OIL PIPELINE WAX DEPOSITION INHIBITION USING CHEMICAL METHODS

NORSERI BINTI MOHD MUSTAFFA

A thesis submitted in fulfillment
of the requirements for the award of the Degree of
Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

December 2010

ABSTRACT

Oil pipeline wax deposition is one of the major problems facing in the crude oil transportation flow line from the offshore to onshore through pipe. The problems occur because of the crude oil fluids temperature is decrease during the transportation process and cause the solidifying process occurs. The deposited wax is normally being removed using pigging process. In the present work, chemical method is introduced as an alternative solution for the wax deposition problems in pipelines. This method used CaCl2.2H2O and NaOCl as the inhibitor. The waxes is initially drowned in the NaOCl solutions to soften the waxes and remove the water content inside the sample; waxes. While drawn the sample, the solution with the waxes is stir to get the condition flowing through the pipeline. Then with fixed molarity of the CaCl2.2H2O solution, it is added to the NaOCl solution which has being reacted with the waxes samples. After a range of period; 24 hours, the result obtained is observed and recorded. This experiment is then repeated with different volume of NaOCl, using heat to study about the heat effect and also using acid to remove the waxes. The experimental results showed that with volume of 50ml NaOCl and 0.0071 M of CaCl2.2H2O, the waxes can break into small pieces and no weight loss to the wall like using 30 ml of NaOCl solutions with 70% weight loss from the initial sample weight. While using the heat, the waxes can be removes in 120s and gets 50% efficiencies for only 30 ml volume of NaOCl. This reaction has being tested gradually to ensure its ability to remove wax from the pipeline. The removal process has being removed using the chemical reactions between CaCl2.2H2O and NaOCl. The reaction of the chemicals and waxes was done in lab scale and the progress has being look properly in schedule time to ensure it properly removed. Inhibition of waxes using chemicals method finally founds it solutions which is means by reaction between Sodium Hypochlorite with Calcium Chloride Dihidrates together with bleaching theory, the problems can be eliminated and this kind of technique is more effectual based on its capability to recycle the chemical used back and need few periods to complete each reactions.

ABSTRAK

Pembuangan dan penghapusan pembentukan lilin minyak asli semasa proses pengangkutan cecair itu daripada laut ke darat adalah salah satu daripada masalah yang seirng dihadapi oleh industri. Masalah ini berpunca daripada perubahan suhu minyak asli itu sendiri dimana ia menyebabkan cecair itu mengalami proses pemejalan molekul yang menyebabkan terbentuknya lilin di dinding- dinding paip tersebut. Biasanya, proses penghapusan lilin ini menggunakan teknik ‘scrapper’ ataupun lebih senang untuk difahami gegelung yang sangat kuat yang dimasukkan dari permulaan paip penghantaran minyak di laut hinggalah ke darat yang memakan masa paling minimum sebulan dan maksimumnya setahun. Namun, dengan menggunakan teknik tindak balas bahan kimia, ia hanya memakan masa 2 minit yg menggunakan haba manakala sehari tanpa haba, dimana tahap keberkesanannya ialah 50% dan 80%. Kesimpulannya, lilin minyak asli tersebut boleh dihapuskan menggunakan tindak balas kimia. Dengan menggunakan kalsium klorida dihidrat dan natrium hypoklorida experimen ini berjaya menghilangkan lilin di dalam saluran paip.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURE

LIST OF ABBREVIATIONS

$CaCl_2.2H_2O$	-	Calcium Chloride Dihidrates
CaOH	-	Calcium Hydroxide
C_{18}	-	Alkanes Group
C_{40}	-	Alkanes Group
CH_2	-	Ethyl
Cl_2	-	Chlorine
Cl^-	-	Chlorine Ion
H^+	-	Hydrogen Ion
H_2O	-	Water
HClO	-	Hypochlorite
NaOCl	-	Sodium Hypochlorite
Na^+	-	Sodium Ion

LIST OF SYMBOLS

º	**-**	Degree
ºC	**-**	Degree Celsius
ºF	**-**	Fahrenheit
$	**-**	Money
%	**-**	Percentage
e^-	**-**	Electron
g	**-**	Gram
M	**-**	Molarity
ml	**-**	Milliliter
n	**-**	Mol
s	**-**	Second
V		Volume

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.7 Background Study

Controlling, preventing and inhibiting wax depositions problems nowadays is one of the critical problems in gas and oil industries as the industry explores and invent in increasingly challenging environments, such as deep water and subarctic conditions based on Simon Richard, SPE, who is the Principle Consultant for EPConsult. Facing the world need and demand, conscientious people today fight to give the best service.

A wax deposition has gives the industry problems during the transportations route because of the shrinking flow area when the deposited waxes become thicker and thicker (Zhang *et al.*, 2009). Based on statement by Xiaoli and Peter (2005) waxes are the combination of linear, branched, and cyclic aliphatic hydrocarbons secluded from petroleum. The crude deposit; wax cause by the presenting the temperature gradient among the pipe wall and the flowing crude oil during transportations progress. Focus on subterranean sea water pipeline, the surroundings around the pipelines is arctic than the crude oil behavior. Its makes the wall absorb heat from the crude oil and transfer to the environment to balance the temperature during the transportation but the heat transfer cannot maintain the temperature entire time during the transportation process which is results the crude oil temperature drops and produce gradient temperature between it surrounding; sea water (Venkatesan *et al*. 2004).

To improve the efficiency of the transportation and saving the crude oil quality, waxes preventing and removing is very important in other to prevent blockage and undesired problems. As an example, considerate the content of the wax can assist during the study to decide the appropriate chemical to break the bond of the wax; make the wax structure becomes small pieces and etc. Pigging is the typical industrial procedure which is using a 'scrapper' device to eliminate the deposited wax from the pipe stockade. If the wax deposit too strong, then such mechanical methods of remediation would prove to be difficult, as exemplified by instances when the pig has been immovable in the pipeline during the clear out process. Hence, when the deposit is hard, thermal methods of remediation may be used either to suspend the wax deposit completely, or to soften the deposit for subsequent pigging (Venkatesan *et al.* 2005). The designed method is based on these three mechanism theory;

a) Mechanism 1 (chemical reaction)

At the beginning of the experiment, $CaCl_2.2H_2O$ will be diluted in water. During the diluting process, the heat release will be observes because in excess heat salt will be produced which can cause the corrosions but calcium chloride dihidrates will produced water to dilute the salt produce make it flow through the flow line during the wax removing process.

b) Mechanism 2 (inhibitor and wax interactions)

The NaOCl solutions will be added to the weighted waxes and stir to soft the waxes. During the stirring process, the changes will be observes and after few moments, $CaCl_2.2H_2O$ solutions will added to the solutions. The sample with the chemical solutions is running until reach the maximum weight losses yield. The remaining waxes will be weight again to check the efficiency of the experiment.

c) Mechanism 3 (wax flowing and chemical damage)

When the wax is totally diluted and removed, the NaOCl will produce NaCl in the pipeline because this chemical when reacted will produced salt and can be remove by the by product, water during the reaction. Although sodium hypochlorite solution is alkaline it does not tend to cause corrosive damage except in large quantities or concentrated solutions. Sodium hypochlorite may release small amounts of chlorine and hypochlorous acid when acidified, but usually in concentrations too small to cause any significant damage (Guy's and St Thomas', 1998).

Consequently, the aimed for this research project to obtain a through understanding of the inhibition of the wax deposition using the chemical methods with chosen chemicals. It is important to ensure that the selected chemical will give positive feedback to guarantee this industrial problem can be solves. We also examine on how the chemical used react to break the bond between the wax molecules based on bleaching concept. The results obtain might be helpful to the transportation process.

1.8 Problems Statements

Frequent problems encounter because of wax deposition are

I. The gradient temperature occurs between the fluids and flow line when the environment condition outside pipe wall changes. The decreasing of the temperature makes the pipe wall undergo the heat transfer process between itself and the environment to maintain the temperature.

II. The low quality of the crude oil purity during the distillation process makes the contents in crude oil still have clay, sea waste and etc from the drilling process which help wax producing during the transportation process.

III. Wax appears thicker and thicker makes the flow area smaller with time going by persuade the transportation capacity and operation safety of the pipelines. It is because it can increase the pressure; blocking area and can cause leakage.

1.9 Research Objectives

These are the objectives that should be accomplished at the end of this study which is 'oil pipeline wax deposition inhibition and using chemical methods'. With the knowledge of chemistry and related fields; as an incoming engineer, observing in detailed and extremely on how to solve this industrial problem; wax deposition, by reach the target perfectly

i. To introduce a chemical solution for the wax deposition problems in pipelines.

ii. To choose a safe chemical compound to remove waxes.

iii. To study the effect of heat to remove waxes

1.10 Expected Results

The results obtained from this research should be:

i. Give positive feedback and might be commercialized
ii. The outcomes must reduces the economical budget based on chemical used and process which is improve the company benefits but reduce the cost
iii. The results should improve the hydrocarbon fluids transportation process to prevent any delay time and waste.

1.11 Scope Of The Research

To fulfill the requirement of this research, the spec to study is customized as shown as in **Table 1.1**. This research scope will guide researcher to guide the researcher and experiment from out of the line.

Table 1.1: Research Scope

Items	**Specified**
Wax Deposition	• forming process • contain and consequence to the chemical • molecule structure and components • characteristics
Selected Chemicals Exp: sodium hypochlorite and calcium chloride dihidrates	• effect to the wax , environment and other realistic consideration • reaction to the wax
Continuous Pipeline	• study in three different environment
Hydrocarbons Fluids	• characteristics
Heat	• heat transfer process between the chemical, wax and crude oil • break of the wax bond (cleavage)
Turbulent Flow	• can increase the aggregation of the wax molecule

1.12 Significance of The Study

The significance of the study is reducing financial problems due to the decreasing wax deposition problems. In addition, the methods that have been used in order to control the wax deposition problem could be applied in other industrial places that working on the same activity which oil or gas pipeline. Thus, the methods might be commercialized which can control the wax deposition problems by having personal operation that the data must be used to help maintain the wall from waxes producing over long period of time.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The complex phenomenon of solid wax deposition in wax saturated crude oils subjected to thermal gradients has been treated in a number of papers under very specific assumptions (e.g. thermo dynamical equilibrium between dissolved wax and the wax suspended in the oil as a crystallized phase) (Antonio *et al.* 2006).

Wax from the crude oil is typically consists of variety of light and transitional hydrocarbons (paraffin's, aromatics, naphthenic, etc.) and diversity of other heavy organic (non-hydrocarbon) compounds, even though at very low concentrations including resins, asphaltenes, diamondoids, mercaptans, organo- metallic's, etc. When the temper of a waxy crude oil is drops, first the heavier fractions of its wax content start to solid out. For waxy crude it is expected to determine its cloud point and pour point according to ASTM methods (Lindsey *et al.,* 1997).

In other to eliminate the wax deposition within the pipeline supposed to identify the content of the wax. There is no typical definition for wax content but it is normally acknowledged that n-alkanes from C_{18} to C_{40} represent waxy material. When if form, at the beginning it like a gel but it becomes thick when it isolated the hydrocarbons molecules from the crude oil. At low temperatures, the wax precipitate as a component in organic deposit cause by the environment outside the pipe wall. The different temperature makes the wax forming increase by time and the flow area becomes smaller and smaller.

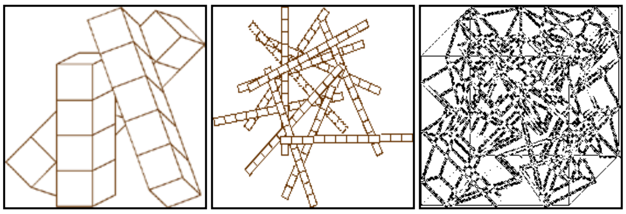

Figure 2.1 Macro crystalline, Microcrystalline, and Crystal Deposit Network of Wax (Mansoori *et al*. 1997)

2.2 Scenery of Wax Deposition

The flowing of the crude oil through the pipeline during the transportation will deposit the wax if the crude oil temperature is lower the cloud temperature and also under the solidifying temperature which is under 35ºC. Cloud temperature is the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a gloomy appearance.

Mostly, the wax component is paraffin but not the pure paraffin. Usually, to recover the wax, the raffinate is mixed with a solvent such as propane and cooled in a series of heat exchangers. Further cooling is provided by the evaporations of propane in the chillers and filter feed thanks. The wax forms crystals, which are continuously removed, filtered, and washed with cold solvent. The solvent is recovered by flashing and steam stripping. The wax is purified by heating with hot solvent, after which it is re-chilled, re-filtered and given a final wash.

Gelled oil-related issues manifest as soon as the external temperature surrounding the pipeline falls below the WAT. A common but erroneous belief is that this situation occurs only in extreme temperature conditions, e.g. Arctic regions. In fact it is common even in warm regions because the WAT may be extremely high, as is the case for waxy crude oils produced in Australia, (Vinay *et al.* 2007) as well as in central Africa.

However, shutdown of the pipeline for maintenance or emergency reasons is not unusual. Static conditions allow time for the temperature to drop in the pipeline. If the shutdown time is too long, the waxy crude oil contained in the pipeline may be eventually severely gelled and restarting the pipeline becomes a significant problem (Frigaard *et al.* 2007). The temperature decrease causes the crystallization of the paraffin compounds and eventually, as the temperature drops below the pour point, the build-up of the gel-like structure in the crude oil bulk.

If the temperature decrease lasts long enough, the waxy crude oil undergoes a thermal shrinkage related to the appearance of gas voids that confers a form of compressibility to the material. Finally, the waxy crude oil restart issue consists of resuming the flow of a compressible gel-like material, usually by injecting some fresh warm oil (expected to be Newtonian and incompressible) at the pipe entry (Chang *et al.* 1999).

Waxy crude oils are well known to have a very complex rheological behaviour. Above the WAT, they behave as a simple Newtonian fluid. As the temperature drops below the WAT, the viscosity starts to increase sharply and to be sensitive to mechanical constraints, in relation to the presence of paraffin crystals and a gel-like structure in the material. Cawkwell and Charles (Cawkwell *et al.* 1989) studied two Canadian arctic crude oils: Cape Allison and Bent Horn.

In the oil and gas industry, the use of pipelines to convey large amounts of crude oil over short or long distances has been extensive. Transportation of conventional (Newtonian, low viscosity, steady physical properties, single-phase, and etc.) crude oils is a relatively easy-to-handle task; however, pipelining crude oils that contain large proportions of high molecular weight compounds such as paraffin can cause many specific difficulties (Uhde *et al* 1971).

2.3 Clean Waxy Crude

Clean waxy crude is defined as a crude oil in which there exist only hydrocarbons and wax as its only heavy organic constituent. As the clean waxy crude flows through a cold pipe or conduit (with a wall temperature below the cloud point of the crude) crystals of wax may be formed on the wall. Wax crystals could then rise in size until the complete inner wall is covered with the possibility of encapsulating oil inside the wax layers. As the wax thickness increases, pressure drop across the pipe needs to be increased to maintain a constant flow rate. As a result, the power requirement for the crude transport will increase. The major blockage problems of clean waxy crude can be professionally inhibited by lagging and heating of the pipe to a temperature above its cloud point (Mansoori *et al*. 1997).

Most of the existing wax deposition problems of the clean waxy crudes are due to the lack of proper insulation and heating systems. As a result application of chemical anti-foulants and frequent use of pigging operation have become necessary.

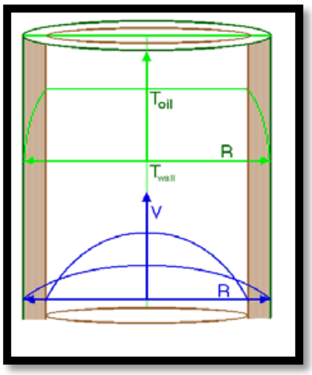

Figure 2.2 Changes in Temperature and Velocity Profiles of a Flowing Crude Oil in a Cooling Pipe Due To Wax Crystal Formation (Mansoori *et al.* 1997)

2.4 Regular Waxy Crudes

Regular waxy crude are not clean and, in addition to wax, they contain other heavy organics such as asphaltenes, resin, etc. These other heavy organics do not generally crystallize upon cooling and, for the most part, they may not have definite solidifying points.

Regular paraffinic or waxy crudes are wide spread in the world and the major complex systems problems related to the production, processing, and transportation of these medium-gravity fluids is not just crystallization of their wax content at low temperatures, but the formation of deposits which do not disappear upon heating and will not be completely removed by pigging.

Depending on their natures, these other heavy organics will have different interactions with wax which could either prevent wax crystal formation or enhance it. To facilitate the production of regular waxy crudes many issues which include the following must be undertaken; to prevent arterial blockage:

a) Detailed fluid properties characterization,

b) Production scheme alternatives,

c) Retrograde condensation and deposition behaviour prediction,

d) Onsets of deposition studies,

e) Equipment and facility options,

f) Design and use of chemical anti-foulants and / or pour-point depressants and blending alternatives.

g) Performance specification and maintenance planning, transportation, storage, and blending studies.

Figure 2.3 shows the part of the deposited waxes inside the pipe which is very thick and makes the flow area smaller than actual size. If this organic deposit did not remove, perhaps it will totally block the area and will cause more unimaginable problems encourage soon.

Figure 2.3 Wax Deposition (Phillips Petroleum Co.)

2.5 Wax Deposition in Crude Oils

The complex observable fact of solid wax deposition in wax saturated crude oils subject to thermal incline has been treated in a number of papers under very specific assumptions (e.g. thermo dynamical equilibrium between dissolved wax and the wax suspended in the oil as a crystallized phase). Most of the complexity is related to the paraffin crystals forming an interlocking gel (Cazaux *et al.* 1998) like structure that changes some of the crude oils rheological features The general framework in which thermo dynamical equilibrium may not exist, the whole system may form a gel-like structure in which the segregated solid wax has no diffusivity, the thermal held may evolve due to a non-negligible difference between the thermal conductivity of the solid wax deposit growing at the cold wall of the container and the conductivity of oil, etc (Fasano *et al.* 2007).

The enormous economic relevance of this phenomenon stimulated several studies, laboratory experiments and field measurements (Azevedo *et al.* 2003). In the framework of a research contract with Enitecnologie, previous research have proposed mathematical models (Correra *et al*. 2004) for the phenomenon and applied them to the interpretation of data form an experimental device called cold finger. Such models were based on the assumption that the segregated crystals can diffuse (though their diffusivity is much smaller than the one of the dissolved wax) and they are at any time in thermo dynamical equilibrium with the solute (Fasano *et al.* 2007).

Other research and study stated that the displacement flow of a weakly compressible waxy crude oil from a pipeline, in the case that the displacing fluid is incompressible and less viscous. They show that fluid compressibility only has a significant effect on the timescale over which all residual fluid is drained from the pipeline, but no noticeable effect on the initial breakthrough of new fluid. They derive analytic estimates for this drainage time, for the cases where either the pressure drop or the displacement rate is fixed (Frigaard *et al.* 2007). In the case of the fixed displacement rate,