CHARACTERIZATION OF NIGERIAN CRUDE OIL WAX

BY

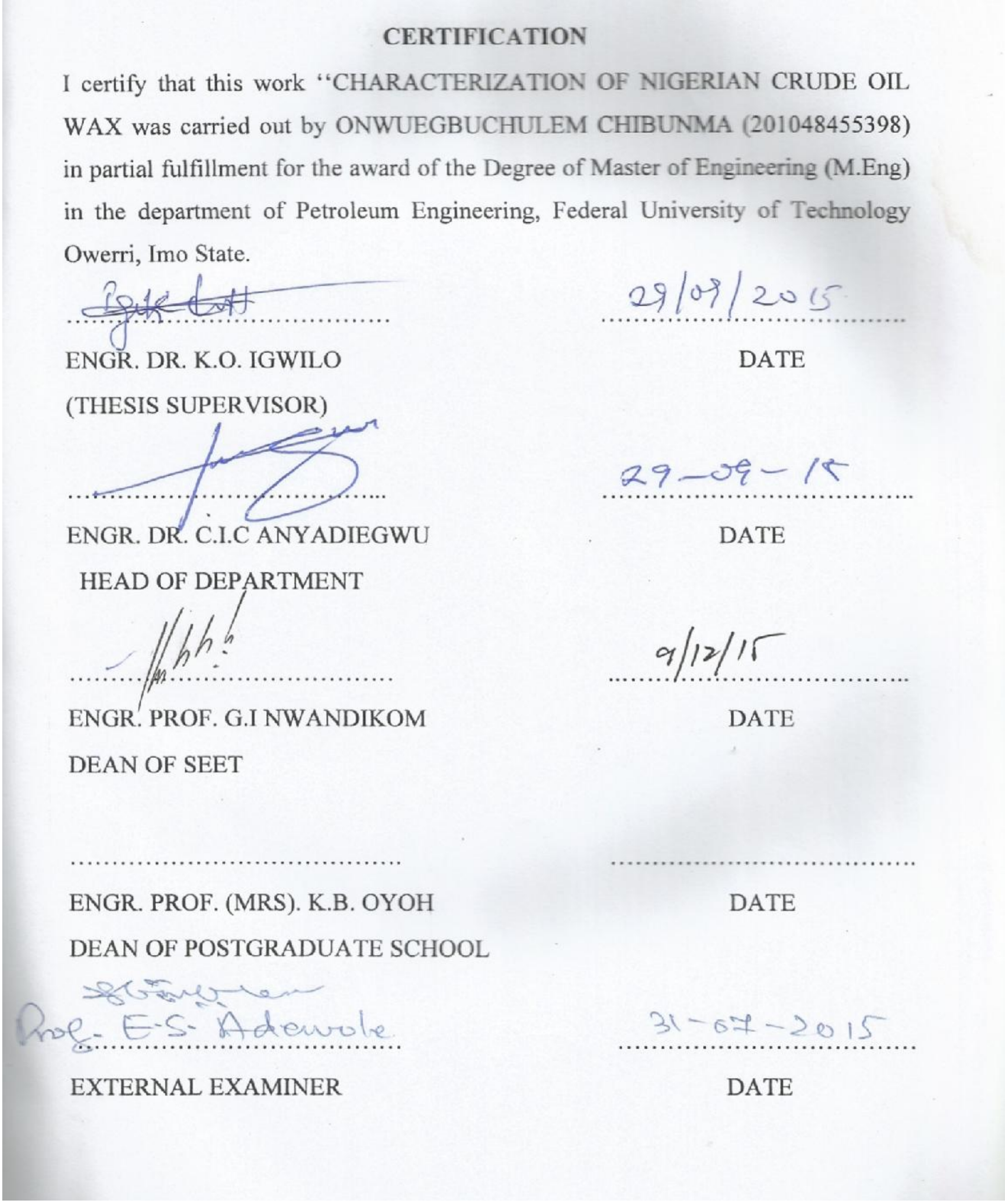
ONWUEGBUCHULEM CHIBUNMA
201048455398

A THESIS SUBMITTED TO THE POST-GRADUATE SCHOOL

FEDERAL UNIVERSITY OF TECHNOLOGY OWERRI

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
AWARD OF MASTER OF ENGINEERING (M.Eng) DEGREE IN
PETROLEUM ENGINEERING

JULY, 2015



CERTIFICATION

I certify that this work "CHARACTERIZATION OF NIGERIAN CRUDE OIL WAX was carried out by ONWUEGBUCHULEM CHIBUNMA (201048455398) in partial fulfillment for the award of the Degree of Master of Engineering (M.Eng) in the department of Petroleum Engineering, Federal University of Technology Owerri, Imo State.

……………………………… 29/09/2015 ………………………………

ENGR. DR. K.O. IGWILO DATE

(THESIS SUPERVISOR)

……………………………… 29-09-15 ………………………………

ENGR. DR. C.I.C ANYADIEGWU DATE

HEAD OF DEPARTMENT

……………………………… 9/12/15 ………………………………

ENGR. PROF. G.I NWANDIKOM DATE

DEAN OF SEET

……………………………… ………………………………

ENGR. PROF. (MRS). K.B. OYOH DATE

DEAN OF POSTGRADUATE SCHOOL

Prof. E.S. Adewole ……………………………… 31-07-2015 ………………………………

EXTERNAL EXAMINER DATE

DEDICATION

TO GOD ALMIGHTY.

ACKNOWLEDGEMENT

I use this opportunity to thank the numerous people who contributed to make this work a success. I thank the entire staff of Petroleum Engineering department, Federal University of Technology, Owerri especially Engr.Dr. C.I.C. Anyadiegwu; my H.O.D, Engr. Dr. K.O. Igwilo; my thesis supervisor, Engr. Prof. B. Obah, Engr.Dr. R.M Aguta , Engr. E .Egele , Engr. M. I. Onyejiekwe, and Engr. C. Nkwocha , your explanations and encouragement were immeasurable.

I thank the entire staff of Petroleum Engineering department, Madonna University,Akpugo campus, Enugu especially Engr. Daniel Egu. You are my family.

I thank the second production crew of Addax Petroleum Nig. Ltd, Izombe Flow Station, Oguta, Imo State for supplying me with field experience and samples for this work. I appreciate you. Thank you Engr Clifford Udogwu and Uche Nwosu.

I thank the staff of Rofenel Laboratories, Port Harcourt for your support and explanations especially Miss Chinyere.

I thank my husband Mr. Chukwuma Amaefule, for being understanding and encouraging throughout this work. You are the very best! I thank my parents Chief (Barr.) & Nneoma B. U Onwu (KSJ). I can never repay you. I thank my big brother Engr. Uche Onwu. Looking at you is enough motivation. I thank my sisters; Dr.(Mrs) Ugo Enwerem and Engr. Amara Onwuegbuchulem. I thank Barr. Kelechi Onwu and Miss Chioma Okoligwe.

I thank my course mates -the 2010 Petroleum M.Eng set; Engr Bob, Engr Okey, Engr Eucharia, Engr Chukwudi, Engr Ugo and Engr Ahamba. Congratulations to you all.

Most of all, I thank the Lord Almighty, who made it possible to produce this research work.

ABSTRACT

Flow assurance is the efficient and successful flow of fluids in pipes. Some of the flow assurance challenges that can be encountered include hydrate formation, which is prevalent offshore, sand deposition, wax precipitation, scale deposits, or emulsion problems. In onshore production facilities in the Niger delta, wax deposition is the major challenge to efficient fluid flow. Consequently, it has been the focus of research to proffer effective predictive control measures to a problem that has been tackled with curative methods like regular pigging, heat treatment and solvent use for decades. This research investigated paraffinic wax deposition using laboratory tests, field simulation with PipeSim, and a mathematical model; ideal solution model with various correlations for melting point temperatures and heat of fusion from Won, Chung and Coutinho's research works. The laboratory test gave agave a result of 3.73%, 4.77% and 3.45%wax content while simulation gave results of 3.71%, 4.78% and 3.49% for samples A, B and C respectively producing a good match with a difference of less than ±0.05 between the two methods.

The ideal solid model gave results of 0.9953, 0.9740, and 0.8424 for Won, Chung and Coultinho's correlations respectively for solid moles calculated at zero degrees celcius. Finally, this research recommends the use of PipeSim software to evaluate and predict wax deposition especially in the absence of laboratory data as well as regular pigging and solvent injection to ensure that wax build up is avoided in facilities handling waxy crudes.

Keywords: Flow assurance, wax deposition, laboratory tests, mathematical correlations, ideal solution model, PipeSim,

LIST OF FIGURES

LIST OF PLATES

LIST OF TABLES

TABLE OF CONTENTS

CHAPTER ONE

CHAPTER TWO

CHAPTER THREE

CHAPTER FOUR

CHAPTER FIVE

CHAPTER ONE

INTRODUCTION

1.0 BACKGROUNG OF STUDY

The term “flow assurance” was coined by Petrobras in early 1990s to mean “guarantee of flow’ (Gao and Chapman 2006). It covers all methods to ensure the efficient delivery of hydrocarbons from wells to collection facilities. It involves the successful and economic flow of hydrocarbons from reservoirs to point of sale. It covers the efficient handling of solid deposits like hydrates, wax, asphalthenes, scale and sand.

Flow assurance includes the analysis of thermal, hydraulic and production chemistry issues, during the flow of fluids through pipelines and processes (Pickering 2009). In this sense, flow assurance works to predict the behavior of fluids as it travels along pipes and processes to highlight issues which could impact safety, integrity, production capacity, and product availability. Flow assurance is to a large extent all about preventing deposits from building up inside the pipe.

Some of the flow assurance issues assailing the oil and gas industry include wax deposition, hydrate formation, sand production, and corrosion issues. The most prevalent of these is wax deposition, which is the blocking of flow lines due to the deposition of heavy organic materials present in the oil (Nathan 1955). Wax deposits are commonly called paraffin though they may be a mixture of both paraffin and asphaltenes (Allen and Roberts 1982). Waxes from Niger Delta crude oils are paraffinic (Leontaritis 1998), while waxes from California, Venezuela and Trinidad crudes are asphaltenic (Allen and Roberts 1982). Wax deposits depend on temperature and pressure, and determining the acceptable operational temperature limits is essential in tackling the problem. Proper identification and characterisation as well as accurate description of the behaviour of various deposits should be a part of field development planning and design of control measures.

All crude oils contain paraffin. The table below demonstrates how paraffin fits into the scheme of crude oil.

Table 1.1 The Constituents of Crude Oil

C number	Type	Example
C_{1-4}	Natural Gases	Methane, Ethane, Propane, Butane
C_{5-8}	Lower Boiling Liquids (40- 120 ^{0} C)	Petroleum Ether, Light Naphtha, Gasoline
C_{9-12}	Higher Boiling Liquids **(**120 – 210 ^{0} C**)**	Kerosine
C_{13-17}	Very High Boiling Liquids **(**210 – 300 ^{0} C**)**	Diesel Fuel
C_{18-35}	Non-volatile liquids Long chain alkanes	Paraffin, Lubricating oils
C_{35+}	Non-volatile liquids, Long chain alkanes, Polycyclic structures	Asphaltenes, Petroleum coke, waxes.

Hydrocarbons of C_{18-35} are labelled paraffin in the table, but they are not the only paraffinic components of the crude oil mixture. All straight chain single bond hydrocarbons are called normal paraffins (n-paraffins) or saturated hydrocarbons. They have the general formula C_nH_{2n+2}. Paraffins also include branched and cyclic alkanes. Paraffins with carbon number C_{18}^{+} are solids at room temperature, but exist in a dissolved state in the crude oil stream at reservoir conditions. When conditions change at the surface, they are precipitated out of the stream. It is this group that are deposited as wax when changes in temperature, pressure and or composition of fluid trigger their precipitation. Crude oils rich in paraffins are called waxy crudes. They produce Macrocrystalline wax deposits. This is prevalent in Nigeria (Ajienka and Ikoku 1990).

Branched chain paraffins have the same number of carbon atoms as the normal paraffins, but their branching makes them exhibit some properties different from their straight chain counterparts. They have lower melting (freezing) temperatures. This means that in a crude oil mixture, the normal paraffins will be precipitated before the iso-paraffins. This observation is important because older wax prediction models like the Won (1980) and Chung(1992) did not account for this difference.

Cyclo-paraffins are called naphtanates. They have higher solubilities than their n-paraffin and iso-paraffin counterparts. They have lower melting points and pour points than their counterparts as well. Aromatic hydrocarbons are of the benzene family. They are cyclic with a double bond. They are mostly liquids and are good solvents for paraffins. Crude oils rich in naphthenic hydrocarbons components (C_{30-60}) produce Microcrystalline wax. This contributes the most to tank-bottom sludge. (Elsharkawy et al, 1999).

Crude oil streams are classified according to which classs of hydrocarbons are the major constituents. Therefore, they are either paraffinic, naphthanic or aromatic. The paraffinic crude stream will most likely produce wax under favourable conditions. Most of the crude oils produced in the Niger Delta are light and contain more of the paraffinic components (Ajienka and Ikoku 1990).

Table 1.2 The Composition of some analysed Crude Oil waxes

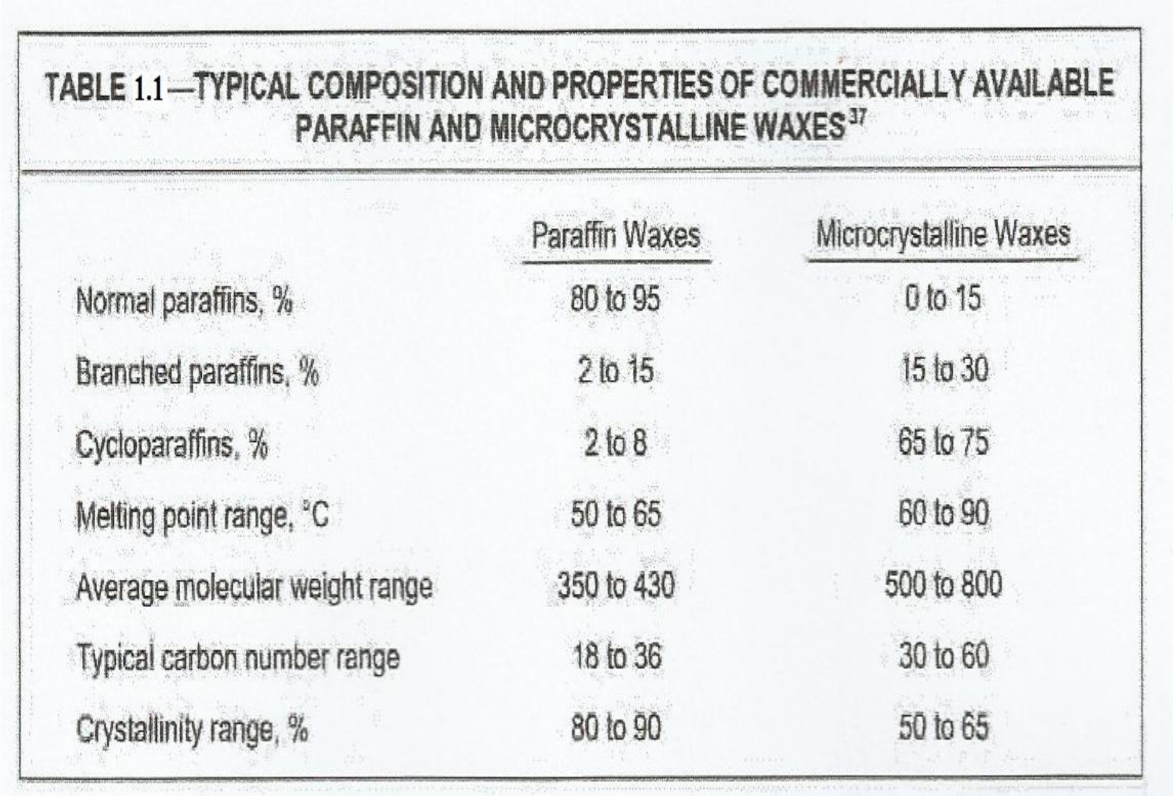


TABLE 1.1—TYPICAL COMPOSITION AND PROPERTIES OF COMMERCIALLY AVAILABLE PARAFFIN AND MICROCRYSTALLINE WAXES[37]

	Paraffin Waxes	Microcrystalline Waxes
Normal paraffins, %	80 to 95	0 to 15
Branched paraffins, %	2 to 15	15 to 30
Cycloparaffins, %	2 to 8	65 to 75
Melting point range, °C	50 to 65	60 to 90
Average molecular weight range	350 to 430	500 to 800
Typical carbon number range	18 to 36	30 to 60
Crystallinity range, %	80 to 90	50 to 65

Source: Petroleum engineering handbook vol 1 by Larry.W.Lake (1952) ("Wax Precipitation from Petroleum Fluids: A Review," pages 557–608, Copyright 2000, with permission from Elsevier Science.)

The table shows the result obtained from the analysis of waxes from sixteen crude oil samples. It indicates that paraffin is the major component of waxes deposited from these crudes.

1.1 STATEMENT OF PROBLEM

Wax deposition is the precipitation, agglomeration and accumulation of organic compounds from the crude oil stream on to the walls of pipelines and in process vessels. Ordinarily, the lighter components which are liquids (C_5-C_{17}) keep the heavier components in solution. This is the condition at the reservoir and even at the surface at high temperatures and pressures.

But when the temperature of the crude oil stream falls to its Wax Appearance Temperature (WAT) wax precipitation commences (Ajienka and Ikoku 1990). Temperature reduction is the most common cause of wax deposition because wax solubility in hydrocarbon fluids decreases as the temperature is lowered (Nghiem and Kohse 2006). Apart from temperature, changes in pressure and fluid composition can trigger wax precipitation. Some of the situations that result in wax precipitation from crude oil include;

Change in oil composition which can be affected by;

1. Mixing with other streams or losing the volatile components
2. Foreign matter in the crude such as silt, scale, salts, and corrosion by-products (iron sulphide and iron oxide) which serve as nuclei around which the paraffin can crystallize. When this mechanism begins, continued growth can proceed.

Temperature drop/cooling rate which can be altered as follows;

3. The temperature of the produced fluid falls below the WAT as it comes up the well bore and into the processing facility. Paraffin may begin to come out of solution and form wax deposits on the tubing and pipe walls.
4. The cooling effect of expanding through an orifice will cause a fall temperature.
5. The cooling produced from radiation of heat from the oil and gas to the surroundings.
6. The cooling from the liberation of dissolved gas form oil.
7. The cooling resulting from the vaporization of lighter constituents.
8. The cooling effect of produced water from wells of higher water cut.

Pressure Changes

1. Decreasing pressures below the crude's bubble point, decreases solubility and thus, increases precipitation

Other factors that enhance wax precipitation and deposition are;

1. Rough, porous, or irregular surfaces can increase deposition.
2. Paraffin Concentration. As the molecular weight of paraffin increases in the solution, the cloud point increases.
3. Molecular mass of paraffin molecules. If the stream contains paraffins of high molecular mass of C_{18}^{+}, it will likely precipitate wax.
4. Occurrence of nucleating materials such as asphaltene, formation fines and corrosion products. These will encourage agglomeration of the precipitated crystals.
5. Water-Oil ratio. Increasing WOR, decreases wax solubility. Wax is not soluble in water. Water losses heat faster and produce a cooling effect.
6. Shear Movement

These phenomena occur regularly in oil production, making wax deposits a constant part of the process. Field operators mostly apply corrective methods to solving wax deposition problems rather than preventive measures. These corrective methods include pigging, re-heating, use of solvents, etc. However, recent researches focus on pre-emtive or proactive methods which hold the promise of better efficiency. These proactive methods include testing to determine acceptable operational parameters, simulating in-situ conditions to predict fluid behaviours, and modelling for various fluid types and varying conditions. One of the tests performed to determine the onset of wax precipitation is cloud point test.

Cloud point test is carried out to determine the WAT of a crude oil sample. The test is performed according to ASTM D2500-66 Although WAT and cloud point are often used interchangeably, the distinction is that the cloud point refers to the temperature at which the first wax crystal are observed in solution. The WAT is generally a slightly lower temperature that represents the point at which the bulk of the wax crystallizes. Still it is possible for it not to pose a threat if the fluid is flowing at a good pressure as the individual crystals will disperse, be carried along in the bulk stream and may not settle nor adhere to a surface. This is in fact the concept of cold flow in oil pipelines offshore. Otherwise, the crystals will agglomerate to form granular particles. The presence of nucleating materials like asphaltenes, formation fines and corrosion products enhance agglomeration as the wax crystals gather around them forming larger particles (Allen, Roberts 1982).These large solid particles may then separate out of the fluid to form deposits. The presence of nucleation sites like rough and porous sites or solids that offer cold spots enhance deposition once these crystals have agglomerated and are pushed out of the stream’s turbulent core towards the pipe wall.

The onset of wax precipitation is sensitive to the crude composition. Wax solubility is affected by the composition of the stream, pressure drop especially below bubble point and of course temperature drop below cloud point. The primary cause of wax deposition is reduced solubility due to changes in the equilibrium conditions of the solution. Determining the characteristics, structure, boiling points, melting points, cloud points, and pour points are important in modelling wax deposition. Wax deposition is particularly problematic in low rate wells. Low flow rates ensure that the oil has a higher resident time in the tubing. This means longer time for heat loss and subsequently wax precipitation and deposition.

1.2 OBJECTIVES OF REASEARCH

This main objective of this research is to evaluate flow assurance in onshore production facilities in the Niger delta. The specific objectives include;

1. To evaluate wax deposition from crude oil using laboratory tests and simulation.
2. To probe the effect of time on amount of paraffin wax deposited.
3. To compare results of wax deposition from laboratory tests and simulation.
4. To compare results from various wax prediction correlations
5. To recommend measures that can improve the efficiency of existing Wax control measures.

1.3 SIGNIFICANCE OF STUDY

The aim of petroleum production is to obtain a pure sample of crude oil from the formation fluid and all its contaminants. Hence, petroleum production is a separation process. This process will not be feasible if the fluid cannot flow due to extreme case of wax deposition or other flow assurance challenges.

Wax deposition has been a major production problem in Nigeria because of the waxy nature of her crude oil. (Leontaritis 1998). In fact, wax deposits have been encountered in almost all the production plants in Nigeria that regular pigging is a constant practice.

If left unchecked, wax deposition will reduce the pipe diameter available for fluid transport, increase the pressure requirement for pumping, plug off entire pipe sections, and cause production loss. In fact wax deposits have been recorded to have plugged a production string at an Ebocha (Adewusi 1996). Even at the reservoir, wax deposition can occur and result in formation damage due to permeability reduction. It can cause a reversal in formation rock wet ability, affecting effective drainage (Svendsen 1993).

The high cost of remediation like wax cutting, pipe heating before restarting, and changing entire pipe sections have forced operators to employ preventive methods. Presently, the trend is the combined use of predictive and preventive methods like modeling to tackle this problem.

1.4 SCOPE AND LIMITATIONS OF WORK

This research discusses flow assurance as unrestricted flow of fluids through conduits. The fluid in consideration is the formation fluid and the focus is on its transport from the well head, through pipes and process to the stock tank and eventually the Tank farm. Within these points, a lot of flow assurance issues arise, but this research is restricted to wax deposition. This samples used in this work were collected from two flow stations, at onshore production facilities in Nigeria. The samples were collected downstream of the pump. The time lapse between sample collection and laboratory testing was more than a week during which the sample was not insulated. These conditions affected the eventual results of the analysis.

PipeSim software was used to simulate field conditions, perform calculations and generate graphs. These results were compared with the laboratory determined results.

Various correlations were compared, but not with laboratory nor simulation results. The reduction of the equilibrium factor equation by removal of many parameters eliminated the basis of comparism. Data, charts and tables used were properly referenced and acknowledgment given to the companies, organizations, institutions and authors from which they were gotten.

All samples were obtained from the Niger Delta area. Any other oil producing region around the world may not find the results in concord with theirs.

CHAPTER TWO

LITERATURE REVIEW

2.0 WAX DEPOSITION AS A FLOW ASSURANCE CHALLENGE

Flow assurance is the technical discipline that guarantees achievement of a lifting and transport system's lifetime production targets; from the near-wellbore to offloading tanks; by predicting, preventing, and solving problems (control) originated by the behaviour of the transported substances (i.e. gases, liquids, and solids either separated or in multiphase conditions) (Alberto DiLullo,2012). Flow assurance is a multidisciplinary concept. Wax deposition is only a small part of flow assurance, but one that is important in areas producing waxy crude oils. It is one of the oldest of oil production problems. In the early 1920s, wax deposits were reported in subsurface production equipment in some wells in the US. (Reistle 1932). More recently, Tube tech international lost about six-figure sums per day when a pig got stuck in wax during a subsea pipeline pigging operation. It took the company a week, using hot tapping method to resolve the problem according to Mike Watson, Tube tech technical director (Offshore technology, 14 March 2012). Paradigm Flow Solutions also reported that pipeline blockages due to wax deposits cost operators tens of millions of dollars every year. Many of such cases have been reported on losses from wax deposition in pipelines.

Wax deposits are either paraffin or asphaltene, though both can be deposited from the same source. Crude oil from Nigeria and other West African countries like Angola and Gabon are waxy, having high content of paraffinic components (Leontaritis1998). It therefore deposits paraffin wax. Paraffin deposition has been reported in various parts of the world. One of the preliminary tests on wax control is aimed at identifying the type of wax as the methods of controlling asphaltene wax deposition are quite different from those for check mating paraffin wax. In Nigeria, paraffin wax problems have been reported from various fields and at different stages of productive life of wells. Pipelines have been known to wax up beyond recovery in Nigeria. Production tubing has also been known to wax up, necessitating frequent wax cutting, using scrapers conveyed by wireline, which is an expensive practice as was the case at an Agip facility at Ebocha, Rivers State (Adewusi, 1997). Billions of dollars has been lost to its prevention and remediation (Oladipo et al 2009). However it is prevalent in fields that have been in production for a long time especially those injecting water for pressure maintenance. This has necessitated regular pigging in these fields.

Paraffin in Crude Oil

Image from uic.edu

PLATE 2.0.1 Wax deposit in Pipeline

2.1 WAX DEPOSITION MECHANISMS

Most crude oil pipelines operate under a turbulent flow regime. In this type of flow, there is a turbulent core and laminar boundary layer adjacent to the pipe wall.

In the turbulent core, temperature, velocity, and wax concentration are independent of radial position. In the laminar boundary layer, there is a high velocity gradient (shear rate) and a decrease in temperature towards the pipe wall. The laminar boundary layer controls the wax deposition rate. Four mechanisms, Molecular diffusion, Shear dispersion Brownian diffusion, and Gravity settling govern wax deposition as precipitated wax is transported from the liquid crude to the pipe wall. Molecular diffusion transports dissolved wax, and shear dispersion transports precipitated wax. If a pipeline is operating within a laminar flow regime, deposition will increase as the velocity of the oil decreases. Under worst-case conditions, the oil will solidify at the pipeline wall and the pipeline will rapidly become choked with wax.

2.1.1 Molecular Diffusion

Where there is a temperature gradient in a crude oil carrying pipeline, molecular diffusion occurs as soon as the pipe wall temperature reaches the cloud point. There is then a wax concentration gradient between a higher level of dissolved wax in the turbulent core of the oil and the lower level of wax still in solution at the pipe wall. This causes dissolved wax to diffuse towards the pipe wall where it is precipitated.

Pipe wall surfaces are inherently rough, providing nucleation sites for deposition. The precipitated wax gradually becomes incorporated into an immobile layer, and as more are diffused, it adds to crystal growth. Deposition only occurs when the oil is being cooled. The equation describing the rate of mass transport caused by molecular diffusion is

$$\frac{dmi}{dt} = -\rho_{oil}\ DiA\frac{dwi}{dT}\frac{dT}{dr} \qquad 2.1$$

mi = mass of component i

t = time

ρ_{oil} =density of oil

D_i = effective diffusion coefficient for component i

A = deposition area,

w_i = weight fraction of component i

r = radial distance.

If the pipe wall temperature is higher than the bulk oil temperature, molecular diffusion can be reversed and waxy residues on the pipe wall can be re-dissolved into the turbulent core.

2.1.2 Brownian (Motion) Diffusion

Small solid wax crystals when suspended will be bombarded continually by thermally agitated oil molecules. These collisions will lead to small random Brownian movements of the suspended particles. If there is a concentration gradient of these particles, Brownian motion will lead to net transport, which is similar to diffusion.

2.1.3 Shear Dispersion

Wax crystals already present in the flowing crude tend to flow at the mean speed of the crude oil. However, close to the pipe wall, shearing of the liquid causes lateral movement of the particles of wax. This lateral movement is called shear dispersion.

This leads to the transport of precipitated wax from the turbulent core to the pipe wall where it may either deposit directly onto the wall surface or link with wax already deposited by molecular diffusion. With shear dispersion, there is no tendency for nucleation to occur at the pipe wall surface. This can lead to a less tenacious deposit than would occur by molecular diffusion. Factors that affect shear dispersion are:

1. Wall shear rate
2. Quantity of precipitated wax
3. Shape and size of wax crystals

Shear dispersion mechanisms only become significant if the precipitated wax content in the turbulent core is high. This only occurs when the bulk oil temperature is well below the cloud point. The rate of mass transport of wax caused by shear dispersion takes the form;

$$\frac{dmw}{dt} = k^* \, c_W Y A \qquad 2.2$$

Mw = mass of wax

k^* = empirical constant

c_W= concentration of precipitated wax at the wall

Y = shear rate.

The form of this equation shows that the deposition rate increases linearly with increasing shear rate.

Although an increase in shear rate tends to encourage more lateral dispersion of wax particles toward the pipe wall (equation 2.2), the increase in shear rate also encourages deposited wax crystals to be stripped off the pipe wall (sloughing). For any given system, equilibrium is reached where deposition approaches a maximum thickness of deposit, provided conditions remain constant. It is considered that molecular diffusion is the dominant process at higher temperatures and shear dispersion will dominate at lower temperatures when shorter chain length (or soft) n-alkanes contribute to the deposition process. It is most likely that both mechanisms proceed simultaneously.

Findings from experiments and modelling of molecular diffusion and shear deposition indicated that wax can be dislodged from pipe wall (Weingarten and Euchner 1988). Sloughing occurs when the wall shear rate exceeds the shear strength of the deposit and may occur both in the laminar and turbulent flow regimes. Studies on effect of high flow rates on paraffin deposition in pipes of different materials confirm this (Jesson and Howel 1958).

2.1.4 Gravity Settling

Wax is denser than oil. So, in a system, the precipitated wax will settle out of the oil stream and be deposited at the bottom. Gravity settling as a wax deposition mechanism has little effect in a flowing system (pipes), but more in stagnant systems like stock tank. In fields where oil was stored in tanks for days due to maintenance works or excess production, wax was reported to have accumulated at the bottom of such tanks.

2.2 RHEOLOGY OF WAXY CRUDE OIL

The Rheology of waxy crude oils is strongly temperature dependant and also shear rate dependant (Aijenka 1983). Above the crude’s cloud point, it exhibits Newtonian fluid behaviour, below the cloud point, waxy crudes exhibits non-Newtonian fluid behaviour because of wax crystallisation (Skovborg et al 1991).

$$T = -\mu Y \tag{2.3}$$

Where

T =Shear stress

μ = viscosity

Y = Shear rate

Between cloud and pour points, the crude is pseudo-plastic (Pedersen et al 1991).

$$\mathrm{T} = PV(-\mathrm{Y}) \qquad 2.4$$

Where

PV = Plastic viscosity

At pour point and below, it becomes a thixotropic/yield plastic fluid

$$\mathrm{T} = \gamma + PV(-\mathrm{Y}) \qquad 2.5$$

Where

$\gamma =$ Yield strength

This explains why increased pump rate is required to restart pipes transporting waxy crudes especially where there is a significant temperature gradient over a long distance.

A good knowledge of the rheology of waxy crude oil is important in the production design for handling waxy crude oils.

There are two clear types of waxy crude oils; clean waxy crude oil and Regular waxy crude oil. Clean waxy crude oil has paraffins as the heavy components. As a result, wax is precipitated when the temperature falls below the cloud point. Designing for wax control of clean waxy crude involves thermal insulation and heating (hot oiling, down hole heaters and surface heater treaters). These methods are effective because the wax is soft and will melt on heating and resume flowing (Nalco 2004). Regions of West Africa, Middle East, and South America like Offshore Argentina have waxy oils (Leontaritis 1998). Regular waxy crude oil have paraffins, and other heavy organics like resins and asphaltene components. As a result, the wax deposited from regular waxy crude hardens with time and so is not effectively handled with pigging.

It will not melt and continue flowing on heating. Regions around the Mediterranean Sea, Offshore Brazil, Columbia, North Sea, North America and Russia have regular waxy oils (Leontaritis 1998).

2.3 CRUDE OIL CLASSIFICATION

Crude oils may be classified according to their content of paraffins(normal and iso-alkanes), Napthanes (cyclo-alkanes) and Aromatic compounds(aromatic hydrocarbons, resins and asphaltenes). These are often referred to jointly as PNA.

2.3.1 PNA Classification

Paraffins: This class includes normal-alkanes (straight chain) and iso-alkanes (branched chain alkanes that are isomers of their straight chain counterparts) that consist of chains of hydrocarbon segments (-CH_2-, -CH_3-) connected by single bonds. Methane (CH_4) is the simplest paraffin. The majority of components present in solid-wax deposits are high-molecular weight paraffins.

Naphthenes: This class includes the cycloalkanes, which are hydrocarbons similar to paraffins but contain one or more cyclic structures. The elements of the cyclic structures are joined by single bonds. Naphthenes make up a large part of microcrystalline waxes.

Aromatics: This class includes all compounds that contain one or more ring structures similar to benzene (C_6H_6). The carbon atoms in the ring structure are connected by six identical bonds that are intermediate between single and double bonds, which are referred to as hybrid bonds, aromatic double bonds, or benzene bonds.

Resin And Asphaltenes Resins and asphaltenes primarily are a subclass of the aromatics, although some resins: may contain only naphthenic rings. They are large molecules consisting primarily of hydrogen and carbon, with one to three sulphur, oxygen, or nitrogen atom per molecule. The basic structure is composed of rings, mainly aromatic with three to ten or more rings per molecules. (McClafin, 1984)

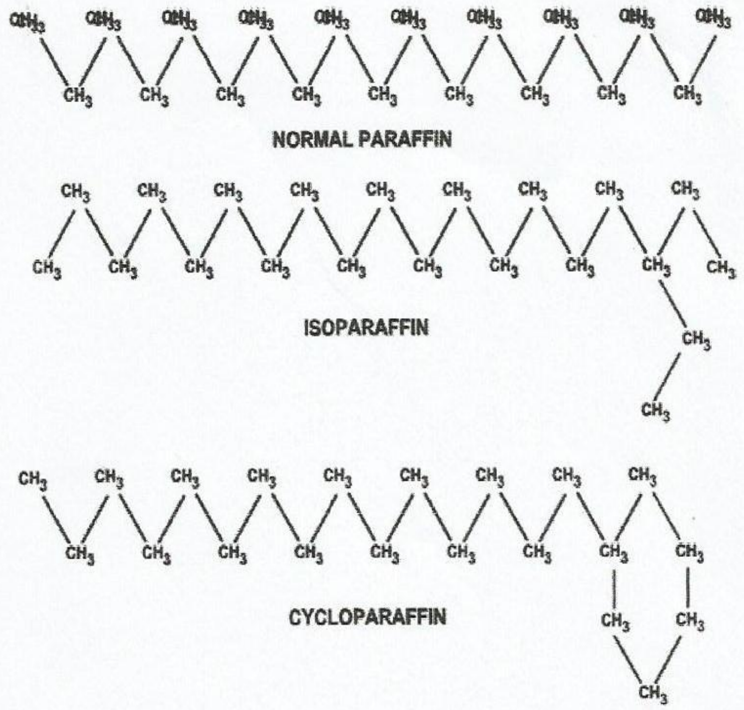


Fig. 2.1 –Example structure of wax-forming components. (Reprinted from *Asphaltenes and Asphalts, 2,* C. Lira-Galeana and A. Hammami, "Wax Precipitation from Petroleum Fluids: A Review," pages 557–608, Copyright 2000, with permission from Elsevier Science.)

Fig PLATE 2.3.1.1 Structure Of Paraffins And Naphthenes

2.3.2 SARA Classification Of Petroleum Constituents

The components of the heavy fraction of a petroleum fluid (the part that readily forms wax) can be separated into four groups: saturates aromatics, resins, and asphaltenes (SARA).

Saturates include all hydrocarbon components with saturated (single-bonded) carbon atoms. These are the n-alkanes, iso-alkanes (paraffins), and cycloalkanes (naphthenes).

Aromatics include benzene and all the derivatives composed of one or more benzene rings.

Resins are components with a highly polar end group and long alkane tails. The polar end group is composed of aromatic and naphthenic rings and often contains heteroatom such as oxygen, sulphur, and nitrogen. Pure resins are heavy liquids or sticky solids.

Asphaltenes are large highly polar components made up of condensed aromatic and naphthenic rings, which also contain heteroatom. Pure asphaltenes are black, non-volatile powders.

The experimental method used to determine the weight fractions of these groups is called **SARA** analysis. (Speight 1991)

2.4 ASPHALTENE CHEMISTRY

Asphaltenes are a class of heavy components in crude oil that are insoluble in non-polar solvents like pentane and hexane unlike other components (paraffins, nephthanes and aromatics), but are soluble in aromatics (Mitchell and Speight, 1973). They have complex polycyclic condensed aromatic ring structures with no exact composition. They have polar macro-cyclic molecules that contain carbon, oxygen, sulphur, and possibly metals with weights up to several thousands. They are soluble in aromatic solvents like carbon tetrachloride and carbon disulphide (Allen and Roberts 1982).

Asphaltene exists in molecule clusters in crude oil as colloidal micelles, kept in solution by resins and maltenes that are also components of crude oil. They have structures similar to those of asphaltene but with lower molecular weights. Crude oils that have high resins content are less likely to deposit asphaltene.

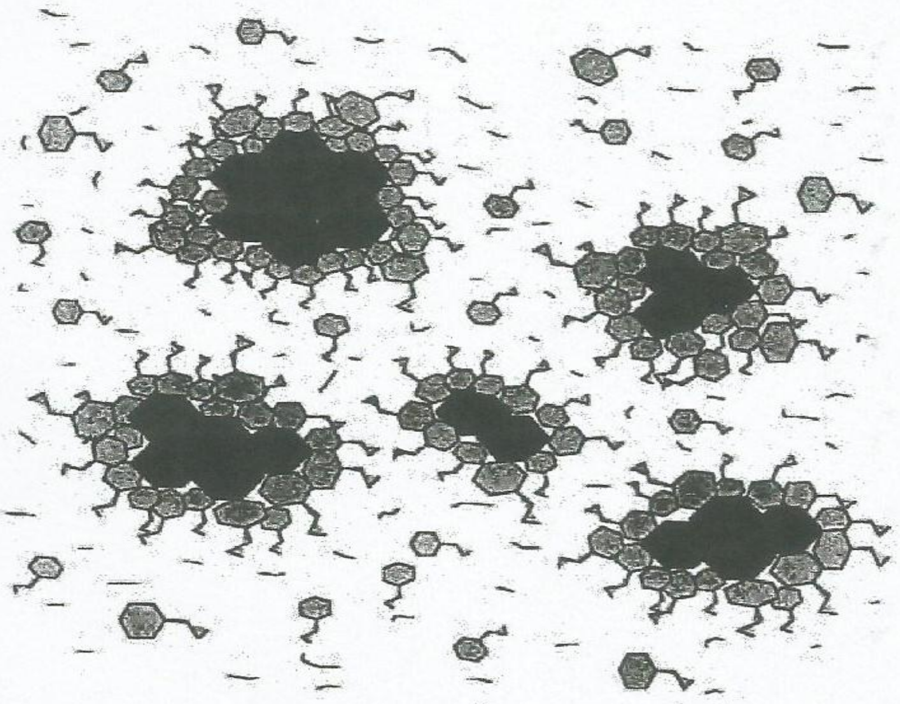


Fig.2.4 —Asphaltene-resin micelles.

PLATE 2.4.1 Asphaltene – Resin Micelles

Source: (Reprinted from *Fuel*, J.G. Speight, R.B. Long, and T.D. Trowbridge, “Factors Influencing the Separation of Asphaltenes From Heavy Petroleum Feedstocks,” pages 616–620, Copyright 1984, with permission from Elsevier Science.)

At stable reservoir conditions, asphaltenes, resins and maltenes are in thermodynamic equilibrium. When this equilibrium is disturbed, they are disassociated and then, asphaltene flocculation occurs (Pfeiffer and Saal, 1940).

2.5 MECHANISM OF FLOCCULATION AND DEPOSITION

Asphaltene precipitation is influenced by interaction between asphaltene and other components of the oil, ie polar and non-polar components, and peptizing agents (resins). Equilibrium changes altering the ratios of the polar and non-polar components can destabilise asphaltene and trigger asphaltene micelle flocculation (Nalco 2004). Asphaltene is soluble in the polar components, so a drop in the concentration of the polar components will enhance asphaltene precipitation. Even after precipitation, asphaltene can remain suspended by peptizing agents like resins causing them to flow with the oil and not be deposited. The fraction of the peptizing agents however affect the suspension of asphaltene in oil (Mansoori 1994). These concentration imbalances can be caused by chemical changes, mechanical changes, or electrical action in the system.

Chemical changes in the system include some of the following:

1. **Mixing crude oils**; This can change the ratio of polar to non-polar components, or resins to asphaltenes. This occurs often in asphaltic crudes that come in contact with gas condensate. Condensate should never be used in clean-outs or work-overs on wells producing asphaltic crude.
2. **Miscible floods**; Miscible solvents tend to be non-polar (CO_2, C_4 - C_6). These non-polar solvents strip the stabilizing agents from the asphaltene causing asphaltene precipitation and deposition on formation surface, resulting in an oil wet surface, reducing relative permeability to oil and reducing oil production (Nghiem and Kohse 2006).
3. **Pressure falls below the bubble point**; When the pressure falls below the bubble point, the gases that were in solution are now in a separate phase. This change will affect the equilibrium of the stabilized asphaltenes.

4. **Acid**; Acid and asphaltic crude are incompatible. Great care must be given to asphaltic crudes during well completion and stimulation.
5. **Gas Lift**; The injected gas can change the chemical composition of the crude. This should be considered and the crude evaluated before installing a gas lift system in a flowing well.

Mechanical changes from shearing and turbulence during fluid transport can affect the system by physically stripping stabilizers off asphaltene, causing flocculation. Even in turbulent flow, there can be localized pressure drop which can have the same effect as bulk pressure drop on asphaltene stability.

Asphaltene deposition can result from the streaming potential phenomenon. Asphaltene molecules are polar and are weakly charged. A streaming potential is set up when these charged particles flow over a surface, disturbing electrical forces and causing aggregation and flocculation. A streaming potential of about 30 mili volts developed in a flow test where black crude oil was forced through a sandstone core. Asphaltene particles were precipitated after the test (Allen and Roberts 1982 ppg13). Streaming potential is a function of surface type, conductivity, flow regime, physical properties of the crude and electrical properties of asphaltene (Al-Safeel 1994). Rough surfaces will have more asphaltene deposits that smooth surfaces. Asphaltene micelles are negatively charged and will selectively deposit on any positively charged material in the system. Streaming potential is affected by the ease of diffusion of the asphaltene particles to the surface, so flow plays a role. The presence of wax particles in the crude encourages asphaltene precipitation as they become the nuclei around which asphaltene molecules deposit.

2.6 CHECKMATING WAX DEPOSITION

Assessing prevalent practices aimed at checking wax and asphaltene deposition reveals that preventive, control and predictive methods are used.

2.6.1 Preventing Wax Deposition

Allen and Roberts (1982) suggested that laboratory analysis should be carried out as a basis for selecting the most economic system for preventing wax deposition from wells completed in each reservoir.

These tests are of two groups. The first determines wax deposition properties of the crude oil and the second screens inhibitors.

Tests that investigate wax deposition properties are called paraffin identification tests. They include; Centrifuge tube test, Hot xylene test, Melt test, and Pentane solubility test. There is also Cloud (Wax appearance test) point test.

The tests that screen inhibitors and monitor deposition include; Paraffin Cold Finger (or Cold Coil) Deposition Test, ASTM D-97 Pour Point Test, Constant Temperature Ramp Down Pour Point Test ,Crude Oil Rheology Test (using different Viscometers to test for various properties in varying temperatures and shear rates), Paraffin Flow Loop, Restart Flow Loop, H.P(High Pressure) Gas Chromatography, DSC (Differential Scanning Calorimeter) Instrument Tests, Etc . For asphaltene, there are Asphaltene flocculation point test, Asphaltene screening test and Asphaltene dispersant test (Nalco 2004).

Before the laboratory tests, field/ system surveys are conducted to identify areas of wax deposition. It is at these points that inhibitors will be injected after screening.

The Chemicals inhibitors used to prevent wax deposition are Crystal modifies. They are polymeric material that modify the shape of paraffin crystals as they come out of solution ensuring that they do not form needles, will not network and will move with the liquid portion of the crude oil.

When at the onset of precipitation wax crystals come out of solution, they take one of the following forms;

1. Needles: In this form, they can network and trap the liquid fraction of the crude.
2. Malcrystals: Poorly shaped crystals that cannot network; they are pumpable.
3. Plates: Plates are pumpable, but it is possible for plates to curl on their edges to form hollow needles that can network.

There are crystal modifiers that work on keeping asphaltenes in solution. Since wax crystals will agglomerate around a nucleus (asphalthene), removing the nucleating agent will prevent agglomeration and deposition (Knox et al 1962). An example of this is Halliburton's Paracheck.

C **A** **B** **D**

PLATE 2.6.1.1 PATTERNS OF PARAFFIN CRYSTAL GROWTH

Pour point depressants are crystal modifiers that work on ensuring that the precipitated wax crystals are not deposited at the pour point temperature (by modifying crystals) but at a much lower temperature.

Another class of chemicals that are used to prevent deposition are Surfactants. They prevent wax deposition in one of two ways. Either by water wetting the pipe surfaces to prevent wax contact with the pipe wall or by acting as solubilising agents for nucleating agents, consequently preventing wax crystals agglomeration. For the first, water producing wells are the best candidates, while the second requires a continuous injection of surfactants. Surfactant screening must be conducted to avoid emulsion problems which could result from the use of surfactants.

Pipe surface contributes to wax deposition. Deposition will occur at a much slower rate on a smooth pipe than on a rough pipe. The use of plastic pipes or plastic (epoxy, phenolic, etc) coated pipes is a preventive measure. But considerations should be given to hot oiling and working pressures especially for pigging. It should be noted that wax accumulation occurs at the same rate on all surfaces after the initial deposition.

Wax deposition can be prevented using methods that ensure that the crude oil temperature does not fall down to the wax deposition temperature. Some of these methods include pipe insulation, heat treating and pipe heating (Shock et al, 1955).

Pipe insulation ensures that the oil retains its heat from the reservoir and does not lose it cold surface environment. This method is however expensive especially where very long distances are involved and not as efficient in very cold environment like in ultra deep offshore.

Inhibiting asphaltene deposition is tackled by preventing asphaltene flocculation because no deposition will occur without flocculation. Asphaltene inhibitors are naphthalene chemicals. They act in the same manner as the resins and maltenes, interacting with the asphaltenes and stabilizing the asphaltene micelles in the crude oil. These asphaltene inhibitors have a stronger association with the asphaltene than the natural resins and maltenes and are able to stabilize the asphaltenes through greater changes in pressure, temperature, shear, and chemical environment. It is important that these asphaltene inhibitors are added to the crude oil before the asphaltenes become destabilized and flocculation occurs. Conventionally, the inhibitor is continuously injected at the wellhead. It may not solve deposition problems at the sand face. So, inhibitor can be squeezed into the formation at intervals.

2.6.2 Controlling Wax Deposition

This involves removing deposited wax perhaps, early enough that it does not cause serious damage to the system. Wax and asphaltene deposits are controlled differently. Wax control methods include;

1. Thermal method
    - Pipe heating
    - Hot oiling
2. Mechanical method
    - Pigging
    - Scraping (Wireline)
3. Chemical method
    - Dilution with low wax content crude oil
    - Use of chemical additives (solvents, and dispersants)

2.6.2.1 Thermal Wax Control methods

These methods apply heat to melt deposited wax and cause it to continue flowing. It could be a continuous application like in down hole heaters. It could be a periodic circulation of hot oil down the casing and up the tubing (Billingsley 1963) called hot oiling. The hot oil heats up the tubing which in turn heats up the wax. It both dissolves and melts wax (Ajienka 1990). In some instances, the oil is pumped down the tubing to get to the sand face and up the casing. This can cause formation damage if melted wax (oil saturated paraffin) enters a formation of temperature less than the hot oil's cloud point. Deposition will occur plugging the formation pores. Hot water and Steam have been effective in removing wax. However the same problem of permeability damage can occur if melted wax flows back into the formation with scales and formation fines. The Huff and Puff steam stimulation EOR is so effective that it eliminates wax re-precipitation in the formation.

The use of heater treaters at production plants, downstream of separators, to heat the oil and keep its temperature well above wax appearance temperatures is a common practise.

2.6.2.2 Mechanical wax control methods

Wax scrapping is the usual choice of remediation for wax plugged wells. It is cheaper and avoids formation damage that may result from the thermal methods. However it can be more expensive if frequent cleanups are required because production will be deferred for each well clean up. To avoid this, scrappers can be attached to sucker rod pumps to remove wax as well is being pumped. Constant scrapping in this case is a more effective control that periodic scrapping. Injecting chemical solvents some hours or days to clean up improves efficiency. However, wax chunks can settle in flow lines and cause blockages. Constant scrapping roughens pipe (tubing) walls encouraging subsequent deposition.

Pigging is a mechanical wax control method employed in surface pipelines. It is pipe cleaning using a ‘pig’ (a device with brushed ends) pushed with a high pressure fluid that brushes off wax from pipe walls and carries them along as it moves. In fields producing waxy crude, pigging is scheduled regularly to ensure that the pig cleans up all deposited wax, avoid wax build up and incidences of stuck pigs.

2.6.2.3 Chemical Wax Control Methods

When waxy crude is diluted with low wax content crude oil, it reduces wax precipitation from the resulting mixture. The low wax content crude is rich in components that act as solvents for wax. Which means that even at conditions favouring precipitation, the mixture will remain in liquid state.

Introducing solvents to dissolve the deposited wax is a common practise especially offshore. Some of the solvents that have been used include; condensate, casing head gasoline, pentane, light gas oil, xylene, toluene, carbon tetrachloride, carbon disulfide, and terpenes. For many years, chlorinated hydrocarbons were the preferred wax solvents used. They include; carbon tetrachloride, trichloroethylene, and perchloroethylene. They were relatively inexpensive, had a high density, and were non-flammable. However, crude treated with these chlorinated hydrocarbons caused problems in the refinery. It was for this reason that their use was discontinued.

Temperature and rate of agitation are two factors that affect every dissolution process. The high the temperature and shear rate the faster the dissolution. For greater efficiency, surveys should be conducted, and points of deposition identified so that the solvent will be injected at those points.

Dispersants will be more effective than solvents when more than a 20% water cut is present. Dispersants perform a different function and are applied differently than solvents. They do not work on removing the deposit, and are not used in a concentrated fashion, like solvents. They are used at ppm treatment levels in a carrier fluid; it is the carrier fluid that removes the paraffin. The carrier fluid might be a paraffin solvent, hot crude, or hot water. The latter two offer a means to introduce heat into the wellbore to melt the paraffin.

Dispersants will not remove paraffin when injected on a continuous basis. Instead, dispersants are used to prevent paraffin deposition in systems that have been cleaned by mechanical, thermal, or chemical means.

Dispersants work by coating the paraffin crystal and the metal surfaces, causing the paraffin crystals to repel each other and the metal surfaces. This approach to paraffin control does not prevent the paraffin crystals from forming but merely keeps them from forming a solid deposit and keeps them moving with the crude.

2.6.2.4 Controlling Asphaltene Deposition

Asphaltene deposits are hard, brittle, dark black, dry solids and heat does not melt them. Therefore, a hot oil treatment will not remove asphaltene deposits. Asphaltene are removed by physical and or chemical means.

Physical methods include

1. Wireline cutting
2. Pigging

3. Hydro blasting
4. Drilling

Chemical methods involve

1. Use of Solvents
2. Use of Dispersants

The advantage of physical removal is that it may be faster and more economical than chemical removal for large volumes of deposit or for lines that are completely plugged. They are the only methods employed in such cases. The disadvantages are the inability of physical methods to remove deposits from the formation face and the cost of deposit hauling and disposal. Physical methods are not used as regular treatments for asphaltene deposits. Removed asphaltene deposits cannot be returned to the production system.

Chemicals are used more regularly in asphaltene treatment (batch and continous applications). They are more convenient. Aromatic solvents are commonly used in the removal of asphaltene deposits, and they can also be used to control the problems caused by the deposits. If the build up of deposits occurs over a long period of time or only occurs after work-overs, the use of periodic solvent soaks may be the more cost-effective approach. On the other hand, if the problem is more severe or frequent, the use of solvents to remove deposits will become less economical compared to the use of dispersants. Dispersants can be applied using batch or continuous methods. Dispersants help the flocculated asphaltene remain dispersed in the oil. The advantage of dispersants is their relative low cost compared to asphaltene inhibitors. The disadvantage is that dispersants do not prevent flocculation from occurring;

instead, they just keep the asphaltenes moving. They may agglomerate and deposit at another point in the system or in the pipeline. Dispersants are surface active and as such, may also contribute to the stabilization of water-in-oil emulsions. So, emulsions are a problem to watch out for in plants where dispersants are used for asphaltene control.

2.7 WAX DEPOSITION AND THERMODYNAMIC SYSTEM EQUILLIBRIUM

Attempts to model crude oil and synthetic oil wax deposition have been made by numerous authors, some of which are an improvement on previous works (Won 1980,1986,1989; Hansen et al 1988; K.S.Perderson et al 1991,1993; Erickson et al 1993; Lira-Gelena et al 1996; Coutinho et al 1996,2001; Chung 1992; etc).

Wax deposition is a thermodynamic process that occurs in stages comprising of the various states of the fluid and fluid-solid mixture. Initially, we may have a vapour-liquid system. As its properties (temperature, composition and pressure) change, there will be resulting changes in state. From vapour-liquid to mostly liquid to liquid-solid and eventually all solid depending on the initial fluid composition. Wax precipitation starts, after the liquid has been saturated with wax molecules at equilibrium. Then further change triggers crystallization and eventually, wax deposition.

2.7.1 System Properties That Affect Change Of State

In thermodynamics, the properties of a system at each point affect its state. In crude oil systems, the properties of concern are the temperature, composition and pressure. It is in this order that they influence.

Temperature: Wax solubility is strongly temperature dependent (Altgelt, Boduszynski, 1994). It increases with increasing temperature. Three temperatures are very important in solid-liquid thermodynamic systems. They are cloud point, melting point and pour point. The cloud(WAT) and pour(WDT) points were discussed in the previous chapters. They are of note and are built into plant design as a preventive measure of checking wax deposition. The melting temperature is relevant when corrective measures like pipe re-start and hot oiling are in use. They are also used in predictive models for calculating equilibrium values.

Composition: Hydrocarbon systems made up of majorly paraffinic components will produce paraffinic wax. Sample characterization is a vital part of wax modelling. Petroleum constituents may be broadly classified as belonging to the C_{6-} or the C_{6+} fraction. The heavy end may be further classified with SARA (saturates, aromatics, resins, and asphaltenes) analysis. Various chromatography methods allow the determination of the mass fractions of single carbon number (SCN) fractions of a fluid. Detailed PNA [paraffinic (P), naphthenic (N), and aromatic (A) fraction] analyses can also be performed. Depending on the details of the analysis, the aromatic fraction may or may not include the resines and asphaltenes. It is also possible to determine the amounts of individual n-alkanes. These types of analyses, although expensive, are especially valuable for wax precipitation modeling because they very accurately define the components of a fluid that will precipitate as wax.

Pressure: Pressure changes usually have a very small effect on wax precipitation temperatures and amounts; however, changes in the original equilibrium composition of the fluids can result in a loss of wax solubility. A fairly consistent trend is that the lightest components in a crude oil act as good solvents for waxes. Liberation of solution gas from a crude oil as pressure decreases below the bubble point of the fluid has been shown to increase the cloud-point temperature of the oil according to Brown et al(1994). In the wax precipitation envelope below, the solid/liquid-phase boundary is nearly vertical, illustrating wax precipitation’s strong dependence on temperature and weak dependence on pressure.

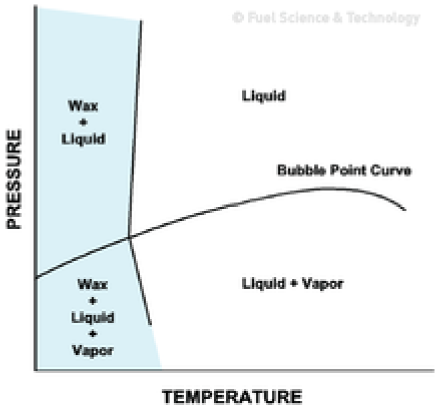


Fig. 2.4 – Pressure-temperature wax precipitation envelopes (Leontaritis,1996)

2.8 ADVANCES IN PREDICTING WAX DEPOSITION

A lot of research has been carried out on wax deposition, studying it from different angles. Nathan (1955) studied the solubility of high molecular weight paraffins. Jeffries-Haris (1969) studied the feasibility of solvent stimulating low gravity oil unto production. Burger et al (1981) studied the use of wax crystal modifiers to control down hole wax deposition. Shock et al (1955) studied the mechanisms of paraffin deposition. They developed temperature-viscosity curves for various crude oil types. Jessen et al (1958) experimentally investigated the relationship between flow rate and wax deposition on various pipe material types. Weingarten and Euchner (1988) studied the effects of shear rate on wax deposition**,** experimentally measured wax deposition rates and compared it to predictions made using the ideal solution model. Keating and Wattenbarger(1994) modelled wax deposition and removal in wells using a well bore simulator. They found that wax removal is caused by equilibrium conditions and not sloughing process.

Scatchard and Hildebrand(1962) developed a single phase multicomponent wax model based on the regular solution theory which considered mixtures with zero-excess entropy provided that there is no volume change of mixing (Prausnitz et al 1999)

Won(1986)'s model determines equilibrium K values using the Soave-Redlich-Kwong (1972) EOS. He then uses a three phase flash algorithm to determine the solid/liquid/vapour phase split as a function of temperature and pressure.

Lira-Galeana et al(1996) developed a thermodynamic model for wax precipitation based on the concept that the precipitated wax is made up of several solid phases, at which each phase consists of a single component or pseudocomponent (single phase multicomponent system).

Pan et al (1997) also used the multisolid-wax model but with a different fluid-characterization procedure. The characterization is based on experimental SCN analysis. Every five consecutive carbon number fractions are lumped together. The relative amounts of the P, N, and A sub-fractions are determined experimentally or with correlations. Melting temperature and enthalpy of fusion properties are assigned to the paraffinic sub-fractions with Won's correlations.

Mei et al (1999)'s research used the mixed activity/fugacity coefficient model with a three-phase flash algorithm, in conjunction with liquid/vapor K values obtained from the Peng-Robinson (1976) EOS.

Perdersen et al (1991) compared experimental wax precipitation as a function of temperature with model predictions for 16 crude oils.

Reddy (1986) used the ideal solubility model to determine the cloud point and amounts of precipitated wax for synthetic fuels.

2.9 MODELLING WAX DEPOSITION

The basics of modelling wax deposition is defining the thermodynamic equilibrium between the phases (solid/liquid). It is expressed as the equality of chemical potential for each component in all phases. For one solid phase in equilibrium with an oil, this condition is given by

$$\mu_{io} = \mu_{is}, \quad i = 1, \ldots, n_c, \qquad 2.7$$

Where:

μ_{io} and μ_{is} are the chemical potentials of component i in the oil and solid phases, respectively

n_c is the number of components.

With the fundamental relation between chemical potential and fugacity of component i (n_c)

$$\left(\mathrm{d}\mu_i = RT\mathrm{d}\ln f_i\right)_T, \tag{2.8}$$

The equilibrium relation also may be expressed in terms of fugacities:

$$f_{io} = f_{is}, \quad i = 1, \ldots, n_c, \tag{2.9}$$

Where f_{io} and f_{is} are the fugacities of component i in the oil and solid phases, respectively.

2.9.1 Pure Solid Component Fugacity

There are no equations of State (EOS) for describing the volumetric behavior of the solid phase as a general function of temperature and pressure; therefore, thermodynamic solid-precipitation models are derived by relating the chemical potential of a pure solid to the chemical potential of the pure liquid at the same pressure and temperature in terms of experimentally known melting properties. Ignoring solid state transitions, and applying the relation between chemical potential and fugacity, we have;

$$\ln\left(\frac{f_{is}}{f_{io}}\frac{f_{io}^0}{f_{is}^0}\right) = \frac{\Delta H_{if}}{RT}\left(1 - \frac{T}{T_{if}}\right) + \frac{1}{R}\int_T^{T_{if}} \frac{\Delta C_{pi}}{T}\mathrm{d}T - \frac{1}{RT}\int_T^{T_{if}} \Delta C_{pi}\mathrm{d}T + \frac{1}{RT}\int_{p_{if}}^{p} \Delta v_i \mathrm{d}p, \tag{2.10}$$

where f_{ik}^0 is the fugacity of pure component *i* in phase state *k* (*k* = *o*, *s*).

$$\frac{f_{io}^0}{f_{is}^0} = \exp\left[\frac{\Delta H_{if}}{RT}\left(1 - \frac{T}{T_{if}}\right) + \frac{1}{R}\int_T^{T_{if}} \frac{\Delta C_{pi}}{T}\mathrm{d}T - \frac{1}{RT}\int_T^{T_{if}} \Delta C_{pi}\mathrm{d}T + \frac{1}{RT}\int_{p_{if}}^{p} \Delta v_i \mathrm{d}p\right]. \tag{2.11}$$

The Solid- liquid equilibrium K factor is defined by

$$K_{is} = \frac{x_{is}}{x_{io}} = \frac{\gamma_{io}}{\gamma_{is}}\frac{f_{io}^0}{f_{is}^0}, \tag{2.12}$$

where:

K_{is} = solid/liquid K value for component i

x_{io} = mole fraction of component i in oil

x_{is} = mole fraction of component i in wax

y_{io} = activity coefficient of component i in oil

y_{is} = activity coefficient of component i in wax

$\boldsymbol{f}^{o}_{io}$= fugacity of pure component i in oil

$\boldsymbol{f}^{o}_{is}$= fugacity of pure component i in wax

Substituting equation 2.11 into equation 2.12, we have;

$$K_{is} = \frac{x_{is}}{x_{io}} = \frac{\gamma_{io}}{\gamma_{is}} \exp\left[\frac{\Delta H_{if}}{RT}\left(1 - \frac{T}{T_{if}}\right) + \frac{1}{R}\int_{T}^{T_{if}} \frac{\Delta C_{pi}}{T} dT - \frac{1}{RT}\int_{T}^{T_{if}} \Delta C_{pi} dT + \frac{1}{RT}\int_{p_{if}}^{p} \Delta v_i dp\right]. \qquad 2.13$$

This is the model for wax deposition. All researchers have used a form of this model. Some, excluding some part of it. Coutinho (1996) and Lira- Gelena (1996) excluded the pressure term.ie the last component of the exponential. They assumed as negligible the contribution of pressure to wax crystallization. Their assumption is in line when considering laminar flow. Chung(1992) excluded both the pressure and heat capacity components. The non idealities of the oil and solid phases can also be considered small (i.e., γ_{io}/γ_{is} = 1) and the solid phase is assumed to be a pure component reducing the expression to the equation of ideal solubility otherwise known as the pure ideal solid model.

$$x_{io} = \exp\left[\frac{\Delta H_{if}}{R}\left(\frac{1}{T_{if}} - \frac{1}{T}\right)\right]. \qquad 2.14$$

Some did include some other components like Nichita et al (1999) and Ungerer et al.(1995) that included enthalpy of transmission components.

2.9.2 Description Of Solid Phase (Solid Solution Models)

The solid phase can either be described as a sum of independent pure (pseudo)components (like in Ratulawski et al,2000; Lira-Gelena et al,1996; and Pan et al,1997) or as a solid solution of all materials that crystallized. Erickson et al,1993; Coutinho et al,1996,2001; Won, 1986; and Hansen et al,1988; considered the solid solution ideal and adopted the regular solution model to describe it.

The Scatchard-Hildebrand (Prausnitz et al 1986) equation for activity coefficients and solubility parameters is

$$\ln \gamma_{ik} = \frac{v_{ik}\left(\delta_{ik} - \bar{\delta}_k\right)^2}{RT}, \qquad 2.15$$

where:

- δ_{ik} = solubility parameter for pure component *i* in phase *k*
- $\bar{\delta}_k$ = volume fraction average solubility parameter for phase *k*

The volume fraction average solubility parameter for a phase is given by:

$$\bar{\delta}_k = \sum_{i=1}^{n_c} \Phi_{ik}\delta_{ik}; \quad \Phi_{ik} = \frac{x_{ik}v_{ik}}{\sum_{j=1}^{n_c} x_{jk}v_{jk}}. \qquad 2.16$$

At conditions far removed from the critical point, the solubility parameter for a component in the oil phase may be expressed in terms of the enthalpy of vaporization and the molar volume of the component.

$$\delta_{io} = \left(\frac{\Delta H_{iv} - RT}{v_{io}} \right)^{1/2} . \tag{2.17}$$

Won(1986) proposed a modified regular solution theory in which the solubility parameter for a component in the solid phase is given by

$$\delta_{is} = \left(\frac{\Delta H_{iv} + \Delta H_{if} - RT}{v_{is}} \right)^{1/2} . \tag{2.18}$$

With Equation 2.15 and assuming that $v_{is} = v_{io}$, the activity-coefficient ratio can be described by

$$\frac{\gamma_{io}}{\gamma_{is}} = \exp\left[\frac{v_{io}}{RT} \left(\left(\delta_{io} - \bar{\delta}_o \right)^2 - \left(\delta_{is} - \bar{\delta}_s \right)^2 \right) \right] . \tag{2.19}$$

Substituting Equation 2.19 into Equation 2.13 and assuming the pressure and heat-capacity terms are negligible gives the final equation used by Won(1986) for the solid/liquid K values as

$$K_{is} = \frac{x_{is}}{x_{io}} = \exp\left[\frac{\Delta H_{if}}{RT} \left(1 - \frac{T}{T_{if}} \right) + \frac{v_{io}}{RT} \left(\left(\delta_{io} - \bar{\delta}_o \right)^2 - \left(\delta_{is} - \bar{\delta}_s \right)^2 \right) \right] . \tag{2. 20}$$

Won also presented correlations for the heat of fusion, temperature of fusion, and molar volume as functions of molecular weight and tabulates values of the solubility parameters for the liquid and solid phases. The correlations are applicable to normal paraffins. The heat of fusion is given by

$$\Delta H_{if} = 0.1426\, M_i T_{if} , \tag{2.21}$$

where M_i is the molecular weight of component i. The heat of fusion from Equation 2.21 is approximately equal to the sum of the heat of fusion and one-half the heat of transition for molecules heavier than C_{22} and approximately equal to the heat of fusion for odd carbon number molecules lighter than C_{22}. The temperature of fusion is given by

$$T_{if} = 374.5 + 0.02617\,M_i - 20172 / M_i, \qquad 2.22$$

and the molar volume is given by

$$v_{io} = M_i / \left(0.8155 + 0.6272 \times 10^{-4} M_i - 13.06 / M_i\right). \qquad 2.23$$

In Won's(1986) model, solid/liquid/vapor equilibrium is determined. Liquid/vapor *K* values are calculated with the Soave-Redlich-Kwong EOS (Soave 1972). These *K* values are used with the solid/liquid *K* values in a three-phase flash algorithm to determine the solid/liquid/vapor-phase split as a function of temperature and pressure. Some others adopted a free energy model to decsibe its non-ideality (like Coultinho 1998, 2000 Coultinho et al 1995,1996 and Pauly et al 2000).

2.9.3 Description Of Liquid Phase (Liquid Solution Models)

For low velocity systems(Laminar flow), the liquid phase is either considered ideal (like in Erikson et al,1993; and Coultinho et al,2001) or is described using a free energy model (like in Won,1986; Hansenet al,1988; Coultinho et al, 1996; and Lira-Gelena et al, 1996).

For the ideal solution model, the activity coefficients are calculated using equation 2.19. Correlations are given for the solubility parameters of paraffins in the oil and solid phases as

$$\delta_{io} = 7.41 + a_1\left(\ln C_i - \ln 7\right) \qquad 2.24$$

and $\delta_{is} = 8.50 + a_2\left(\ln C_i - \ln 7\right).$ 2.25

where C_i is the carbon number of component *i*.

The the enthalpy of formation is given by;

$$\Delta H_{if} = a_3(0.1426\, M_i T_{if}), \qquad 2.26$$

And the heat capacity difference given by;

$$\Delta C_{pi} = a_4 M_i + a_5 M_i T. \qquad 2.27$$

Constants a_1 through a_5 were determined by a least-squares fit to the data of Pedersen et al(1991)as:

- $a_1 = 0.5914\ (\mathrm{cal/cm^3})^{0.5}$
- $a_2 = 5.763\ (\mathrm{cal/cm^3})^{0.5}$
- $a_3 = 0.5148$
- $a_4 = 0.3033\ \mathrm{cal/(g{\bullet}K)}$
- $a_5 = 0.635\times10^{-4}\ \mathrm{cal/(g{\bullet}K^2)}$

Some authors described the liquid phase using an equation of state(like in Lira-Gelena,1996; Mei et al (1999)Pan et al,1997; and Pauly et al,2000). Mei et al (1999) for instance, used the Pen-Robinson EOS(1976), calculated solid solubilities with the correlation from Thomas et al(1992), enthalpy of fussion, temperature of fussion and molecular volume from Won(1986), and heat capacity from Pedersen(1995)'s correlation. Brown et al(1994) used the Soave-Redlich-Kwong EOS(1972) is used to determine the fugacity coefficients for liquid and vapor phases. These models then use a flash vaporization algorithm to calculate the solid content of the mixtures at given temperatures and pressure

CHAPTER THREE

MATERIALS AND METHODS

3.0 METHODOLOGY

Temperature, more than any other factor, influences wax precipitation from oil and subsequent deposition on pipe walls. The temperature at which precipitation starts is the cloud point also known as WAT. The temperature at which deposition starts is the pour point also known as the WDT. Three samples collected from different fields in the Niger delta, ten days after pigging, were Characterized and tested (cooled) and their wax contents determined at 0^0C. A pipeline simulator PIPESIM software was used to simulate field conditions and determine the wax content of the samples at various temperatures, and wax content at 0^0C with time. The simulator results were compared with the laboratory results on a spreadsheet.

3.1 LABORATORY TESTS (CONTROL)

3.1.1 Sample Characterization

The samples were analysed using Gas Chromatography to determine their SCN (Single Carbon Number) fractions. Fluid properties like molecular weights and densities were determined. Flow parameters like viscosity, water cut and wax content were determined for each sample (Tables 3.1.1 to 3.1.6) The results obtained from the laboratory experiments were used as the controls against which other results were compared.

3.1.2 Wax Content Laboratory Test

The paraffin cold finger deposition test was used to determine the sample wax content. The samples were cooled to 0^0C (273 k) and the amount of wax precipitated was scrapped and measured. 100g, ie 0.1kg sample was used for the test. The amount of wax deposited at 0^0C was measured and given in percentage (%) of the sample. Results are shown in Tables 3.1.2, 3.1.4 and 3.1.6 of the Appendix.

3.2 SIMULATION USING PIPESIM

3.2.1 Wax Content Determination Using PIPESIM

The software PipeSim was used to simulate field conditions using data on Pipe dimensions, Pigging schedule, pump pressures and heat transfer rates. With these conditions and the fluid composition, PipeSim modelled the process (Fig 3.2.1 of Appendix) and calculated amount of deposited wax at 0^0C for each of the sample.

Table 3.2.1 Data for Simulation (sample A)

Ambient temperature	20^oc
Validation/source temperature	0^oc
Thermal conductivity (Bare and in ground)	150 Btu/hr/ft
Pipe dimensions	10inches x 19.4km
Pump discharge pressure	100psi
Density of sample A Sample collection time	806 kg/m^3 10 days after pigging(240 hours)
Calculated Wax volume in sample A	0.00016 ft^3 = 0.0002 ft^3

Table 3.2.2 Data for Simulation (sample B)

Ambient temperature	20^oc
Validation/source temperature	0^oc
Thermal conductivity (Bare and in ground)	150 Btu/hr/ft
Pipe dimensions	10inches x 19.4km
Pump discharge pressure	100psi
Density of sample A Sample collection time	836 kg/m^3 10 days after pigging (240 hours)
Calculated Wax volume in sample A	0.00303 ft^3 = 0.003 ft^3

Table 3.2.3 Data for Simulation (sample C)

Ambient temperature	20^oc
Validation/source temperature	0^oc
Thermal conductivity (Bare and in ground)	150 Btu/hr/ft
Pipe dimensions	10inches x 19.4km
Pump discharge pressure	110psi
Density of sample A Sample collection time	830 kg/m^3 10 days after pigging(240 hours)
Calculated Wax volume in sample A	0.00015 ft^3 = 0.0002 ft^3

3.2.2 Wax Content Determination With Time

The simulation end time was extended from 240 hrs (10 days) to 720 hrs (30 days) and eventually to 4months, at the same operating conditions of temperature, pressure and flow rate to determine the effect of time on the volume of wax deposited. Results gotten were converted to percentage to account for the part volume of sample taken

(0.1 kg) during laboratory experiment. This was used to recommend a time range for pipeline pigging.

3.2.3 Calculating Cloud Point

PipeSim was also used to determine the cloud point of the samples. Simulation for Critical Wax Deposition Temperatures (CWDT) was run and the values in the tables 3.2.3.1 to 3.2.3.3 obtained.

3.3 MODELLING WAX DEPOSITION WITH VARIOUS CORELATIONS

The equilibrium factor equation which is the foundation of all wax deposition models is given by

$$K_{is} = \frac{x_{is}}{x_{io}} = \frac{\gamma_{io}}{\gamma_{is}} \exp\left[\frac{\Delta H_{if}}{RT}\left(1 - \frac{T}{T_{if}}\right) + \frac{1}{R}\int_{T}^{T_{if}} \frac{\Delta C_{pi}}{T} \mathrm{d}T - \frac{1}{RT}\int_{T}^{T_{if}} \Delta C_{pi} \mathrm{d}T + \frac{1}{RT}\int_{p_{if}}^{p} \Delta v_i \mathrm{d}p\right]. \qquad 3.3.1$$

All the parameters are as defined in chapter two. The Activity coeffient is given by

$$\frac{\gamma_{io}}{\gamma_{is}} = \exp\left[\frac{v_{io}}{RT}\left(\left(\delta_{io} - \bar{\delta}_o\right)^2 - \left(\delta_{is} - \bar{\delta}_s\right)^2\right)\right]. \qquad 3.3.2$$

All the parameters are also as defined in the previous chapter.

The equilibrium K factor was narrowed down, for this investigation, to the equation for ideal solubility (equation 2.14) which assumes that the molar volume (pressure term) and heat capacity parameters are negligible, the non-idealities of the oil and solid phases are small and that the solid phase is a pure component. Equation of ideal solubility *Xi* is given as;

$$x_{io} = \exp\left[\frac{\Delta H_{if}}{R}\left(\frac{1}{T_{if}} - \frac{1}{T}\right)\right]. \qquad 3.3.3$$

Consequently, results from the model could not be compared with those obtained through experiment and simulation.

3.3.1 WON'S CORRELATIONS

Won(1986) correlation for finding the enthalpy of fusion and the melting point temperature are given as;

$$T_i^f = 374.5 + 0.02617 * \text{Mwi} - \frac{20172}{Mwi} \qquad 3.3.4$$

$$\Delta H_i^f = 1.14 * 0.1426 * \text{Mwi} * T_i^f \qquad 3.3.5$$

3.3.2 CHUNG'S CORRELATIONS

Chung(1992) made slight adjustment to Won's equation for heat of fusion

$$\Delta H_i^f = 0.9 * \text{Mwi} \wedge 0.55 * T_i^f \qquad 3.3.6$$

3.3.3 COUTINHO'S CORRELATION

Coutinho's equation for melting point temperature is given by

$$T_i^f = 421.63 - 1936112.63 \exp(-7.8945\ (N-1)^{0.07194}) \qquad 3.3.7$$

And the enthalpy of fusion is given as

$$\Delta H^f = 1000\ (3.7791\ \text{N} - 12.654) \qquad 3.3.8$$

Where "N" is the carbon number.

For n-paraffins below a carbon number of 42 (but greater than 4), the melting temperature is given as:

$$T_i^f = 421.63 - 1936112.63 \exp(-7.8945\ (N-1)^{0.07194}) \qquad 3.3.9$$

The enthalpy of fusion can be obtained from the following correlation,

$$\Delta H^f = 1000\ (-0.00355N^3 + 0.2376\ N^2 - 3.6209\text{N} + 18.5391) \qquad 3.3.10$$

These models were used with a flash equilibrium algorithm to determine solid moles in a sample of crude oil at 0^0C.

3.4 EQUILIBRIUM FLASH VAPORIZATION CALCULATION

The equilibrium or flash vaporization calculations are made for a mixture that separates into liquid and solid phase at a certain temperature and pressure, with the solid and liquid being in equilibrium.

Taking, F = moles of feed

S = moles of solid

L = moles of liquid

Z = mole fraction of a constituent in the feed

Wi = mole fraction of a constituent in the solid

Xi = mole fraction of a constituent in the liquid

i = any constituent.

At equilibrium

$$K_i = \frac{W_i}{X_i} \qquad 3.4.1$$

Performing the overall material balance of the system shows that

$$F = S + L \qquad 3.4.2$$

Doing the material balance on a constituent indicates that

$$Zi\ F = Wi\ S + Xi\ L \qquad 3.4.3$$

From equation 3.4.1,

$$Xi = \frac{Wi}{Ki} \qquad 3.4.4$$

Substituting equation 3.4.4 into 3.4.3

$$Zi\ F = Wi\ S + \frac{Wi\ L}{Ki}$$

$$Zi\ F = Wi\ (S + \frac{L}{Ki}) \quad = \quad Wi\ (\frac{ki\ S + L}{Ki})$$

$$Wi = \frac{Zi\,F\,Ki}{Ki\,S + L} \qquad 3.4.5$$

Let F = 1 then equation 3.4.5 becomes

$$Wi = \frac{Zi\,Ki}{Ki\,S + L} \qquad 3.4.6$$

From equation 3.4.2

$$L = F - S \qquad 3.4.7$$

Substituting equation 3.4.7 into 3.4.6

$$Wi = \frac{Zi\,Ki}{Ki\,S + F - S} \qquad 3.4.8$$

Since F = 1 then equation 3.4.8 becomes

$$Wi = \frac{Zi\ Ki}{Ki\,S + 1 - S}$$

$$Wi = \frac{Zi\,Ki}{S\,(Ki - 1) + 1} \qquad 3.4.9$$

From equation 3.4.8

$$Wi = Ki\ Xi \qquad 3.4.10$$

Substituting equation 3.4.10 into 3.4.3

$$Zi\ F = Ki\ Xi\ S + Xi\ L$$

$$Zi\ F = Xi\ (Ki\ S + L)$$

Then $Xi = \frac{Zi\,F}{Ki\,S + L}$ 3.4.11

From equation 3.4.2

$$L = F - S \qquad 3.4.12$$

Substitute equation 3.4.12 into 3.4.11

$$Xi = \frac{Zi\,F}{Ki\,S + F - S}$$

$$Xi = \frac{Zi\,F}{Ki\,S - S + F} \qquad 3.4.13$$

Let F = 1 then equation 3.4.13 becomes

$$Xi = \frac{Zi}{S\,(Ki-1\,)+\,1} \qquad 3.4.14$$

Given the following values

- Composition of the sample (feed)
- Equilibrium constant (Ki)
- Temperature and pressure
- And assumed value of S

Therefore, subtracting equation 3.4.14 from 3.4.9 i.e. Wi - Xi

$$\frac{Zi\,Ki}{S\,(Ki\,-1)+1} - \frac{Zi}{S\,(Ki-1\,)+\,1} = \frac{Zi\,Ki\,-Zi}{S\,(Ki-1\,)+\,1} = \sum\frac{Zi\,(\,ki-1)}{S\,(Ki-1\,)+\,1} \qquad 3.4.15$$

Using Newton Raphson iteration method

$$\frac{\partial}{\partial s}\left[\sum\frac{Zi\;\,(Ki-1)}{S\,(Ki-1\,)+\,1}\right] = \sum\frac{Zi\,(Ki\,-1)^2}{[S\,(Ki\,-1)+\,1]^{\,2}} \qquad 3.4.16$$

Hence,

$$S_2 = S_1 + \frac{\sum\frac{Zi\;\,(Ki-1)}{S\,(Ki-1\,)+\,1}}{\sum\frac{Zi\,(Ki\,-1)^2}{[S\,(Ki\,-1)+\,1]^{\,2}}} \qquad 3.4.17$$

A MathLab programme was written to calculate the moles of solids in a sample of crude.

3.5 MathLab Programme for various correlations

3.5.1 Won’s model (Sample 1)

```
z  = [3.99 0.7 0.13 0.12 0.14 0.24 0.24 1.08 1.93 8.06 7.14 12.28 13.06 13.6 12.79
8.96 7.71 3.09 1.69 1.48 0.54 0.25 0.13 0.07 0.03 0.01 0.01 0.01 0.01 0.01 0.01
0.02]/100;
Mi = [16 30 44 58 58 72 72 84 96 107 121 134 147 161 175 190 206 222 237 251
263 275 291 300 312 324 337 349 260 372 382 580];
Tif = 374.5+(0.02617.*Mi)-(20172./Mi);
Hf = 1.14.*0.1426.*Mi.*Tif;
T = 0+273;
R = 8.314;
k =(exp(Hf/(R.*T).*1-T./Tif));
for s = 0.001:0.0001:0.1
   C = sum((z.*(k - 1))./(s.*(k - 1) + 1))/sum((z.*(k - 1).^2)./((s.*(k - 1) + 1).^2));
   A = abs(s+C);
   tol = abs(A-s);
   if tol < 0.00001
      break
   end
   disp([tol s])
end
```

3.5.2 Chung’s model (Sample 1)

```
z  = [3.99 0.7 0.13 0.12 0.14 0.24 0.24 1.08 1.93 8.06 7.14 12.28 13.06 13.6 12.79
8.96 7.71 3.09 1.69 1.48 0.54 0.25 0.13 0.07 0.03 0.01 0.01 0.01 0.01 0.01 0.01
0.02]/100;
Mi = [16 30 44 58 58 72 72 84 96 107 121 134 147 161 175 190 206 222 237 251
263 275 291 300 312 324 337 349 260 372 382 580];
Tif = 374.5+0.02617.*Mi-(20172./Mi);
Hf = 0.95.*Mi.^0.53.*Tif;
T = 0+273;
R = 8.314;
k =(exp(Hf/(R.*T).*1-T./Tif));
for s = 0.001:0.0001:0.1
   C = sum((z.*(k - 1))./(s.*(k - 1) + 1))/sum((z.*(k - 1).^2)./((s.*(k - 1) + 1).^2));
   A = abs(s+C);
   tol = abs(A-s);
   if tol < 0.00001
      break
   end
   disp([tol s])
end
```

3.5.3 Coutinho’s model (Sample 1)

```
% for coutinho for C2 to C30
z  = [3.99 0.7 0.13 0.12 0.14 0.24 0.24 1.08 1.93 8.06 7.14 12.28 13.06 13.6 12.79
8.96 7.71 3.09 1.69 1.48 0.54 0.25 0.13 0.07 0.03 0.01 0.01 0.01 0.01 0.01 0.01
0.02]/100;
T = 0+273;
R = 8.314;
N = [5 5 6:30];
Tf = 421.63-1936112.63.*exp(-7.8945.*((N-1).^0.07194));
Hf = 1000*(-0.00355.*N.^3+0.2376.*N.^2-3.6209.*N+18.539);
k = [0 0 0 0 0 exp(Hf/(R.*T).*1-T./Tf)];
for s = 0.001:0.0001:1
    C = sum((z.*(k - 1))./(s.*(k - 1) + 1))/sum((z.*(k - 1).^2)./((s.*(k - 1) + 1).^2));
    A = abs(s+C);
    tol = abs(A-s);
    if tol < 0.00001
        break
    end
    disp([tol s])
end
```

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 RESULTS

The laboratory tests run to determine wax content of the fluid samples have the results on tables 3.1.1 to 3.3.2 of the Appendix. A summary of the results are presented below. This result is the control against which other methods are validated.

Table 4.1 Wax Content of Samples

Samples	**Wax content(% wt of sample)**
A	**3.73**
B	**4.77**
C	**3.45**

The PipeSim simulated wax deposition was run at 0^0C and for 240 hours (10 days) because the samples were collected ten days after pigging. The results are presented in Figures 4.1 to 4.3 of the Appendix. Below is a summary of the results in comparism against the control:

Table 4.2 Comparism of wax content results

Sample	**Laboratory result**	**PipeSim result**
A	3.73%	3.71%
B	4.77%	4.78%
C	3.45%	3.49%

Graphical presentations of this comparism for each sample is shown in figures 4.14 to 4.16 of the Appendix

4.1 Wax deposition with Time

Wax content simulation time as extended to 30 days (720hrs, one month) and then to 4months for each sample. The graphs are presented in Figures 4.4 to 4.6 of the Appendix. A summary of wax deposits with time is presented in the graph below. These results indicates that it would be dangerous to ignore pigging the pipeline transporting this crudeoil up to four months (unless another control method like chemical injection is in place). It is advisable to pig monthly to avoid incidences of stuck pigs.

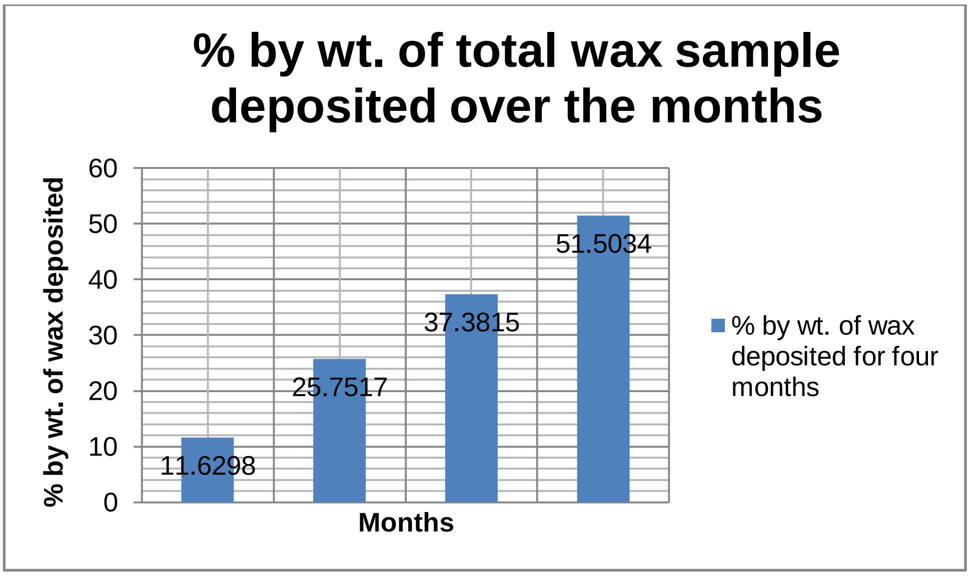


Figure 4.2.7 Simulated percentage wax content with time for sample A

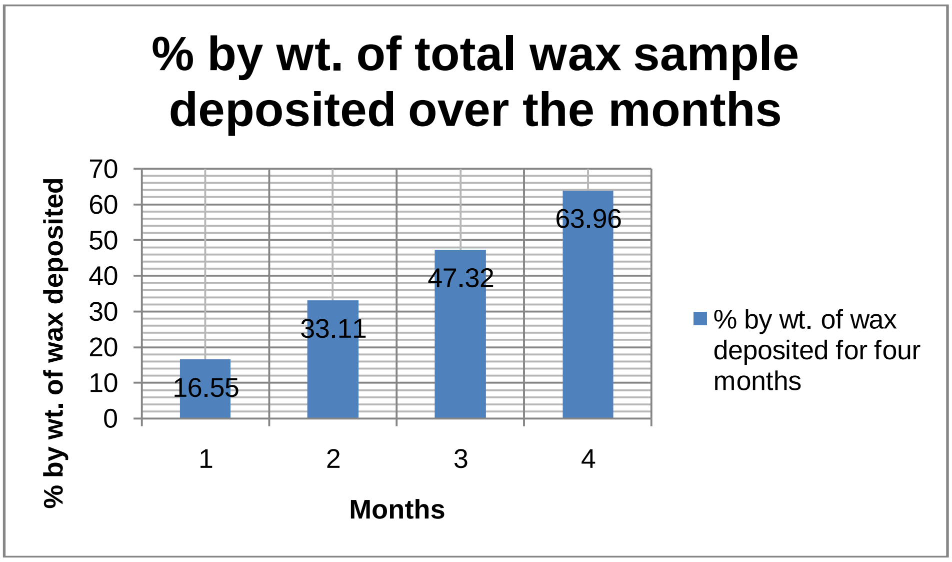


Figure 4.2.8 Simulated percentage wax content with time for sample B

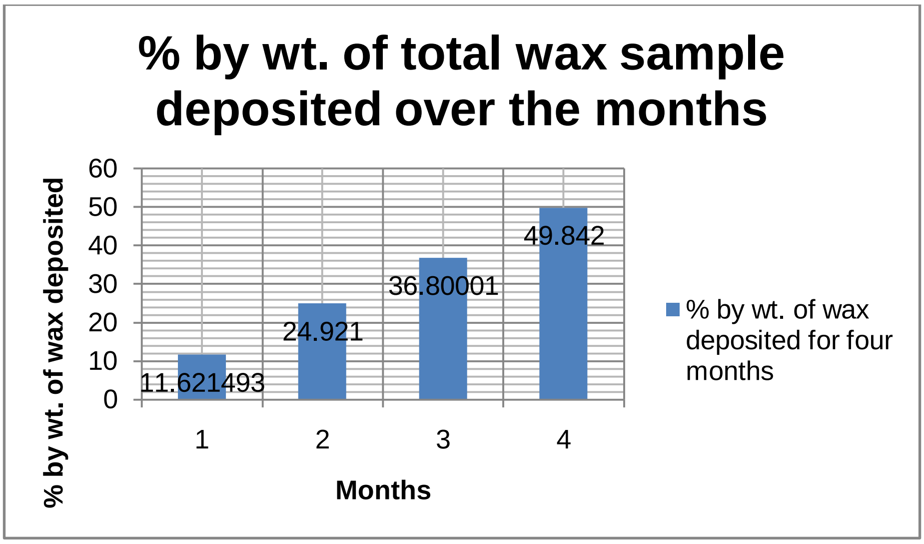


Figure 4.2.9 Simulated percentage wax content with time for sample C

4.2 Cloud Point Determination using PipeSim

The results of the Critical wax deposition temperature determination using PipeSim were presented in table 4.3.1 of the Appendix.

4.3 Comparism of correlations

From the MATLAB programme generated to perform the equilibrium flash calculation, the results for the various models were presented graphically for temperature range of -10^{0}C to 60^{0}C in Appendix 4.(Figures 4.3.1 to 4.3.3) The Comparison of mole fractions in solid phase for the Won, Chung and Coutinho models were summarised in the table below:

Table 4.4.1 Moles of solid from various corelations

Moles of solids Si at 0^{0}C	**Sample 1**
Won	**0.9953**
Chung	**0.9740**
Coutinho	**0.8424**

4.4 DISCUSSION AND ANALYSIS OF RESULTS

Wax deposition was investigated using three different methods; Laboratory tests, Simulation with PipeSim and Mathematical correlations. Wax depositions evaluated at 0^0C were compared.

The laboratory tests results are the control. They include sample compositions with mole fractions, density, viscosity and wax content in weight percent of the samples (Tables 3.1.1 to 3.3.2 of the Appendix). The wax contents were measured at 0^0C. The wax volume was calculated using mass of the wax content and the density of the sample. This volume was converted to cubic ft (ft^3).

The Simulation which took cognisance of field conditions (Figures 3.1), time of sample collection and sample compositions, determined the amount of wax that can be deposited at zero degrees Celsius (Figures 4.1.1 to 4.1.3) for each sample. Simulation and control results were compared and showed a good match (Table 4.2 and figures 4.1.4 to 4.1.6) with a difference of less than $\pm$0.05%.

Having determined wax content after ten days (24 hours), the simulation end time was extended to determine wax deposition after longer periods of one (figures 4.2.1, 4.2.3 and 4.2.5) and four months (figures 4.2.2, 4.2.4 and 4.2.7). The results of simulated wax content after one and four months indicate possible deposition rates. Hence, it can be used to draw schedules for pigging. The graphical representations of simulated percentage wax content with time (figures 4.2.7 to 4.2.9) indicate that wax left unchecked in a pipeline conveying crude oil samples A, B, and C will wax up to about 50% in four months. This poses such consequences as pipe replacement, production deferment, back pressure that can kill low pressure/low rate wells, inefficiency of control methods like pipe re-start because of wax aging, etc

The simulation was also run to determine the Critical wax deposition temperature (Tables 3.4 to 3.6 and 4.3). The essence of this is that it should be inbuilt in the plant design ensuring that the fluid temperature does not fall as low as this value. This can be achieved using heater treaters.

Mathematical correlations for melting point temperatures and heat of fussion from Won(1980), Chung(1992), and Coutinho's(1996) research works were used in Mathlab programmes to calculate moles of solid that can be deposited out of the first sample at -10^{0}C to 60^{0}C(3.8 Mathematical models). At zero degrees Celsius, the numbers of moles of solids according to the different models were compared (Table 4.4.1). The result from Won's model gave the highest estimate of the solids moles. It is the oldest of the three models and more recent works have made improvements on it having confirmed that it gives an over-estimate of solid moles when compared with other models and laboratory results (Lira-Gelena 1996, Pedersen et al 1991). The Chung model which is an improvement on Won's model gave a lesser estimate. The Coutinho model which is the most recent of the three gave the least estimate.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.0 CONCLUSION

1. Wax deposition which is the most prevalent flow assurance issue in production facilities was investigated with crude oil samples from the Niger delta region.
2. The sample compositions indicate paraffinic nature of crude oil waxes from this region.
3. Wax content of the samples were measured at the laboratory at 0^0C
4. PipeSim software was used to simulate operating conditions and consequently, calculate wax content at 0^0C. It also simulated wax deposition as a function of time.
5. The results from laboratory tests were compared with PipeSim results, producing a good match with less than ±0.5% difference for each of the samples.
6. The simulated percentage wax content with time indicate that if wax deposition is left unchecked in a pipeline conveying crude oil samples A, B, and C will wax up to about 50% in four months. This poses such consequences as pipe replacement, production deferment, back pressure that can kill low pressure/low rate wells, inefficiency of control methods like pipe re-start because of wax aging.
7. The results of Solid moles calculated from the mathematical models indicate that the Won and Chung models over estimate amount of wax deposits when compared to the Coultinho model.

8. The inconclusive application of the mathematical models based on equilibrium correlations gave results that deviated greatly from the control even as activity coefficients and pressure parameters were yet to be included.

5.1 RECOMMENDATION

1. Prarffinic wax deposition strongly depends on temperature, so fluid heat loss should be minimized in plant design through pipe insulation.

2. Fluid temperatures should be maintained above the WDT and possibly above the WAT. Heater treaters should be included in plant design. Hot oiling and pipe heating can also be employed as a control measure to melt already deposited wax.

3. Solvents and other chemicals used to checkmate wax deposition should be field tested for optimal results and to minimize aggravating wax deposition problems and emulsions.

4. Regular pigging is recommended in plants handling waxy crudes to avoid incidences of stuck pigs, and mitigate against wax build up.

5. Wax content calculated with PipeSim software gave a good match with the control and so can be used for predictions where laboratory data is not readily available. It was also used to predict wax depositions in the pipeline with time, indicating that when left too long, as in the case of 4months, over 50% of the pipeline will be filled with wax. This can be used to prepare pigging schedules and plan other wax control measures.

5.2 Contributions to Knowledge

1. Samples from Niger delta were used in this work, analysing their wax forming tendencies and successfully determining wax content with PipeSim softwear which agreed with the Control result. PipeSim can therefore be used to predict wax content and prepare preventive and or control methods to tackle it.
2. The ideal solubility model using Won, Chung and Coutinho’s correlations gave results that greatly deviated from the Control even as activity coefficients and pressure parameters were yet to be included.

NOMENCLATURE

A = Depositional area

C_w = Concentration of precipitated wax

D_i = Effective diffusion coefficient

ρ_{oil} = Density of oil

μ_i = Chemical Potential

F = mole of feed

f_i^s = Fugacity of component in solid phase

f_i^l = Fugacity of component in liquid phase

K = Equilibrium constant

L = Mole of liquid

Mi = Mass component

Mw = molar weight

N = Carbon number

P = pressure

r = radial distance

R = Gas constant

S = Mole of solid

T = Temperature of the sample

t = Time

T^f = melting point temperature

Vi = molar volume of component i

Wi = Weight fraction

Wsi = Weight fraction of component in solid phase in the mixture

Wti = Weight fraction of component in the solid phase

Xi = mole fraction of constituent in solid phase.

Y = shear rate

y_i = Activity coefficient

Z = mole fraction

ΔH^f = Heat of fusion/enthalpy

ΔH^v = Heat of vaporization/enthalpy

ΔCp = Difference of heat capacity

δ^l = Solubility parameter for liquid

δ^s = Solubility parameter for solid

$\bar{\delta}$ = Average solubility

F = moles of feed

S = moles of solid

L = moles of liquid

i = any constituent.

mi = mass of component i

t = time

ρ_{oil} =density of oil

Di = effective diffusion coefficient for component i

A = deposition area,

wi = weight fraction of component i

r = radial distance.

LIST OF ABBREVIATIONS

ASTM	American Society for Testing Materials
Cn	Organic Compound of n carbon atoms
CnHn	Hydrocarbon of n carbon atoms and n hydrogen atoms
n-paraffins	Normal paraffins or Saturated straight chain paraffins
iso-paraffins	Branched chain paraffins
IB/1000BBL	Pounds per thousand barrels
WAT	Wax Appearance Temperature
PIG	Pipeline Inspection (and cleaning) Tool
PPM	Parts per Million
EOS	Equation of State
EOR	Enhanced Oil Recovery
WDT	Wax Deposition Temperature
SCN	Single Carbon Number
SARA	Saturates Aromatics Resins and Asphaltene
PNA	Paraffins Napthanates and Aromatics
CWDT	Critical Wax Deposition Temperature

REFERENCES

Adewusi .A. Victor (1997) ‘Prediction of wax deposition potential of hydrocarbon systems from viscosity-pressure correlations’ Sience Direct vol 76(12) : 1079-1083, doi:10.1016/S0016-2361(97)00083-5 Elsevier Ltd.

Alberto Di Lullo (2012) ‘Discover a Career: Flow Assurance’ THE WAY AHEAD Magazine Vol. 8 // No. 1 // 2012 pg 24-25

A.Hammami, J. Ratulowski, and J. A. P. Coutinho(2003)’ Cloud points: can we measure or model them’ Oilphase-DBR.,A Schlumberger Company, 9419-20 Avenue, Edmonton, Canada T6N 1E5

Ahmed Hanmani, Mike Raines "Paraffin Deposition from Crude Oils: Compassion of Laboratory Results to Field Data" SPE 28776 Presented at SPE Annual Technical Conference San Antonio Texas. October 1999.

Ajienka, J. A. (1983) The effect of Temperature on rheology of Waxy crude oils and its implication in production operation, Ph. D Dissertation, University of Port-Harcourt, Nigeria.

Ajienka, J.A. and Ikoku, C.V, (1997). Waxy crude oil handling in Nigeria: practices, problems and prospects, Energy sources , Vol. 12. No. 4. pp. 463-478.

Altgelt K.H, Boduszynski M. “Composition and analysis of heavy petroleum fractions” New York: Dekker, 1994.

Allen O.T, Roberts A.P (1982) ‘Wax Deposition’ Production Operations Vol 2. 2nd Edition, Oil and Gas Consultants Inc. Oklahoma

Billingsley, D.L “How To Control Paraffin Wax In Shallow Pumping Wells’’. World Oil, July 1963

Brown, T.S., Niesen, V.G., and Erickson, D.D. 1994. The Effects of Light Ends and High Pressure on Paraffin Formation. Presented at the SPE Annual Technical Conference and Exhibition, New Orleans, 25-28 September. SPE-28505-MS.

Burger , Perkin and Sriegler, (1981). ‘Studies of wax deposition in the Trans Alaska pipeline’, Journal of Petroleum TBechnology, June (1075-1086).

Chung T.H, (1992) ‘Thermodynamic Modelling for Organic Solid Precipitation’ SPE 24851, 67th Annual Technical Conference and Exhibition-Washington DC, October 1992.

Coutinho, J.A.P. and Stenby, E.H. 1996. Predictive Local Composition Models for Solid/Liquid Equilibrium in n-Alkane Systems: Wilson Equation for Multicomponent Systems. Industrial Engineering Chemistry Research **35**: 918.

Elijah Taiwo, John Otolorin and Tinuade Afolabi (2012). Crude Oil Transportation: Nigerian Niger Delta Waxy Crude, Crude Oil Exploration in the World.

Elsharkawy A.M, Al-sahhaf T.A, Fartim M.A(1999) "wax deposition from middle east crudes" Engineering. Vol, 18, No. 04. December, 2001. Pg. 411-422.; 79:104-55.

Erickson, D.D., Niesen, V.G., and Brown, T.S. 1993. Thermodynamic Measurement and Prediction of Paraffin Precipitation in Crude Oil. Presented at the SPE Annual Technical Conference and Exhibition, Houston, 3-6 October. SPE-26604-MS.

Flory, P.J. 1953. *Principles of Polymer Chemistry*. Ithaca, New York: Cornell University Press.

Gao S. ,Chapman G.W (2006)' Detecting Gas Hydrate Behaviour in Crude oil using NMR' J. Phy. Chem. B 110 (13): 6549-6552.

Hansen, J.H., Fredenslund, A., Pedersen, K.S. et al. 1988. A thermodynamic model for predicting wax formation in crude oils. *AIChE J*. **34** (12): 1937-1942.

J. A.P. Coutinho, J. Pauly and J. Daridon (2003) 'Modelling phase equilibria in systems with organic solid solutions' Presented at Departamento de Química da Universidade de Aveiro, 3810-193 Aveiro, Portugal and Laboratoire des Fluides Complexes, Université de Pau et des Pays de l'Adour, 64013 Pau Cedex, France.

Jessen, F.W and Howell, J.N; "Effect of Flow Rate on Paraffin Accumulation in Plastic, Steel and Coated Pipe" Trans. AIME 1958, 80 – 84

Keating J.F. and Wattenbarger R.A.: "The Simulation of Paraffin Deposition and Removal in Wellbores", paper SPE 27871 presented at the 1994 SPE Western Regional meeting, Long Beach, California, 23-25 march.

Knox, J.A., Waters, A.B., and Arnold, B.B.: 'Checking Paraffin deposition by Crystal Growth Inhibition' SPE 443, 37th Annual Fall Meeting, Los Angeles, Califonia, 1962.

Larry .W.D (1952) 'Petroleum engineering handbook vol 1 "Wax Precipitation from Petroleum Fluids: A Review," pages 557–608, Reprinted 2000.

Leontaritis, K.J. 1996. The Asphaltene and Wax Deposition Envelopes. Fuel Sci. Technol. Int. **14** (1-2): 13-39.

Leontarities, K.J. "Challenges and Solutions to asphaltene and wax deposition:Major economic problem for production operations" Offshore magazine, volume 58, issue 9, January, 1998.

Lira-Galeana, C., Firoozabadi, A., and Prausnitz, J.M. 1996. Thermodynamics of wax precipitation in petroleum mixtures. AIChE J. **42** (1): 239-248.

Long X. Nghiem and Bruce F. Kohse 'Asphalteen and Waxes', Petroleum Enginering Handbook Volume 1(2006),Society of Petroleum Engineering, Richardson Texas, USA.

Mansoori G.A ''The Occurance of Asphaltene Throughout Production Cycle: A Comprehensive Description of Mechanisms and Factors Influencing Heavy Organic Deposition'' ADSPE #2 October, 1994.

Mei, H., Kong, X., Zhang, M. et al. 1999. A Thermodynamic Modelling Method for Organic Solid Precipitation. Presented at the SPE Annual Technical Conference and Exhibition, Houston, 3-6 October. SPE-56675-MS.

Mitchell D.L and Speight J.G, " The solubility of Asphaltenes in Hydrocarbon solvents", fuel (April 1973) 149.

Nalco Energy Services (2004) 'Paraffins' and 'Asphaltene' Oil field ChemicalsTraining Manual. Capex College, Nalco Energy Services, Sugar land, Texas.

Nathan, C.C (1955) 'Solubility studies on High molecular Weight Paraffin Hydrocarbons Obtained from Petroleum Rod Waxes' Trans. AIME Vol. 204

Nichita, D.V., Goual, L., and Firoozabadi, A. 1999. Wax Precipitation in Gas Condensate Mixtures. Presented at the SPE Annual Technical Conference and Exhibition, Houston, Texas, USA, 3-6 October. SPE-56488-MS.

Oladiipo A., Bankole A. and Taiwo E (2009) Artificial Neural Network Modeling of Viscosity and Wax Deposition Potential of Nigerian Crude Oil and Gas Condensates. 33rd Annual SPE International Technical Conference and Exhibition in Abuja, Nigeria, August 3-5, 2009. SPE 128600

Pan, H., Firoozabadi, A., and Fotland, P. 1997. Pressure and Composition Effect on Wax Precipitation: Experimental Data and Model Results. *SPE Prod & Operations* **12** (4): 250-258. SPE-36740-PA.

Pedersen, W.B., Hansen, A.B., Larsen, E. et al. 1991. Wax precipitation from North Sea crude oils. 2. Solid-phase content as function of temperature determined by pulsed NMR. *Energy Fuels* **5** (6): 908-913.

Peng, D.-Y. and Robinson, D.B. 1976. A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals* **15** (1): 59–64.

Pfeiff J.P. and Saal R.N.: “ Asphaltic Bitumen as colloidal system,” physical chemistry (1940) 44, 139.

Prausnitz, J. M., R. N. Lichtenthaler, and E. G. Azevedo(1986). Molecular Thermodynamics of Fluid Phase Equilibria, Chap. 9, Prentice-Hall, Englewood Cliffs, NJ (1986).

Prausnitz, J.M., Lichtenthaler, R.N., and de Azevedo, E.G. 1999. *Molecular Thermodynamics of Fluid-Phase Equilibria*, third edition. Upper Saddle River, New Jersey: International Series in the Physical and Chemical Engineering Sciences, Prentice Hall PTR.

Reddy, S.R. 1986. A thermodynamic model for predicting n-paraffin crystallization in diesel fuels. *Fuel* **65** (12): 1647-1652.

Reistel, C.E. “paraffin and congealing oil problem” Bull USBM (1932), No. 348.14 March 2014, ‘Smart solutions to subsea pipeline blockages’ Offshore technology Jornal.

Speight J.G, Long R.B, and Trowbridge T.D, “Factors Influencing the Separation of Asphaltenes From Heavy Petroleum Feedstocks,” Elsevier Science, 1984.

Speight, J.G.: The Chemistry and Technology of Petroleum, Marcel Dekker, New York City (1991).

Saad Al-Safeel ‘‘Electro Kinetic Aspects of Asphaltene Deposition in Petroleum Reservoir’’ ADSPE #26 October, 1994.

Shock D.A, Sudbury, I.D. and Crockett J.J (1955), “Studies of Mechanism of Paraffin Deposition and its Control”. JPT (sept).

Soave, G. 1972. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci*. **27** (6): 1197–1203.

Skovborg .K, Schou Pedersen and Roenningsen H.P. 1991. Wax precipitation from North Sea crude oils. 4. Thermodynamic modeling. *Energy Fuels* **5** (6): 924-932.

Svendsen J.A, "Mathematical Modelling of Wax Deposition in Oil Pipeline Systems" Alche Journal, August, 1993.

Thomas, F.B., Bennion, D.B., Bennion, D.W. et al. 1992. Experimental And Theoretical Studies Of Solids Precipitation From Reservoir Fluid. *J Can Pet Technol* **31** (1): 22. PETSOC-92-01-02.

Ungerer, P., Faissat, B., Leibovici, C. et al. 1995. High pressure-high temperature reservoir fluids: investigation of synthetic condensate gases containing a solid hydrocarbon. *Fluid Phase Equilibrium*. **111** (2): 287-311.

Walas, S.M. 1985. *Phase Equilibria in Chemical Engineering*. Boston, Massachusetts: Butterworth Publishers.

Watson M.(2012)‘Smart solutions for Subsea Pipeline blockages’14th March 2012 Offshore Technology Journal

Weingarten, J.S. and Euchner, J.A. 1988. Methods for Predicting Wax Precipitation and Deposition. *SPE Prod Eng* **3** (1): 121-126. SPE-15654-PA.

Won K.W(1980) ‘Thermodynamic for solid-liquid vapour Hydrocarbon Equillibrium:Wax phase formation from Heavy Hydrocarbon Mixtures’ *Fluid Phase Equilibrium* 30 pg.265-279

Won, K.W. 1986. Thermodynamics for solid solution-liquid-vapor equilibria: wax phase formation from heavy hydrocarbon mixtures. *Fluid Phase Equilibrium*. **30** (0): pg 265-279.

APPENDIX

TABLE 3.1.1 SAMPLE A FLUID COMPOSITION

Sample A	**Separator Oil composition.**
Component	**Mole %**
N_2	0.15
CO_2	0.32
H_2S	0.00
C_1	3.99
C_2	0.70
C_3	0.13
i-C_4	0.12
n-C_4	0.14
i-C_5	0.24
n-C_5	0.24
C_6	1.08
C_7	1.93
C_8	8.06
C_9	7.14
C_{10}	12.28
C_{11}	13.06
C_{12}	13.60
C_{13}	12.79
C_{14}	8.96
C_{15}	7.71
C_{16}	3.09
C_{17}	1.69
C_{18}	1.48
C_{19}	0.54
C_{20}	0.25
C_{21}	0.13
C_{22}	0.07
C_{23}	0.03
C_{24}	0.01
C_{25}	0.01
C_{26}	0.01
C_{27}	0.01
C_{28}	0.01
C_{29}	0.01
C_{30}+	0.02
TOTAL	**100.00**
M.wt(g/gmol)	152.11
Density (g/cm^3)	0.806
M.Wt C_7+[g/gmol]	161.09
Mol % of C_7+	92.88

TABLE 3.1.2 SAMPLE A CRUDE OIL FLOW ASSURANCE PARAMETERS

Parameter	METHOD	VALUE
Base Sediment and Water (%)	ASTM D97	<0.01
Copper Corrosion	ASTM D130	Slightly Tarnished (1A)
Wax Content (%) @ 0^0C	ASTM D5452	3.73

TABLE 3.1.3 SAMPLE B FLUID COMPOSITION

Sample B	Recombined Separator Oil
Component	**Mole %**
C_2	0.083
C_3	1.594
i-C_4	1.436
n-C_4	4.708
i-C_5	3.271
n-C_5	3.548
C_6	5.668
C_7	9.260
C_8	11.832
C_9	6.757
C_{10}	5.831
C_{11}	4.412
C_{12}	3.674
C_{13}	3.701
C_{14}	3.522
C_{15}	3.578
C_{16}	2.466
C_{17}	2.166
C_{18}	2.818
C_{19}	1.867
C_{20}	1.524
C_{21}	1.368
C_{22}	1.281
C_{23}	1.192
C_{24}	1.144
C_{25}	1.141
C_{26}	0.987
C_{27}	1.005
C_{28}	0.998
C_{29}	1.095
C_{30}+	6.076
TOTAL	100.000
M.wt(g/gmol)	180.5260
Density(gm/cm^3)	0.8360
M.Wt C_7+[g/gmol]	208.9875
Mol % of C_7+	79.6927

TABLE 3.1.4 SAMPLE B CRUDE OIL FLOW ASSURANCE PARAMETERS

Parameter	METHOD	VALUE
Base Sediment and Water (%)	ASTM D97	<0.01
Copper Corrosion	ASTM D130	Slightly Tarnished (1A)
Wax Content (%) @ 0^0C	ASTM D5452	4.77

TABLE 3.1.5 SAMPLE C FLUID COMPOSITION

Sample C	**Recombined Separator Oil**
Component	**Mole %**
C_2	0.077
C_3	1.907
i-C_4	1.540
n-C_4	4.962
i-C_5	3.492
n-C_5	3.464
C_6	5.758
C_7	9.263
C_8	11.797
C_9	6.714
C_{10}	5.800
C_{11}	4.407
C_{12}	3.727
C_{13}	3.691
C_{14}	3.547
C_{15}	3.609
C_{16}	2.491
C_{17}	2.170
C_{18}	2.847
C_{19}	1.879
C_{20}	1.535
C_{21}	1.375
C_{22}	1.284
C_{23}	1.185
C_{24}	1.141
C_{25}	1.122
C_{26}	0.967
C_{27}	0.982
C_{28}	0.956
C_{29}	1.047
C_{30}+	5.266
TOTAL	100.00
M.wt(g/gmol)	176.0354
Density(gm/cm^3)	0.8307
M.Wt C_7+[g/gmol]	204.9982
Mol % of C_7+	78.7996

TABLE 3.16 SAMPLE C CRUDE OIL FLOW ASSURANCE PARAMETERS

Parameter	METHOD	VALUE
Base Sediment and Water (%)	ASTM D97	<0.01
Copper Corrosion	ASTM D130	Slightly Tarnished (1A)
Wax Content (%) @ 0^0C	ASTM D5452	3.45

ANALYSIS FOR SAMPLE A

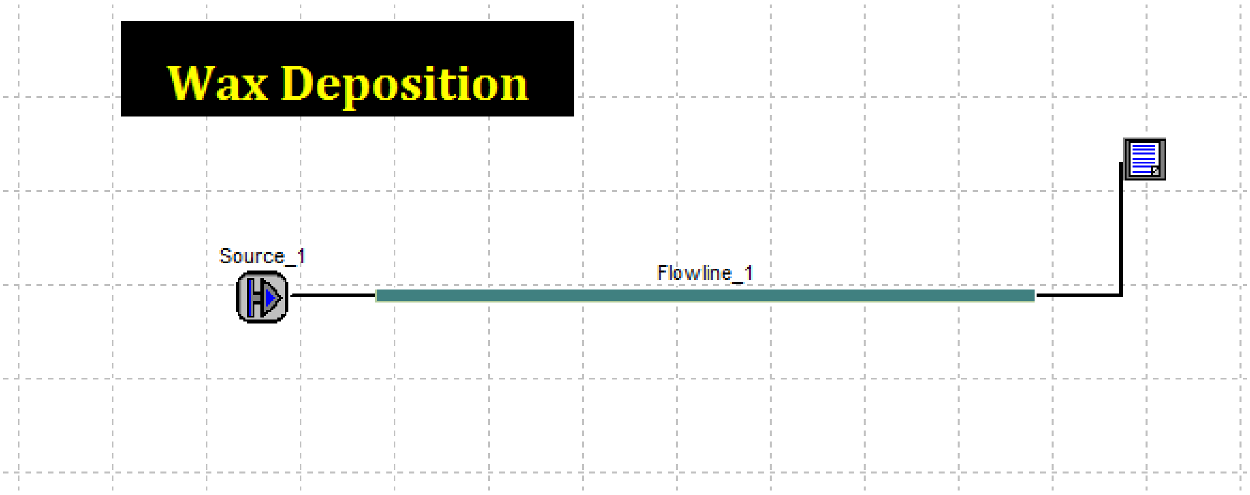
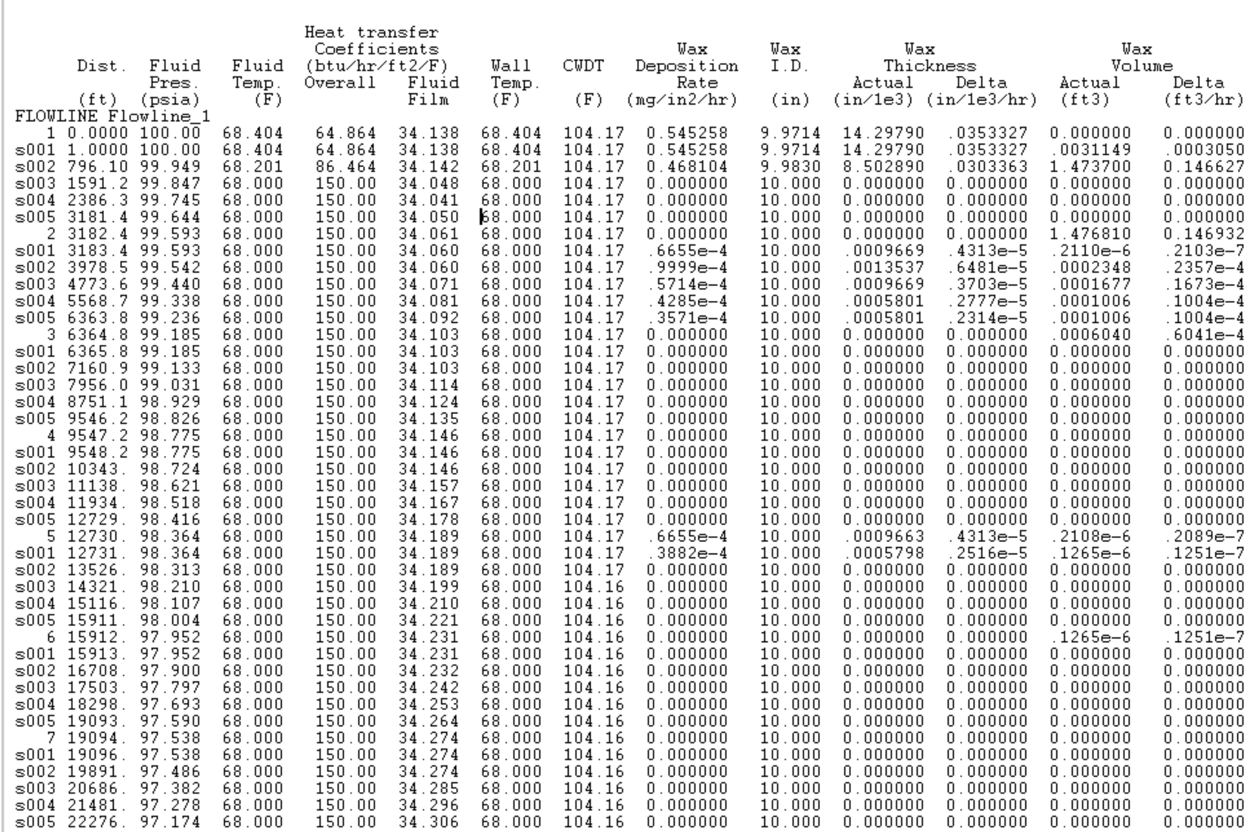


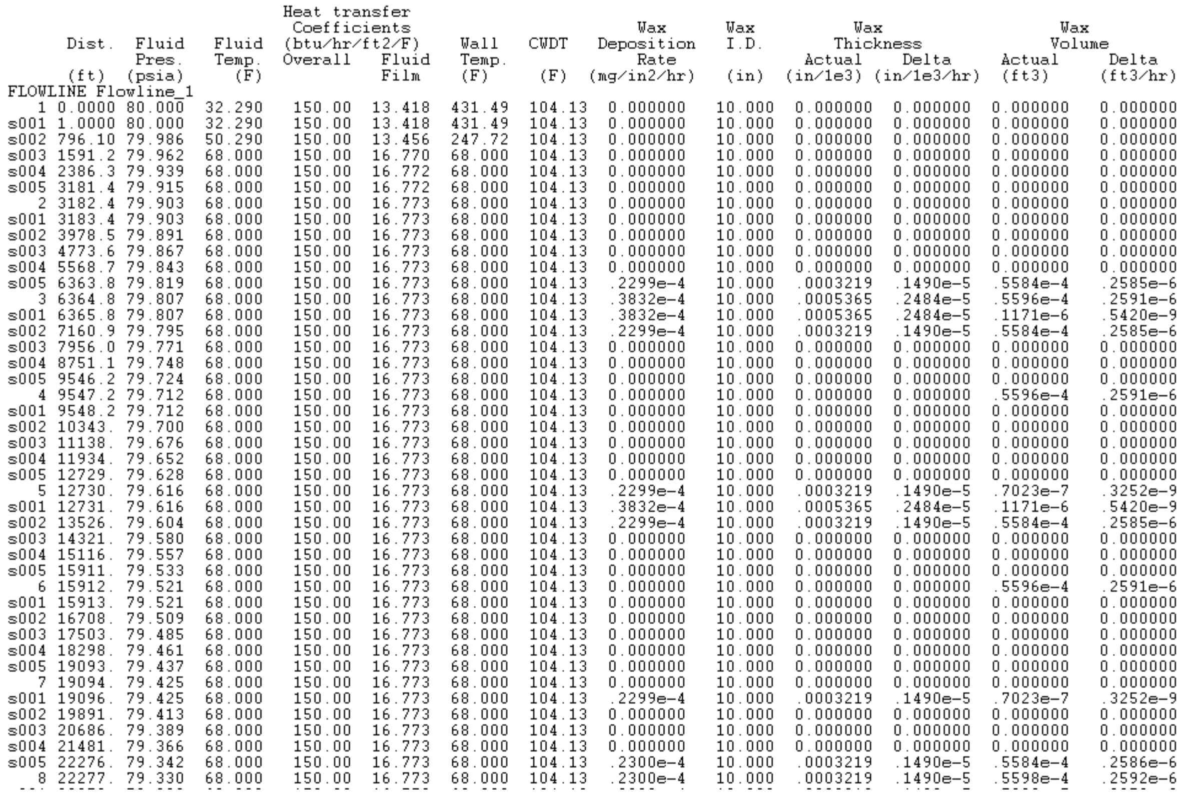
Figure 3.2.1 - Schematic of the Pipeline model in PIPESIM

Table 3.2.3.1 Critical Wax Deposition Temperature (CWDT) for Sample A



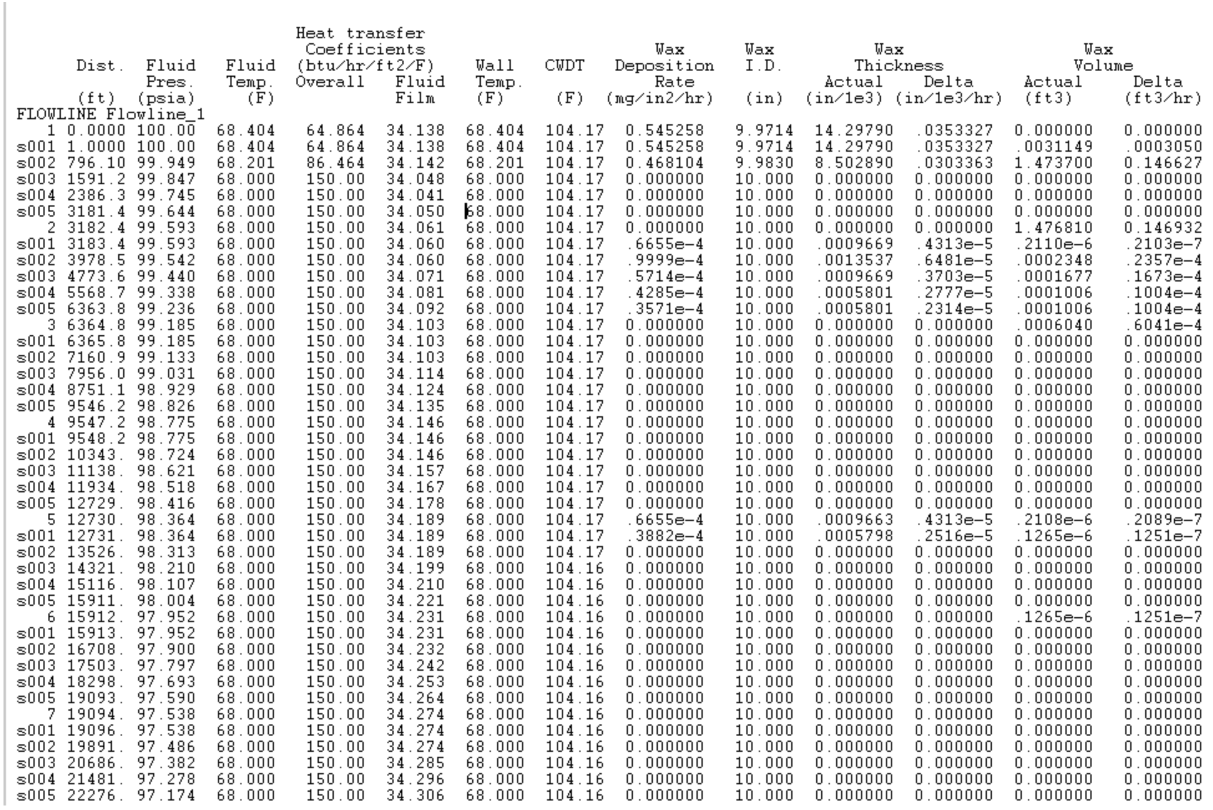
```
                                 Heat transfer
                                  Coefficients                          Wax          Wax          Wax                        Wax
       Dist.  Fluid    Fluid     (btu/hr/ft2/F)     Wall    CWDT    Deposition    I.D.       Thickness                  Volume
              Pres.    Temp.     Overall   Fluid    Temp.             Rate                 Actual     Delta          Actual      Delta
       (ft)   (psia)    (F)                Film     (F)      (F)   (mg/in2/hr)     (in)   (in/1e3) (in/1e3/hr)    (ft3)       (ft3/hr)
FLOWLINE Flowline_1
   1 0.0000 100.00    68.404    64.864    34.138   68.404  104.17   0.545258     9.9714   14.29790   .0353327     0.000000    0.000000
s001 1.0000 100.00    68.404    64.864    34.138   68.404  104.17   0.545258     9.9714   14.29790   .0353327     .0031149    .0003050
s002 796.10 99.949    68.201    86.464    34.142   68.201  104.17   0.468104     9.9830   8.502890   .0303363     1.473700    0.146627
s003 1591.2 99.847    68.000    150.00    34.048   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 2386.3 99.745    68.000    150.00    34.041   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 3181.4 99.644    68.000    150.00    34.050   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
   2 3182.4 99.593    68.000    150.00    34.061   68.000  104.17   0.000000     10.000   0.000000   0.000000     1.476810    0.146932
s001 3183.4 99.593    68.000    150.00    34.060   68.000  104.17   .6655e-4     10.000   .0009669   .4313e-5     .2110e-6    .2103e-7
s002 3978.5 99.542    68.000    150.00    34.060   68.000  104.17   .9999e-4     10.000   .0013537   .6481e-5     .0002348    .2357e-4
s003 4773.6 99.440    68.000    150.00    34.071   68.000  104.17   .5714e-4     10.000   .0009669   .3703e-5     .0001677    .1673e-4
s004 5568.7 99.338    68.000    150.00    34.081   68.000  104.17   .4285e-4     10.000   .0005801   .2777e-5     .0001006    .1004e-4
s005 6363.8 99.236    68.000    150.00    34.092   68.000  104.17   .3571e-4     10.000   .0005801   .2314e-5     .0001006    .1004e-4
   3 6364.8 99.185    68.000    150.00    34.103   68.000  104.17   0.000000     10.000   0.000000   0.000000     .0006040    .6041e-4
s001 6365.8 99.185    68.000    150.00    34.103   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s002 7160.9 99.133    68.000    150.00    34.103   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s003 7956.0 99.031    68.000    150.00    34.114   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 8751.1 98.929    68.000    150.00    34.124   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 9546.2 98.826    68.000    150.00    34.135   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
   4 9547.2 98.775    68.000    150.00    34.146   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s001 9548.2 98.775    68.000    150.00    34.146   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s002 10343. 98.724    68.000    150.00    34.146   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s003 11138. 98.621    68.000    150.00    34.157   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 11934. 98.518    68.000    150.00    34.167   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 12729. 98.416    68.000    150.00    34.178   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
   5 12730. 98.364    68.000    150.00    34.189   68.000  104.17   .6655e-4     10.000   .0009663   .4313e-5     .2108e-6    .2089e-7
s001 12731. 98.364    68.000    150.00    34.189   68.000  104.17   .3882e-4     10.000   .0005798   .2516e-5     .1265e-6    .1251e-7
s002 13526. 98.313    68.000    150.00    34.189   68.000  104.17   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s003 14321. 98.210    68.000    150.00    34.199   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 15116. 98.107    68.000    150.00    34.210   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 15911. 98.004    68.000    150.00    34.221   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
   6 15912. 97.952    68.000    150.00    34.231   68.000  104.16   0.000000     10.000   0.000000   0.000000     .1265e-6    .1251e-7
s001 15913. 97.952    68.000    150.00    34.231   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s002 16708. 97.900    68.000    150.00    34.232   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s003 17503. 97.797    68.000    150.00    34.242   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 18298. 97.693    68.000    150.00    34.253   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 19093. 97.590    68.000    150.00    34.264   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
   7 19094. 97.538    68.000    150.00    34.274   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s001 19096. 97.538    68.000    150.00    34.274   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s002 19891. 97.486    68.000    150.00    34.274   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s003 20686. 97.382    68.000    150.00    34.285   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 21481. 97.278    68.000    150.00    34.296   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 22276. 97.174    68.000    150.00    34.306   68.000  104.16   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
```

Table 3.2.3.2 Critical Wax Deposition Temperature (CWDT) for Sample B



```
                                 Heat transfer
                                  Coefficients                          Wax          Wax          Wax                        Wax
       Dist.  Fluid    Fluid     (btu/hr/ft2/F)     Wall    CWDT    Deposition    I.D.       Thickness                  Volume
              Pres.    Temp.     Overall   Fluid    Temp.             Rate                 Actual     Delta          Actual      Delta
       (ft)   (psia)    (F)                Film     (F)      (F)   (mg/in2/hr)     (in)   (in/1e3) (in/1e3/hr)    (ft3)       (ft3/hr)
FLOWLINE Flowline_1
   1 0.0000 80.000    32.290    150.00    13.418   431.49  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s001 1.0000 80.000    32.290    150.00    13.418   431.49  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s002 796.10 79.986    50.290    150.00    13.456   247.72  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s003 1591.2 79.962    68.000    150.00    16.770   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 2386.3 79.939    68.000    150.00    16.772   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 3181.4 79.915    68.000    150.00    16.772   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
   2 3182.4 79.903    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s001 3183.4 79.903    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s002 3978.5 79.891    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s003 4773.6 79.867    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 5568.7 79.843    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 6363.8 79.819    68.000    150.00    16.773   68.000  104.13   .2299e-4     10.000   .0003219   .1490e-5     .5584e-4    .2585e-6
   3 6364.8 79.807    68.000    150.00    16.773   68.000  104.13   .3832e-4     10.000   .0005365   .2484e-5     .5596e-4    .2591e-6
s001 6365.8 79.807    68.000    150.00    16.773   68.000  104.13   .3832e-4     10.000   .0005365   .2484e-5     .1171e-6    .5420e-9
s002 7160.9 79.795    68.000    150.00    16.773   68.000  104.13   .2299e-4     10.000   .0003219   .1490e-5     .5584e-4    .2585e-6
s003 7956.0 79.771    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 8751.1 79.748    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 9546.2 79.724    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
   4 9547.2 79.712    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     .5596e-4    .2591e-6
s001 9548.2 79.712    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s002 10343. 79.700    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s003 11138. 79.676    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 11934. 79.652    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 12729. 79.628    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
   5 12730. 79.616    68.000    150.00    16.773   68.000  104.13   .2299e-4     10.000   .0003219   .1490e-5     .7023e-7    .3252e-9
s001 12731. 79.616    68.000    150.00    16.773   68.000  104.13   .3832e-4     10.000   .0005365   .2484e-5     .1171e-6    .5420e-9
s002 13526. 79.604    68.000    150.00    16.773   68.000  104.13   .2299e-4     10.000   .0003219   .1490e-5     .5584e-4    .2585e-6
s003 14321. 79.580    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 15116. 79.557    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 15911. 79.533    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
   6 15912. 79.521    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     .5596e-4    .2591e-6
s001 15913. 79.521    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s002 16708. 79.509    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s003 17503. 79.485    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 18298. 79.461    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 19093. 79.437    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
   7 19094. 79.425    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s001 19096. 79.425    68.000    150.00    16.773   68.000  104.13   .2299e-4     10.000   .0003219   .1490e-5     .7023e-7    .3252e-9
s002 19891. 79.413    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s003 20686. 79.389    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s004 21481. 79.366    68.000    150.00    16.773   68.000  104.13   0.000000     10.000   0.000000   0.000000     0.000000    0.000000
s005 22276. 79.342    68.000    150.00    16.773   68.000  104.13   .2300e-4     10.000   .0003219   .1490e-5     .5584e-4    .2586e-6
   8 22277. 79.330    68.000    150.00    16.773   68.000  104.13   .2300e-4     10.000   .0003219   .1490e-5     .5598e-4    .2592e-6
```

Table 3.2.3.3 Critical Wax Deposition Temperature (CWDT) for Sample C



```
                            Heat transfer
                             Coefficients                          Wax        Wax           Wax                      Wax
       Dist.  Fluid   Fluid (btu/hr/ft2/F)    Wall    CWDT     Deposition    I.D.        Thickness                  Volume
              Pres.   Temp. Overall    Fluid   Temp.              Rate              Actual      Delta       Actual      Delta
       (ft)  (psia)     (F)            Film    (F)      (F)   (mg/in2/hr)    (in)  (in/1e3)  (in/1e3/hr)   (ft3)       (ft3/hr)
FLOWLINE Flowline_1
   1 0.0000 100.00  68.404    64.864  34.138  68.404  104.17  0.545258    9.9714  14.29790  .0353327  0.000000    0.000000
s001 1.0000 100.00  68.404    64.864  34.138  68.404  104.17  0.545258    9.9714  14.29790  .0353327  .0031149    .0003050
s002 796.10 99.949  68.201    86.464  34.142  68.201  104.17  0.468104    9.9830  8.502890  .0303363  1.473700    0.146627
s003 1591.2 99.847  68.000    150.00  34.048  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s004 2386.3 99.745  68.000    150.00  34.041  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s005 3181.4 99.644  68.000    150.00  34.050  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
   2 3182.4 99.593  68.000    150.00  34.061  68.000  104.17  0.000000    10.000  0.000000  0.000000  1.476810    0.146932
s001 3183.4 99.593  68.000    150.00  34.060  68.000  104.17  .6655e-4    10.000  .0009669  .4313e-5  .2110e-6    .2103e-7
s002 3978.5 99.542  68.000    150.00  34.060  68.000  104.17  .9999e-4    10.000  .0013537  .6481e-5  .0002348    .2357e-4
s003 4773.6 99.440  68.000    150.00  34.071  68.000  104.17  .5714e-4    10.000  .0009669  .3703e-5  .0001677    .1673e-4
s004 5568.7 99.338  68.000    150.00  34.081  68.000  104.17  .4285e-4    10.000  .0005801  .2777e-5  .0001006    .1004e-4
s005 6363.8 99.236  68.000    150.00  34.092  68.000  104.17  .3571e-4    10.000  .0005801  .2314e-5  .0001006    .1004e-4
   3 6364.8 99.185  68.000    150.00  34.103  68.000  104.17  0.000000    10.000  0.000000  0.000000  .0006040    .6041e-4
s001 6365.8 99.185  68.000    150.00  34.103  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s002 7160.9 99.133  68.000    150.00  34.103  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s003 7956.0 99.031  68.000    150.00  34.114  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s004 8751.1 98.929  68.000    150.00  34.124  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s005 9546.2 98.826  68.000    150.00  34.135  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
   4 9547.2 98.775  68.000    150.00  34.146  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s001 9548.2 98.775  68.000    150.00  34.146  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s002 10343. 98.724  68.000    150.00  34.146  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s003 11138. 98.621  68.000    150.00  34.157  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s004 11934. 98.518  68.000    150.00  34.167  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s005 12729. 98.416  68.000    150.00  34.178  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
   5 12730. 98.364  68.000    150.00  34.189  68.000  104.17  .6655e-4    10.000  .0009663  .4313e-5  .2108e-6    .2089e-7
s001 12731. 98.364  68.000    150.00  34.189  68.000  104.17  .3882e-4    10.000  .0005798  .2516e-5  .1265e-6    .1251e-7
s002 13526. 98.313  68.000    150.00  34.189  68.000  104.17  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s003 14321. 98.210  68.000    150.00  34.199  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s004 15116. 98.107  68.000    150.00  34.210  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s005 15911. 98.004  68.000    150.00  34.221  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
   6 15912. 97.952  68.000    150.00  34.231  68.000  104.16  0.000000    10.000  0.000000  0.000000  .1265e-6    .1251e-7
s001 15913. 97.952  68.000    150.00  34.231  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s002 16708. 97.900  68.000    150.00  34.232  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s003 17503. 97.797  68.000    150.00  34.242  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s004 18298. 97.693  68.000    150.00  34.253  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s005 19093. 97.590  68.000    150.00  34.264  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
   7 19094. 97.538  68.000    150.00  34.274  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s001 19096. 97.538  68.000    150.00  34.274  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s002 19891. 97.486  68.000    150.00  34.274  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s003 20686. 97.382  68.000    150.00  34.285  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s004 21481. 97.278  68.000    150.00  34.296  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
s005 22276. 97.174  68.000    150.00  34.306  68.000  104.16  0.000000    10.000  0.000000  0.000000  0.000000    0.000000
```

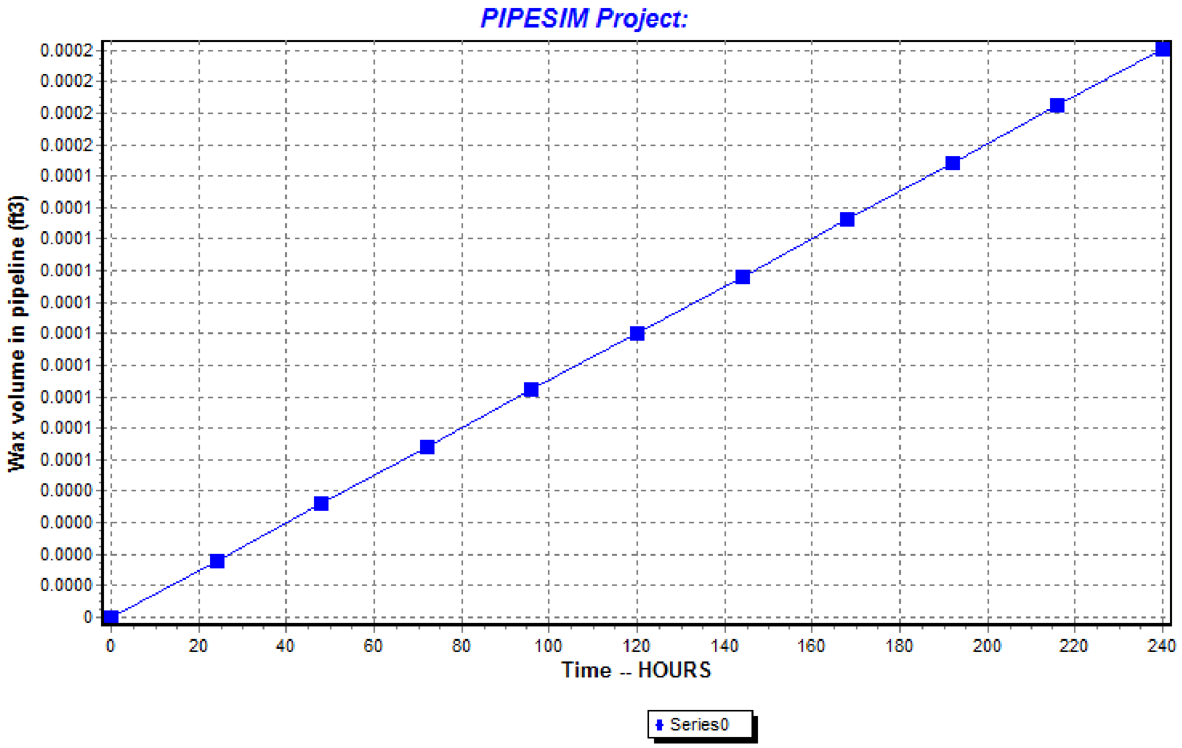


Figure 4.1.1 - Wax deposition volume in pipeline after 10 days for sample A

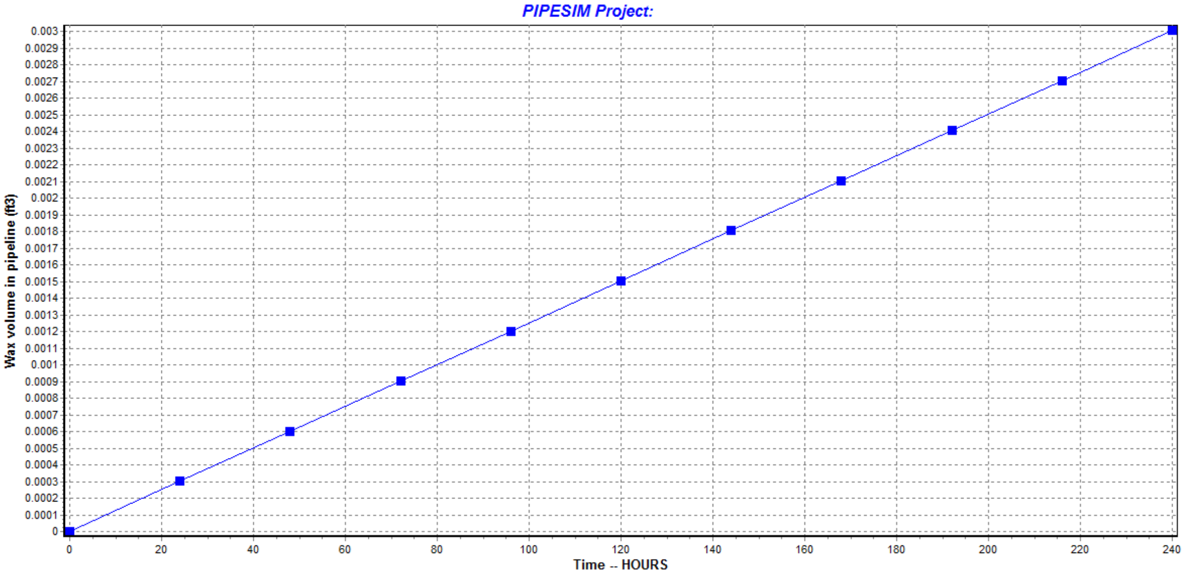


Figure 4.1.2 - Wax deposition volume in pipeline after 10days for sample B

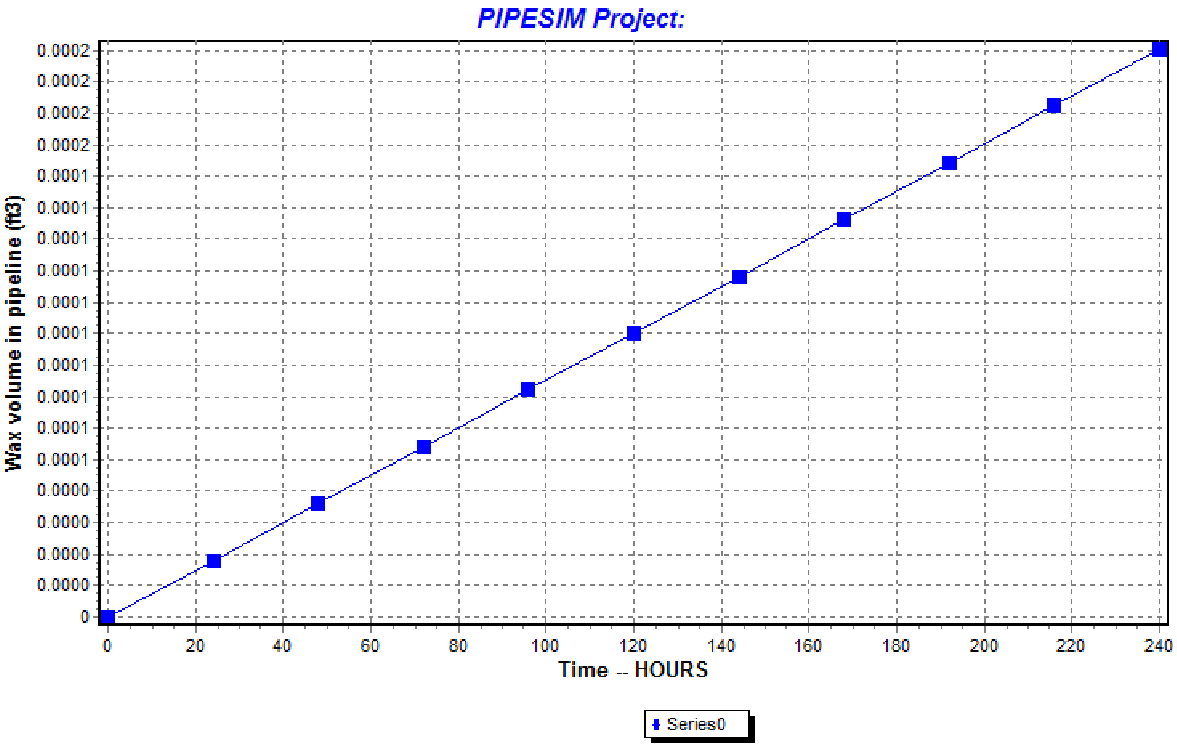


Figure 4.1.3 - Wax deposition volume in pipeline for 10 days for sample C

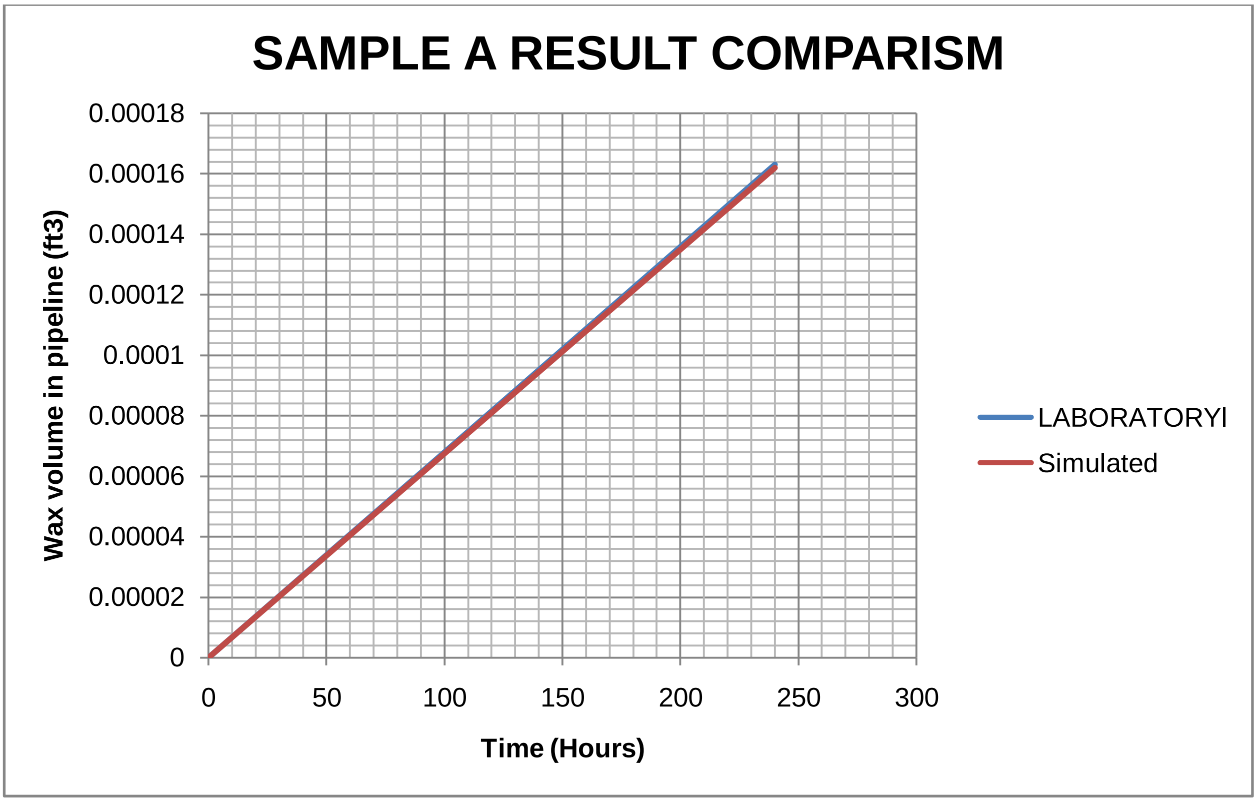


Figure 4.1.4- Comparism of Simulated and Control results for Sample A

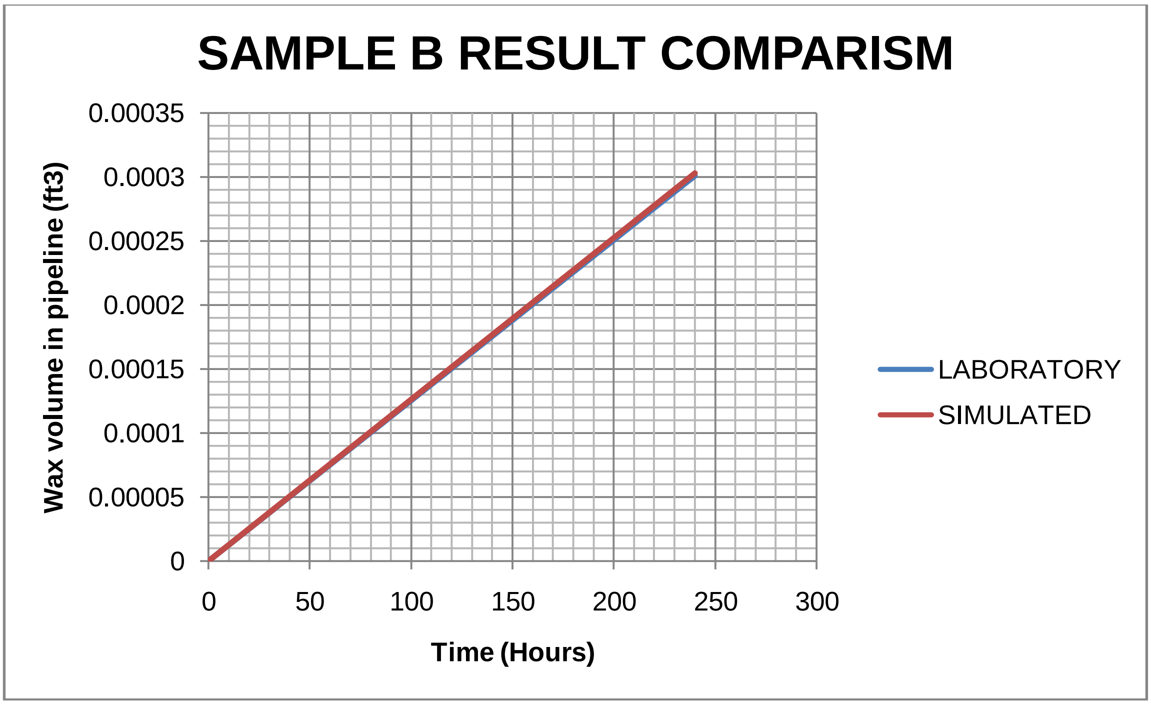


Figure 4.1.5- Comparism of Simulated and Control results for Sample B

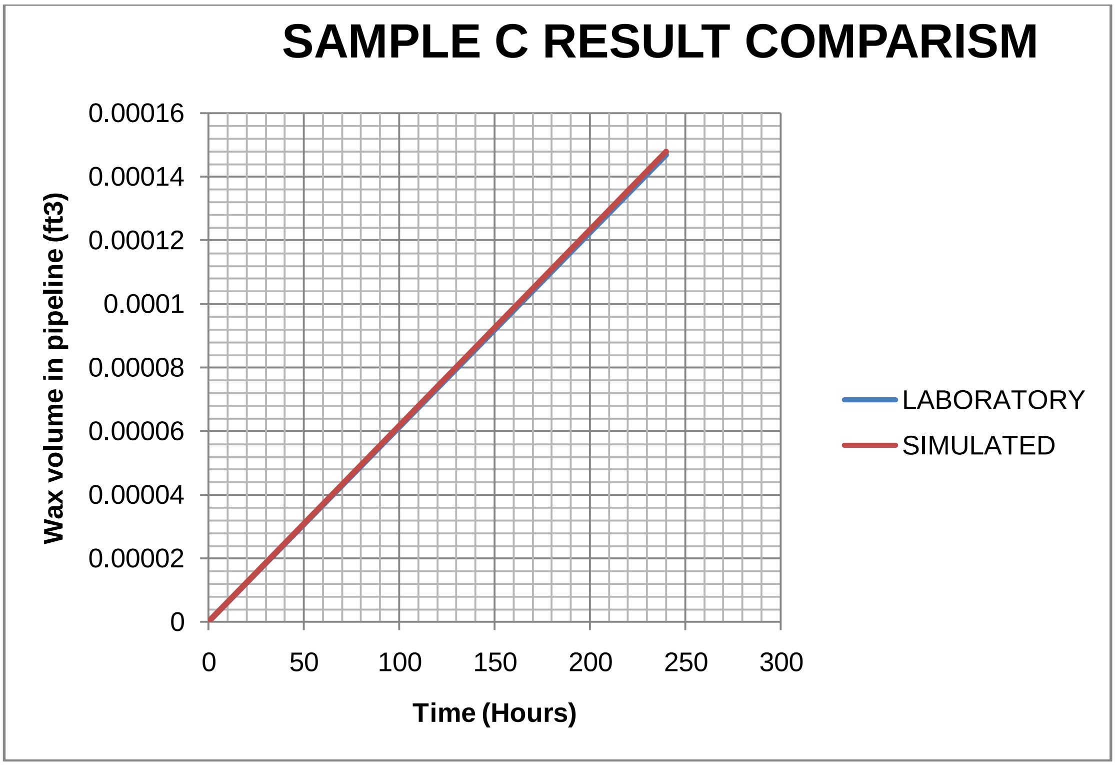


Figure 4.1.6- Comparism of Simulated and Control results for Sample C

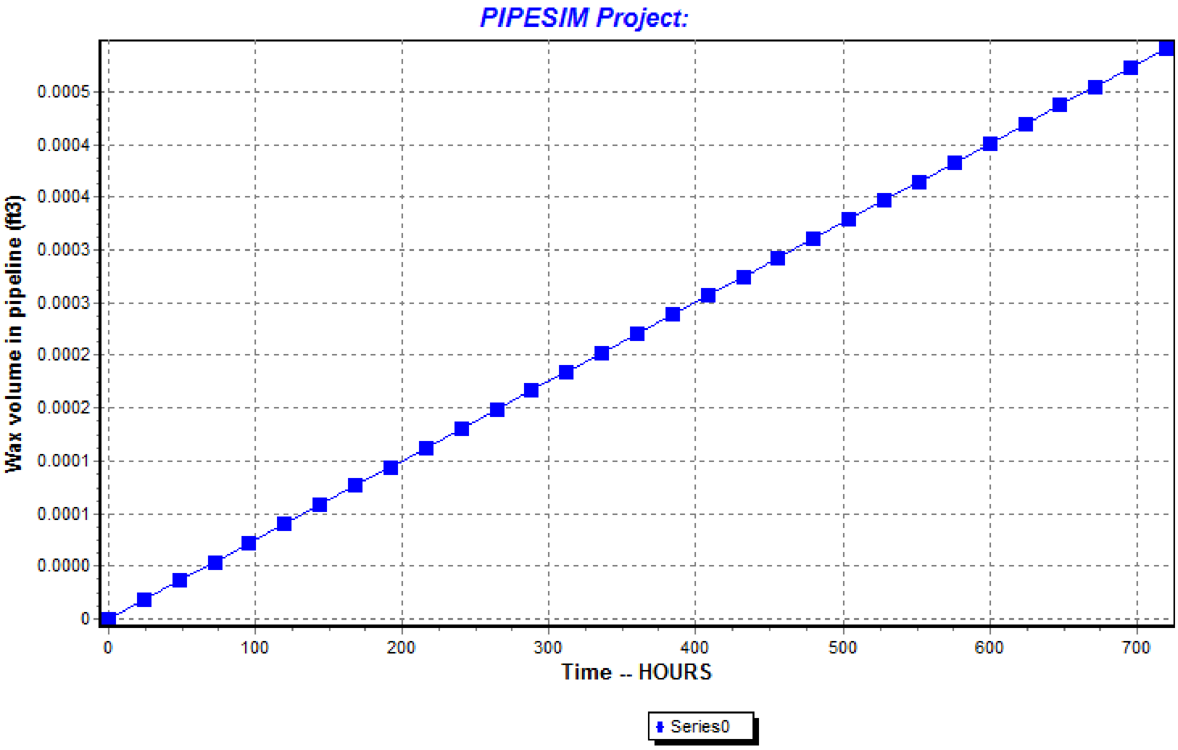


Figure 4.2.1 - Wax deposition volume in pipeline for 1 month for sample A

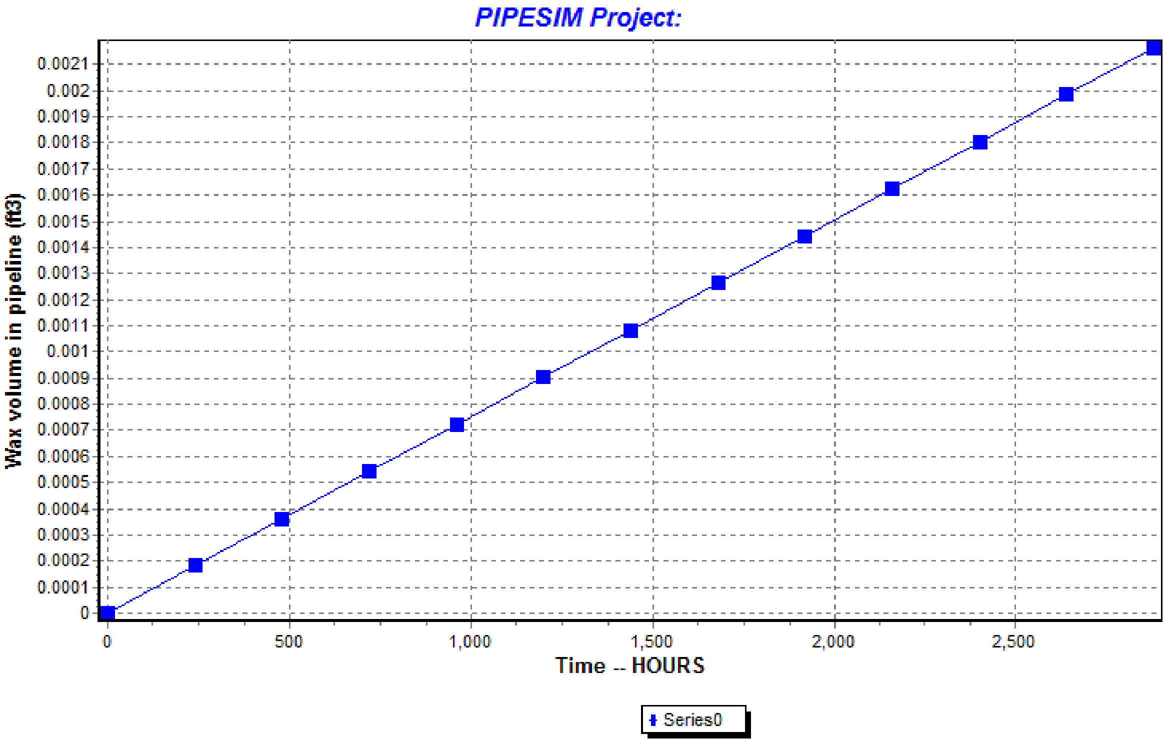


Figure 4.2.2 - Wax deposition volume in pipeline for 4 months for sample A

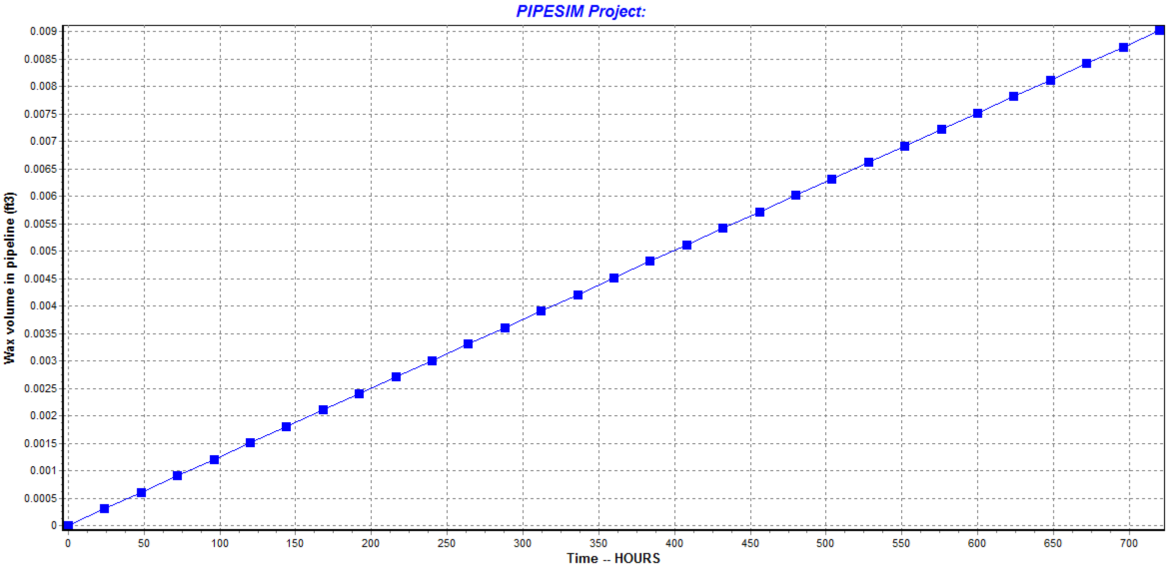


Figure 4.2.3 - Wax deposition volume in pipeline for 1 month for sample B

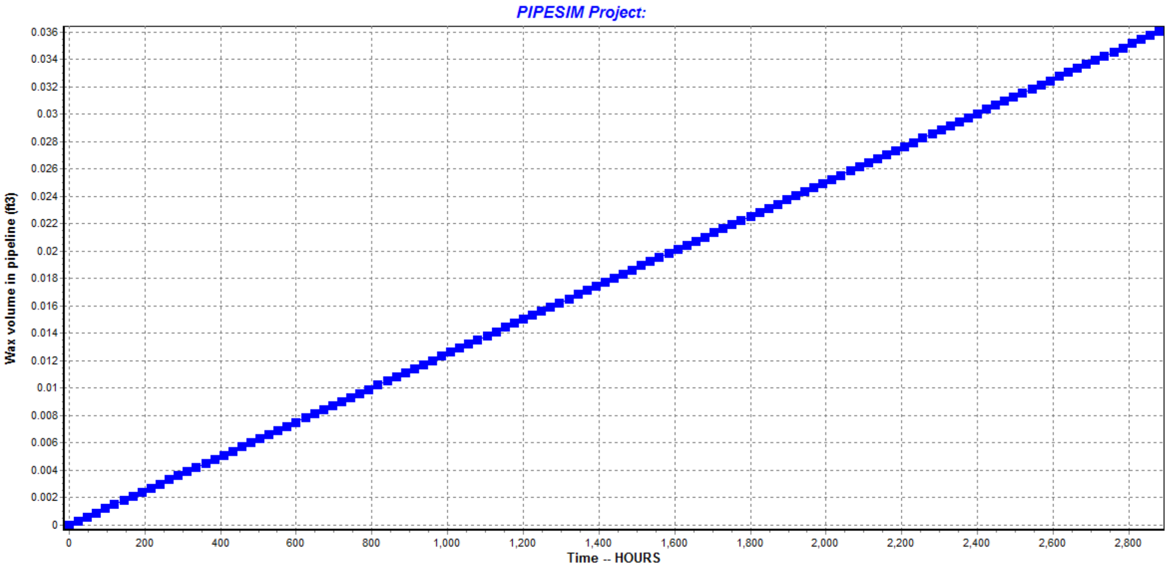


Figure 4.2.4 - Wax deposition volume in pipeline for 4 months for sample B

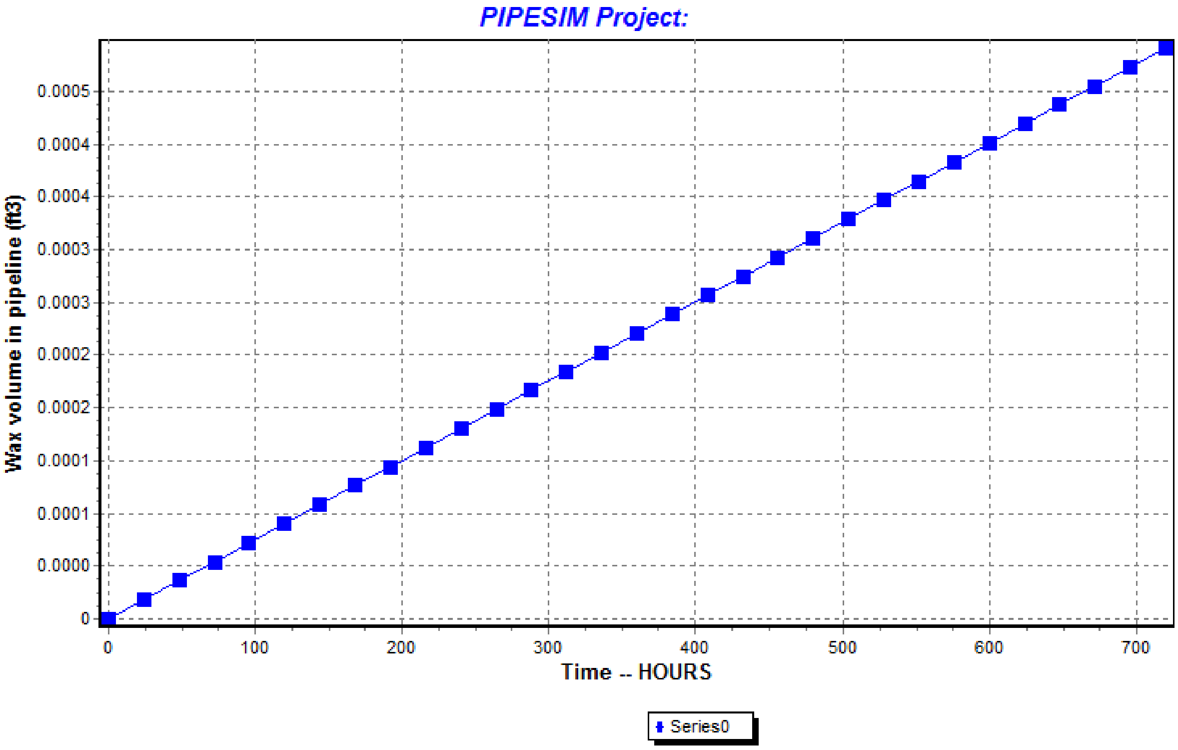


Figure 4.2.5- Wax deposition volume in pipeline for 1 month for sample c

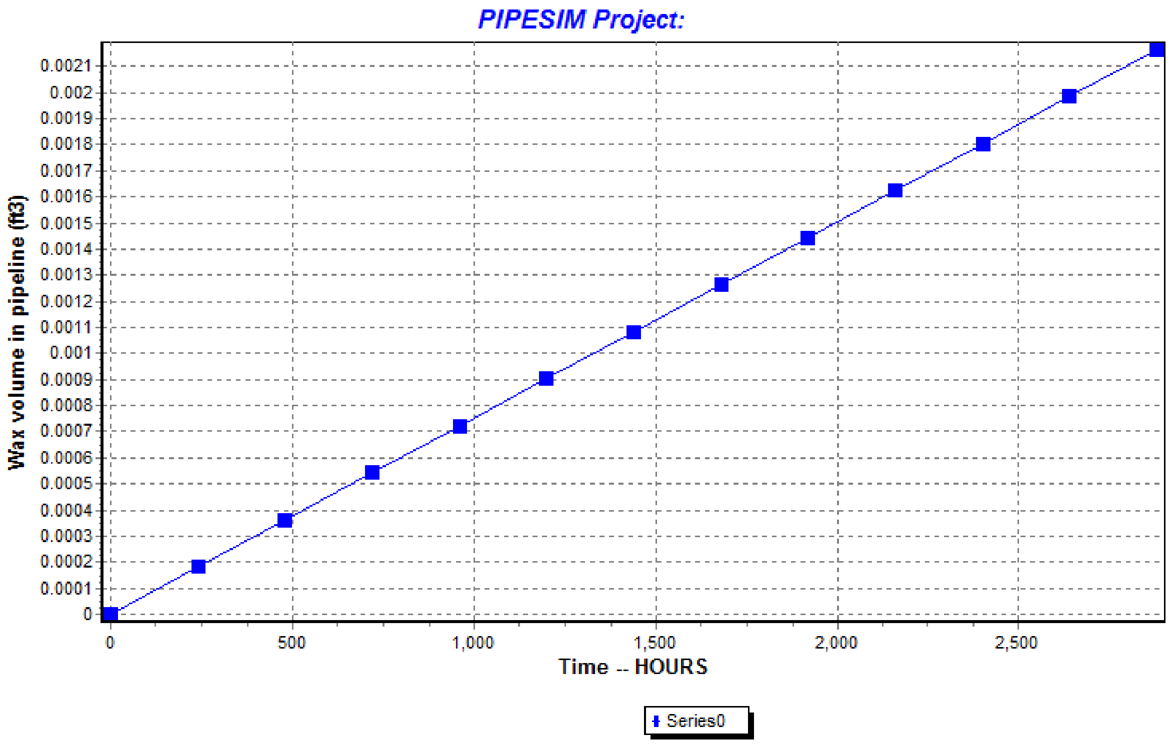


Figure 4.2.6- wax deposition volume in pipeline for 4-months for sample C

Table 4.3.1 Critical Wax Deposition Temperature (CWDT) Results

Samples	**CWDT**
A	**104.2^{o}F = 40^{o}C**
B	**104.1^{o}F = 40^{o}C**
C	**104.2^{o}F = 40^{o}C**

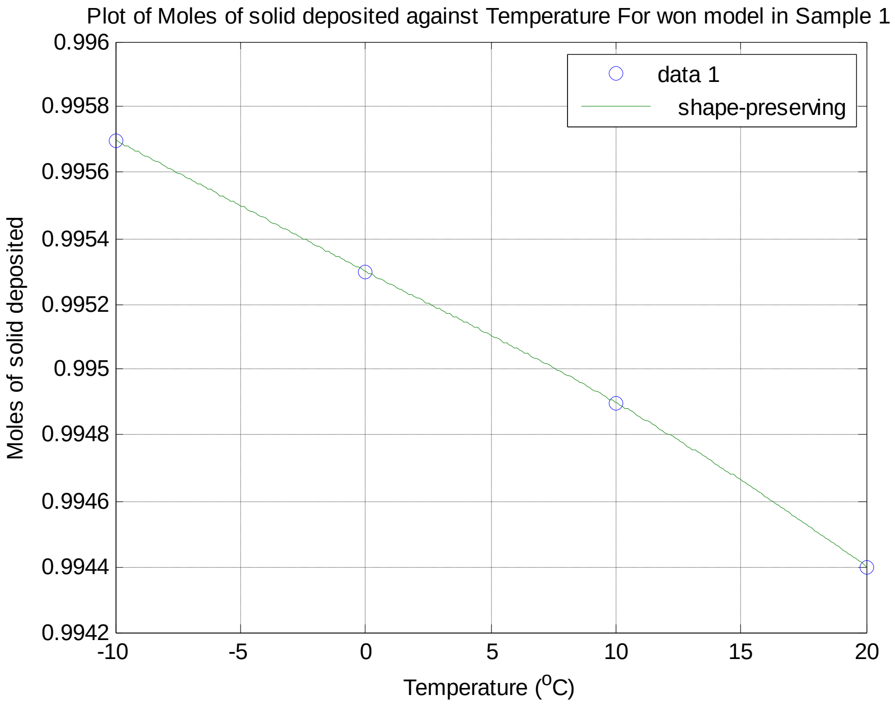


FIGURE 4.4.1 Moles of solids deposited for Won model

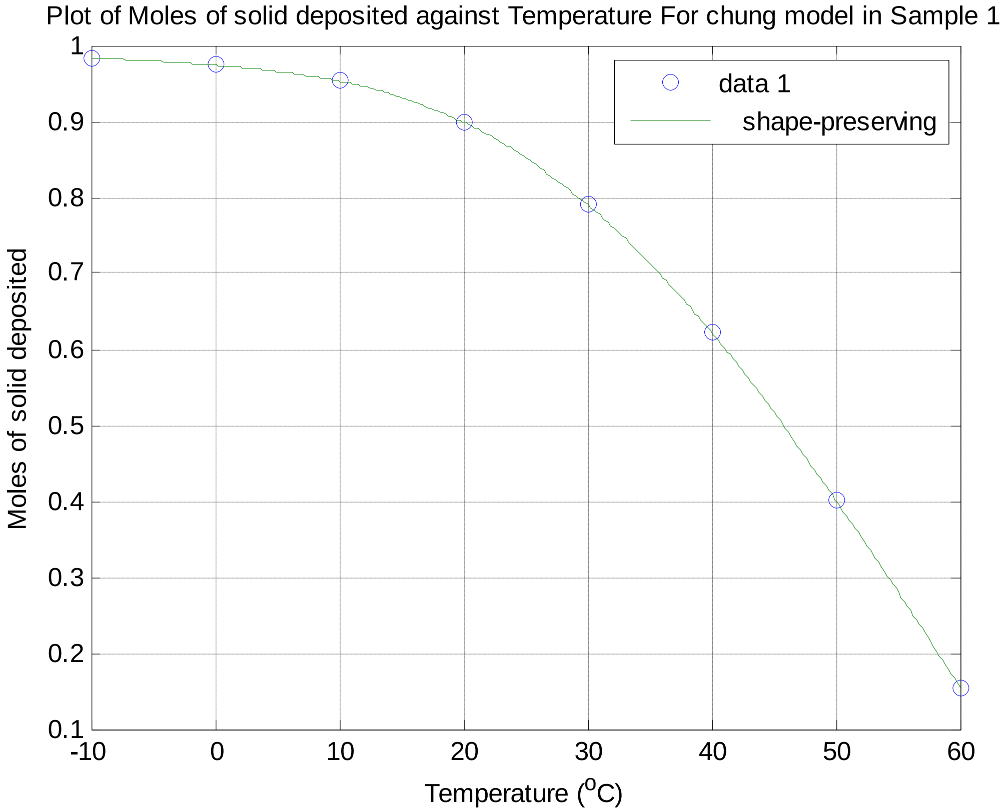


FIGURE 4.4.2 Moles of solids deposited for Chung model

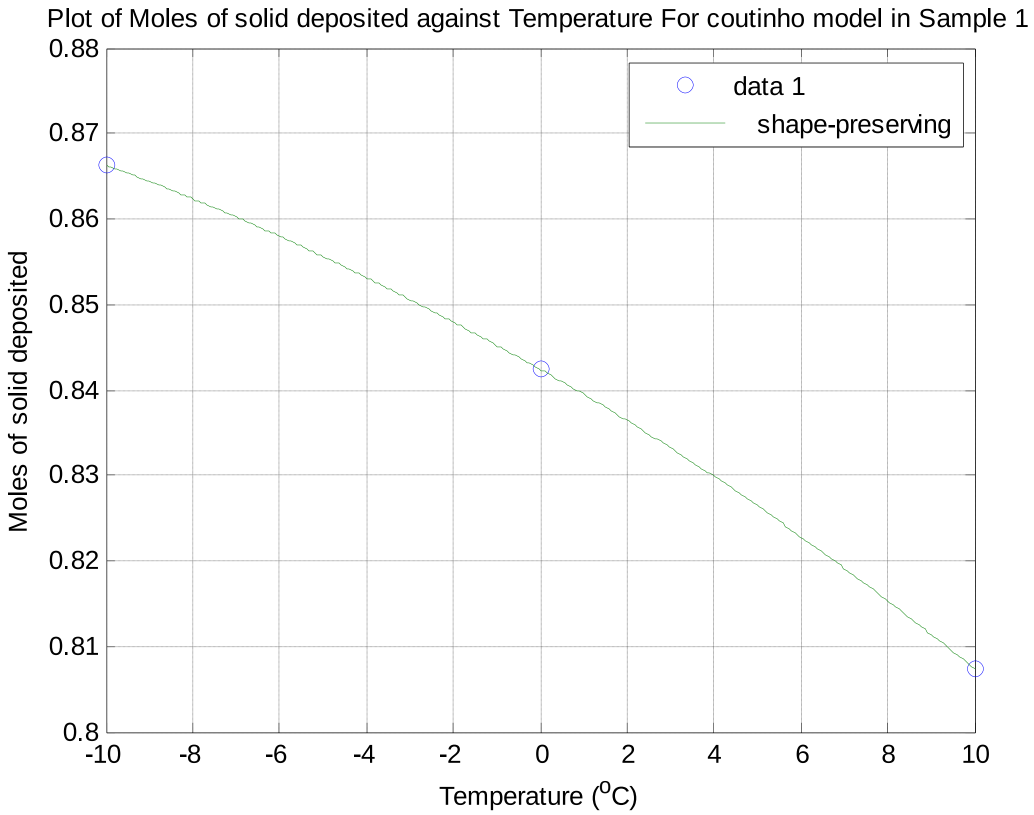


FIGURE 4.4.3 Moles of solids deposited for Coutinho model