

EVALUATION OF WAX DEPOSITION PREVENTION FOR CRUDE OIL PRODUCTION FROM MAE SOON OIL FIELD



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Georesources and Petroleum
Engineering
Department of Mining and Petroleum Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2018
Copyright of Chulalongkorn University

การประเมินผลการป้องกันการสะสมตัวของไขมันในการผลิตน้ำมันจากแหล่งแม่สุน



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมทรัพยากรธรณีและปิโตรเลียม ภาควิชาวิศวกรรมเหมืองแร่และปิโตรเลียม

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2561

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

Thesis Title EVALUATION OF WAX DEPOSITION
 PREVENTION FOR CRUDE OIL PRODUCTION
 FROM MAE SOON OIL FIELD
By Mr. {Htet Myat Min
Field of Study Georesources and Petroleum Engineering
Thesis Advisor Assistant Professor Kreangkrai Maneeintr, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in
Partial Fulfillment of the Requirement for the Master of Engineering

..... Dean of the Faculty of
Engineering
(Associate Professor Supot Teachavorasinskun,
D.Eng.)

THESIS COMMITTEE

..... Chairman
(Assistant Professor Jirawat Chewaroungroj, Ph.D.)
..... Thesis Advisor
(Assistant Professor Kreangkrai Maneeintr, Ph.D.)
..... External Examiner
(Pichit Vardcharragosad, Ph.D.)



จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

เสถ เมียด มิน : การประเมินผลการป้องกันการสะสมตัวของไขน้ำมันในการผลิตน้ำมันจากแหล่งแม่สุ่น.
 (EVALUATION OF WAX DEPOSITION PREVENTION FOR
 CRUDE OIL PRODUCTION FROM MAE SOON OIL FIELD) อ.ที่
 ปริญญาหลัก : ศศ.ดร.เกรียงไกร มณีอินทร์

น้ำมันดิบที่มีไขถูกพบได้โดยทั่วไปในแหล่งกักเก็บปิโตรเลียม น้ำมันดิบที่มีการเกิดไขเป็นหนึ่งในปัญหาหลักในการไหลในท่อส่งน้ำมันสำหรับการผลิตน้ำมันและแก๊ส ประเด็นดังกล่าวทำให้เกิดปัญหาการตกตะกอนของไข และทำให้เกิดปัญหาใหญ่ในด้านความสูญเสียในเชิงเศรษฐศาสตร์ อันได้แก่ การผลิต เวลา และค่าใช้จ่ายในการดูแลรักษา ดังนั้นจึงเป็นเรื่องที่สำคัญในการจัดการปัญหาการเกิดไขในท่อขนส่ง โดยเฉพาะอย่างยิ่งบริเวณพื้นที่ด้านบนในช่วงฤดูหนาว ในการศึกษาในครั้งนี้ สารเอ็น-เฮบเทน และสารโพลีมาเลอิกแอนไฮไดรด์ อัลวันออกตะเดเคน หรือ เอ็มเอ ที่ใช้เป็นตัวยับยั้งการเกิดไขที่มีค่าความเข้มข้นต่างๆ จะถูกใช้ในการวัดผลของอุณหภูมิที่จุดเท อุณหภูมิปรากฏไข และการเกิดไขของน้ำมันดิบจากแหล่งแม่สุ่น และจะใช้ค้นหาผลของตัวแปรต่างๆ เช่น อุณหภูมิ ความเข้มข้น และชนิดของสารยับยั้งที่มีต่อเรื่องดังกล่าว

เอ็น-เฮบเทน มีบทบาทในการลดอุณหภูมิที่จุดเท อุณหภูมิปรากฏไข และการเกิดไข สำหรับการศึกษาในครั้งนี้พบว่า ปริมาณรวมของไขที่เกิดขึ้นจะลดลงเมื่อใช้สารที่ความเข้มข้นเพิ่มขึ้น ดังนั้นการเพิ่มความเข้มข้นของสารจะประสิทธิภาพที่ดีขึ้นในการยับยั้งปัญหาเรื่องการเกิดไข ในทางตรงกันข้าม สารเอ็มเอ จะแสดงผลที่ใช้ลดอุณหภูมิปรากฏไข และการเกิดไขจากน้ำมันดิบแม่สุ่น จากผลที่ได้สารนี้จะแสดงประสิทธิภาพต่ำในการลดอุณหภูมิที่จุดเท เนื่องจากสารสามารถละลายได้น้อยในน้ำมันดิบที่มีปริมาณไขสูง

หลังจากการทดสอบใช้สารเดี่ยวในการวัดค่าต่างๆ จะมีการทดสอบการใช้สารผสมของ เอ็น-เฮบเทน และ เอ็มเอ ในการหาค่าต่างๆ เพื่อที่จะได้ผลที่ดีขึ้นในการป้องกันการเกิดไขพบว่า เอ็น-เฮบเทน จำนวน 10 เปอร์เซ็นต์ และ เอ็มเอ จำนวน 5,000 พีพีเอ็ม จะให้สภาวะที่เหมาะสมในการป้องกันการเกิดไข เนื่องจากสภาวะดังกล่าวนี้จะเกิดไขในปริมาณต่ำโดยใช้สารจำนวนไม่มาก

จุฬาลงกรณ์มหาวิทยาลัย
 CHULALONGKORN UNIVERSITY

สาขาวิชา วิศวกรรมทรัพยากรธรณีและ
 ปิโตรเลียม

ปีการศึกษา 2561

ลายมือชื่อนิสิต

.....

ลายมือชื่อ อ.ที่ปรึกษาหลัก

5971238021 : MAJOR GEORESOURCES AND PETROLEUM
ENGINEERING

KEYWORD Wax Deposition Pour point temperature Wax appearance

D: temperature Wax inhibitor MA N-heptane

Htet Myat Min : EVALUATION OF WAX DEPOSITION PREVENTION
FOR CRUDE OIL PRODUCTION FROM MAE SOON OIL FIELD.

Advisor: Asst. Prof. Kreangkrai Maneeintr, Ph.D.

Waxy crude oils are normally found in petroleum reservoirs. Crude oil with the wax formation is one of the crucial problems for flow assurance of pipeline transportation in oil and gas production. This issue can commonly cause wax deposition problem and it has made a huge amount of economic losses such as production, time and maintenance cost. Therefore, it is a critical aspect to deal with wax deposition for crude oil flow assurance, especially at the surface region in cold climate. In this study, n-heptane and poly (maleic anhydride-alt-1-octadecane) or MA as the inhibitors with different concentrations will be measured the effect on pour point, wax appearance temperature and wax deposition of Mae Soon crude oil and investigated the effects of parameters such as temperature, concentration and types of inhibitors for these aspects.

N-heptane plays a key role in the reduction of pour point, wax appearance temperature and wax deposition of this study. It is also found that the amount of total wax deposits decreases when this chemical concentration increases. Consequently, an increasing concentration provides a better performance for inhibition of wax deposition problems. On the other hand, MA also shows the results for the reduction of wax appearance temperature and wax deposition of Mae soon crude oil. According to the results, it offers low performance for pour point reduction because it cannot be soluble well in the higher wax content of crude oil. After each individual inhibitor are measured for the reduction of pour point, wax appearance temperature and wax deposition, the mixtures of n-heptane and MA are investigated to have better results for wax deposition prevention. It is found that 10% n-heptane and 5000 ppm MA provides the optimal condition for wax deposition prevention based on this study because it can show low wax deposition with less amount of chemical consumption. The results can be used as fundamental data and the investigation can expand into combination with another type of inhibitors.

Field of Study: Georesources and
Petroleum Engineering

Academic 2018
Year:

Student's Signature

.....

Advisor's Signature

.....

ACKNOWLEDGEMENTS

Firstly, I would like to thank my thesis advisor Asst. Prof. Dr. Kreangkrai Maneeintr of the Department of Mining and Petroleum Engineering at Chulalongkorn University. The author also wishes to thank all the professors and faculty members in the Department of Mining and Petroleum Engineering.

I appreciate to Scholarship Program for ASEAN Countries of Chulalongkorn University and Chevron Thailand Exploration and Production, Ltd. for the financial support.

I would also like to thank my friends from Georesources Engineering and Civil Engineering for help and good friendship.

Finally, I would like to thank my parents for providing me and always stay beside me no matter what happens.

Htet Myat Min

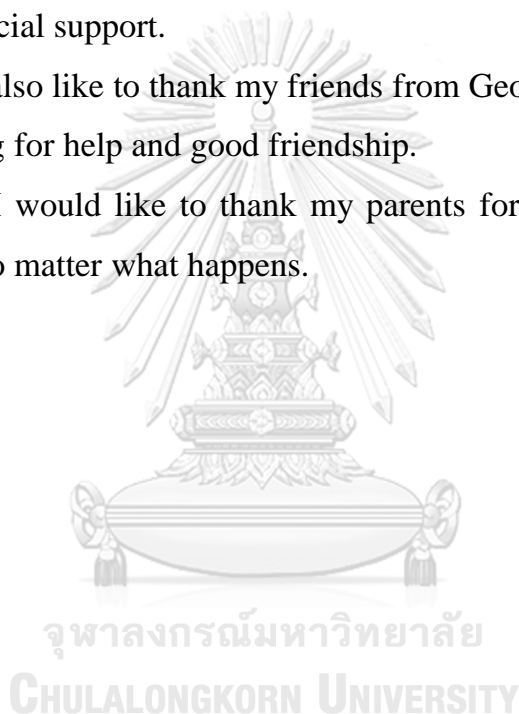


TABLE OF CONTENTS

	Page
ABSTRACT (THAI)	iii
ABSTRACT (ENGLISH).....	iv
ACKNOWLEDGEMENTS.....	v
TABLE OF CONTENTS.....	vi
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS.....	xii
NOMENCLATURE	xiii
GREEK LETTER	xv
CHAPTER 1 INTRODUCTION	1
1.1 Classification of petroleum products	1
1.2 Paraffin wax in crude oil and wax precipitation	2
1.3 Paraffin wax production problems and prevention.....	4
1.4 Objectives and scope of this study.....	5
CHAPTER 2 THEORY AND LITERATURE REVIEW	7
2.1 Paraffin wax.....	7
2.2 Waxy precipitation.....	7
2.2.1 Wax Appearance Temperature	7
2.2.2 Pour Point Temperature.....	8
2.3 Wax deposition	8
2.3.1 Wax Deposition Mechanisms.....	8
2.3.2 Factors Affecting Wax Deposition.....	13
2.3.3 Control and Remediation.....	14
2.4 Wax deposition prevention by chemical method.....	16
2.4.1 Chemical Method	16

2.4.2 WAT Measurement Techniques.....	19
2.4.3 Wax Deposition Prevention and Removal Techniques	21
CHAPTER 3 EXPERIMENT	26
3.1 Materials, equipment and experimental procedure.....	26
3.1.1 Pour Point testing	27
3.1.2 Wax Appearance Temperature (WAT)	29
3.1.3 Wax Deposition Test	31
3.2 Methodology.....	33
CHAPTER 4 RESULTS AND DISCUSSION.....	36
4.1 Characteristics of original crude oil from Mae Soon.....	36
4.2 Effect of MA as a wax inhibitor	37
4.2.1 Effect of MA on crude oil pour point.....	37
4.2.2 Effect of MA on crude oil wax appearance temperature.....	39
4.2.3 Effect of MA on crude oil wax deposition	42
4.3 Effect of N-heptane.....	43
4.3.1 Effect of n-heptane on crude oil pour point	43
4.3.2 Effect of n-heptane on crude oil wax appearance temperature	45
4.3.3 Effect of n-heptane on crude oil wax deposition.....	49
4.4 Effect of mixture of MA and N-heptane.....	51
4.4.1 Effect of mixture on crude oil pour point.....	51
4.4.2 Effect of mixture on crude oil wax appearance temperature.....	52
4.4.3 Effect of mixture on crude oil wax deposition	55
CHAPTER 5 CONCLUSIONS AND RECOMMENDATION	58
5.1 Conclusions.....	58
5.2 Recommendation	59
REFERENCES	60
VITA.....	64

LIST OF TABLES

	Page
Table 3-1: Composition of oil sample (Saengnil, 2015).....	26
Table 3-2: Density of crude oil sample (Saengnil, 2015)	27
Table 3-3: Experimental operating conditions for pour point.....	33
Table 3-4: Experimental operating conditions for wax appearance temperature test..	34
Table 3-5: Experimental operating conditions for wax deposition test	34
Table 4-1: Wax appearance temperature of original Mae Soon crude oil	37
Table 4-2: Wax deposits amount of Mae Soon crude oil.....	37
Table 4-3: Effect of MA concentration on crude oil pour point	39
Table 4-4: Effect of shear rate on wax appearance temperature of crude oil with MA	42
Table 4-5: Wax deposits from the crude oil with MA	43
Table 4-6: Effect of n-heptane concentration on crude oil pour point.....	44
Table 4-7: Effect of shear rate on wax appearance temperature of crude oil with	49
Table 4-8: Wax deposits from the crude oil with n-heptane.....	51
Table 4-9: Effect of mixture concentration on crude oil pour point	52
Table 4-10: Effect of shear rate on wax appearance temperature of crude oil with mixture	55
Table 4-11: Wax deposits from the crude oil with mixture	56

LIST OF FIGURES

Page

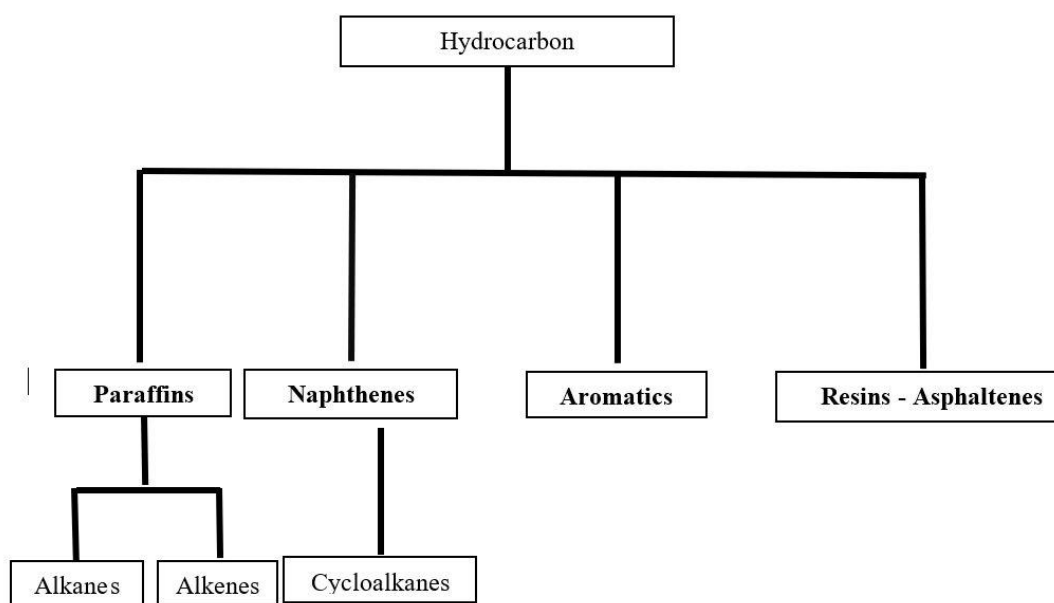


Figure 1-1: Hydrocarbon Classification.....	2
Figure 1-2: Macrocrystalline wax (Mansoori, 1996).....	3
Figure 1-3: Microcrystalline wax (Mansoori, 1996).....	4
Figure 2-1: Illustration of how wax molecules diffuses to aggregate into the deposits layer (Siljuberg, 2012)	10
Figure 2-2: Long wax particles located in shear flow (Siljuberg, 2012)	11
Figure 3-1: Equipment for pour point test	28
Figure 3-2: Brookfield Viscometer LV DV2T model	29
Figure 3-3: Julabo Glycol solution bath.....	30
Figure 3-4: Flowchart of wax appearance temperature determination	30
Figure 3-5: Rod finger for wax deposition test.....	31
Figure 3-6: Julabo immersion circulator.....	32
Figure 3-7: Equipment set up for wax deposition.....	32
Figure 3-8: Flowchart of methodology	35

Figure 4-1: Effect of shear rate on wax appearance temperature of original Mae Soon crude oil	36
Figure 4-2: Effect of MA on crude oil pour point	38
Figure 4-3: Effect of shear rate on wax appearance temperature of crude oil at MA 3000 ppm	40
Figure 4-4: Effect of shear rate on wax appearance temperature of crude oil at MA 4000 ppm	40
Figure 4-5: Effect of shear rate on wax appearance temperature of crude oil at MA 5000 ppm	41
Figure 4-6: Comparison the effect of MA concentrations on wax appearance temperature of Mae Soon crude oil at 24 s^{-1} shear rates	41
Figure 4-7: Effect of MA concentration on the amount of wax deposits	43
Figure 4-8: Effect of n-heptane on crude oil pour point	44
Figure 4-9: Effect of shear rate on wax appearance temperature of crude oil at 5% N-heptane	46
Figure 4-10: Effect of shear rate on wax appearance temperature of crude oil at 10% N-heptane	46
Figure 4-11: Effect of shear rate on wax appearance temperature of crude oil at 15% N-heptane	47
Figure 4-12: Effect of shear rate on wax appearance temperature of crude oil at 20% N-heptane	47
Figure 4-13: Effect of n-heptane concentrations on wax appearance temperature of Mae Soon crude oil at 24 s^{-1} shear rates	48
Figure 4-14: Effect of n-heptane concentration on amount of wax deposit	50
Figure 4-15: Effect of temperature on amount of wax deposit of crude oil with	50
Figure 4-16: Effect of shear rate on wax appearance temperature of crude oil at 10% N-heptane and 4000 ppm MA	53
Figure 4-17: Effect of shear rate on wax appearance temperature of crude oil at 10% N-heptane and 5000 ppm MA	53
Figure 4-18: Effect of shear rate on wax appearance temperature of crude oil at 10% N-heptane and 7500 ppm MA	54
Figure 4-19: Effect of the mixture concentration on wax appearance temperature of crude oil at 24 s^{-1} shear rates	54

Figure 4-20: Effect of mixture concentration on amount of wax deposit.....56



LIST OF ABBREVIATIONS

MA	Poly (maleic anhydride-alt-1-octadecene)
WAT	Wax Appearance Temperature
DSC	Differential Scanning Calorimeter
CPM	Cross Polar Microscopy



NOMENCLATURE

a	Brownian particle diameter (m)
A_w	Area of wax deposition (m^2)
C_1	Function of oil constant
D_B	Brownian diffusion coefficient (m^2/s)
dC/dr	Wax concentration gradient ($1/m$) of wax concentration over pipe radial coordinate r (m)
dC/dr	Concentration gradient over the pipe radial coordinate ($1/m$)
dC/dT	Solubility coefficient of the wax crystal in the oil phase ($1/^\circ C$)
dM_w/dt	Rate of wax deposited (kg/s)
D_s	Shear dispersion coefficient (m^2/s)
dT/dr	Radial temperature gradient of the wall ($^\circ C/m$)
D_w	Diffusion coefficient of the wax in the oil phase (m^2/s)
g	Acceleration due to gravity (m/s^2)
K_p	Power-law consistency index
M	Molecular weight of the oil solvent (g/mol)
M_B	Mass of deposited wax due to Brownian diffusion (kg)
n	power-law index

N	Avogadro's number (1/mol)
ΔP	Density difference (kg/m ³) between the settling wax and the oil
R	Gas constant (J/mol.K)
T _a	Absolute temperature (K)
U	Settling velocity (m/s)
V	Wax molar volume (cc/g mole)



GREEK LETTER

ρ_w	Density of the solid wax (kg/m^3)
μ	Dynamic viscosity (cP)
μ	Oil viscosity (Ns/m^2)
ξ	Association parameter representing the effective molecular weight of the solvent with respect to molecular diffusion
γ	Oil shear rate at the pipe wall (1/s)
φ_w	Wax particle diameter (m)
φ_w	Wax volume fraction out of the solution at the wall

SUBSCRIPTS

a	Absolute
B	Brownian
P	Power-law
s	shear
w	wax

CHAPTER 1

INTRODUCTION

1.1 Classification of petroleum products

The petroleum chemicals are divided into 4 groups namely, paraffins, naphthenes, aromatics and resins-asphaltenes. Besides, paraffins group can also be separated into three classes namely, alkanes, alkenes, alkynes as shown in Figure 1.1 (McCain, 1990).

Paraffins

Alkanes has general formula C_nH_{2n+2} in hydrocarbon homologous series. In this compound, the atoms of carbon are connected in continuous or branches with more than two carbon atoms. Moreover, these alkanes compound are also called paraffin hydrocarbons, and these are straight chain (normal) hydrocarbon (McCain, 1990).

Alkenes are composed of branched hydrocarbon chain and the basic formula for alkenes is C_nH_{2n} . Moreover, the basic formula of alkynes is C_nH_{2n-2} and it has triple bond with longest chain.

Naphthenes (Cycloalkanes)

The cycloalkanes are called naphthenes, cycloparaffins or alicyclic hydrocarbons and the basic formula of cycloalkanes is C_nH_{2n} . This class is known as naphthenes. This compound of hydrocarbon is known as naphthenes.

Aromatics

Aromatics is mainly composed of benzene ring. Moreover, the basic structure of aromatic compounds is made up of benzene ring as the fundamental structure. Benzene structure contains a flat molecule that has six hydrogen atoms arranged in hexagonal ring. Generally, benzene ring has six corner of carbon atom and each carbon atom is attached to one hydrogen atom.

Resins and Asphaltenes

Resin and asphaltenes contain larger molecules, mainly hydrogen and carbon with sulfur, oxygen and carbon ranges of one to three atoms per molecule. The primary structure is composed of rings, aromatic with three to ten or more rings in each molecule. The appearance of asphaltenes are solid, dry, black powders and nonvolatile. However, the appearance of resins are heavy liquids or sticky solids and volatile as hydrocarbons of the same size (McCain, 1990).

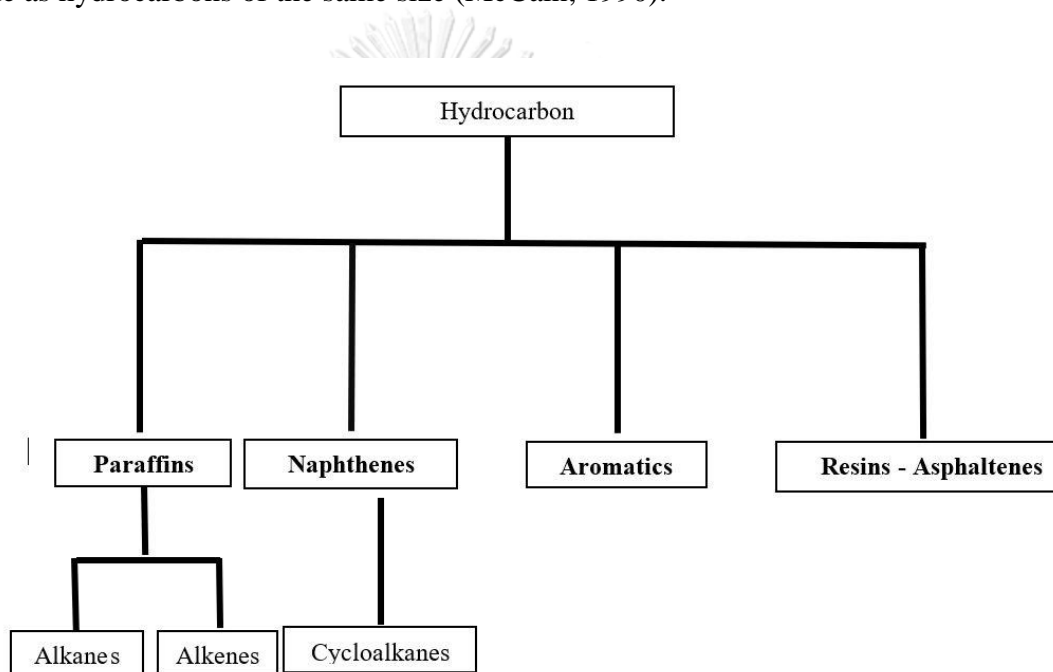


Figure 1-1: Hydrocarbon Classification

1.2 Paraffin wax in crude oil and wax precipitation

Waxy crude oils are widely found in onshore and offshore petroleum fluid reservoirs. Crude oil from wax formation is one of the crucial problems for flow assurance of transportation pipeline in oil and gas production (Aiyejina et al., 2011). In crude oil production and transportation sector, this issue can commonly cause wax deposition problem and it has made huge amount of economic losses (Sanjay et al., 1995).

Generally, petroleum crude oil has different constituents comprising paraffinic, naphthenic, intermediate and asphaltenes. Both paraffinic and intermediate crude oil which has linear, branched and ring carbon structures are origin of petroleum waxes. Basically, crude oil contains paraffin hydrocarbons(C18-C36) which are known as macrocrystalline wax and naphthenic hydrocarbon (C30-C60) which are known as microcrystalline wax (Speight, 2014). In macrocrystalline waxes, these are composed of straight chain saturated hydrocarbons from carbon numbers 18 to 36 and large percentage of branched and cyclic hydrocarbons with 30 to 60 are contained in the microcrystalline waxes as shown in Figure 1.2 and 1.3 (Mansoori, 1996).

A waxy crude oil commonly comprises

- (1) Different type of middle class and light hydrocarbons (paraffins, aromatics, naphthenic, etc.)
- (2) Macro and microcrystalline wax
- (3) Different kind of another heavy organic compound such as resins, asphaltenes, diamondoids, organometallics, etc. (Totten et al., 2003).

As the crude oil temperature decreases, the wax components start to precipitate out of the crude oil and this temperature is known as wax appearance temperature (WAT). If the crude oil temperature is still dropped to pour point that fluid cannot flow at this condition, the wax fragments will freeze. Therefore, these two points is critical for the crude oil.

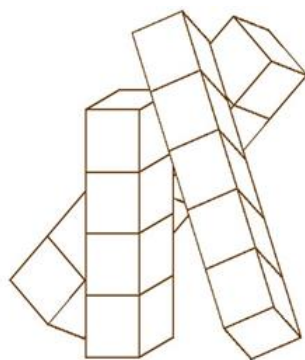


Figure 1-2: Macrocrystalline wax (Mansoori, 1996)

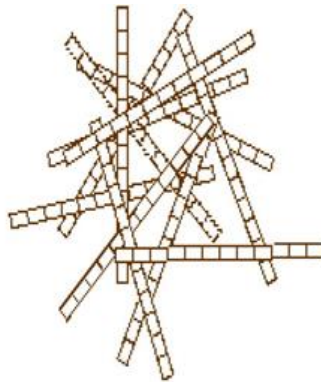


Figure 1-3: Microcrystalline wax (Mansoori, 1996)

The wax precipitation from crude oil throughout production and transportation might create different kind of issues. One of the most discovered issues is solid wax deposition on well stream and pipeline. This problem takes place when (1) the temperature of pipeline wall is decreased to wax appearance temperature of the crude oil, (2) a negative outspread temperature gradient exists in the fluid flow, (3) wax crystals can adhere to the wall because of high wall friction, (4) asphaltence from the crude oil has expanded after the contact with pipeline wall and bound together with wax crystals (Totten et al., 2003).

1.3 Paraffin wax production problems and prevention

The origin of the production problems from paraffin wax is an increasing concentration of heavy wax components within aging and deeper reservoirs. Varying fluid velocities results into viscosity effects, wax deposition in the formation and tubing, and block formation by deposited asphaltenes and waxes. Moreover, the downhole and surface equipment are all negatively affected by paraffin waxes with emulsions, solids and corrosion by-products. However, paraffin wax deposition during production stage is one of the critical problems for solving and in many occurrences. The natural reservoir flow is ceased because of paraffin wax blockage (Becker, 1997).

There are a lot of methods that have been applied to reduce the wax deposition. Generally, they can be divided into three groups (a) mechanical method (b) thermal method and (c) chemical method. In chemical method, there are four different kinds of wax inhibitors for preventing and removing wax deposition and wax

gelling namely wax crystal modifier, pour point depressant, dispersant and solvent (Kelland, 2014). Among them, the usage of chemicals is common in the field because they can be applied easily rather than other techniques. According to Kelland (2014), (1) ethylene polymers and copolymers, (2) comb polymers and (3) branched polymers with long alkyl groups are used as both wax crystal modifier and pour point depressants. Maleic-Anhydride-alt-1-octadecene (comb polymer type) demonstrate the reduction in the amount of wax deposits effectively compared to other chemicals because the viscosity or van der Waals (vdW) interaction of crude oil would be controlled by adding amount of Maleic-Anhydride-alt-1-octadecene ratio (Ridzuan et al., 2016).

On the other hand, n-heptane solvent is one of the common solvents that is used to maintain flowable condition and to dissolve the precipitated heavy organic of crude oil. Furthermore, the precipitated heavy organic of crude oil is decreased as the higher carbon number of n-alkane solvent is used (Udourioh et al., 2014). In the process of bringing crude oil to the surface, the flow of velocity is too slow while waxy crude oil passes through low temperature zone. In addition, production engineers must plan to maintain fluid flow condition in the surface pipeline. The chemicals are frequently used for this problem to reduce the pour point of crude oil and to maintain the fluid flow condition.

1.4 Objectives and scope of this study

Crude oil is involved in different compositions and properties according to their original source. In this study, the paraffin waxes dissolved in wax removal chemicals at various concentrations are investigated to handle wax deposition. The main objectives of this study are

- (1) To investigate the effect of working temperatures between 35, 45 and 55°C and analyze of chemical concentrations on wax deposition of crude oil from Mae Soon at Fang oil field.
- (2) To measure pour point temperature and wax appearance temperature at various conditions.
- (3) To evaluate the chemical concentration with less wax deposits.

The contribution of this research work is to understand on wax deposition problems in the production pipeline in Thailand crude oil and provide important data to handle this issue.

The rest of the contents in this thesis is presented in the following chapters. Chapter 2 presents theory and literature review describing important parameters of wax deposition such as pour point and wax appearance temperature. The experiment and methodology are explained in this chapter 3. The result and discussion will be mentioned in Chapter 4. Finally, the conclusions and recommendation will be presented in Chapter 5.



CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Paraffin wax

The wax in the petroleum crude primarily composes of paraffin hydrocarbons (C18-C36) and naphthenic hydrocarbons (C30-C60). The wax components in the hydrocarbon can remain different states depending on their temperature and pressure. These components start to precipitate out of the crude oil and form crystal which are known as macrocrystalline wax and the wax crystals from naphthenes which are known as microcrystalline waxes (Totten et al., 2003).

2.2 Waxy precipitation

Petroleum wax formation contain two stages: nucleation and crystal growth. As the temperature of the petroleum fluid is lowered to the level where wax molecules can be precipitated out of the crude oil, the wax molecules grow as clusters. Wax particles proceed to adhere and detach from these clusters till they reach certain a crucial size and become stable. These clusters are called nuclei and the development of cluster formation is known as nucleation. When the nuclei are formed, and the temperature is still below the WAT, the crystal-growth process becomes when wax molecules fall in a plate-like structure (Fanchi, 2007).

2.2.1 Wax Appearance Temperature

As the temperature of the petroleum fluid is decrease to the wax appearance temperature (WAT), the wax molecules grow as clusters. Once these nuclei reach certain a crucial size, they become stable and another combination of molecules results in crystal growth. This point is also referred to as wax crystallization temperature or wax appearance temperature. Wax appearance temperature is considered as the crucial parameter. If high WAT is detected during field production, it indicates the potential for wax deposition issues (Fanchi, 2007).

The various methods for determination of WAT have been developed (Kruka et al., 1995). Kruka et al. (1995) divides WAT measurement techniques into four groups which are (1) optical observation methods (CPM, NIR) (2) heat detection methods (DSC), (3) viscosity deviation measurement (viscometry) and (4) density alteration methods. However, other methods have been developed such as (5) mechanical methods (sonic testing, filter-plugging), (6) electromagnetic methods (NMR).

2.2.2 Pour Point Temperature

When the liquid petroleum is still mobile at the lowest temperature and this temperature is known as pour point temperature (Nadkarni and Nadkarni, 2007). Pour point of crude oil can be evaluated by ASTM D5853-11 method. Pour point of crude oil is one of the critical factors because it can cause economic losses and wellbore damage. Therefore, it always needs to assess the condition of crude oil.

2.3 Wax deposition

The precipitation of paraffin wax and deposition are the important factors in the production, transportation, and processing of crude oil because it can reduce the flow ability and block pipeline on the surface equipment. Moreover, the wax deposition in the pipeline and surface equipment causes falling pressure; thus, requiring maximum pump power and declining the production capacity.

2.3.1 Wax Deposition Mechanisms

At the early stage of wax deposition investigation, four mechanisms of wax deposition are initially proposed by (Burger et al., 1981).

(1) Molecular Diffusion

Crude oil flow conditions will be considered as a laminar flow throughout the pipeline and a thin laminar sub-layer adjacent to the pipe wall is developed. When the bulk crude oil is cooled, temperature gradient will be across the inside layer of pipeline. The temperature is under the point which solid wax particles come out from the solution and then the flowing fluid will contain precipitated wax particles.

Moreover, the fluid state will be in equilibrium with the solid phase. As a result, the solid particles exist with the fluid in this stage. Subsequently, the concentration gradient of dissolved wax will occur near the pipe wall due to temperature changes and the dissolved wax molecules will be transported toward the pipe wall by molecular diffusion (Theyab, 2018).

Wax gel formation and aging effect of the deposited wax contain as the two stages in the wax deposition process. Non-hydrocarbon and hydrocarbon solid and liquid particles contain in the wax deposit process depending on characteristics of crude oil. Wax deposition is caused by entrapped crude oil that can diffuse the wax molecules into the wax gel deposit at the same time crude oil molecules out of wax gel deposit as counter-diffusion as shown in Figure 2.1. The higher carbon number of crude oil fraction transform crystal form into a gel with the entrapped crude oil molecules inside the wax gel. Consequently, molecular diffusion is important for hardening of wax gel deposits and aging of wax gel that is caused by agglomeration of wax deposits because of diffusion and counter-diffusion (Theyab, 2018).

Molecular diffusion equation

Paraffin wax precipitation is occurred when dissolve wax molecules and the cool pipeline surface strike at the point. Heat flux conditions of flow line is dominated by molecular diffusion as a primary mechanism. According to Fick's law of diffusion, molecular diffusion of solid paraffin wax in oil and gas fluid flow condition can be modelled. Therefore, the wax deposition rate can be stated by the following equation:

$$\frac{dM_w}{dt} = \rho_w D_w A_w \frac{dC}{dr} = \rho_w D_w A_w \frac{dC}{dT} \frac{dT}{dr} \quad (2.1)$$

Where dM_w/dt is the rate of wax deposited (kg/s), ρ_w is solid wax density (kg/m³),

D_w is the diffusion coefficient of the wax in oil phase (m²/s),

A_w is the area of wax deposition (m²),

dC/dr is the wax concentration gradient (1/m) of wax concentration over pipe radial coordinate r (m),

dC/dT is the solubility coefficient of the wax crystal in the oil phase (1/°C) and

dT/dr is the radial temperature gradient of the wall (°C/m).

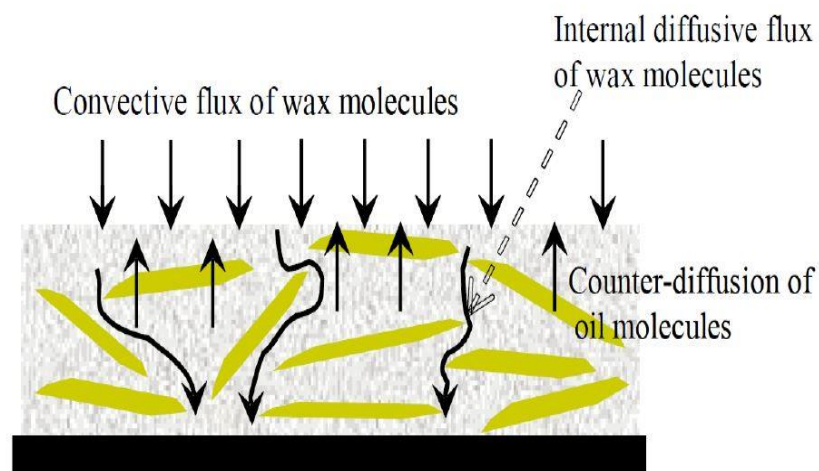


Figure 2-1: Illustration of how wax molecules diffuse to aggregate into the deposits layer (Siljberg, 2012)

(2) Shear Dispersion

The tiny wax particles are suspended when the fluid is flowing in laminar flow. These particles usually spread out toward the surrounding fluid. When the particles reach at the center of the stream line, the particle rotates with an angular velocity that is half of fluid shear rate as shown in Figure 2.2. If the particles start to change a solid state, the reduction effect will cause in both of linear and angular velocities. The circulatory motion is occurred onto a layer of fluid adjacent to particles by rotating fluid owing to the fluid viscosity. Then, surrounding particles is affected by drag force because of circulating fluid region. In a shear field, each particle are passes and interact with surrounding particles in slower or faster moving streamlines. The particle which depart from the original stream line to another result in large temporary displacements when only two particles are present far from a wall. However, there is

no adjacent displacement, when the particles pass through to another and return to their original streamline. Besides, the concentration of wax particles is high, the multi particle interaction will occur. The multi- particles which colloid each other lead to dispersion of particles. Shear dispersion can be modelled by following equation: (Theyab, 2018)

$$\text{Dispersion coefficient} \quad D_S = \gamma \frac{d_w^2 \phi_w}{10} \quad (2.2)$$

Where γ is the shear rate of crude oil at the pipe wall s^{-1} ,

d_w is the wax particle diameter (m),

ϕ_w is the volume fraction of wax out of solution at the wall and

D_s is the shear dispersion coefficient (m^2/s).

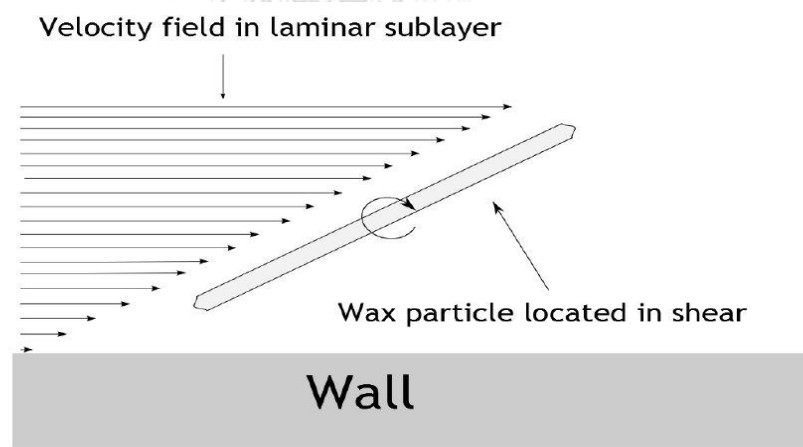


Figure 2-2: Long wax particles located in shear flow (Siljuberg, 2012)

(3) Brownian Diffusion

When crude oil molecules will force thermally to the suspended wax crystals, random small Brownian movements of the suspended particles will be occurred by these collisions. Then, the Brownian movement will induce a net transport which is similar to diffusion, when the concentration gradient of these particles takes place in the crude oil. Briefly, precipitated wax suspended in waxy crude oil flow is forced by

agitated oil molecules. Then, when concentration gradient is occurred for the wax solid particles, motion of precipitated particles is started to the path of decreasing concentration modelled by Fick's law of diffusion. Therefore, the amount of deposited wax due to Brownian diffusion can be stated by following equation. (Theyab, 2018)

$$\frac{dM_B}{dt} = \rho_W D_B A_W \frac{dC}{dr} \quad (2.3)$$

Where M_B is the weight of deposited wax owing to Brownian diffusion (kg),

$\frac{dC}{dr}$ is the concentration gradient gradient over the pipe (1/m),

A_W is wax deposition area (m^2) and

D_B is the Brownian diffusion coefficient (m^2/s).

(4) Gravity Settling

The precipitated wax particles are heavier than the surrounding fluid phase. Thus, they will in a gravity field and can be deposited on the bottom of the pipe wall or tanks. Although the mixture begins with uniform, then, the precipitated wax particles deposits settling will take place because of gravity force. Gravity settling have been proposed to be negligible as flowing fluid causing the dispersion of precipitated wax particles. Thus, gravity settling is eliminated. On the other hand, it is assumed that gravity settling will show wax deposition rate at shut-in conditions or storage tanks or low flow rates. The modified stokes's law of settling crystals in a pseudoplastic fluid generate the settling velocity U (m/s) as following equation; (Theyab, 2018)

$$U = \left[\frac{g \Delta P a^{(1+n)}}{18 K_p} \right]^{1/n} \quad (2.4)$$

Where ΔP is the density difference between the settling wax particles and the crude oil (kg/m^3),

n is the power law index, a is the particle diameter,

g is the acceleration due to gravity (m/s^2) and

K_p is the power-law index.

2.3.2 Factors Affecting Wax Deposition

(1) Effect of temperature

Temperature is the one of the most crucial point in wax precipitation and deposition because it has direct relationship with the paraffin wax solubility. Paraffin wax solubility decreases as the temperature decreases. Once the surrounding temperature around the production pipe is usually less than the temperature of crude oil inside the pipe. Consequently, there is a heat loss through the pipe wall to the ambient because of existing temperature changes between crude oil and colder pipe wall. This temperature changes cause to wax deposition while the temperature of pipe wall drops below the cloud point.

Paraffin molecules close the pipe wall crystallize out of the crude oil as the temperature of wall drops below cloud point. Thus, the dissolved paraffin molecules are reduced around the wall because of inducing a radial concentration gradient. According to the diffusion theory, dissolved paraffin molecules in oil diffuse towards the pipe wall. As a result, additional wax precipitation and further deposition is caused, and this circumstance leads to increasing wax deposit thickness with time (Anchorage et al., 2008).

(2) Effect of crude oil composition

Crude oil consists of saturates, aromatics, resins and asphaltenes (SARA). The solid deposition and crude oil stability are determined by SARA. Saturates are adaptable in nature: normal paraffin is the most flexible class among of them because of straight chain compounds. The iso-paraffins similarly act a high level of adaptability but it is formed as a more unstable wax. Cyclo-paraffins (naphthenes) are least flexible and do not contribute to wax deposition because of their structure. Aromatics help to be soluble high molecular weight saturates especially asphaltenes. Light ends of saturates equally assist to keep high molecular weight ends in solution.

As the light ends of saturates depart from the reservoir firstly during the beginning of production, this varies the original crude oil composition, resulting in decreased solubility of the paraffin waxes. This loss of solubility may lead to deposition of wax (Anchorage et al., 2008).

(3) Effect of pressure

Pressure is one of the main essential parameters during the exploitation of reservoir fluids. The reservoir pressure is decline during production stage and also the flow line pressure drops the whole path from reservoir to the surface. The lighter components precipitate out of reservoir fluid as pressure drops. This causes an increase in solute solvent ratio since light ends assist as solvent to the wax compound. Therefore, the solubility of wax is decreased with the loss of these light ends (Anchorage et al., 2008).

(4) Effect of flow rate

When moving oil stream has longer residence time in the flow line, this circumstance leads to heat loss to the surroundings and provide enough time for wax precipitation and deposition. Jessen and Howell (1958) believed that the flow in the laminar regime makes more wax deposition. On the other hand, wax deposition decreases when the flow changes to turbulent (Anchorage et al., 2008).

(5) Effect of gas/oil ratio

Gas/oil ratio impacts on wax deposition according to pressure changes. Solution gas assists to maintain wax in the solution as gases remain in the solution above the bubble point (Anchorage et al., 2008).

2.3.3 Control and Remediation

A few strategies have been developed to reduce the wax problems. Three methods are generally used as shown in below:

1) Mechanical Methods

Pigging is often used for removing severe wax deposits in flowlines and pipelines. There is various type of pig designs for removing blockage wax deposits such as foam pig, bristle pigs and aggressive pigs. The function of the pig is scraping off the wax deposits along the pipeline and let the wax disperse along the crude oil flowline. This technique can be stated as a cost-effective method for removing wax deposition in the flowline and pipelines. Generally, pigging program can be run by regular schedule of the system (Numura, 2005).

Wireline cutting with scrubber is used to reduce organic deposition case inside the tubing, but the drawbacks of this techniques are uneconomical for oil fields and time-consuming operation (Numura, 2005).

2) Thermal Methods

Thermal methods for wax deposition are usually used into three ways (i) hot oiling (ii) hot water technique and (iii) direct heating.

Hot oiling is often used as a popular method for removing deposited wax in the flowline and downhole. Heating temperature of hot oil is maintained above the melting point of desired waxy crude oil and then circulate the hot oil along all production facilities, thereby the wax dissolved in the crude oil. On the other hand, the drawback of this technique is to care about the flash point of crude oil and sufficient amount of hot oil depending on the depth of well is needed to dissolve the wax (Thota & Onyeana, 2016).

Hot water technique does not provide the wax soluble efficiency like the previous technique. This technique is usually used combining with surfactants. One of the benefits of this technique is that water can be heated up at specific degree than oil (Thota & Onyeana, 2016).

Direct heating technique is using electric current that passes through the pipeline to generate heat. Some researchers mentioned this technique one of the

reliable techniques for transportation pipelines of Deepwater well (Thota & Onyeonuna, 2016).

3) Chemical Method

Wax inhibitors can be divided into four group namely wax crystal modifiers, pour point depressants (PPD), dispersants and solvents (Allen & Roberts, 1989).

Wax crystal modifiers group has special chemical structure which is produced artificially to modify wax aggregation. Moreover, there are structures with segments in to interact with forming wax crystals in this former inhibitor group. Hence, this chemical transforms molecules to replace the wax molecules, thereby it can reduce the size of the wax crystal group of crude oil by hindering (Numura, 2005).

Pour point depressants are high molecular weight polymers and small amount of concentration of PPD can affect wax crystal structure for interacting crystal morphology. These chemicals show significant reduction of pour point, viscosity and yield stress reduction but these chemicals may not reduce wax deposition rates (Numura, 2005).

Dispersants are known as surface active agents such as polyesters, amine ethoxylates. These chemicals perform by each segment by repairing the surface of pipeline wall. However, the primary work of these chemicals are to assist the wax crystal dispersed as separated particles (Numura, 2005).

In the last inhibitor, the hydrocarbon solvents are mostly used to dilute waxy crude oil. They provide the better flow condition by soaking waxy the fluid and wax precipitation can become less amount of original stage by doing this way. These wax inhibitors will be discussed in detail in next section.

2.4 Wax deposition prevention by chemical method

2.4.1 Chemical Method

1) Crystal modifiers have uniform molecular structure to the wax. They compose of polymeric compounds that have one or more hydrocarbon chain like wax

and polar portion. It is known that crystal modifier molecules replace to wax molecules position by co-precipitating or co-crystallizing on the crystal lattices through the hydrocarbon chains. The chemicals that influence on WAT are known as wax inhibitors or wax crystal modifiers. A steric hindrance is placed on the crystal which can interrupt aggregation of wax crystals and the crystal growth. Besides, they also frequently reduce the pour point of crude oil (B Wei, 2005). The effective polymers are used as a wax crystal modifiers and field test and laboratory test can provide the suitable chemical for related oilfield (Allen & Roberts, 1989).

2) For pour point depressants (PPD), there are four stages namely nucleation, adsorption & co-crystallization and solubilization between pour point depressant and wax interaction. The crude oil temperature is below WAT, high molecular weight of polymeric PPD molecules interfere with low molecular weight of wax molecules and behave as crystalline nucleus. As a consequence, the group of sub-critical crystalline nucleus become larger and this aggregation is known as polynucleation. In adsorption stage, polymeric PPD co-crystallize to form wax crystal during wax molecules are absorbed on the surface of PPD. At the same time, the solvent portion attempt to coat with wax molecules in the process of co-crystallization. The main function of polymeric PPD is to alter the wax crystals morphology. When the process is reached at the solubilization stage, the molecular layer is formed absorbing low polarity material by polar group on the surface of the mixture. Besides, the second layer known as solvation layer is formed near the first layer to prevent the interaction between the wax crystals (Li et al., 2018).

The wax crystal structure is modified by PPD and it is reduced growth of wax crystals. PPD reduces the viscosity, yield stress and pour point of crude oil, meanwhile, it cannot reduce the wax deposition rate (Kang et al., 2014).

3) Wax dispersants are known as surfactants which inhibit the wax molecules attach to on the surface of pipeline. This chemical can change the wettability of the surface to water wet or it make the crystals growth to a weak layer and let them to disperse with turbulent flow in the pipeline. Some wax dispersants are applied as a function of adsorbing and water-wetting on the surface of the pipe.

Generally, the role of wax dispersants is soaking up wax crystals to hinder the growing process by doing so the tendency for sticking up of wax molecules together on the pipe surface can be reduced. Moreover, the best designation of wax dispersants can handle severe wax deposits problem and they can provide the better flow condition for crude oil in the pipeline (Kelland, 2014).

Dispersants and surfactants have a uniform molecular structure. One end of the dispersant molecule is attracted to the paraffin, but the other end is soluble in oil or water depending on the phase in which the paraffin is to be dispersed. Dispersants split wax crystals into smaller particles, and reduce the deposition rate and prevent it by reduction wax adhesion to the pipe wall (Kang et al., 2014).

4) Solvents are used to disintegrate the solid components of the crude oil. Especially, light hydrocarbon solvents such as n-heptane are soluble in the waxy crude oil because they have similar hydrocarbon structures. Furthermore, solvents can combine with the other additive and those mixture designations can assist to reduce not only wax deposition but also asphaltenes. On the other hand, selecting of solvents can be done easily with small laboratory test (Allen & Roberts, 1989). Consequently, solvents can improve the solubility of waxy crude oil and dissolve deposited wax in the crude oil (Kang et al., 2014).

According to purpose of prevention and removing for wax deposition and wax gelling, the chemical designation will provide different mechanism. Some chemical affect WAT of crude oil and other chemicals affect pour point of crude oil. However, there is an overlap between these two groups according to the chemistry and mechanism of chemical. Therefore, some chemicals as known as wax crystal modifiers can function as PPD.

The major group of wax crystal modifiers and PPDs can be expressed as flows:

- (1) Ethylene polymers and copolymers
- (2) Comb polymers such as maleic anhydride-alt-one-octadecene
- (3) Miscellaneous branched polymers with long alkyl group (Kelland, 2014).

2.4.2 WAT Measurement Techniques

Plenty of research studies on WAT have been investigated depending on accuracy and reliability of each method and observed different results. Among of these methods, cross-polar microscopy, differential scanning calorimeter (DSC) and viscometry methods are commonly studied and make comparison by lots of researchers (Kruka et al., 1995; Roenningsen et al., 1991; Ruwoldt et al., 2018).

(1) Cross Polar Microscopy (CPM)

The magnification lenses are used to extend the detection limit to the tiny crystal sizes and then light of cross-polarized is used for detecting the solid particles of dark oil. This technique can detect the wax crystals while they form into the black crude oil. In contrast with other methods, the highest value of WAT is supplied in this method and CPM method is based on operator visual detection of onset wax crystals. Therefore, the results of measurement can be varied by different operators (Huang et al., 2016).

(2) Differential Scanning Calorimeter (DSC)

The precipitated wax onset temperature is measured when the heat of crystallization releases from the crude oil and then detect the onset temperature of the exothermic peak in terms of liquid-solid transition in an exothermic process. DSC approach captures the liberated thermal from the waxy crude oil meanwhile wax crystallization process (Huang et al., 2016).

(3) Viscometry Method

For this method, at above WAT, the crude oil act as a Newtonian fluid and the temperature of the Newtonian range can be described by the following Arrhenius type equation.

$$\mu = Ae^{\frac{E_a}{RT}} \quad (2.5)$$

As the temperature is below WAT, the molecules of wax crystals occur in the crude oil and then they disturb the flow properties of the bulk oil. As the temperature is slightly below the WAT, the crude oil change as a non-Newtonian fluid and the viscosity is increased. The viscometry method applies the change in the slope in the viscosity vs temperature curve. As the crude oils are generally shear-thinning, the determination of WAT is not considered to use high shear rate (Roenningsen et al., 1991).

Roenningsen et al. (1991) made the comparison of WAT results value with different three methods, CPM, DSC and viscometry methods. All measurement is conducted each cooling rate $0.5^{\circ}\text{C}/\text{min}$ for CPM, $10^{\circ}\text{C}/\text{min}$ for DSC and $12.5^{\circ}\text{C}/\text{h}$; at 100 s^{-1} shear rates with different operating temperature. As the results of all measurements, the WAT temperature values from CPM are higher than other techniques and DSC is the lowest. This can be explained that the precipitated wax particles cannot be detected with DSC and viscometry in the earlier stage whereas CPM detected a change in the fluid with transmitted light.

Kok et al. (1996) presented the experimental results of the WAT determination by DSC, CPM and viscometry method. The experiment is carried out with same cooling rate 2K min^{-1} for CPM and DSC but 0.5K min^{-1} for viscometry at 110 s^{-1} shear rates. The WAT result of CPM is also higher for this study compared with other two techniques. However, the author suggested that DSC and CPM should be used together to understand WAT of crude oil and viscometry should be used when the effect of inhibitors are studied.

Neto et al. (2010) measured the WAT with photoelectric signal method and rheological method. In both experiments, the temperature and cooling rate are set the same condition (from 60°C to 5°C , $0.1^{\circ}\text{C}/\text{min}$ cooling rate). According to the results, WAT result from the viscometry is lower than photoelectric signal method which is higher WAT value because this method detects the solid phase as soon as it is built.

Theyab and Diaz (2016) studied the effect of inhibitors on pour point and WAT with viscometer. The test is conducted at a cooling range from 55°C down to

0°C at a rate of 5°C/min and shear rate of 120 s⁻¹. According to results, the inhibitors show reduction WAT in the same concentration with different mixtures.

According to Ruwoldt et al. (2018), the changes in cooling rate interfere for WAT determination. The three different methods (DSC, CPM and viscometry) are used to investigate the effect of cooling rate on WAT. Operating temperatures are set depending on fluids and cooling rate varied 5, 10, 15 and 20°C/min for each method. The shear rate of viscometer is set at 25 s⁻¹. All the results of their different cases showed that the higher cooling rate results in lower WAT. Therefore, at the higher cooling rate, WAT detection is delayed owing to wax precipitation that is not pronounced.

In this study, WAT measurement with and without inhibitors will be conducted at cooling rate of 12°C/hour, temperature range from 75°C to 35°C at three shear rates (6 s⁻¹, 12 s⁻¹, 24 s⁻¹). The reason for setting cooling rate of 12°C/hour is that higher cooling rate can delay the WAT detection according to Ruwoldt et al. (2018). For the temperature, the range is followed the original reservoir condition. The parameters for shear rate is set below 100 s⁻¹ because the crude oil is generally shear thinning (Roenningsen et al., 1991) and higher shear rate can reduce the crystal size dimensions (Venkatesan et al., 2005).

2.4.3 Wax Deposition Prevention and Removal Techniques

Several ways are used to reduce wax gelling and the build-up of wax deposition downhole and in flowlines.

1. Insulation
2. Mechanical removal
 - a. Pigging of transportation lines
 - b. Wireline cutters downhole
3. Heating
 - a. Downhole
 - b. Flowline
4. Shock chilling (cold flow)

5. Wax inhibitors, pour-point depressants (PPDs), dispersants and wax solvers
6. Magnets
7. Microbial treatment
8. Ultrasonic

Pipeline pigging is commonly used to remove the build-up of wax deposits at regular operating intervals. Moreover, pigging is performed as a conjunction for wax inhibitor treatment. Wireline cutting is performed with simple procedure inside downhole, but this operation takes longer time for well shutting down. In insulating technique, the transported fluid is maintained above the wax deposition temperature. However, pipeline heating is expensive, and this option should be chosen for subsea multiphase transportation.

In shock chilling or cold flow method, this technique is maintaining the precipitated wax in the bulk fluid rather than deposits on the pipe walls. Magnets and electromagnets are used to reduce the viscosity of crudes oil and they are widely used in Asia. The effect of water and salinity can also influence in this wax removal technique. In microbial treatment, organic acids and biosurfactants assist to disperse the wax and soluble in produced fluid. Microbial treatment is one of the expensive techniques to remove the wax from downhole. However, the performance of this method provides good results for wells in China. Ultrasonic method is also suggested for removal of wax deposits in the downhole and it is especially proposed for long section wax prevention instead of the chemical methods (Kelland, 2014).

In the chemical techniques, there are a lot of different chemicals that have been investigated on their performance. Hence, these are frequently used in the downhole and pipeline to reduce the wax deposition rate. Some techniques such as flow loop and cold finger have been developed for determining wax deposition and evaluation wax inhibitors.

Generally, flow loop and cold finger apparatus are commonly used in study of wax deposition rate. However, flow loop test is significantly required large amount of sample and manpower. Instead, small-scale system like cold finger is popular in the

among some investigators because this testing can perform the multitude of deposition test with a small amount of sample volume and minimum time requirements. Commonly, the performance of paraffin wax inhibitors for flow line deposition are determined with cold finger testing (Jennings & Weispfennig, 2005).

Jennings and Weispfennig (2005) studied the effect of shear and temperature on wax deposition for gulf of Mexico crude oil with cold finger apparatus. The experiment is carried out to measure the deposition rate as a function of time and shear rate. The results show that the temperature differential existing between crude and colder deposition surface can cause more deposition rate. Therefore, the concentration of wax increases as shear increases, and the shear rate is directly proportional to the wax deposition rate.

(Kasumu & Mehrotra, 2015) inspect solids deposition from one-phase and two-phase waxy mixtures by using cold finger apparatus. This experiment is performed by different time duration from 0.1s to 24 hours with two shear rates (250 rpm and 500 rpm). In this study, the researcher has found that the deposit mass decreases with an increase in stirrer speed and liquid-solid interface temperature is equal to the wax appearance temperature of the solution throughout the deposition process.

Ridzuan et al. (2015) examine the effect of shear rate and inhibitors on wax deposition of Malaysian crude oil. The cold finger testing for wax deposition is conducted at 50°C for 2 hours. The temperature for water bath is maintained at constant temperature but the shear rate is varied from 0 to 400. In this study, the author mention about different types of inhibitors can affect and increase the pour point. Hence, it is found that the total wax deposit decreases when shear rate increases.

(Chi et al., 2017) conducted the wax deposition experiment to investigate the flow field (cold finger and flow loop) effect on the wax deposition and the performance of the wax inhibitors. The experiment is carried out with different time 2,8,20 and 24 hours at the same shear rate, constant temperature and the same concentration with different chemicals. It is found that the performance of chemical 1

and 2 decrease the wax deposits mass indicating the cold finger apparatus can assess the efficiency of wax inhibitors. On the other hand, the wax content is always higher in cold finger testing. It is stated that different carbon number distribution in the wax deposits can cause different mass influx of different components to the wax deposit interface.

Li et al. (2018) express that comb-type copolymers such as maleic anhydride are popular and their performance on viscosity and pour point of crude oil is perceived. Comb polymers structures comprises of nonpolar section such as long chain alkyl groups and polar section such as aromatic base, ester bond and so on. The interaction between paraffin waxes molecules and PPD molecules can be enhanced due to incorporation between nonpolar groups and paraffin waxes. The nonpolar sector can be inserted simultaneously into wax crystal structure that influence the development of wax crystals forming. At the same time, polar sector can interact with the stronger asphaltene components in the crude oil. On the other hand, the polar section can build up the interaction between collid asphaltene molecules and the wax crystal to provide more nucleation center for wax components in the crude oil.

According to Hoffmann and Amundsen (2013), wax deposition can be reduced by adding wax inhibitors and it would help for less frequency for pipeline pigging. Moreover, they found that different chemical concentration can provide different effect to the wax deposition and the optimal ration can be found from the usage of different inhibitors concentration. In this study, wax deposition is reduced about 60% to 90% by adding different inhibitors ratio. On the other hand, it is stated that adding higher amount of inhibitors concentrations cannot provide the better performance instead of optimal concentration.

Yang et al. (2015) state that the wax inhibitors performance relies on the polymer atomic weight. Addition of highest molecular weight copolymers leads to the best performance for crude oil with a broad range of normal paraffins and a smaller carbon number. On the one hand, the lowest molecular weight of copolymers provides the better performance for crude oil with a narrow range of normal paraffins and a larger carbon number.

Dehaghani and Badizad (2016) investigate the effect of n-heptane solvent to reduce heavy crude oil viscosity. N-heptane is lack of polar molecules and as a result, it cannot interact the high fraction part of crude oil. In addition, there is zero value of n-heptane polar number according to Hansen parameters. It is intended that there would be no polar interaction between high solid particles of crude oil and n-heptane molecules nor hydrogen bonding. However, n-heptane can significantly reduce heavy oil viscosity in increasing solvent volumes compared to other solvents.

Udourioh et al. (2014) study the heavy organics deposition mechanism from precipitation of crude oil by using both single n-alkane solvents (n-pentane, n-hexane and n-heptane solvents) and binary mixture of n-alkane solvents. In the single solvents results, there is a decrease in the quantity of precipitate as the n-alkane solvent carbon number is increase.

Most researchers focus on temperature, shear rate and coolant rod temperature for determination of wax deposition. In this research, the wax deposition conditions of the fluid without shear rate and coolant rod will be investigated while temperature vary from 55°C, 45°C and 35°C with and without inhibitors. Furthermore, the single and mixed solvents are also studied and investigated for wax deposition prevention.

CHAPTER 3

EXPERIMENT

3.1 Materials, equipment and experimental procedure

Crude oil sample is obtained from Mae Soon area at Fang oil field, the Northern oil field in Thailand. The viscosity of oil is 34 cp at 70°C and the density of oil is 0.85 g/cm³ with the acid number of 0.89 mg KOH/g (Saengnil, 2015).

The composition of oil ranges from C7 to C35+ alkane and the distribution are as shown in Table 3.1.

Table 3-1: Composition of oil sample (Saengnil, 2015)

Component	Percent by weight (%)
C7	0.05
C8	0.68
C9	0.93
C10	1.00
C11	1.45
C12	1.84
C13	3.06
C14	3.52
C15	4.86
C16	3.87
C17	4.71
Pristane (C ₁₉ H ₄₀)	2.44
C18	3.49
Phytane (C ₂₀ H ₄₂)	0.82
C19	3.89
C20	4.41
C21	4.81
C22	4.48

C23	4.97
C24	4.26
C25	4.42
C26	4.33
C27	4.56
C28	3.58
C29	3.97
C30	3.72
C31	3.27
C32	2.87
C33	3.64
C34	1.7
C35+	4.40

Table 3-2: Density of crude oil sample (Saengnil, 2015)

Temperature (°C)	Oil density (g/cm ³)
70	0.850
80	0.849
90	0.848

Poly(maleic anhydride-alt-1-octadecane) or MA and N-heptane with 95% purity are purchased from Sigma-Aldrich to be used as wax removal and wax inhibitors for this studies, respectively.

3.1.1 Pour Point testing

Equipment

The temperature measurements are performed by Kimo thermocouple data loggers' model KTT 220 and thermocouples J-Type with $\pm 0.4^{\circ}\text{C}$ accuracy and temperature ranging from 0 to 1300°C .

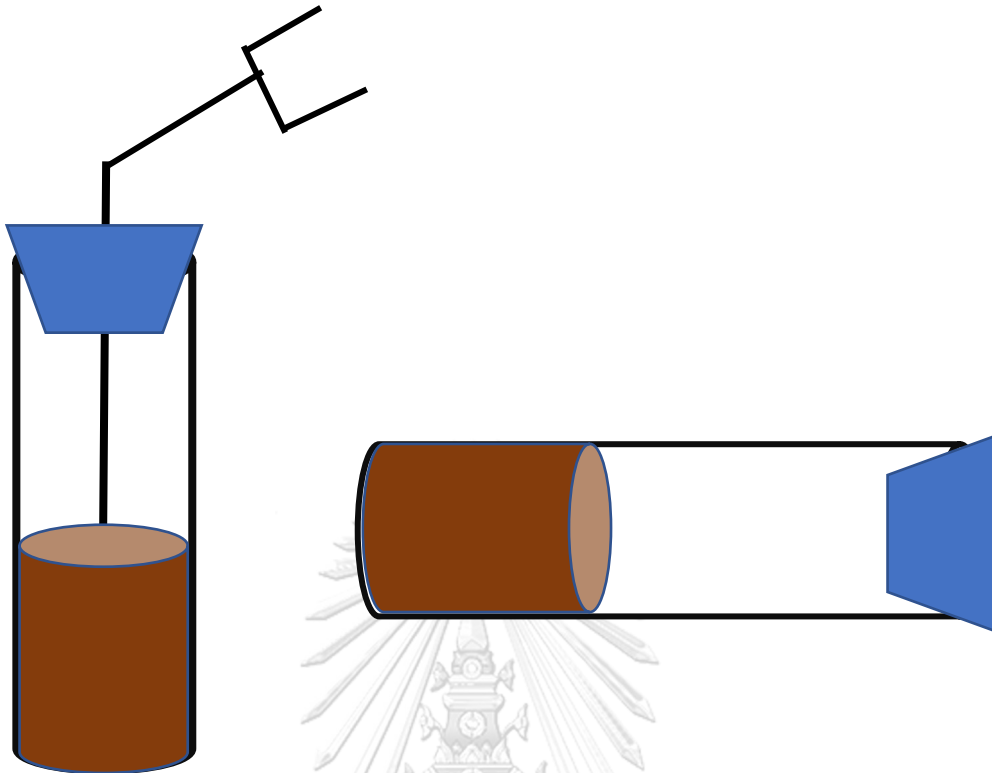


Figure 3-1: Equipment for pour point test

Crude oil temperature is controlled by using temperature controller bath Julabo immersion circulator ME model heating or cooling bath machine with ± 0.01 accuracy.

Experimental Procedure

Pour point of crude oil is tested following ASTM D 5853-11 (Nadkarni & Nadkarni, 2007). The test sample is heated at least 20°C above expected pour point with water bath and close the test tube with the cork carrying thermocouple. The temperature is reduced in the multiple of 3°C and begins to examine the appearance of sample when the temperature of the test sample is 9°C above the expected pour point. The test tube is tilted just enough to ascertain every 1°C down whether there is movement of the sample in the test tube or not. If the movement of the test sample is shown, the test tube is replaced immediately in the water bath and repeat a test for the flow at the next temperature, 3°C lower. When the test sample shows no movement even the test tube is held in a horizontal position for 5 s, that temperature is recorded

the observed reading of the test temperature. Pour point is the lowest temperature at which movement of the sample is observed under conditions of the test.

3.1.2 Wax Appearance Temperature (WAT)

Equipment

Brookfield viscometer model DV2TLV with spindle number 52Z (4.6 to 92130 cp) is used to perform the viscosity measurements as shown in Figure 3.2. Moreover, Julabo F26 model heating or cooling bath machine with ± 1 accuracy is utilized to control temperature and glycol is used as a heating and cooling media as shown in Figure 3.3.



Figure 3-2: Brookfield Viscometer LV DV2T model



Figure 3-3: Julabo Glycol solution bath

Wax Appearance Temperature Determination Procedure

WAT is measured by using viscometer. First of all, the crude oil is heated up to 80°C about 1 hour before commencing the test and then crude oil with and without inhibitor is transferred to the viscometer cup. After the test is carried out, the temperature is cooled down ranging from 80°C to 40°C with three different shear rates and constant cooling rate. The experimental procedure is shown in Figure 3.4.

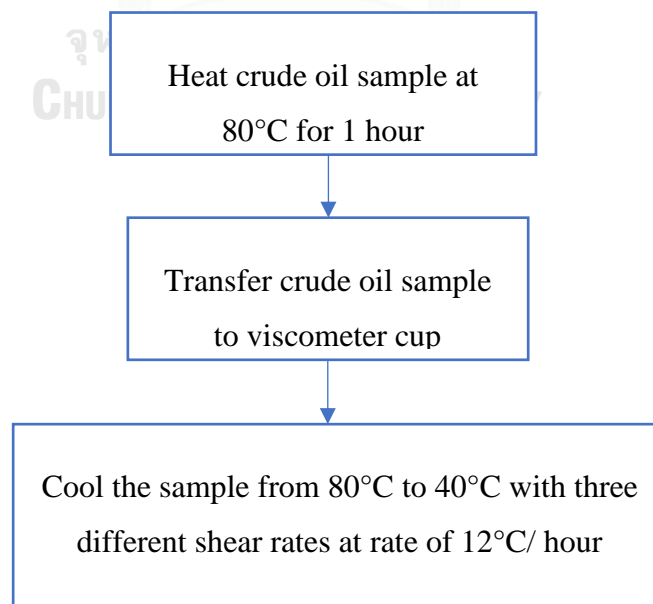


Figure 3-4: Flowchart of wax appearance temperature determination

3.1.3 Wax Deposition Test

Equipment

Rod finger, a 25 cm long of copper stick, is equipped at rubber cork together with thermocouple J-type. It is designed to evaluate the wax inhibitors performance as shown in Figure 3.5.

Crude oil temperature is controlled by using temperature controller bath Julabo immersion circulator ME model heating or cooling bath machine with ± 0.01 accuracy. It is utilized to control temperature and water is used as a heating and cooling media as shown in Figure 3.6 and Figure 3.7.



Figure 3-5: Rod finger for wax deposition test



Figure 3-6: Julabo immersion circulator



Figure 3-7: Equipment set up for wax deposition

Wax deposition test procedure

Wax deposition determination is conducted by cold finger technique. The weight of the naked rod is measured. Crude oil is melted down at 65°C for 1 hour before commencing wax deposition test with and without inhibitors. Transfer sample into test tube and close with cork carrying cold finger and thermocouple. After preparation mixture for wax deposition test, it is conducted for 3-hour period with different temperatures and concentrations to investigate the temperature gradient

effect. Wax deposits mass would be measured by the precision 4 digits weighing machine. The experiment is repeated for 3 times and gets the average result.

3.2 Methodology

This study has divided into 3 parts which are pour point, wax appearance temperature and wax deposition of crude oil with and without chemical.

The methodology of this research is presented below:

- (1) Review theory and literature
- (2) Get the samples, design the equipment and order the chemicals
- (3) Set up the equipment and run each test of the experiment
- (4) Investigate the effect of deposition time, temperature and chemical concentration on wax deposition, pour point and wax appearance temperature of crude oil
- (5) Analyse, discuss and conclude the results that is obtained from the experiment

Table 3-3: Experimental operating conditions for pour point test

Parameter	Value
Type of chemical	MA, N-heptane and Mixture
Concentration for MA (ppm)	3000, 4000, 5000
Concentration for N-heptane (wt.%)	5, 10, 15, 20
Concentration for Mixture	10% of n-heptane and 4000 ppm of MA 10% of n-heptane and 5000 ppm of MA 10% of n-heptane and 7500 ppm of MA

Table 3-4: Experimental operating conditions for wax appearance temperature test

Parameter	Value
Type of chemical	MA, N-heptane and Mixture
Concentration for MA (ppm)	3000, 4000, 5000
Concentration for N-heptane (wt.%)	5, 10, 15, 20
Concentration for Mixture	10% of n-heptane and 4000 ppm of MA 10% of n-heptane and 5000 ppm of MA 10% of n-heptane and 7500 ppm of MA
Temperature (°C)	40 to 80
Shear rate (s ⁻¹)	6, 12, 24

Table 3-5: Experimental operating conditions for wax deposition test

Parameter	Value
Type of chemical	MA, N-heptane and Mixture
Concentration for MA (ppm)	3000, 4000, 5000
Concentration for N-heptane (wt.%)	5, 10, 15, 20
Concentration for Mixture	10% of n-heptane and 4000 ppm of MA 10% of n-heptane and 5000 ppm of MA 10% of n-heptane and 7500 ppm of MA
Temperature (°C)	35, 45, 55

Methodology flowchart of the study can be shown in Figure 3.8

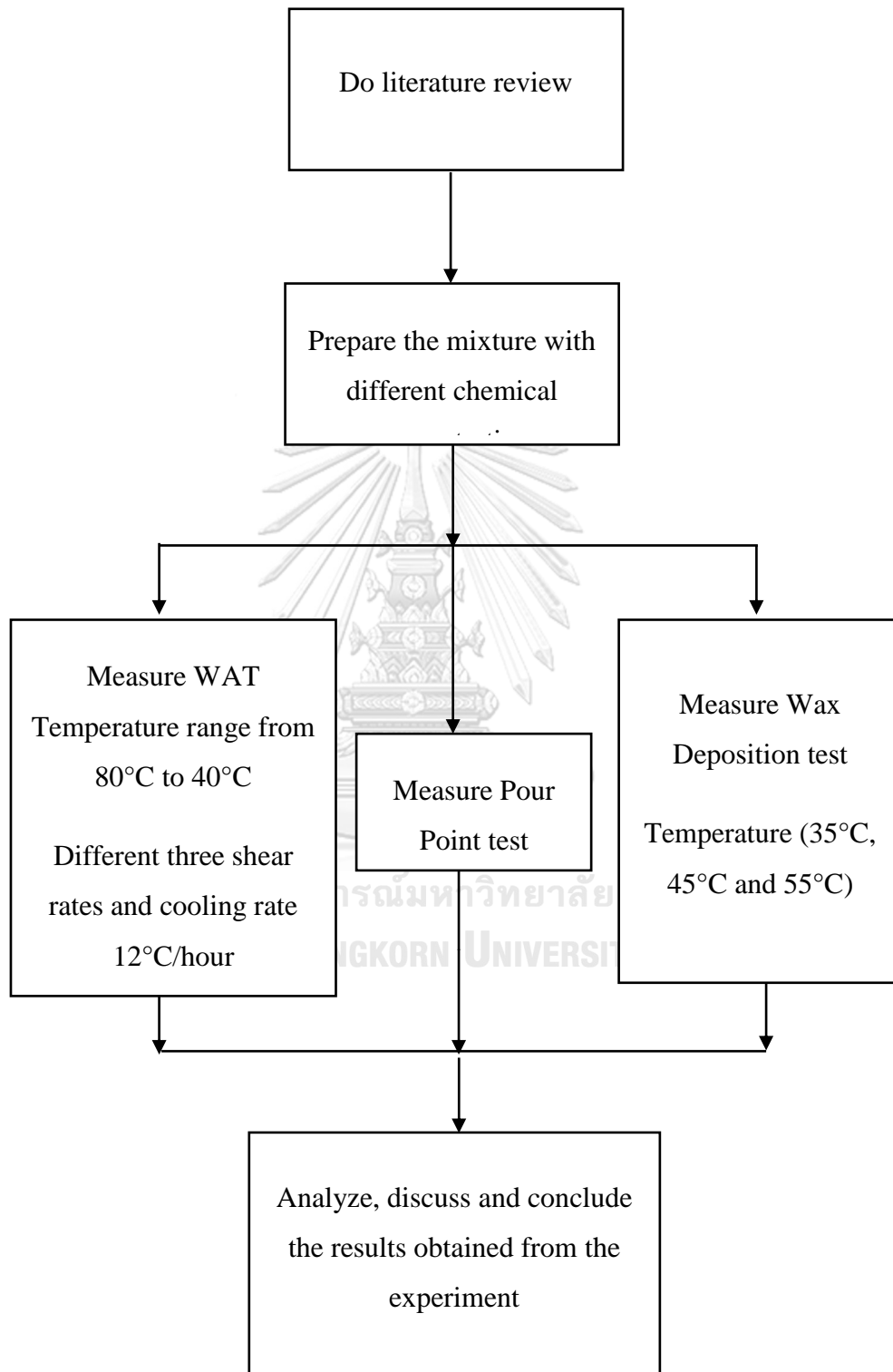


Figure 3-8: Flowchart of methodology

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characteristics of original crude oil from Mae Soon

Physical characteristics of Mae Soon crude oil contain higher wax content and it is solid state condition at room temperature. The pour point temperature of Mae Soon crude oil is 36°C. The wax appearance temperature of Mae Soon crude oil is 43°C for 24 s⁻¹ shear rates, 47°C for 12 s⁻¹ shear rates and 49°C for 6 s⁻¹ shear rates, respectively as shown in Figure 4.1 and Table 4.1. Crude oil is measured the amount of wax deposits by cold finger method and the results show that wax is deposited for 1.05 grams and 0.6786 grams at 45°C and 55°C, respectively as shown in Table 4.2. Furthermore, at 35°C, oil becomes solid.

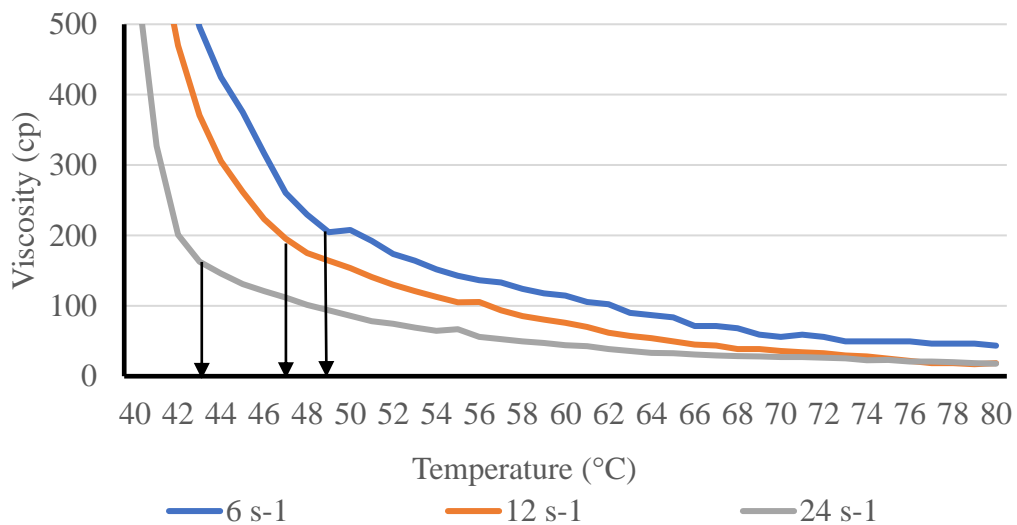


Figure 4-1: Effect of shear rate on wax appearance temperature of original Mae Soon crude oil

Table 4-1: Wax appearance temperature of original Mae Soon crude oil

Mae Soon Crude Oil	24 s ⁻¹ shear rates	12 s ⁻¹ shear rates	6 s ⁻¹ shear rates
Wax Appearance Temperature (°C)	43	47	49

Table 4-2: Wax deposits amount of Mae Soon crude oil

Mae Soon crude oil	Amount of wax deposits (gram)	
Temperature (°C)	35	N/A
	45	1.0500
	55	0.6786

4.2 Effect of MA as a wax inhibitor

4.2.1 Effect of MA on crude oil pour point

The pour point of original Mae Soon crude oil is at 36°C and the physical characteristics of crude oil exist the solid condition at the surface temperature. In this study, MA as a wax inhibitor is used to investigate the ability of pour point reduction of Mae Soon crude oil. The results of crude oil pour point using different concentrations of MA are compared in Figure 4.2 and Table 4.3. It can be clearly seen from the results that there is no significant reduction of pour point Mae Soon crude oil

by using MA inhibitor and it is found that only one degree Celsius reduced at 5000 ppm concentration in the range of this study.

According to Kelland (2014), the poor performance of MA pour point depression can be obtained when the wax is made up of C₂₄₊ alkanes. Furthermore, if wax inhibitor does not contain a similar length side chains, the inhibitor is difficult to influence on very long-chain alkanes wax. Based on Table 3.1, the crude oil wax of Mae soon has very long waxes (C₃₀₊), the inhibitor performance is relatively low.

Pedersen and Rønningsen (2003) provides the reason that wax with high molecular weight molecules cannot be interfered by the wax inhibitor molecules. If the polymer wax inhibitor cannot supply longer alkyl side chain lengths to prevent wax crystal forming. Therefore, MA has less effect on pour point reduction of this case.

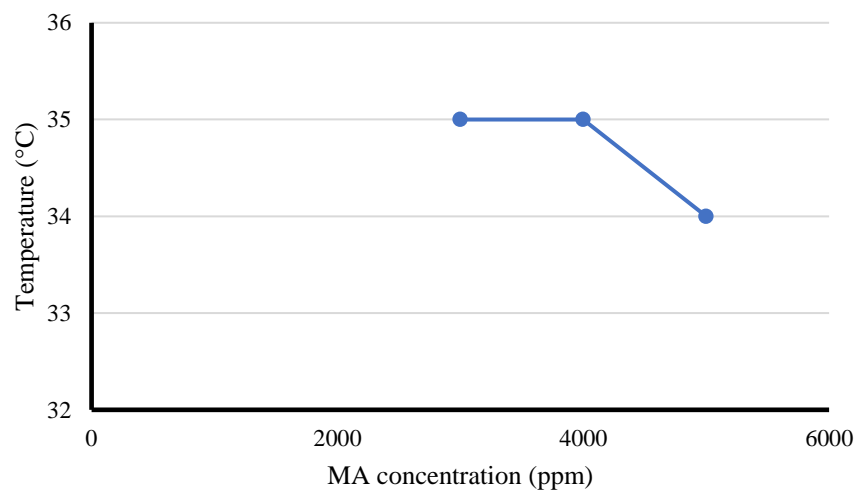


Figure 4-2: Effect of MA on crude oil pour point

Table 4-3: Effect of MA concentration on crude oil pour point

MA (ppm)	Pour Point Temperature (°C)
3000	35
4000	35
5000	34

4.2.2 Effect of MA on crude oil wax appearance temperature

Wax appearance temperature (WAT) of crude oil with MA inhibitor is determined from the changing the slope line by viscometry method from Chapter 2, which the viscosity line start to change the slope sharply from the line to the curve when it starts from the the non-Newtonian fluid to Newtonian region. Wax precipitation rate is faster when higher cooling rate is used.

The results of this measurement are presented in Figure 4.3 to Figure 4.6 and Table 4.4. The results show that 5000 ppm concentration of MA can reduce wax appearance temperature effectively from 43°C of original crude oil WAT to 41°C at 24 s⁻¹ shear rates and this concentration with two shear rates also reduce 42°C and 43°C respectively for each 12 s⁻¹ and 6 s⁻¹ shear rates. In addition, high wax appearance temperature is obtained when concentration is decreases according to the results. Hence, the concentration of MA can affect WAT of crude oil as shown in Figure 4.6. On the other hand, the effect shear rate should be considered as one of the factors in the determination of this test because higher shear rate reduces the viscosity and provides a better result. Jennings and Weispfennig (2005) explain the reason why increasing shear rate can provide not only increasing shear stress at wax accumulation surface but also spreading out the heat transfer.

In this study, MA serves as a wax crystal modifier. Wax crystal modifier that has similar molecular structure to paraffin wax substitutes wax crystal position in the wax crystal networking group and then it obstructs the new coming wax molecules

that are coming for agglomeration (Theyab & Diaz, 2016). A reasonable explanation for the polymer wax inhibitor effect is that these inhibitor molecules occupy position on the crystal network and then self-assemble as a group which can hinder the growth of wax crystallization (Bing Wei, 2014).

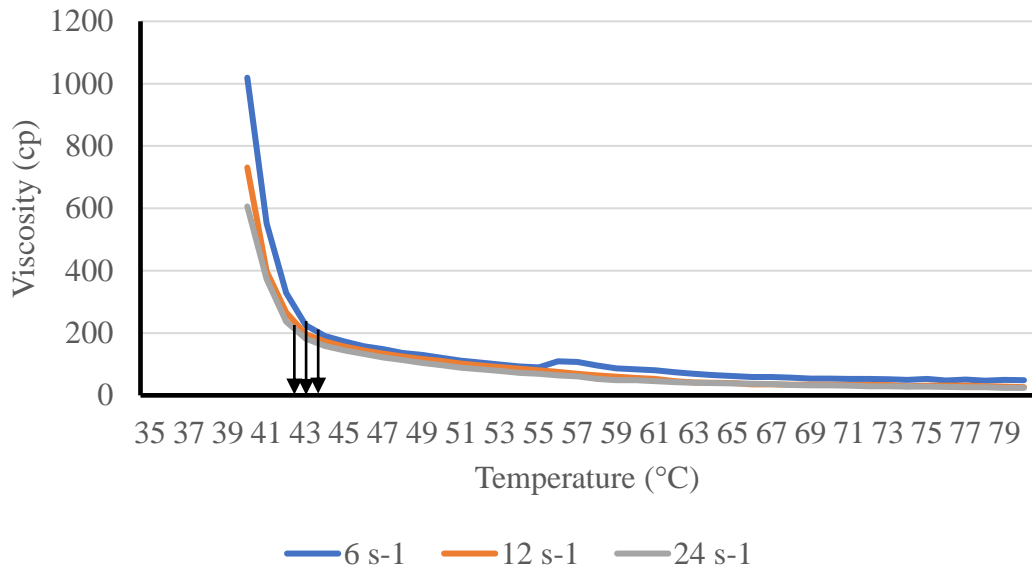


Figure 4-3: Effect of shear rate on wax appearance temperature of crude oil at MA 3000 ppm

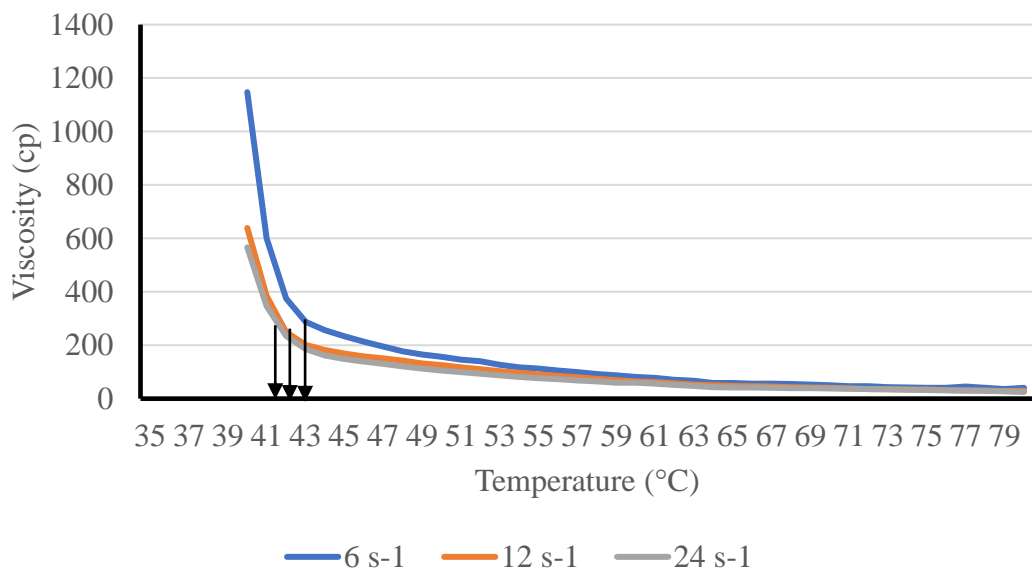


Figure 4-4: Effect of shear rate on wax appearance temperature of crude oil at MA 4000 ppm

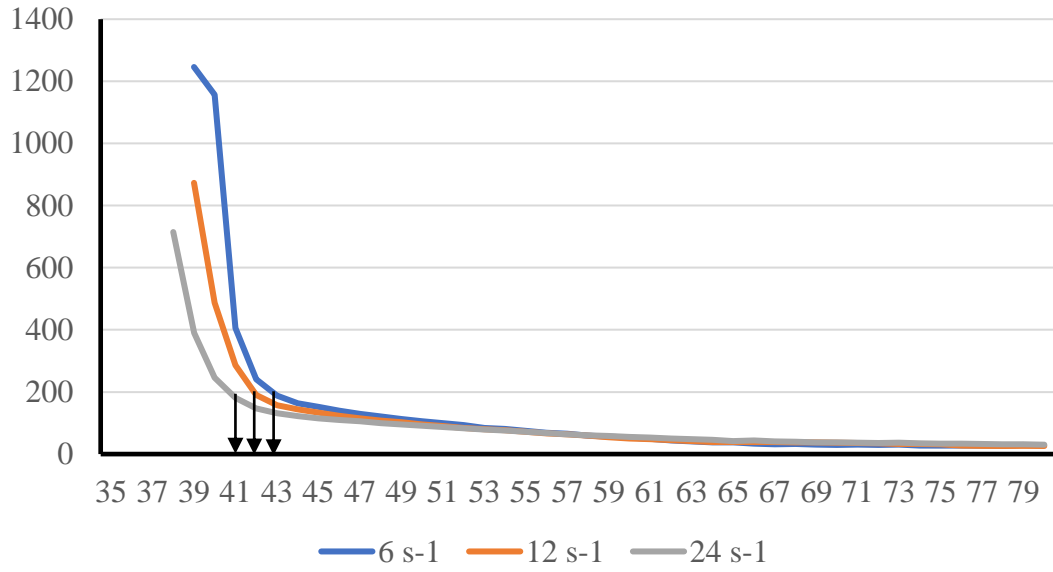


Figure 4-5: Effect of shear rate on wax appearance temperature of crude oil at MA 5000 ppm

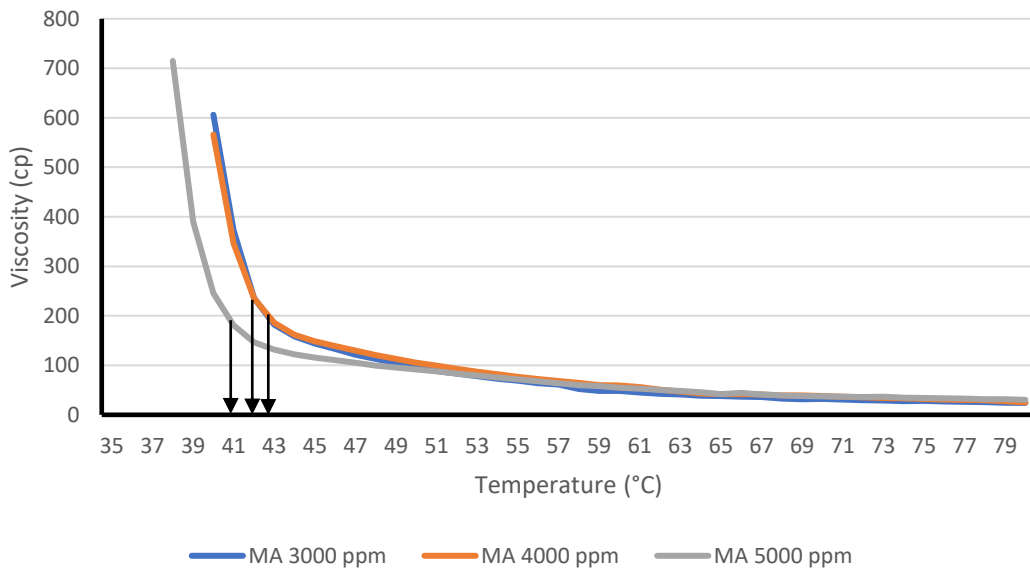


Figure 4-6: Comparison the effect of MA concentrations on wax appearance temperature of Mae Soon crude oil at 24 s⁻¹ shear rates

Table 4-4: Effect of shear rate on wax appearance temperature of crude oil with MA

	Wax Appearance Temperature (°C)		
	24 s ⁻¹ shear rates	12 s ⁻¹ shear rates	6 s ⁻¹ shear rates
Crude Oil	43	47	49
MA 3000 ppm	43	43	44
MA 4000 ppm	42	42	43
MA 5000 ppm	41	42	43

4.2.3 Effect of MA on crude oil wax deposition

The amount of wax deposits from original Mae soon crude oil are 0.6786 g at 55°C and 1.05 g at 45°C and the physical characteristics of crude oil depends on waxy components (Mansoori, 1996). Furthermore, there are many factors to consider on wax deposition. According to the results from Figure 4.7 and Table 4.5, the amount of wax deposits is slightly lowered by using the different concentration of MA wax inhibitor ranging from 3000 ppm to 5000 ppm at both 55°C and 45°C. It can be inferred that for 3000 and 4000 ppm concentrations of MA show the less significant reduction of wax deposits. Nevertheless, at 5000 ppm concentration of MA, the decline of wax deposit is more decreases. In addition, the effect of concentration of wax inhibitor can reduce the amount of wax deposition for 40.09%, 42.29% and 56.83% for MA at 3000, 4000 and 5000 ppm, respectively compared to original oil.

In addition, for temperature, the results show that the more wax are precipitated when the temperature is decreased from 55°C to 45°C as shown in Table 4.5. As a result, the amount of wax deposits is obtained more at lower temperature. Furthermore, decreasing temperature from 55°C to 45°C can increase the amount of wax deposition for 124.67%, 131.46% and 159.06% for MA at 3000, 4000 and 5000

ppm, respectively. Consequently, the bulk crude oil temperature plays an important role in wax deposition to maintain fluid stage.

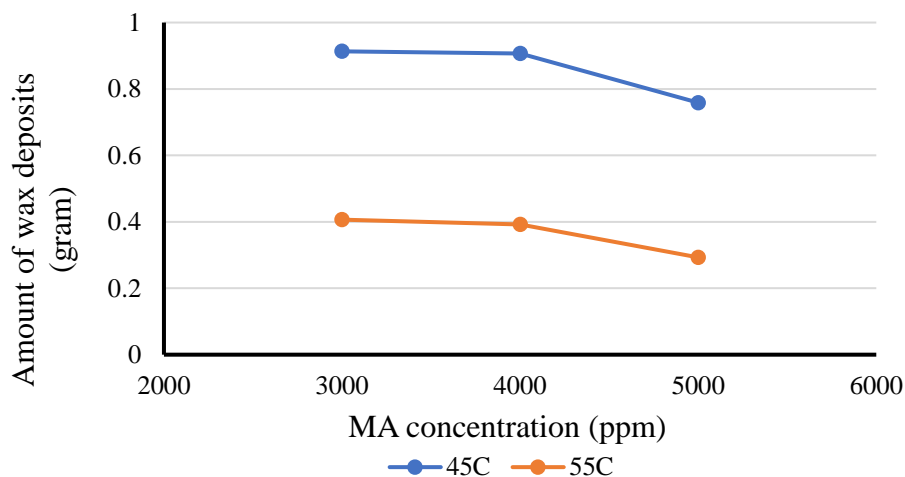


Figure 4-7: Effect of MA concentration on the amount of wax deposits

Table 4-5: Wax deposits from the crude oil with MA

Chemical MA		Amount of wax deposits (gram)			
Concentration (ppm)		3000	4000	5000	Crude oil
Temperature (°C)	35	N/A	N/A	N/A	N/A
	45	0.9133	0.9064	0.7588	1.0500
	55	0.4065	0.3916	0.2929	0.6786

4.3 Effect of N-heptane

4.3.1 Effect of n-heptane on crude oil pour point

Numura (2005) tested the pour point reduction of Fang crude oil with 3.8% to 50% concentration ratio of n-heptane compared to n-pentane and n-hexane solvents and n-heptane provided the better results for pour point reduction temperature of Fang oilfield. In this study, n-heptane solvent is employed as a pour point depressant at different concentrations for 5%-20% to investigate the pour point reduction. The results show that there is a significant pour point reduction in increasing n-heptane

concentration as presented in Figure 4.8 and Table 4.6. The concentration of n-heptane at 20% offers the lowest pour point temperature at 22°C. Consequently, the higher n-heptane concentration provides the better pour point reduction for Mae soon crude oil. It can be concluded that higher concentration can provide lower pour point temperature of crude oil from the results.

Table 4-6: Effect of n-heptane concentration on crude oil pour point

N-heptane Concentration (%)	Pour Point Temperature (°C)
5	34
10	30
15	26
20	22

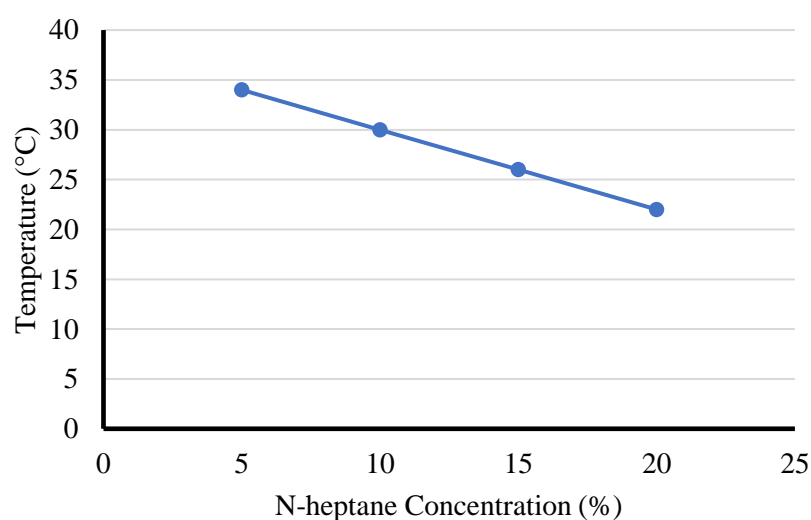


Figure 4-8: Effect of n-heptane on crude oil pour point

4.3.2 Effect of n-heptane on crude oil wax appearance temperature

The results of the effect of n-heptane on WAT are presented in Figure 4.9 to Figure 4.13 and Table 4.7. From the result, it is clearly seen that the highest concentration at 20% of n-heptane for this study acquires WAT at 38°C and followed by 39°C, 41°C and 42°C for 15%, 10% and 5% of n-heptane concentration at 24 s⁻¹ shear rates, respectively. The different concentrations of n-heptane are compared at 24 s⁻¹ shear rates to study the effect of concentration of n-heptane on crude oil wax appearance temperature as shown in Figure 4.13. It is observed that increasing concentration of n-heptane offers the reduction of WAT more than the lower concentration comparing at the same shear rate as shown in Figure 4.13.

According to the results, the higher shear rate provides low WAT in different concentration. Therefore, it becomes one of the aspects of determination of WAT. The relation between shear rate and WAT is that the wax aggregation becomes larger as the temperature decreases and these sizes are reduced by increasing shear rate. Therefore, shear rate assists to reduce the size of agglomerate into dispersed particles (Adeyanju & Oyekunle, 2012).

N-heptane solvent can provide the lowest viscosity compared to other solvents (Dehaghani & Badizad, 2016). Therefore, it can be concluded that n-heptane shows a better performance in viscosity and yield stress reduction of waxy crude oil because the wax can be soluble in the hydrocarbon solvent.

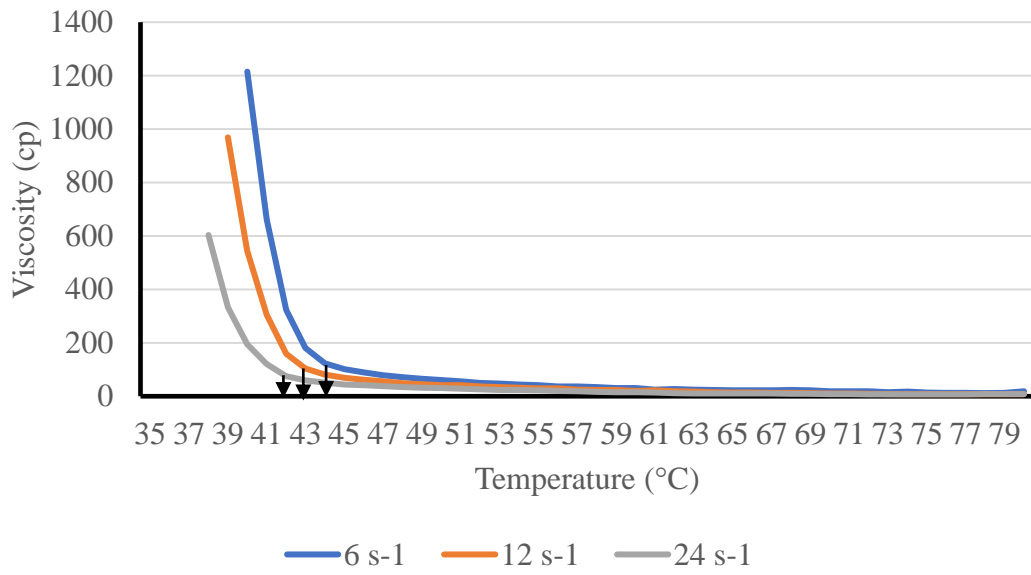


Figure 4-9: Effect of shear rate on wax appearance temperature of crude oil at 5% N-heptane

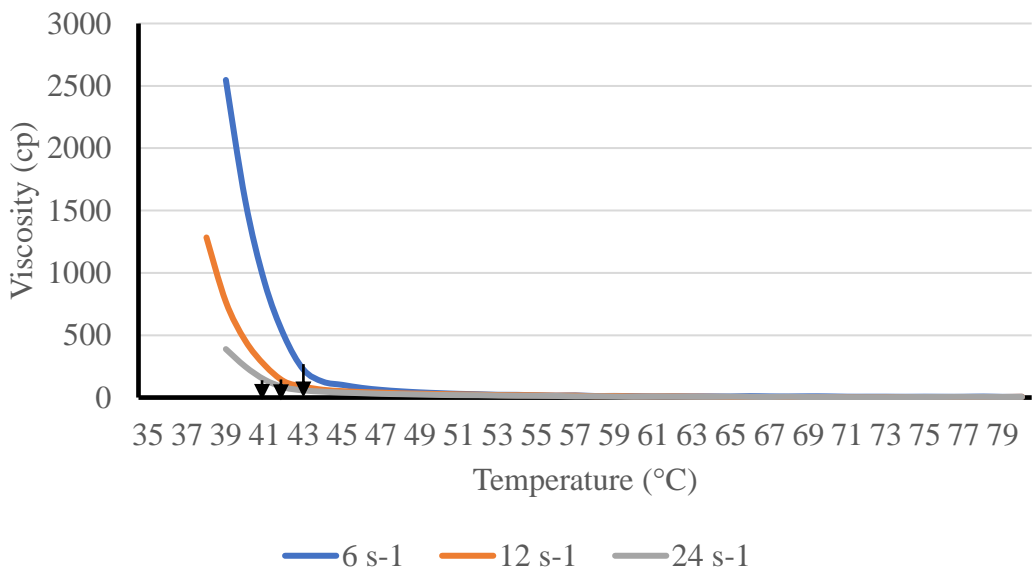


Figure 4-10: Effect of shear rate on wax appearance temperature of crude oil at 10% N-heptane

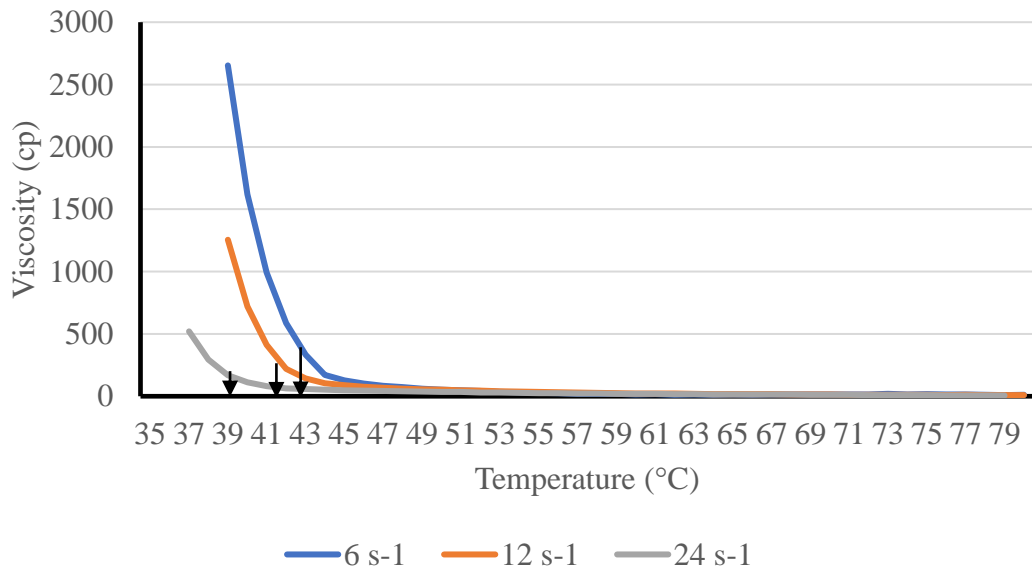


Figure 4-11: Effect of shear rate on wax appearance temperature of crude oil at 15% N-heptane

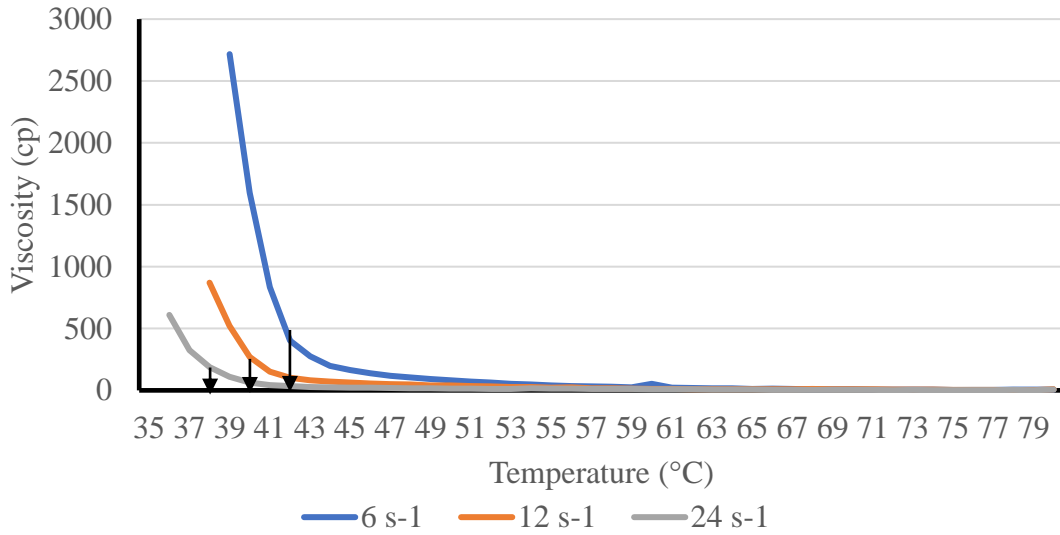


Figure 4-12: Effect of shear rate on wax appearance temperature of crude oil at 20% N-heptane

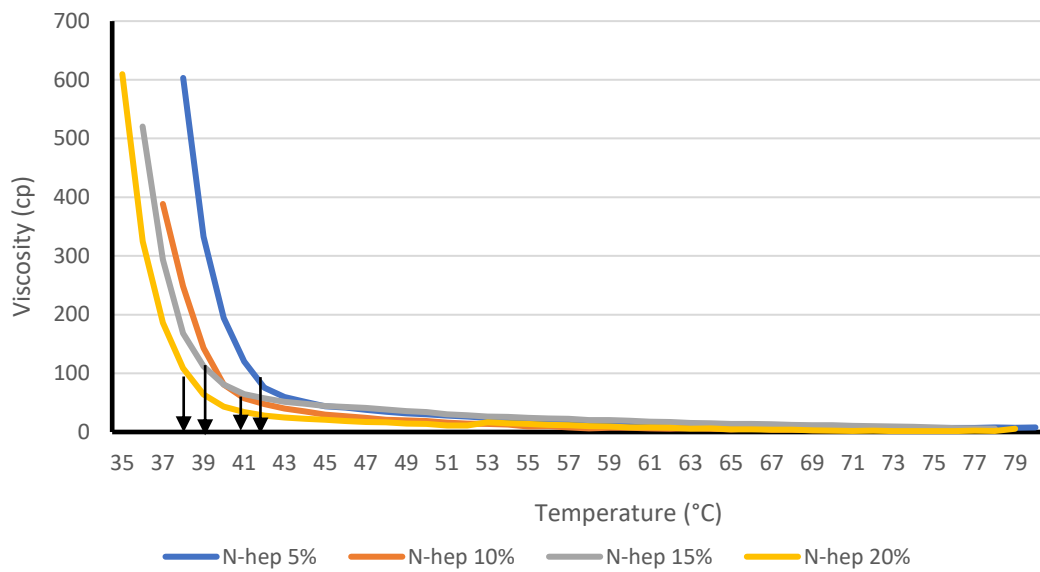


Figure 4-13: Effect of n-heptane concentrations on wax appearance temperature of Mae Soon crude oil at 24 s^{-1} shear rates

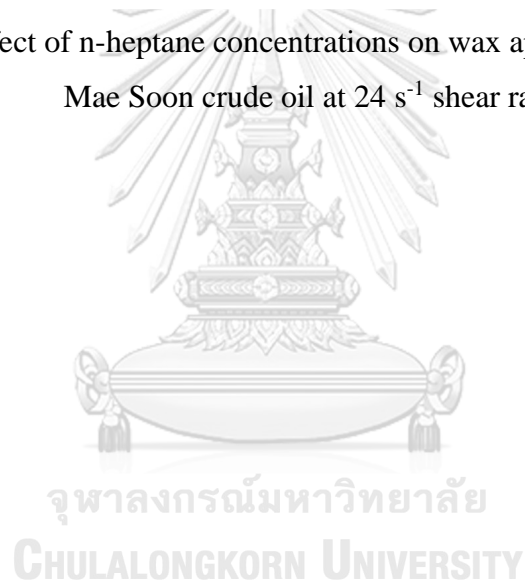


Table 4-7: Effect of shear rate on wax appearance temperature of crude oil with
N-heptane

	Wax Appearance Temperature (°C)		
	24 s ⁻¹ shear rates	12 s ⁻¹ shear rates	6 s ⁻¹ shear rates
Crude oil	43	47	49
N-hep 5%	42	43	44
N-hep 10%	41	42	43
N-hep 15%	39	42	43
N-hep 20%	38	40	42

4.3.3 Effect of n-heptane on crude oil wax deposition

The results of the effect of n-heptane on wax deposition are shown in Figure 4.14 to Figure 4.15 and Table 4.8. It is obvious that the amount of wax deposits is decreased as n-heptane concentration increases at different temperatures because as n-heptane is one of the light hydrocarbon solvents, it can dilute the paraffin wax components in the crude oil. Therefore, an increase in n-heptane concentration can obtain the better solubility for wax components. It can be shown that the effect of concentration of wax inhibitor can reduce the amount of wax deposition for 54.93%, 62.93%, 65.10% and 75.44% for n-heptane at 5%, 10%, 15% and 20% respectively compared to original oil.

On the one hand, the lower temperature at 35°C provides twice amount of wax deposits compared to the higher temperature and it is observed that the high concentration of n-heptane is needed when the operation is lower temperature. Only 20% and 15% of n-heptane concentration obtained the effective conditions when the temperature is decrease to 35°C. Furthermore, decreasing temperature from 55°C to

45°C can increase the amount of wax deposition for 25.14%, 34.99%, 27.61% and 58.18% for at 5%, 10%, 15% and 20%, respectively. Therefore, the effect of temperature of crude oil plays as one of the important factors in wax deposition.

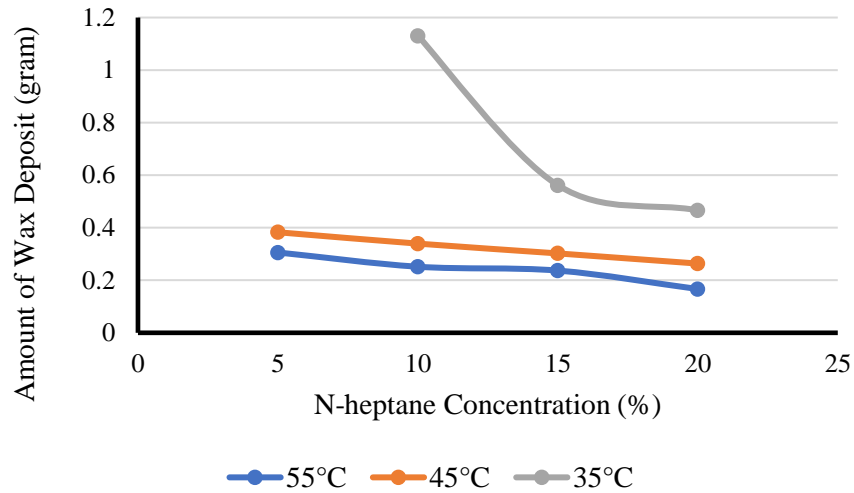


Figure 4-14: Effect of n-heptane concentration on amount of wax deposit

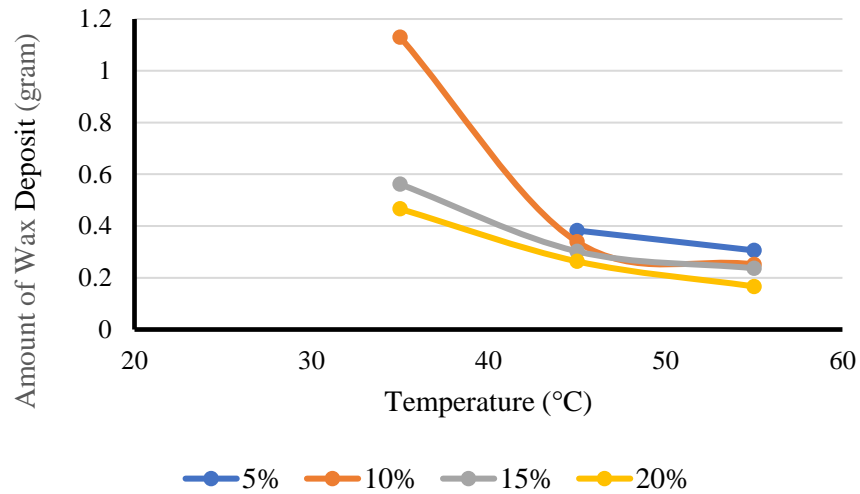


Figure 4-15: Effect of temperature on amount of wax deposit of crude oil with n-heptane

Table 4-8: Wax deposits from the crude oil with n-heptane

Chemical N-heptane		Amount of wax deposits (gram)				
Concentration (%)		5	10	15	20	Crude oil
Temperature (°C)	35	N/A	1.1306	0.5617	0.4663	N/A
	45	0.3827	0.3395	0.3022	0.2635	1.0500
	55	0.3058	0.2515	0.2368	0.1666	0.6786

4.4 Effect of mixture of MA and N-heptane

4.4.1 Effect of mixture on crude oil pour point

The designation of mixture is considered from the concentrations that provided better results from MA and n-heptane. First of all, as 4000, 5000 ppm of MA are chosen to use in the mixture plan because these concentrations provide the effective reduction of wax deposits between the range of MA wax inhibitor in this study and 7500 ppm of MA is added to observe the effect of increasing MA concentration in the mixture plan. On the one hand, 10% of n-heptane concentration that has not much different reduction of wax deposits compared to 15% is chosen to investigate the effect of combination.

The result of the effect of mixture on pour point is presented in Table 4.9. The results show that pour point reduction temperature is the same at 30°C even though in the different concentration of MA with 10% of n-heptane ratio as shown in Table 4.3. It can be explained that n-heptane can reduce the pour point of crude oil in the same way as non-polar part of wax inhibitor in the combination of two wax inhibitors, but MA inhibitor cannot relatively reduce the pour point according to former results. Consequently, the results can be concluded that MA has less effect on pour point reduction even it is mixed with n-heptane.

Table 4-9: Effect of mixture concentration on crude oil pour point

Mixture Concentration	Pour Point Temperature (°C)
N-hep 10% and MA 4000	30
N-hep 10% and MA 5000	30
N-hep 10% and MA 7500	30

4.4.2 Effect of mixture on crude oil wax appearance temperature

The results of the effect of mixture on WAT are presented in Figure 4.16 to Figure 4.19 and Table 4.10. The results show that a reduction of wax appearance temperature with this mixture and the mixture of 7500 ppm MA with 10% n-heptane ratio acquires wax appearance temperature at 37°C at 24 s⁻¹ shear rates and followed by 39°C, 41°C for 12 s⁻¹ and 6 s⁻¹ shear rates, respectively. For the mixture of 4000 ppm MA with 10% n-heptane, WAT is obtained a little higher compared to the former mixture. It can be explained that the higher concentration of mixture offers the lower wax appearance temperature according to the results in Figure 4.19. Moreover, it is indicated that the combination of chemical effect is also performed in this study. On the one hand, the shear rate can reduce the viscosity of fluid and it can provide better results when it combines with the mixture.

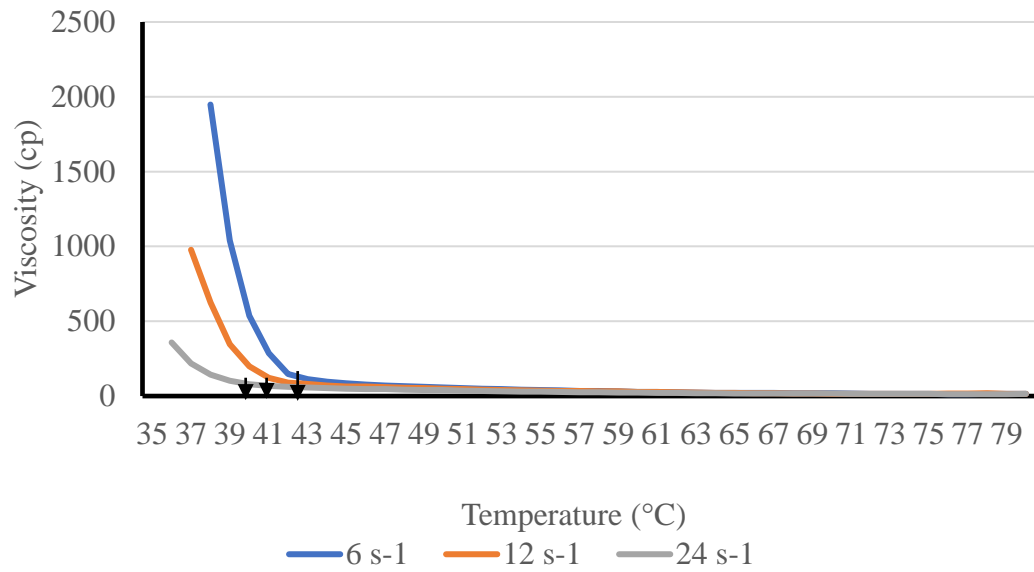


Figure 4-16: Effect of shear rate on wax appearance temperature of crude oil at 10% N-heptane and 4000 ppm MA

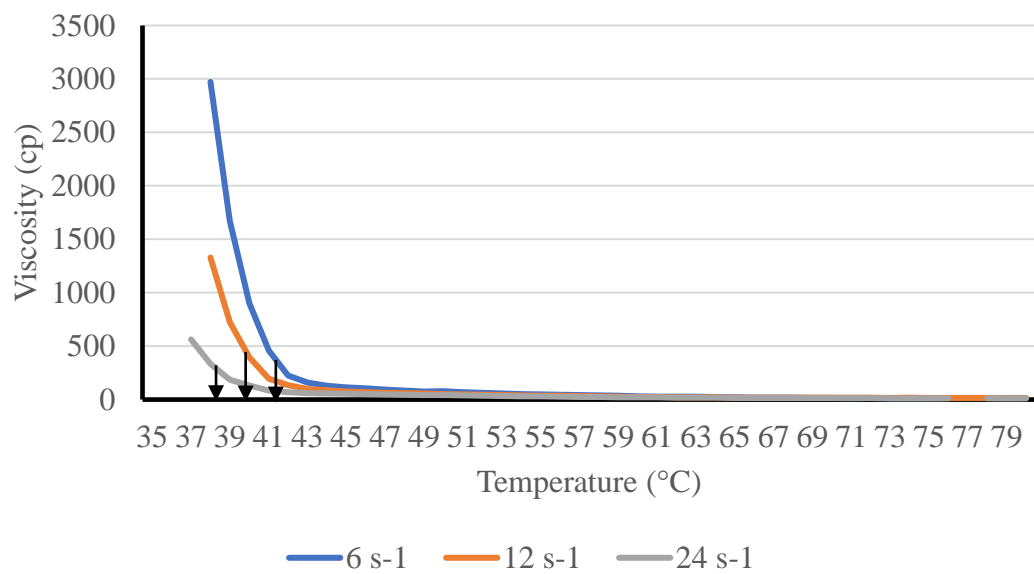


Figure 4-17: Effect of shear rate on wax appearance temperature of crude oil at 10% N-heptane and 5000 ppm MA

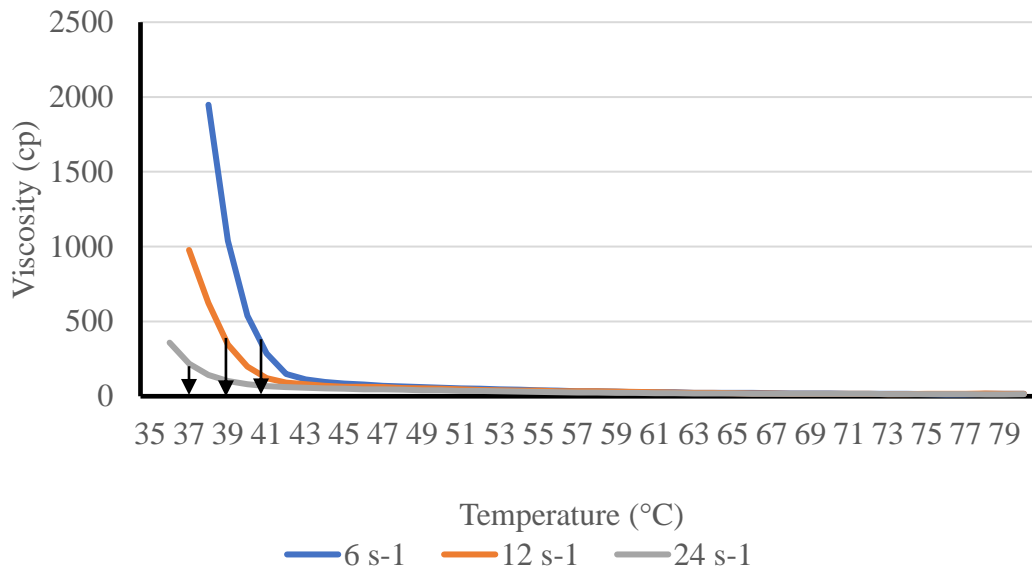


Figure 4-18: Effect of shear rate on wax appearance temperature of crude oil at 10% N-heptane and 7500 ppm MA

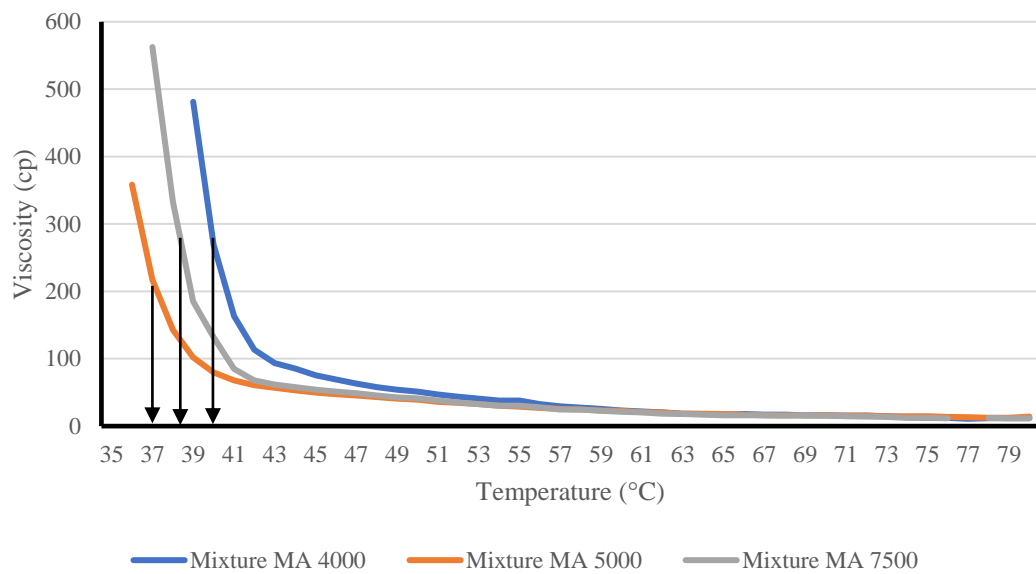


Figure 4-19: Effect of the mixture concentration on wax appearance temperature of crude oil at 24 s⁻¹ shear rates

Table 4-10: Effect of shear rate on wax appearance temperature of crude oil with mixture

	Wax Appearance Temperature (°C)		
	24 s-1	12 s-1	6 s-1
Crude Oil	43	47	49
Mixture MA 4000	40	41	43
Mixture MA 5000	38	40	41
Mixture MA 7500	37	39	41

4.4.3 Effect of mixture on crude oil wax deposition

The results of the effect of the mixture on crude oil wax deposition are presented in Figure 4.20 and Table 4.11. According to the results, the mixture of 10% n-heptane and 7500 ppm MA reduces more amount of wax deposition compared with other mixtures in both 45°C and 55°C temperature. It can be shown that the effect of concentration of mixture can reduce the amount of wax deposition for 65.72%, 76% and 82.74% for mixture at 4000, 5000 and 7500 ppm with n-heptane 10%, respectively compared to original oil.

Furthermore, the temperature has the effect on wax deposition prevention because the wax deposits become less as the temperature decreases. Finally, it can be concluded that the mixture combination shows the better performance for wax deposition compared to the results single chemicals in this study. Decreasing temperature from 55°C to 45°C can increase the amount of wax deposition for 35.25%, 52.70% and 78.30% for at 4000, 5000 and 7500 ppm with n-heptane 10%, respectively. Therefore, the effect of temperature of crude oil plays as one of the important factors in wax deposition.

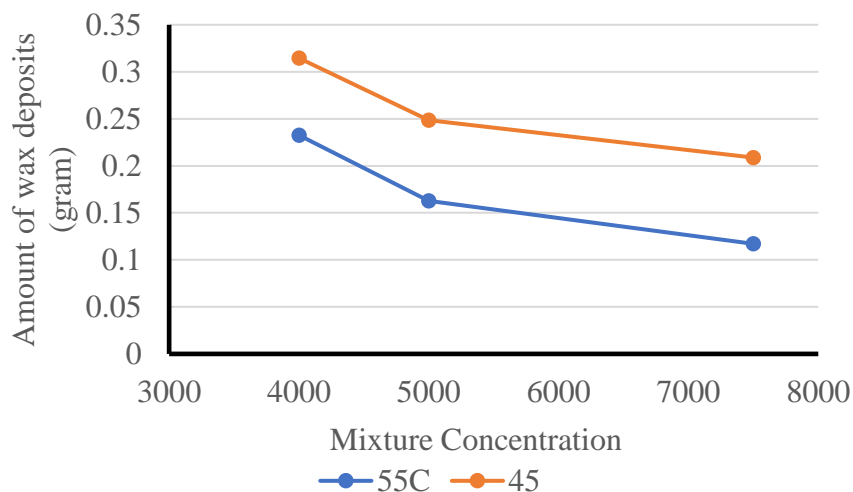


Figure 4-20: Effect of mixture concentration on amount of wax deposit

Table 4-11: Wax deposits from the crude oil with mixture

Chemical		Amount of wax deposits (gram)			Crude oil
Different MA Concentration (ppm) with n-heptane 10%		4000	5000	7500	
Temperature (°C)	35	N/A	N/A	N/A	N/A
	45	0.3146	0.2486	0.2088	0.6786
	55	0.2326	0.1628	0.1171	1.0500

In conclusion, based on the results from this study, 10% n-heptane and 5000 ppm MA is the optimum for reducing the wax deposits among all conditions. Because MA provides lower WAT and less amount of wax deposits and n-heptane offers reduction in pour point, wax appearance temperature and wax deposition in this study. Moreover, these two concentrations consume less, and the operating cost may be lower based on economic point of view.

In addition, the effect of chemical combination should be investigated to find the new results. In this study the mixture of n-heptane and MA offers better

performance for the reduction of wax deposition than individual chemical. Therefore, the range of chemical mixture can be expanded to find the extensive results and it can obtain suitable operating condition.



CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

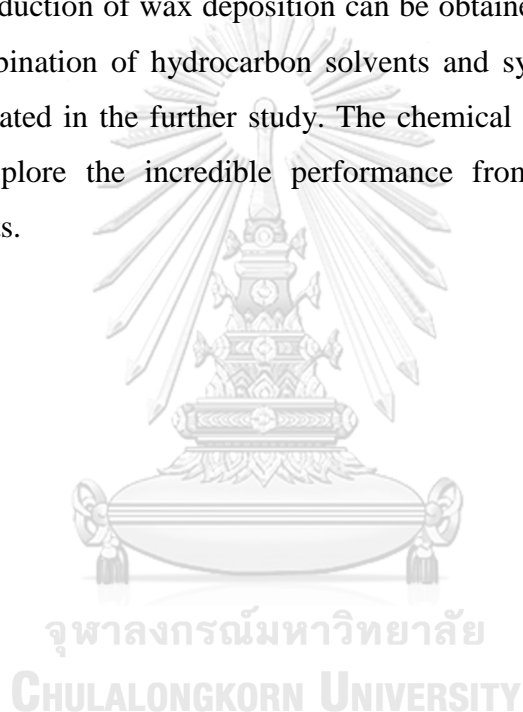
The following conclusions can be expressed as shown below.

1. Temperature is considered as one of the most important factors in the studying of wax deposition of Mae Soon crude oil because from the results the temperature can reduce significantly the amount of wax deposition for up to 159.06% of MA 5000 ppm, 58.16% of 20% n-heptane and 78.30% of MA 7500 ppm with 10% n-heptane from the wax deposition test. Also, it can reduce the viscosity and gelling of waxy crude oil.
2. MA concentration used in this study are 3000, 4000 and 5000 ppm. The results show that MA at lower concentration has less effect on wax deposition reduction, but these concentrations still show the viscosity reduction for wax appearance temperature. On the other hand, the better results for wax deposition and wax appearance temperature are obtained with 5000 ppm based on this study of Mae Soon crude oil at Fang oilfield.
3. The concentration of n-heptane is used at 5%, 10%, 15% and 20%. The results show that an increase in concentration of n-heptane provides the higher reduction of pour point, wax appearance temperature and wax deposition. Increasing the amount of wax inhibitor has the better results for wax deposition. However, any further increase of inhibitor concentration from 10% to 15% has only small additional effect. Furthermore, the amount of inhibitor used at 20% is very high and the cost of chemical consumption is increased significantly. Therefore, based on this study, the recommended concentration for n-heptane is 10%.

5.2 Recommendation

Future studies on the current topic are recommended in order to investigate two or more chemicals that can improve pour point reduction and wax deposition reduction of Mae Soon crude oil. Especially, light hydrocarbon solvents which are economical for usage would be recommended for future study in removing wax deposition of Mae Soon crude oil.

The various solvents should be investigated to determine whether the better performance on reduction of wax deposition can be obtained at low concentration. In addition, the combination of hydrocarbon solvents and synthesis polymer chemical should be investigated in the further study. The chemical comparison study is being encouraged to explore the incredible performance from two or more chemical combination effects.



REFERENCES

- Adeyanju, O., & Oyekunle, L. (2012). An experimental study of rheological properties of nigerian waxy crude oil. *Petroleum Science and Technology*, 30(11), 1102-1111.
- Aiyejina, A., Chakrabarti, D. P., Pilgrim, A., & Sastry, M. (2011). Wax formation in oil pipelines: A critical review. *International Journal of Multiphase Flow*, 37(7), 671-694.
- Allen, T., & Roberts, A. (1989). Production Operations: Well Completions, Workover, and Stimulation, Oil & Gas Consultants Intl. In: Inc.
- Anchorage, U. o. A., Energy, U. S. D. o., Laboratory, N. E. T., Scientific, U. S. D. o. E. O. o., & Information, T. (2008). *Evaluation of Wax Deposition and Its Control During Production of Alaska North Slope Oils*: United States. Department of Energy.
- Becker, J. (1997). *Crude oil waxes, emulsions, and asphaltenes*: Pennwell Books.
- Burger, E., Perkins, T., & Striegler, J. (1981). Studies of wax deposition in the trans Alaska pipeline. *Journal of Petroleum Technology*, 33(06), 1,075-071,086.
- Chi, Y., Daraboina, N., & Sarica, C. (2017). Effect of the Flow Field on the Wax Deposition and Performance of Wax Inhibitors: Cold Finger and Flow Loop Testing. *Energy & Fuels*, 31(5), 4915-4924.
- Dehaghani, A. H. S., & Badizad, M. H. (2016). Experimental study of Iranian heavy crude oil viscosity reduction by diluting with heptane, methanol, toluene, gas condensate and naphtha. *Petroleum*, 2(4), 415-424.
- Fanchi, J. R. (2007). *Petroleum Engineering Handbook: Asphaltenes and Waxes*. Richardson, TX Society of Petroleum Engineers.
- Hoffmann, R., & Amundsen, L. (2013). Influence of wax inhibitor on fluid and deposit properties. *Journal of Petroleum Science and Engineering*, 107, 12-17.
- Huang, Z., Zheng, S., & Fogler, H. S. (2016). *Wax deposition: experimental characterizations, theoretical modeling, and field practices*: CRC Press.
- Jennings, D. W., & Weispfennig, K. (2005). Effects of shear and temperature on wax deposition: Coldfinger investigation with a Gulf of Mexico crude oil. *Energy & Fuels*, 19(4), 1376-1386.

- Kang, P.-S., Lee, D.-G., & Lim, J.-S. (2014). *Status of wax mitigation technologies in offshore oil production*. Paper presented at the The Twenty-fourth International Ocean and Polar Engineering Conference.
- Kasumu, A. S., & Mehrotra, A. K. (2015). Solids Deposition from Wax–Solvent–Water “Waxy” Mixtures Using a Cold Finger Apparatus. *Energy & Fuels*, 29(2), 501-511.
- Kelland, M. A. (2014). *Production chemicals for the oil and gas industry*: CRC press.
- Kok, M. V., Létouffé, J.-M., Claudy, P., Martin, D., Garcin, M., & Volle, J.-L. (1996). Comparison of wax appearance temperatures of crude oils by differential scanning calorimetry, thermomicroscopy and viscometry. *Fuel*, 75(7), 787-790.
- Kruka, V., Cadena, E., & Long, T. (1995). Cloud-point determination for crude oils. *Journal of Petroleum Technology*, 47(08), 681-687.
- Li, N., Mao, G., Shi, X., Tian, S., & Liu, Y. (2018). Advances in the research of polymeric pour point depressant for waxy crude oil. *Journal of Dispersion Science and Technology*, 39(8), 1165-1171.
- Mansoori. (1996). Paraffin / Wax and Waxy Crude Oil. The Role of Temperature on Heavy Organics Deposition from Petroleum Fluids.
- McCain, W. D. (1990). *The properties of petroleum fluids*: PennWell Books.
- Nadkarni, R., & Nadkarni, R. (2007). *Guide to ASTM test methods for the analysis of petroleum products and lubricants*: ASTM International West Conshohocken.
- Neto, A. D., Gomes, E., Neto, E. B., Dantas, T., & Moura, M. (2010). Determination of wax appearance temperature (WAT) in paraffin/solvent systems by photoelectric signal and viscosimetry. *Brazilian Journal of Petroleum and Gas*, 3(4), 149-157.
- Numura, P. (2005). *The Influence of Wax Inhibitors on Thai Crude Oils*: Chulalongkorn University.
- Pedersen, K. S., & Rønningsen, H. P. (2003). Influence of wax inhibitors on wax appearance temperature, pour point, and viscosity of waxy crude oils. *Energy & Fuels*, 17(2), 321-328.
- Ridzuan, N., Adam, F., & Yaacob, Z. (2015). Effects of Shear Rate and Inhibitors on Wax Deposition of Malaysian Crude Oil. *Oriental Journal of Chemistry*, 31(4), 1999-2004.

- Ridzuan, N., Adam, F., & Yaacob, Z. (2016). Evaluation of the inhibitor selection on wax deposition for Malaysian crude oil. *Petroleum Science and Technology*, 34(4), 366-371.
- Roenningsen, H. P., Bjoerndal, B., Baltzer Hansen, A., & Batsberg Pedersen, W. (1991). Wax precipitation from North Sea crude oils: 1. Crystallization and dissolution temperatures, and Newtonian and non-Newtonian flow properties. *Energy & Fuels*, 5(6), 895-908.
- Ruwoldt, J., Kurniawan, M., & Oschmann, H.-J. (2018). Non-linear dependency of wax appearance temperature on cooling rate. *Journal of Petroleum Science and Engineering*, 165, 114-126.
- Saengnil, S. (2015). *Interfacial tension measurement on light oil from Fang oilfield with alkaline solution*. Chulalongkorn University,
- Sanjay, M., Simanta, B., & Kulwant, S. (1995). Paraffin problems in crude oil production and transportation: a review. *SPE Production & facilities*, 10(01), 50-54.
- Siljubergh, M. K. (2012). *Modelling of Paraffin Wax in Oil Pipelines*. Institutt for petroleumsteknologi og anvendt geofysikk,
- Speight, J. G. (2014). *The chemistry and technology of petroleum*: CRC press.
- Theyab, M. (2018). Wax deposition process: mechanisms, affecting factors and mitigation methods. *Open Access J Sci*, 2(2), 112-118.
- Theyab, M., & Diaz, M. (2016). Experimental Study of the Effect of Inhibitors on Wax Deposition. *Journal of Petroleum & Environmental Biotechnology*, 7, 310.
- Thota, S. T., & Onyeonuna, C. C. (2016). Mitigation of Wax in Oil Pipelines. *International Journal of Engineering Research and Reviews*, 4(4), 39-47.
- Totten, G. E., Westbrook, S. R., & Shah, R. J. (2003). Fuels and lubricants handbook: technology, properties, performance, and testing. *ASTM International*.
- Udourioh, G., Ibezim-Ezeani, M., & Ofodile, S. (2014). Comparative investigation of heavy organics precipitation from crude oil using binary mixtures and single n-alkane organic solvents. *Journal of Petroleum Gas Exploration Research*, 4(4), 53-59.
- Venkatesan, R., Nagarajan, N., Paso, K., Yi, Y.-B., Sastry, A., & Fogler, H. (2005). The

- strength of paraffin gels formed under static and flow conditions. *Chemical Engineering Science*, 60(13), 3587-3598.
- Wei, B. (2005). Recent advances on mitigating wax problem using polymeric wax crystal modifier. *Journal of Petroleum Exploration and Production Technology*, Vol 5(No 4), 391-401.
- Wei, B. (2014). Recent advances on mitigating wax problem using polymeric wax crystal modifier. *Journal of Petroleum Exploration and Production Technology*, 5(4), 391-401.
- Yang, F., Zhao, Y., Sjöblom, J., Li, C., & Paso, K. G. (2015). Polymeric wax inhibitors and pour point depressants for waxy crude oils: a critical review. *Journal of Dispersion Science Technology*, 36(2), 213-225.



VITA

NAME	Htet Myat Min
DATE OF BIRTH	23 June 1990
PLACE OF BIRTH	Yangon Region, Myanmar.
INSTITUTIONS ATTENDED	Department of Petroleum, West Yangon Technological University, Yangon city.
HOME ADDRESS	No 23, Myintzu street, Htann Pin Gone, Sawbwar Gyi Kone Ward, Insein Township, Yangon, Myanmar.
AWARD RECEIVED	ASEAN Scholarship



จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY