents experimental work. The results of the experiment are provided in Chapter 4. Finally, the conclusions and recommendation section are shown in Chapter 5.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Wax deposition

2.1.1 Pour-point temperature

The lowest temperature which the waxy crude oil still have ability to flow is called pour-point temperature (Min, 2018). The procedure to evaluate the pour-point temperature is presented in ASTM D5853-11 standard method. This pour point is one of main factors to cause the flow assurance problem artificial blockage for petroleum production. Thus, it is important to investigate the pour point of each condition.

2.1.2 Wax appearance temperature

To maintain the bulk oil temperature greater than the wax appearance temperature (WAT) is the most effective way for wax deposition prevention because this temperature is the point which forming wax comes out of the fluid to find out.

The probability for precipitation of the crude oil is required by measuring WAT. In addition, the experiment to measure WAT is by differential scanning calorimetry (DSC), cross polar microscopy (CPM) and viscometry method (Kok, Létoffé et al. 1996) and ultrasonic wave (Jiang et al., 2014). The WAT getting from CPM is measured as there is first crystal observed from polarized light (Taheri-Shakib, Rajabi-Kochi et al. 2018). For DSC, the heat alteration profile released is determined to obtain WAT in the cooling process. Also, WAT from viscosity method is measured by obviously significantly changing of viscosity.

Visual inspection method

Figure 2.1 illustrates the experimental model of ASTM D2500 and the limitation of this method is required the transparent fluid with cold finger thickness 40 mm and a cloud point is also lower than 49 °C. This method sensitivity is from operator, amount and size of wax. Firstly, the sample is heated to the temperature above WAT and then, the temperature of sample with cold finger decreases with circulating cooling. As the temperature reaches to WAT, there is the presence of wax deposits on the cold surface which can determine wax deposition encountered in the pipeline (Smith, 2011)

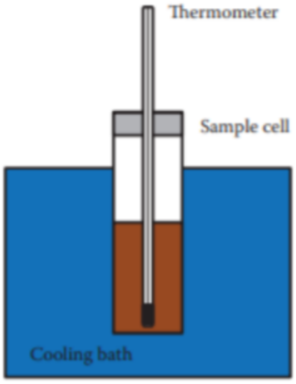


Figure 2.1 The ASTM D2500 model which measure WAT by visual inspection (Smith, 2011)

In addition, the visual method which is the ASTM-D2500 (Olisemeke, 2018). It needs the transparent samples which is immersed in the controlling temperature bath with decreasing temperature in 1°C each time for forming crystal that is WAT benchmark by visual inspection.

For an inhibitor, it required exactly analysis of WAT and wax component because the component also influences crude oil WAT. Moreover, the component of wax which is carbon fraction has major influence on the WAT and also higher carbon number results in greater wax component melting point (Dobbs 1999).

Cross poly microscopy or CPM

To extend the limitation of detection small size of wax crystals, this method supports the visual measurement by using a magnifying lens with cross-polarized light and the cross polarized one cannot pass through the black oil but optical of wax crystal is anisotropic. With rotating the polarization plane, it permits some part of the light through the oil. When there is present of wax crystal under CPM, it appears to be bright. The oil sample for testing with CPM can use with relation dim color as shown in the Figure 2.2 (Yang et al., 2015). The round shape of wax crystals is found in crude oil with low WAT with nonpolar structure (Dimitriou et al., 2015).

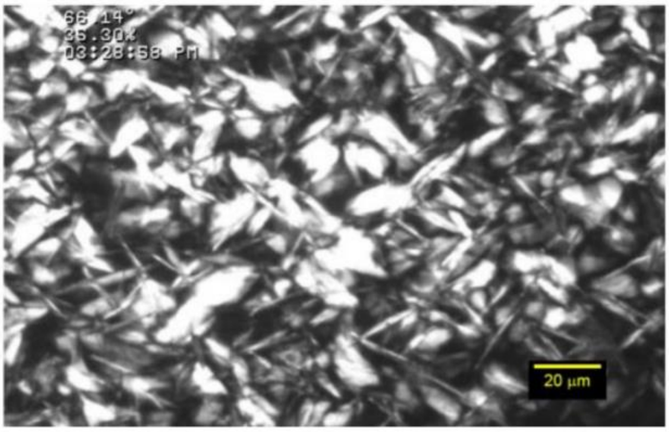


Figure 2.2 Illustrate waxy oil gel under cross polar microscope (Dimitriou et al., 2015)

Wax concentration is the main impact on WAT and WAT increases with an increment of wax concentration and the high wax content exhibits no intermediate alteration of phase between solid and liquid. From the experiment, the wax content having less than 15% expresses the intermediate changing that can be observed before the wax entirely solidifying (Ali 2019). There are two major types of rheological model which are Newtonian fluid and non-Newtonian fluid. The definition of Newtonian fluid stands for shear stress is direct-change with shear rate. Also, the viscosity is defined as the shear stress divided by the shear rate. Thus, the viscosity of Newtonian fluid is remained constant as changing the shear rate. Figure 2.3 shows the Newtonian fluid and non-Newtonian fluid (Pedersen, Rønningsen et al. 2000).

Light transmission can be determined WAT for light transmittance (LT) which the light can pass through the sample with determined temperature. As the temperature of light transmission decreases, this point is recorded as WAT and also Fourier transform infrared spectroscopy can use the properties of wax which is absorption properties of infrared (Li ,2010). Also, the combined effect of increasing shear rate and pressure have the great effect on decreasing WAT (Ali 2019).

Differential Scanning Calorimeter (DSC)

As there is the crystallization process, the heat of the lattice energy is released. Then, the differential scanning calorimeter detects the temperature with the peak of heat released. This temperature point is the phase transition between liquid and solid phases and this temperature point evaluate as WAT (Huang, Zheng et al. 2016).

Viscometry Method

This method uses the knowledge of rheology of waxy crude oil at higher and lower of WAT temperature. For the temperature higher than WAT temperature, the fluid behavior is Newtonian fluid. In other hand, the temperature below WAT leads to crystallization of crude oil and the presence of crystal will change the crude oil flow behavior to be non-Newtonian fluid which cause increasing of crude oil viscosity. WAT is determined by changing of slope between temperature and viscosity. Because of shear thinning, the shear rate for WAT experiment should not be high (Roenningsen, Bjoerndal et al. 1991).

Rønningsen et al. (1991) performed the comparative study with DSC, CPM and viscosity method with the cooling rate 12.5 °C/h, 10 °C/h and 0.5 °C/h . The result reveals that CPM yield the highest WAT. The reason is that it requires certain amount of wax crystal for both DSC and viscometry method to detect the viscosity and thermal alteration and also DSC provides the lowest WAT value among these three methods.

Theyab and Diaz (2016) performed the experiment of pour point and viscometry method for WAT in order to study the effect of inhibitor. Firstly, the sample is warmth up to 60 °C to dissolve the wax and then the temperature of the experiment is cooling from 55 °C to 0 °C with 120 s^{-1} of shear rate. The result reveals that inhibitors have influence to WAT and pour-point reduction for the same concentration with various prepared samples.

Ruwoldt et al. (2018) conducted the study about the effect of cooling rate alteration on WAT determination with CPM, DSC and viscometry method. Also, the cooling rate of all methods are 5, 10 and 15 C and 20 °C /min with 25 s^{-1} of shear rate. The result reveals that the lower WAT is caused by the higher cooling rate. The reason behind this phenomenon is that the higher cooling rate leads to delay the precipitation process than the lower cooling rate.

The formulation for pseudoplastic fluid without a yield stress is determine with 2 parameter functions. Moreover, Herscel-Bulkey model is for pseudoplastic with yield stress.

$$T_{xy} = \tau_0 + \eta_p (\frac{dv_x}{dy}) \tag{2.1}$$

τ_0 is the yield stress and n is a shear rate (Pederson & Rønningsen, 1999).

Viscoelastic material is the non-Newtonian fluid with a yield stress which is Bingham plastic and Casson fluids. At the low temperate, crude oil with wax is viscoelastic behavior.

Newtonian fluid and Bingham plastic have the similar linear relationship between shear rate and shear stress. The difference is that Bingham plastic relationship have certain pressure or shear stress to initiate the flow and influence of shear rate by increasing shear rate with decreasing viscosity (shear thinning). At shear rate 200 s^{-1}, the oil with precipitated wax exhibits as Bingham plastic fluid. The formulation for a Bingham plastic fluid is shown in Equation 2.2:

$$\eta = A + \frac{B}{\sqrt{\frac{dV_x}{dy}}} + \frac{C}{\sqrt{\frac{dV_x}{dy}}} \qquad (2.2)$$

τ_0 is the Bingham yield stress and η_p is a plastic viscosity. (Pedersen, Rønningsen et al. 2000).

Another rheological fluid model, the Casson model, is the same with Herscel-Bulkley. It is included a yield stress with non-linear curve. This model can be valid in the case of shear rate lower than 200 s^{-1} of non-Newtonian precipitated oil.

$$\eta = A + \frac{B}{\sqrt{\frac{dV_x}{dy}}} + \frac{C}{\sqrt{\frac{dV_x}{dy}}} \qquad (2.3)$$

In addition, A, B and C are the constants. Moreover, the Newtonian and non-Newtonian fluid behaviors are shown in the Figure 2.3.

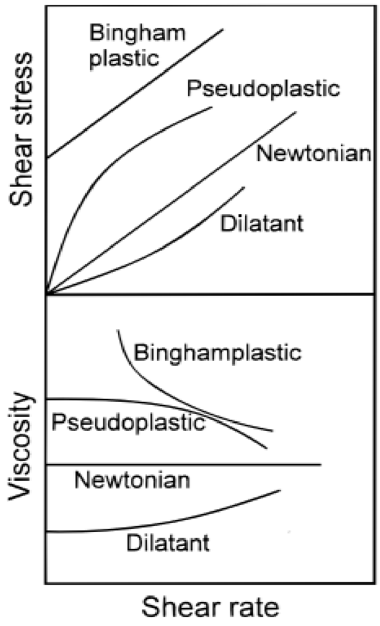


Figure 2.3 illustrate Newtonian and three non-Newtonian behaviors
(Pederson & Rønningsen , 1999)

While both pseudoplastics which viscosity decreasing with shear rate and dilatant fluid which is increasing with shear rate show non-linear behavior and the reason that CPM value is normally higher than viscometry method is that fine wax crystal is formed when there is cooling process present. Also, these forming wax crystal process is found earlier than the WAT of viscometry method which there is sharp changing of viscosity of the oil (Kok, Létoffé et al. 1996).

2.1.3 Wax deposition mechanisms

Normally, there are 4 kinds of wax deposition mechanisms that have been proposed by the researchers which compose of molecular diffusion, gravity setting, Brownian diffusion and shear dispersion (Theyab, 2018).

These mechanisms assumed that the oil flowing regime is laminar flow which flows through the pipe wall. As there is cooling process caused by surrounding environment, there is a temperature gradient which the highest temperature is at center of the bulk oil while the lowest temperature is at the location near the pipe wall. If anywhere of the bulk oil temperature is lower than wax appearance temperature (WAT) which is the highest bulk oil temperature that wax precipitates out of the crude oil. It results in concentration gradient of wax which is dissolved wax in the crude oil reaches to the pipe wall at lower temperature. Then, the wax in the crude oil will dissolve out of the crude oil. Then, there will be equilibrium between solid phase and liquid phase after a period of precipitation.

There are 2 stages of wax deposition. First, gel is formed and entrapped the crude oil, gel, water, gum which depend on crude oil composition. While aging process traps oil in the wax formation causing the diffusion of wax molecule in the deposit, the counter-diffusion diffuses oil out of the gel formation as shown in Figure 2.4. There are certain carbon numbers of hydrocarbon that can be precipitated if the value of carbon number is beyond which the stable wax crystal can form the gel formation. And others hydrocarbon will be trapped in the wax formation. Thus, in the gel formation, the carbon number below the critical number decreases and another one increased is carbon number beyond the critical number resulting in reducing the trapped oil and harden the wax formation. This process is called aging. For aging process, the molecular diffusion is the dominating the process (Theyab, 2016).

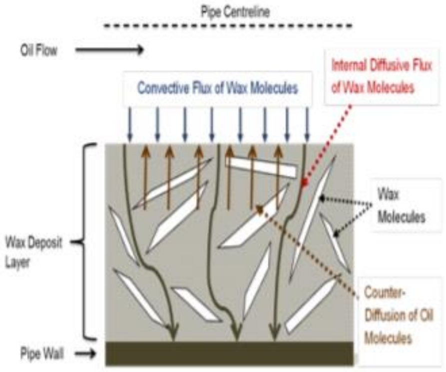


Figure 2.4 Mechanism of molecular diffusion (Theyab, 2016)

For the Fick’s law of diffusion, the rate of wax deposition can be determined as following equation

$$\frac{dM_w}{dt} = p_w D_W A_W \frac{dC}{dT}\frac{dT}{dr} \tag{2.4}$$

dMw/dt (kg/s) stands for the rate of wax deposited. Pw presents the density of solid wax (kg/m3). While Dw is represented the diffusion coefficient of wax in the oil phase. Aw is area of wax deposition (m2), dC/dT is the solubility coefficient of wax crystal in oil phase (1/°C) and the last one is dT/dr is temperature profile of the cold surface (°C/m). Also, the formular of diffusion coefficient is as following equation;

$$D_B = \frac{RT_a}{6\pi\mu aN} \tag{2.5}$$

R is the gas constant (J/mol.K), Ta is the absolute temperature (K). μ is the dynamic viscosity (cP). a represents Brownian particle diameter (m) and N stands for Avogadro’s number (1/mol).

As the temperature gradient is present in the system due to different temperature between bulk oil and cold surface or in let coolant temperature, this leads higher viscosity of the oil leading to decrease in diffusion coefficient. Thus, after a period of wax deposition, the temperature decreases due to heat loss to the surrounding. From decreasing diffusion coefficient, it confirms that the rate of wax deposition decreases (Theyab, 2018).

Shear dispersion

In the laminar flow regime, the suspended particles move in the direction of surrounded particles with mean velocity which is at the center of the particle and rotating with half of the speed. As the particles with rotated motion reaching to the location near the cold surface which have more wax particles precipitate out of the crude oil leads to higher viscosity, its velocity will be decreased. These rotated particles impact to others surrounding particles to circulate the motion due to its own drag force. Thus, all of influenced particles will rotate and apply the drag force to the wax crystal. Thus, the shear dispersion reduces wax deposition.

If there is two particles present in the system which have low Reynolds number of laminar flow regime, these two particles are out of their original streamline and pass through each other with curve movement and then they will return to their earlier streamline. In other hand, there are a large number of wax particles in the system lie the same phenomenon with the earlier. There are a large number of particles collision. There are lateral motion present in the system and dispersion of wax particle (Theyab, 2018) and the mechanism is illustrate as shown in Figure 2.5.

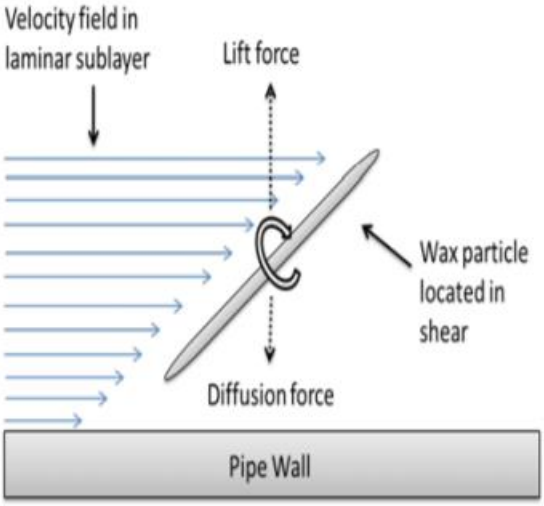


Figure 2.5 Wax particle with rotating motion (Siljuberg, 2012)

Brownian diffusion

As the oil particle is excited by higher temperature in the bulk oil, it is resulting in movement and collision with random motion of the oil particle to the wax crystal due to precipitation with the effect of thermal gradient. If there is concentration gradient, it will result in net movement of wax crystal in the direction of opposite to the molecular diffusion that the net motion will be toward the lower concentration of wax. Its deposition nature expressed as mathematics is the same with molecular diffusion (Theyab, 2018).

Gravity setting

This mechanism dominates wax deposition when there is no flow or in the stock tank and precipitated waxy crystal region has higher density than the fluid phase. The particle will sediment to the bottom of pipe or tank with the starting rate of wax deposition and declining rate of wax deposition. In the end, the rate of wax deposition will be no more. In the oil field, it reveals that these mechanisms can be ignore because shear dispersion results in lateral movement of wax particle and dispersion of wax particle. Thus, there is no wax particle available for setting.

Shear dispersion governs the wax deposition phenomenon by lateral motion of the particle in the case that there is the presence of the flow which also called shear flow. Also, shear dispersion is the main mechanism if the temperature is lower than cloud point or wax appearance temperature (Fasano, 2004).

However, in the turbulent flow regime, shear stripping governs the wax deposition and also, there shear forces is higher than laminar flow. Also, shear force leads to the reduction of wax deposits resulting in lower velocity and deposition thickness. Thus, both of these two wax deposition mechanisms have ability to support wax inhibitor performance (Ragunathan, Husin et al. 2020).

2.1.4 Factors affecting wax deposition

Pressure

During the production, it is normal for reservoir pressure decline as time passes and the light hydrocarbon fraction which acts as wax solution in the crude oil is likely to produce first. Thus, the solubility of oil is reduced. The wax content will be higher as the pressure drops and WAT also increases. Thus, the region above the bubble point, the changing of the pressure influence wax deposition. Below the bubble point which means it is two phase flow (If it is assumed to be dead oil, there is oil and solution gas in the system), the influence of light hydrocarbon dissolves back to the solution as the pressure increases so that the WAT decreases. The influence of pressure is trivial in the case of stock tank. However, pressure promotes oil solubility leading to lesser wax deposition (Valinejad, 2013).

Temperature differential and cooling rate

The one of main factors that influences to the wax deposition is temperature differential and cooling rate (Creek et al., 1999; Hammami & Raines, 1999). The wax deposition is found only when surface temperature is below the wax appearance temperature. As cold surface or inlet coolant temperature decreases, the wax deposition increases even crude oil temperature is above the wax appearance temperature. As wax deposits on the cold surface with high rate at the initial state, the rate is consequently lower at the later stage (Misra et al. 1995). The reason is that the layer of wax generated from these phenomenon act as thermal insulator. The same concept is used with thermal method to prevent wax deposition which reduces heat loss to surrounding temperature. In other word, it maintains the oil temperature. Thus, this lowers thermal gradient for molecular diffusion. Thereby, wax particle available for deposition becomes lesser. The size and number of wax crystals are also one of factors effecting of wax deposition. Higher cooling rate leads to smaller of wax crystal with large number of wax crystals formed because there are large number of wax crystals available. While the cooling rate is lower, more uniform of wax crystals is formed which lead to smaller surface area and free energy. The higher temperature difference also influences both higher and lower melting wax crystal in the porous with full amount of oil (Theyab, 2018).

Crude oil composition

Oil composition is one of influence factors (Sighal et al., 1991) of wax deposition for viscoelastic and yield stress properties which result in effect of pour point and viscosity. The issues caused from this oil composition are as following; the light hydrocarbon fraction like methane, ethane and propane causes hydrate formation which causes high pressure at the lower temperature. In the higher molecular weight cases, there are changing phases of alkane and iso-paraffin from liquid phase to solid phase to macro crystalline and micro crystalline solid. Also, the concentration of paraffin, light end and nucleating in the crude oil influence wax deposition (Zerpa, 2011).

Flow rate

In the laminar flow regime, wax deposition increases with an increase in the flow rate because there are more particles passing through on one location. Thus, there are more possibilities for wax particle deposit due to higher concentration on the inlet coolant. On other hand of turbulent flow regime, the higher flow rate decreases wax deposition because of shear dispersion governed in the turbulent flow which its definition of Reynolds number is greater than 2000. With shear dispersion and higher flow rate, wax crystal with higher shear is broken into small crystal. Also, lesser wax crystal causes chaotic flow of turbulent flow as show in Figure 2.6. Thus, it leads to the reduction of wax deposition due to the lowering adhesion to the pipe wall. The higher flow rate leads to higher influence of shear dispersion resulting in firm attachment of wax crystal on the pipe wall which leads to more compact and harder and it is hard to remove wax deposit (Bott et al, 1977). The low flow rate generates the issue because of the longer time of the oil in place which mean there is higher heat loss to the surrounding. Thus, it leads to higher amount of precipitation of wax particle and also, wax deposition. Thus, the recommended minimum flow rate to perform lab experiment is 0.56 ft/sec (Theyab, 2018). In addition, the deposit thickness of turbulent flow condition is lesser than laminar flow up to 60%. (Santos et al., 2021).

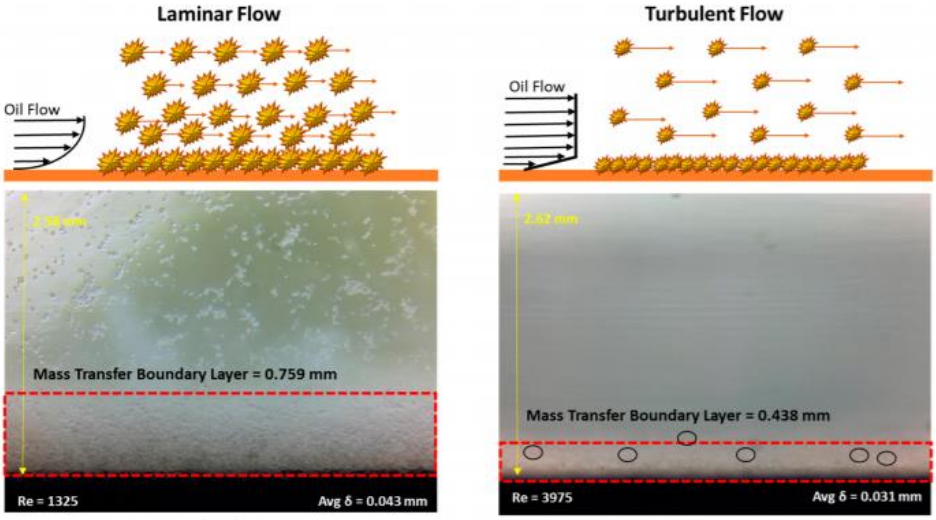


Figure 2.6 The deposition thinness for turbulent condition in the left-hand side and turbulent flow for right hand side with Temperature of bulk oil = 37.8 C and Inlet coolant temperature = 31.3 C (Santos et al., 2021).

Experimental time

The one of most influenced parameters for wax deposition is wax deposition inside the pipelines (Kasumu, 2014; Noville, 2012). For laboratory experiment, the thermal steady state is found in less than 30 minutes under laminar flow condition. While turbulent flow condition is 21-24 hours after start to perform. The amount of increment wax deposition is considered insignificant to perform after the time passing 4 hours because most of wax deposit on the pipe wall. During two hours after beginning to perform the wax deposition experiment, most of wax particles deposit on the inlet coolant after that there are reduction of wax deposition because of lesser paraffin content in the crude oil. On the other hand, it is found that wax deposition increases with the time. Assumed that wax deposition deposits one place, the fresh oil deposits on this place coming after another because of oil production. Even though, oil content changes with production time because light particles come out of reservoir first while heavier fraction leaves out of reservoir later but it does not change mush compared to laboratory oil which the same bulk oil continues to deposit on the inlet coolant at the point of the time. For the fresh oil of the oil field, it grants a great opportunity for wax deposit on the pipe wall (Theyab, 2018). Santos et al. (2021) studied about the effect of the time and wax deposition with visual observation of flow dynamic and deposition. Also, the sample used to perform the experiment is Exssol D-60 mineral mixed with CSP-165 food grade wax. The result shows that wax deposition rate is declined as time progresses as shown in Figure 2.7.

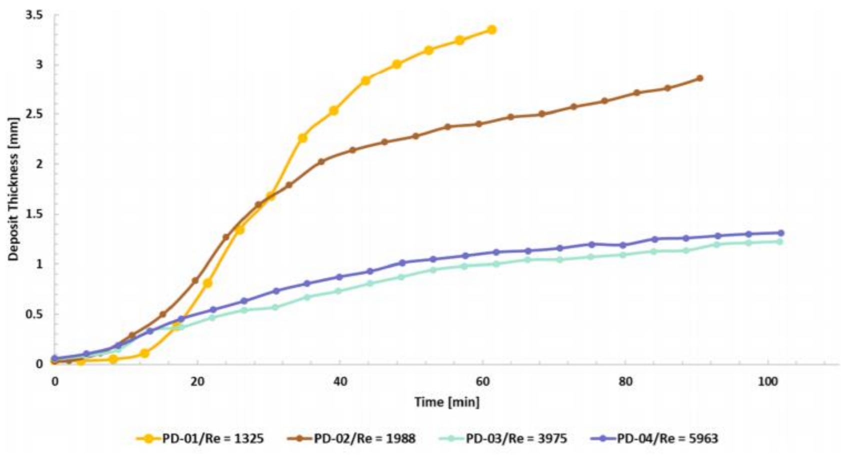


Figure 2.7 The decline rate of wax deposition as the time progress

(Santos et al., 2021)

Pipe surface properties

Wax deposition deposits on the pipe wall and wax crystal adheres to the pipe surface by its roughness. Also, it is not from the metal itself. As the paraffin wax deposits on the surface, there is absorption force which depends on free energy of both paraffin and surface. Despite no direct actual correlation between absorption and the roughness, adhesion bond should relate to total surface area and surface roughness and the temperature difference between wall and fluid. Another factor is low friction of internal pipe leading to decrease wax deposition. The cohesive force plays the minor role for wax crystal adhered to the pipe wall while adhesion force is at least equal or greater than the first one (Theyab, 2018).

Polar crude component

The hydrocarbon with polar fraction which are asphaltene, resin and aromatic is considered to be cost effective flow improver. Asphaltene function is not only phase separation of waxy crude oil by gravity setting and also reduce gelation temperature. However, the mechanism of interaction between polar asphaltene with wax molecule is not totally comprehend (Ragunathan et al., 2019).

2.1.5 Control and remediation

For controlling and remediation management, 3 method of the management is shown in Figure 2.8.

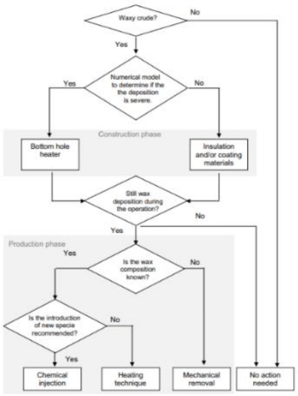


Figure 2.8 The step for making decision to choose the suitable wax deposition management method (Sousa, Matos et al. 2020)

The mechanical method

The mechanical method is straight forward method to remove paraffin wax deposit on the pipe wall by using mechanical devise which are scrapper and cutter (Sousa et al., 2019). The cutting function is cut the deposit in the tubing and this cutting deposit is reached to the surface by production fluid and another one is scrapping and take the deposit out of the tubing. Figure 2.9 and 2.10 illustrate the scraper and pigging.

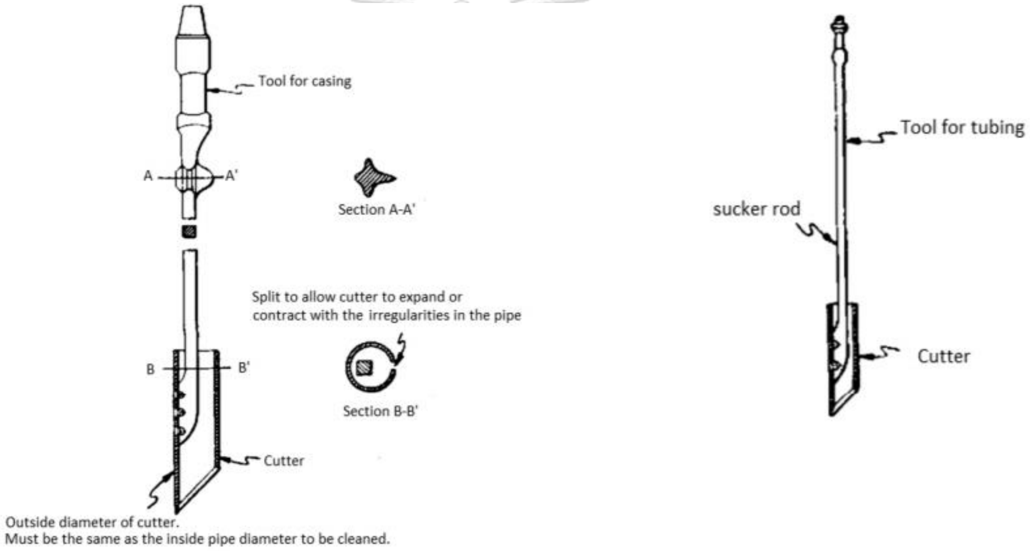


Figure 2.9 The left cutting for the casing and right cutting for the tubing which can operate without interfere the hydrocarbon production (Sousa, Matos et al. 2020).

After utilizing the mechanical method with cutting or scrapping, it turns out that the possibility for wax deposition is higher because the roughness of the pipe wall metal is higher due to contract between these two and pipe wall. These is also the risk that wax plug because of cumulative of scraped wax. Also, chemical soak can be utilized with mechanical method to solve hard deposit case (Sousa, Matos et al. 2020).

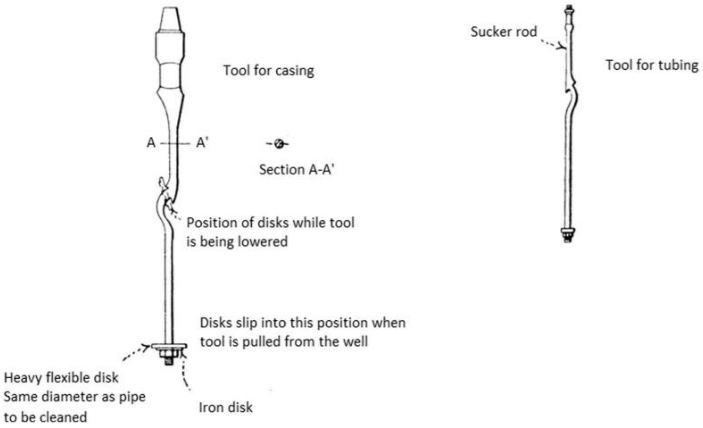


Figure 2.10 The scrapping with hook which the left is for casing and the right is for tubing (Sousa, Matos et al. 2020)

Figure 2.11 shows the deposit distribution of the pipe earlier and during the pigging at the negative temperature difference. It shows that the deposit is found at the bottom part of the pipe (Yang, Lu et al. 2020).

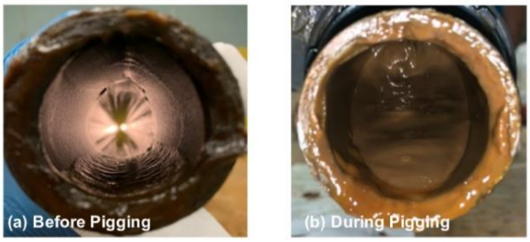


Figure 2.11 The image of deposition distribution inside the pipe before and during pigging. T_{bulk} oil is equal to 94.5 F and T_{inlet} coolant is equal to 98 F with Reynolds number is equal to 4000 (Yang, 2020)

However, the mechanical method may generate issue. If there is wireline break, the scrapper will be inside the well (Sousa, Matos et al. 2020). This method appears to be unfeasibility if it is required to operate this mechanical method regularly. In the industry, it is preferred to use hot oiling rather than this method because the effectiveness of hot oiling is higher than mechanical method for 67% g (Khandekar, 2015).

The thermal method

The main purpose of this technique is to maintain and supply heat in order to dissolve the precipitated wax back into the bulk oil and promote the flow assurance of hydrocarbon fluid from the tubing reaching to the surface. However, it should control the heat generated to rise the oil temperature because the temperature beyond flash point results in petroleum coke.

Others than using the bottom-hole heater, the others two method is hot oiling and stream circulation. For hot oiling, the produced oil is heated and injected back into the well. The light hydrocarbon fraction evaporates during the heating process. Thus, this process lowers the gross value of produced oil. As injecting the hot oil, the heat will lose to the surrounding during the oil flowing from tubing to casing. If the high waxy crude oil temperature is below the WAT, the wax deposition is present. Other components which can deposit are clay, iron sulphide, iron oxide.

Another method of thermal method is hot water circulation. Because of the greater heat capacity of water comparing to the oil at the same temperature, it becomes a low-cost medium to transfer the heat to the waxy crude oil in the well. Another advantage of utilizing method is that there is no contamination within the water (Khandekar, 2015).

The disadvantage of this method is the lack of solvent ability and also requires surfactant to disperse wax into the stream. Also, the surfactant needs to contract with waxy particles. Unless, the mixture will generate a large amount of water-wet wax particle. To ensure flow ability by avoiding emulsion, a large amount of demulsifying agent is needed to be added in to the well for two-phase flow.

The next method is injecting steam into the wax formation, the steam is injected to the place between tubing and casing. This method is required to the location below the lowest point of accumulative deposit in order to heat the oil with 55 to 65 °C. The time for steam taking the effect is 3-6 hrs and the injecting pressure is higher than formation without damaging the formation and causing the emulsifying issue. Moreover, it requires to stop the production to perform this method and this method is not economical or practical comparing to utilize scraper of mechanical method. All of the thermal methods show that there is no long-term advantage for wax deposition prevention (Straub et al, 1989).

The chemical method

For wax deposition prevention, the chemical method is the preferred method in the industry. There are 4 kinds of these chemicals which are dispersant, crystal modifier, solvent and surfactant. Dispersant is used for dispersing the precipitated particle. Also, the solvent function is for dissolving the paraffinic wax. Crystal modifier alters wax crystal morphology and size and also the growth of the crystal. Also, it changes rheological properties such as viscosity, yield stress and pour point of crude oil. Because of various composition in the waxy crude oil, there are no exact universal chemical. Thereby, each individual crude oil has to be specifically designed for suitable inhibitor with concerning about the formation and reservoir condition. Also, the environmental safety to ensure that there is no toxic effect from inhibitor have to evaluate to avoid potential hazard (Bimuratkyzy, Sagindykov et al. 2016).

2.2 Wax deposition prevention by chemical method

Among the three wax deposition control and radiation methods, the chemical method is the favorite choice for the industry because of limitation of others methods (Aiyejina, 2015)

2.2.1 Wax dispersant

Because of adhesion force which related to both surface roughness and wax crystal free energy stated earlier being the main factor for wax attach to the pipe wall surface, wax adhesion force reduction caused by surfactant covers on the pipe surface. The surfactant changes wettability of pipe surface or forms the layer resulting in wax deposit. This is the mechanism of shear dispersion for laminar flow and shear stripping for turbulent flow.

It is not only covering to the pipe surface but it also absorbs into the wax crystal structure. Later, these crystals with wax dispersant will form 3-D structure. The effect of this chemical is reducing the growth crystal morphology by altering of wax crystal shape from spherical to plate structure and also 3-D network formation which leads to promote the fluid flow ability (Jafari Ansaroudi, Vafaie-Sefti et al. 2013). The effectiveness of wax dispersant is only using this inhibitor without polymer inhibitor because polymeric inhibitor characteristic prevents the wax from setting and depositing at the cold surface.

Some of surfactants with the effect of presence of water which are sulfonates and fatty amine ethoxylates also exhibit the wax dispersant. Wax dispersion effects which are interaction between wax particle and hydrophilic group of surfactant lead to smaller size resulting in prevention of wax agglomeration and deposition (Ahmed, 2018; Maithufi, 2011).

2.2.2 Pour point Depressant (PPD)

Wax deposition reduction of this chemical is resulting in van der Waal forces and co-crystalizing with wax crystal which modify size and shape of wax crystal. Its advantages are cost effective for flow assurance in the hydrocarbon production (Wang et al., 1999).

Also, their characteristics of PPD are described as following; 1. the non-polar part which is alkyl chain with carbon number ranging from 14-25 exhibit wax-like part so in order to co-crystallizes with waxy oil. 2. the polar part which has opposite effect to wax crystal inhibits the progress of crystallization. 3. polymer which causes sterically hindered to control the size of crystal (Wang et al., 1999) and PPD can be shown in Figure 2.12.

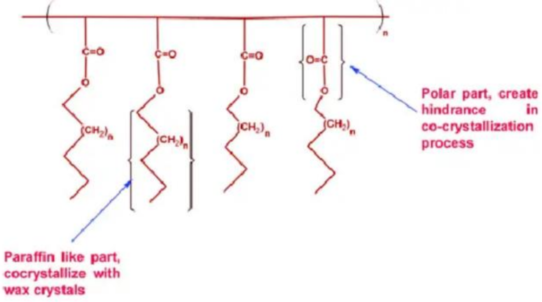


Figure 2.12 The PPD structure (Hemant et al., 2008)

The sterically hindered effect of polymer obstructs the interlocking between wax crystals to form the network of wax crystal. Thus, smaller size and changing shape are more unfavorable to wax crystallization resulting in pour point reduction (Hemant et al., 2008). Thereby, it weakens the wax formation and promote the effective of wax removal by shear force. It does not affect on WAT reduction because crystallization does not impede with this inhibitor. In other words, it retards the growth of wax crystal (Huang, 2015). That means as this inhibitor absorbs into the molecule, it will prevent other wax molecules to attach further.

Poly vinyl acetate or EVA is the most used PPD in the industry. There are two processes of wax deposition reduction mechanism. The polar group of EVA is VA which comprises of two active oxygen atoms. The increment of solubility comes from these two active atoms interacting with long chain paraffin resulting in the van der Waal force leading to gel strength reduced. Thereby, this phenomenon causes reduction of wax deposition (Taiwo et al., 2019; Ridzuan et al., 2019) and another mechanism is non-polar part, alkyl which interact with long chain paraffin wax. According to the non-polar part mechanism described earlier, this results in changing wax crystallization process with size and shape and also pour point reduction (Yang, Zhao et al. 2015).

The comb polymer is another type which can divide further into two polymer groups. The first one is Maleic anhydride copolymer (MAC) and the other type is polyacrylate methacrylate (PA or PMA). For the optimum effect on wax deposition prevention, the length of comb polymer chain should be alike to wax crystal. There is no effect of polyvinyl backbone. However, the modified backbone influences polymeric structure which has function for pour point and crystallization reduction (Sivakumar, 2012) and the mechanism of comb polymer to the paraffin and asphaltene is shown in Figure 2.13.

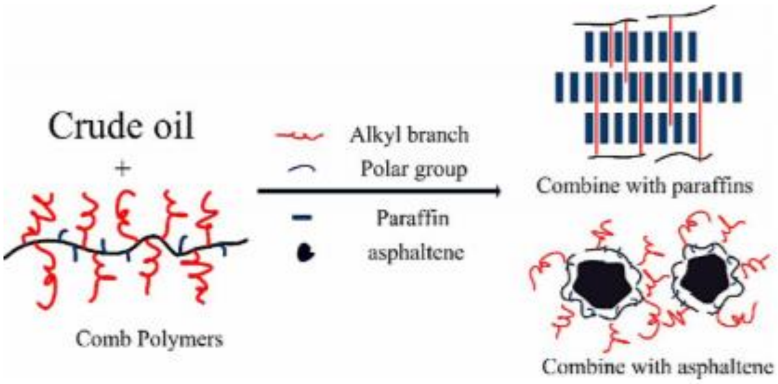


Figure 2.13 The mechanism between comb polymer

with both paraffin and asphaltene (Na li et al., 2017)

The longer chain of alkyl in the all comb polymers which are MAC, PA, PMA has higher effect to wax crystal size reduction than small chain because the longer chain results in more solubility of copolymer. Thus, the measured pour point reduction in the case of using concentration with 10000 ppm is from 27°C to -3°C.

MAC is not only pour-point reduction inhibitor and also lesser deposition rate and yield stress of wax gel. If the comb polymer is not suitable with paraffin chain length, there is no the effect for preventing interlock of wax crystal. For the wider range of paraffin chain and low carbon number, it is recommended to use the high molecular weight copolymer. While the short range of paraffin chain has high carbon number, it is recommended to utilize low molecular weight of polymer (Li et al., 2012).

PPD is reported to be limited for wax inhibitor performance. To eliminate this limitation with increasing interest among researchers on nanotechnology which have potential as wax deposition inhibitors, the mechanism of nanoparticle can change the nucleation site and also crystal growth. Thus, its effectiveness is higher than using only EVA (Wang., 2011).

The combined effect of PPD with utilizing organic solvent is that the viscosity reduction promotes flowability. An example of organic solvent is as following; xylene, toluene based chemical. Bello (2006) studied the use of Trichlotoethylene-xylene(TEX) mixing with Nigerian crude oil. With 0.1 %wt of TEX, there is some effect of WAT reduction and reduced from 0.050 to 00015 g/g for wax deposition reduction. However, the safety has to take into account because of toxicity of these organic solvent and also flammability of low flash point (Straub et al., 1989; Woo et al., 1984).

To find the suitable effect of chemical inhibitor with Malaysian oil, Ridzuan et al. (2016) perform the comparative study with various inhibitors such as poly (ethylene-co-vynyl acetate) of EVA, cocaminde diethanolamine (C-DEA), poly (maleic anhydride-alt-1-octadecene or PMAO and cyclohexane. The wax deposition is evaluated by cold finger method and viscosity method. The results show that EVA exhibits the highest effectiveness of inhibitor upon wax deposition reduction by minimum amount of wax deposit.

Wei et al. (2016) studied about utilizing the novel wax is star-like crystal modifier derived from β-cyclodextrin and performs the experiment. The result is that this type of crystal modifier can effectively reduce wax deposition and crystal size with yield stress reduction in the highly waxy oil.

2.2.3 Wax crystal modifier

In the nucleation process, wax crystal absorbs the wax crystal modifier in order to change the growth. The surface behavior of wax crystal results in forming micelle-like aggregate. Thus, the small nuclei with lower the supersaturation of crude oil resulting from the micelle-like aggregate leads to form smaller wax crystal and is stable. In addition, the possibility of forming 3-D wax crystal is diminished to form 3-D network so that the pour point decreases (Marie, 2005; Naiya, 2015) and the interaction between wax crystal modifier and wax crystal are shown in Figure 2.14.

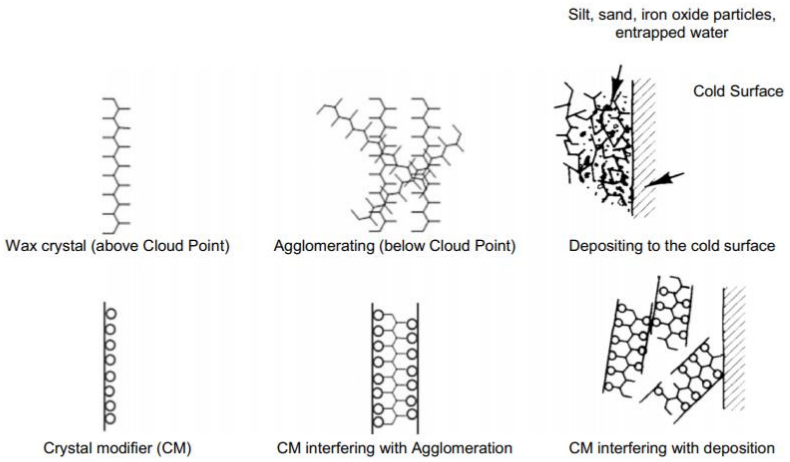


Figure 2.14 Co-crystallization of wax crystal modifier and wax crystal (Wei and Technology 2015)

Wei (2015) stated that wax crystal modifier promotes the pour-point reduction by altering wax morphology to be spherulite shape. Thus, the pour-point is decreased. There are several examples of wax crystal modifiers which are crystalline amorphous structure such as polyethylene butene (PEB) and polyethylene butene, poly alkyl methacrylate, methacrylic acid ester (Ashbaugh, 2002).

2.2.4 Solvent

This type of chemical function is for dissolving of the precipitated wax. The oldest method of wax management is using benzol, gasoline and kerosene within the well. The solvent cost is the parameter to determine suitability of solvent. Moreover, the solvent can be getting back in the form of crude oil but the gross profit when using the solvent should be subtracts with total solvent cost. The disadvantage of this method is that it can only apply to the well with pumping but it is found difficulty for injectivity of solvent to the well with natural flowing well (Straub et al., 1989).

Straub et al. (1989) performed the comparative experiment to test various solvents which are xylene, diesel, toluene, oil and kerosene. The results reveal that xylene has superior effect upon dissolvability of the paraffin wax comparing to other chemicals. The reaction between solvent and wax particle depends on paraffin wax, solvent type and temperature. For low asphaltene fraction in the waxy crude oil, the solvents utilized as solvent are kerosene or consolidate.

2.3 Emulsion

The emulsion is the homogeneous mixture of two immiscible fluid which are oil and water coupling with emulsion and shear force applied by fluid flow. Because of droplet-droplet interaction within the emulsion, the viscosity is higher than single phase of both oil and water (Bai, 2005).

Some studies conclude that the effect of brine does not have any effect to wax deposition condition experiment. With various mixing speeds as preparing the emulsion, brine has the similar deposition which mean whatever speeds and brine solution with the same water cut have ability to comparable properties and do not interfere the deposition with the parameter range.

Visintin et al (2008) used the crude oil with high paraffin fraction with 8% distilled water and 2 %wt. of NaCl. The size distribution is measured by Lasentec FBRM and Rheological measurement is determined by using a controlled strain rheometer. The result shows that there is the certain water cut percentage which promotea the gel formation led to increment of pour point and the yield strength. Also, at the fraction of water above threshold, the emulsion distinguishes from crude oil which is found that pour point and yield stress increased abruptly as shown in Figure 2.15.

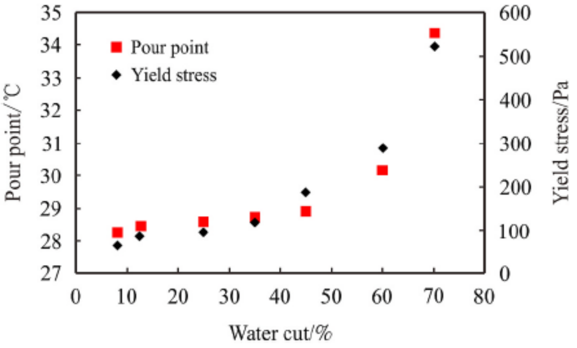


Figure 2.15 The effect of water content on both yield stress and pour point (Visintin et al, 2008)

Other researchers study also support Visintin’s work in that the presence of water results in increasing pour point and yield stress which promote the gel formation and the explanation of this behavior is the 3D network formation between waxy crude oil and water (Paso et al., 2009; Olivera et al., 2010)

Bruno et al. (2008) performed the flow loop of both South Pelto crude oil and Garden Banks condensate deposition test and phase inversion test. The results show that water cut increases with the decrease in deposit thinness. Moreover, the water content in the trapped deposit has lower content than original water cut of bulk emulsion. Moreover, the result of phase inversion illustrates that the viscosity of oil-in-water emulsion increases as water cut increases until it reaches to the certain points after that the viscosity drops sharply due to phase inversion which the emulsion changes its type from water-in-oil emulsion to oil-in-water emulsion and the phase inversion determination is shown in Figure 2.16.

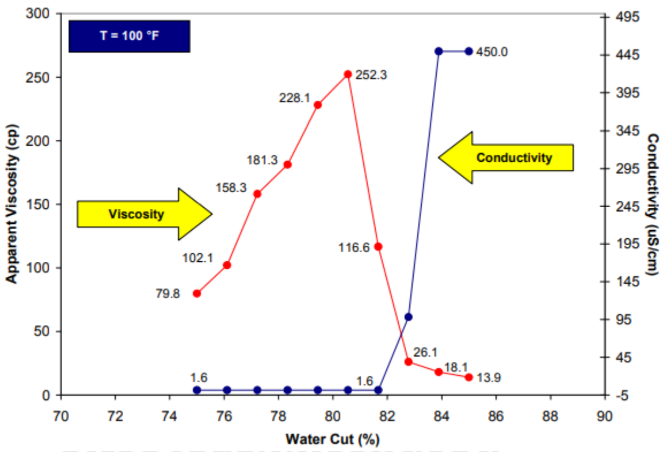


Figure 2.16 Phase inversion of South Pelto emulsion (Bruno et al., 2008)

Moreover, at high water cut, the deposition is found as very thin and hard deposit. Thus, this suggests that available diffusion mechanism is not enough to explain crude oil at high water cut.

Zhang et al (2010) stated that WAT increases with increase in the water cut until one threshold and WAT will be decreased. However, there is no explanation for this phenomenon yet.

Piroozian et al., (2016) support the effect of water in waxy crude oil leading to increase in WAT by performing the differential scanning calorimeter with emulsion from Terengganu crude oil.

2.3.1 Viscosity of emulsion

The viscosity of emulsion is normally greater than that of single phase because rheological properties of emulsion exhibit non-Newtonian behavior because of droplet within the emulsion.

The main factor influences to the viscosity of emulsion such as temperature, concentration, viscosity of disperse phase, viscosity of continuous phase, average droplet size. The one of the most important factors affecting on the viscosity is water cut because dispersed phase of emulsion results in non-Newtonian behavior and another important parameter is temperature (Juntarasakul 2015).

Rønningsen (1995) performed the viscosity experiment and correlation with water-in-oil emulsion from North Sea crude oil and the result reveals that viscosity increases with decreasing of shear rate and temperature. While the water cut is direct variation with viscosity.

2.3.2 Effect of shear rate on emulsion viscosity

For non-Newtonian behavior, the viscosity is also the function of shear stress. Also, non-Newtonian behavior can be further divided into shear thickening and shear thinning. For shear thickening, the viscosity increases with shear rate increases. For shear thickening, the viscosity decreases with shear rate increases.

2.3.3 Effect of cold finger temperature

For flow loop and cold finger, these two methods are designed to evaluate the wax deposition. The disadvantage of flow loop is to utilize the experiment with a lot of crude oil and effort. On the other hand, the cold finger method needs small amount of crude oil. Thus, this method is preferred among the researchers (Jennings, Weispfennig et al. 2005).

The cold finger experiment is the experiment consisted of generated cold surface equipment. This equipment normally comprises a chamber which cooling fluid can flow in and out (KENNETH, NORRIS et al. 1960).

Wax deposition test with cold finger apparatus normally consists of an oil tank and two water baths and the 1st water bath supplies the cold flow to the cold finger while 2nd water bath controls the bulk oil temperature. Thus, this leads to the temperature difference between cold surface of cold finger and the bulk oil and the apparatus in shown in Figure 2.17 (Kaifeng et al., 2015).

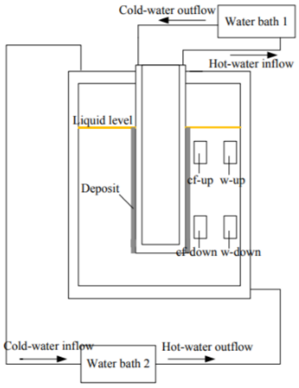


Figure 2.17 Cold finger apparatus for wax deposition test (Kaifeng et al., 2015)

In the case of maintaining temperature difference to be constant with the same water cut, the wax deposition decreases with an increase in temperature of the bulk emulsion. In addition, the greater temperature difference with the same water cut leads to increase wax deposition (Zhang, Gong et al. 2010).

2.4 Literature review

Jenning and Weispfenning (2005) performed the experiment to measure the wax deposition by cold finger apparatus with the thermal and shear rate effect and the result is that the higher temperature difference between inlet coolant and crude oil leads the greater wax deposition. Also, shear rate is direct variation with concentration of wax leading to increase wax deposition rate.

Hoffmann and Amundsen (2013) study reveals that wax inhibitor with various concentrations can reduce the frequency of using the mechanical method. The result of this study shows that the efficiency of wax inhibitor for wax deposition reduction is from 60% to 90% coupling with inhibitor concentration. In other word, the high concentration can yield the better performance comparing to optimal concentration.

Udourioh et al. (2014) performed WAT measurement following with ASTM/IP with Nigeria delta crude oil with the effect of single solvent and n-alkane solvents of n-pentane, n-hexane and n-heptane. The result reveals that wax precipitation decreases as increasing carbon number of n-alkane solvent.

According to Min (2018), the experiments are pour point, WAT and wax deposition measurement. For WAT measurement, the crude oil from Fang is measured with and without the inhibitor. The temperature is cooled from 75 °C to 35 °C at all three shear rates (6 s^{-1}, 12 s^{-1} and 24 s^{-1}). For cooling rate, it is set to be 12 °C /hour because detection delay of WAT occurs at the higher cooling rate. The temperature range is following by reservoir temperature. Also, the shear rate is lower than 100 s^{-1} because crude oil is shear thinning (Rønningsen et al., 1991). Pour-point measurement method follows the ASTM D5949. Wax deposition experiment utilizes cold finger method which the cold surface is copper rod with cock above the tube containing the sample. The result of this study is that n-heptane has ability to reduce pour point, WAT and wax deposition. In addition, crystal modifier which is poly (maleic-anhydried-alt-1-octadecene) or PMAO has an effect of pour point, WAT and wax deposition reduction and it is concluded that the best inhibitor combination of n-heptane and PMAO are 10%wt and 5000 ppm.

Aye (2019) follows Min (2018) with the correlation of WAT as gap of the research. The results show that an increase in the amount of n-heptane as inhibitor results in pour point, WAT and wax deposition reduction. Also, increasing shear rate results in decreasing WAT.

Juntarasakul (2015) performed viscosity measurement and oil correlation with its emulsion from Fang oil field. Light microscope is utilized for droplet size distribution and viscometry measurement is used with LVDV2T. The conclusion of this study is the most influence parameter for viscosity of oil and its emulsion is temperature as it compared to water cut and shear rate. The greater viscosity is caused by the higher water cut because the more presence of water droplets. Also, shear rate increases with and decrease in viscosity because the oil exhibits non-Newtonian fluid. For stability, higher temperature leads to the larger of droplet size. Thus, the stability of emulsion is less. Also, high water cut results in smaller droplet which make the emulsion more stable.

2.5 Research Gap

From the literature review, it shows that there is no investigation about effect of emulsion on wax deposition of the crude oil from Fang oil field. In the oil field, there is the presence of water produced with hydrocarbon fluid resulting in emulsion formation. To cover wax deposition with effect of emulsion, it requires to explore this point of view.

CHAPTER 3

EXPERIMENT

3.1 Materials

3.1.1 Oil properties

For this study, oil sample is collected from Mae Soon area, Fang oil field, Northern oil field of Thailand. At the 60°C the measured viscosity and density of the crude oil are 33.51 cp and 0.815 g/cm^3, respectively (Min, 2018). The component of crude oil is analyzed by Intertek and the composition of crude oil ranges from C1 to C35$^+$ as shown in Table 3.1.

Table 3.1 Composition of oil sample from Fang oilfield analyzed by Intertek

Component	Percent by weight (%)
n-C	0
n-C2	0
C3s	0
i-C4	0
n-C4	0
i-C5	0.19
C5s	0.55
C6s	0.92
C7s	2.29
C8s	2.97

C9s	3.83
C10s	3.51
C11s	3.78
C12s	3.7
C13s	3.4
C14s	4.44
C15s	5.59
C16s	3.74
C17s	4.1
Pristanes	1.44
C18s	3.23
Phytanes	0.42
C19s	3.39
C20s	3.91
C21s	3.85
C22s	3.59
C23s	3.68
C24s	3.17
C25s	3.39
C26s	3.2
C27s	3.19
C28s	2.91
C29s	2.82
C30s	3.13
C31s	2.76
C32s	2.29
C33s	1.78
C34s	0.9
C35s plus	3.94
Total	100

3.1.2 Wax inhibitors

For the wax inhibitors of this study, poly (maleic anhydride-alt-1-octadecane) or PMAO and N-heptane are utilized illustrated in Figure 3.1.

Figure 3.1 Wax inhibitor and distilled water

3.2 Experimental equipment and procedure

3.2.1 Emulsion preparation

The preparation of emulsion is performed by mixing oil and water respected to water volume fraction or water cut in the sample with constant speed of electric mixer for 15 min.

3.2.2 Pour point measurement

Pour point test equipment

The experiment is conducted test tube with cork coupled with Thermocouple data logger model KTT 200 in order to measure the temperature and thermocouple J-Type with ± 0.4 °C accuracy. The controlling temperature bath is performed to control the sample temperature to the research temperature and the pour point measurement apparatus is illustrated from Figure 3.2.

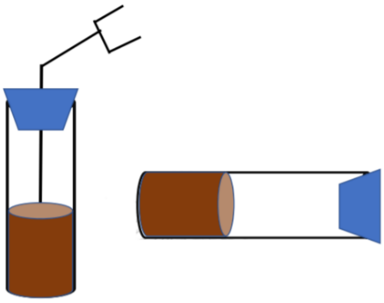


Figure 3.2 pour point apparatus (Min 2018)

Experiment procedure of pour point

ASTM D 5853-11 method is used for pour point evaluation and procedure is as follows. Firstly, the minimum temperature to melt the oil sample is 20 °C beyond the pour point. Secondly, the emulsion is prepared by mixing oil and water by electric mixer. After that, 15 cc of sample is poured to the tube. Then, the test tube is closed with the cock with probe and thermocouple. Next, the testing tube is hanged by cramp of the sand and immersed the tube into the water bath. Later, the sample is reducing its temperature for 3°C each time to observe its rheology of the sample. The test tube is tilted horizontally to see the movement of the sample. If the movement of the sample start to move slowly. The temperature is reduced 1°C each time next experiment. If there is no movement of the sample after horizontal tilting for 5 seconds, that temperature is recorded as pour point temperature.

Experiment condition of pour point

The experiment is performed with various conditions at concentration percent by weight varying 0%, 5%, 10%, 15% and 20% in case of n-heptane, while poly (maleic anhydride-alt-1-octadecane) concentration is from 0 ppm, 2500 ppm, 5000 ppm and 7500 ppm. Also, emulsion is from 0%, 20%, 40%, 60% and 80% to investigate the full effect of pour point reduction.

3.2.3 Wax appearance temperature (WAT)

Viscometry method is used for WAT measurement to determine the viscosity at each temperature with specific shear stress.

Wax appearance temperature equipment

Julabo F26 model water bath with ± 1 accuracy with glycol as media is used to control the temperature. Also, the measurement of viscosity is performed by Brookfield viscometer DV2TLV using conical spindle which its number is 52Z. This spindle can measure viscosity from 4.6 to 92130 cp and viscometer and Julabo water bath is illustrated in Figure 3.3 and Figure 3.4, respectively.

Figure 3.3 Brookfield viscometer LV DV2T model

Viscosity calibration

The instrument has to be calibrated before running the experiment with standard solution. The calibration performed with spindle number 52Z. Test period is 90 minutes and recorded every 3 minutes.

Experiment procedure of wax appearance temperature

Firstly, the sample is melted for restoring the liquid state. Next, prepare the emulsion mixture by mixing the oil and water with electric mixer. Then, the sample is prepared with various chemical concentrations which also depends on the types of chemical. Also, the Brookfield Viscometer LV DV2T measures the viscosity with shear rate at 3, 6, 12 rpm. After that, temperature at water bath is set at 70 °C. Next, crude oil sample is transmitted to viscometer cup. By cooling down the sample, the sample viscosity is measured from the setting temperature to the viscometry limit range of each shear rate which range of 3, 6 and 12 are 1550, 3101 and 6202 cp, respectively with cooling rate 12 °C/hour and the result is recorded each time reduced the temperature.

Figure 3.4 Julabo controlling temperature bath

Experiment condition of wax appearance temperature

The experiment condition are performed with various at concentrations percent by weight varying 0%, 5%, 10%, 15% and 20% in case of n-heptane, while poly (maleic anhydride-alt-1-octadecane) concentration is from 0 ppm, 2500 ppm, 5000 ppm, 7500 ppm and 10000 ppm. Also, emulsion is from 0%, 20%, 40%, 60% and 80%. Moreover, shear rate is conducted at 3 s-1, 6 s-1, 12 s-1. In addition, the temperature is from 15 °C above the viscometry limit range of each shear rate which range of 3, 6 and 12 are 1550, 3101 and 6202 cp, respectively.

3.2.4 Wax deposition measurement

To evaluate the wax deposition, cold finger technique is conducted to test amount of wax deposited on the cold surface which this study is u-tube copper rod.

Wax deposition test equipment

The test is performed by the tube which can contain the oil sample inside when it is immersed in the water bath and the u-tube copper rod with the cap which prevent formed water droplet from condensation of air humidity contracting with cold surface of copper rod. In addition, the temperature is controlled by Julabo immersion circulator ME model. Also, the media is water and a probe which use with thermocouple J-Type with ± 0.4 °C accuracy and the wax deposition apparatus is shown in Figure 3.5.

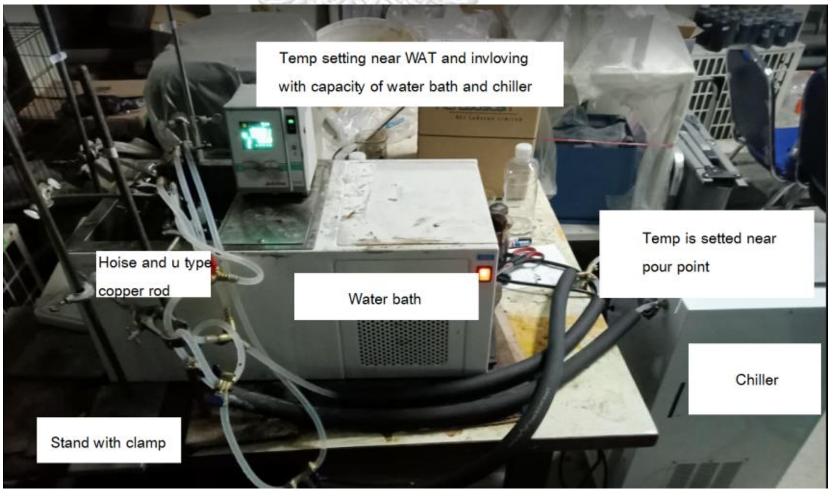


Figure 3.5 Wax deposition apparatus.

Wax deposition test procedure

Firstly, the crude oil is melted down to be liquid state and above the WAT to remove thermal history and make it to be homogeneous mixture. There is no existing wax particles which do not dissolve. Then, the sample which is crude oil and its emulsion is injected into the tube inside the water bath. The experiment is conducted with and without inhibitor. Also, the chiller is set the temperature 20°C, 25°C, 30°C as simulating the working temperature and the Julabo water bath is set the temperature at 50°C which this setting temperature is beyond WAT of the crude oil. The outflow of the chiller which connects with hoist to guide the medium flow to the u-tube copper rod which act as inlet coolant and the u-tube copper rod is immersed in the water bath. After opening the chiller pump with the setting temperature for 3 hours, the wax deposit is drew off from the u-tube copper rod and weigh to evaluate the effect.

Experiment condition of wax deposition

The experiment condition is performed with various at concentration percent by weight varying 0%, 5%, 10%, 15% and 20% in case of n-heptane, while poly (maleic anhydride-alt-1-octadecane) concentration is from 0 ppm, 2500 ppm, 5000 ppm, 7500 ppm and 10000 ppm. Also, emulsion is from 0%, 20%, 40%, 60% and 80%. In addition, the temperature of chiller is from 20 °C, 25 °C and 30 °C. Moreover, the temperature of water bath is 50 °C. Also, the experimental time is 3 hours.

3.3 Methodology

There are 3 main experiments of this study which consists of pour point measurement, wax appearance temperature and wax deposition measurement to satisfy the research objective and the procedure is presented below:

1. Review theory and literature
2. Collect the sample from Fang oil field
3. Set up the equipment and condition which described in the equipment and procedure section
4. Perform the experiment to explore the emulsion on various parameter such as pour point temperature, wax appearance temperature, wax deposition and chemical
5. Analyze and discuss the results

Methodology flow chart of this study is illustrated in Figure 3.6

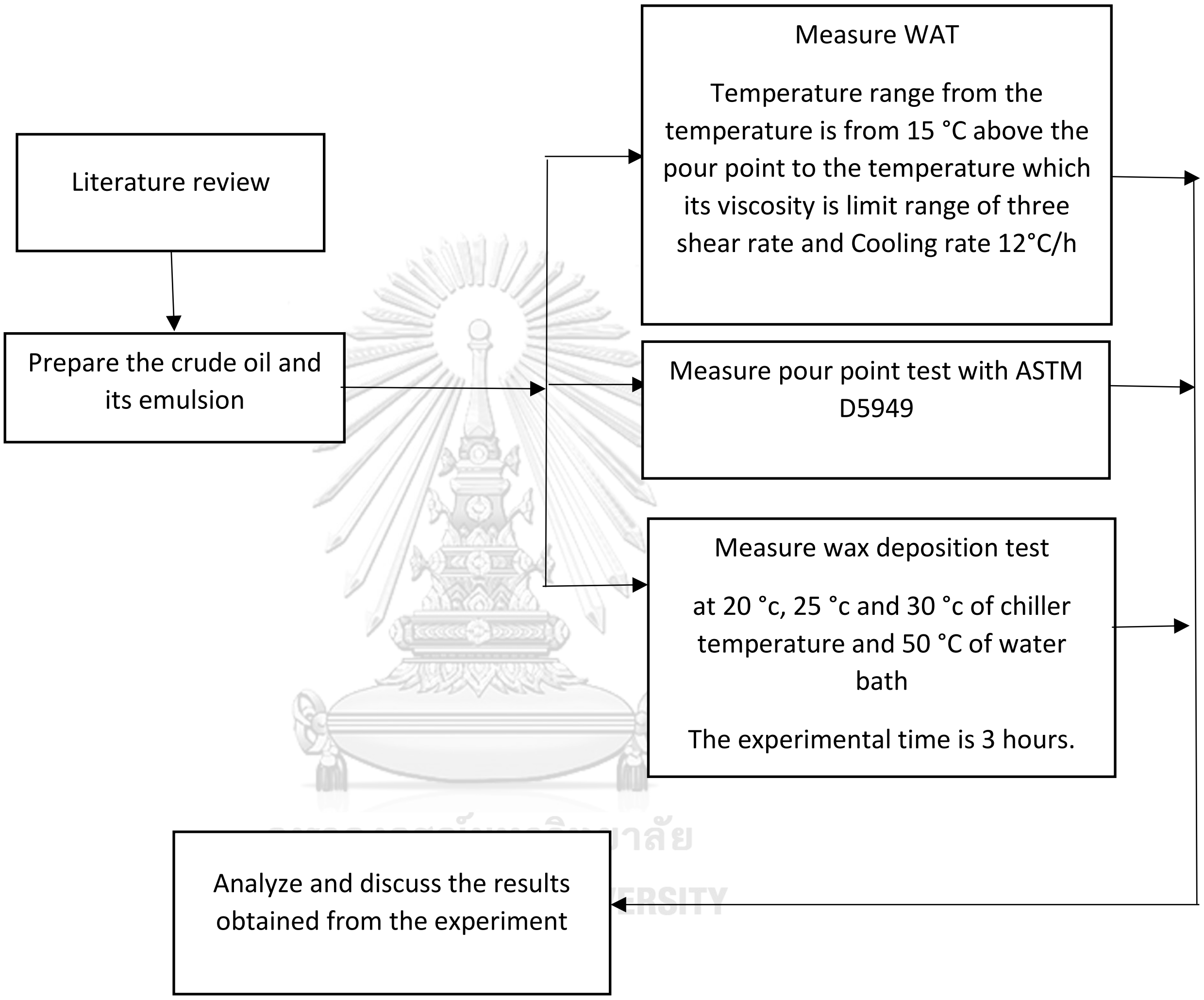


Figure 3.6 The Methodology flow chart

Chapter 4

RESULTS AND DISCUSSION

4.1 Characteristics of crude oil and its emulsion from Fang oilfield

Oil from Fang composes of high wax content as mentioned in Chapter 3. Also, pour point temperature of Fang crude oil is 36.2 °C. To calculate wax appearance temperature (WAT), the explanation is described in the Appendix A. WAT of Fang with 3, 6 and 12 s^{-1} shear rate are 41.2 °C, 40.8 °C and 40.6 °C, respectively as shown in the Table 4.1 and Figure 4.1. At low temperature, the fluid behavior acts as Newtonian fluid. For cooling process, the initial temperature which alteration of viscosity depends on the shear rate significantly is at WAT temperature. As the cooling temperature passes through wax appearance temperature or WAT, there is the presence of wax particles which precipitate out of crude oil at the temperature below WAT. This reason leads the rheological behavior of crude oil changing from independent to dependence flow behavior of crude oil.

For wax deposition, Firstly, the temperature difference which is illustrated in the form like 20 °C /50 °C is the difference between and the cooling temperature circulated on the cold surface for wax deposition test (20 °C) and the outside temperature to control the oil sample into the liquid form (50 °C).

Wax deposition is evaluated by cold finger technique and the result is illustrated in Table 4.2 and the cold surface temperature ranges from 20 ˚C – 30 ˚C. It turns out that amount of wax deposition decreases as temperature increases.

Table 4.1 Wax appearance temperature of Fang crude oil

Fang crude oil/ shear rates	3 s^{-1}	6 s^{-1}	12 s^{-1}
WAT (°C)	41.2	40.8	40.6

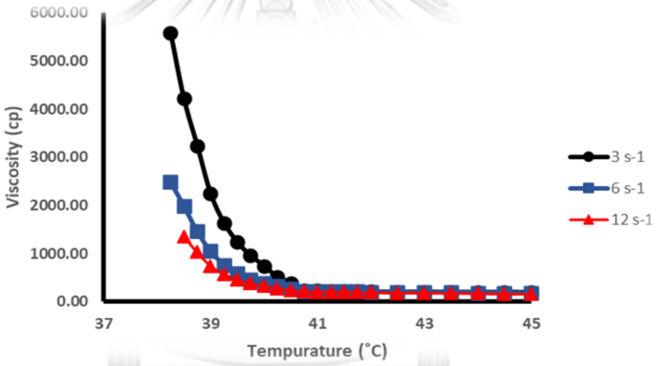
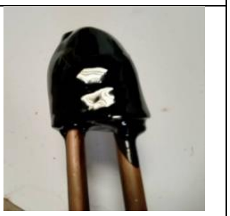


Figure 4.1 Effect of shear rate on WAT of original Fang crude oil

Table 4.2 Amount of wax deposit from Fang crude oil

Fang Crude Oil		Amount of Wax Deposits (g)	Images
Temperature (℃)	20	14.5092	
	25	12.2861	
	30	8.1199	

Also, water-in-oil emulsion is found in most of oilfield. Moreover, Lockhart and Correra (2005) study reveals that water cut increases upon the progress of production and most of researcher study about emulsion inversion reveals that this point can be between 40%-80% which are 50%, 55%, 60%, 70% and 80% for Cheng et al (2019), Zhang et al (2017), Baozhi et al (2017), Wanfen et al (2020) and Kokal (2006), respectively. Thus, the water cut condition for this study is set between 0% - 80%.

The pour-point temperatures of Fang emulsion varying at 20%, 40%, 60% and 80% are 37.3 °C, 38.5 °C, 41.3 °C, and 45.3 °C, respectively as shown in Figure 4.2. The reason of pour-point temperatures which increase with an amount water cut, is that the presence of emulsion increases the rheological property of crude oil such as viscosity and gel strength (Olivera et al., 2010; Paso et al., 2009). An increase in water cut leads to an increase in fraction of the droplet in the emulsion. Also, it results in higher number of droplets in the emulsion causing the higher droplet-droplet interaction and greater interfacial area between the two phases of oil and water (Juntarasakul, 2015).

There is no clear statement about relationship between viscosity and pour point. However, both of parameters is rhetorical properties of the crude oil. To explain the relation between viscosity and pour point of emulsion, it can be explained from wax content relation with both viscosity and pour point. In the waxy crude, Lao (2017) reveals that the amount of wax content increase leads to viscosity increases. In addition, more wax content leads to higher pour point. The higher viscosity retards the ability to flow (Juntarasakul, 2015). Also, lesser ability to flow leads to higher the lowest flowability temperature.

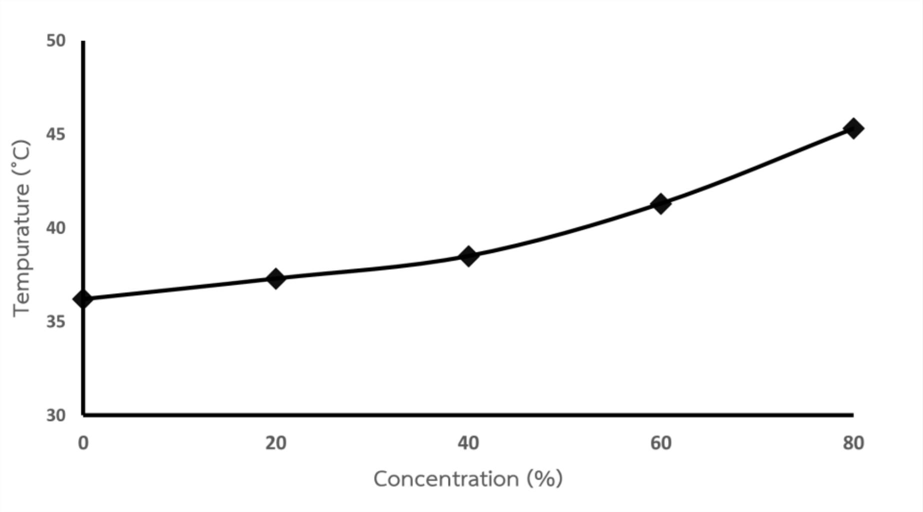


Figure 4.2 Effect of emulsion on pour point and temperature of original Fang crude oil

Figure 4.3 to 4.5 show the viscosity alteration and Figure 4.6 illustrates WAT with various water cut levels. The rheology of this crude oil and its emulsion exhibits Newtonian fluid at the high temperature. Theoretically, shear rate does not have significant effect on the viscosity. At low temperature, the rheology of this crude oil and its emulsion exhibits non-Newtonian fluid. Thus, viscosity is dependent with shear rate. For non-Newtonian fluid, the rheology of the sample exhibit shear thinning that viscosity decreases with increase of shear rate for shear rate lesser than 100 s^{-1} shear rate (Min, 2018). Also, this study utilizes 3 s^{-1}, 6 s^{-1}, and 12 s^{-1} shear rate. From the result viscosity decrease with increase shear rate.

Table 4.3 presents the result of WAT for shear rate at 3-12 s^{-1} and water ranging from 0-80%. For effect of shear rate on WAT, WAT slightly decreases with increasing shear rate. By increasing shear rate from 3 s^{-1} to 12 s^{-1} shear rate at 0% water cut case, WAT decreases from 41.2 ˚C to 40.6 ˚C. The reason is that increasing shear rate will promote heat transfer (Jennings and Weispfenning, 2005). Also, Piroozian (2021) supports that increasing shear rate causes the bond of aggregated crystal molecules within the oil phase broken.

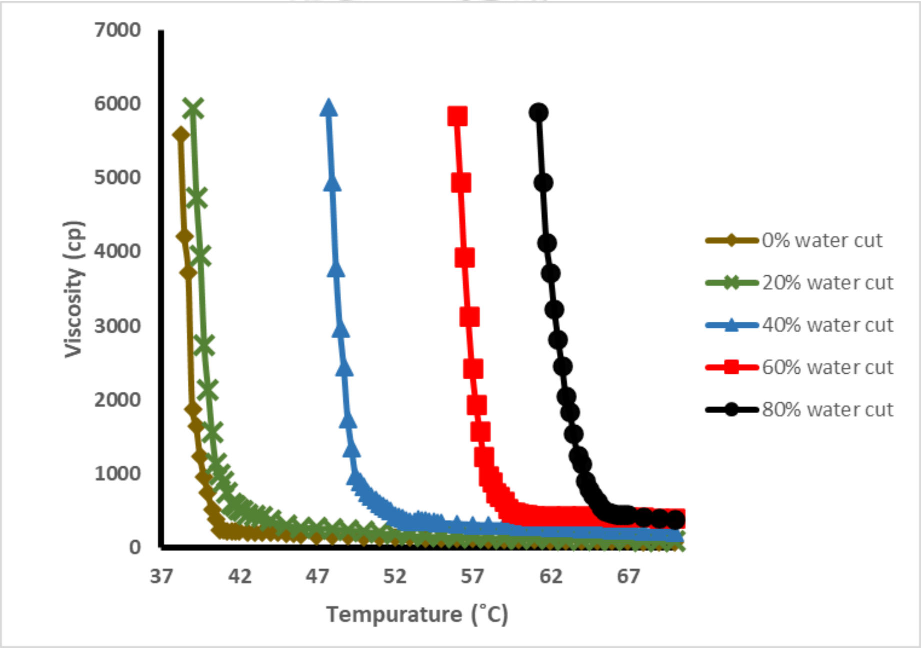


Figure 4.3 Effect of emulsion on viscosity alteration and temperature of original Fang crude oil at 3 s^{-1}

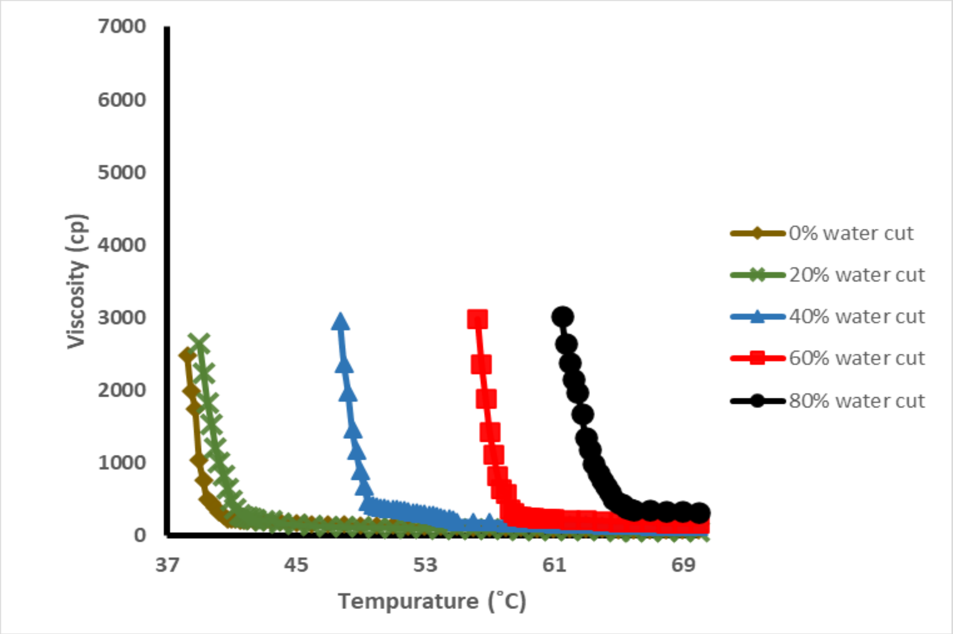


Figure 4.4 Effect of emulsion on viscosity alteration and temperature of original Fang crude oil at 6 s^{-1}

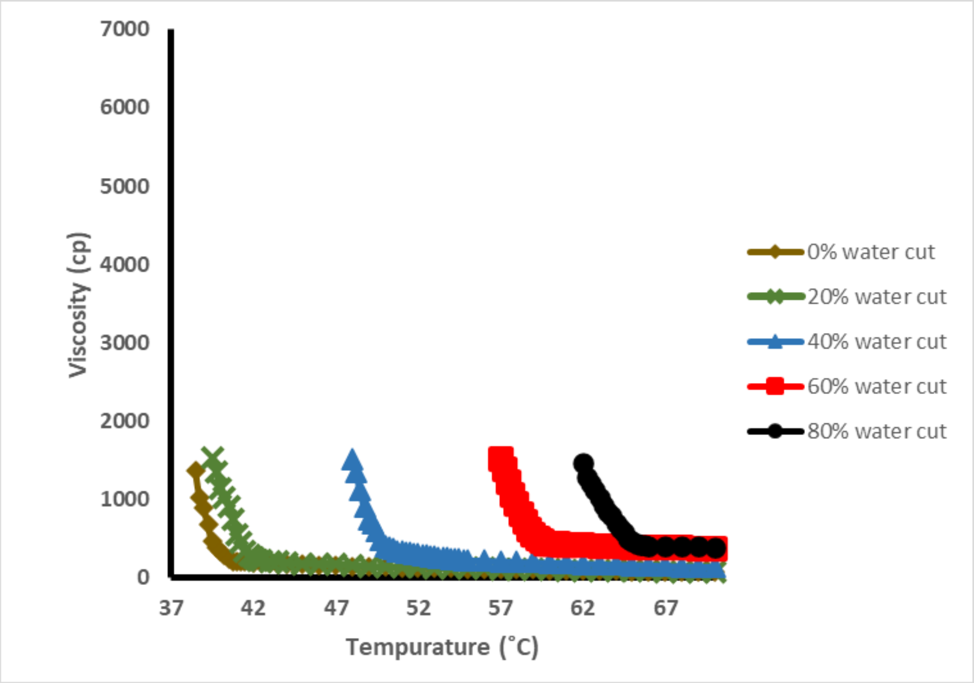


Figure 4.5 Effect of emulsion on viscosity alteration and temperature of original Fang crude oil at 12 s^{-1}

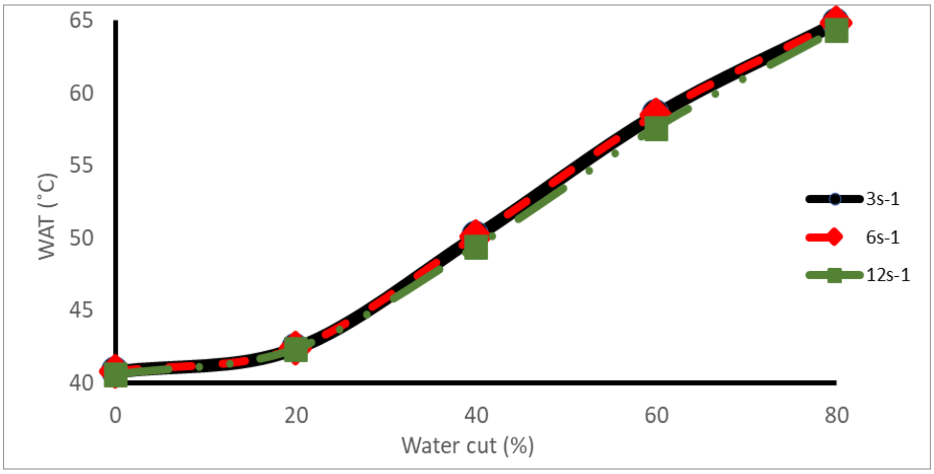


Figure 4.6 Effect of emulsion on viscosity alteration and temperature of original Fang crude oil at shear rate ranging from 3 s^{-1} to 12 s^{-1}

Table 4.3 Wax appearance temperature of Fang crude oil and its emulsion

Fang crude oil/ shear rate	3 s^{-1}	6 s^{-1}	12 s^{-1}
0%	41.2	40.8	40.6
20%	42.7	42.4	42.4
40%	50.7	50.1	50.1
60%	58.7	58.5	58.5
80%	65.2	64.8	64.8

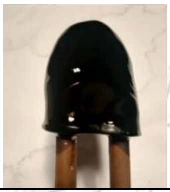
The wax deposition experiment of crude oil and its emulsion ranges from 0%-80% water cut. Also, the circulating medium supplied from chiller are set from 20 °C to 30 °C within the cold finger which illustrates the working condition of the oil field. The surrounding medium of the oil sample is set to be 50 °C to melt down the oil sample in liquid phase at all time.

The results of the effect of emulsion on wax deposition are shown in Table 4.4 and Figure 4.7

The amount of wax deposit initially increases with an increase in the amount of water cut and decreases after 40% water cut as illustrated in the Figure 4.7. The reason because there are several factors influenced to lower the deposit thickness. Couto et al. (2008) explains that the presence of water influences the amount of wax deposit on water-wet surface rending to reduce. On the other hand, there is no difference in the amount of wax deposition on the oil-wet surface. Also, another factor effect on the wax deposition is the gelation point. Zhou et al. (2015) illustrates that the gelation point increases with an increase in the wax deposition point and states that gelation characteristic is considered as the main factor of wax deposit. The substance trapped within 3-D network of the deposit in the water-in-oil emulsion not only crude oil but it is emulsion as well. This reason can be proven by Zhou et al. (2015) for microscope experiment that wax crystal resides within the 3-D network but nor within the droplet. Thus, the amount of wax deposition increases. This explanation also supports this study about increasing pour point also leading to amount of wax deposition increases.

For temperature aspect, the lower temperature leads to the higher wax deposition (Theyab, 2018). This can be explained by molecular diffusion. As the cold surface of the cold finger temperature is lower, there is more precipitated wax particles out of crude oil. Thus, it is lower dissolved wax particle concentration within the region near the cold surface and also higher the concentration in the distance region far from the cold surface. This leads to promote the influence of molecular diffusion to cause more wax deposition on the cold surface.

Table 4.4 Emulsion and temperature effect on amount of wax deposit

Water cut (%)	Amount of wax deposit (gram)		
	Temperature 20°C /50°C	Temperature 25°C /50°C	Temperature 30°C /50°C
0	14.5092 	12.2861 	8.1199 
20	14.722 	12.5429 	9.0455 
40	15.1433 	14.8537 	11.1118 
60	14.9267 	12.9745 	11.2824 
80	14.6623 	12.137 	9.9683 

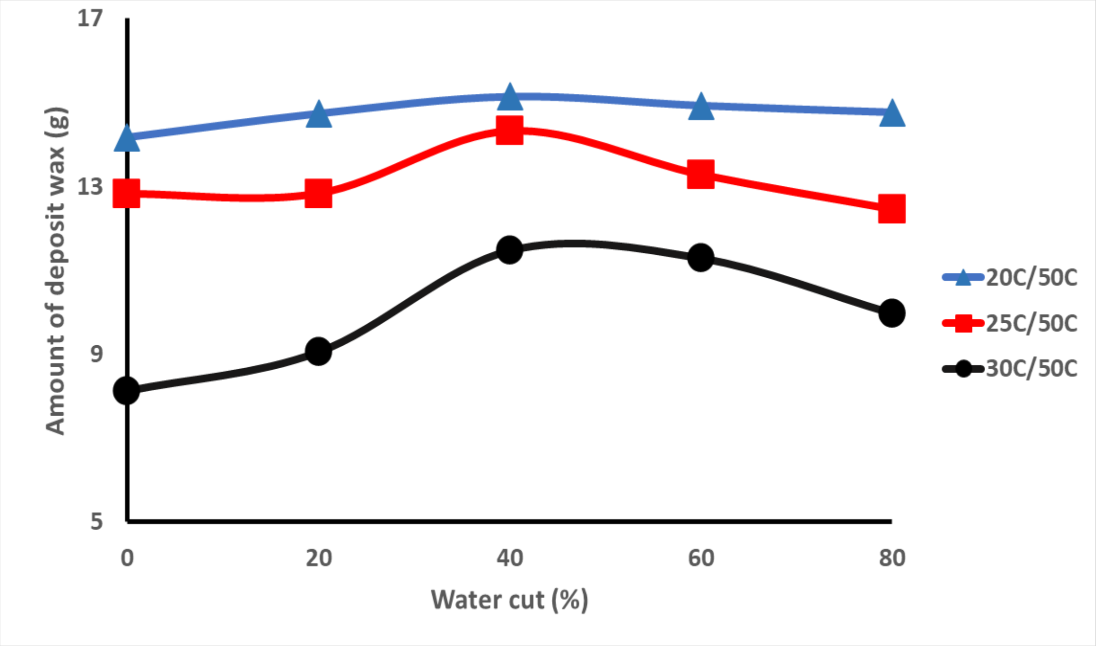


Figure 4.7 Effect of emulsion on the amount of wax deposit

4.2 Pour-point measurement

4.2.1 Results of n-heptane on pour-point

Numura (2005) conducted the pour point measurement study of Fang crude oil with several solvents such as n-heptane, n-hexane and n-pentane. Also, the concentration condition of this study is varying from 3.8% to 50%. The result shows that the highest pour point reduction among chemical used in this study is n-heptane.

Also, Min (2018) performs the pour-point measurement ranging between 5%-20% n-heptane and the result shows that concentration of n-heptane increases with an decrease in pour point. In addition, n-heptane with 20% can reduce the pour point temperature of crude oil from Fang oilfield up to 22 °C.

In order to extend the scope of Min (2018), to study with emulsion perspective, the setting condition for this experiment is varying between 5%-20% and comparing with crude oil case and emulsion case of Fang crude oil.

For the inhibitor performance on pour point, it is defined as the percentage of pour point reduction by using inhibitor comparing to pour point of original crude oil and its emulsion without inhibitor treatment. Therefore, the inhibitor performance on pour point can be calculated by equation 4.1;

$$\text{Inhibitor performance on pour point} = \frac{T_f - T_t}{T_f} x100 \qquad (4.1)$$

T_f is the pour point of the original crude oil and its emulsion without the inhibitor treatment. Also, T_t is the pour point of the oil and its emulsion with the inhibitor treatment.

For the result, the effect of n-heptane and its emulsion on pour point are shown in the Table 4.5 and the inhibitor performance of pour point by using n-heptane is shown in the Table 4.6. The concentration can be reduced to 21.1°C, 23.4°C, 27.7C°C 34.2°C and 40.8°C for water cut from 0-80% with 20% n-heptane as shown in Figure 4.8. Thus, the pour point decreases with an increase in n-heptane concentration of both crude oil and its emulsion.

Even though, the effect of h-heptane concentration can reduce the pour-point temperature, the used amount of chemical for 20 % is high considering with chemical cost. Thus, the selected chemical concentrations in order to use chemical for further study are 10% and 15% n-heptane.

The effect of the emulsion on pour point is that the presence of water cut leads to increase pour point. The reason is explained by Visintin et al. (2008) that the presence of the inter-linkage of the water droplet leads to the increasing stability of emulsion. Also, the wax crystal network growth surrounds the water droplet and wax crystal. Moreover, the enlargement of the wax crystal network also confines the water and the gel is formed. At low temperature, Paso et al. (2009) suggested that the molecular adsorption of wax crystal increase leads to an increment of the water wettability of wax crystal surface. Thus, there is more absorption of wax crystal onto the oil-water interface. Thus, this mechanism can infer that the presence of emulsion leads to significant elevation of pour point, viscosity and yield stress.

To explain the inhibitor performance on pour-point reduction, a decrease in inhibitor performance with an increase in water cut as illustrated in the Table 4.6 can be explained that oil phase decrease with an increment of water phase and n-heptane which is a solvent type of wax inhibitor will interact only oil phase. The lower oil fraction leads to possible decreasing amount of oil to treat with n-heptane. Thus, an increase in water cut leads to the lower performance of wax inhibitor as illustrated in the Table 4.6 and Figure 4.8.

Table 4.5 Effect of n-heptane concentration on crude oil and its emulsion pour point

Water cut (%)/ n-heptane (wt%)	Pour point (°C)				
	0%	5%	10%	15%	20%
0	36.2	32.3	29.4	24.5	21.1
20	37.3	33.5	30.9	26.4	23.4
40	38.5	35.1	33.5	30.2	27.7
60	41.3	39.2	37.8	35.8	34.2
80	45.3	44.1	43.2	41.6	40.8

Table 4.6 Inhibitor performance of n-heptane on pour point of crude oil and its emulsion

Water cut (%)/ n-heptane (wt%)	Inhibitor performance on pour point reduction (%)			
	5%	10%	15%	20%
0	10.77	18.78	32.32	41.71
20	10.19	17.16	29.22	37.27
40	8.83	12.99	21.56	28.05
60	5.08	8.47	13.32	17.19
80	2.65	4.64	8.17	9.93

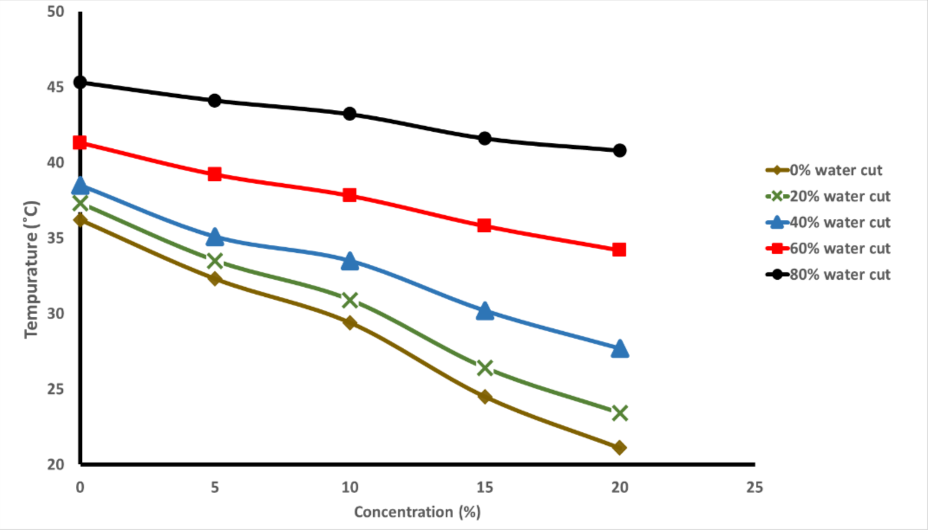


Figure 4.8 Effect of n-heptane on crude oil and its emulsion pour point

4.2.2 Results of PMAO on pour-point

Min (2018) performs pour-point reduction experiment with PMAO by varying PMAO concentration from 3000 to 5000 ppm. The result reveal that PMAO concentration increases with little decline of pour point.

In order to extend the scope of Min (2018) by studying with emulsion perspective, the PMAO concentration for this experiment is varying between 2,500-10,000 ppm and comparing with crude oil case and emulsion case from Fang crude oil.

From the result shown in the Table 4.10 for pour-point reduction and Table 4.11 for inhibitor performance of PMAO on pour-point reduction comparing to without chemical case, the result of crude oil and its emulsion can be obviously seen that there is less pour-point reduction of PMAO with increasing PMAO concentration. Also, it is found that the highest pour-point reduction is at 7500 ppm. In addition, the pour point can be reduced up to 30.6 °C, 33.2 °C, 35.0 °C, 38.9 °C and 43.8°C for 0%, 20%, 40%, 60% and 80%, respectively. At the concentration greater than 7,500 ppm, the pour point becomes higher at 10,000 ppm of PMAO concentration comparing to pour point 7,500 ppm.

The reason is that the effect of PMAO has less effect on pour-point reduction comparing to n-heptane as a solvent explained by Kelland (2014). The performance of PMAO have a less effect in case of wax with the composition of C24+ for n-alkanes as shown in Table 4.8. Also, the influence to pour-point reduction becomes lesser as wax inhibitor side chain are not the same with the wax.

For the long chain alkane, the wax inhibitor performance is even lesser. If inhibitor side chain cannot contain longer alkyl side chain to hinder wax crystal to form. Wax inhibitor can no longer interfere the co-crystallization of wax inhibitor (Pedersen and Rønningsen (2003)).

For the result from Table 4.8, the inhibitor performance of PMAO decreases with an increase in the water cut. As mention earlier, PMAO interacts with wax crystal through similar side chain. Also, PMAO interacts with oil phase. Water cut increases with a decrease in oil phase. Thus, total wax particles containing in the oil sample become less when it compares with less water content. Thus, the effect of wax particle decreases as greater water content as illustrated in Table 4.8 and Figure 4.9.

Table 4.7 Effect of PMAO concentration on crude oil and its emulsion pour point

Water cut (%)/PMAO (ppmw)	Pour point (°C)				
	0	2500	5000	7500	10000
0	36.2	35.0	33.4	30.6	34.8
20	37.3	36.3	35.1	33.2	36.7
40	38.5	37.6	36.5	35.0	37.7
60	41.3	40.8	40.0	38.9	40.7
80	45.3	45.0	44.6	43.8	44.8

Table 4.8 Inhibitor performance of PMAO on pour point of crude oil and its emulsion

Water cut (%)/PMAO (ppmw)	Inhibitor performance on pour point reduction (%)			
	2500	5000	7500	10000
0	3.31	7.73	15.47	3.87
20	2.68	5.90	10.99	1.61
40	2.34	5.19	9.09	2.08
60	1.21	3.15	5.81	1.45
80	0.66	1.55	3.31	1.10

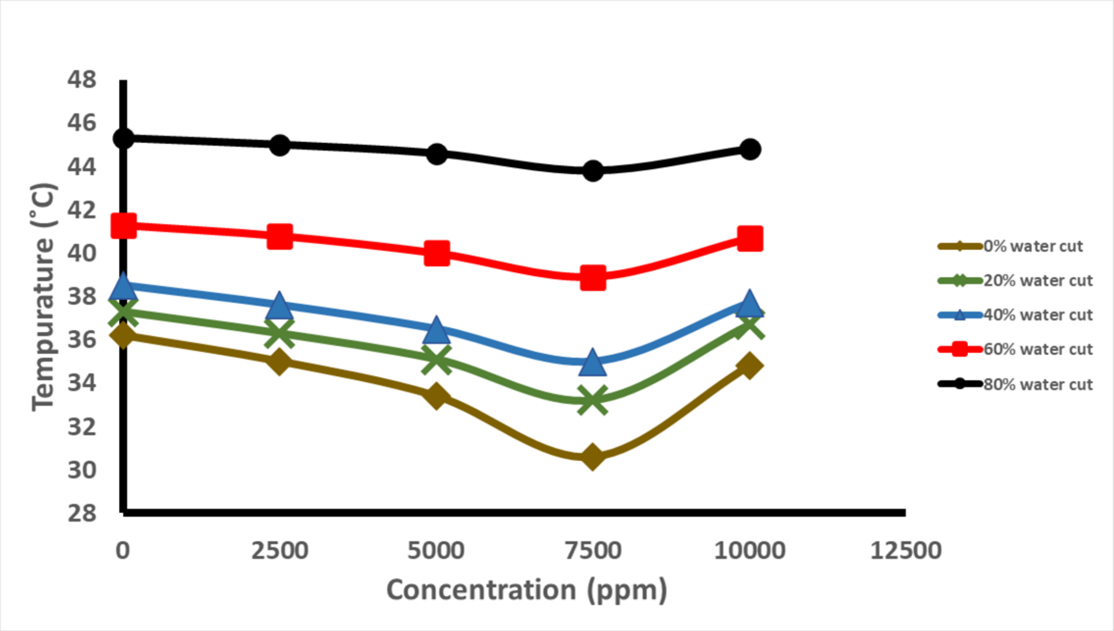


Figure 4.9 Effect of PMAO on crude oil and its emulsion pour point

4.3 Wax appearance temperature measurement

4.3.1 Results of n-heptane on WAT

Wax appearance temperature (WAT) of crude oil with n-heptane inhibitor is determined from viscometry method by definition of WAT as the rate of change of the slope from Chapter 2. The viscosity starts to change the slope gradually from the curve. Wax precipitation rate is faster when higher cooling rate is used (Rønningsen et al., 1991).

The viscosity method is employed and the rate of change of slope determine WAT of each condition which the slope begins to change sharply and the WAT calculation is described in Appendix A. Cooling rate is set to be 12.5 °C as mention in

Chapter 2 to fix the wax precipitation rate of each case to be the same in order to compare the result of every cases.

The viscosity and temperature relationship of W/O emulsion is similar to waxy crude oil. The reason is because the factors affecting emulsion viscosity and rheological properties of emulsion are properties of continuous phase, dispersed phase, temperature and pressure (Li et al., 2010).

The inhibitor performance on WAT can be defined as the percentage of WAT reduction by using inhibitor comparing to WAT of original crude oil and its emulsion without inhibitor treatment. To calculate inhibitor performance, it can be calculated as the equation 4.2;

$$\text{Inhibitor performance on WAT} = = \frac{WAT_f - WAT_t}{WAT_f} x100 \qquad (4.2)$$

WAT_f is WAT of the oil and its emulsion without the inhibitor treatment.

WAT_t is WAT of the oil and its emulsion with the inhibitor treatment.

The results of effect of n-heptane on crude oil and its emulsion at 3 s^{-1} shear rate are illustrated in the Table 4.12-4.14 and Figure 4.13-4.17. For the effect of n-heptane on crude oil and its emulsion at 6 s^{-1} and 12 s^{-1} shear rate are shown in Appendix B. The viscometry method performs under 5%-20% of n-heptane concentration at shear rates from 3-12 s^{-1}. The results show that the lowest WAT of this study is provided from 20% n-heptane with all cases of water cut. From Table

4.12, the WATs at 3 s^{-1}shear rate of 20% n-heptane are 36.9°C, 37.5°C, 45.4°C, 53.9°C and 61.8 °C for 0%, 20%, 40%, 60% and 80% water cut, respectively. The results also reveal that the higher n-heptane concentration uses, the lower WAT can be obtained at the same shear rate. Also, increasing water cut can increase the WAT at the same shear rate.

Dantas et al. (2009) stated that the reduction of WAT is probably due to interaction between waxy oil and the solvent. To explain this phenomenon, n-heptane is light hydrocarbon used to dissolve the wax particles in oil and its emulsion. Also from Min (2018) study, the presence of wax crystal leads to increase the viscosity of the sample. With disappearance of wax crystal and an increase in solubility by adding n-heptane, the overall viscosity of the sample is decreased. The solubility of wax particle increase leads to a decrease in the possibility of wax particle precipitated out of oil phase. Thus, WAT also decreases. Also, shear stress increase leads to WAT decrease as spanning the heat transfer and shear stress (Jennings and Weispfenning, 2005).

For inhibitor performance of n-heptane, it can be explained that as water cut increases, the number of wax particles within the same volume of the sample decreases due to a decrease in of oil fraction in the emulsion. Also, the n-heptane is light hydrocarbon interacting only oil phase contained the wax crystal. This can be concluded that the inhibitor performance of n-heptane reduces as water cut increases as illustrated in Table 4.12 to Table 4.14. The results are also confirmed from Figure 4.10 to 4.12.

For the viewpoint of emulsion effect on WAT, WAT increases with an increase in water cut. The researchers also investigated the effect of emulsion on the wax appearance temperature (Piroozian et al. 2016; Li and Gong, 2010). WAT increases with water cut because the water droplet grants additional nucleation for precipitated wax and wax crystal precipitate on the droplet (Visintin et al., 2008).

It can be concluded that the presence of water leads to an increase in WAT for all shear rated as illustrated in the Table 4.9 to Table 4.11

Also, the water cut increase leads to oil fraction decrease. Thus, the influence of n-heptane acting as solvent becomes less. Thus, the inhibitor performance of WAT comparing to the oil and its emulsion without treating with chemical become less as water cut increases for all n-heptane concentrations and shear rates as shown in the Table 4.12 to Table 4.14.

Figure 4.18 to Figure 4.21 show the shear rate increases with a decrease in viscosity For shear thinning effect, the reason why oil and emulsion viscosity decrease with increase with shear rate is explained by Metzger (2011) and suggested that apply shear to wax crystal particle. Then, the wax crystal shape is altering to be more oval shape. Thus, the flowability is increase.

For the effect of shear rate on WAT, shear rate increases with slightly decreasing of WAT. For shear rate from 3 s^{-1} to 12 s^{-1} shear rate at 20% water cut with 5% n-heptane, WAT slightly decreases from 41.3 ˚C to 40.6 ˚C as shown in the Table 4.9 – 4.11. The reason is that increasing shear rate will promote heat transfer (Jennings and Weispfenning, 2005). Also, Piroozian et al. (2021) supports that the bond of aggregated crystal molecules within the oil phase is broken by increase shear rate. The effect of shear rate on the inhibitor performance of n-heptane is insignificant as illustrated in the Table 4.12 – 4.14.

Table 4.9 Effect of n-heptane of crude oil and its emulsion on WAT at 3 s^{-1} shear rate

Water cut (%) / n-heptane (wt%)	Wax Appearance Temperature (°C)				
	0	5	10	15	20
0	41.2	40.2	38.6	37.9	36.9
20	42.7	41.3	40.0	38.4	37.5
40	50.7	48.6	47.6	46.6	45.4
60	58.7	57.2	56.1	54.6	53.9
80	65.2	64.8	64.1	62.9	61.8

Table 4.10 Effect of n-heptane of crude oil and its emulsion on WAT at 6 s^{-1} shear rate

Water cut (%) / n-heptane (wt%)	Wax Appearance Temperature (°C)				
	0	5	10	15	20
0	40.8	39.8	38.0	37.1	36.4
20	42.4	40.8	39.2	37.8	37.0
40	50.1	48.2	47.4	46.5	45.4
60	58.5	57.0	55.7	54.4	53.2
80	64.8	64.4	63.6	62.5	61.4

Table 4.11 Effect of n-heptane of crude oil and its emulsion on WAT at 12 s^{-1} shear rate

Water cut (%) / n-heptane (wt%)	Wax Appearance Temperature (°C)				
	0	5	10	15	20
0	40.6	39.2	37.9	36.9	36.2
20	42.4	40.6	38.3	37.8	36.6
40	49.4	48.2	47.2	46.1	45.4
60	57.6	56.6	55.6	54.1	53.2
80	64.3	63.6	62.7	61.3	60.9

Table 4.12 Effect of inhibitor performance of n-heptane concentration for crude oil and its emulsion on WAT at 3 s^{-1} shear rate

Water cut (%) / n-heptane concentration (wt%)	Inhibitor performance on WAT (%)			
	5	10	15	20
0	2.54	6.52	8.14	10.48
20	3.38	6.37	10.01	12.25
40	4.00	6.01	8.02	10.41
60	2.51	4.42	6.85	8.12
80	0.63	1.83	3.54	5.26

Table 4.13 Effect of inhibitor performance of n-heptane concentration for crude oil and its emulsion on WAT at 6 s^{-1} shear rate

Water cut (%) / n-heptane concentration (wt%)	Inhibitor performance on WAT (%)			
	5	10	15	20
0	2.37	6.85	9.05	10.79
20	3.75	7.56	10.91	12.73
40	3.85	5.52	7.29	9.44
60	2.65	4.78	7.01	9.07
80	0.62	1.81	3.51	5.23

Table 4.14 Effect of inhibitor performance of n-heptane concentration for crude oil and its emulsion on WAT at 12 s^{-1} shear rate

Water cut (%) / n-heptane concentration (wt%)	Inhibitor performance on WAT (%)			
	5	10	15	20
0	3.54	6.63	9.08	10.87
20	4.16	9.51	10.73	13.67
40	2.44	4.42	6.74	8.18
60	1.65	3.54	6.05	7.68
80	1.06	2.48	4.67	5.33

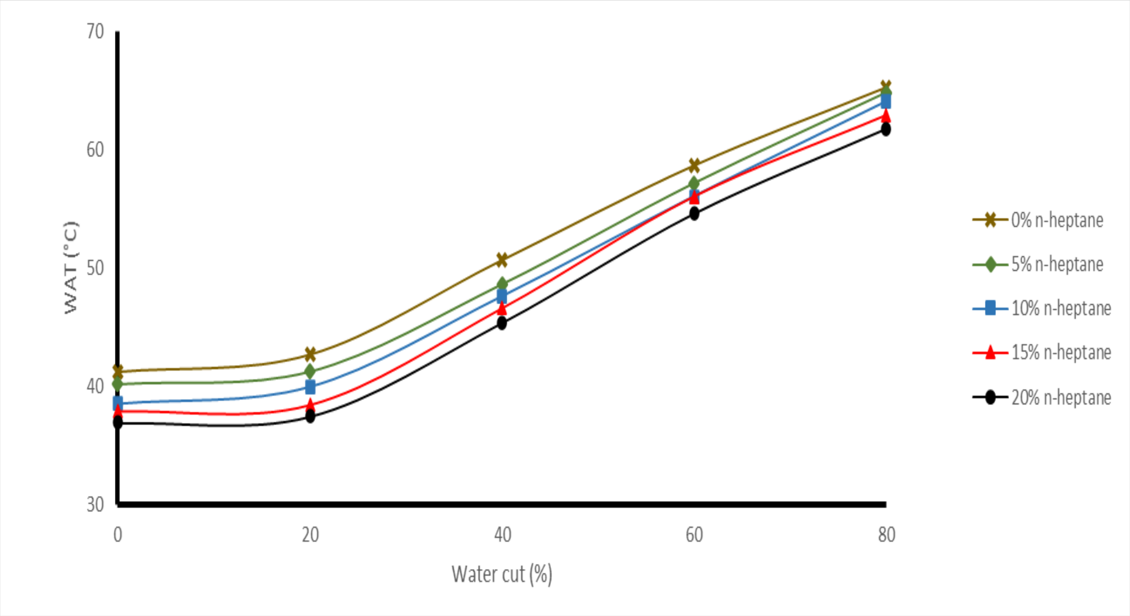


Figure 4.10 Effect of n-heptane on crude oil and its emulsion WAT at 3 s^{-1} shear rate

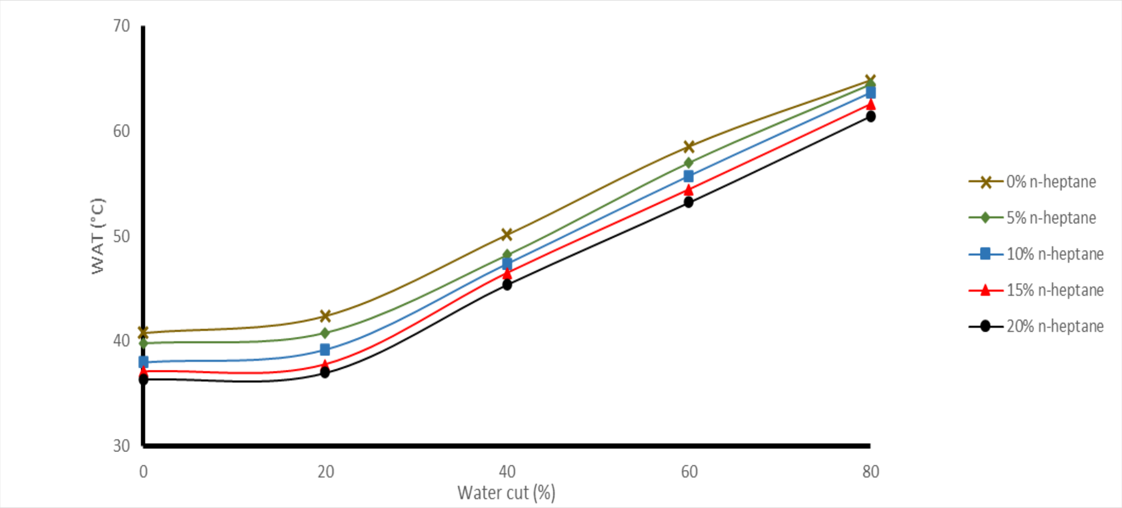


Figure 4.11 Effect of n-heptane on crude oil and its emulsion WAT at 6 s^{-1} shear rate

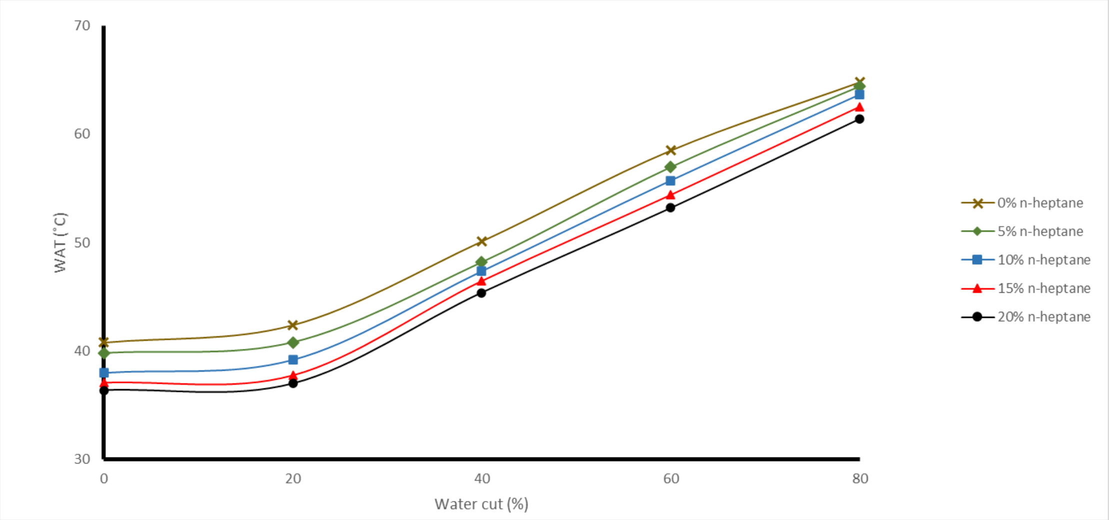


Figure 4.12 Effect of n-heptane on crude oil and its emulsion WAT at 12 s^{-1} shear rate

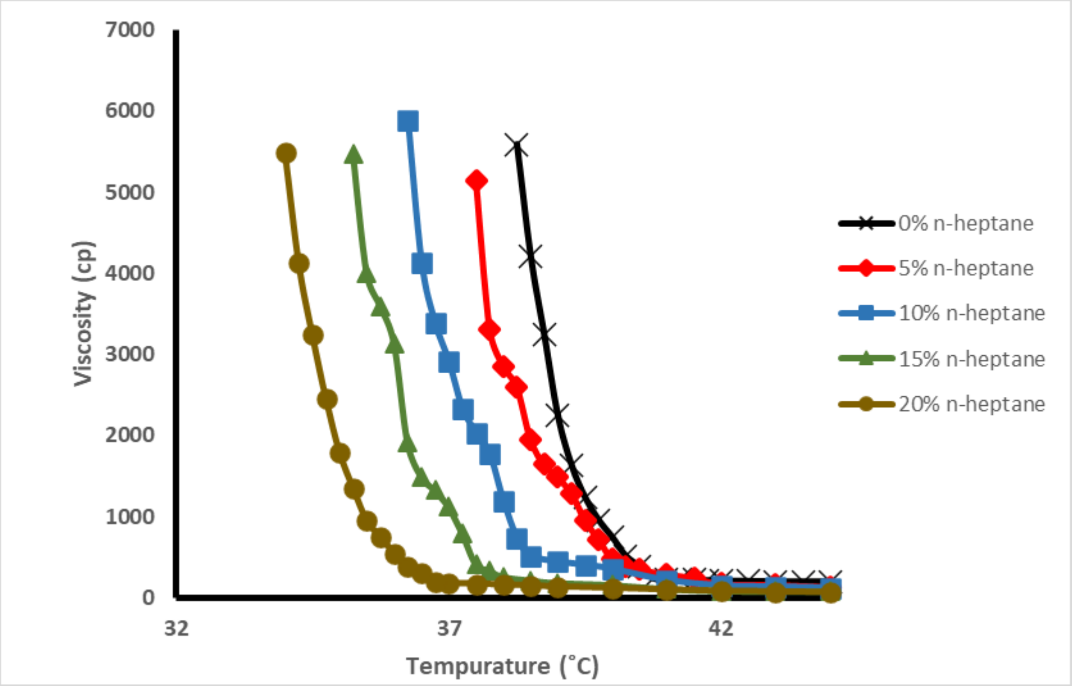


Figure 4.13 Effect of n-heptane concentrations on WAT of crude oil at 3 s^{-1} shear rate

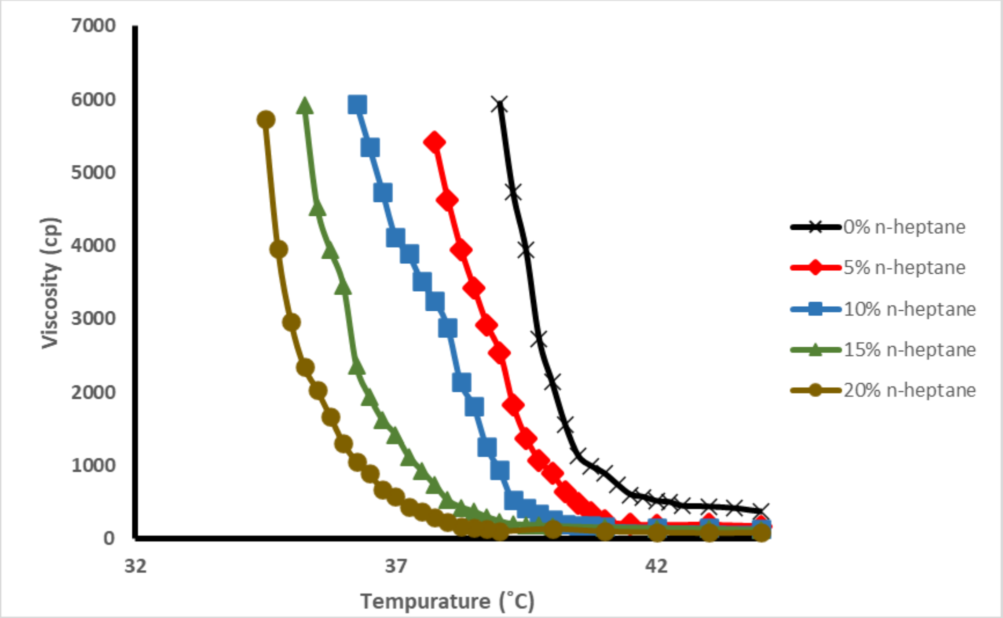


Figure 4.14 Effect of n-heptane concentrations on WAT of 20% water cut emulsion at 3 s^{-1} shear rate

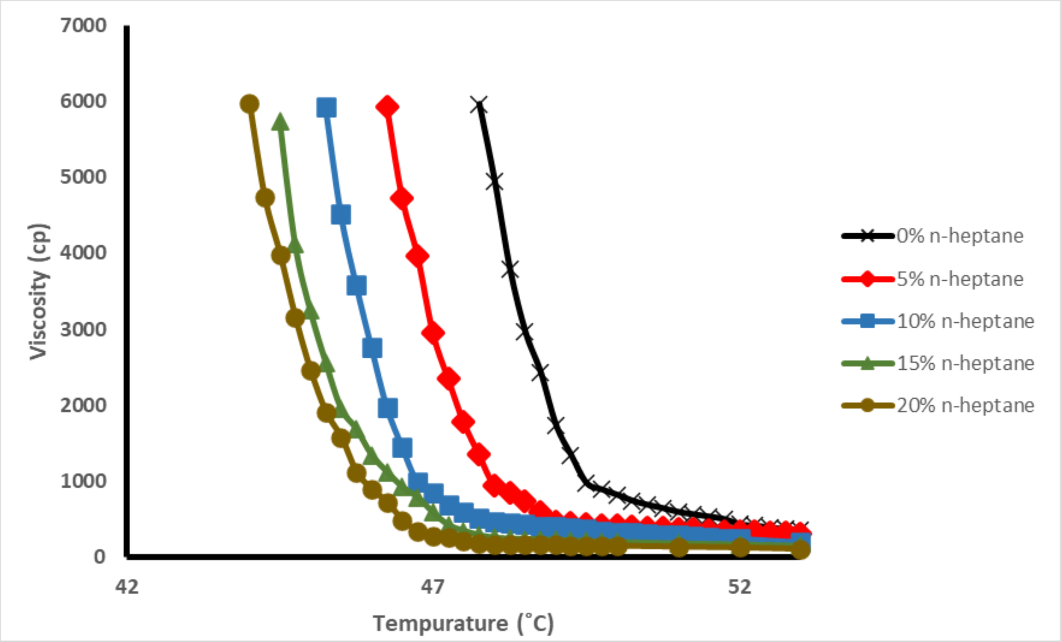


Figure 4.15 Effect of n-heptane concentrations on WAT of 40% water cut emulsion at 3 s^{-1} shear rate

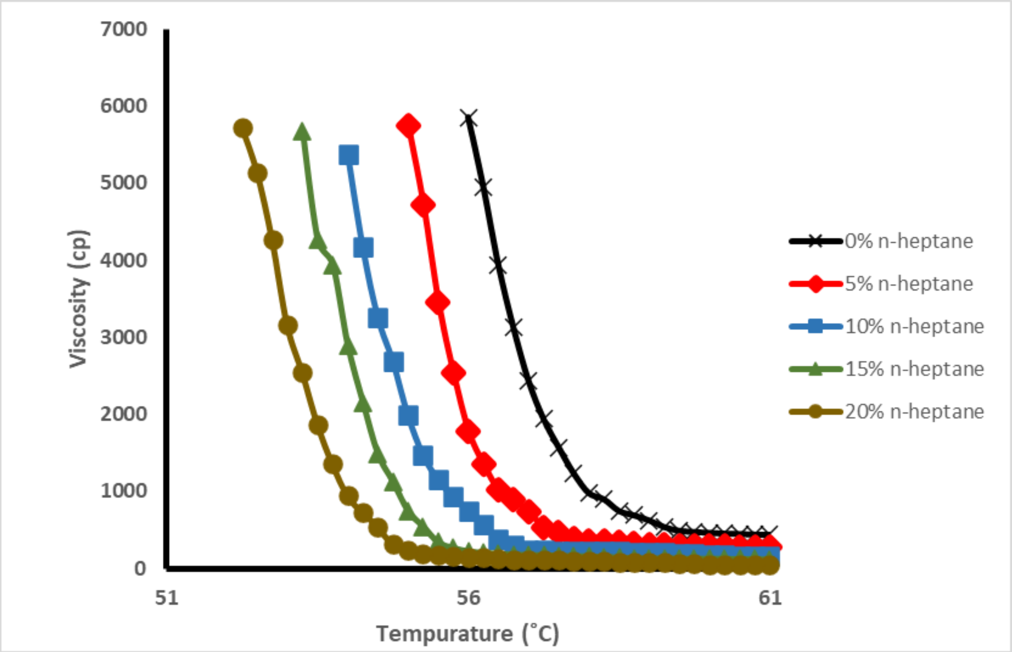


Figure 4.16 Effect of n-heptane concentrations on WAT of 60% water cut emulsion at 3 s^{-1} shear rate

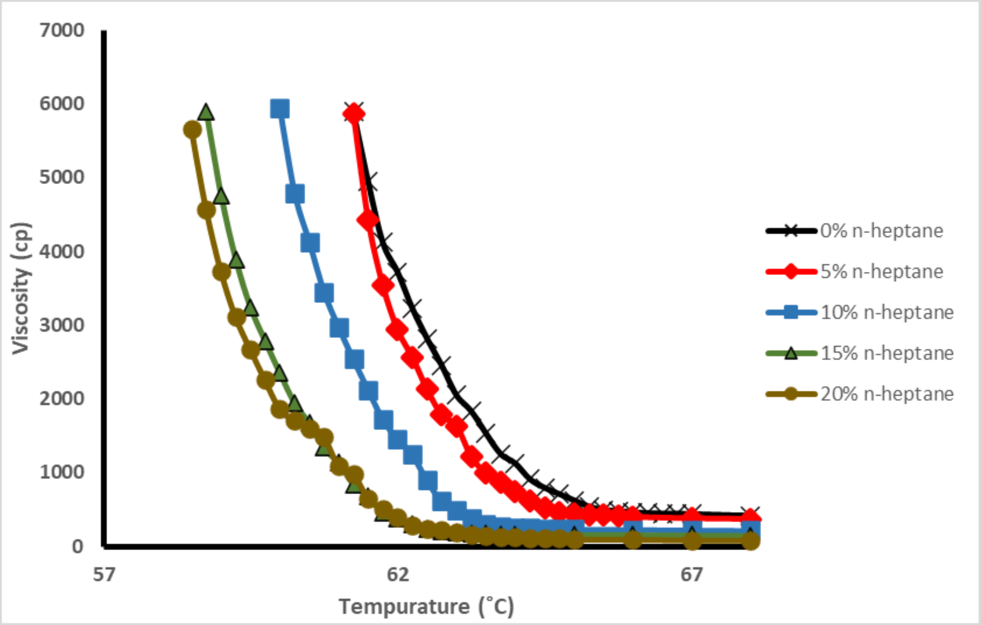


Figure 4.17 Effect of n-heptane concentrations on WAT of 80% water cut emulsion at $3\ s^{-1}$ shear rate

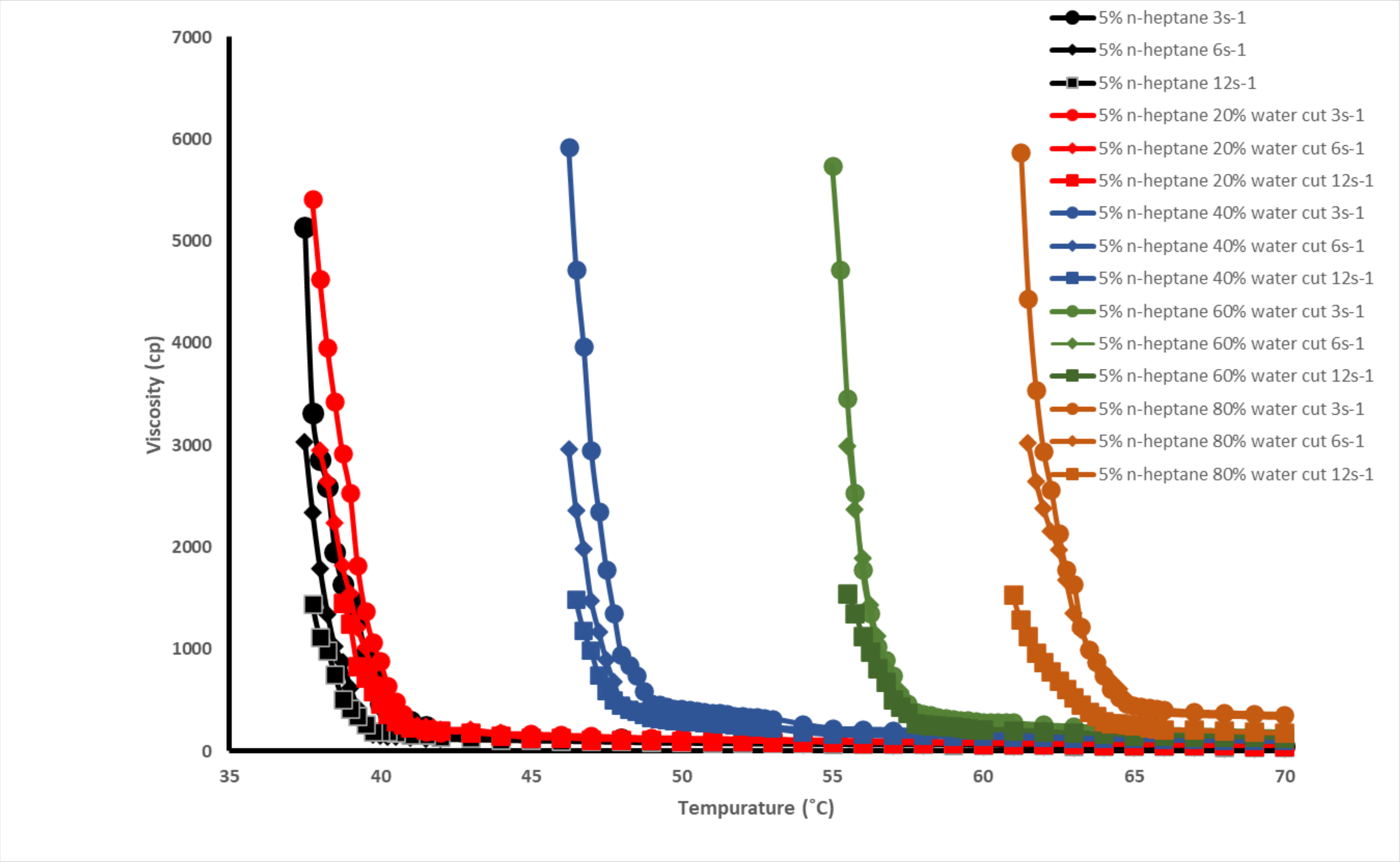


Figure 4.18 Effect of shear rate on 5% n-heptane concentrations varying 0%-80% water cut at 3,6,12 s^{-1} shear rate

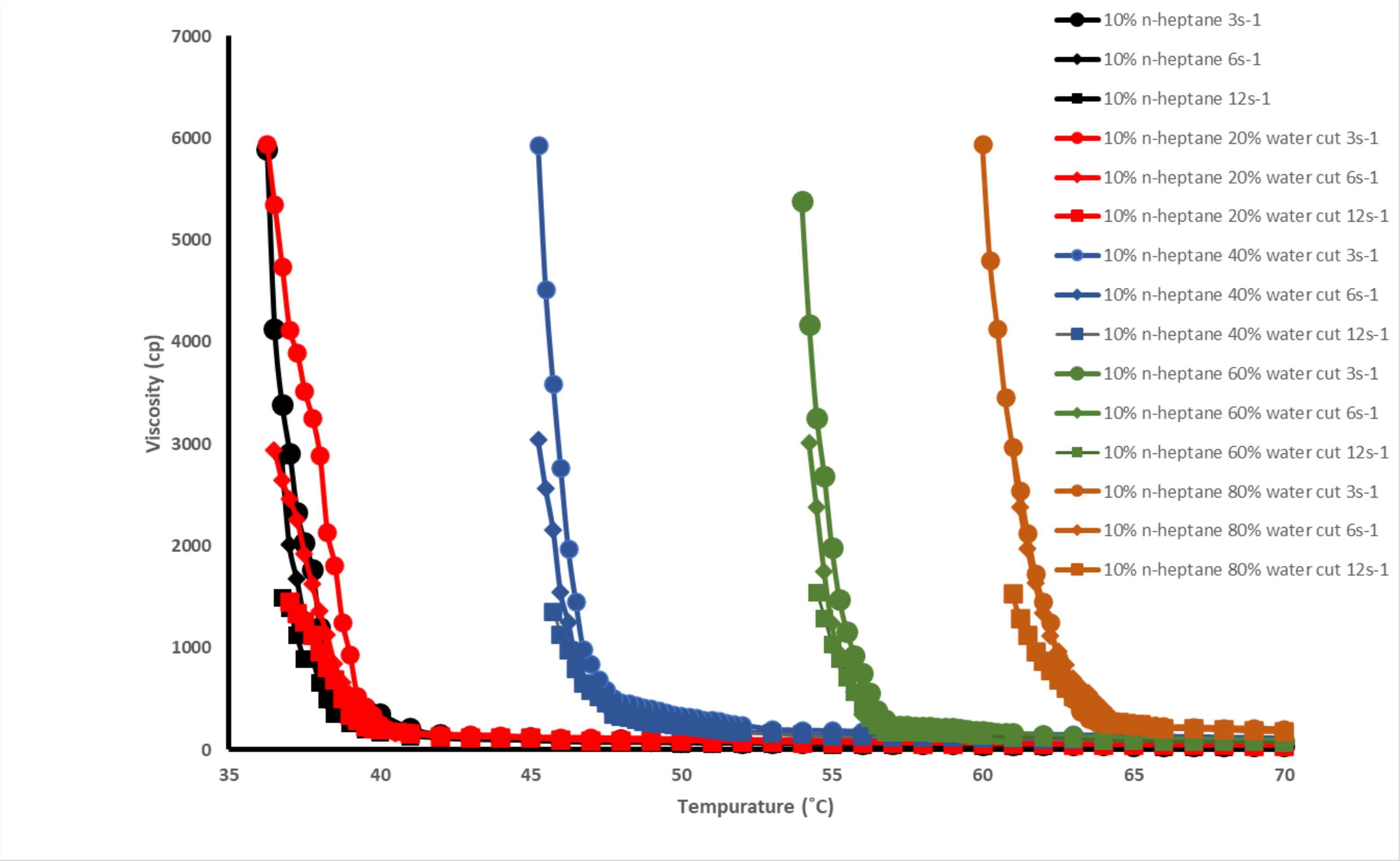


Figure 4.19 Effect of shear rate on 10% n-heptane concentrations varying 0%-80% water cut at 3,6,12 s^{-1} shear rate

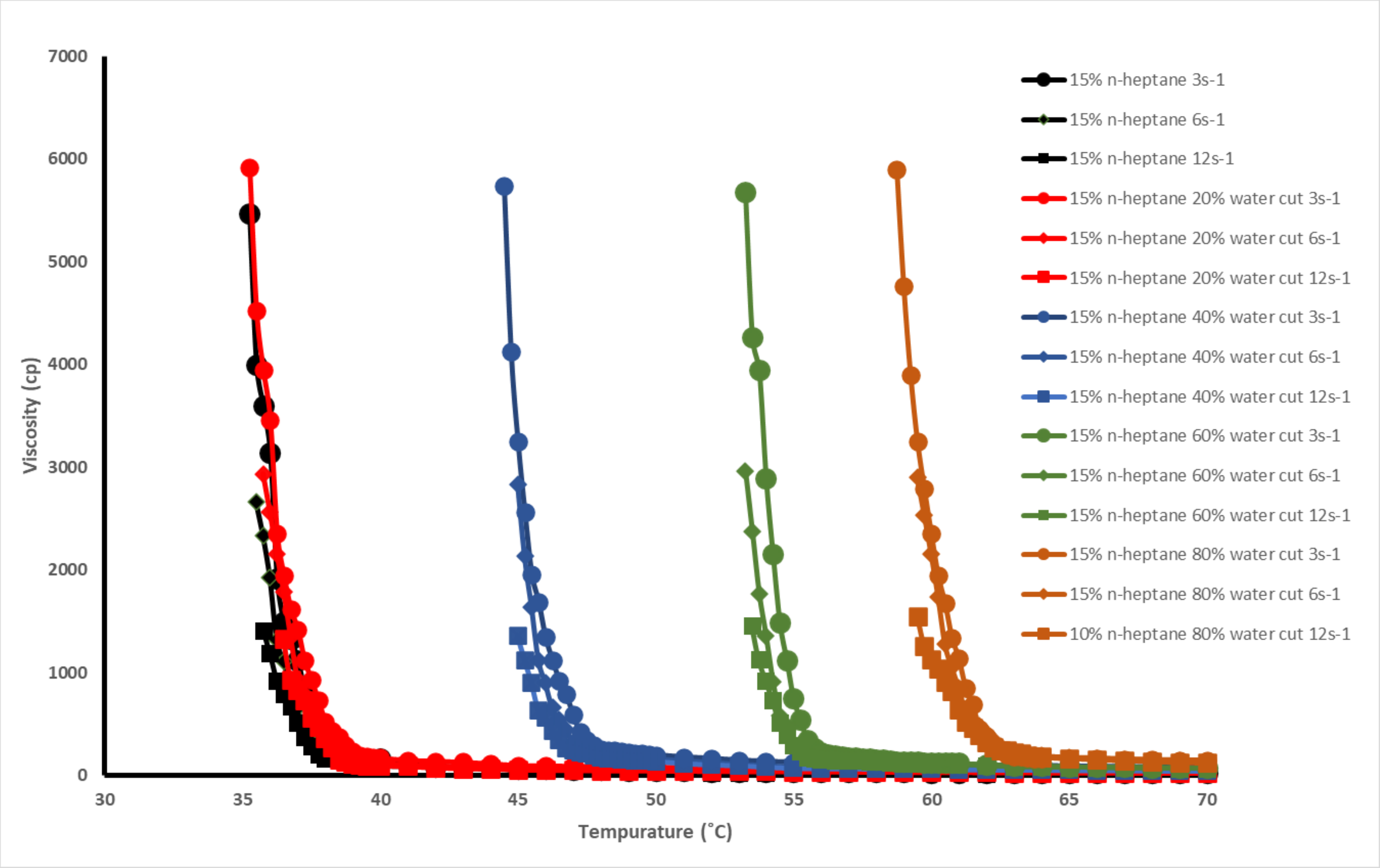


Figure 4.20 Effect of shear rate on 15% n-heptane concentrations varying 0%-80% water cut at 3,6,12 s^{-1} shear rate

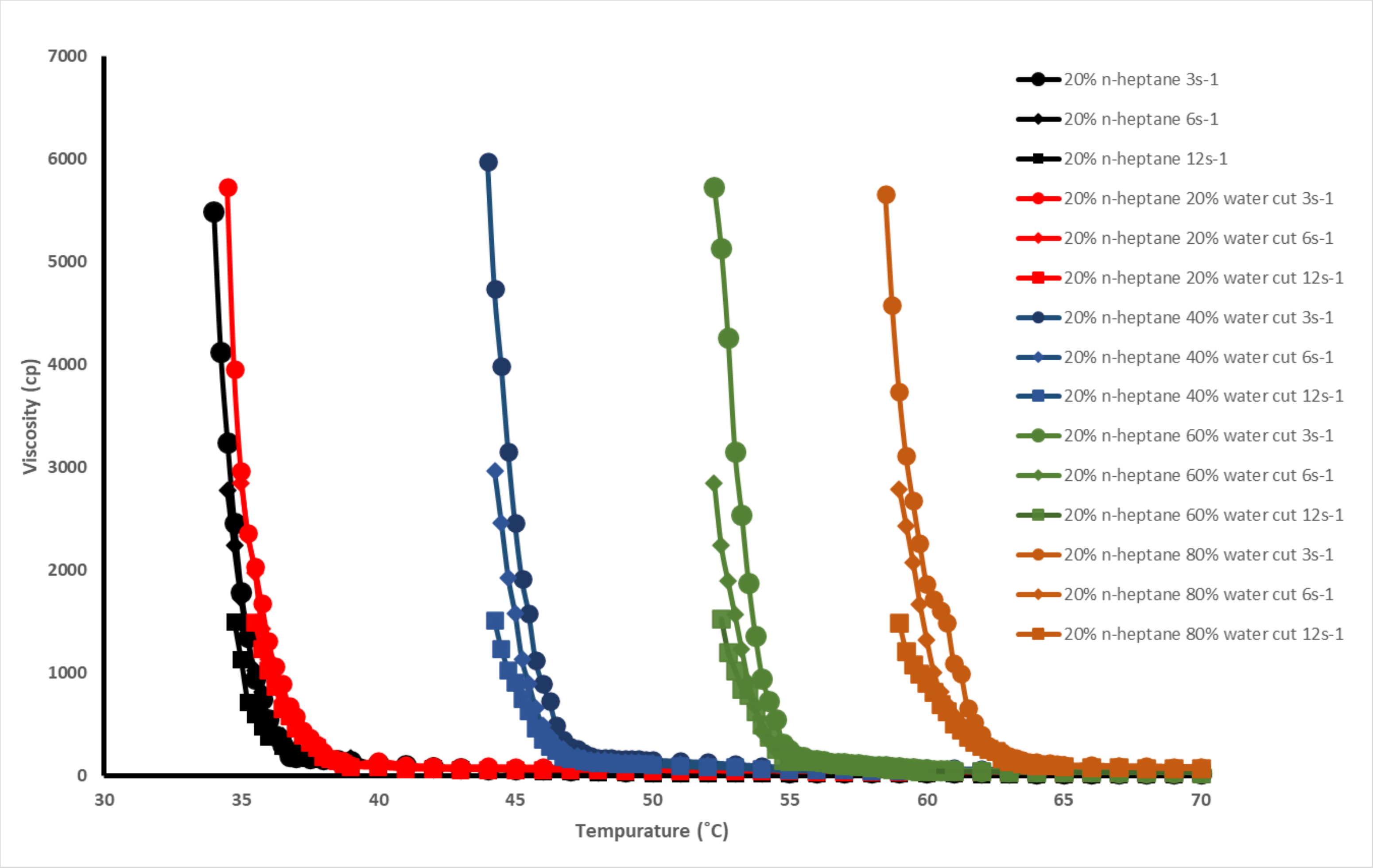


Figure 4.21 Effect of shear rate on 20% n-heptane concentrations varying 0%-80% water cut at 3,6,12 s^{-1} shear rate

4.3.2 Results of PMAO on WAT

For wax crystal modifier type, PMAO is selected as polymer wax inhibitor which its mechanism is disrupt the growth of wax crystal by changing wax crystal's morphology from plate-like to needle-like. It will match to the wax crystal in the inter-lock position instead of another wax crystal to form 3-D network (Theyab, 2016). As the inhibitor inter-locking with wax crystal, it leads to obstruct 3-D network the further forming network with others wax crystal (Wei, 2015).

The results of the crude oil and its emulsion for WAT are illustrated in Table 4.15-4.20 and Figure 4.25-4.36 present the result of emulsion effect on WAT with concentration of PMAO ranging from 2,500-10,000 ppm at shear rates from 3-12 s^{-1}, respectively. The results of PMAO ranging from 2,500-10,000 ppm on crude oil and its emulsion at 6 s^{-1} and 12 s^{-1} shear rate are illustrated in Appendix B. The results show that WAT can be reduced from 41.2 °C, 42.7 °C, 50.7 °C, 58.7 °C and 65.2°C to 38.2 °C, 39.5 °C, 46.8 °C, 55.8 °C and 62.9 °C for water cut ranging from 0%, 20%, 40%, 60% and 80%, respectively with the concentration of PMAO at 7500 ppm at 3 s^{-1} shear rates and other result will be shown in Table 4.15.

However, at 10,000 ppm PMAO, the results show that WATs are 39.7 °C, 41.3 °C, 48.5 °C, 57.5 °C and 64.0 °C for water cut at 0%, 20%, 40%, 60% and 80%, respectively which means wax can precipitate more at the higher temperature than that of PMAO at 7,500 ppm.

Ragunathan et al. (2020) stated that the wax crystal modifier type inhibitor can interact with others polymer if the concentration of the polymer is too high. Thus, the available potential number of polymers can interact with other polymer are decreased. This mean that excessive concentration of polymer performance can be lowered than that of the optimum concentration at 7,500 ppm. From this study, it reveals that the concentration of PMAO at 10,000 ppm is too high. The highest performance of PMAO concentration of this study is 7,500 ppm.

The result reveals that there is little effect of PMAO concentration on WAT of the crude oil and its emulsion. Also, the effect of shear rate is that the higher shear rate leads to the greater WAT reduction for each condition. The increasing shear rate increase shear stress at the place wax deposit and span the heat transfer (Jennings and Weispfenning, 2005).

The possible explanation about reduction of inhibitor performance coupling with the effect the emulsion is because the water fraction within the sample becomes greater and results in the reduction of oil fraction of the sample. Thus, the influence of WAT reduction comparing to the oil and its emulsion without chemical becomes less for all concentrations and shear rates as shown in the Table 4.15 to 4.17.

As mentioned earlier about effect of emulsion on WAT with two supported researchers (Piroozian et al. 2016; Li and Gong, 2010), it can be concluded that water cut increases with increasing WAT as shown in Table 4.18 – Table 4.20. Increasing water cut causes increasing WAT because the water droplets grant additional nucleation for precipitated wax and wax crystals precipitate on the droplet (Visintin et al., 2008).

Also, Figure 4.22 to Figure 4.24 illustrate the diminishing effect of PMAO on the WAT of oil and its emulsion for each condition.

For effect of shear rate on WAT, shear rate increases with slightly decreasing WAT. For shear rate from 3 s^{-1} to 12 s^{-1} shear rate at 20% water cut with 2500 ppm of PMAO, WAT slightly decreases from 40.7 °C to 40.0 °C as shown in the Table 4.15 – 4.17. The reason is the same with effect of shear rate on WAT of oil and its emulsion without chemical treatment and n-heptane. The effect of shear rate on inhibitor performance of n-heptane is slightly different as illustrate in the Table 4.18 – 4.20.

Table 4.15 Effect of PMAO concentration of crude oil and its emulsion on WAT at 3 s^{-1} shear rate

Water cut (%) / PMAO (ppmw)	Wax Appearance Temperature (°C)				
	0	2500	5000	7500	10000
0	41.2	40.7	39.9	38.2	39.7
20	42.7	40.7	40.5	39.5	41.3
40	50.7	49.8	48.1	46.8	48.5
60	58.7	58.2	57.1	55.8	57.5
80	65.2	64.6	63.6	62.9	64.0

Table 4.16 Effect of PMAO concentration of crude oil and its emulsion on WAT

at 6 s^{-1} shear rate

Water cut (%) / PMAO (ppmw)	Wax Appearance Temperature (°C)				
	0	2500	5000	7500	10000
0	40.8	40.7	39.0	38.2	39.0
20	42.4	40.8	40.1	38.7	41.1
40	50.1	49.4	47.7	46.5	49.7
60	58.5	58.1	56.5	55.7	57.2
80	64.8	63.9	63.2	62.0	63.7

Table 4.17 Effect of PMAO concentration of crude oil and its emulsion on WAT at 12 s^{-1} shear rate

Water cut (%) / PMAO (ppmw)	Wax Appearance Temperature (°C)				
	0	2500	5000	7500	10000
0	40.6	40.0	38.9	37.4	39.2
20	42.4	40.7	40.0	38.6	41.2
40	49.4	48.9	47.6	46.4	48.2
60	57.6	57.2	56.8	55.7	57.0
80	64.3	63.9	63.2	62.0	63.7

Table 4.18 Effect of inhibitor performance of PMAO concentration for crude oil and its emulsion on WAT at 3 s^{-1} shear rate

Water cut (%) / PMAO concentration (ppmw)	Inhibitor performance on WAT (%)			
	2500	5000	7500	10000
0	2.54	6.52	8.14	10.48
20	3.38	6.37	10.01	12.25
40	4.00	6.01	8.02	10.41
60	2.51	4.42	6.85	8.12
80	0.63	1.83	3.54	5.26

Table 4.19 Effect of inhibitor performance of PMAO concentration for crude oil and its emulsion on WAT at 6 s^{-1} shear rate

Water cut (%) /PMAO concentration (ppmw)	Inhibitor performance on WAT (%)			
	2500	5000	7500	10000
0	2.37	6.85	9.05	10.79
20	3.75	7.56	10.91	12.73
40	3.85	5.52	7.29	9.44
60	2.65	4.78	7.01	9.07
80	0.62	1.81	3.51	5.23

Table 4.20 Effect of inhibitor performance of PMAO concentration for crude oil and its emulsion on WAT at 12 s^{-1} shear rate

Water cut (%) / PMAO concentration (ppmw)	Inhibitor performance on WAT (%)			
	2500	5000	7500	10000
0	3.54	6.63	9.08	10.87
20	4.16	9.51	10.73	13.67
40	2.44	4.42	6.74	8.18
60	1.65	3.54	6.05	7.68
80	1.06	2.48	4.67	5.33

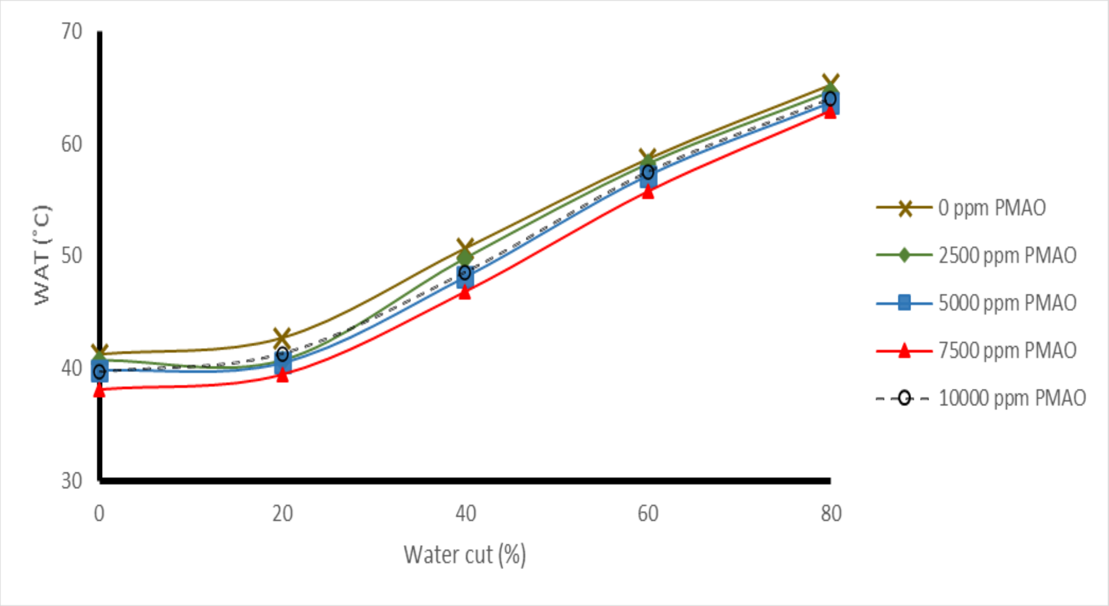


Figure 4.22 Effect of PMAO on crude oil and its emulsion WAT at 3 s^{-1} shear rate

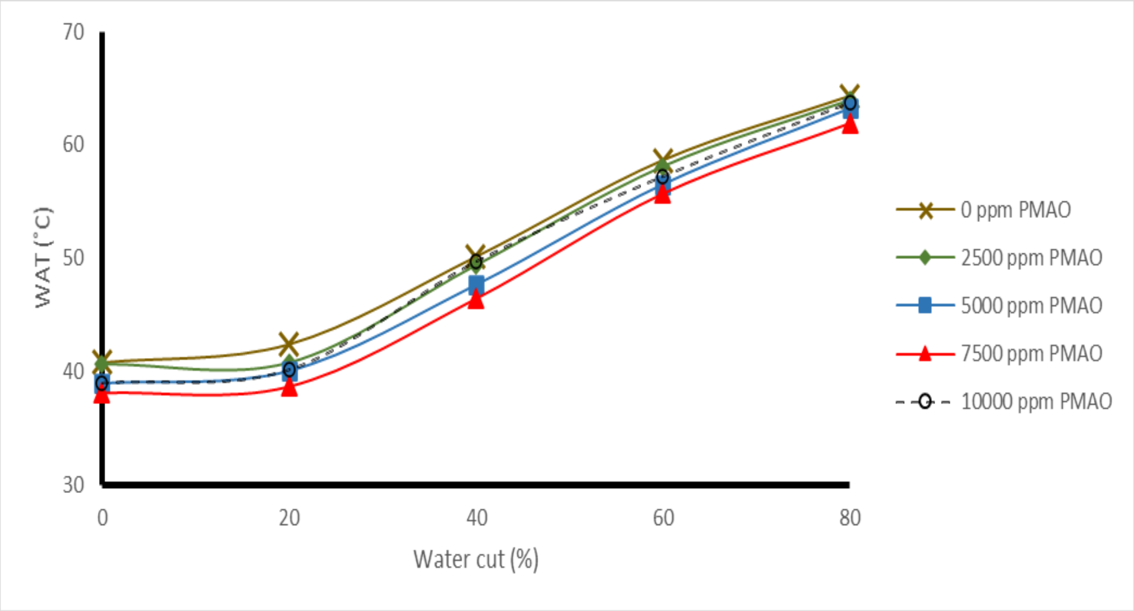


Figure 4.23 Effect of PMAO on crude oil and its emulsion WAT at 6 s^{-1} shear rate

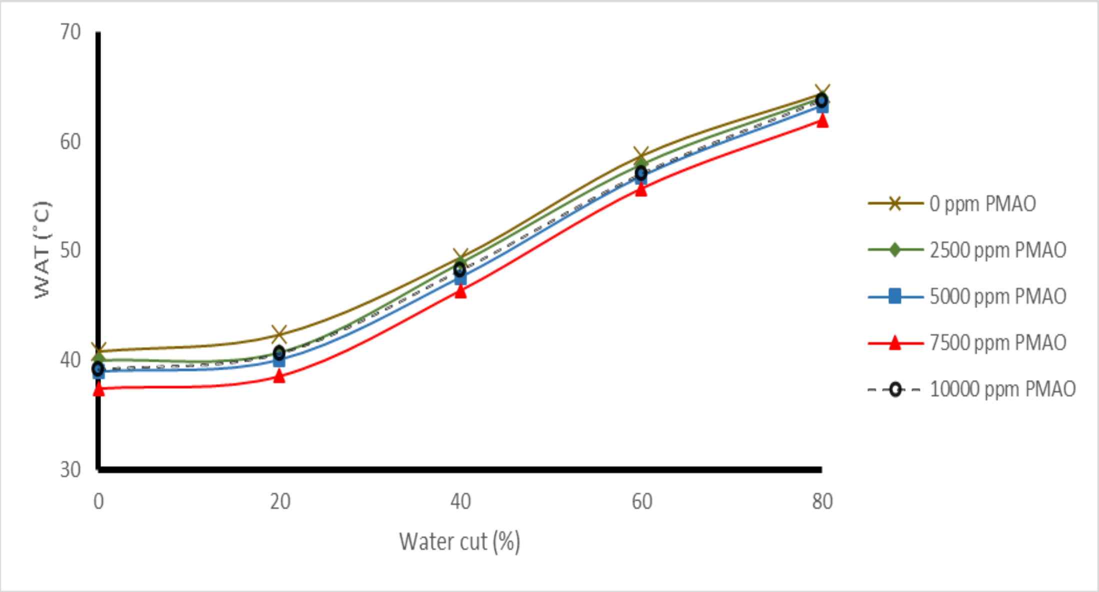


Figure 4.24 Effect of PMAO on crude oil and its emulsion WAT at 12 s^{-1} shear rate

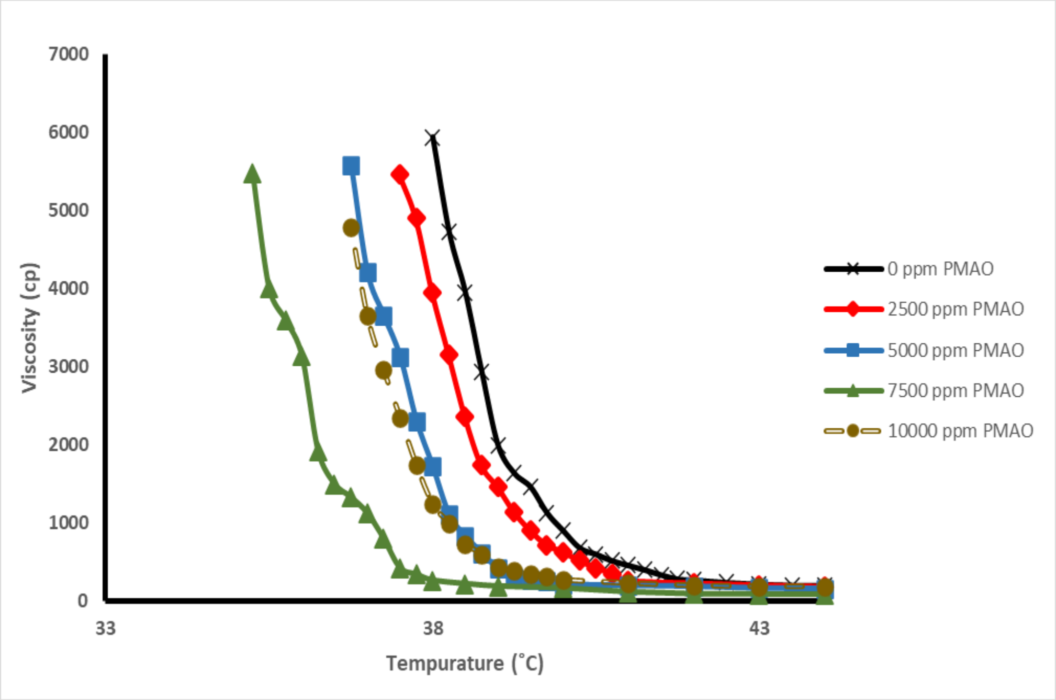


Figure 4.25 Effect of PMAO concentrations on WAT of 0% crude oil at 3 s^{-1} shear rate

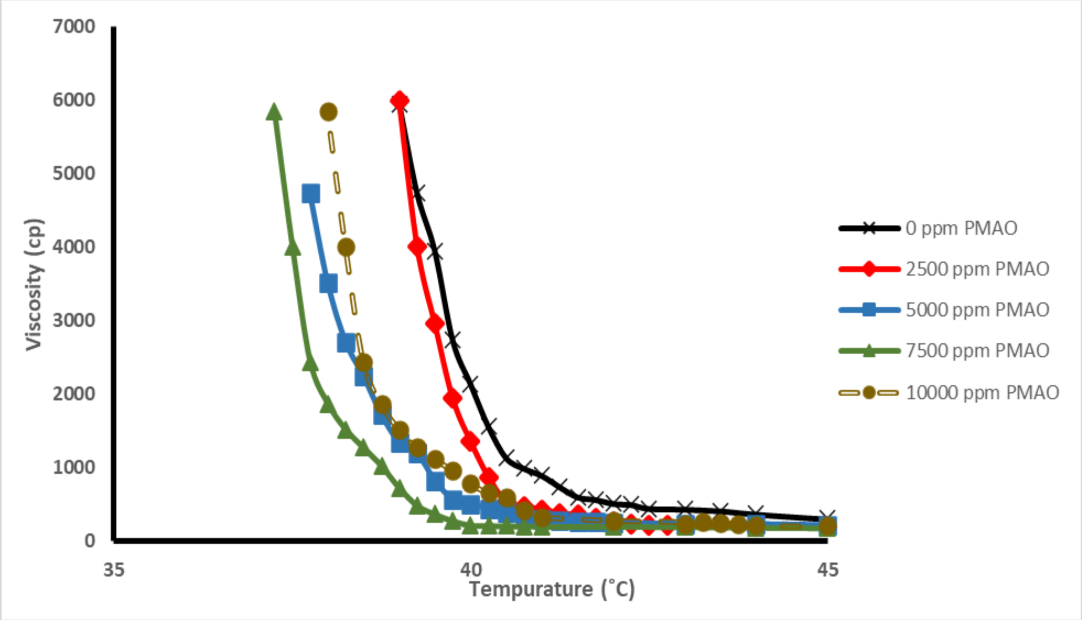


Figure 4.26 Effect of PMAO concentrations on WAT of 20% water cut emulsion at 3 s^{-1} shear rate

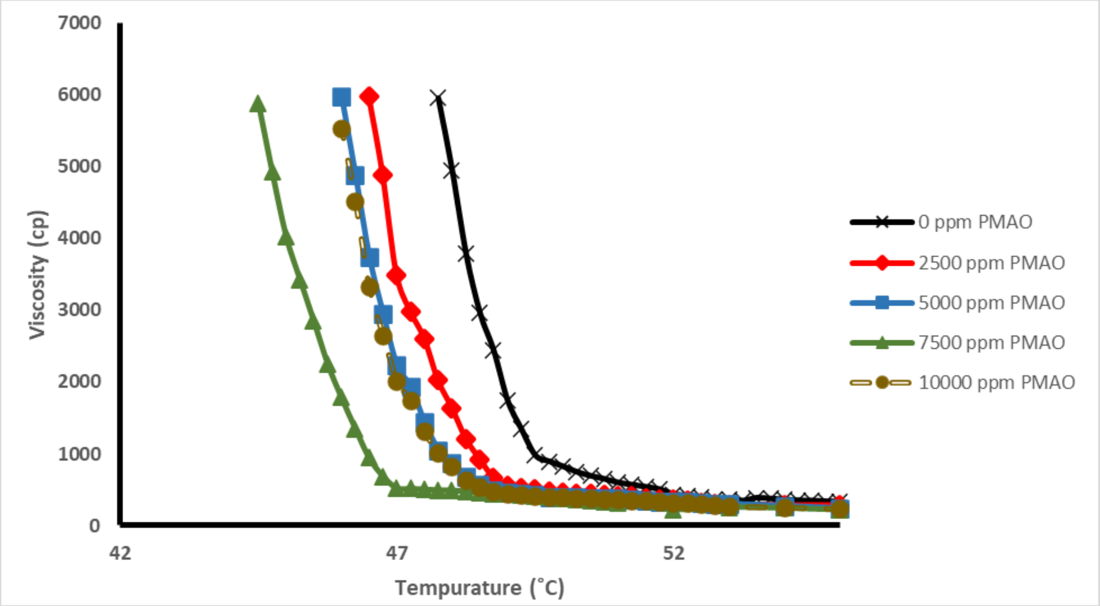


Figure 4.27 Effect of PMAO concentrations on WAT of 40% water cut emulsion at 3 s^{-1} shear rate

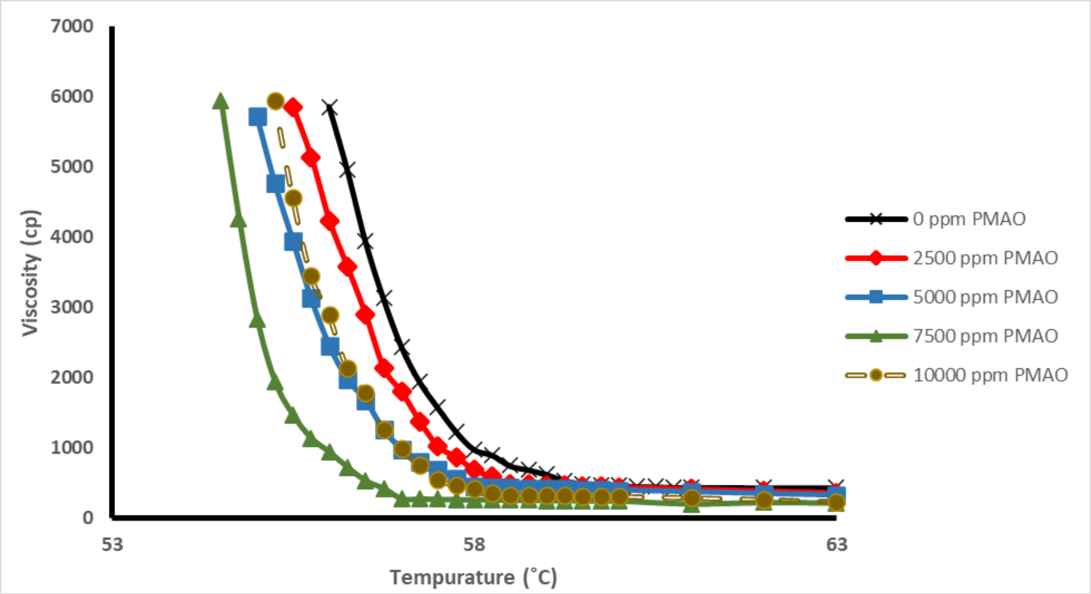


Figure 4.28 Effect of PMAO concentrations on WAT of 60% water cut emulsion at 3 s^{-1} shear rate

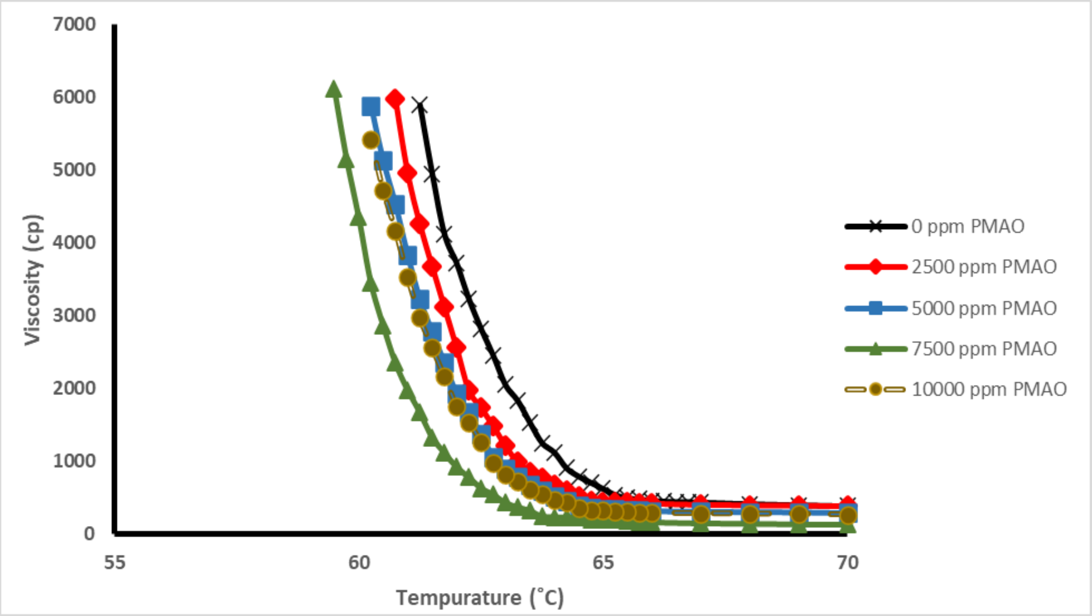


Figure 4.29 Effect of PMAO concentrations on WAT of 80% water cut emulsion at 3 s^{-1} shear rate

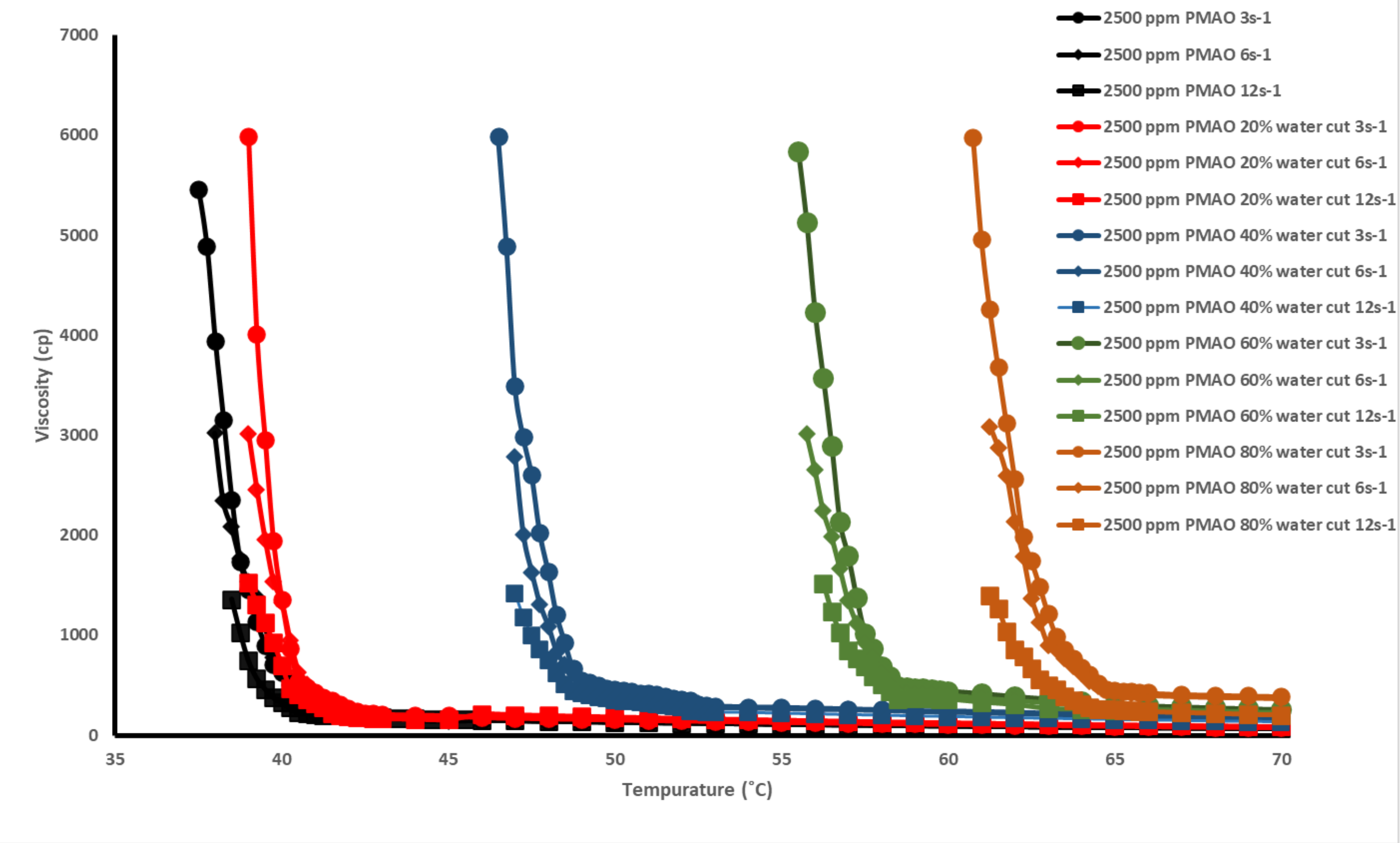


Figure 4.30 Effect of shear rate on 2500 ppm PMAO concentrations varying 0%-80% water cut at 3,6,12 s^{-1} shear rate

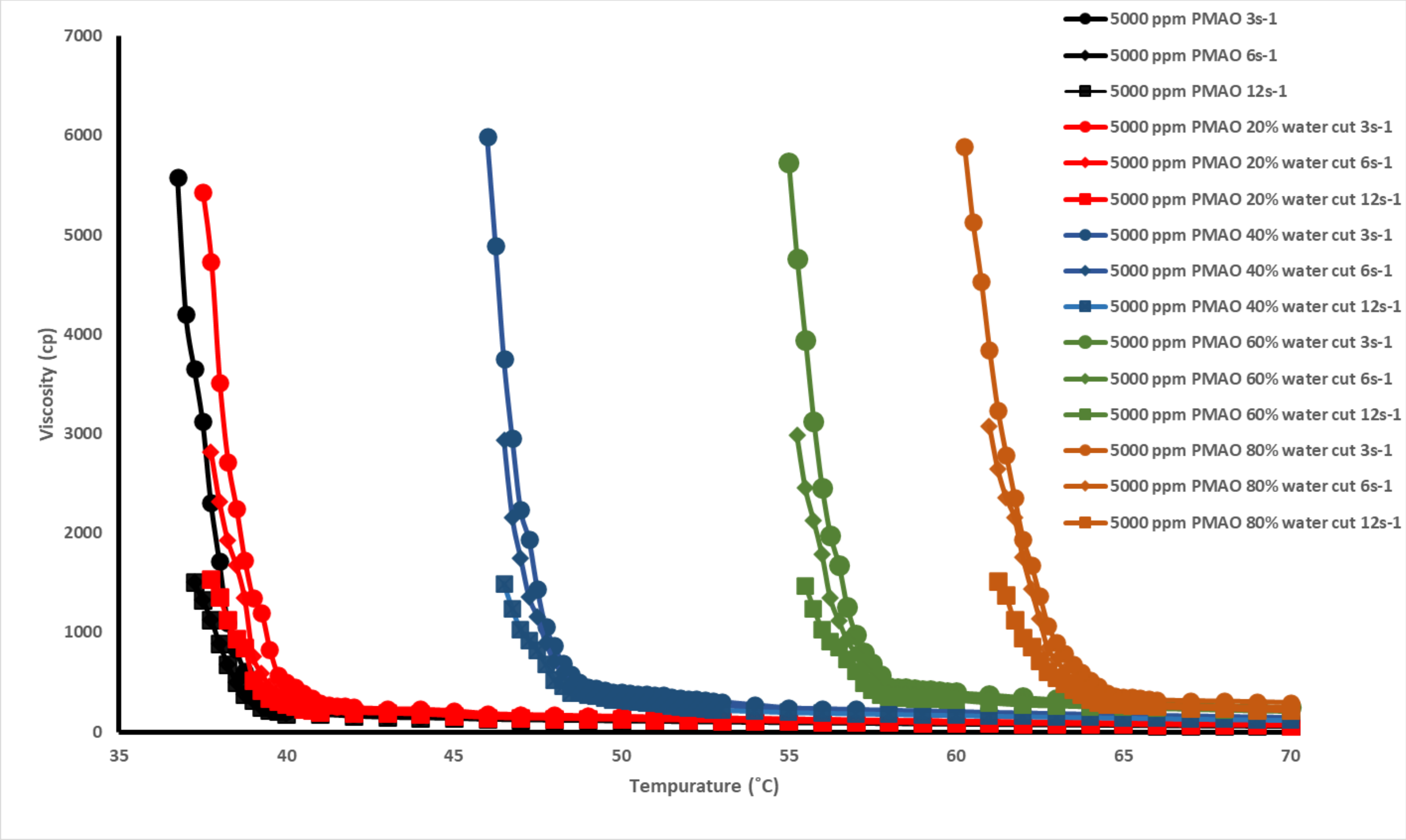


Figure 4.31 Effect of shear rate on 5000 ppm PMAO concentrations varying 0%-80% water cut at 3,6,12 s^{-1} shear rate

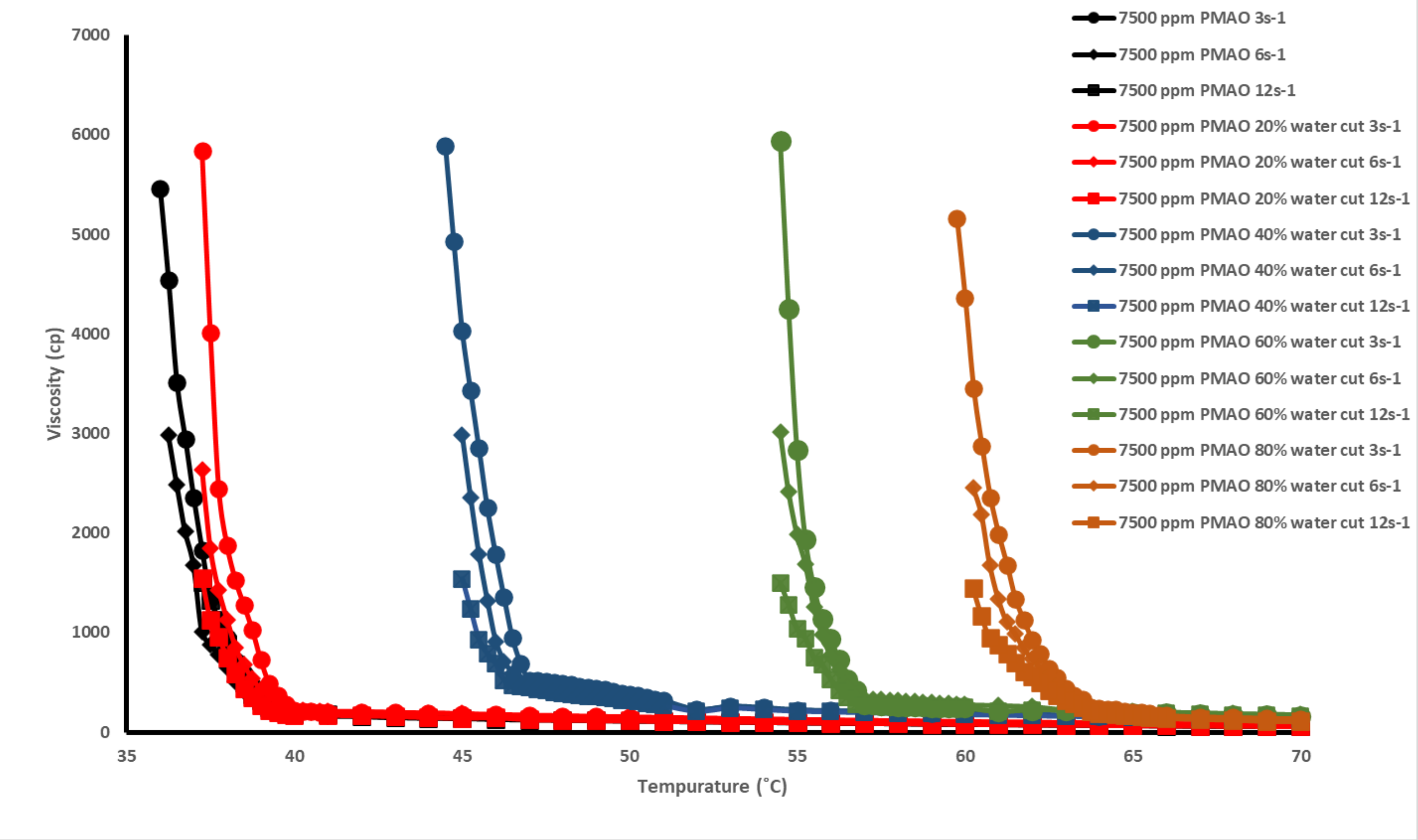


Figure 4.32 Effect of shear rate on 7500 ppm PMAO concentrations varying 0%-80% water cut at 3,6,12 s^{-1} shear rate

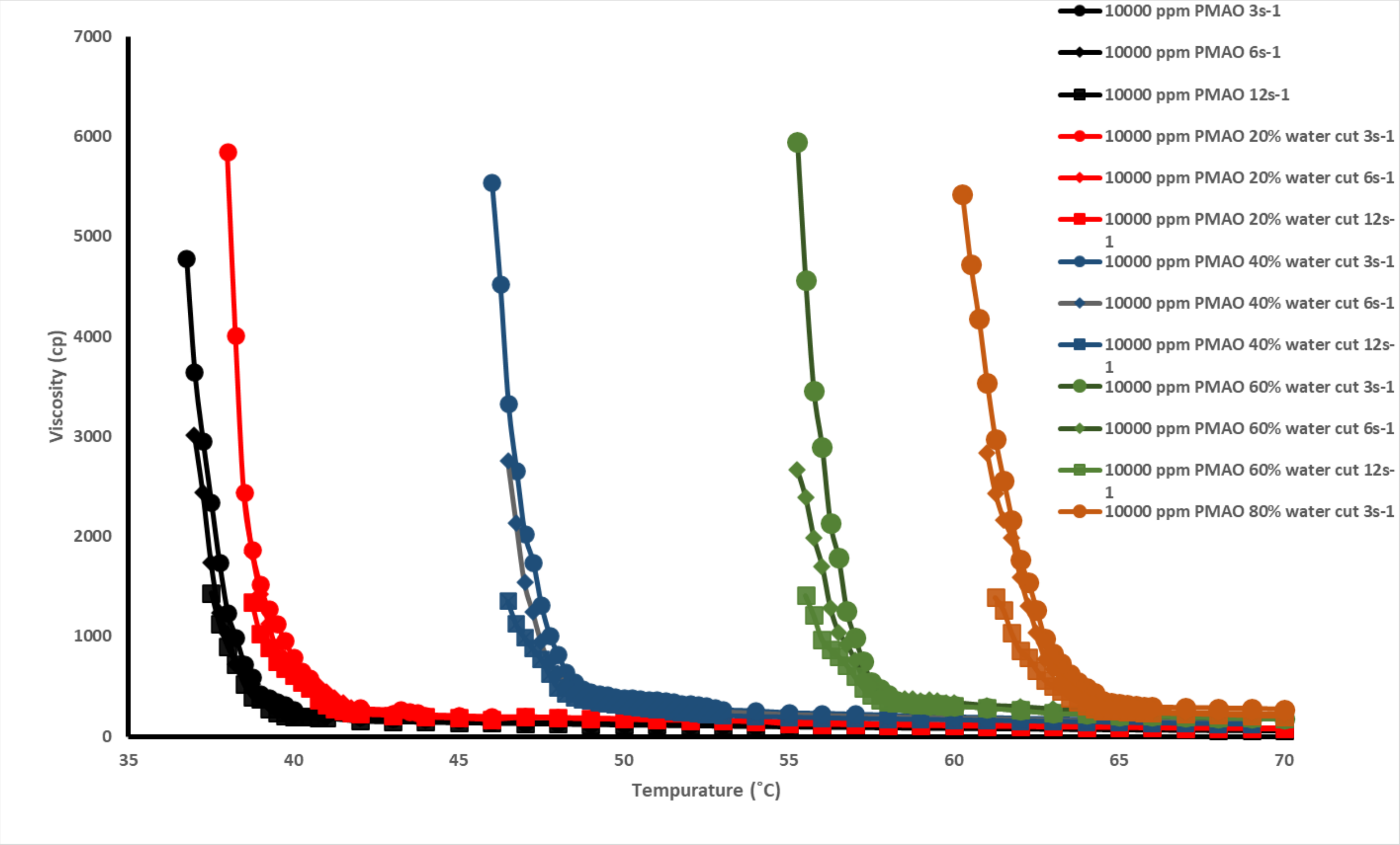


Figure 4.33 Effect of shear rate on 10000 ppm PMAO concentrations varying 0%-80% water cut at 3,6,12 s^{-1} shear rate

4.4 Wax deposition measurement

4.4.1 Results of n-heptane on wax deposition

The wax deposition experiment of crude oil and its emulsion range from 0%-80%. Also, the circulating medium supplied from chiller is set from 20 °C to 30 °C inside the cold finger tube representing the working condition of the oil field. The surrounding medium of the oil sample is set to be 50 °C to melt down the oil sample in liquid phase at all time.

For the inhibitor performance on wax deposition, it is defined as the percentage of the amount of wax deposition reduction by using inhibitor comparing to that of original crude oil and its emulsion without inhibitor. Also, the inhibitor performance on wax deposition will be shown in abbreviation as %Perform which will be shown in each table of wax deposition section. To calculate the inhibitor performance, it can be calculated as presented in the equation 4.3;

$$\text{Inhibitor performance on wax deposition} = \frac{W_f - W_t}{W_f} x100 \qquad (4.3)$$

W_f is the amount of wax deposition of the original oil and its emulsion without the inhibitor treatment.

W_t is the amount of wax deposition and its emulsion with the inhibitor treatment at various conditions.

In addition, for wax deposition, the temperature difference which is illustrated in the form like 20 ˚C/50 ˚C is the difference between and the cooling temperature circulated on the cold surface for wax deposition test (20 ˚C) and the outside temperature to control the oil sample into the liquid form (50 ˚C) .

The result of the effect of emulsion on wax deposition are shown in Table 4.21 and Figure 4.34 to Figure 4.36. Also, the amount of wax deposition varying from 0%, 20%, 40%, 60% and 80% are 14.5081 g, 14.727 g, 15.1381 g, 14.9207 g and 14.7595 g, respectively.

Table 4.21 to 4.25 show the effect of n-heptane on various emulsion conditions ranging from 0-80% with different temperature from 20°C-30°C. The concentration of n-heptane is varying from 5-20%. The figures of wax deposition of each case are also provided in the Table 4.21 to Table 4.25. Also, the inhibitor performance of n-heptane on wax deposition is also shown in the table with its abbreviation as %Perform.

The result presents that the amount of wax deposit decreases with an increase in the concentration of n-heptane at the various temperature as shown in the Figure 4.34 to Figure 4.39. The reason is that n-heptane is one of n-alkane solvent and it has the composition of the light hydrocarbon fraction that can dilute wax particles or increase wax solubility within oil. At the lower concentration of n-heptane, the amount of wax is higher. As the temperature of cold finger becomes lower, the amount of wax deposit on the cold finger will be larger.

In one hand, the temperature at 30 °C provides the less amount of wax deposit comparing to the lower temperature. For flow assurance of oil production, the low operation temperature is requiring the higher concentration of n-heptane. There is significantly decline of wax deposition in the case of 15% and 20%. However, the amount of 20% n-heptane in order to use as a wax inhibitor is high as well leading to the high operating cost. Thus, n-heptane concentration plays a major role for wax deposition reduction.

From the pour point aspect, the reason as explained earlier leads to the increasing pour point with increasing water cut because of the greater magnitude of rheology property. Thus, it is easily to form the gel as the pour point is lowered. This reason leads to an increase in the amount of wax deposition as water cut increases (Wang et al., 2013) as described in the Table 4.21-4.25.

For temperature difference of cold surface and the sample, it is obviously seen that an increase in temperature difference leads to a greater amount of wax deposition on the cold finger and the trend of emulsion and crude oil share the same similarity. Also, these two factors promote molecular diffusion and play a major role of wax deposition among 4 mechanisms. Thus, the wax deposition rate is reduced as temperature increases (Zhang et al., 2010).

For sensitivity of water cut to wax deposition, the results of water cut ranging from 0%-40% contribute that water cut increases with a higher amount of wax deposition. From Visintin et al, (2008) as water droplets provide the additional nucleation site, the wax deposition contains trapped water. Thus, the amount of wax deposit is founded to be higher than that of less water cut cases.

In contrast, for wax deposition at high water cut ranging from 40%-80%, the amount of wax deposit decreases with an increasing water cut. The reason is that water cut increases with an incremental number of droplets within emulsion and this water droplets can block the path of dissolve wax diffusion (Bruno et al., 2008) and the results are shown in Figure 4.34 to 4.36.

The calculation of Inhibitor performance is from the amount of wax deposit comparing with oil and its emulsion without chemical. According to result of inhibitor performance with water cut varying from 40% to 80%, it is increased with an increase in water cut.

The two factors impacting on the reduction of the amount of wax deposit are precipitated wax blocking the diffusion path and water droplet absorbing with dissolved wax and wax crystal. The former is blocking the diffusion path due to the occurrence of molecular diffusion through oil phase only. Thus, the higher water cut, the greater inhibiting of wax deposit. The wax particles and crystals absorb on to water droplet on the droplet surface. Thereby, the diffusion path is obstructed (Fan et al. 2017).

Thus, with the combined effect of these phenomena, this can explain why inhibitor effect increases with an increasing water cut ranging from 40%-80% for wax deposition.

Table 4.21 Amount of wax deposit with n-heptane as a wax inhibitor and crude oil

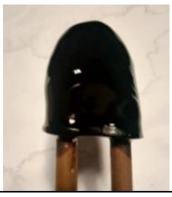
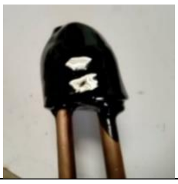
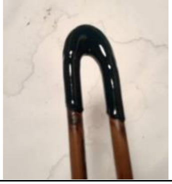
n-heptane		Amount of wax deposit					
		Temperature 20°C /50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
Concentration (wt%)	0	14.1531 		12.8126 		8.1199 	
	5	13.2497 	6.38	11.9456 	6.77	7.5695 	6.78
	10	12.0245 	15.04	10.8741 	15.13	6.7843 	16.45
	15	10.2327 	27.70	9.1650 	28.47	4.9019 	39.63
	20	8.1255 	42.59	7.1076 	44.53	3.8731 	52.30

Table 4.22 Amount of wax deposit with n-heptane as a wax inhibitor and 20% emulsion

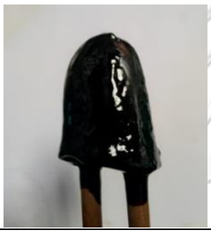
N-heptane		Amount of wax deposit					
		Temperature 20°C /50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
Concentration (wt%)	0	14.7270 		12.8214 		9.0455 	
	5	13.8366 	6.05	11.8367 	7.68	8.2549 	8.74
	10	12.3184 	16.35	10.7214 	16.38	6.9788 	22.85
	15	10.5942 	28.06	9.2124 	28.15	5.4124 	40.16
	20	8.4390 	42.70	7.3035 	43.04	3.9412 	56.43

Table 4.23 Amount of wax deposit with n-heptane as a wax inhibitor and 40% emulsion

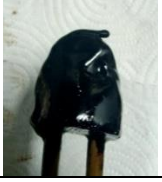
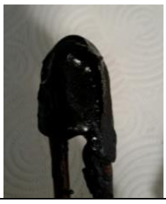
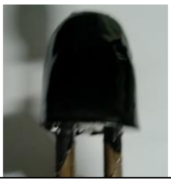
N-heptane		Amount of wax deposit					
		Temperature 20°C/50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
Concentration (wt%)	0	15.1381 		14.3246 		11.4653 	
	5	14.5203 	4.08	13.1412 	8.26	10.0352 	12.47
	10	12.9226 	14.64	11.7726 	17.82	8.5412 	25.50
	15	11.8310 	21.85	10.9741 	23.39	6.8427 	40.33
	20	9.5840 	36.69	8.8941 	37.91	5.2314 	54.37

Table 4.24 Amount of wax deposit with n-heptane as a wax inhibitor and 60% emulsion

N-heptane		Amount of wax deposit					
		Temperature 20°C /50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
Concentration (wt%)	0	14.9207 		13.2745 		11.2867 	
	5	13.8535 	7.25	11.8397 	10.81	9.2538 	17.93
	10	12.3263 	17.39	10.7981 	18.66	7.5373 	33.19
	15	10.5411 	29.35	9.3526 	29.54	5.8623 	48.04
	20	8.4353 	43.47	7.4426 	43.93	4.7132 	58.23

Table 4.25 Amount of wax deposit with n-heptane as a wax inhibitor and 80% emulsion

N-heptane		Amount of wax deposit					
		Temperature 20°C/50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
Concentration (wt%)	0	14.7595 		12.4412 		9.9683 	
	5	13.1453 	10.94	11.0533 	11.36	8.1241 	18.50
	10	10.8426 	26.54	9.0122 	27.57	5.9834 	39.98
	15	9.3487 	36.66	7.8741 	36.71	4.9741 	50.10
	20	7.8410 	46.87	5.8679 	52.83	3.3207 	66.69

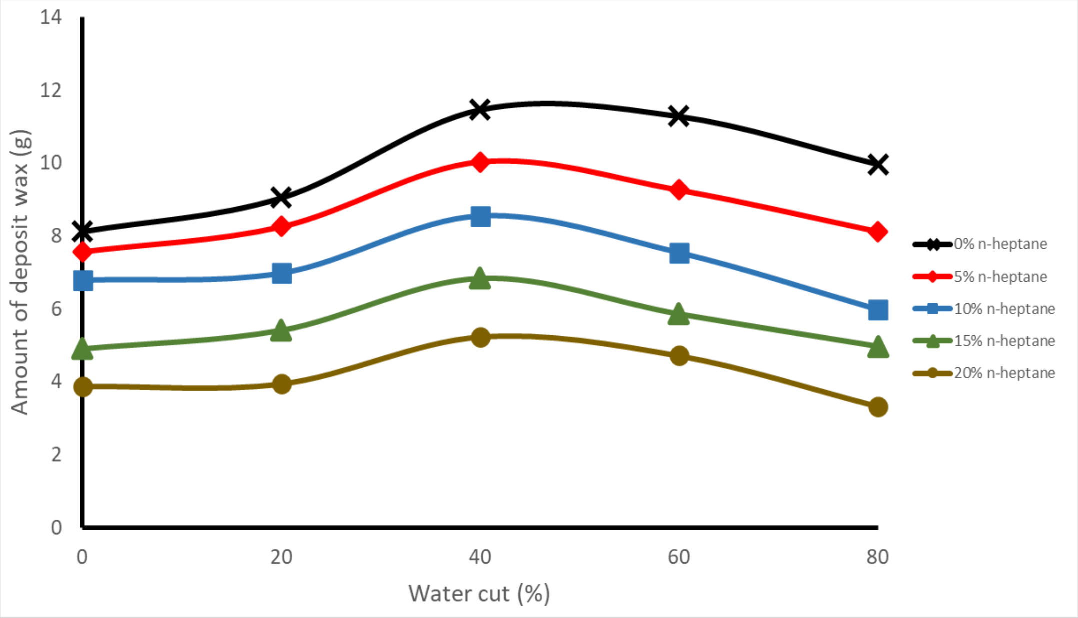


Figure 4.34 Effect of n-heptane concentration on the amount of wax deposit at 30˚C/50˚C

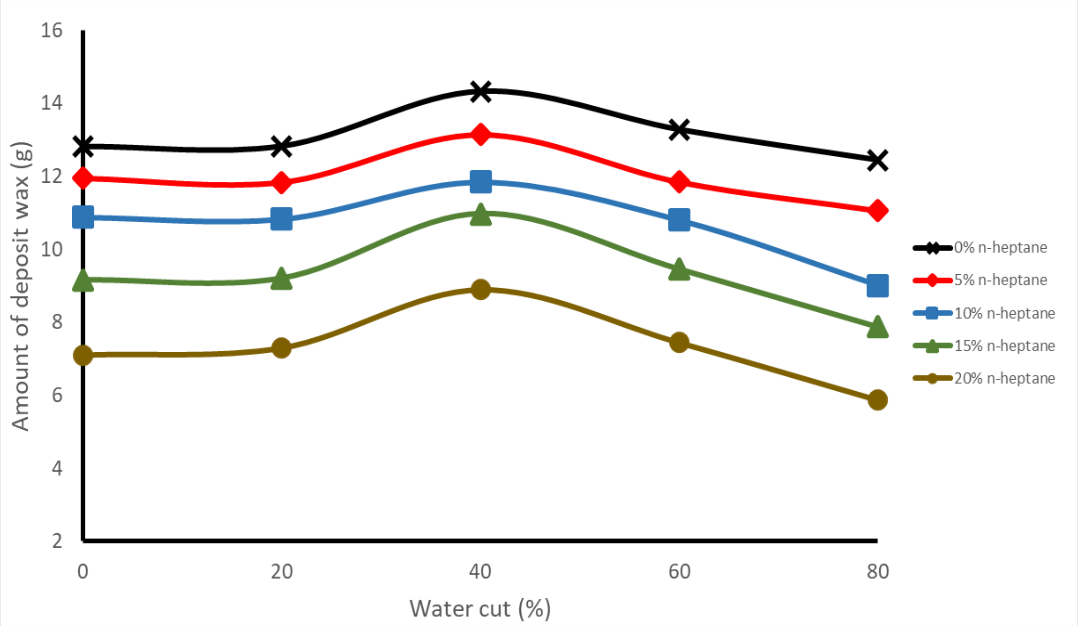


Figure 4.35 Effect of n-heptane concentration on the amount of wax deposit at 25˚C/50˚C

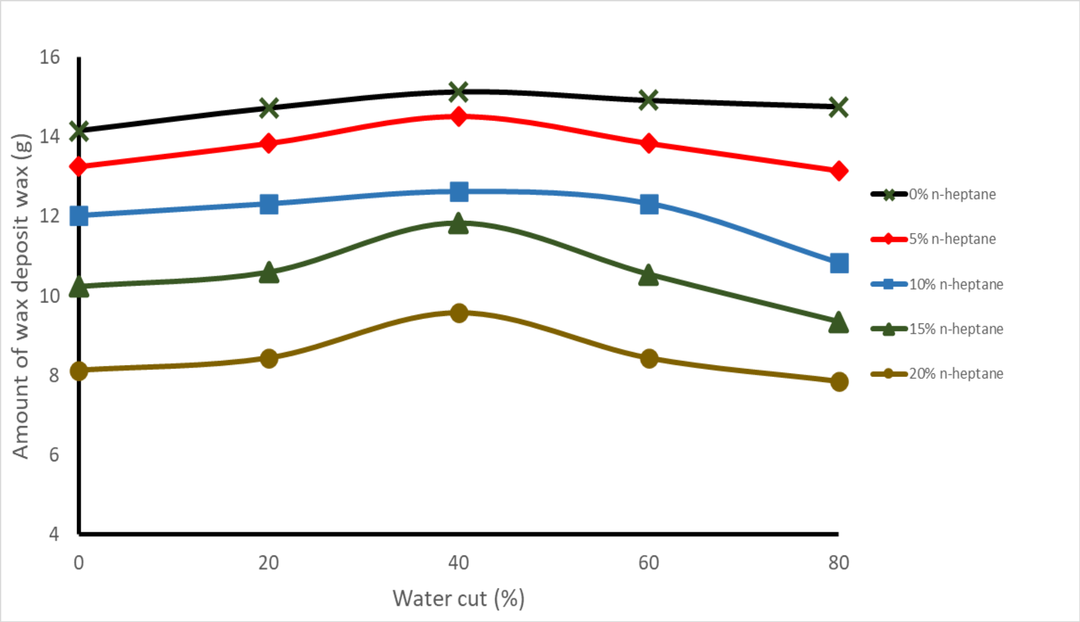


Figure 4.36 Effect of n-heptane concentration on the amount of wax deposit at 20˚C/50˚C

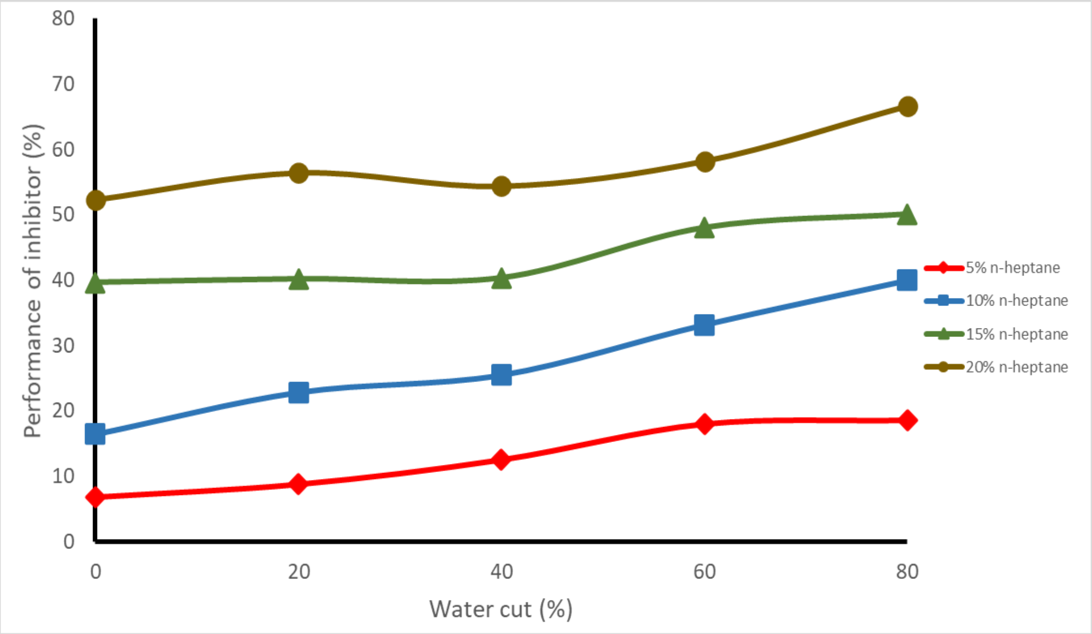


Figure 4.37 Performance n-heptane concentration on wax deposit at 30˚C/50˚C

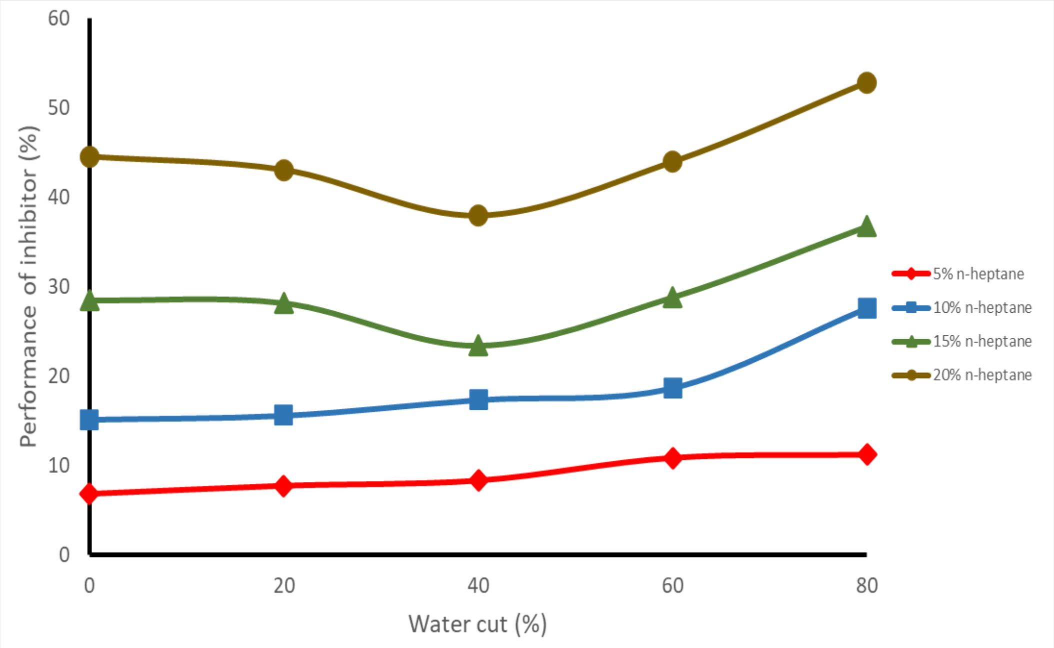


Figure 4.38 Performance n-heptane concentration on wax deposit at 25˚C/50˚C

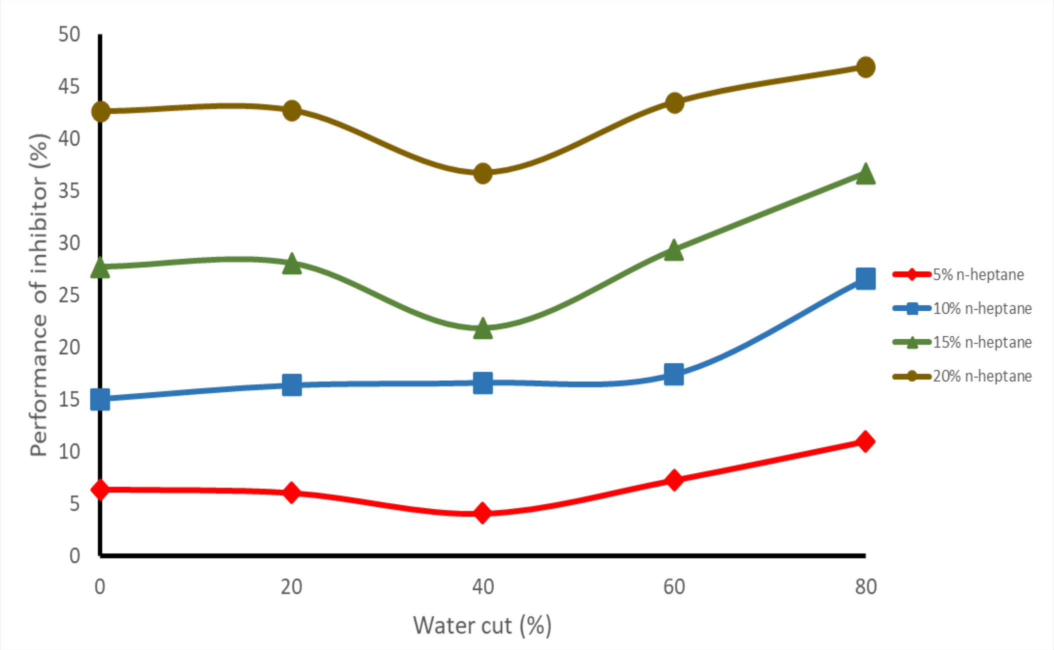


Figure 4.39 Performance n-heptane concentration on wax deposit at 20˚C/50˚C

4.4.2 Results of PMAO on wax deposition

The results of effect of PMAO are shown in the Table 4.26 to Table 4.30 and Figure 4.40 to Figure 4.45. The amount of wax deposition slightly decreases with an increase in the concentration of PMAO from 2,500 ppm to 7,500 ppm for each temperature condition. On the other hand, the amount of wax increases with PMAO concentration at 10,000 ppm.

This means that there is the optimum concentration which exhibits the best performance in term of amount of wax deposit at 7,500 ppm. The reason for higher concentration at 10,000 ppm leading to the lower wax deposition reduction performance is stated by Hoffmann (2013). From this work, it is informed that an excessive amount of inhibitor can exhibit slightly reduction. The reason is the same with explanation as the effect of PMAO on WAT that excessive of PMAO result in its molecule interact with others molecule. Thus, the number of polymer acted as polymer decrease. Thus, the performance of inhibitor decrease explained by Ragunathan et al. (2020).

In addition, it can be seen that the results show less wax components precipitated when the temperature is increased from 20 °C to 30 °C as shown in Table 4.26 to Table 4.30. As a result, from both factors, the amount of wax deposits is acquired less deposit at higher temperature and concentration of PMAO until it reaches 7,500 ppm.

At the low concentration and low temperature, the amount of wax deposit and gel strength are high. However, at the higher concentration to optimal concentration, the amount of wax deposit decreases with softer gel strength and also the amount of wax deposit illustrates in the Table 4.26 to Table 4.30.

For temperature difference, the higher temperature difference causes the concentration gradient close to cold region. According to molecular diffusion, more wax deposit is measured on the cold surface (Mansourpoor et al., 2019).

For the performance inhibitor with the effect of water cut ranging from 0%-40%, it is initially decreases as water cut increases as shown in Figure 4.46 to 4.48. The reason is that water cut increases resulting in lesser wax crystals (Chen et al., 2020). Thus, chemical inhibitor effect to wax deposition become lesser.

For the effect of inhibitor performance with water cut varying from 40% to 80%, it is increases with an increasing water cut. The amount of wax decreases due to decline of oil fraction resulting in reduction effect of inhibitor.

Table 4.26 Amount of wax deposit with PMAO as a wax inhibitor

PMAO		Amount of wax deposit					
		Temperature 20°C /50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
Concentration (ppmw)	0	14.5092 		12.8126 		8.1199 	
	2500	13.1834 	9.14	11.6158 	9.34	7.0619 	13.03
	5000	11.9652 	17.53	10.5537 	17.63	6.3181 	22.19
	7500	9.5808 	33.97	7.8412 	38.80	4.9421 	39.14
	10000	12.2412 	15.63	10.6779 	16.66	6.1987 	23.66

Table 4.27 Amount of wax deposit with PMAO as a wax inhibitor and 20% emulsion

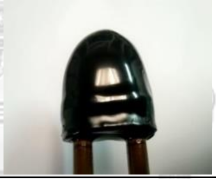
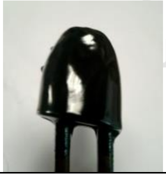
PMAO		Amount of wax deposit					
		Temperature 20°C /50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
Concentration (ppmw)	0	14.7220 		12.8214 		9.0455 	
	2500	13.8764 	5.74	12.0458 	6.05	7.9642 	11.73
	5000	12.6472 	14.09	10.9637 	14.49	7.1874 	22.90
	7500	10.1187 	31.27	8.421 	34.32	5.8742 	33.55
	10000	12.7241 	13.57	11.0471 	13.84	7.0124 	24.20

Table 4.28 Amount of wax deposit with PMAO as a wax inhibitor and 40% emulsion

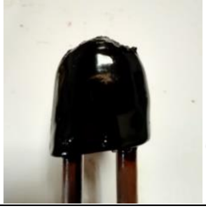
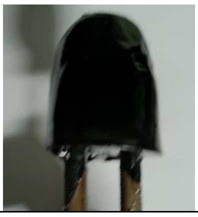
PMAO		Amount of wax deposit					
		Temperature 20°C /50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
Concentration (ppmw)	0	15.1443 		14.325 		11.4653 	
	2500	14.4867 	4.34	13.6872 	4.45	10.3463 	9.76
	5000	13.1241 	13.34	12.3774 	13.60	9.3412 	18.53
	7500	10.7624 	28.93	9.9842 	30.30	7.7474 	32.43
	10000	13.3842 	11.62	12.4471 	13.31	9.2141 	19.63

Table 4.29 Amount of wax deposit with PMAO as a wax inhibitor and 60% emulsion

PMAO		Amount of wax deposit					
		Temperature 20°C /50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
Concentration (ppmw)	0	14.9267 		13.2745 		11.2824 	
	2500	13.8398 	7.28	12.2141 	7.99	9.8742 	12.48
	5000	12.3274 	17.41	10.7452 	19.05	8.5758 	23.99
	7500	9.9546 	33.31	8.4247 	36.53	7.0937 	37.13
	10000	12.5759 	15.75	10.6741 	19.59	8.5412 	24.30

Table 4.30 Amount of wax deposit with PMAO as a wax inhibitor and 80% emulsion

PMAO		Amount of wax deposit					
		Temperature 20°C /50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
Concentration (ppmw)	0	14.6623 		12.5412 		9.9683 	
	2500	13.2416 	9.69	11.0842 	11.62	8.5782 	13.95
	5000	11.6741 	20.38	9.6913 	22.72	7.3741 	26.02
	7500	9.2471 	36.93	7.6412 	39.07	5.7439 	42.38
	10000	11.6313 	20.67	9.5026 	24.23	7.3221 	26.55

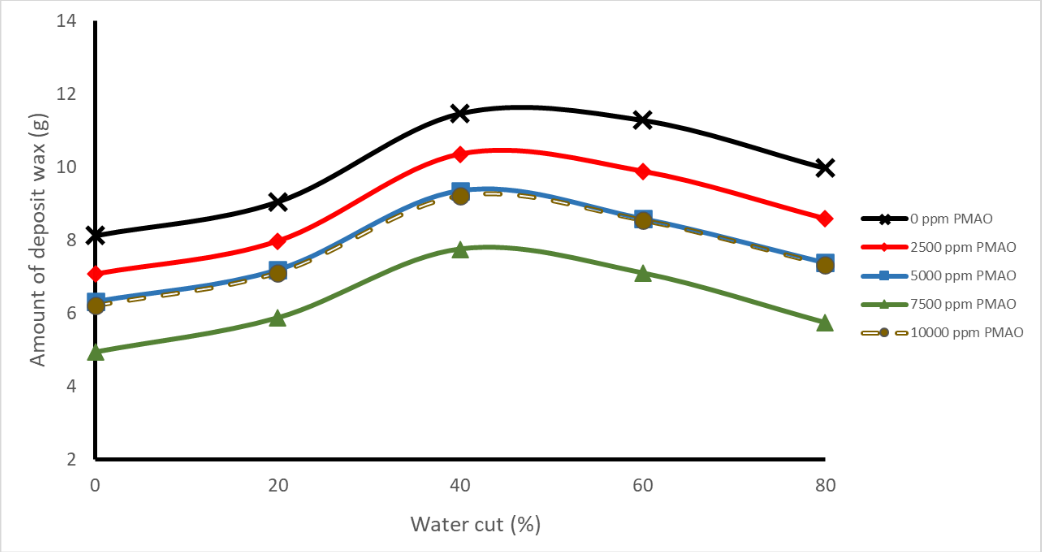


Figure 4.40 Effect of PMAO concentration on the amount of wax deposit at 30˚C/50˚C

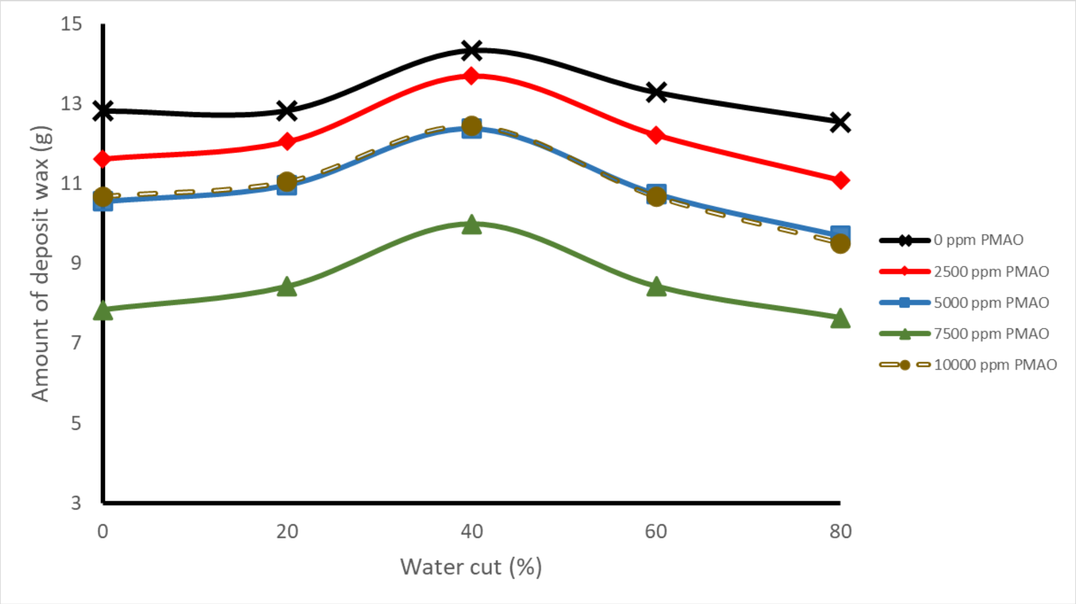


Figure 4.41 Effect of PMAO concentration on the amount of wax deposit at 25˚C/50˚C

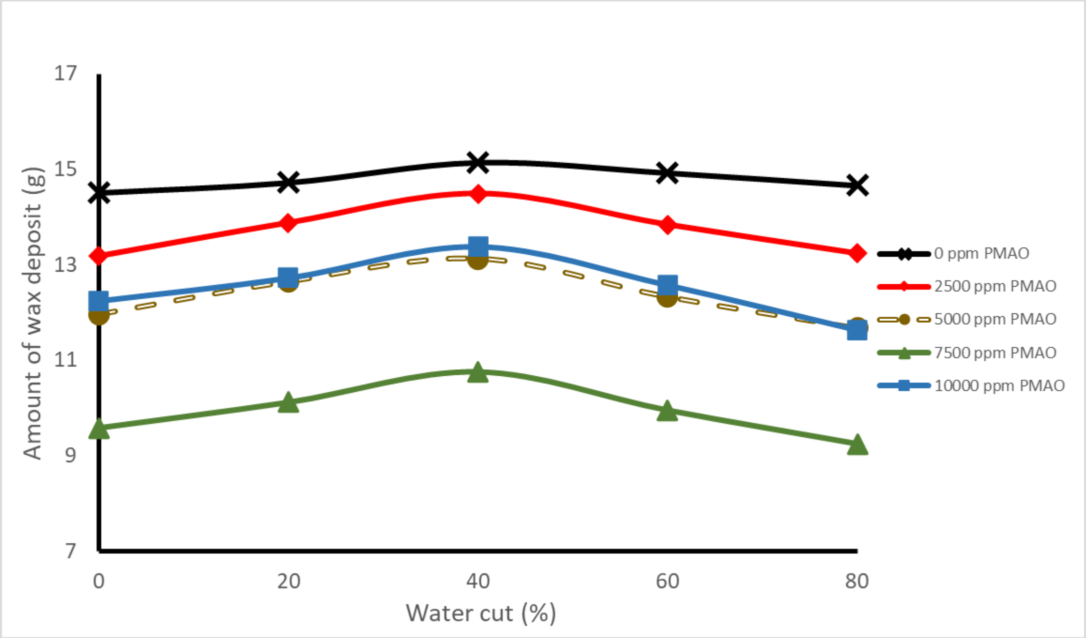


Figure 4.42 Effect of PMAO concentration on the amount of wax deposit at

20˚C/50˚C

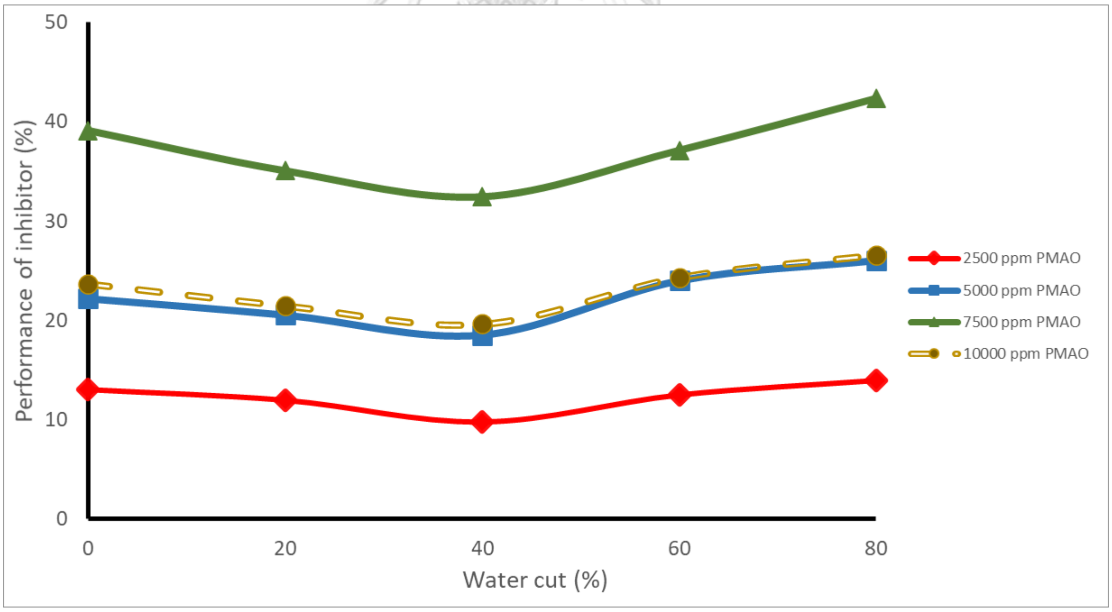


Figure 4.43 Performance PMAO concentration on wax deposit at 30˚C/50˚C

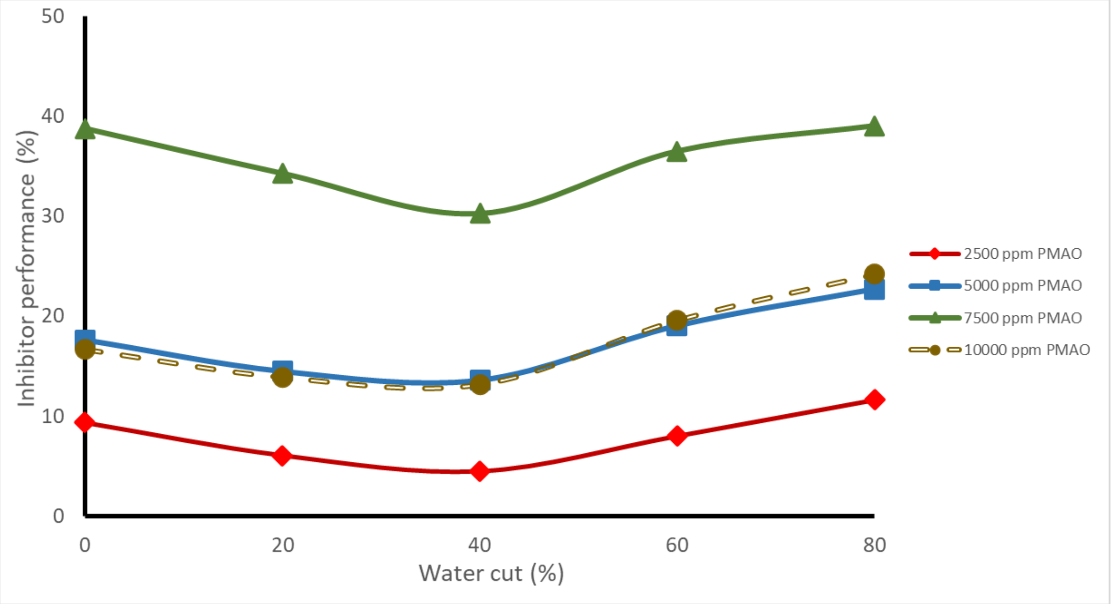


Figure 4.44 Performance PMAO concentration on wax deposit at 25˚C/50˚C

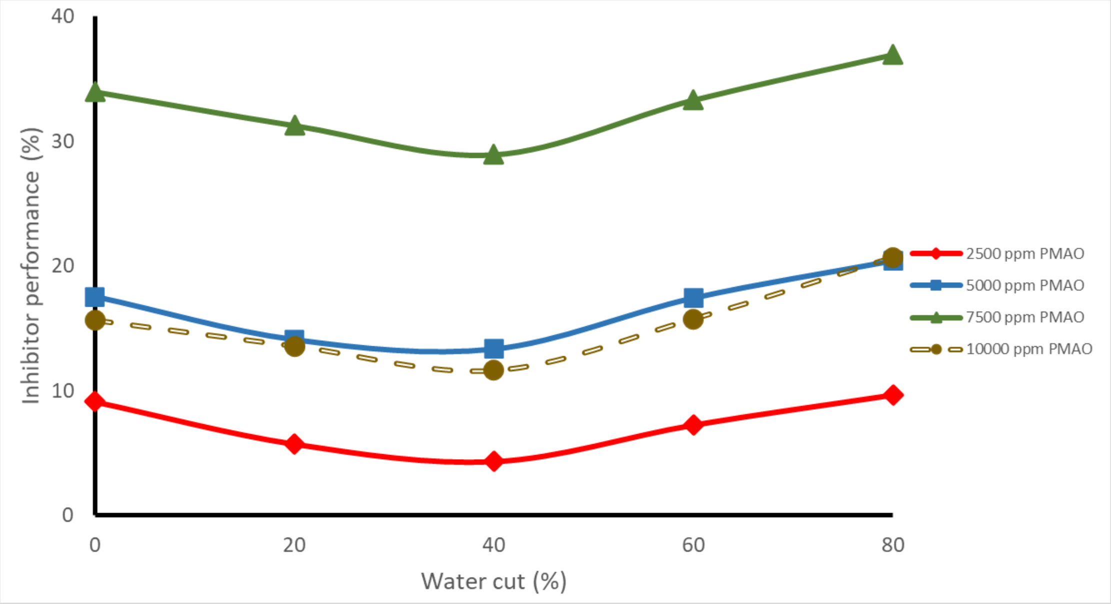


Figure 4.45 Performance PMAO concentration on wax deposit at 20˚C/50˚C

4.5 Mixture of wax inhibitors

4.5.1 Results of mixture of wax inhibitors on pour point

The selected of each chemical concentration in order to be effective and economical are 10% and 15% for n-heptane and 7500 ppm for PMAO. The mixture is performed the pour point measurement to investigate the effect of chemical mixture and the performance of wax deposition prevention. As the result of single chemical, selected chemical concentrations grant the higher performance.

Table 4.31 to Table 4.32 and Figure 4.46 illustrate the effect of emulsion coupling with chemical effect on pour point. The result illustrates that there is insignificant pour-point reduction with the effect of mixture comparing to effect of n-heptane for each condition.

The reason is that n-heptane provides the pour-point reduction as explained earlier. Also, PMAO has low performance for pour-point reduction in the both cases of single and mixing with n-heptane.

The presence of emulsion increases the rheology properties as described earlier. Thus, increasing water cut leads to increasing gel point and also pour point of emulsion. The greater water cut leads to increase pour point as illustrated in Table 4.31. Also, the same explanation of oil fraction decreases as increasing water cut; thus, resulting in the reduction of performance of inhibitor as shown in Table 4.32.

Table 4.31 Effect of mixture concentration on crude oil and its emulsion pour point coupling with mixture of chemical

Water cut (%)/n-heptane (wt%)	Pour point (°C)			
	n-heptane (%wt)		n-heptane(%wt) + 7500 ppm PMAO	
	10	15	10	15
0	29.4	24.5	29.3	24.4
20	30.9	26.4	30.7	26.3
40	33.5	30.2	32.9	29.7
60	37.8	35.8	35.6	33.5
80	43.2	41.6	38.3	36.7

Table 4.32 Performance of pour point reduction on crude oil and its emulsion pour point coupling with mixture of chemical

Water cut (%)/n-heptane (wt%)	Inhibitor performance on pour point reduction (%)			
	n-heptane (%wt)		n-heptane(%wt) + 7500 ppm PMAO	
	10	15	10	15
0	18.78	32.32	19.06	32.60
20	17.16	29.22	17.69	29.49
40	12.99	21.56	14.55	22.86
60	8.47	13.32	13.80	18.89
80	4.64	8.17	15.45	18.98

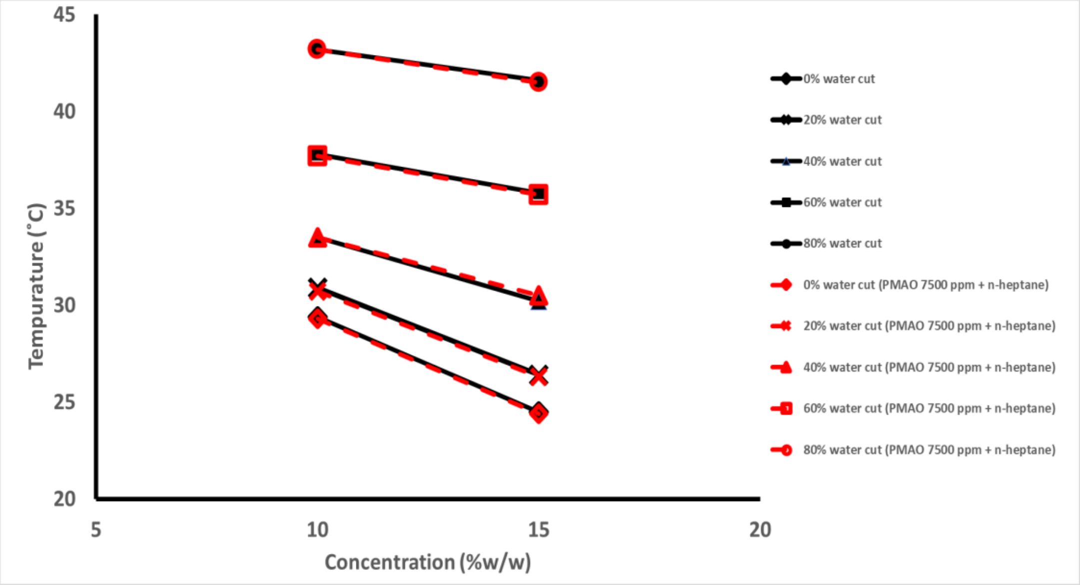


Figure 4.46 Effect of mixture concentration on crude oil and its emulsion pour point

4.5.2 Results of mixture of wax inhibitors on WAT

For the result of mixture on WAT at 3 s^{-1} shear rate, it is illustrated in Table 4.33 to Table 4.38 and Figure 4.47 to Figure 4.56. The results provide that the combination of mixture yields the better result than single n-heptane. For effect of mixture on crude oil and its emulsion at 6 s^{-1} and 12 s^{-1} shear rate are illustrated in Appendix B.

15% of heptane with 7,500 ppm yields slightly higher performance for WAT reduction than that of 10% with 7,500 ppm. This can be concluded that WAT decreases as the concentration of mixture increases. The result indicates that the combined effect of chemical between solvent and crystal modifier can influence the lower WAT.

WAT increases with amount of water cut because the water droplets grant the additional nucleation for precipitated wax and wax crystal precipitated on the droplet (Visintin et al., 2008).

For the effect of shear rate on WAT, shear rate increases with slightly decreasing WAT. For shear rate from 3 s^{-1} to 12 s^{-1} shear rate at 20% water cut with 10% n-heptane and 7500 ppm of PMAO, WAT slightly decreases from 39.1 °C to 38.4 °C as shown in the Table 4.33 – 4.35. The reason is the same with effect of shear rate on WAT of oil and its emulsion without chemical treatment and n-heptane.

For the effect of shear rate on the inhibitor performance of n-heptane, the effect is relatively insignificant as illustrated in the Table 4.36 – 4.38.

Table 4.33 Effect of mixture on WAT of crude oil and its emulsion at 3 s^{-1} shear rate

Water cut (%) / concentration	Wax Appearance Temperature (°C)				
	n-heptane (wt%)			n-heptane (wt%) + 7500 ppmw PMAO	
	0	10	15	10%	15%
0	41.2	38.6	37.9	37.2	36.2
20	42.7	40.0	38.4	39.1	37.5
40	50.7	47.6	46.6	46.8	46.1
60	58.7	56.1	54.6	55.5	60.0
80	65.2	64.1	62.9	62.8	61.8

Table 4.34 Effect of mixture on WAT of crude oil and its emulsion at 6 s^{-1} shear rate

Water cut (%) / concentration	Wax Appearance Temperature (°C)				
	n-heptane (wt%)			n-heptane (wt%) + 7500 ppmw PMAO	
	0	10	15	10%	15%
0	40.9	38.0	37.1	36.9	35.9
20	42.4	39.2	37.8	38.9	37.3
40	50.1	47.4	46.4	45.8	45.3
60	58.5	55.7	54.4	55.2	53.8
80	64.8	63.4	62.5	62.4	61.7

Table 4.35 Effect of mixture on WAT of crude oil and its emulsion at 12 s^{-1} shear rate

Water cut (%) / concentration	Wax Appearance Temperature (°C)				
	n-heptane (wt%)			n-heptane (wt%) + 7500 ppmw PMAO	
	0	10	15	10%	15%
0	40.6	37.9	36.9	36.2	35.5
20	42.4	38.3	37.8	38.4	37.3
40	50.1	47.2	46.0	45.4	45.0
60	58.5	55.6	54.1	54.8	53.7
80	64.8	62.7	61.3	62.2	60.9

Table 4.36 Inhibitor performance of mixture and n-heptane on WAT of crude oil and its emulsion at 3 s^{-1} shear rate comparing to without chemical condition

Water cut (%) / concentration (%)	Inhibitor performance on WAT (%)			
	n-heptane (%wt)		n-heptane(%wt) + 7500 ppm PMAO	
	5	10	15	20
0	2.54	6.52	8.14	10.48
20	3.38	6.37	10.01	12.25
40	4.00	6.01	8.02	10.41
60	2.51	4.42	6.85	8.12
80	0.63	1.83	3.54	5.26

Table 4.37 Inhibitor performance of mixture and n-heptane on WAT of crude oil and its emulsion at 6 s^{-1} shear rate comparing to without chemical condition

Water cut (%) / concentration (%)	Inhibitor performance on WAT (%)			
	n-heptane (%wt)		n-heptane(%wt) + 7500 ppm PMAO	
	5	10	15	20
0	2.37	6.85	9.05	10.79
20	3.75	7.56	10.91	12.73
40	3.85	5.52	7.29	9.44
60	2.65	4.78	7.01	9.07
80	0.62	1.81	3.51	5.23

Table 4.38 Inhibitor performance of mixture and n-heptane on WAT of crude oil and its emulsion at 12 s^{-1} shear rate comparing to without chemical condition

Water cut (%) / concentration (%)	Inhibitor performance on WAT (%)			
	n-heptane (%wt)		n-heptane(%wt) + 7500 ppm PMAO	
	5	10	15	20
0	3.54	6.63	9.08	10.87
20	4.16	9.51	10.73	13.67
40	2.44	4.42	6.74	8.18
60	1.65	3.54	6.05	7.68
80	1.06	2.48	4.67	5.33

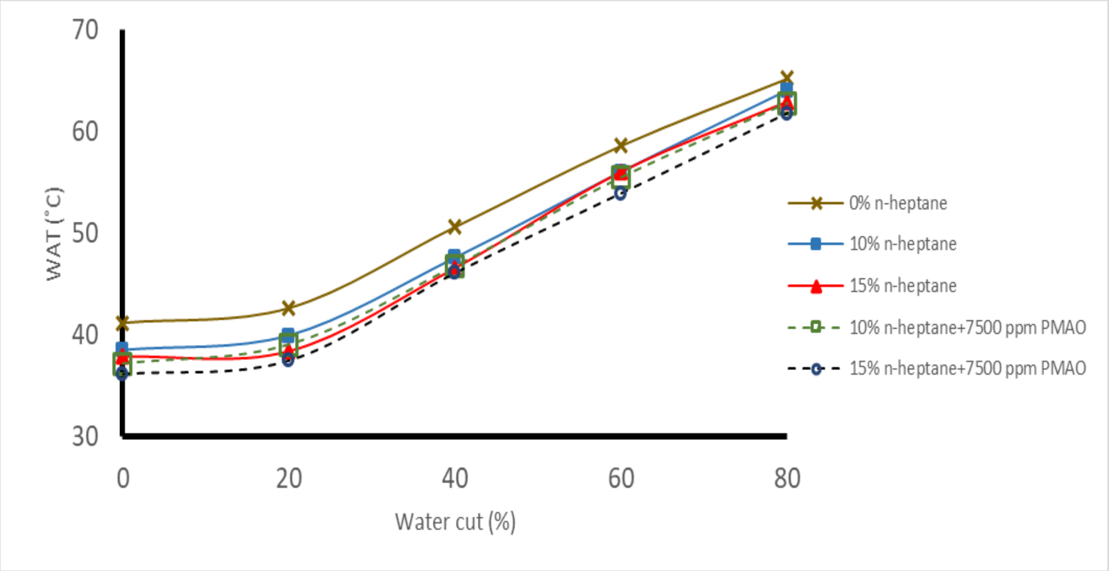


Figure 4.47 Effect of emulsion coupling with mixture concentration on WAT at 3 s^{-1} shear rate

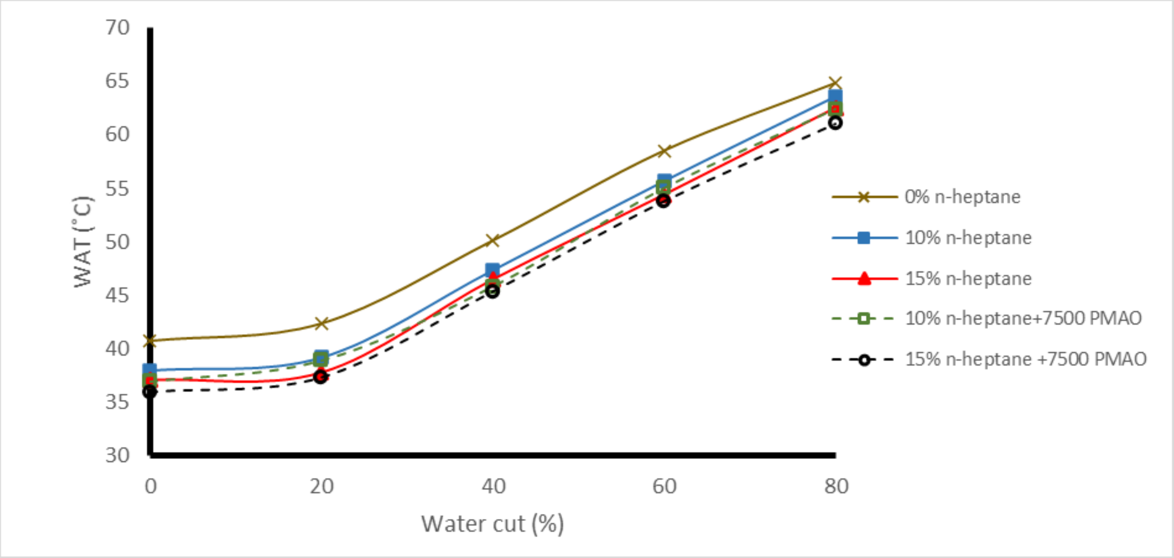


Figure 4.48 Effect of emulsion coupling with mixture concentration on WAT at $6\ s^{-1}$ shear rate

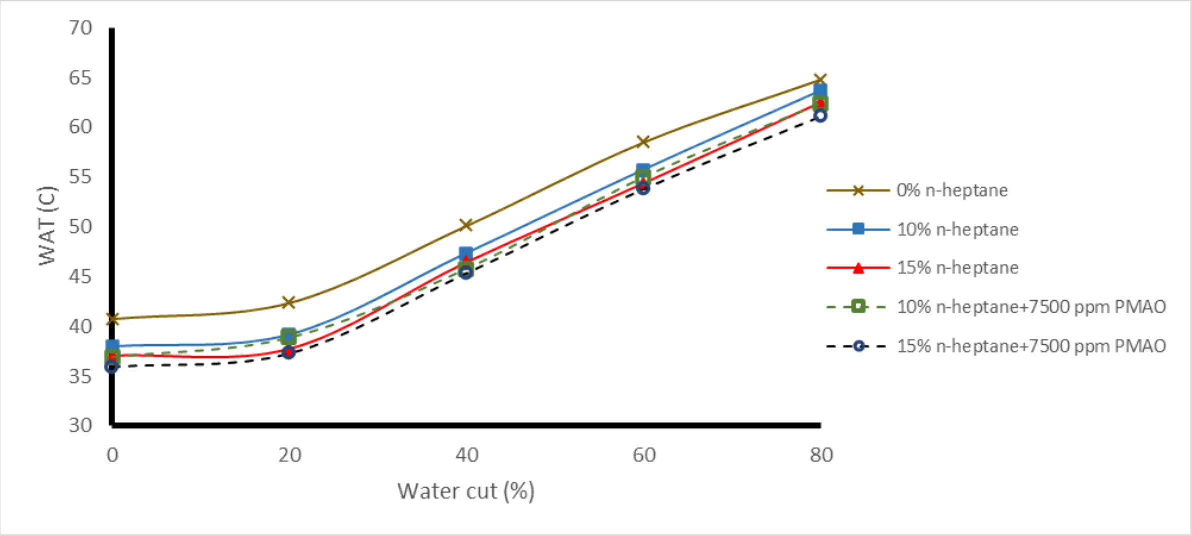


Figure 4.49 Effect of emulsion coupling with mixture concentration on WAT at $12\ s^{-1}$ shear rate

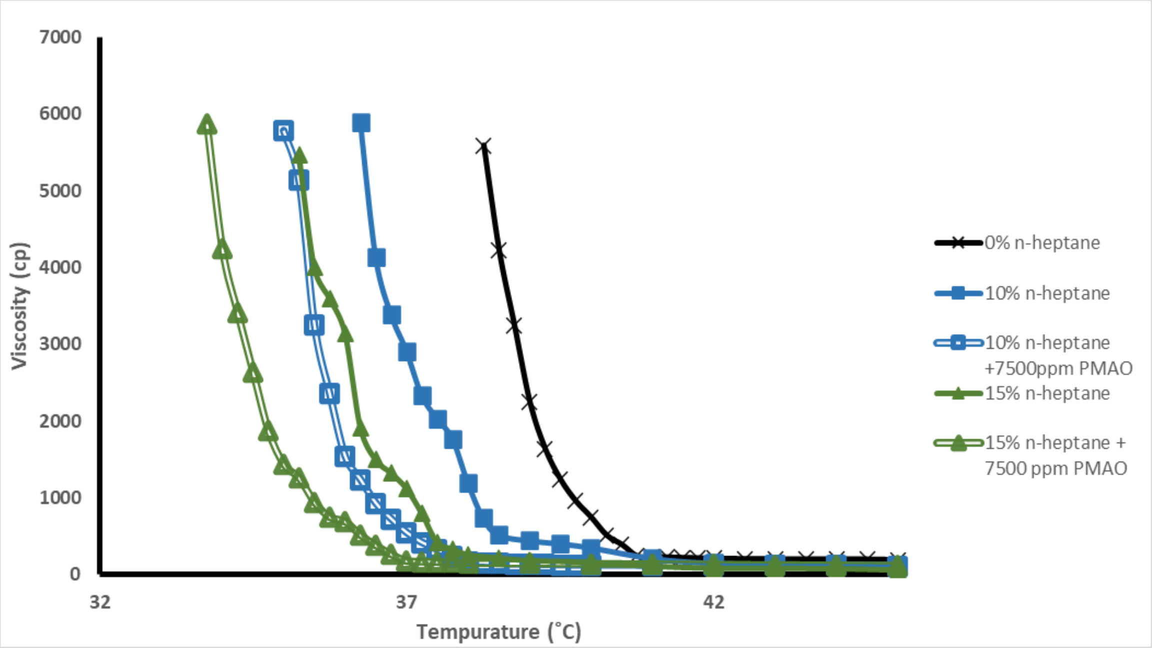


Figure 4.50 Effect of the mixture on WAT of crude oil at 3 s^{-1} shear rate

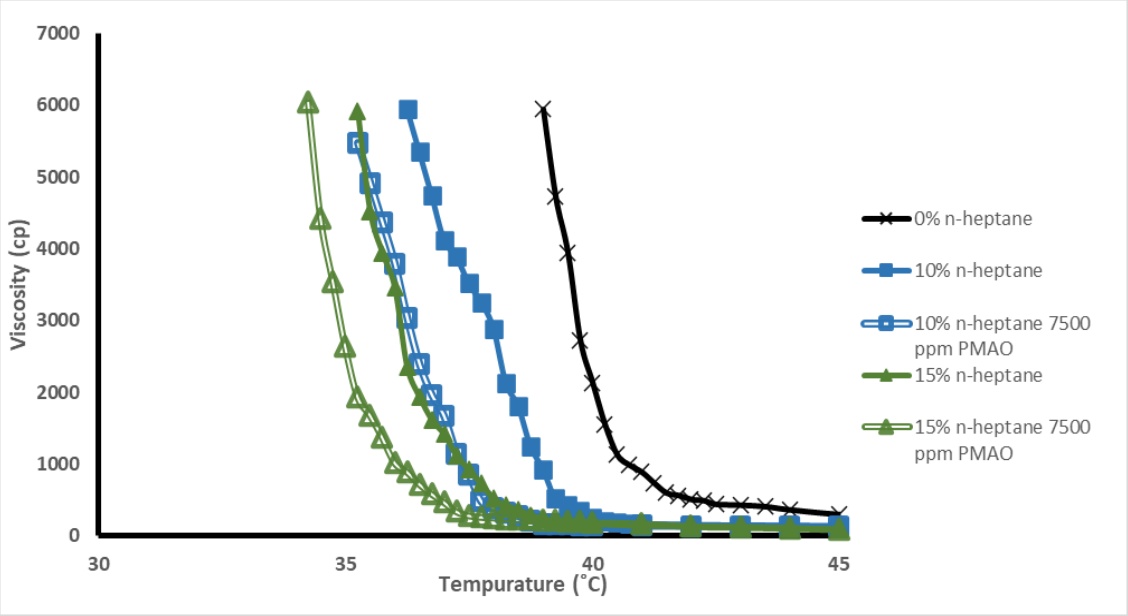


Figure 4.51 Effect of the mixture on WAT of emulsion water cut 20% at 3 s^{-1} shear rate

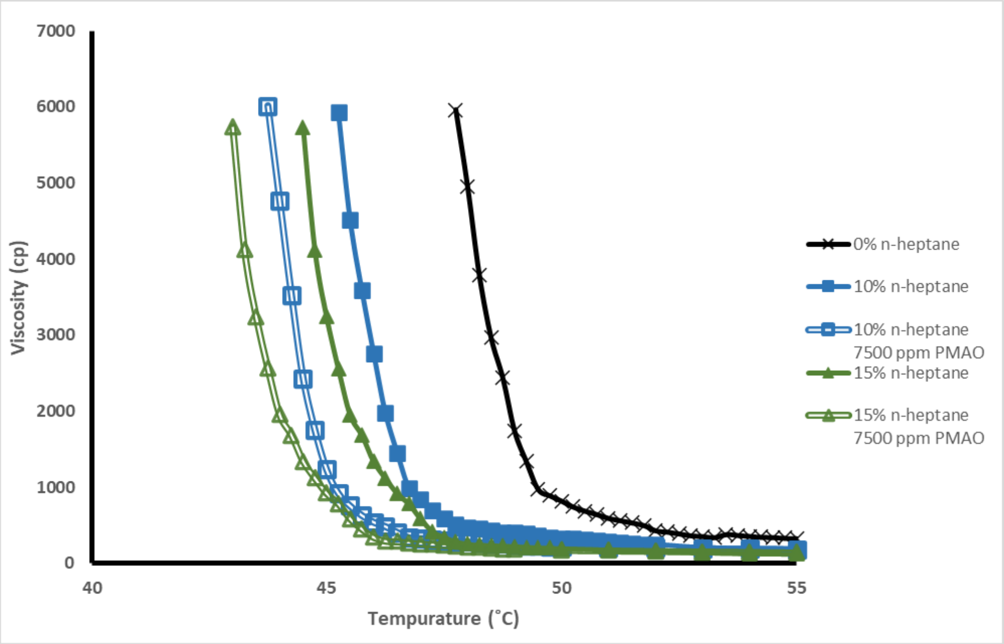


Figure 4.52 Effect of the mixture on WAT of emulsion water cut 40% at 3 s^{-1} shear rate

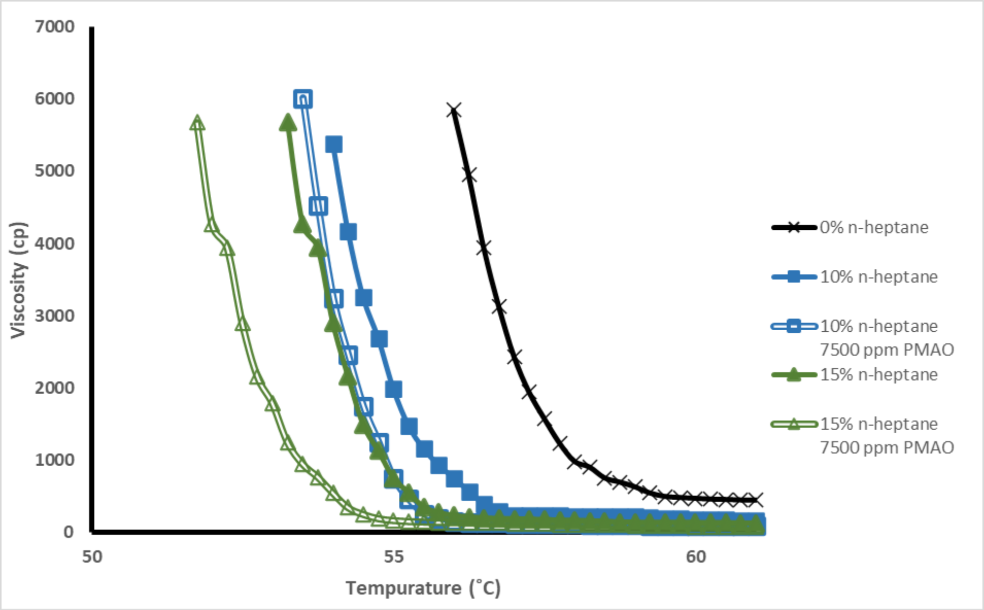


Figure 4.53 Effect of the mixture on WAT of emulsion water cut 60% at 3 s^{-1} shear rate

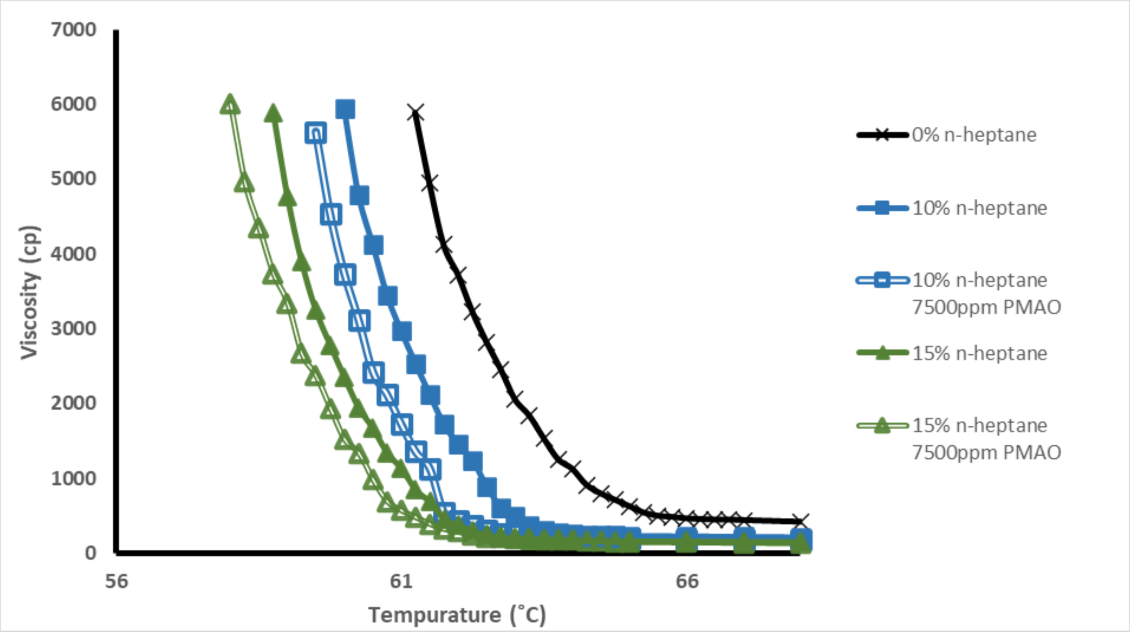


Figure 4.54 Effect of the mixture on WAT of emulsion water cut 80% at 3 s^{-1} shear rate

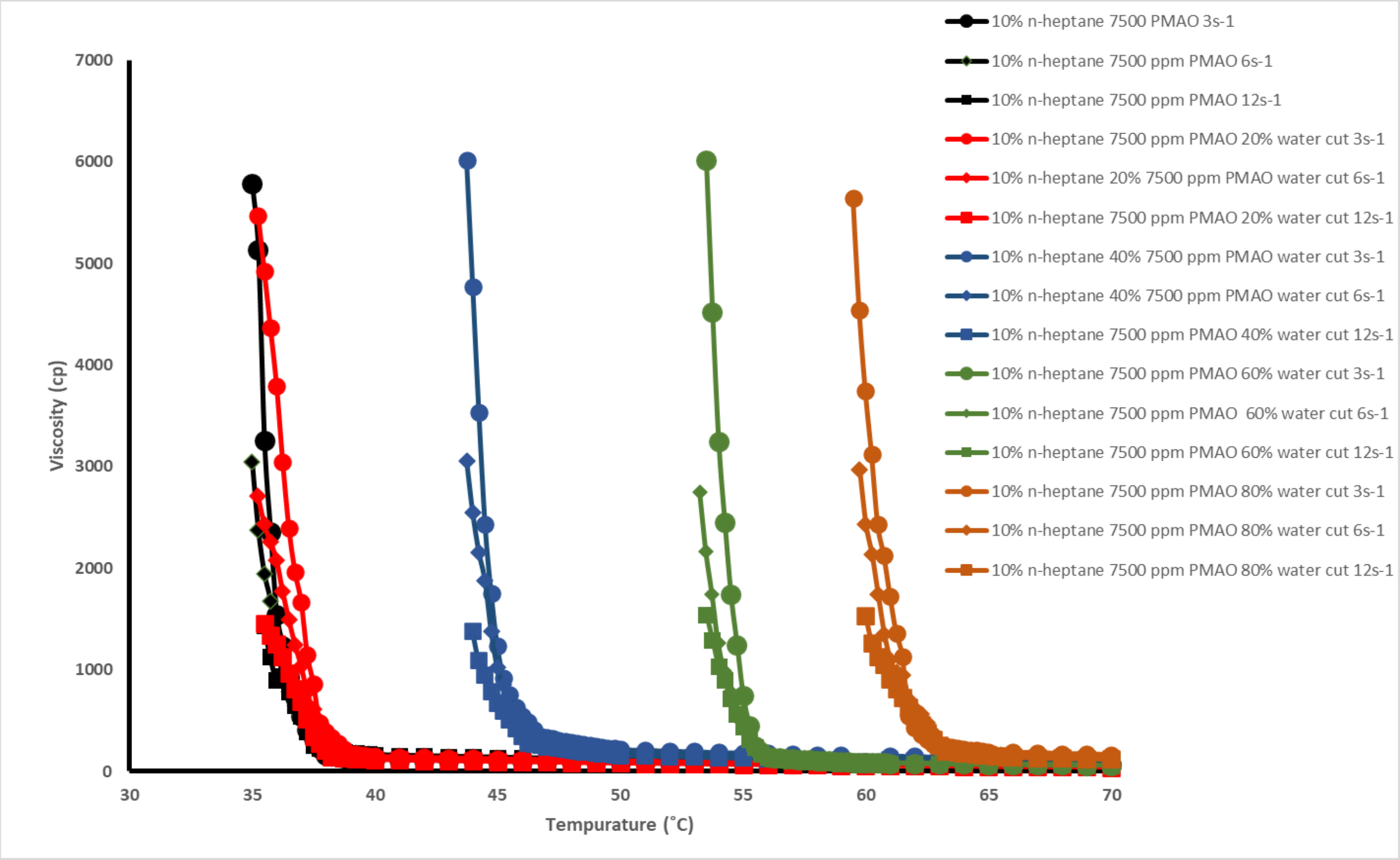


Figure 4.55 Effect of shear rate on WAT of crude oil and its emulsion at 10% n-heptane and 7500 ppm PMAO with 3 s^{-1},6 s^{-1} and 12 s^{-1}

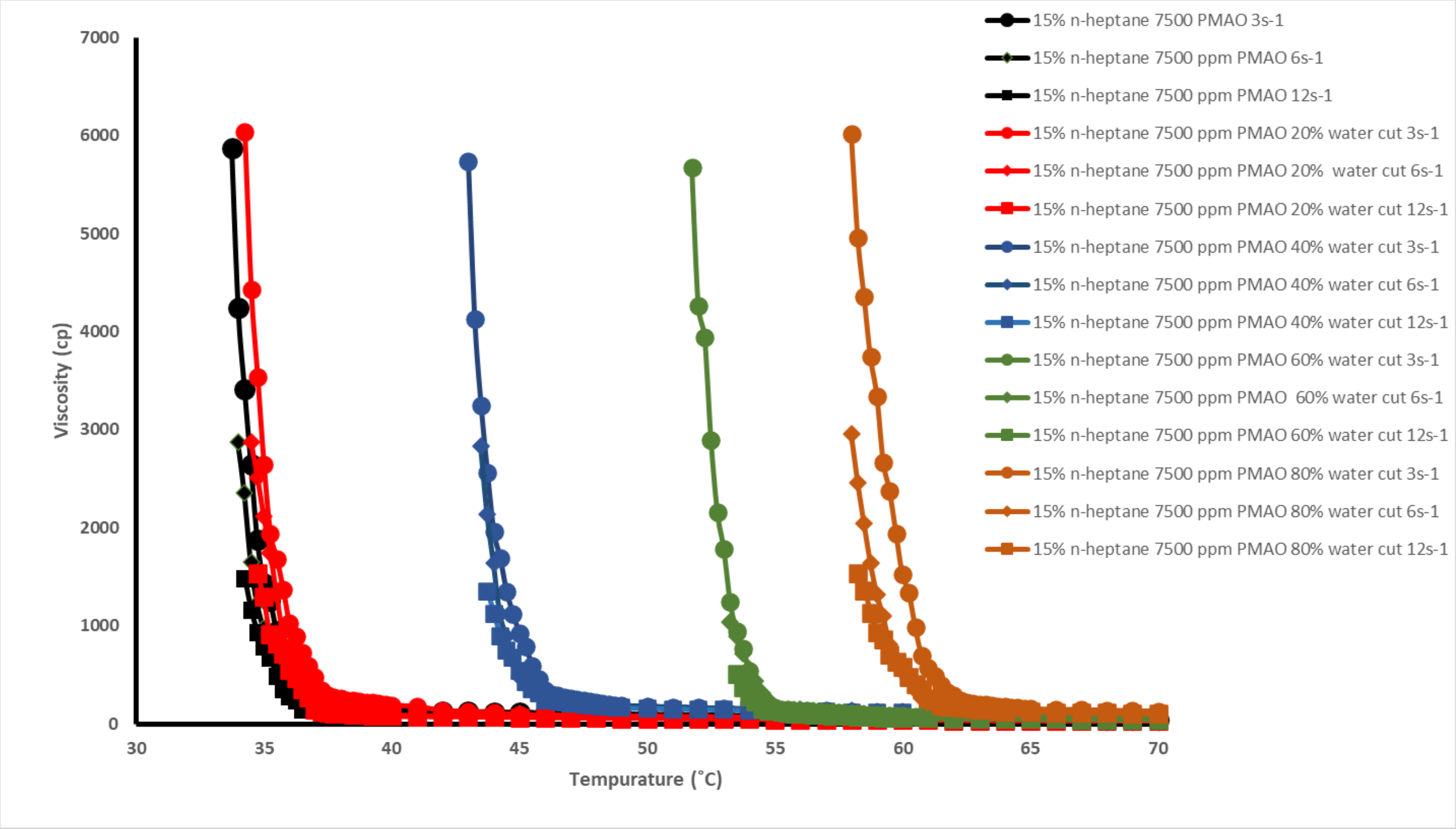


Figure 4.56 Effect of shear rate on WAT of crude oil and its emulsion at 15% n-heptane and 7500 ppm PMAO with 3 s^{-1},6 s^{-1} and 12 s^{-1}

4.5.3 Results of mixture of wax inhibitors on wax deposition

For the results of mixture coupling with water cut on wax deposition, it is illustrated in the Table 4.39 to Table 4.43 and Figure 4.57 to Figure 4.62. The result illustrates that the amount of wax deposition with combination of n-heptane and PMAO yields the better result than that of the single chemical.

From the result, the combination of two chemical reduces gel strength and amount of wax deposition. The effect of n-heptane can dilute the wax particles and PMAO as a co-crystallize to inhibit crystal growth. The combination of the two chemicals provides more effect on wax deposition.

For the presence of emulsion, the droplets of water increases with an increasing water cut (Juntarasakul, 2015). Higher water cut leads to greater number of droplets. Thus, the molecular diffusion will be hindered by blocking the path of this mechanism from water droplet.

For the temperature difference which illustrated by comparing amount of wax deposition of all cases in Figure 4.57 to Figure 4.57, it reveals that the amount of wax deposition decreases at higher temperature.

In addition, the same explanation of inhibitor performance of mixture for wax deposition related to water cut exhibits the same behavior with the single chemical. Zhou et al. (2015) suggested that the gelation point, one of the factors influencing the wax deposition becomes greater and the studied result also revealed that wax deposition initially increases with an increase in the water cut.

For 0%-40% water cut result of wax deposition, when water cut increases, the higher amount of wax deposition can be obtained. Visintin et al. (2008) explained that the more nucleation site is provided from water droplet. After that, water is trapped within wax crystal network. Thus, the water cut increases with the rising amount of wax deposition.

For 40%-80% water cut result of wax deposition, the amount of wax deposit decreases with an increasing water cut. The higher dispersed phase from increasing water cut can obstruct the diffusion path explained by Bruno et al (2008) and the result is shown in Figure 4.57 to 4.59.

For cold surface of cold finger decreased from 30 °C to 20 °C, wax deposition increases due to an increment of both concentration gradient and temperature gradient. Due to lowering temperature of cold surface, higher temperature gradient result in the greater concentration gradient of dissolved wax. At the temperature below the WAT, the dissolve wax precipitate out of the the oil phase. Then, the amount of dissolved wax reduces leading to lower concentration gradient in redial direction. Thus, the dissolved wax moves toward the cold surface due to molecular diffusion. Thereby, this mechanism produces more wax crystal precipitation and greater deposition at same water cut from 0% to 80% (Zhu, 2008).

The performance for 15% n-heptane combining with 7500 ppm PMAO exhibits the better performance from the amount of wax deposition reduction comparing to mixture at 10% n-heptane and single n-heptane as illustrated in Figure 4.60 to Figure 4.62 for all temperature conditions. Also, at the high water cut, the inhibitor performance of wax inhibitor on wax deposition also increases.

For the effect of inhibitor performance with water cut varying from 40% to 80%, it is increases with increasing water cut.

Table 4.39 Amount of wax deposit with n-heptane and mixture as a wax inhibitor and crude oil

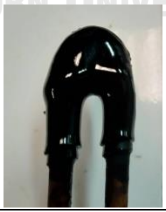
Concentration (%)		Amount of wax deposit					
		Temperature (°C) 20°C/50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
n-heptane (wt%)	0	14.1531 		12.8126 		8.1199 	
	10	12.0245 	15.04	10.8741 	15.13	6.7843 	16.45
	15	10.2327 	27.70	9.1650 	28.47	4.9019 	39.63
n-heptane (wt%) + 7500 ppmw PMAO	10	7.3366 	48.16	5.7256 	55.31	3.3172 	59.15
	15	4.8363 	65.83	2.9358 	79.09	1.8365 	77.38

Table 4.40 Amount of wax deposit with n-heptane and mixture as a wax inhibitor and emulsion water cut 20%

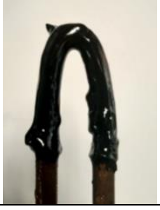
Concentration (%)		Amount of wax deposit					
		Temperature 20°C /50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
n-heptane (wt%)	0	14.7270 		12.8214 		9.0455 	
	10	12.3184 	16.35	10.7214 	16.38	6.9788 	22.85
	15	10.5942 	28.06	9.2124 	28.15	5.4124 	40.16
n-heptane (wt%) + 7500 ppmw PMAO	10	8.0053 	45.64	6.1356 	52.15	3.0167 	66.65
	15	6.2916 	57.28	3.9401 	69.27	1.6185 	82.11

Table 4.41 Amount of wax deposit with n-heptane and mixture as a wax inhibitor and emulsion water cut 40%

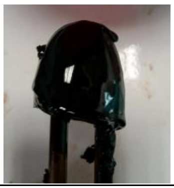
Concentration (%)		Amount of wax deposit					
		Temperature 20°C /50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
n-heptane (wt%)	0	15.1381 		14.3246 		11.4653 	
	10	12.9226 	14.64	11.7726 	17.82	8.5412 	25.50
	15	11.8310 	21.85	10.9741 	23.39	6.8427 	40.32
n-heptane (wt%) + 7500 ppmw PMAO	10	9.2801 	38.70	7.3750 	48.52	4.1718 	63.61
	15	7.3170 	51.67	4.9381 	65.53	3.7166 	67.58

Table 4.42 Amount of wax deposit with n-heptane and mixture as a wax inhibitor and emulsion water cut 60%

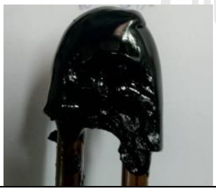
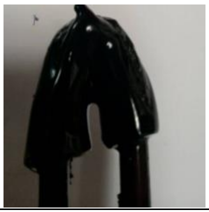
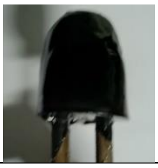
Concentration (%)		Amount of wax deposit					
		Temperature (°C) 20°C /50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
n-heptane (wt%)	0	14.9207 		13.2755 		11.2824 	
	10	12.3263 	17.39	10.7981 	18.66	7.5373 	33.19
	15	10.5411 	29.35	9.3526 	29.54	5.8623 	48.04
n-heptane (wt%) + 7500 ppmw PMAO	10	8.1166 	45.60	6.9386 	47.73	3.9156 	65.29
	15	6.4771 	56.59	4.7176 	64.46	3.3367 	70.43

Table 4.43 Amount of wax deposit with n-heptane and mixture as a wax inhibitor and emulsion water cut 80%

Concentration (%)		Amount of wax deposit					
		Temperature 20°C /50°C	% Perform	25°C /50°C	% Perform	30°C /50°C	% Perform
n-heptane (wt%)	0	14.7595 		12.4412 		9.9683 	
	10	10.8426 	26.54	9.0112 	27.57	5.9834 	39.98
	15	9.3487 	36.66	7.8741 	36.71	4.9741 	50.10
n-heptane (wt%) + 7500 ppmw PMAO	10	6.8276 	53.74	5.487 	55.90	3.0056 	69.85
	15	5.2200 	64.63	4.0160 	67.72	2.6053 	73.86

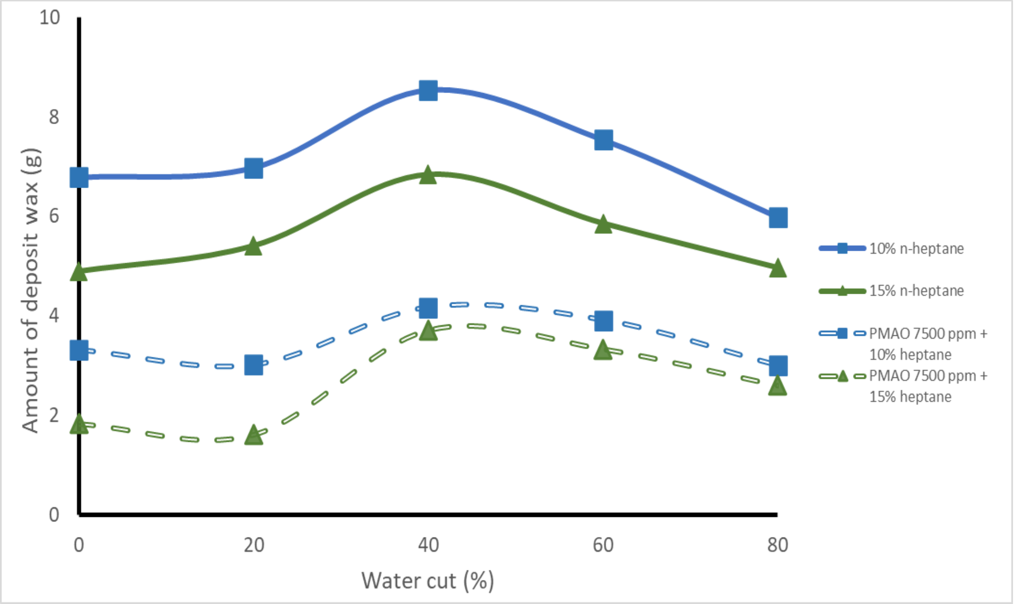


Figure 4.57 Effect of n-heptane and mixture concentration on the amount of wax deposit at 30 °C /50 °C

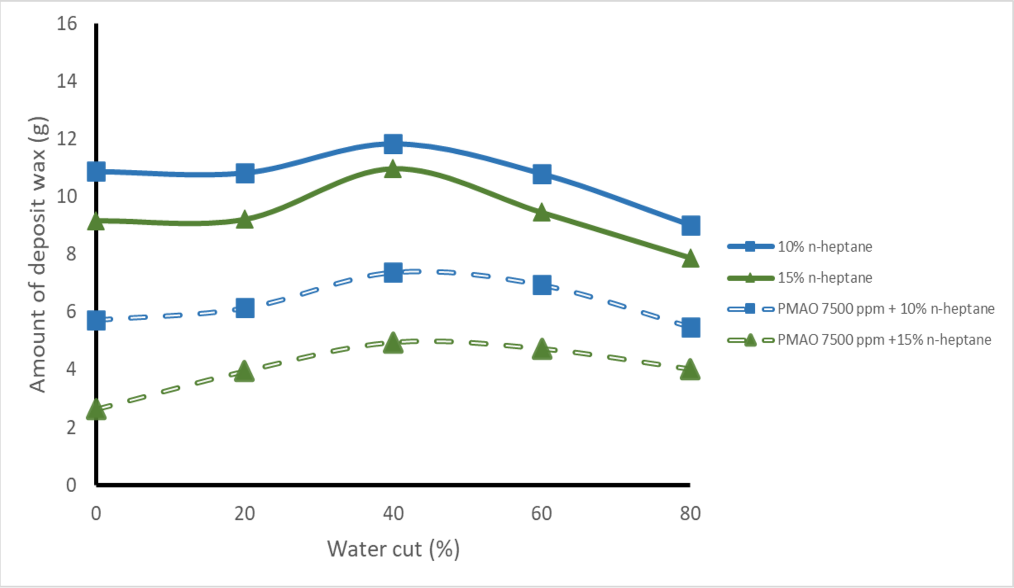


Figure 4.58 Effect of n-heptane and mixture concentration on the amount of wax deposit at 25 °C /50 °C

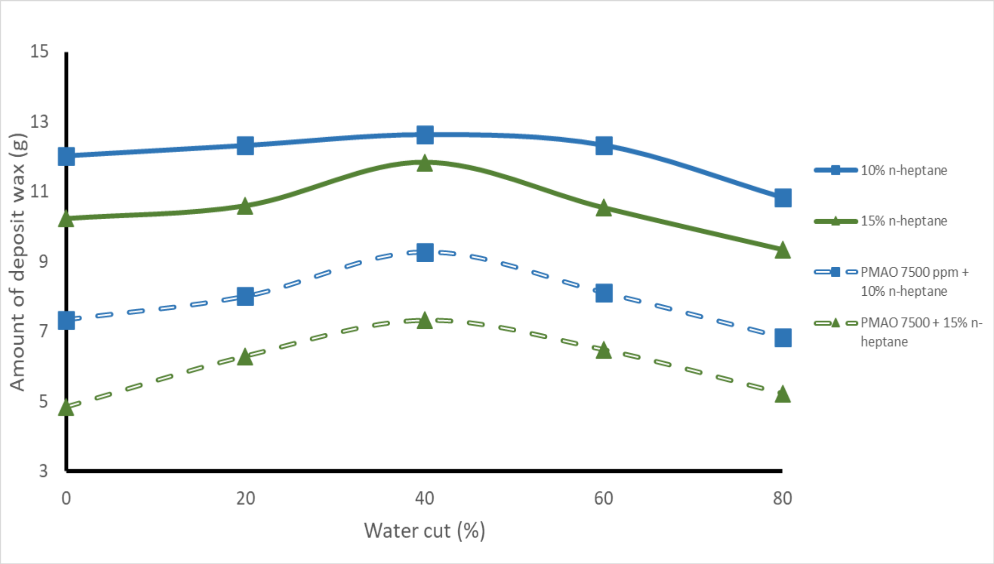


Figure 4.59 Effect of n-heptane and mixture concentration on the amount of wax deposit at 20 °C /50 °C

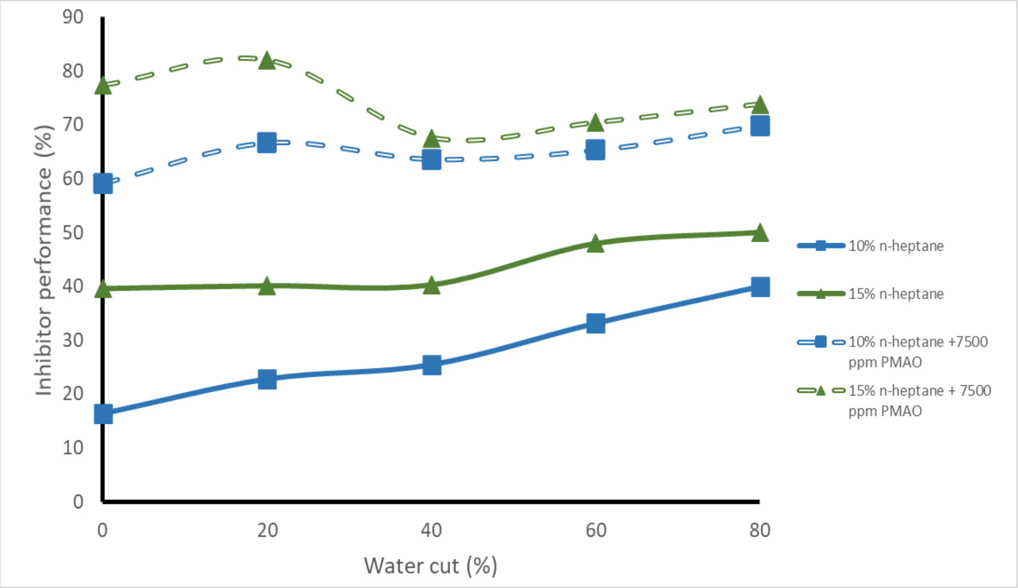


Figure 4.60 Performance of n-heptane and mixture concentration on the amount of wax deposit at 30°C/50 °C

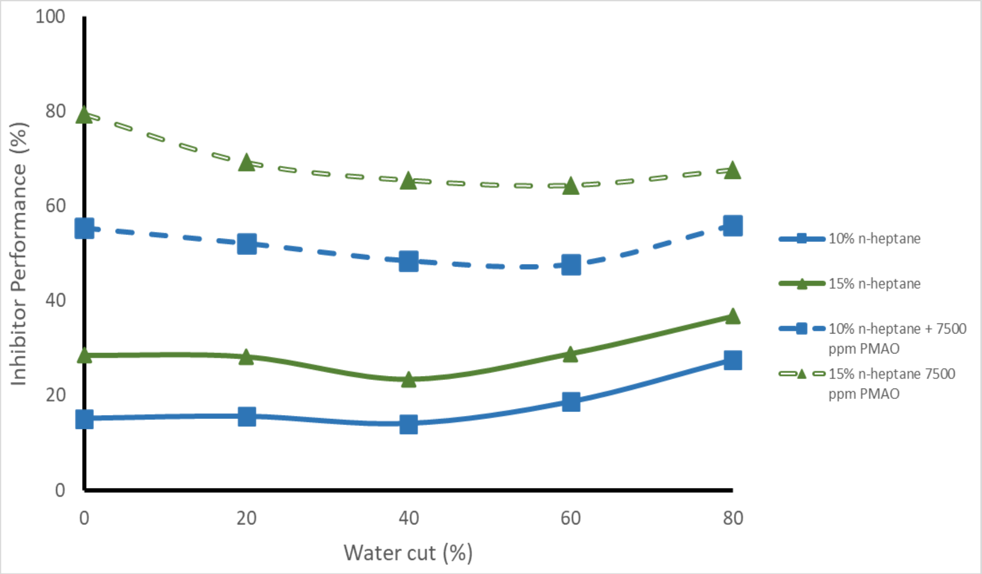


Figure 4.61 Performance of n-heptane and mixture concentration on wax deposit

at 25 °C /50 °C

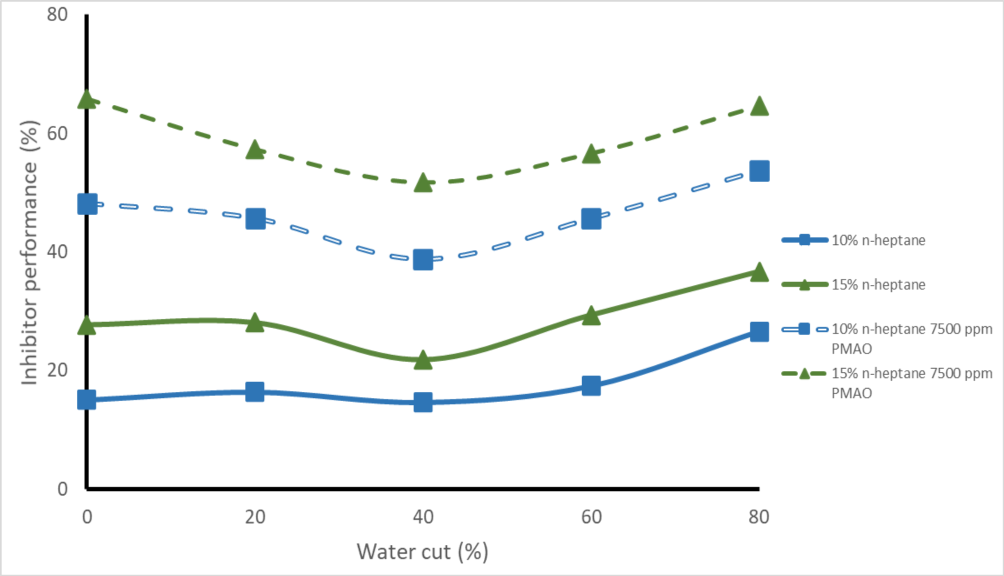


Figure 4.62 Performance of n-heptane and mixture concentration on wax deposit

at 20 °C /50 °C

Chapter 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

This study is performed to manage the wax deposition issue. It can alleviate the wax deposition problem coupling with the emulsion effect at the working temperature. According to the result of this study, it can be summarized as follows:

1. Based on original oil, for the emulsion effect on pour point, the higher water cut results in the greater pour point. Pour point increases from 36.2°C to 45.3°C for water cut ranging from 0%-80%. For the emulsion effect on WAT, WAT increases with increasing water cut ranging from 0%-80%. WAT increases from 40.8°C to 64.8°C at 3 s^{-1} shear rate. For the effect of shear rate on WAT, WAT slightly decreases with increasing shear rate. WAT decrease 41.2 °C to 40.6 °C for 3 s^{-1} to 12 s^{-1} shear rate.
2. For the effect of emulsion on wax deposition for original oil, the increasing water cut from 0%-40% results in an increasing amount of wax deposition. Wax deposition decreases from 14.5092 g to 15.1381 g for water cut ranging from 0% to 40% at 20°C /50°C which are the cooling temperature for wax deposition test (20°C) and outside temperature to control the oil sample into the liquid form (50°C). For wax deposition with water cut ranging from 40%-80%, the water cut increases with a decrease in wax deposition. Wax

deposition decreases from 15.1381 g to 14.7595 g with increased water cut from 40% to 80% at 20°C /50°C. For temperature effect on wax deposition varying cold surface temperature from 20°C-30°C at 50°C of sample temperature, wax deposition decreases with increasing cold surface temperature. Also, the amount of wax deposit decreases from 14.5092 g to 8.1199 g at 0% water cut.

3. For the effect of n-heptane from 5%-20% to the pour point and wax appearance temperature coupling with emulsion ranging from 0-80%, it shows that pour-point reduction and WAT decrease with an increasing n-heptane concentration. For inhibitor performance of pour point and WAT, it increases with an increasing n-heptane concentration. However, the magnitude of the performance is smaller as the water cut increases. For shear rate effect on WAT at the same n-heptane concentration, WAT decreases with increasing shear rates from 3 s^{-1} to 12 s^{-1} shear rate comparing at the same water cut. For shear rate effect on inhibitor performance at the same shear rate ranging from 3 s^{-1} to 12 s^{-1} shear rate with n-heptane cases, there is less effect of shear rate on inhibitor performance comparing at the same water cut.
4. For the effect of n-heptane from 5%-20% on wax deposition with water cut from 0%-80%, it shows that the wax deposition decreases with an increase in n-heptane concentration. The inhibitor performance of n-heptane on

wax deposition increases with an increase in n-heptane concentration. For temperature effect on wax deposition varying cold surface temperature from 20°C-30°C for n-heptane cases, the wax deposition decreases with increasing cold surface temperature. N-heptane concentrations at 10% and 15% provide the high performance and less chemical consumption for pour point reduction WAT, and wax deposition comparing to that at 20%. Therefore, they are selected to study further for mixed chemicals with PMAO.

5. For the effect of PMAO from 2500 ppm to 10000 ppm on the pour point and WAT with respect of emulsion varying from 0-80%, it reveals that PMAO has less effect of pour-point reduction and has slightly higher influence on WAT. For inhibitor performance of pour point and WAT, it increases with an increase in PMAO concentration until the concentration at 10,000 ppm the performance becomes lowered. For the shear rate effect on WAT with PMAO cases, WAT slightly decreases with increasing shear rate from 3 s^{-1} to 12 s^{-1} shear rate at the same PMAO concentration and water cut. For the shear rate effect on inhibitor performance with PMAO case, there is less effect of shear rate on inhibitor performance at the same water cut.
6. For the effect of PMAO from 2500 ppm to 10000 ppm on wax deposition with water cut from 0%-80%. It shows that PMAO has comparatively high effect on wax deposition. The inhibitor performance of PMAO on wax

deposition increases with an increase in PMAO concentration until the concentration at 10,000 ppm the performance becomes lowered. For the effect of temperature on wax deposition varying cold surface temperature from 20°C-30°C, wax deposition decreases with an increasing cold surface temperature. Based on the results, the optimum condition for pour-point reduction, WAT, and wax deposition from PMAO is 7500 ppm. Also, the increased water cut diminishes the inhibitor performance.

7. For mixed solution between 10% or 15% of n-heptane and 7500 ppm of PMAO, based on the results of pour point, the pour points of mixed chemicals are slightly reduced for all cases comparing each single chemical. For, the inhibitor performance on pour point, the mixed chemical inhibitor performance has slightly higher than n-heptane at the same single n-heptane concentration from 10%-15%. For, WAT of mixture, the effect of n-heptane at 10% is close to that of at 15% n-heptane. Also, 15% n-heptane with 7500 ppm yields the WAT reduction greater than 10% n-heptane with 7500 ppm PMAO. For inhibitor performance of 10% with 7500 PMAO is close to 15% n-heptane. However, 15% n-heptane with 7500 ppm of PMAO has a greater inhibitor performance than 10% n-heptane. For the shear rate effect on WAT with mixture, WAT slightly decreases with increasing shear rate from 3 s^{-1} to 12 s^{-1} shear rate comparing at the same water cut. For the shear rate effect on inhibitor performance with mixture

case, there is less significant effect of shear rate on inhibitor performance comparing at the same water cut. Also, the effect of water cut from 0-80% is the same as the previous results in that at higher water cut, the pour point and WAT become lowered.

8. For wax deposition, the amount of wax deposit of 15% of n-heptane with 7500 ppm of PMAO is less than that of at 10% of n-heptane with 7500 ppm of PMAO. Also, the amount of wax deposit is decreasing greater than 15% n-heptane. In addition, the inhibitor performance for 10% n-heptane with 7500 ppm is greater than that at 15% n-heptane. For the temperature effect on wax deposition varying cold surface temperature from 20°C-30°C with the mixture, the wax deposition decreases with an increasing cold surface temperature. For mitigating the wax deposition at Fang oil field for all cases of water cut, it is recommended to use 15% of n-heptane with 7500 ppm of PMAO for high inhibitor performance. However, in term of chemical consumption, it is recommended to use 10% of n-heptane with 7500 ppm of PMAO for economical consideration.

5.2 Recommendation

For further study related to research, it is recommended to develop correlation or to use the existing correlations to predict pour point, WAT, and wax deposition.

In order to investigate and to optimize the combined effect of wax deposition in Fang oil field, the combined effect of n-heptane with other effective chemicals is suggested.

APPENDIX

APPENDIX A

WAT Calculation

Firstly, viscosity vs temperature graph is drawn from viscometry measurement result as illustrate in the figure below.

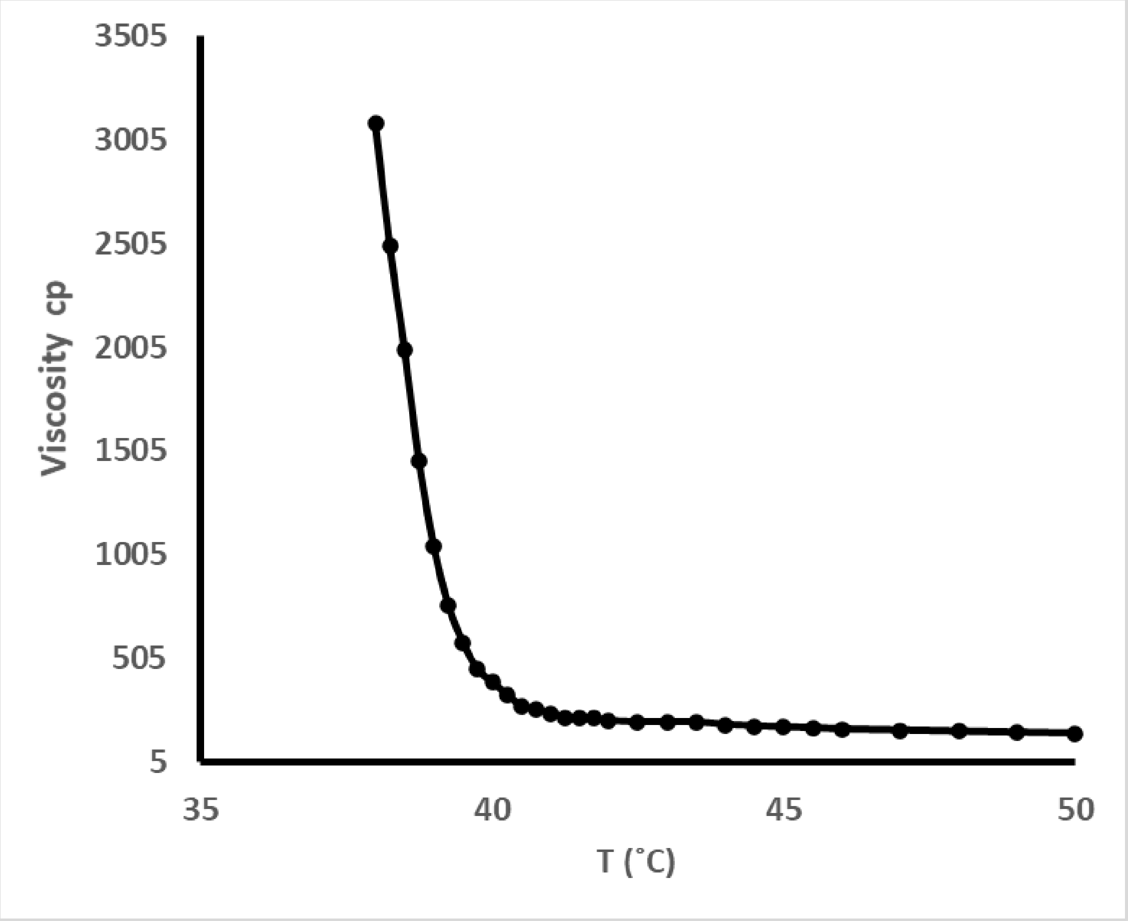


Figure A1 Viscosity vs temperature result of crude oil without chemical at 6 s^{-1} shear rate

The next step is draw Ln(viscosity) vs 100/T (1/°C). In order to determine the WAT, it can be observe that WAT is the temperature that viscosity is changed or deviated by the straight line of hydrocarbon at high temperature. Then, the temperature range is selected and it should be cover the deviation region from straight line to construct the trendline.

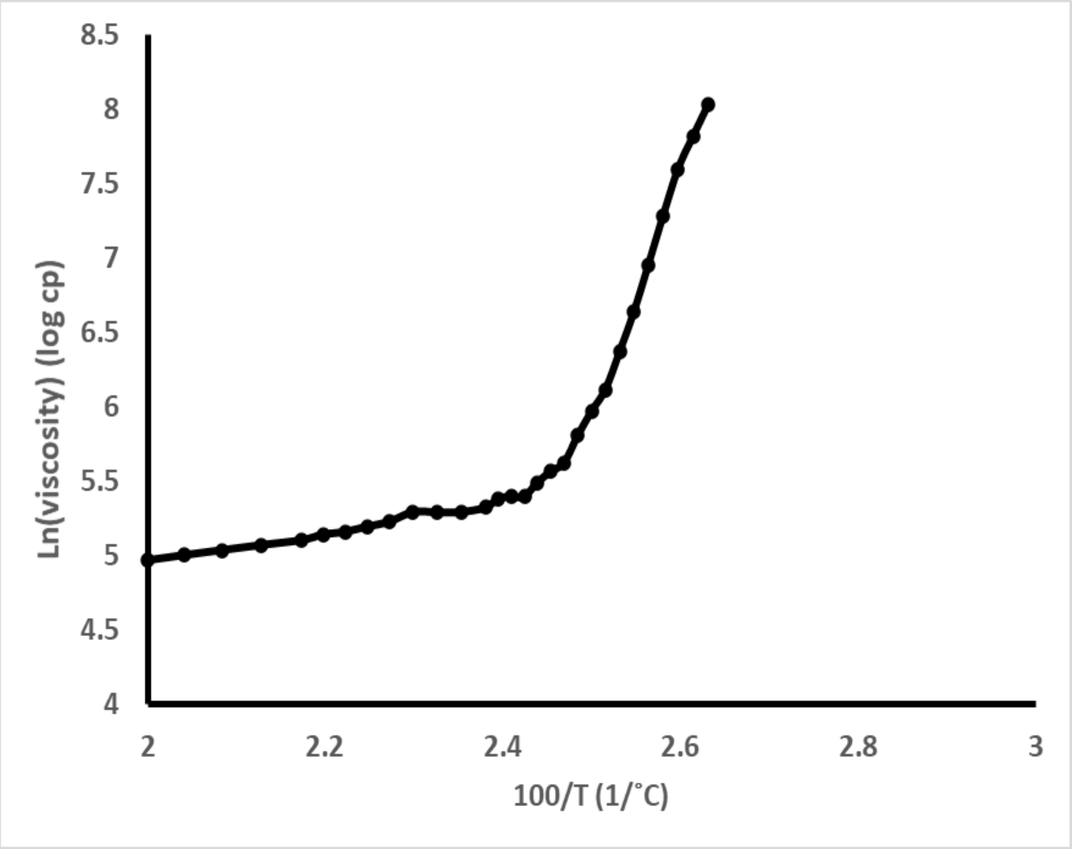


Figure A2 Ln(viscosity vs 100/T (1/°C) result of crude oil without chemical at 6 s^{-1} shear rate

After selecting temperature range to fit the trend line, the most suitable temperature range of this study is 2°C. Also, the preferable trend line of this study is 4^{th} polynomial equation.

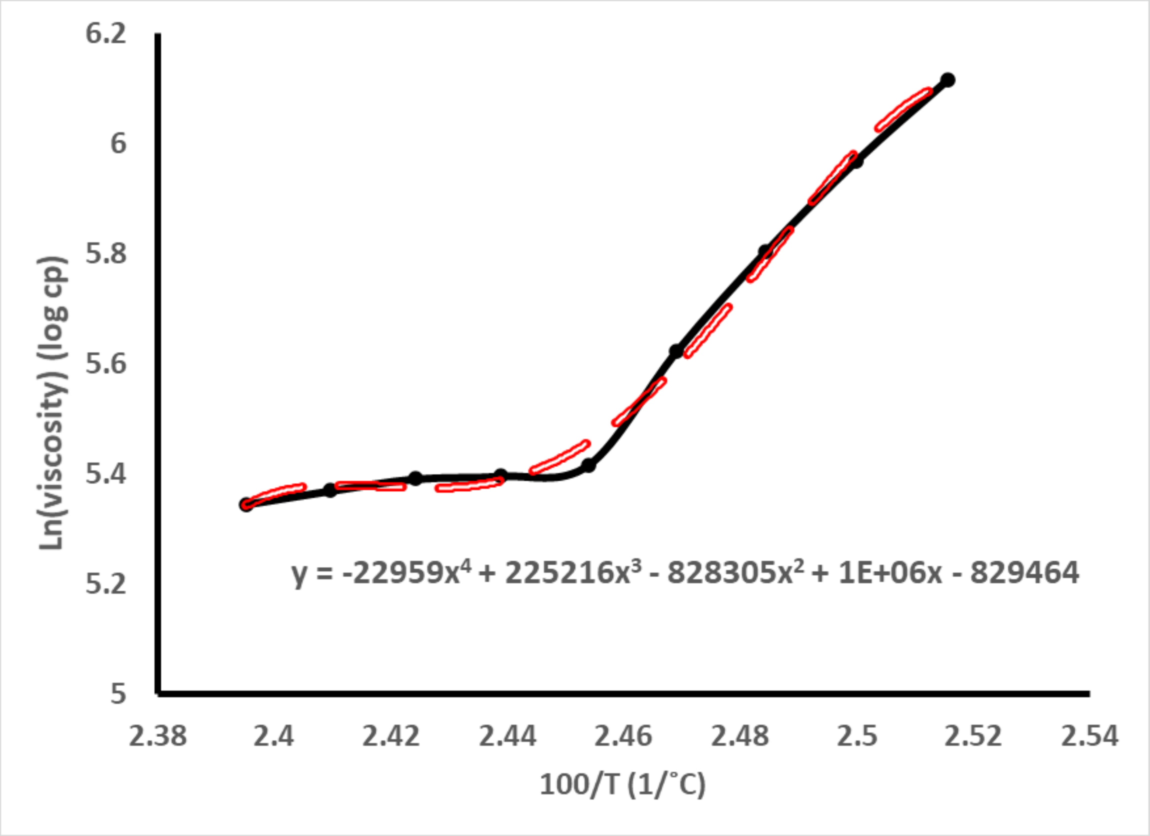


Figure A3 Ln(viscosity vs 100/T (1/˚C) result of crude oil without chemical at 6 s^{-1} shear rate with temperature ranging 2˚C

The equation from the trendline is selected and perform the second derivative of this equation and also draw the graph of second derivative in order to find maximum and minimum of the curve. From the definition of WAT, WAT is the maximum or minimum point of second derivative curve of the graph.

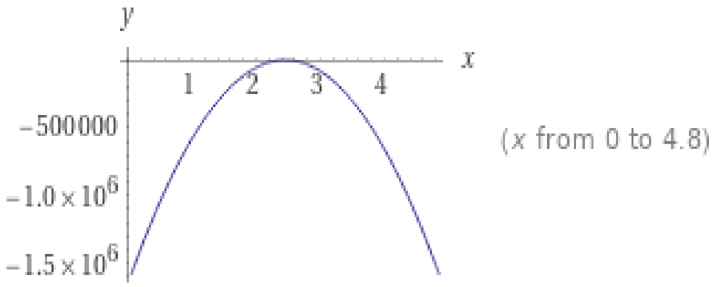


Figure A4 Second derivative graph illustrate maximum change of viscosity or the location to determine WAT

After the maximum or minimum value of the graph is acquired, WAT is getting from 1/(maximum or minimum of this value).

Equation: $-22959x^4 + 225216x^3 - 828305x^2 + 1E{+}06x - 829464$

Second derivative: $-2\,(828305 - 675648x + 137754x^2)$

Maximum/ minimum of the second derivative graph: 2.4537 (1/ ˚C)

WAT: 40.78 ˚C

APPENDIX B

Effect of inhibitor on WAT with water cut ranging from 0%-80% at 6 s-1 and 12 s-1 shear rate

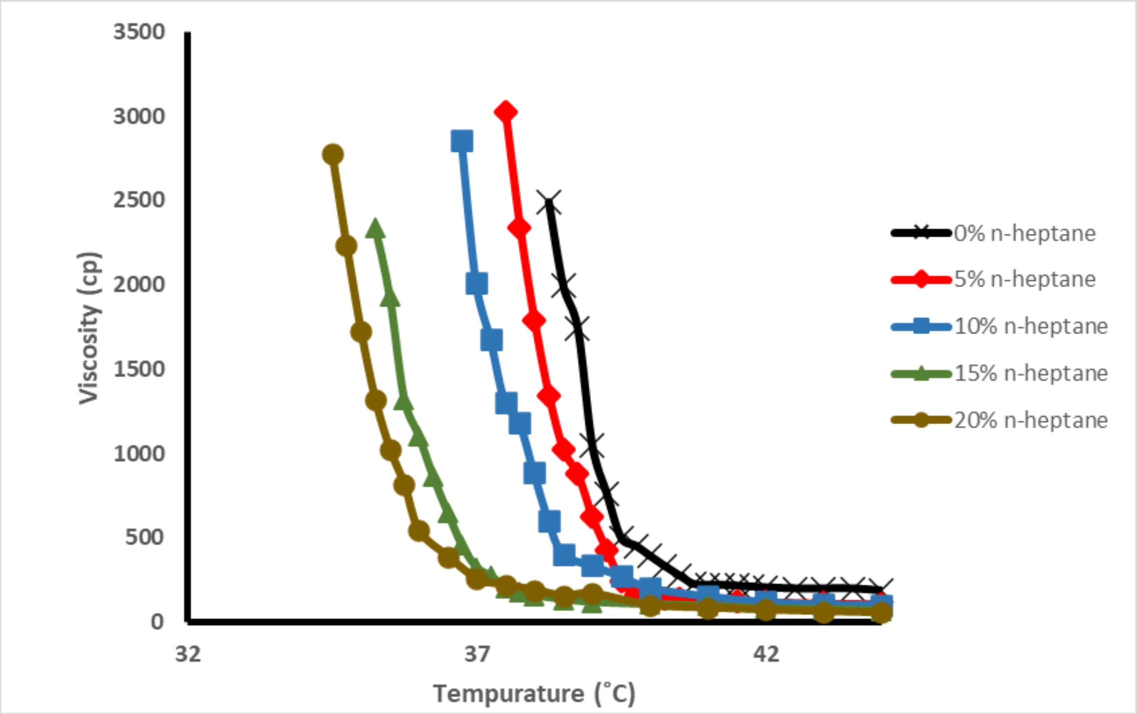


Figure B1 Effect of PMAO concentrations on WAT of 0% water cut at 3 s^{-1} shear rate

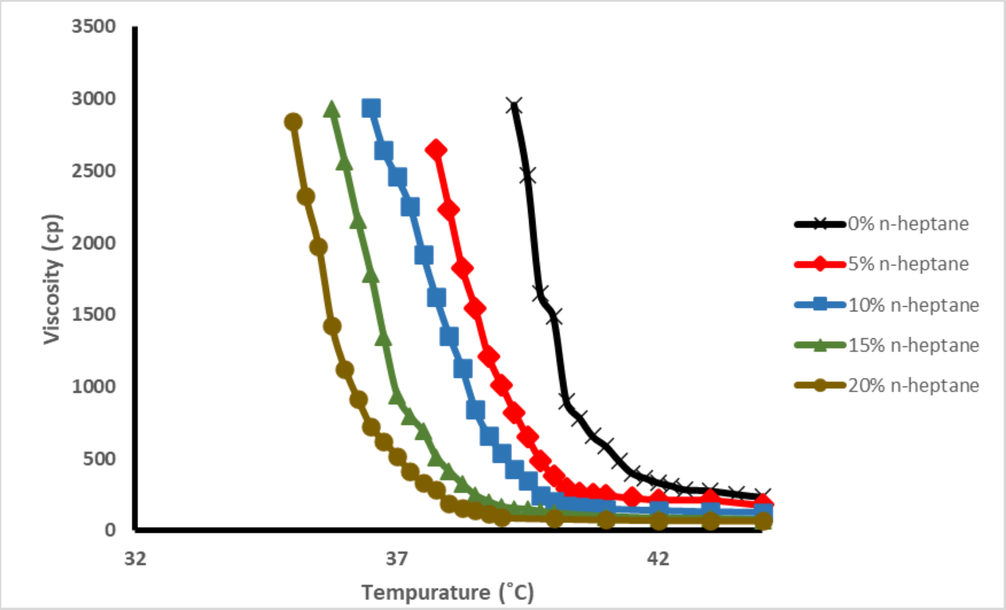


Figure B2 Effect of n-heptane concentrations on WAT of 20% water cut at 6 s^{-1} shear rate

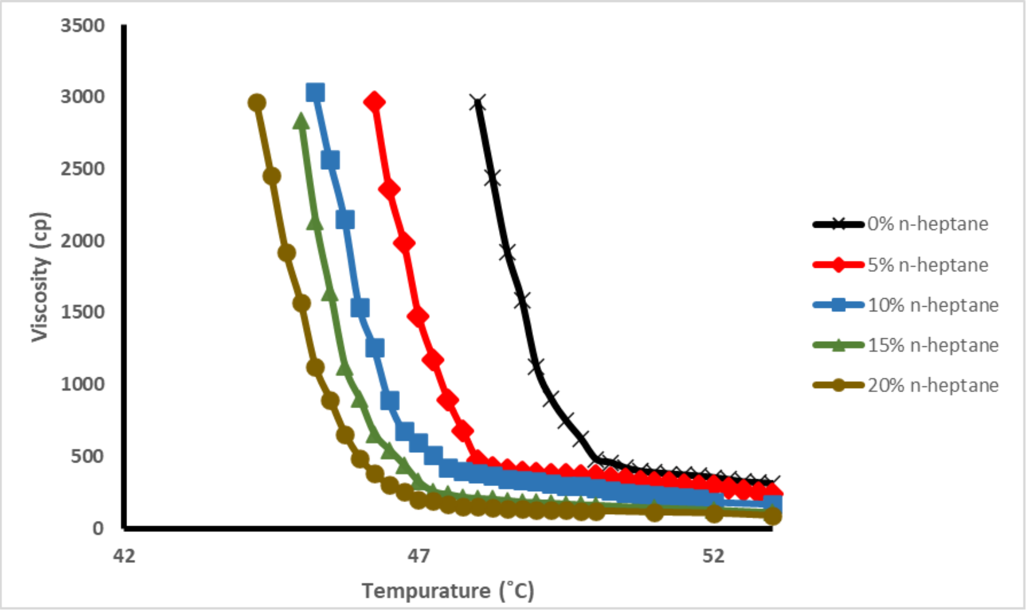


Figure B3 Effect of n-heptane concentrations on WAT of 40% water cut at 6 s^{-1} shear rate

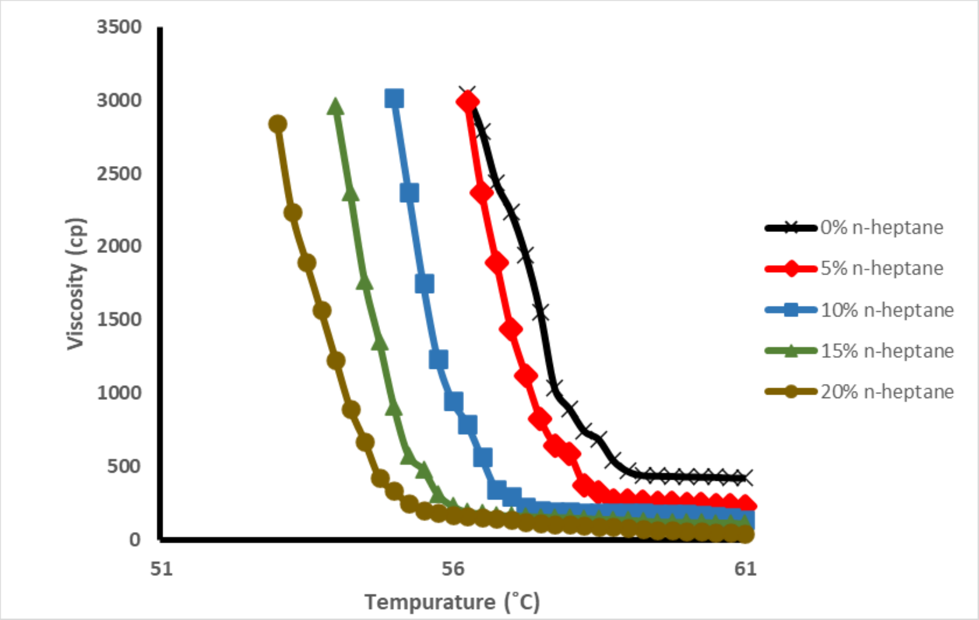


Figure B4 Effect of n-heptane concentrations on WAT of 60% water cut at 6 s^{-1} shear rate

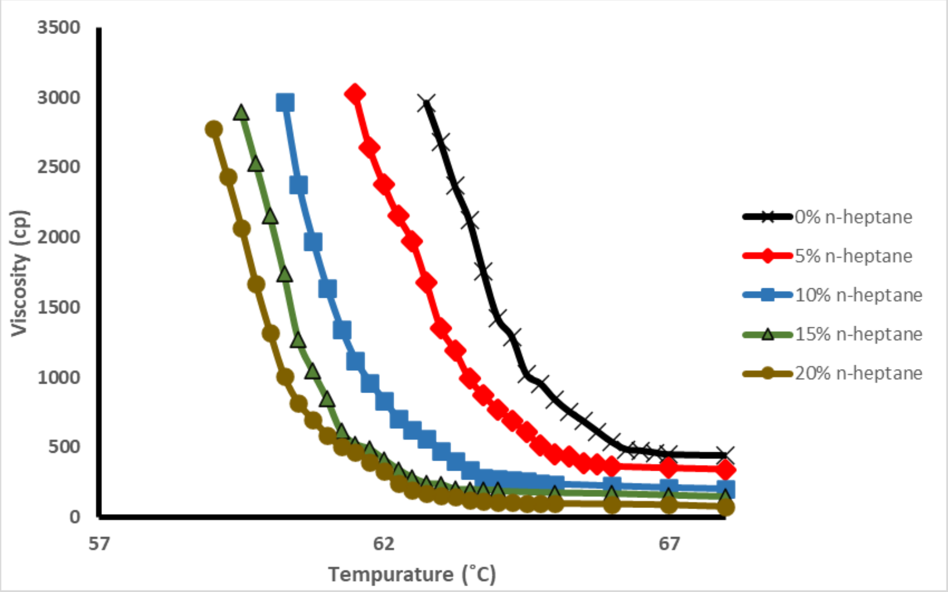


Figure B5 Effect of n-heptane concentrations on WAT of 80% water cut at 6 s^{-1} shear rate

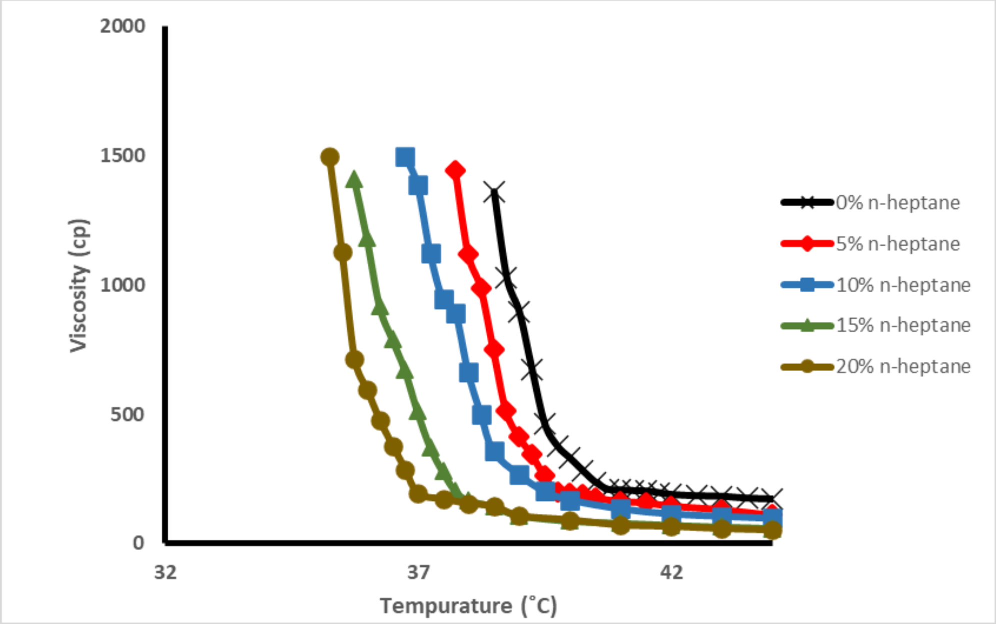


Figure B6 Effect of n-heptane concentrations on WAT of 0% water cut at 12 s^{-1} shear rate

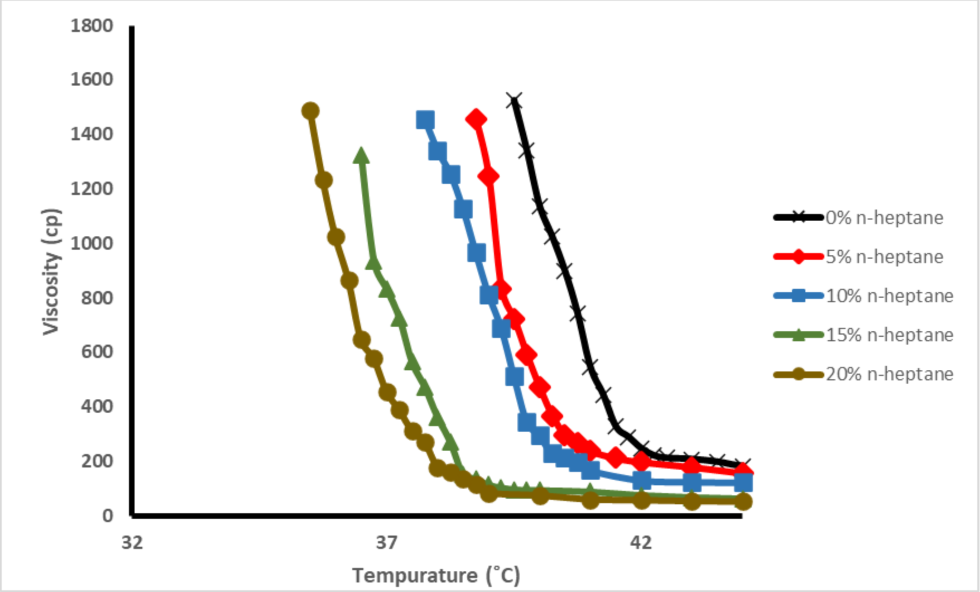


Figure B7 Effect of n-heptane concentrations on WAT of 20% water cut at 12 s^{-1} shear rate

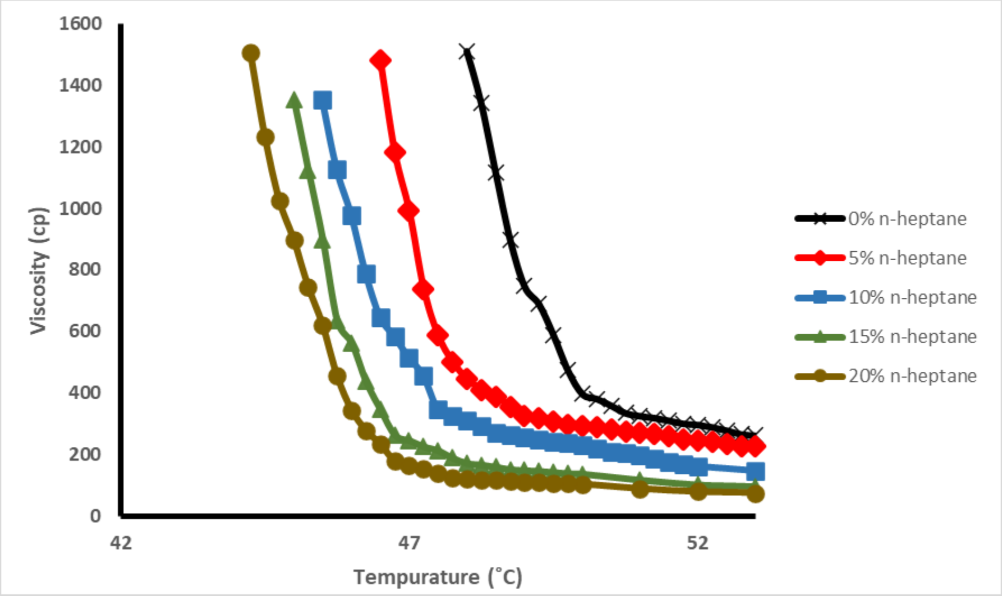


Figure B8 Effect of n-heptane concentrations on WAT of 40% water cut at 12 s^{-1} shear rate

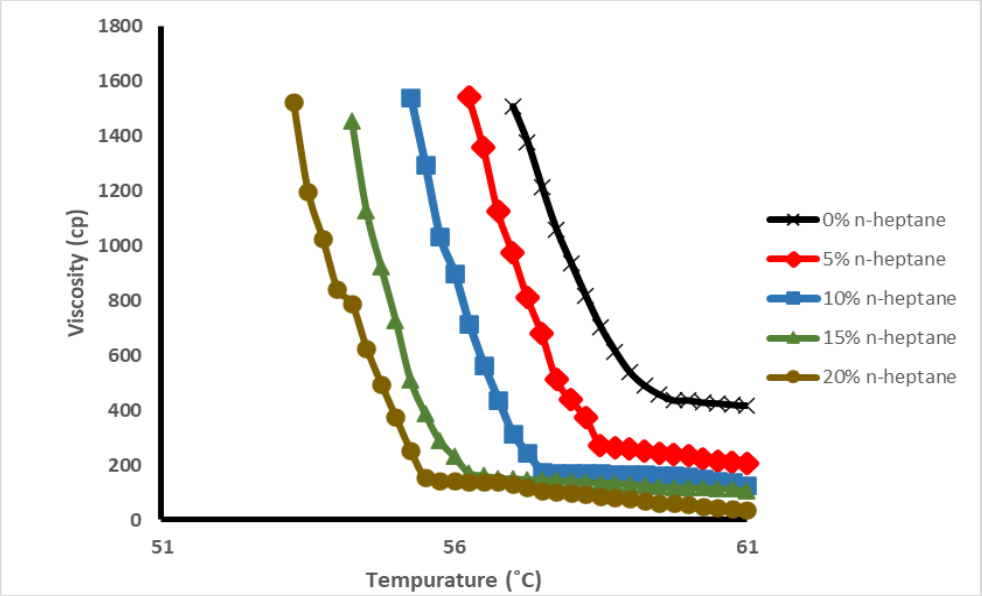


Figure B9 Effect of n-heptane concentrations on WAT of 60% water cut at 12 s^{-1} shear rate

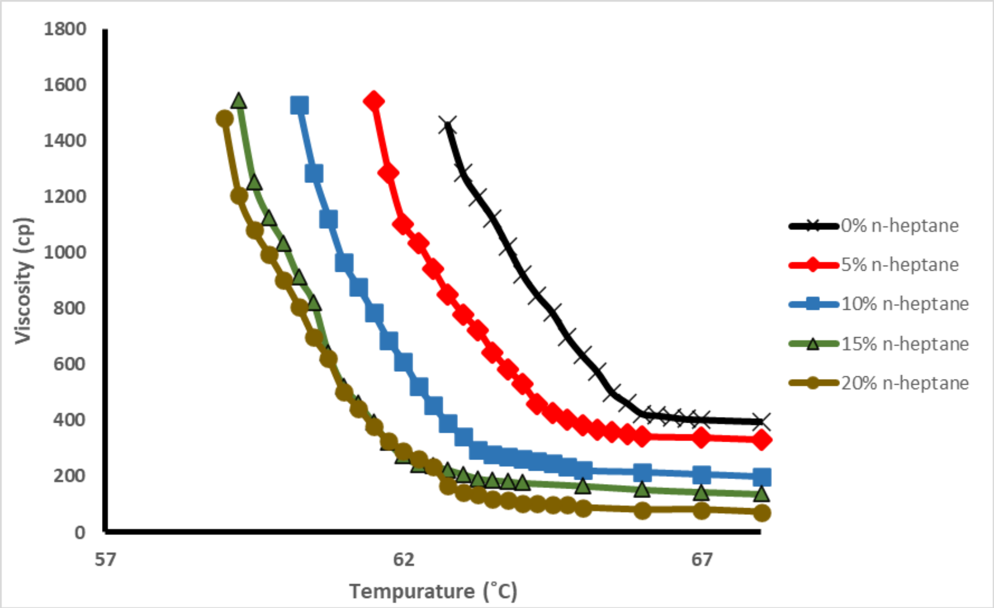


Figure B10 Effect of n-heptane concentrations on WAT of 80% water cut at 12 s^{-1} shear rate

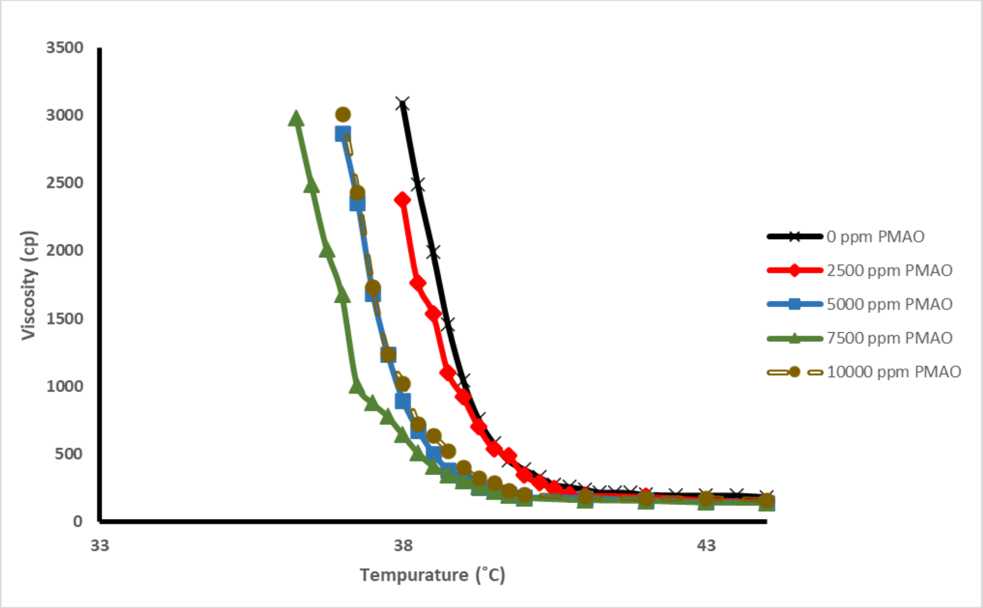


Figure B11 Effect of PMAO concentrations on WAT of 0% water cut at 6 s^{-1} shear rate

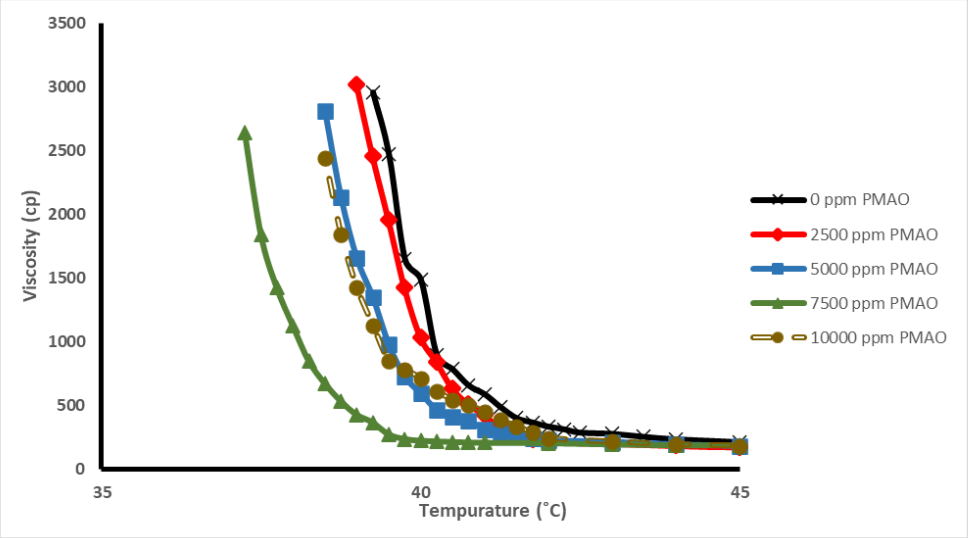


Figure B12 Effect of PMAO concentrations on WAT of 20% water cut

at 6 s^{-1} shear rate

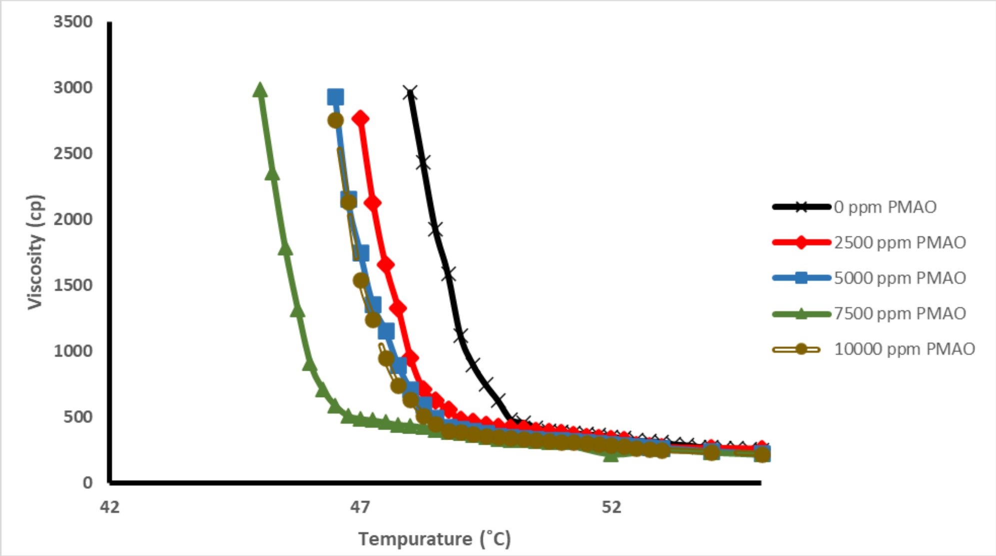


Figure B13 Effect of PMAO concentrations on WAT of 40% water cut

at 6 s^{-1} shear rate

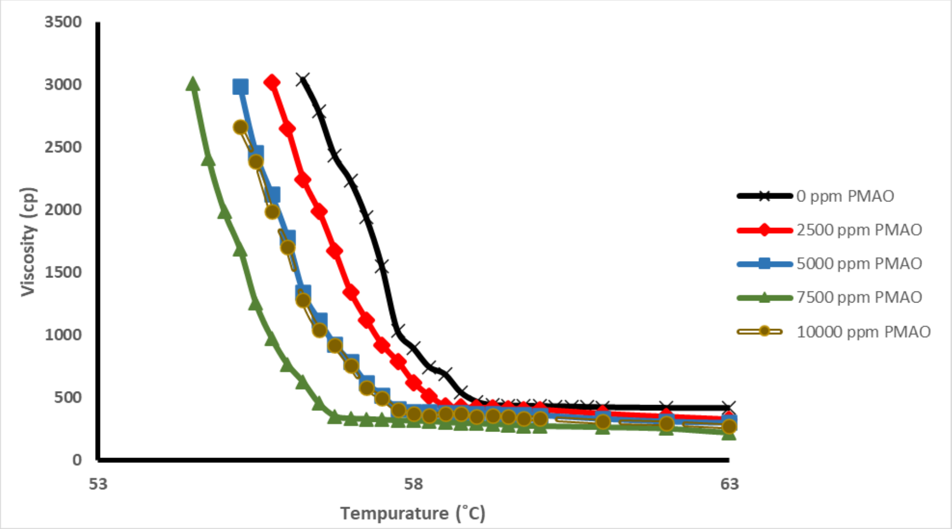


Figure B14 Effect of PMAO concentrations on WAT of 60% water cut at 6 s^{-1} shear rate

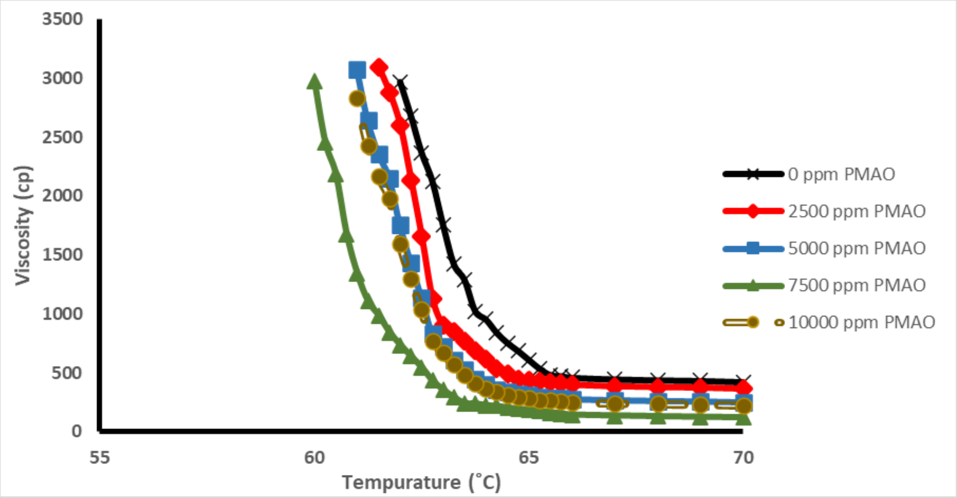


Figure B15 Effect of PMAO concentrations on WAT of 80% water cut at 6 s^{-1} shear rate

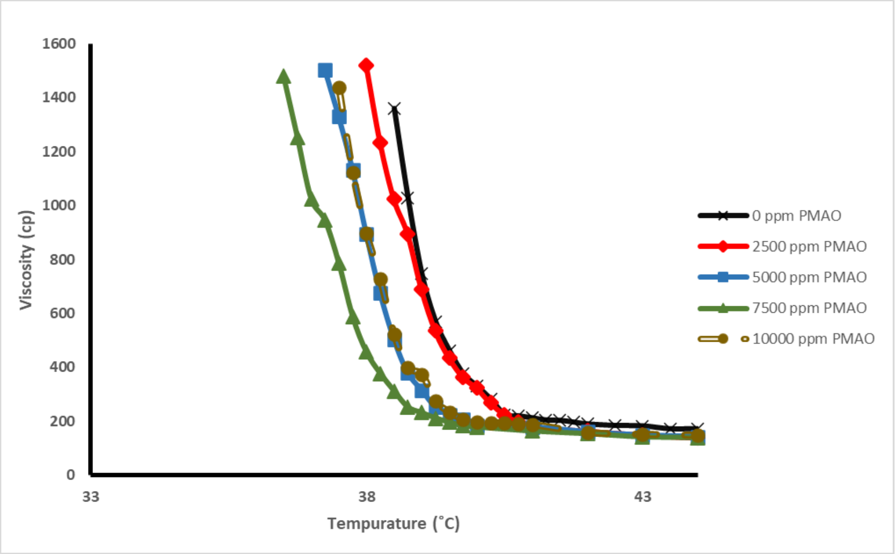


Figure B16 Effect of PMAO concentrations on WAT of 0% water cut

at 12 s^{-1} shear rate

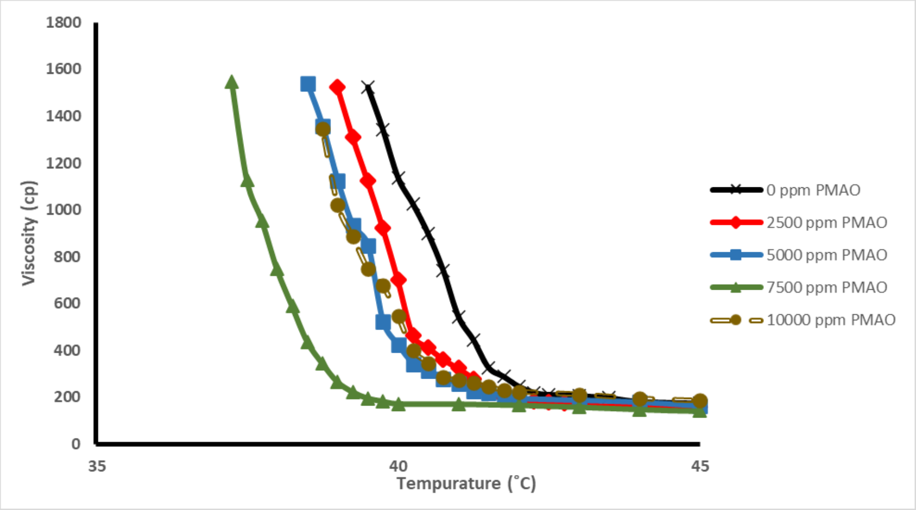


Figure B17 Effect of PMAO concentrations on WAT of 20% water cut

at 12 s^{-1} shear rate

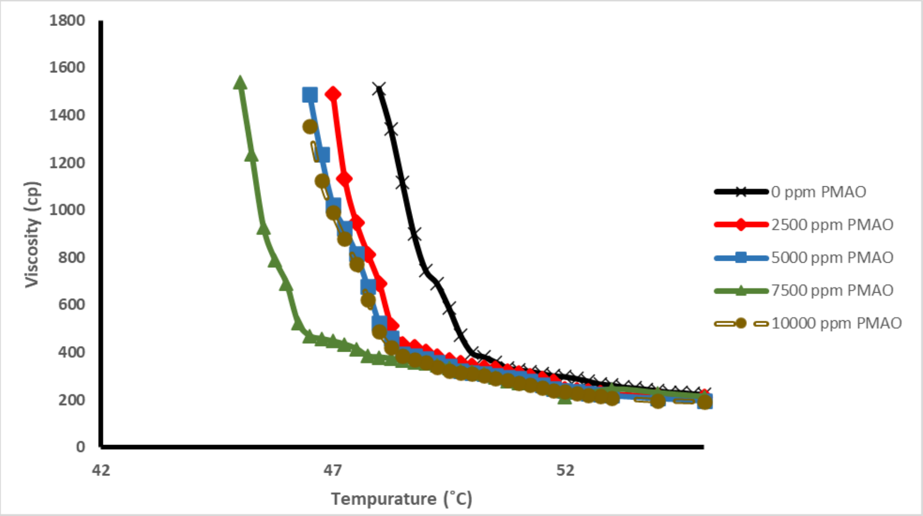


Figure B18 Effect of PMAO concentrations on WAT of 40% water cut

at 12 s^{-1} shear rate

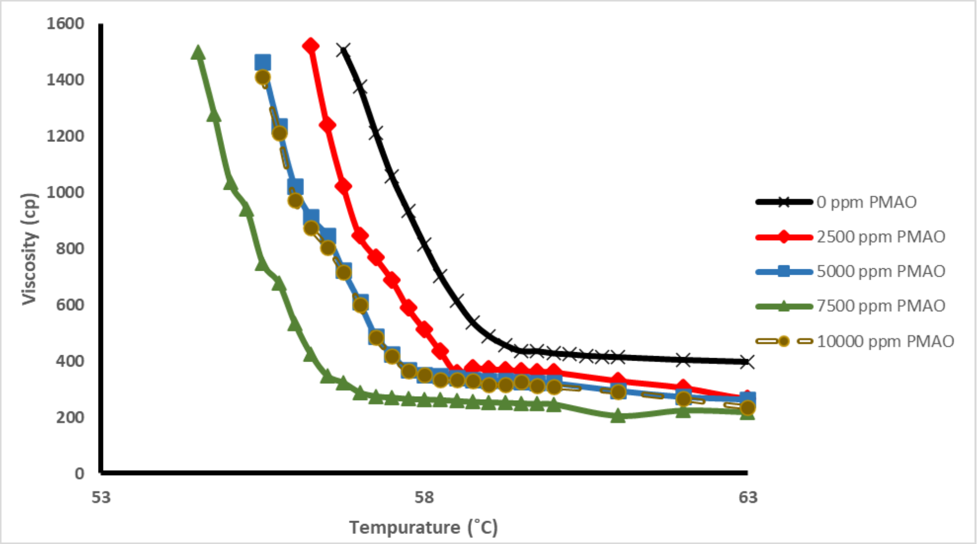


Figure B19 Effect of PMAO concentrations on WAT of 40% water cut

at 12 s^{-1} shear rate

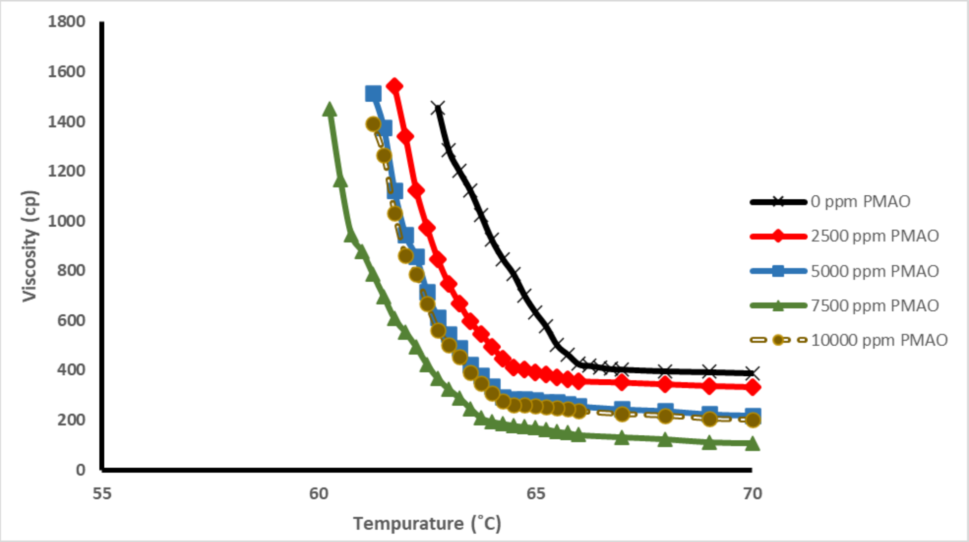


Figure B20 Effect of PMAO concentrations on WAT of 60% water cut

at 12 s^{-1} shear rate

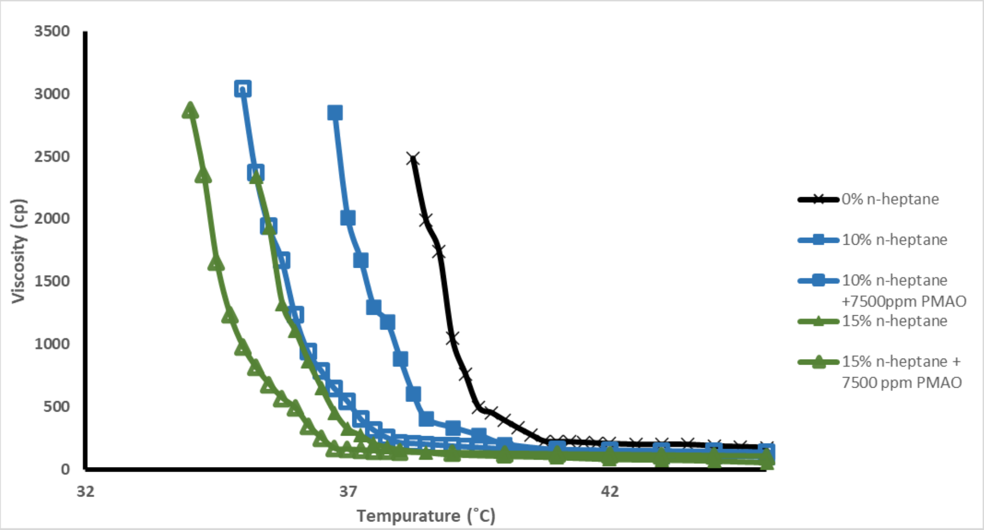


Figure B21 Effect of n-heptane and mixture concentrations on WAT of 0% water cut

at 6 s^{-1} shear rate

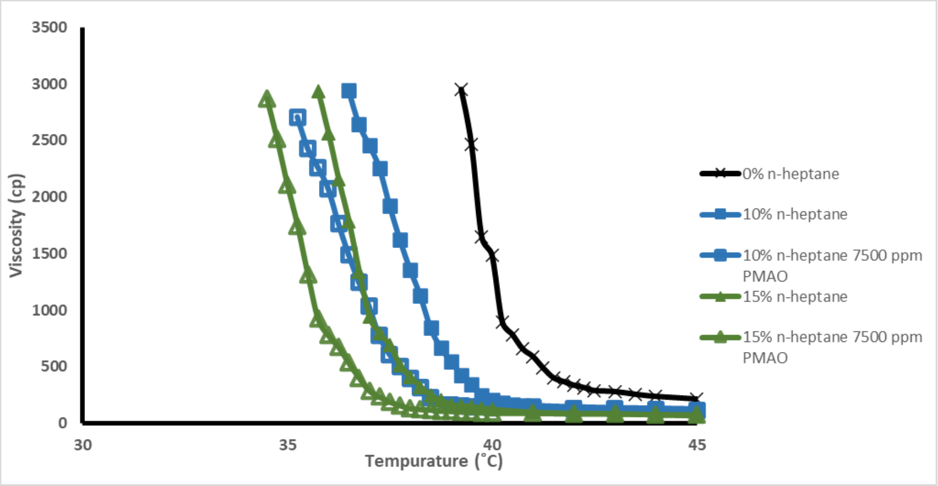


Figure B22 Effect of n-heptane and mixture concentrations on WAT of 20% water cut at 6 s^{-1} shear rate

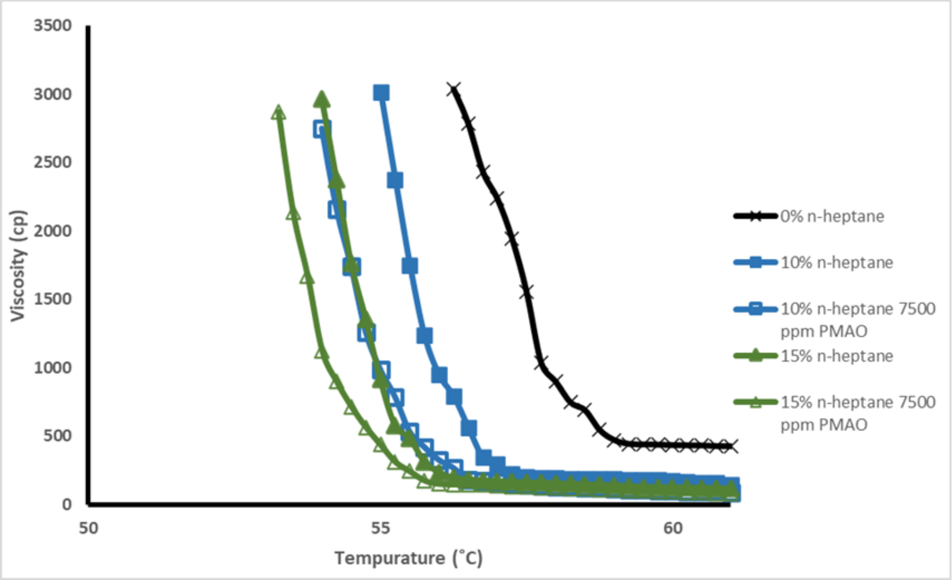


Figure B23 Effect of n-heptane and mixture concentrations on WAT of 40% water cut at 6 s^{-1} shear rate

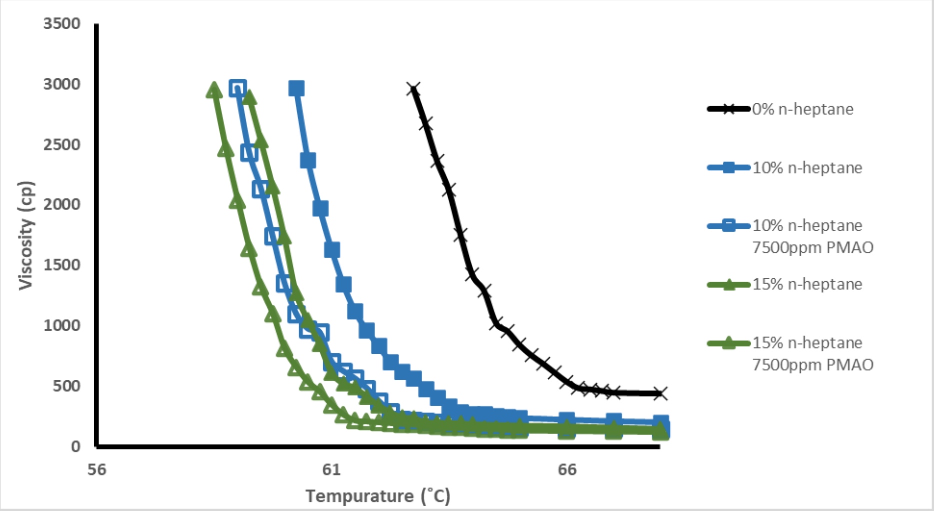


Figure B24 Effect of n-heptane and mixture concentrations on WAT of 60% water cut at 6 s^{-1} shear rate

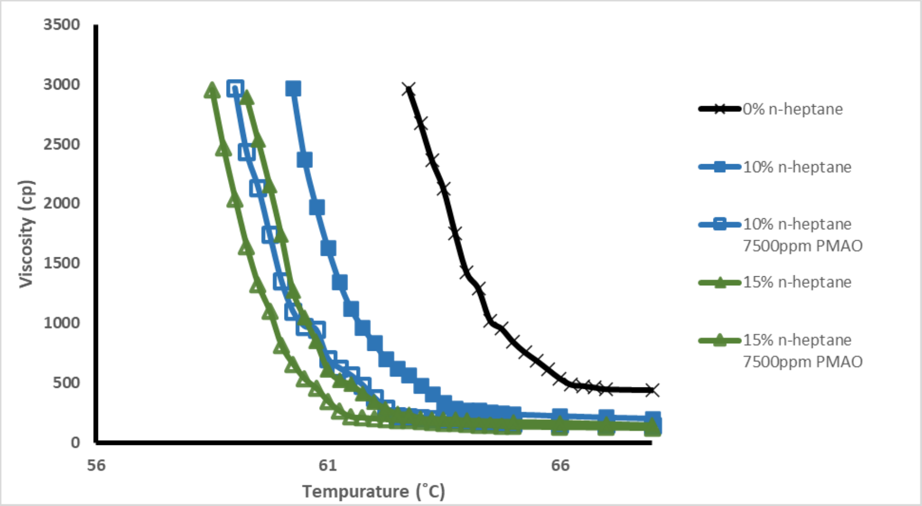


Figure B25 Effect of n-heptane and mixture concentrations on WAT of 80% water cut at 6 s^{-1} shear rate

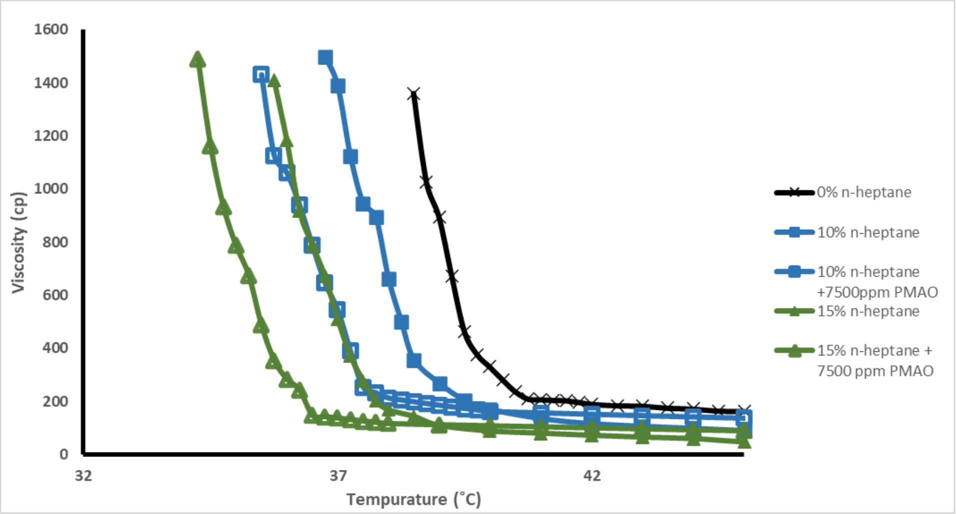


Figure B26 Effect of n-heptane and mixture concentrations on WAT of 0% water cut at 12 s^{-1} shear rate

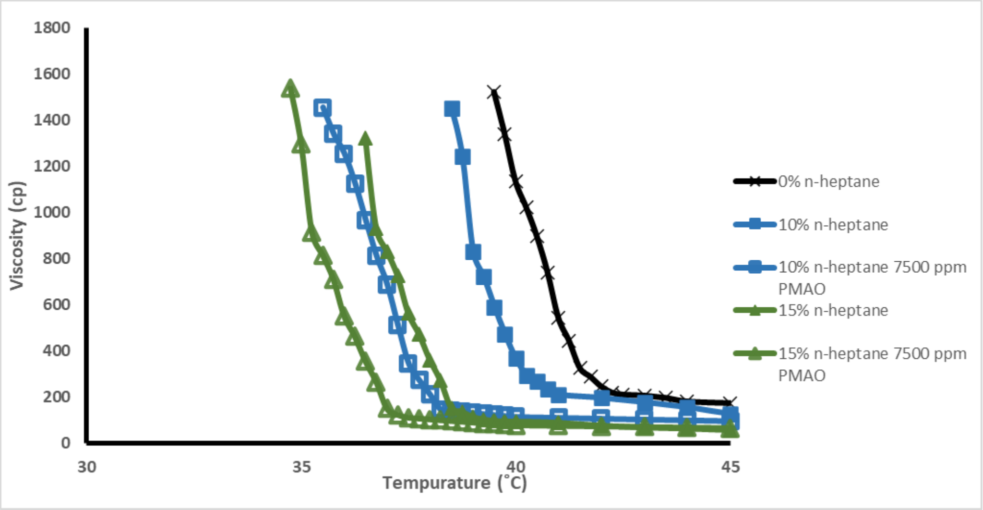


Figure B27 Effect of n-heptane and mixture concentrations on WAT of 20% water cut at 12 s^{-1} shear rate

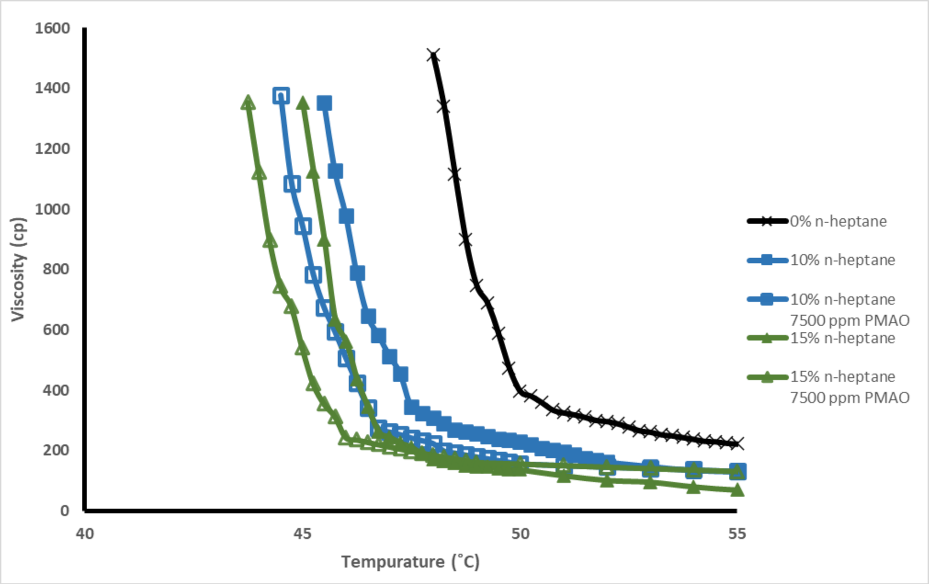


Figure B28 Effect of n-heptane and mixture concentrations on WAT of 40% water cut at 12 s^{-1} shear rate

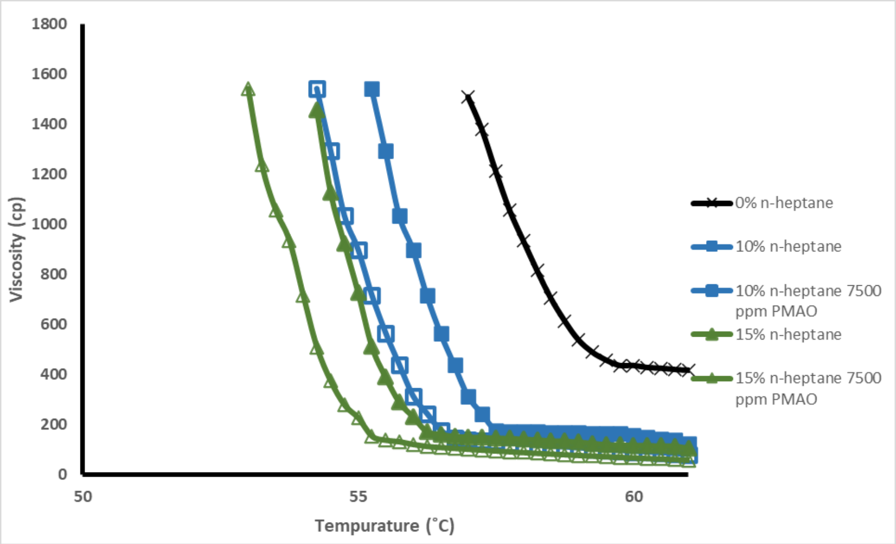


Figure B29 Effect of n-heptane and mixture concentrations on WAT of 60% water cut at 12 s^{-1} shear rate

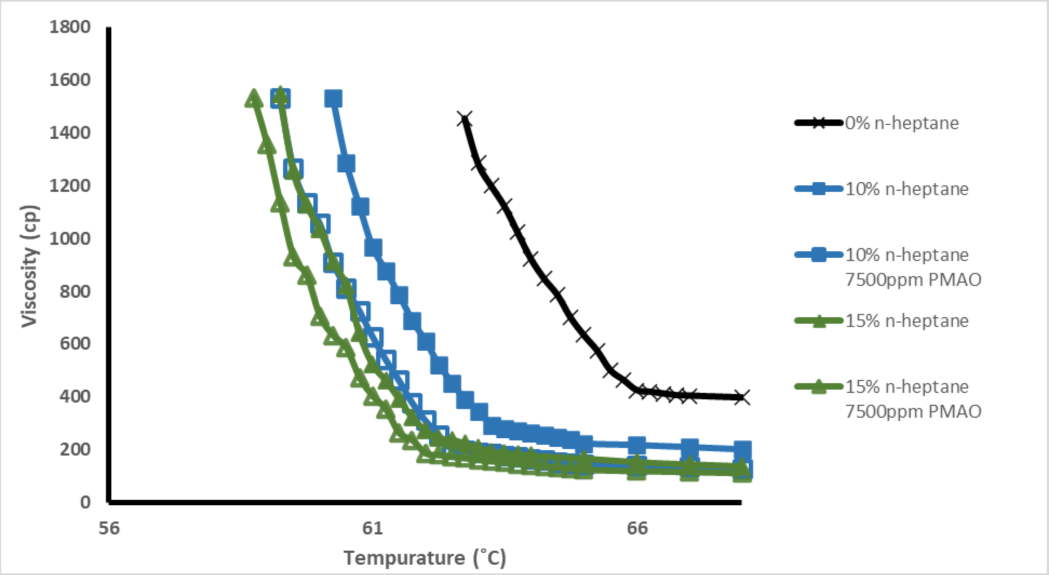


Figure B30 Effect of n-heptane and mixture concentrations on WAT of 80% water cut at 12 s^{-1} shear rate

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