EXPERIMENTAL ASSESSMENT OF PREDICTIVE WAX DEPOSITION MODELS IN SIMULATION SOFTWARE

by

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CERTIFICATION OF APPROVAL

Experimental Assessment of Predictive Wax Deposition Models in Simulation Software

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A project dissertation submitted to the

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Approved by,

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

_____
(AHMAD EZAT ADHA B ABD AZIZ)

ABSTRACT

One of the most relevant flow assurance issue in oil transportation is indeed the phenomena of wax deposition. Wax deposition occur when the temperature along the pipeline falls below a point where it is described as Wax Appearance Temperature(WAT) of the oil. The deposition may cause a lot of problems to the industry and definitely will involve expensive cause to overcome the problem. The main objective of this study is to compare wax deposition predicted by a simulation model to operational data.

Literature reviews was conducted extensively in order to have a better understanding regarding the topic and developments regarding this topic in recent years. The objective and scope of studies is determined. A Gantt chart is also constructed to measure the progress of the project. Forecasted result and outcome from this project are informations to determine which wax deposition method in certain software are the most reliable on predicting wax deposition to be use in Petroleum industry.

Prediction of wax deposition indeed help to minimize the cost of operating such equipment. The model used for the wax deposition simulations in this study is described below. The properties of the fluids used in the study are presented and discussed. Then the simulation results are presented and compared to the existing field experience data.

Finally, some conclusion are drawn. This simulation will enable prediction of wax deposition such as its wax deposition rate and thickness of deposition. A main conclusion of this paper is that wax deposition under field condition is not as severe as predicted by the model. This information will be greatly appreciated since it can assess remediation or prevention strategies, such as, the models can be used to evaluate insulation effectiveness or to estimate pigging frequency.

ACKNOWLEDGEMENT

Firstly I would like to thank Allah SWT for giving me blessings throughout my Final Year Project in the year of 2013. Without His blessing, i will definitely not be able to carry out and finish this project. I would also like to genuinely thank Universiti Teknologi PETRONAS for the opportunity to complete my Final Year Project for semester May 2013. The project enhance my knowledge theoretically as well as in practical area. Upon completion of the project, titled Experimental Assessment of Predictive Wax Deposition in Simulation Software, I am able to apply some theoretical knowledge into an experimental as well as simulation software. Utmost appreciation is expressed to Dr. Aliyu Sulaimon Adebayo, my supervisor, for the continuous guidance and support upon completion of the project. The two semesters Final Year Project delivers an experience to develop my personal skills through anticipation in planning and execution of the project. It also give a closer exposure to hands-on experimental lab environment. The opportunity to work with supervisors, lecturers and team mates within the university enhances communication skill and introduces me to work culture. Greatest gratitude to everybody that was directly or indirectly involved during the project. The successful completion of this project hopefully contributes to Universiti Teknologi Petronas in fulfilling its organizational objectives. Again, I would like to thank Universiti Teknologi PETRONAS especifically to Dr. Aliyu Sulaimon Adebayo on the permission to publish this Final Year Dissertation Report.

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INTRODUCTION

1.1   Background of study

Wax deposition in production facilities and pipelines is a problem that costs the upstream petroleum industry billions of dollars worldwide every year. The deposits can plug pipelines and seize equipment, leading to costly downtime and expensive remediation techniques.

1.2   Problem statement

There are a lot of simulation software that can be used to predict wax deposition. Beside that, there are also numbers of wax deposition model that can be use in softwares. All wax models overstimates the wax deposition compared to the field confdition, but there are a few models that predict sufficiently close with the field condition data and it is important to know which wax models it is since better prediction will definitely improve the operational cost.

1.3   Objectives

The main objective of the project is :

- To simulate a model from data given in which to predict wax depostion.
- To demonstrate which simulation software and wax deposition model are the sufficiently reliable on wax deposition prediction

1.4   Scope of study

- Charaterization of Crude Oil
- Wax Appearance Temperature
- Wax Deposition Simulation Softwares

CHAPTER TWO

LITERATURE REVIEW

2.1   Paraffin wax

Crude oils and natural gas fluids are composed of nearly 100% hydrocarbons. A series of naturally occurring hydrocarbons with the chemical formula C_nH_{2n+2} are known as paraffins. In most crude oils, the paraffins align as long straight chain molecules. However, they can also form branched or cyclic structures. A collection of normal paraffins, with 16 or more carbon atoms ($\geq$C16) that form crystalline solid substances at 68 ˚F (20 ˚C), are known as wax. The amount of wax contained in a crude oil sample varies, depending on the geographic source of the crude(James Outlaw et al. 2011).

2.2   Wax precipitation and deposition

Wax precipitation during crude oil flow causes wax deposition and flow restriction (Mohammed 2011). Wax depostion during the flow of waxy crude oil through subsea pipelines occurs as a result of the precipitation of wax molecules adjacent to the cold pipe wall. Thus, wax deposition can only occur when the inner pipe wall temperature is below cloud point temperature. The precipitated wax molecules near the pipe wall start to form an incipient gel at the cold surface. The incipient gel formed at the pipe wall is a 3-D network structure of wax crystals and contains a significant amount of oil trapped in it. The incipient gel grows as time progresses while there are radial thermal and mass transfer gradients as a result of heat losses to the surrounding as shown in Figure-1.
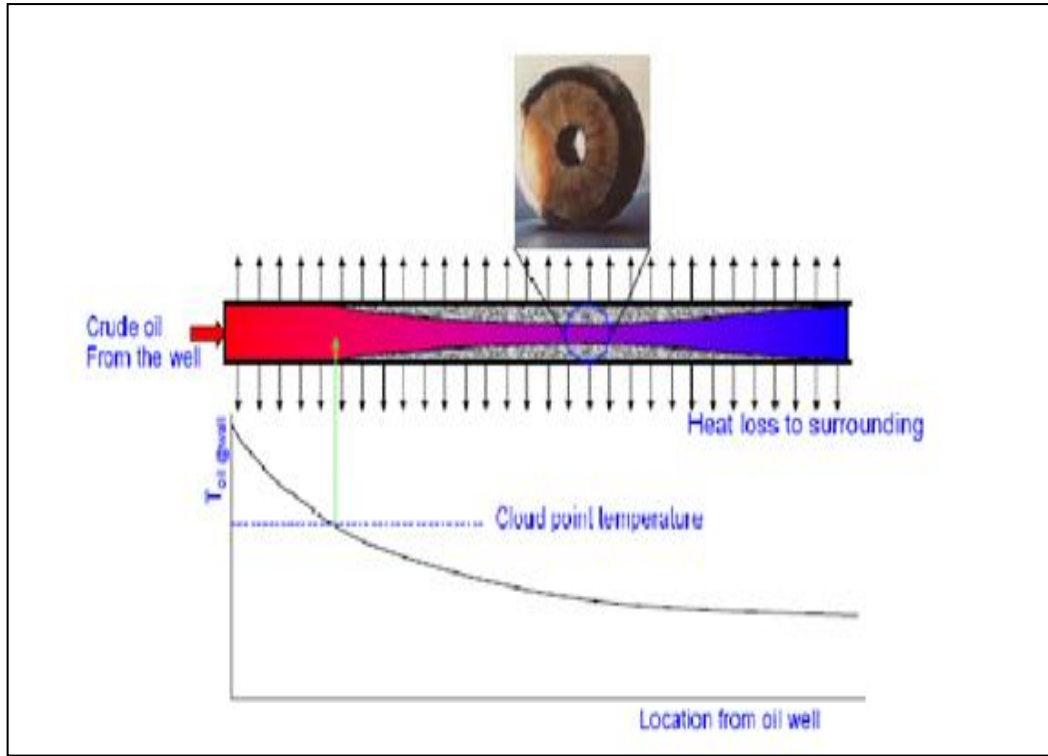
Figure 2.1 : Wax depostion occur when the inner temperature of the pipeline is below
the cloud point temperature(Lee. 2008)

2.3   Wax mechanism

The ability of solid particles to diffuse towards the cold wall is a critical issue with
respect to the formation of stable cold slurry that will not adhere to the walls. The
main proposed mechanisms of transport of solids inside a fluid stream were reported
by Merino-Garcia and his team(2008). These Mechanisms include : shear dispersion,
Brownian diffusion, gravity, thermophoresis and turbopherisis.

All those mechanisms (Borghi et al. 2005) would tend to drive particles towards the
wall, but it was concluded that their were small compared to the other two
mechanisms. Without temperature gradients, liquids molecules do not participate in
deposition. Due to the fact that only negligible deposition is observed, solids are
considered to essentially remain in the bulk and not deposit. This negligible quantity
that does deposit may come from the waxes that were in direct contact with the wall,
so that diffusion was not needed to transport them.

2.4   Methods to determine WAT

Several techniques are available to measure WAT, which are Standard American Society for Testing Materials (ASTM) D2500 – 88 or IP 219/82, Viscometry, Cold Finger, Differential Scanning Calometry (DSC), Filter Plugging (FP), Fourier Transform Infrared (FTIR), Cross Polar Microscopy (CPM), and Light Transmission (LT). Several studies has been carried out to compare the different methods of WAT measurement (Monger-Mc Clure et al. 2004). The ASTM methods for instant rely on visual observation of the wax crystals. They require the fluids to be transparent, resulting it not realiable ti measure WAT of opaque or dark oils. Cross Polar Microscopy (CPM), Light Transmittance, Differntial Scanning Calorimetry and Viscometry are used to measure WAT for dark oils. The sensitivity of Differential Scanning Calorimetry and Viscometry is dependent on the amount of precipitated wax, Cross Polar Microscopy depends on the size of the wax crystals and Light Transmittance depends on the number of wax crystals.

Cross Polar Microscopy(CPM)

CPM is commonly used for determining wax appearance temperature of crude oil (Hammami and Raines 1999; Ferworn et al. 1997). It works on the principle that the wax cystals rotate the plane of polarized light (the crystals are refered to as anisotropic). The use of two prisms in a cross-polar microscope allows the field of view within the microscope to initially appear black, but, when the crystals are introduced to the system, they appear as a white spots because of the rotation of polarized light. This can be used to determine the size and structure of any anisotropic wax crystals (Kané et al. 2002). This direct microscopic view of wax crystals is used to detect the formation of crystals as small as 1μm(Hammami and Raines 1999).

2.5   Wax Deposition Predictive Simulators

Various simulators like TUWAX, OLGA's wax deposition module, PvTsims Depowax etc. include some of the progress made in our understanding of the thermodynamic equilibrium and deposition mechanisms of wax. These software packages cannot be completely relied because the model used in the software has their own assumptions and limitations (A. Singh et al 2011). For example, Singh et al (2000) models works very well within laminar flow but for turbulent region it needs to be modified (Venkatesan 2003). Since the complexity of the wax phenomenon these simulators do not capture all of the physics and tend to ignore some of the critical aspects while simplifying the modeling parameters

Validation of wax deposition models have been the focus of several research projects published in the 1iterature. Model systems comprised of food grade waxes dissolved in model oils (a blend of mineral oil and Kerosene) were used by several researchers (Singh et al. 2000, Venkatesan, 2003, and Lee 2008) to perform the laboratory deposition experiments utilizing a flow loop system. These researchers were able to fit the modeling parameters to match their experimental data. However, limited attempts were made to validate the wax deposition models for real crudes using laboratory data. Tulsa University Paraffin Deposition (TUPDP) consortium has extensively utilized South Pelto crude and Garden Bank condensate (Lund, 1998, Matzain 1998, Apte et al. 2001, Hernandez, 2003, Couto et al, 2006. Espinoza, 2006. Bruno et al, 2008) to obtain experimental data to further study to predict wax deposition. Recently a detailed experimental study was presented on a North Sea condensate (43 API) using a 1aboratory now loop system by Hofmann and Amundsen (2010). In another waxy study, a west African waxy crude (36 API) tested in flow loop deposition setup by Alboudwarej at all (2006). With these studies, significant progress made on wax prediction but scale-up of the data to the real cases still remains as a problem.

Very few attempts have been made to validate the wax deposition models using feld data su etal. 1998, Klienhas et al, 2000). Instead of true field scale systems, these studies utilized side streams and loops at the well site to generate data using fresh produced fluids. Labes-Carrier et al (2002) and Bagatin al (2008) utilized some of the operational experience and qualitative information to validate wax deposition predictions.

2.6   Wax Content

High Temperature Gas Chromatography (HTGC) can be used to characterize the molecular weight distribution of both the n-alkane and the all hydrocarbons as a function of the carbon number present in the stock tank sample (A. Singh et al 2011). The results are presented as the weight percent of all hydrocarbon containing a given carbon aumber and the weight percent ofa-parafin (Fig. 2.2). Because the normal n-aikanes precipitate at higher temperatures than the so-alkanes of the same carbon number, they are responsible for higher cloud points and wax deposition issues
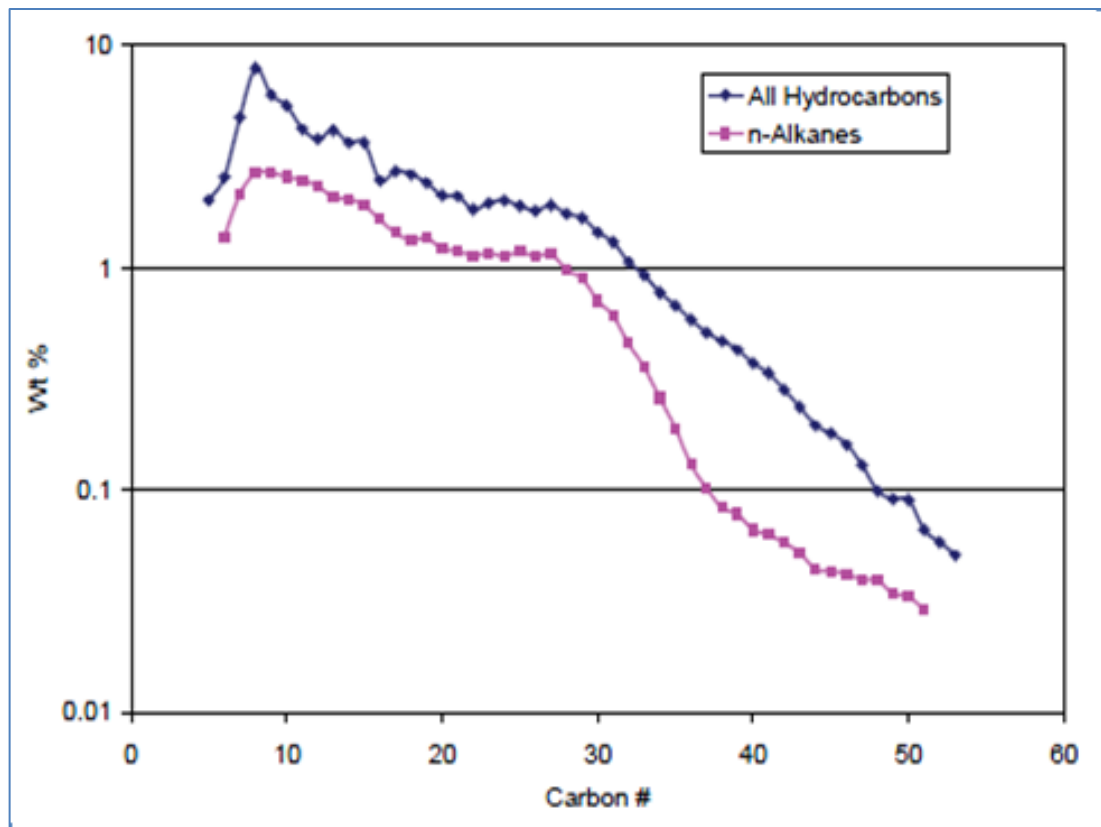
Figure 2.2 : Weight Percent Distribution of n-Alkanes and All Hydrocarbon.
Adapted from A. Singh et al (2011)

2.7 Wax Appearance Temperature (WAT)

Wax Appearance Temperature (WAT), which is also known as cloud point is an important parameter to see weather there will be precipitation or not (Ayoub 2000). It is the temperature of which wax crystals started to form. The most important parameters that affect the hydrocarbon cloud point temperature are the apparent molecular weights of solution and solute, and solute weight fraction. Majority of existing wax models (Coutinho, 1998; Vafaie-Sefti et al., 2000; Coutinho and Daridon, 2001; Azevedoand Teixeria, 2003) and experimental measurements (Pedersen et al., 1991; Chevallier et al., 2000; Roehner and Hanson, 2001; Wu et al., 2002) are based on WAT. Viscosity measurements indicate that crude oils exhibit Newtonian behavior at temperature above WAT and Non-Newtonian elsewhere (A. M. Elsharkawy, 1999).

WAT can be measured by using Cross Polar Microscopy (CPM). The sample will be preheated to $82°C$ (180^0F) to remove any themal history and introduced inside a microscope capillary that has been placed on the stage at 80^0C (176^0F). PPT of the stock tank sample can be measured by using ASTM D5853-95 procedure with the "beneficiated" method that requires preheating the crude to $82°C$ to remove the thermal history and then gradually cooling the sample until it no longer pours. The "benefciated" method is usually the most applicable for crude production situations where the crude is flowing hot and then allowed to cool when flow is stopped.

2.8 Wax Models

Several models have been presented in the literature for the prediction of WAT and amount of wax formed at different temperatures (Weingarten and Euchner, 1986). These models generally overestimate the WAT and amount of wax formed below the cloud-point temperature (Lira-Galaena, 1996). Won(1995) used regular solution theory to describe the non-idealities in oil and wax phases. Hansen et al.(1988) applied polymer solution theory of Flory(1953) for the description of oil phase while the wax phase was assumed to be an ideal. The cloud points obtained using the model of Won were somewhat higher than those measured. Countinho et al. (1995) proposed a model in which the solid state is described by local composition. Ungerer et al. (1995) hypothesis that each component of the heavy fraction of crude oil can crystallize pure wax leading to several solid wax phases. Finally Pedersen (1991) has

presented a thermodynamic model based on equation of state to predict the wax formation at different conditions. Results reported by Pedersen(1995) shows that the model successfully matches the experimental data for wax deposition for the North Sea crudes. Hamouda et al.(1993) reported that wax deposited in pipeline at higher temperature than those measured in laboratory where pipeline wall roughness and/or the presence of nucleation sites, such as solid, corrosion products etc., plays great role for depositing wax from undersaturated fluids.

2.9   Viscosity of the Stock Tank Oil

Haake Rs 150 Rheometer with a rotational pressure cell can be used to measure the viscosity of the crude saturated with separator gas at 150 psig to simulate the pipelne operating conditions(A. Singh et al 2011). Figure 2.3 shows the measured viscosity data for the live crude with some gas dissolved at different shear rates rangng from 30 and 1.0001/sec. It can be noted that the viscosity of the crude begins to rapidly increase when the crude cool below 60°C and even more rapidly below 35°C. The fluid behaves almost Newtonian at temperature above 60°C. However, the fluid turns non-Newtonian below WAT due to the presence of the wax crystals. The default viscosity predicted by the TUWAX program matches very well with the single phase viscosity of the crude above 60°C. Below 60°C. The presence of wax crystals changes the rheology of the slurry by making it highly viscous non-Newtonian fluid. The viscosity of the continous medium of the slurry is expected to follow the default viscosiy prediction below 60°C.
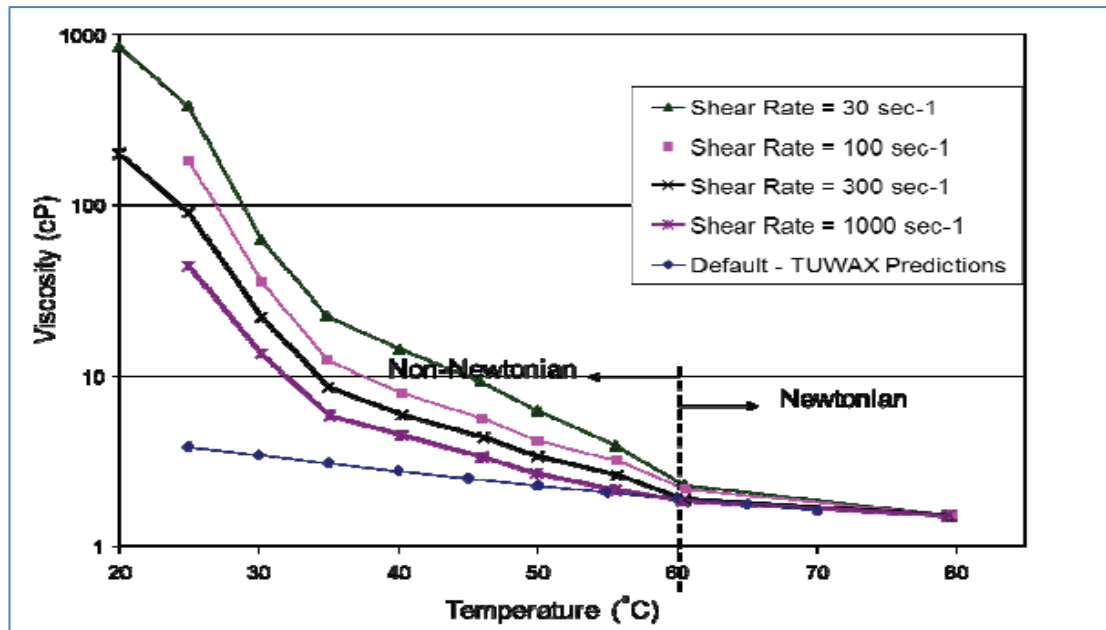
Figure 2.3: Viscosity vs Temperature of Live Crude Oil. Adapted from A. Singh et al (2011)

2.10 TUWAX Thermodynamic Modeling

TUWAX uses HTGC analysis results of the sample as input to develop a thermodynamic model of the waxy cude oil and identify which carbon number n-alkanes will precipitate at a given temperatre and pressure if gas is dssolved in solution. The WAT is defned as the temperature and pressure at which 0.02 mole% of the crude precipitate out as the solid state.

Table 2.1 : Summary of Results of Crude Properties. Adapted from A. Singh et al (2011)

Crude Property	Measurement Technique	Values
API @ 60^OF	Anton Paar DMA 5000	45
Density (g/cc)	Anton Paar DMA 5000	0.8
Cloud Point (WAT)	Cross-Polarized Microscopy	58^OC (136^OF)
	Anton Paar DMA 5000	57^OC (135^OF)
	TU MSI Model	55.5^OC (132^OF)
WAT in Pipeline	Live Oil TU MSI Model	55^OC (131^OF)
STO Pour Point (PPT)	ASTM D5853-95 Beneficiated Method	29^OC (85^OF)
Wax Content (%)	HTGC n-C19+	17
Asphaltene Content (%)	IP 143	0.03

2.11 Live oil composition

In order to study the behavior of the crude in the subsea pipeline, the composition of the live oil will be estimated. Depending on the pipeline operating conditions, the liquid phase may contain some light ends that are not present in the stock tank sample (A. Singh et al 2011). It is important to estimate the additional light ends that will be present in the pipelne fluid relative to the stock tank sample since they may have some effect on the wax deposition rate.

The general procedure used was to develop a good thermodynamic model of the reservoir fluid and then flash it to the separator pressure and temperature conditions to estimate the composition of the pipeline fuid. Figure 4 shows the analysis of the separator oil composition obtained at 150 psig and 60^0F from TUWAX program. This live oil is expected to contain 2.3% of light C1-C4 components that are missing in the stock tank analysis.
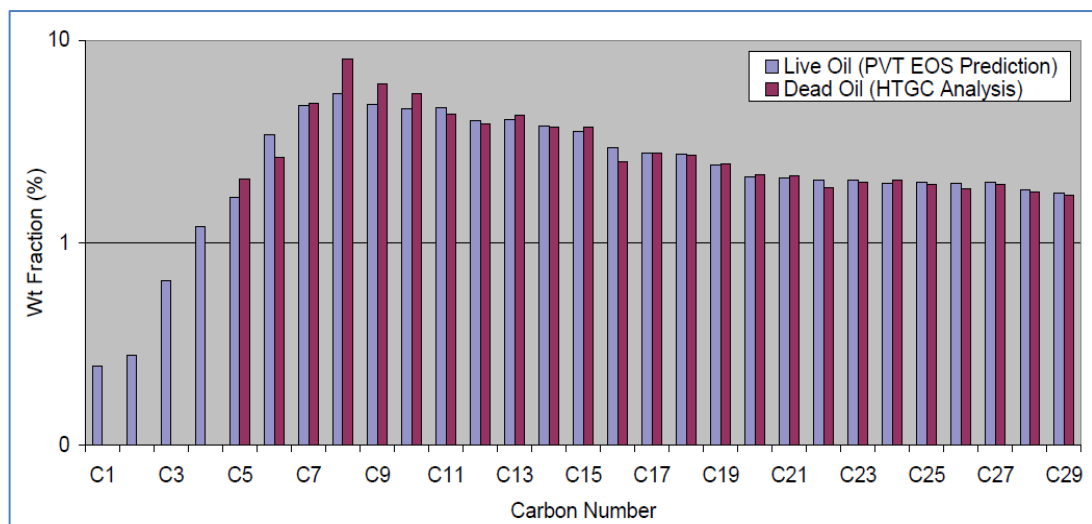
Figure 2.4 : Live and Dead Crude Oil Compositions. Adapted from A. Singh (2011)

2.12 Wax Precipitation vs Temperature

Figure 2.5 shows the TUWAX predictions of solid weight fractions as a function of temperature (A. Singh et al 2011). Note that the precipitated solid fraction of 0.02 mo1e% was predicted at the WAT of 55°C. The curve increases rapidly below 35°C. The faction of solids at the pipeline exit temperature of 29°C is predicted to be 6 wt%. The presence of 6 wt% solid cristals result in an increase in the bulk viscosity of the slurry by one to two orders of magnitude.
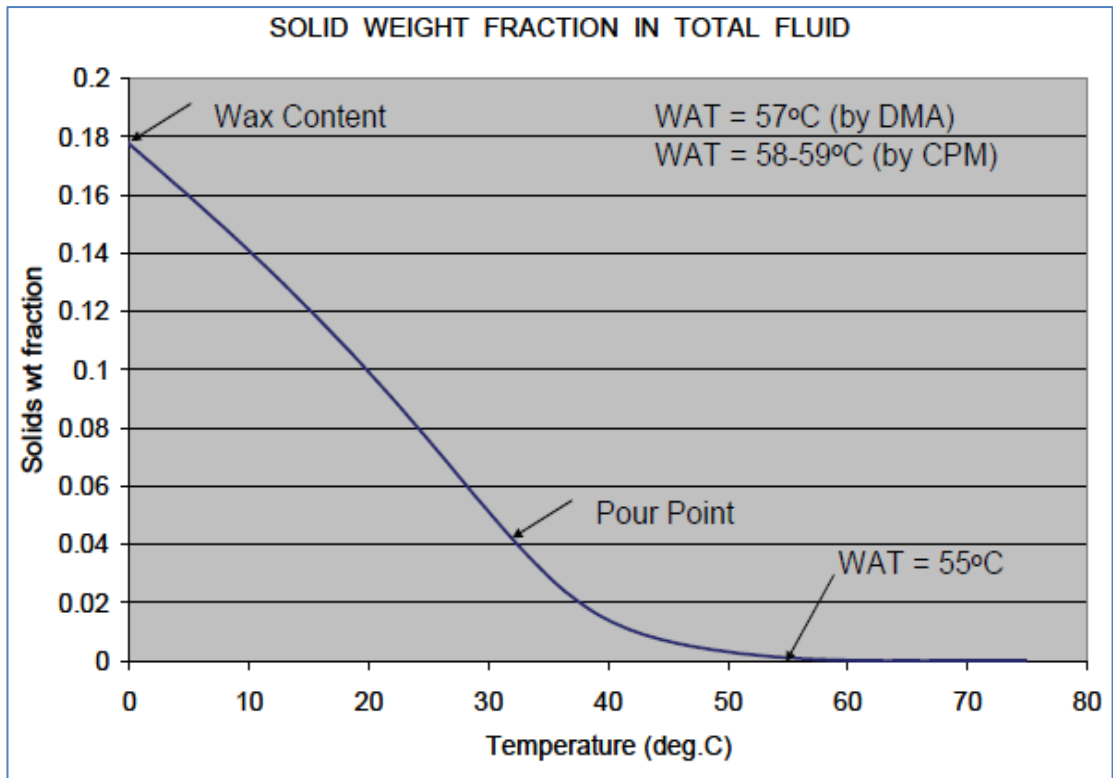
Figure 2.5 : Solid Weight Fraction vs Temperature. Adapted
from A. Singh et al (2011)

CHAPTER THREE

METHODOLOGY

3.1 Project Work

PVT-P Software

Wax Amount Calculation

This calculation can be initiated by selecting the Wax Amount (Multiphase Flash) from the Calculation of Solid menu. There are two modes available for data input, which is Automatic and User Selected. This mode can be changed by using the radio buttons.

Data Input : Automatic

The limits of the temperature and pressure ranges to be covered as well as the number of points to be calculated for each variable can be insert in the data entry boxes provided. The wax formation is only significantly affected by temperature and is not significantly affected by pressure.

Data Input : User Selected

The ranged input is replaced by a grid where any mixture of pressures and temperatures can be entered.

Wax Appearance Temperature Calculation

This calculation can be initiated by selecting the Wax Amount (Multiphase Flash) from the Calculation of Solid menu. There are two modes available for data input, which is Automatic and User Selected. This mode can be changed by using the radio buttons. Data entry boxes are provided for entering the limits of the temperature and pressure ranges to be covered and the number of points to be calculated for each variable. The points will be spread evenly throughout the pressure ranges selected.

Stream Selection

There will be a list box in the range calculation (CCE) that allows the user to select any combination of streams to calculate. A stream is the main structure for holding data within a PVT file. A project must have at least one stream. Each stream is independent with the following data contained within it:

- Composition
- Calculation data
- Referrence data
- Match data
- Regression data

There also will be major model options displayed in the Range Calculation dialog. Only one set are allowed per file. Preference Dialog will be displayed by clicking on the "Change" Button. There will be various Wax Models that can be selected by the user in the combo box within the preferences dialog. Important component properties can be reset back to the default values outlined by the model's author by clicking on the Reset Props button.

Pressure Range

The lower pressure limit of the calculation has been set at 0 psig (14.7 psia). If a value below this limit is entered the following message will appear

Wax Model

A model for wax formation were initialy proposed by Won based on an ideal solution. Basic equations are derive as follow:

$$f = \gamma_2 x_2 f_2^0$$

where

x_2 is the mole % solute in the solvent or solubility,

γ_2 is the liquid-phase activity coefficient and

f_2^0 is the standard state fugacity.

if it is assumed that the solvent and solute are very similar making

$\gamma_2 = 1$, and equation 1 becomes

$$x_2 = \frac{P_{1(pure\_solid)}}{P_{2(subcooled\_liquid)}}$$

with P being the vapour pressure and x_2 now referred to as the *ideal solubility*.

Note that the problem is analysed in terms of a subcooled liquid and a thermodynamic cycle Further detailed analysis are done by Prausnitz(1969).
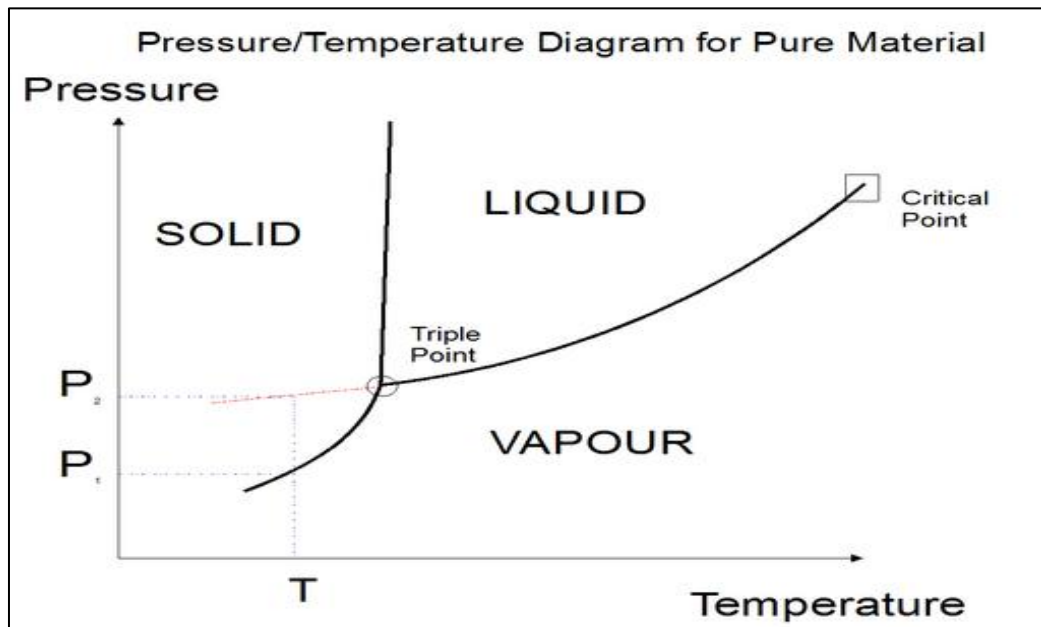
Figure 3.1 : Pressure vs temperature diagram

The problem can be more generally solved using the thermodynamic cycle shown in figure below.
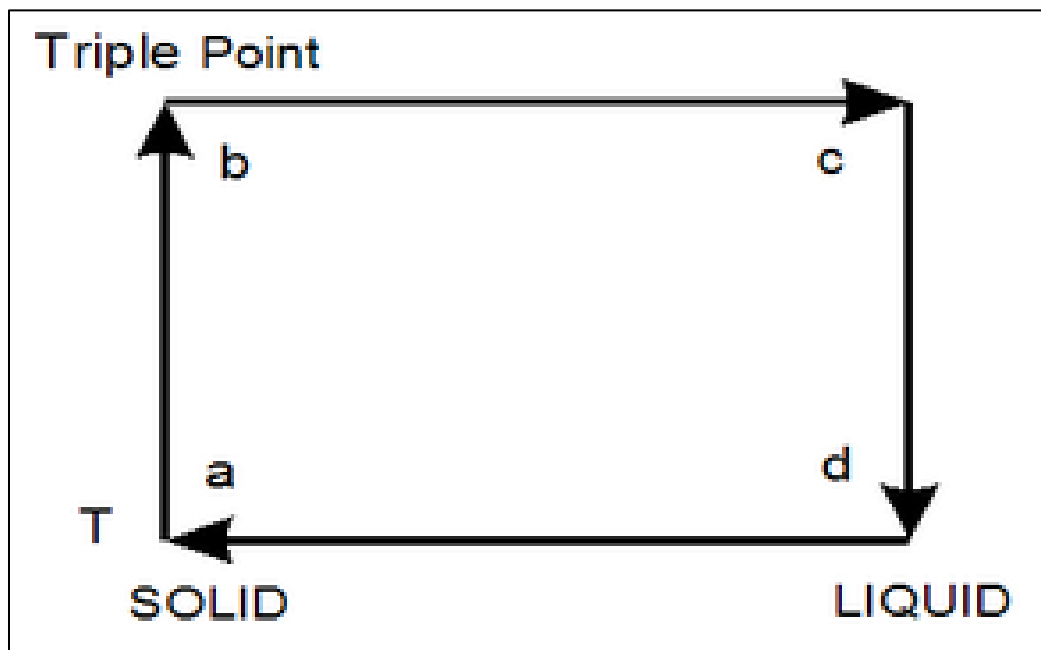
Figure 3.2 : Thermodynamic Cycle

However, there are some assumption that need to be taken in consideration.

Assumption 1

Assuming negligible solubility of the solvent in the solid then equation 1 can be written as

$$x_2 = \frac{f_2^S}{\gamma_2 f_2^L}$$

Assumption 2

It is assumed that the fugacities depend only on the solid forming component and are independent of the nature of the solvent. The thermodynamic cycle allows the ratio of the two fugacities to be calculated. The change in Gibbs free energy going from a to d is given by:

$$\Delta G_{a \to d} = RT \ln\left(\frac{f_2^L}{f_2^S}\right)$$

and also can be written

$$\Delta G_{a \to d} = \Delta H_{a \to d} - T\Delta S_{a \to d}$$

Using the thermodynamic cycle a->d is replaced by a->b->c->d . enthalpy becomes:

$$\Delta H_{a \to d} = \Delta H_{a \to b} + \Delta H_{b \to c} + \Delta H_{c \to d}$$

This can be rewritten in terms of the Heat of Fusion(Melting) and the specific heats in going from temperature T to the triple point.

$$\Delta H_{a \to d} = \Delta h_f + \int_{T_t}^{T} \Delta C_p dT + T\int_{P}^{P_t} \left(\frac{d\Delta v}{dT}\right) dP - \int_{P}^{P_t} \Delta v dP$$

Assumption 3

The volume change at the melting point is assumed to be negligible and these terms are ignored, giving:

$$\Delta H_{a \to d} = \Delta h_f + \int_{T_t}^{T} \Delta C_p \, dT$$

The entropy cycle can be written as:

$$\Delta S_{a \to d} = \Delta S_{a \to b} + \Delta S_{b \to c} + \Delta S_{c \to d}$$

which in a similar way to enthalpy becomes

$$\Delta S_{a \to d} = \Delta S_f + \int_{T_t}^{T} \frac{\Delta C_p}{T} \, dT - \int_{P}^{P_t} \frac{d\Delta v}{dT} \, dP$$

Assumption 4

Again the volume change is assumed to be negligible giving

$$\Delta S_{a \to d} = \Delta S_f + \int_{T_t}^{T} \frac{\Delta C_p}{T} \, dT$$

The entropy change at fusion is defined as:

$$\Delta S_f = \frac{\Delta H_f}{T_t}$$

Substituting the results of the cycle in eqn 2 and rearranging gives the equation which acts as the fundamental for many wax models:

$$\ln\left(\frac{f_2^L}{f_2^S}\right) = \frac{\Delta H_f}{RT_t}\left(\frac{T_t}{T} - 1\right) - \frac{\Delta c_p}{R}\left(\frac{T_t}{T} - 1\right) + \frac{\Delta c_p}{R}\ln\left(\frac{T_t}{T}\right)$$

Assumption 5

For most materials the melting point line is nearly parallel with the Pressure axis allowing the triple point temperature to be replaced with the melting point.

$$\ln\left(\frac{f_2^L}{f_2^S}\right) = \frac{\Delta H_f}{RT_t}\left(\frac{T_{melt}}{T} - 1\right) - \frac{\Delta c_p}{R}\left(\frac{T_{melt}}{T} - 1\right) + \frac{\Delta c_p}{R}\ln\left(\frac{T_{melt}}{T}\right)$$

Assumption 6

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Implicit in the use of this equation is that the thermodynamics of a pure substance in an ideal solution can be extended to a mixture where the solvent is non-ideal and the solid is neither ideal nor a pure single species. Some points to note about this equation is that it is dominated by the Melting Point value. In essence this value determines when the solid may start to form. The other important term is the Heat of Melting which plays a role both in the formation temperature and the amount of solid formed. In its simplified form, this equation as used by Won overestimates both the Wax Appearance Temperature and the amount of wax formed. The various models question the assumptions built into this model extending the equation in various ways to remove these errors.

MODEL DETAILS SECTION

Won Original

Won derived and expressed equation as follows:

$$K_i^{SL} = \frac{S_i}{x_i} = (\frac{\gamma_i^L}{\gamma_i^S}) \exp[\frac{\Delta H_f}{RT_t}(1 - \frac{T}{T_{melt}}) + \frac{\Delta c_p}{R}(1 - \frac{T_{melt}}{T} + \ln(\frac{T_{melt}}{T})) + \int_0^P \frac{\Delta v}{RT}dP]$$

where x_i are the mole fractions of i in the liquid and solid respectively.

Won simplified this equation by assuming the second and third terms were equal to zero and the ratio of activity coefficients

$$(\frac{\gamma_i^L}{\gamma_i^S})$$

was equal to 1.

This leaves a fairly simply equation which unfortunately exaggerates both the Wax Appearance Temperature and the amount of wax formed.

$$K_i^{SL} = \frac{S_i}{x_i} = \exp[\frac{\Delta H_f}{RT_t}(1 - \frac{T}{T_{melt}})]$$

Within the model the required values for Melting Points and Heats of Melting are taken from the following correlations

$$T_{melt} = 374.5 + 0.02617 \, .M_i - \frac{20172}{M_i}$$

and

$$\Delta H^f = 0.1426 \, .M_i T_i^m$$

where x_2 is the molecular Weight of component i.

Won with Solubility Parameters

Won has later suggested that the assumption

$$\left(\frac{\gamma_i^L}{\gamma_i^S}\right)$$

was equal to 1 was in valid as it lead to and overestimation of the solubilities of C5 to C10 in the solid solution. Instead he proposed an estimation of the activity coefficients based on modified regular solution theory. This gives a method of estimating the activity ratio based on solubility parameters

$$\frac{\gamma_i^L}{\gamma_i^S} = \exp\left[\frac{v_i}{RT} \{ (\bar{\delta} - \delta_i)_L^2 - (\bar{\delta} - \delta_i)_S^2 \} \right]$$

where

$$v_i = \frac{M_i}{d_{25}^L}$$

x_2 is the molecular Weight of component i and

d_{25}^L is the liquid density of the component at 25 degrees C estimated by:

$$d_{25}^L = 0.8155 + 0.6272 \, e - 04 \, M_i - 13.06 / M_i$$

The paper gives estimates of the solid and liquid solubility parameters δ up to C40.

$\bar{\delta}$ is the average solubility parameter for the respective phase

Within this model the Won uses the correlations outlined in his original model for estimating melting points and heats of melting.

Chung Original

This model is very similar to Won with Sol Params above. The difference lies in the assumption that the all the species in the solid are very similar and that the activity coefficient of the solid can therefore be set to 1. Equation in Won Original is modified by the introduction of solubility parameters to be:

$$K_i^{SL} = \frac{S_i}{x_i} = \exp[\frac{\Delta H_f}{RT}(1 - \frac{T}{T_{melt}}) + \frac{v_i}{RT}(\bar{\delta} - \delta_i)_L^2 + \ln(\frac{v_i}{V_m}) + 1 - (\frac{v_i}{V_m})]$$

with

$$V_m = \sum x_i v_i$$

Within this model the author uses the correlations outlined in won original for estimating melting points and heats of melting. In addition the following correlations are suggested for molar volume and liquid solubility parameter.

$$v_i = M_i / (0.8155 + 0.6272\, e - 04\, M_i - \frac{13.06}{M_i})$$

and

$$\delta_i^L = 6.993 + 0.781\,\beta - 0.049\,\beta^2 - 10.235 / \beta$$

where

$$\beta = \ln(M_i)$$

and

x_i is the molecular Weight of component i

Chung Modified

This model is very similar to Won with Sol Params above. The difference lies in the correlations listed below:

$$\Delta H^f = 0.9 T_i^m (M_i^{0.55})$$
$$v_i = 3.8 (M_i^{0.786})$$

and

$$\delta_i^L = 6.743 + 0.938\,\beta - 0.0395\,\beta^2 - 13.039\,/\,\beta$$

Pedersen Wax

The model is derived from the simplified version of equation used by Won i.e.

$$\ln\left(\frac{f_2^L}{f_2^S}\right) = \frac{-\Delta H_f}{RT_t}\left(1 - \frac{T_{melt}}{T}\right)$$

Substituting fugacity coefficients for fugacities, this equation becomes:

$$f_i = x_i \phi_i \, p \, \exp\left[\frac{-\Delta H_f}{RT_t}\left(1 + \frac{T}{T_{melt}}\right)\right]$$

where

x_i is the fugacity of component i in the solid phase

ϕ_i^L is the liquid fugacity coefficient of component i

x_i is the solid phase mole fraction of component i

and p is the pressure.

The basis for the model is the presumption that not all the high molecular weight material can form waxes. The fraction which is allowed to do so within the model comes from an empirical relationship :

$$z_i^S = z_i^{total}\left[1 - (A + B - Mi).\left(\frac{p - p_i^p}{p_i^p}\right)^C\right]$$

Where

z_i^S is the fraction of

z_i^{total} allowed to become wax,

x_i is the C7+ molecular weight

γ_2 is the SG of component i

and

ϕ_i^L is the SG of an equivalent paraffin given by:

$$\rho_i^p = 0.3915 + 0.0675 \ln(M_i)$$

A B and C are constants with the following values. A = 0.8824 , B= 0.0005354 and C=0.1144. The component melting points and heats of melting are calculated using correlations proposed by Won.

$$T_i^m = 374.5 + 0.02617 \, M_i - \frac{20172}{M_i}$$

and

$$\Delta H_i^m = 0.1426 \, M_i T_i^m$$

Compositional data was taken from the literature review since the compositional data for the project are not available due to time constrain.

Table 3.1 : Compositional Data for Middle East("*Determination and Prediction of Wax Deposition from Kuwaiti Crude Oils*" Adel M. Elsharkawy, SPE, Taher A. Al-Sahhaf, Mohamed A. Fahim, and Wafaa Al-Zabbai, Kuwait University)

Oil Component	A
N2	0
H2S	0.13
CO2	0.03
C1	0.02
C2	0.34
C3	1.62
i-C4	0.81
n-C4	3.28
i-C5	2.19
n-C5	4.10
C6	7.19
C7	80.29

Multi-Phase Flash

Multi-Phase systems are needed when wax or asphaltenes are present in the oil. Other than that, this system also will be needed when there is high concentration of CO_2 at low temperatures. Thus, getting familiar with the system is necessary to ensure that the project will proceed smoothly. As for the time being, these are the methodology that was able to achieved. Continuation of development of the methodology will always be done by time to time.

PIPESIM Production System Analysis Software

Shell Method

Wax Properties Setup - This dialog allows the user to change data for prediction of wax in the model.

Wax Properties - required

- Density. Must be supplied if the max. wax plug DP/max. volume stopping option is used. Reasonable value: 55 lb/ft3
- Thermal Conductivity. Reasonable value: 0.15 Btu/hr/ft2/F
- Yield Strength. Reasonable value: 0.3 psi

CWDT (critical wax deposition temperature) - required

- Deposition temperature against pressure

Modeling Parameters

- A & B constants against temperature
- Rate model - required
- Model to use, Default #1

Wax Deposition Limits - This dialog sets limits for the wax deposition calculations

General :

- Start/Restart time - The starting time
- Reporting interval - When reports are required. This will govern the maximum time step that can be used.

- Termination Model - The simulation will finish when the first stopping criteria is met

- End time - the finish time for the simulation if no other stopping criteria is met

- Maximum PigDP / Maximum Wax Volume

- Maximum Wax Thickness

- Minimum Production Liquid rate/gas rate/mass rate

- Maximum System DP- The system pressure drop is exceeded

Timestep Calculation criteria

- Minimum step - smallest time step

- Relaxation parameter

- Step size

- DP factor

- Minimum Dx

- Set Dx

- HTC Limit

BRITISH PETROLEUM (BP) Method

Wax Properties Setup - This dialog allows the user to change or input data for prediction of wax in the model.

Wax Properties - required
- Conductivity Multiplier
- Yield Strength. Reasonable value: 0.3 psi

Properties Filename - required
- File that contains the wax properties data - *.thm file
  Diffusion Coefficient Method - required
- Wilke-Chang - requires a Diffusion Coefficient Multiplier
- Hayduk-Minhas - requires a Diffusion Coefficient Multiplier
- User supplied - requires a Diffusion Constant

Oil Fraction in Wax   - required
Roughness Multiplier   - required

Shear Multiplier   - required

Wax Deposition Limits - This dialog sets limits for the wax deposition calculations

Schlumberger DBR Method

Wax Properties Setup - This dialog allows the user to change or input data for prediction of wax in the model.

The only required input is the Properties Filename:

- File that contains the wax properties data - *.DBRWax file

However, this file is generated using a third party package DRR Solids version 4.1 and above

Wax Deposition Limits - This dialog sets limits for the wax deposition calculations

Wax Deposition Limits - Sets limits for the wax deposition calculations

General

- Start/Restart time - The starting time
- Reporting interval - When reports are required. This will govern the maximum time step that can be used.

Termination Mode - The simulation will finish when the first stopping criteria is met.

- End time the finish time for the simulation if no other stopping criteria is met
- Maximum Pig DP / Maximum Wax Volume
- Maximum Wax Thickness
- Minimum Production - Liquid rate/gas rate/mass rate
- Maximum System DP - The system pressure drop is exceeded

Timestep Calculation criteria

- Step size

3.2   Process Flow Chart

```
                    ┌──────────────────────┐
                    │  Background of Study  │
                    └──────────────────────┘
                              │
                    ┌──────────────────────┐
                    │   Define Problem      │
                    │   Statements          │
                    └──────────────────────┘
                              │
                    ┌──────────────────────┐
                    │  Background of Study  │
                    └──────────────────────┘
                              │
                    ┌──────────────────────┐
                    │   Define Objectives   │
                    └──────────────────────┘
                              │
        ┌──────────────────────────────────────┐
        │   Study on Literature Review:         │
        │                                       │
        │      • Paraffin wax                   │
        │      • Wax Precipitation and          │
        │        Deposition                     │
        │      • Wax Appearance                 │
        │        Temperature                    │
        │      • Methods to determine           │
        │        WAT                            │
        └──────────────────────────────────────┘
                              │
        ┌──────────────────────────────────────┐
        │   Proposal Defense Presentation       │
        └──────────────────────────────────────┘
                              │
   ┌──────────────────────────────────────────────┐
   │ Interim Report                                 │
   │     • Perform detailed study on literature     │
   │       review                                   │
   │     • Construct detailed methodology           │
   │     • Plan experimental procedure              │
   │     • Prepare necessary equipments and         │
   │       tools                                    │
   └──────────────────────────────────────────────┘
                              │
   ┌──────────────────────────────────────────────┐
   │ Experiment Methodology                         │
   │     • Prepare necessary materials and          │
   │       equipment                                │
   │                                                │
   └──────────────────────────────────────────────┘
```

```
              │
    ┌─────────────────────────┐
    │ Progress Report         │
    │    • Summarize progress │
    │      of the project     │
    └─────────────────────────┘
              │
    ┌─────────────────────────┐
    │ Run simulation software │
    └─────────────────────────┘
              │
    ┌─────────────────────────┐
    │ Data Analysis           │
    │    • Collect, analyze and│
    │      discuss the data   │
    │      material           │
    └─────────────────────────┘
              │
    ┌─────────────────────────┐
    │ Pre-SEDEX Presentation  │
    └─────────────────────────┘
              │
    ┌─────────────────────────┐
    │ Analysis and Discussion │
    └─────────────────────────┘
              │
┌───────────────────────────────────────────┐
│ Discuss and analyze the outcome of the experiment │
└───────────────────────────────────────────┘
              │
    ┌─────────────────────────┐
    │ Conclusion              │
    │    • Conclude the       │
    │      project            │
    └─────────────────────────┘
              │
    ┌─────────────────────────────────┐
    │ Produce a Technical Paper on the project │
    └─────────────────────────────────┘
              │
    ┌─────────────────────────┐
    │ Submit final-draft Dissertation │
    └─────────────────────────┘
              │
    ┌─────────────────────────┐
    │ Viva Presentation       │
    └─────────────────────────┘
              │
    ┌─────────────────────────┐
    │ Project Dissertation    │
    └─────────────────────────┘
```

CHAPTER FOUR

RESULTS AND DISCUSSION

PIPEsim Software

Oil Sample : Oil A
Wax deposition method : Shell

Figure 4.1 : Wax deposition rate vs temperature (Shell Method)

From the graph shown above, the deposition rate start to increase rapidly at the temperature of 103° F. This temperature represents the wax appearance temperature
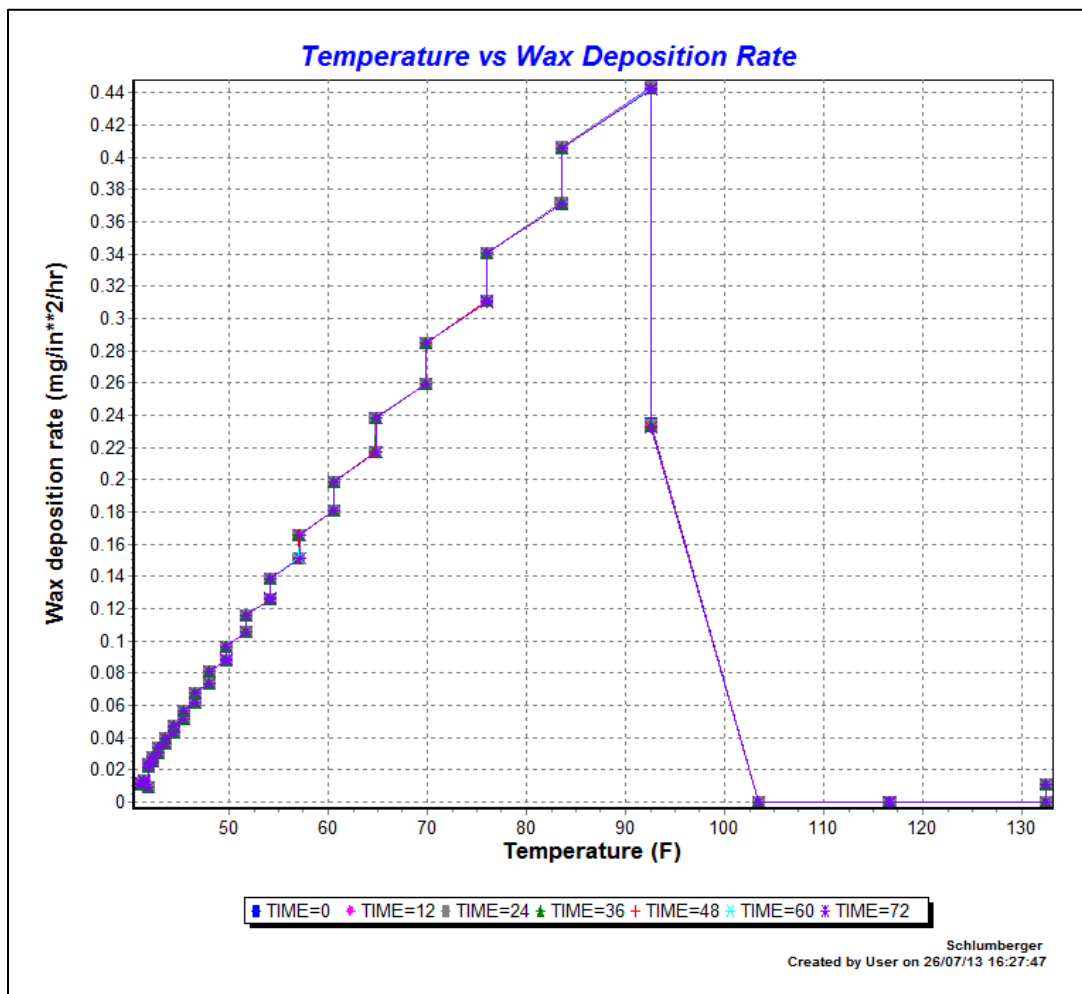
predicted by the PIPEsim software using the Shell Wax Deposition Method. The wax appearance temperature then were compared with the value that was obtained experimentally.
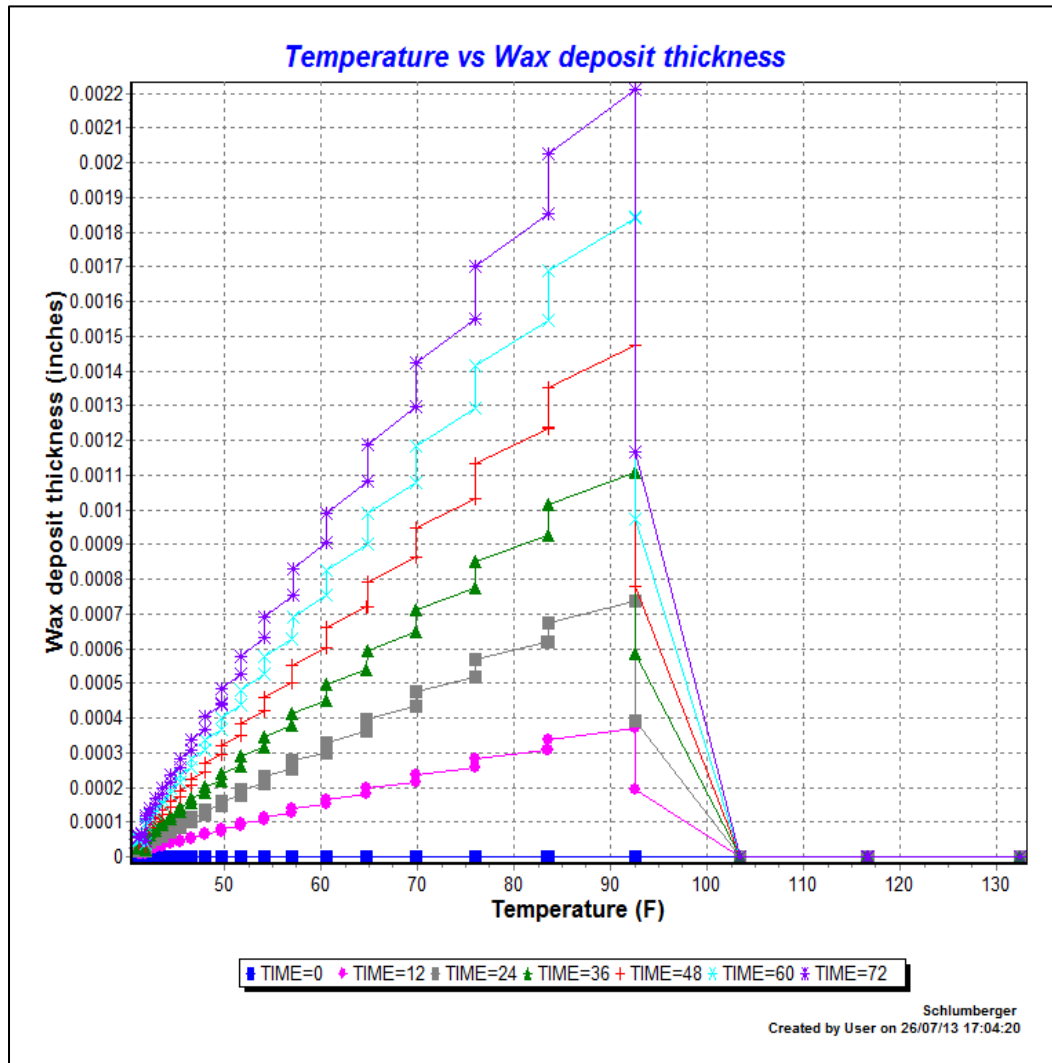
Figure 4.2 : Wax deposit thickness vs temperature(Shell Method)

From this plot, the deposit thickness started to increase at the temperature of 103° F. This happen since the temperature of the fluid model has reach WAT and the paraffin wax started to deposit. Above the temperature of 103° F, the wax deposit thickness is zero because at sufficiently high temperature, crude oils are indeed Newtonian. This means there are no deposition of paraffin wax. The wax deposit thickness is highest at the temperature of 92.63^{o} F because at this temperature the wax deposition rate is the highest. The time variable shows that by time, the wax deposited thickness will increase and will reach the highest thickness at the temperature of 92.63^{o} F. The wax deposition thickness depends on composition of

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oil, temperature, pressure and velocity of fluid. From the graph above, it is clearly shown the effect of temperature to wax deposit thickness. As temperature decrease from 92.63 ^{o} F , the thickness of wax deposited started to decrease gradually due to decrease in rate of wax deposition.
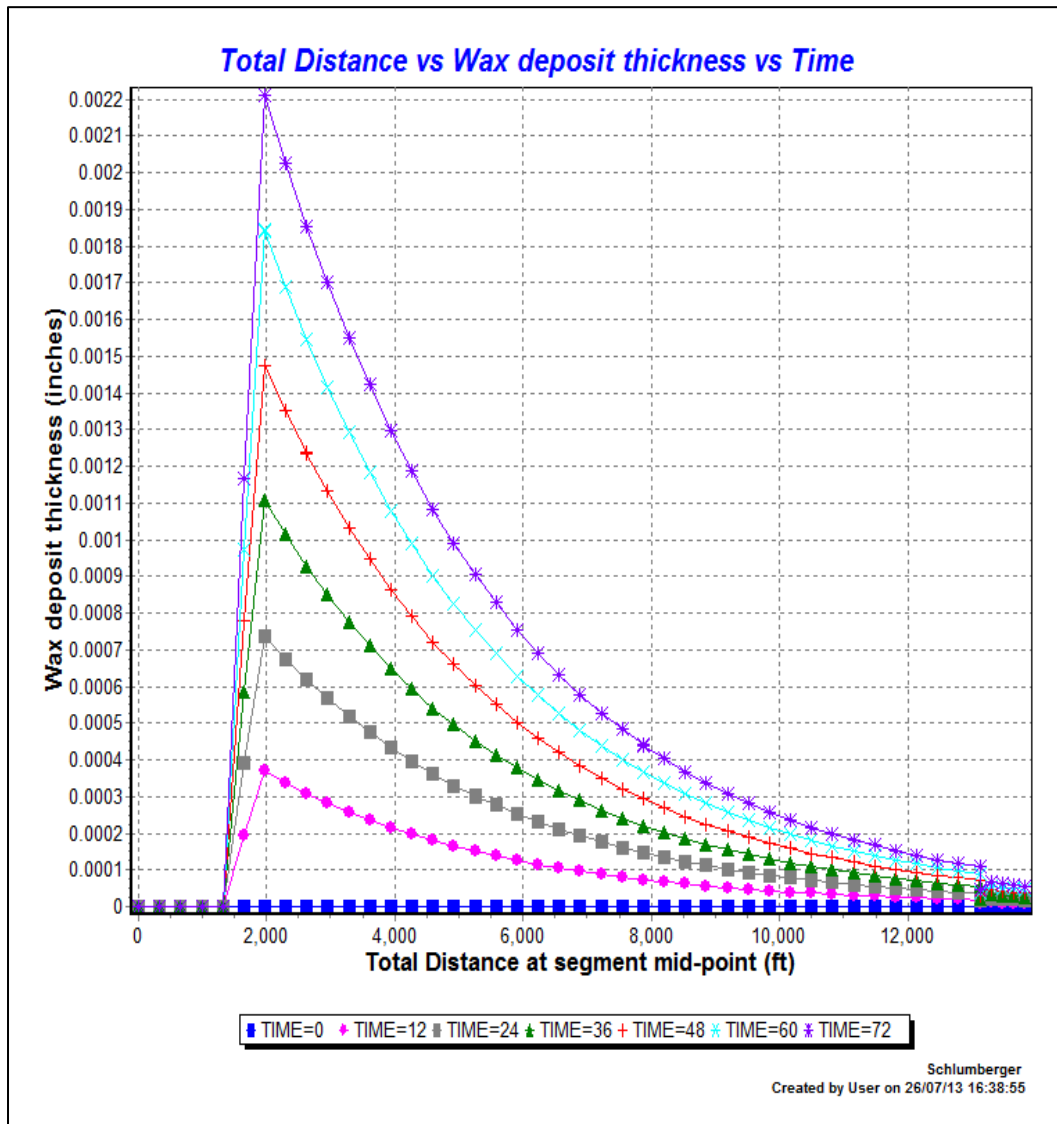

Figure 4.3 : Wax deposit thickness vs total distance vs time(Shell Method)

The graph above shows the wax deposition thickness against the total distance at segment mid-point. The wax deposition thickness has the highest value at the distance of 1968ft at every time interval. At the distance of 12000ft and above, there are paraffin wax deposited but the thickness of it is quite low. As the distance decrease from 12000ft, the wax deposited thickness increase gradually. This is

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because as the distance decrease, the temperature of the crude oil also decrease resulting the wax deposition increase. According to Catherine et al.(2002), a maximum wax layer thickness of 0.0787402-0.11811 inches are often used as a criterion. This is due to the danger of getting the pig stuck in the pipeline if the wax layer gets too thick.
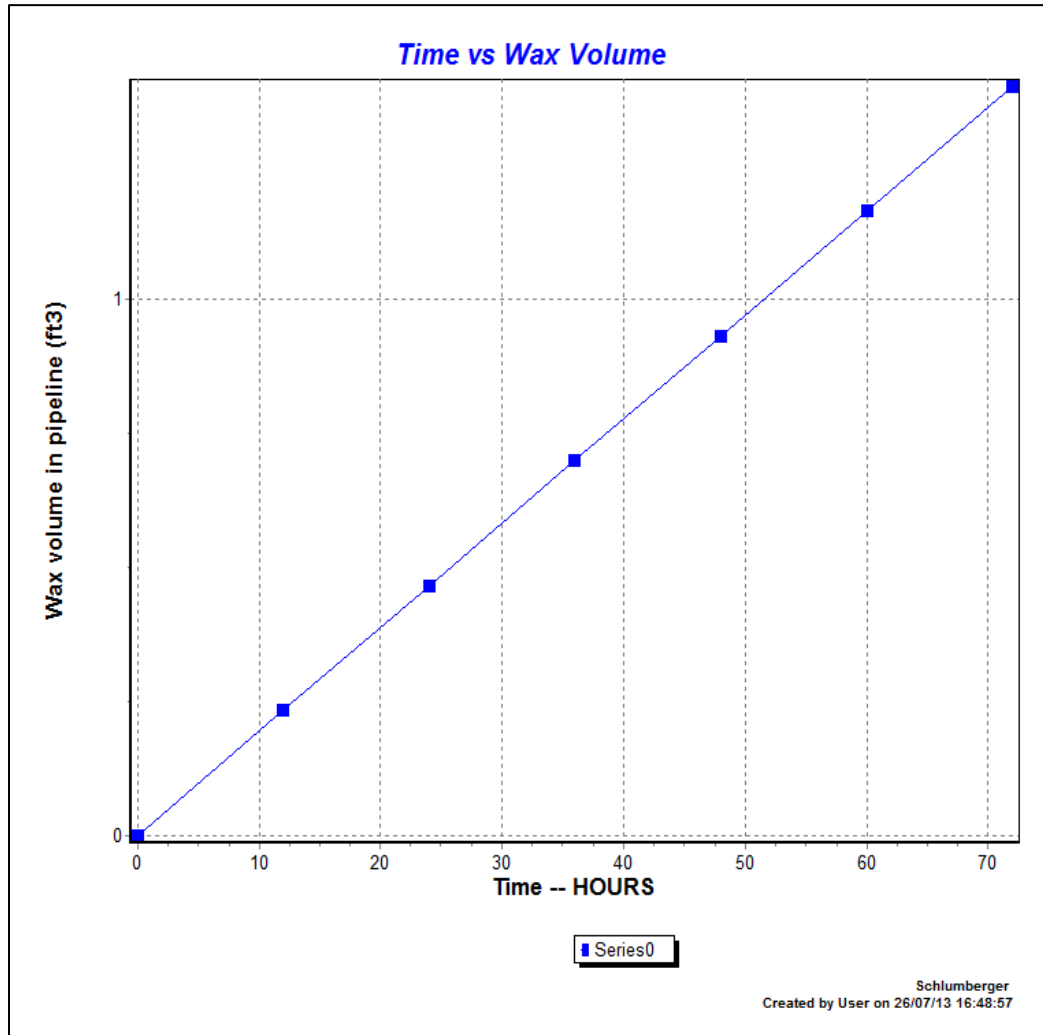

Figure 4.4 : Wax Volume in pipeline vs Time(Shell Method)

The graph above shows that the wax volume exist in pipeline is directly proportional to the time. At the time of 12 hours, the volume of wax exist in the pipeline is 0.2325ft^3. The volume increases to 0.4651 ft^3 after 24hours. At the time of 36 hours, the volume is 0.6976 ft^3. At the interval of 48 hours, 60 hours and 72 hours, the volume of wax deposited in the pipeline is 0.9300 ft^3, 1.1624 ft^3 and 1.3948 ft^3 respectively.

Oil Sample : Oil A
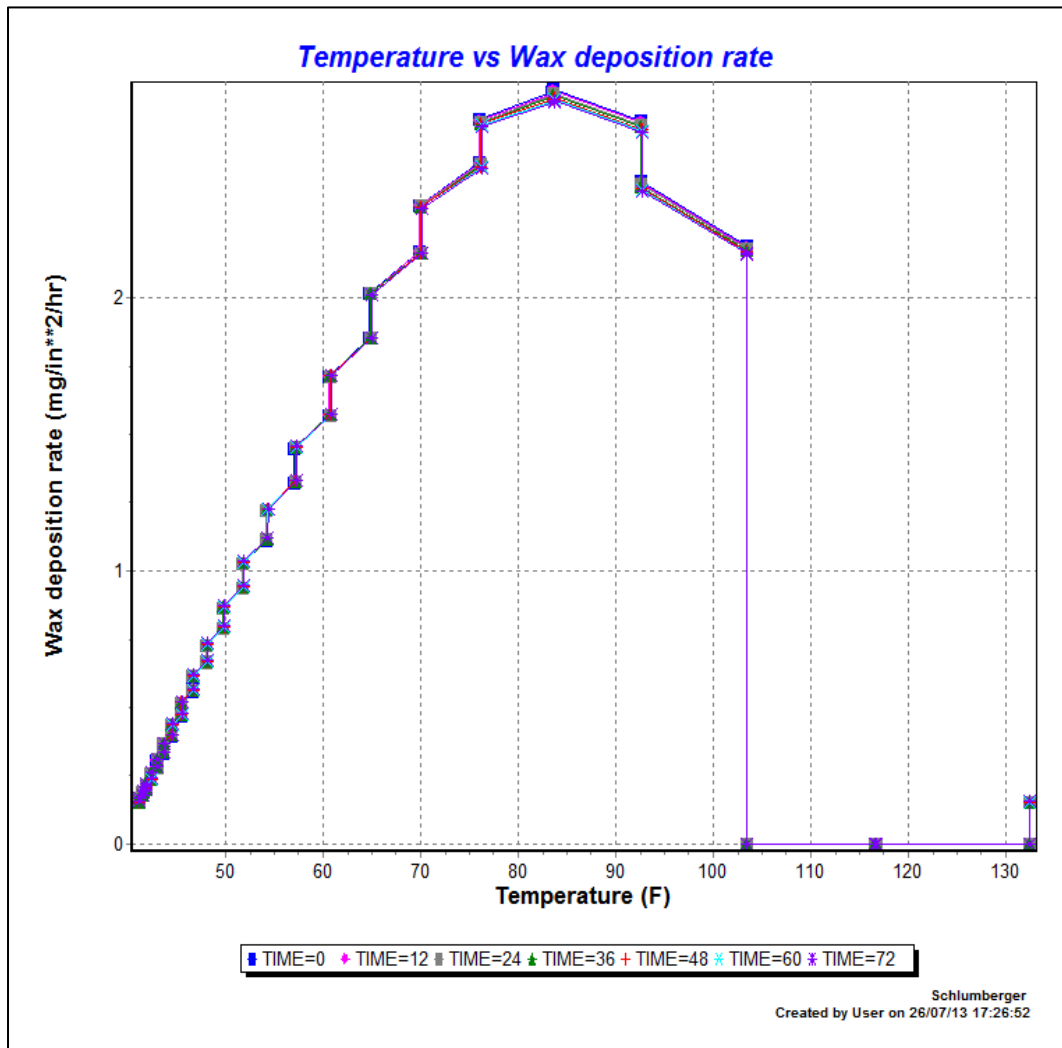**Wax deposition method : Bristish Petroleum (BP)**

Figure 4.5 : Deposition Rate vs Temperature (BP Method)

From the graph shown above, the deposition rate start to increase rapidly at the temperature of 104° F. This temperature represents the wax appearance temperature predicted by the PIPEsim software using the British Petroleum (BP) Wax Deposition Method. The wax appearance temperature then were compared with the value that was obtained experimentally.
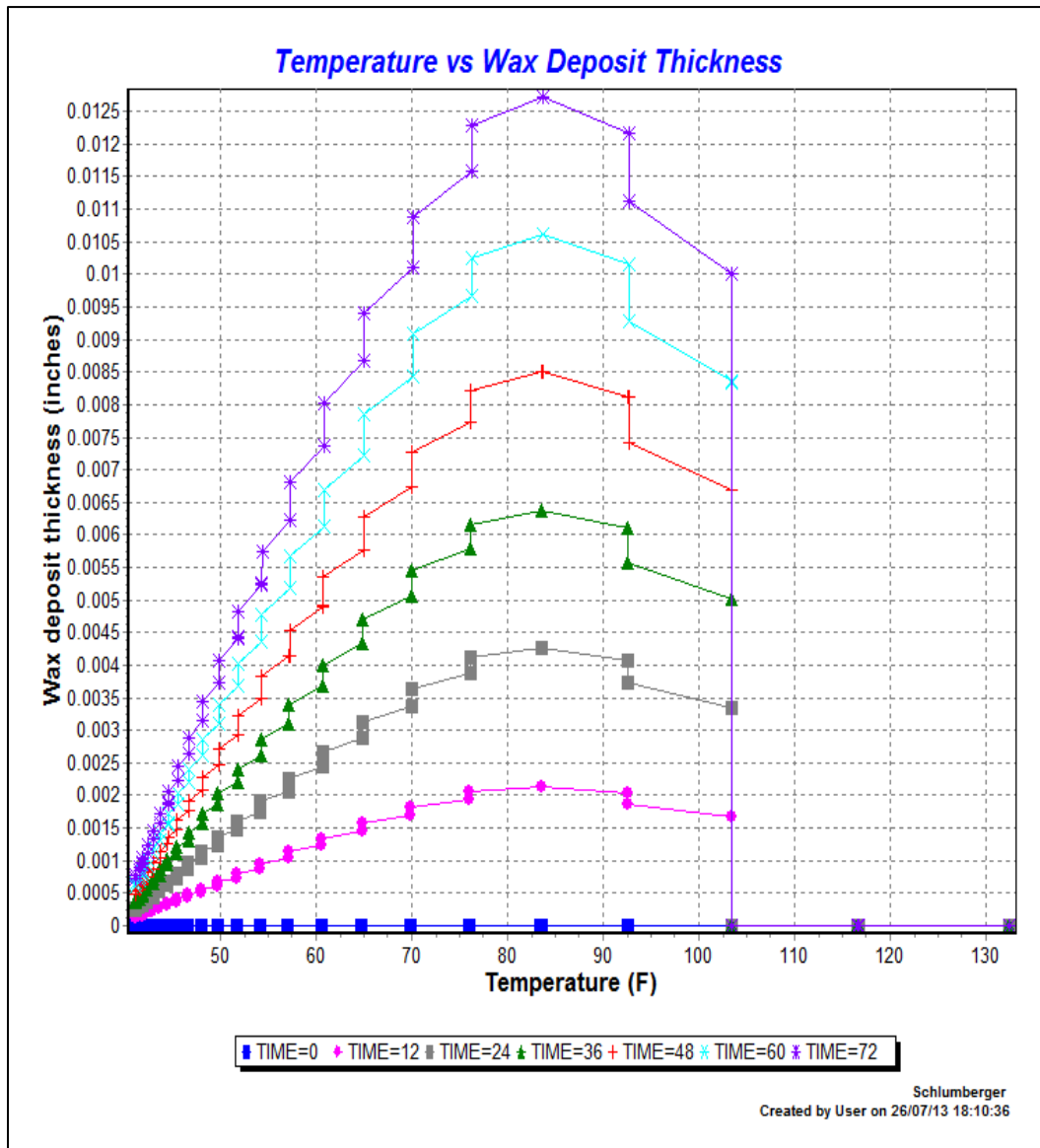
Figure 4.6 : Wax deposit thickness vs temperature (BP Method)

From this plot, the deposit thickness started to increase at the temperature of 104° F. This happen since the temperature of the fluid model has reach WAT and the paraffin wax started to deposit. Above the temperature of 104° F, the wax deposit thickness is zero because at sufficiently high temperature, crude oils are indeed Newtonian. This means there are no deposition of paraffin wax. The wax deposit thickness is highest at the temperature of 83.79^o F because at this temperature the wax deposition rate is the highest. The time variable shows that by time, the wax deposited thickness will increase and will reach the highest thickness at the temperature of 83.79^o F. From the graph above, it is clearly shown the effect of temperature to wax deposit thickness. As temperature decrease from 83.79^o F , the

thickness of wax deposited started to decrease gradually due to decrease in wax deposition rate.
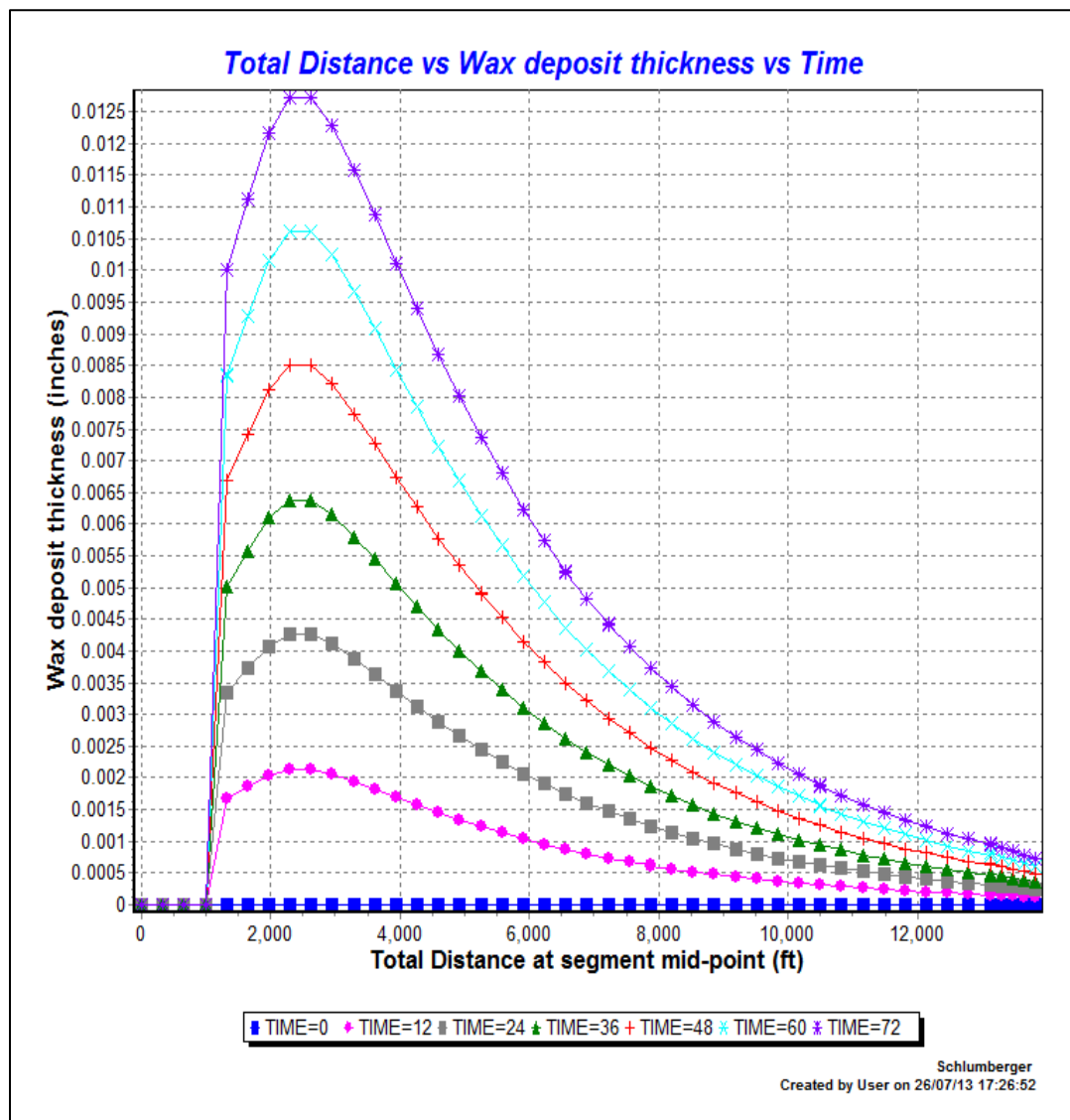

Figure 4.7 : Wax deposit thickness total distance vs time(BP Method)

The graph above shows the wax deposition thickness against the total distance at segment mid-point. The wax deposition thickness has the highest value at the distance of 2296ft at every time interval. At the distance of 12000ft and above, there are paraffin wax deposited but the thickness wax deposited are quite low. As the distance decrease from 12000ft, the wax deposited thickness increase gradually. This is because as the distance decrease, the temperature of the crude oil also decrease resulting the wax deposit thickness increase. According to Catherine et al.(2002), a maximum wax layer thickness of 0.0787402-0.11811 inches are often used as a

criterion. This is due to the danger of getting the pig stuck in the pipeline if the wax layer gets too thick.
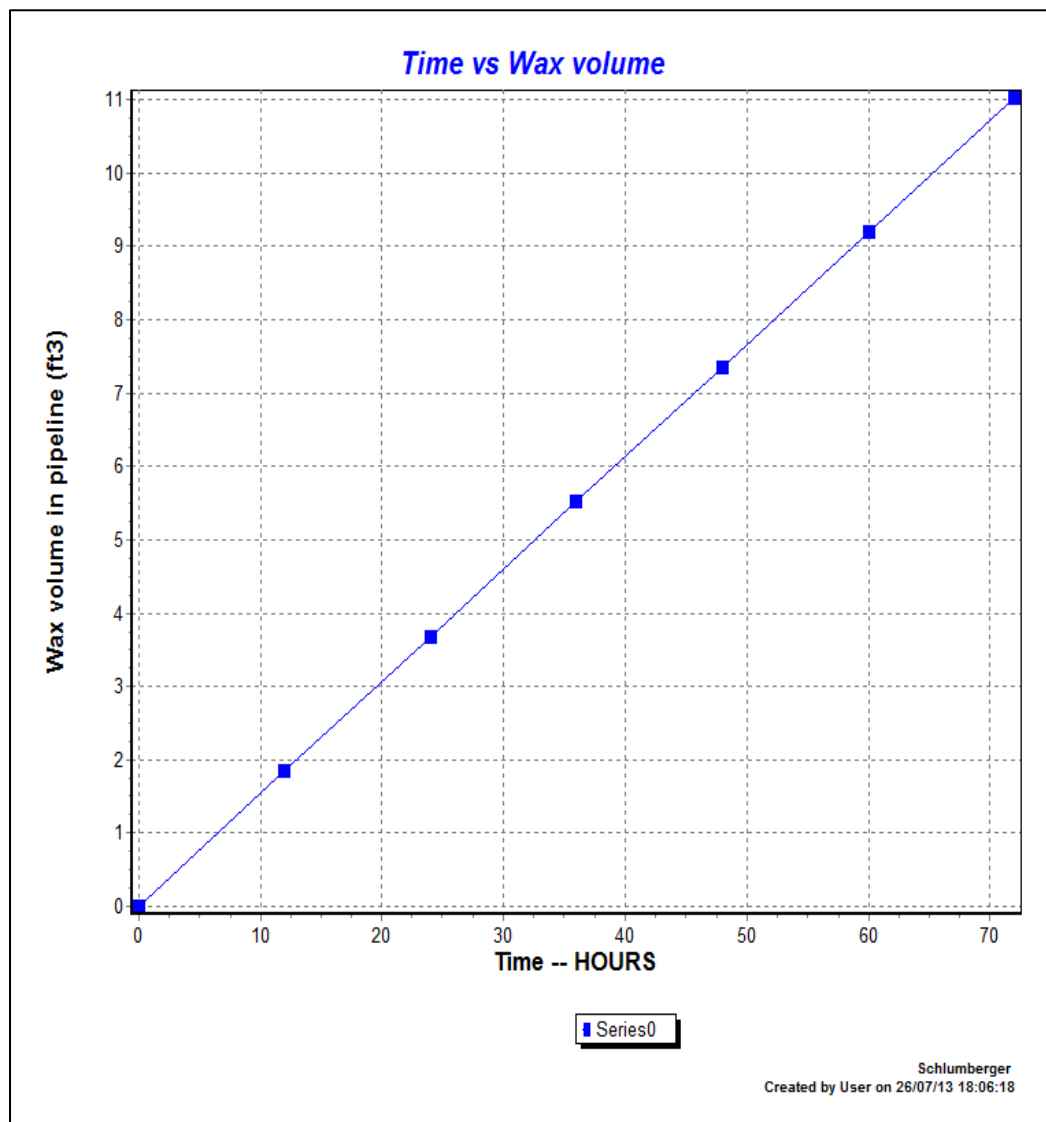

Figure 4.8 : Wax volume in pipeline vs time(BP Method)

The graph above shows that the wax volume exist in pipeline is directly proportional to the time. At the time of 12 hours, the volume of wax exist in the pipeline is $1.838ft^3$. The volume increases to $3.676ft^3$ after 24hours. At the time of 36 hours, the volume is $5.5138ft^3$. At the interval of 48 hours, 60 hours and 72 hours, the volume of wax deposited in the pipeline is $7.3510ft^3$, $9.1879ft^3$ and $11.0244ft^3$ respectively.

Oil Sample : Oil A
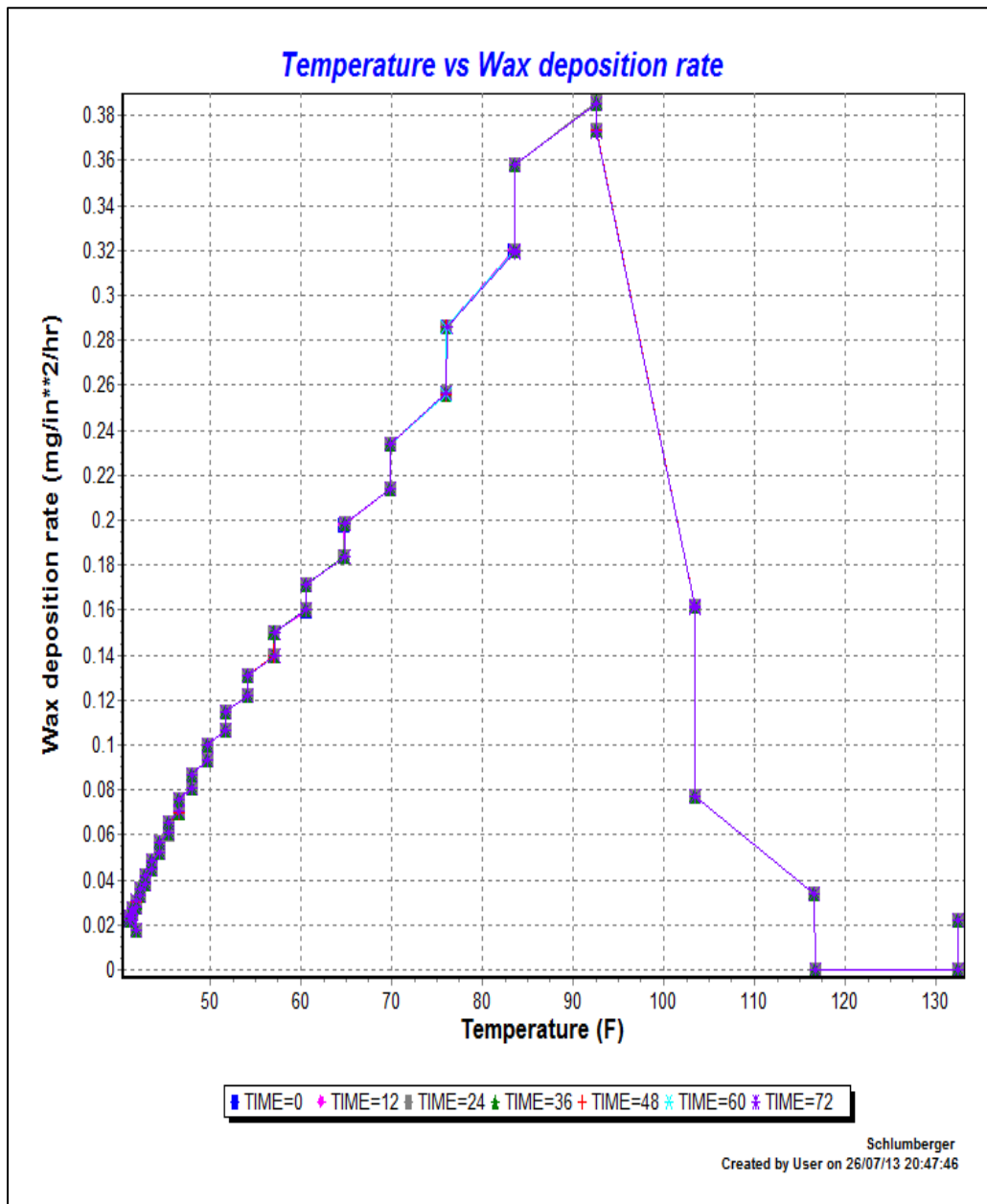
Wax deposition method : Schlumberger DBR

Figure 4.9 : Wax deposition rate vs temperature (Schlumberger DBR Method)

From the graph shown above, the deposition rate start to increase rapidly at the temperature of 116° F. This temperature represents the wax appearance temperature predicted by the PIPEsim software using the Schlumberger DBR Wax Deposition Method. The wax appearance temperature then were compared with the value that was obtained experimentally.
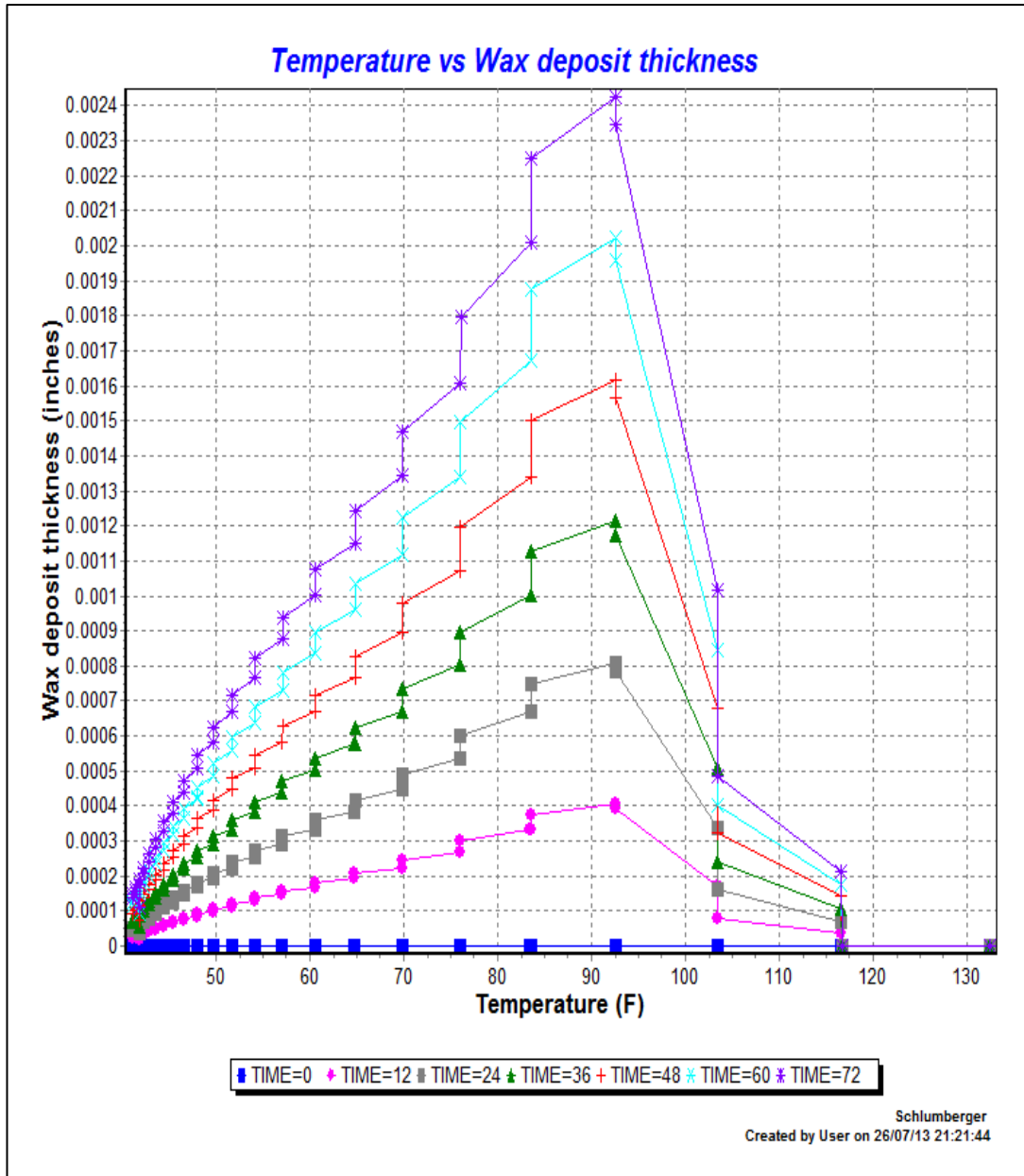
Figure 4.10 : Temperature vs Wax Deposit thickness (Schlumberger DBR Method)

From this plot, the deposit thickness started to increase at the temperature of 116° F. This happen since the temperature of the fluid model has reach WAT and the paraffin wax started to deposit. Above the temperature of 116° F, the wax deposit thickness is zero because at sufficiently high temperature, crude oils are indeed Newtonian. This means there are no deposition of paraffin wax. The wax deposit thickness is highest at the temperature of 92°F because at this temperature the wax deposition rate is the highest rate. The time variable shows that by time, the wax deposited thickness will increase and will reach the highest thickness at the temperature of 92°F. The wax deposition thickness depends on composition of oil,

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temperature, pressure and velocity of fluid. From the graph above, it is clearly shown the effect of temperature to wax deposit thickness. As temperature decrease from 92^oF, the thickness of wax deposited started to decrease gradually due to decrease in wax deposition rate.
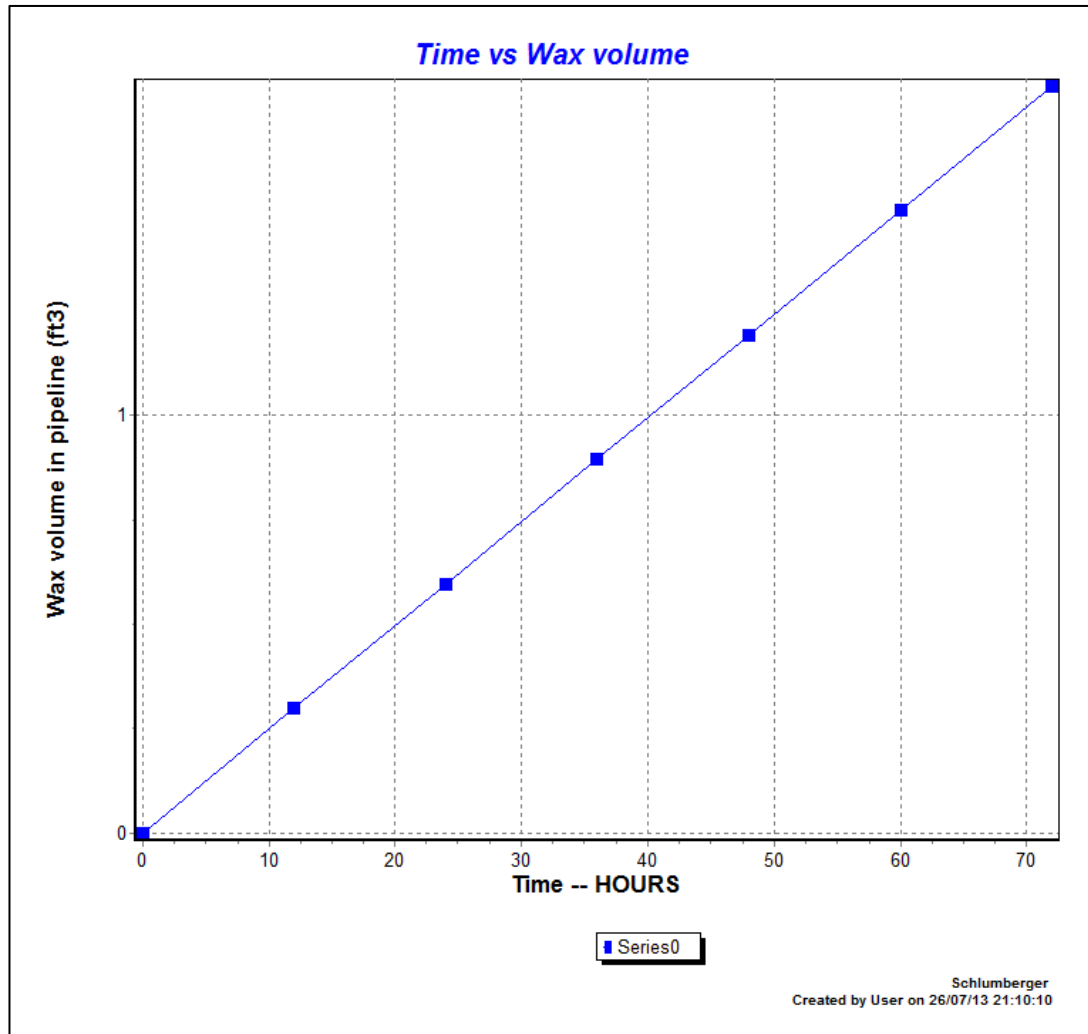

Figure 4.11 : Time vs Wax Volume in pipeline (Schlumberger DBR Method)

The graph above shows that the wax volume exist in pipeline is directly proportional to the time. At the time of 12 hours, the volume of wax exist in the pipeline is $0.2977ft^3$. The volume increases to $0.5955ft^3$ after 24hours. At the time of 36 hours, the volume is $0.8932ft^3$. At the interval of 48 hours, 60 hours and 72 hours, the volume of wax deposited in the pipeline is $1.1909ft^3$, $1.488ft^3$ and $1.7864ft^3$ respectively.
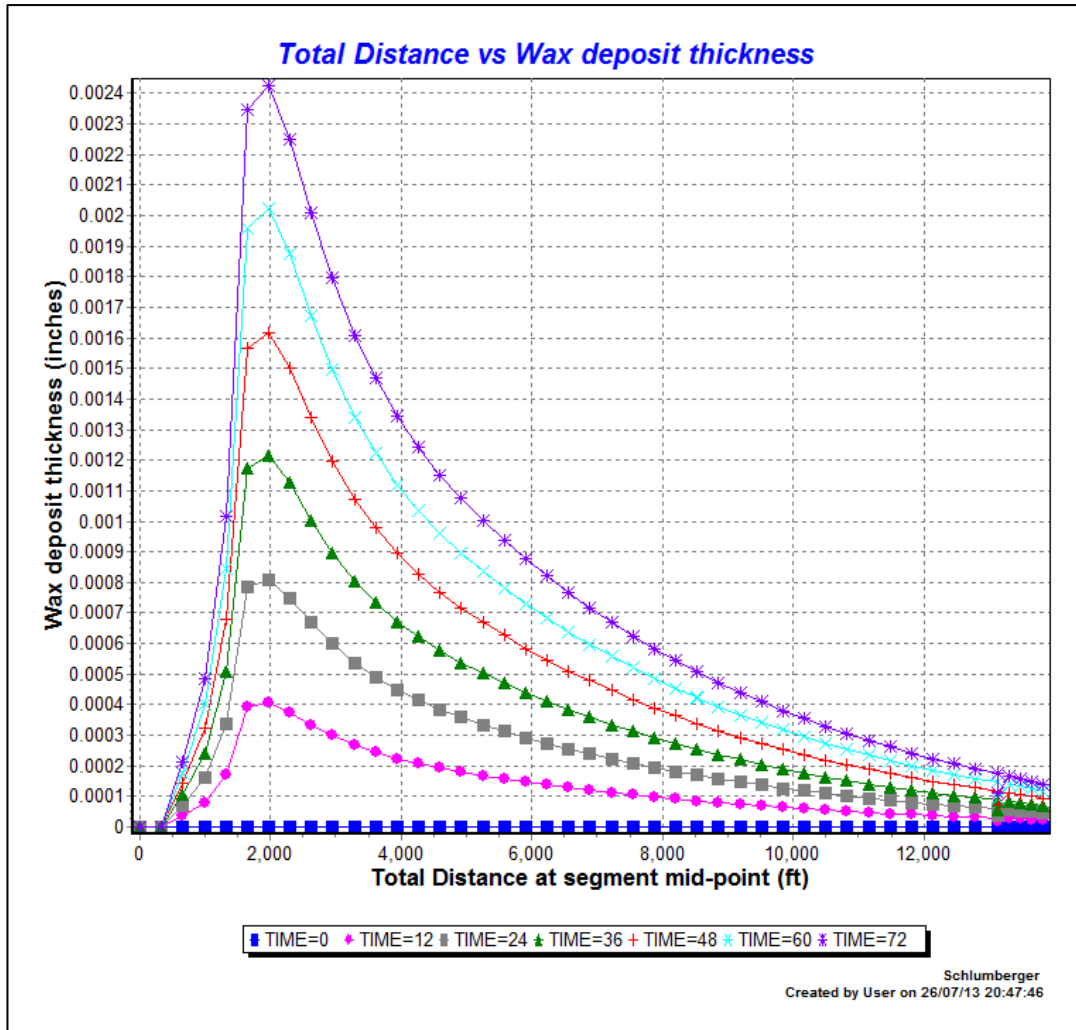
Figure 4.12 : Total Distance vs Wax Deposit Thickness vs Time (Schlumberger DBR Method)

The graph above shows the wax deposition thickness against the total distance at segment mid-point. The wax deposition thickness has the highest value at the distance of 1968ft at every time interval. At the distance of 12000ft and above, there are paraffin wax deposited but the thickness wax deposited are quite low. As the distance decrease, the wax deposited thickness increase gradually. This is because as the distance decrease, the temperature of the crude also decrease resulting the wax deposit thickness increase.

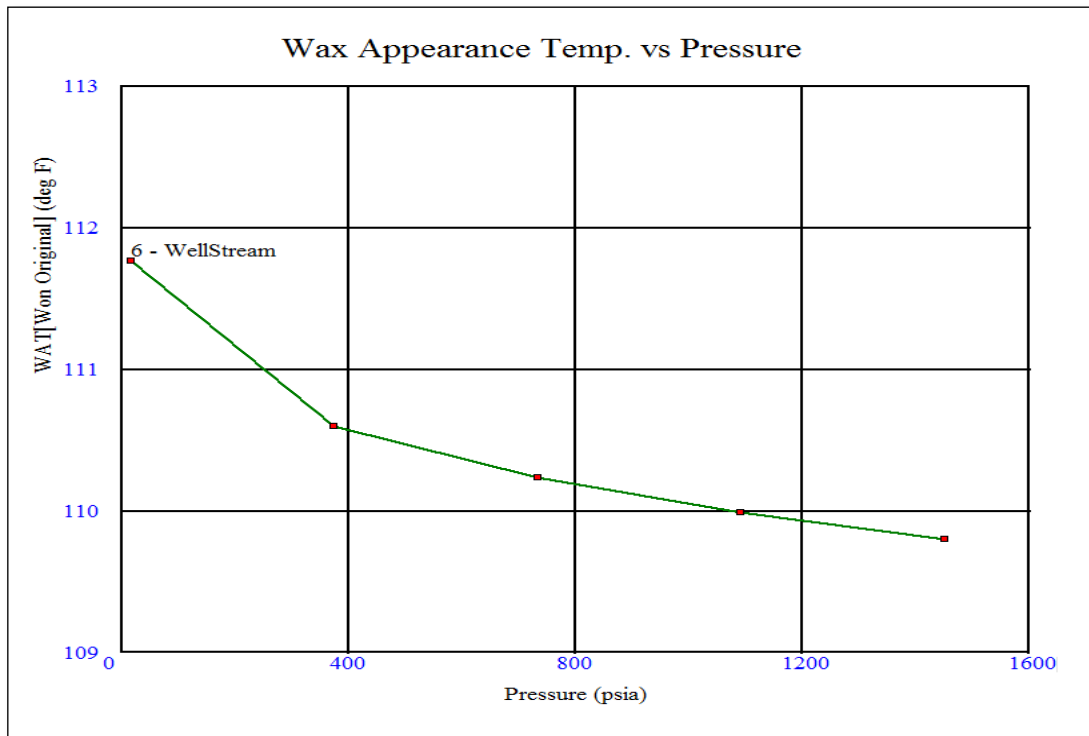**Petroleum Experts : PVT-P Software**

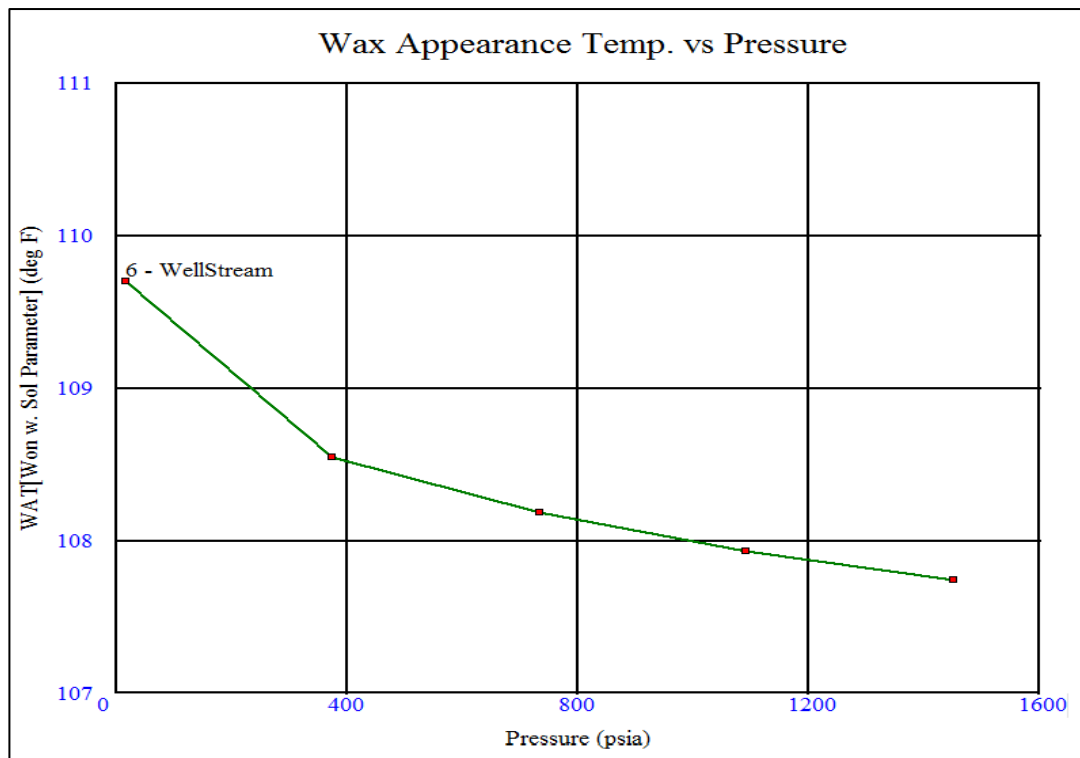Figure 4.13 : Wax appearance temperature by Won Original against pressure

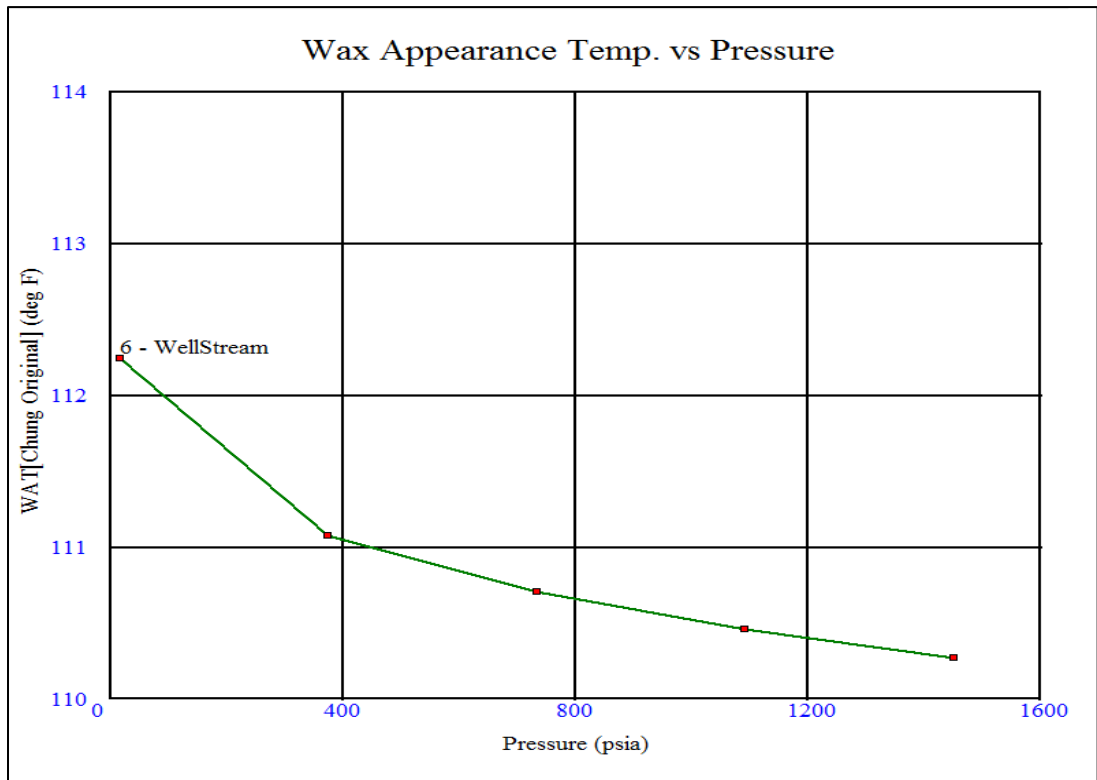Figure 4.14 : Wax appearance temperature by Won with Solubility Parameter against pressure

Figure 4.15 : Wax appearance temperature by Chung Original method against
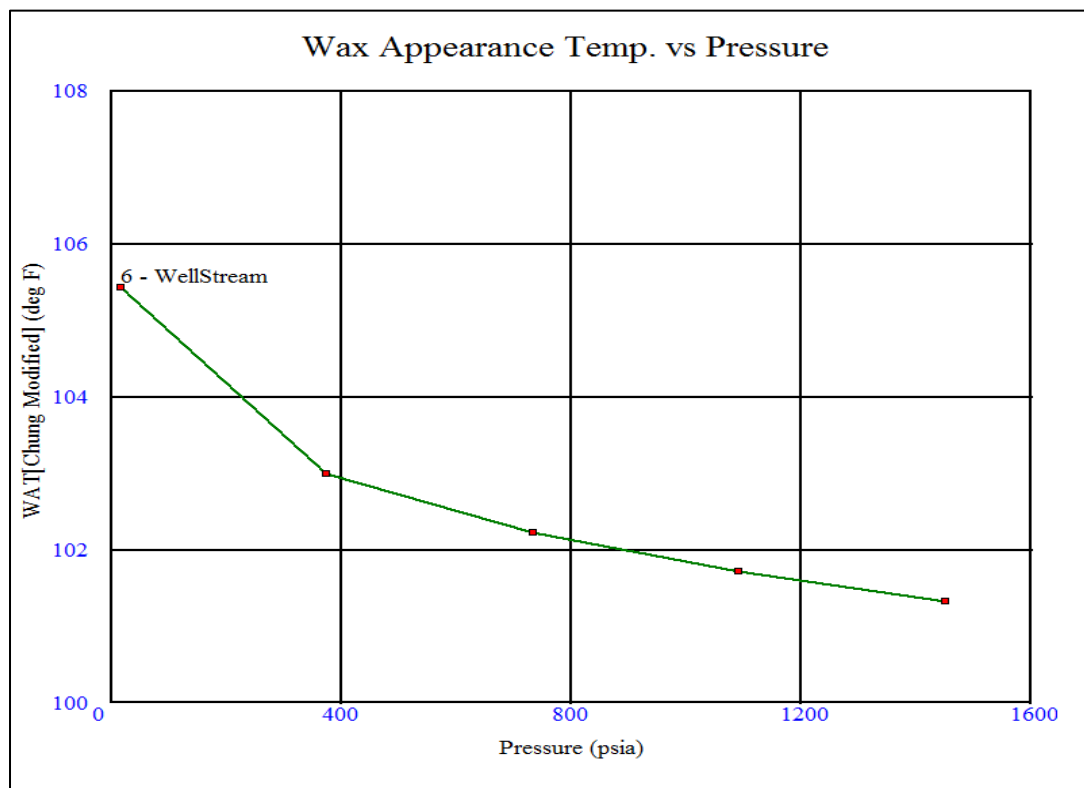pressure

Figure 4.16 : Wax appearance temperature by Chung Modified method against
pressure
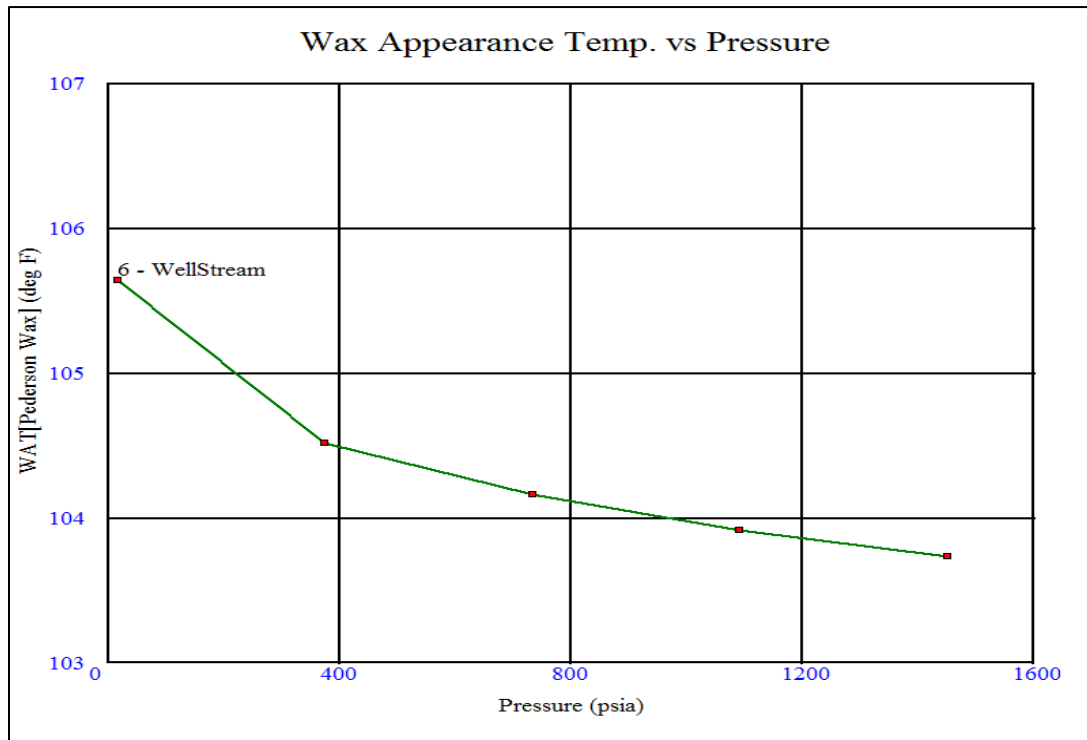
Figure 4.17 : Wax appearance temperature by using Pederson Wax method against pressure

Figure 4.13 shows the graph of Wax Appearance Temperature (WAT) predicted by using Won Original method against pressure. Figure 4.14 shows the graph of wax appearance temperature (WAT) predicted by using Won with Solubility Parameter method against pressure. Figure 4.15 shows the graph of wax appearance Temperature (WAT) predicted by using Chung Original method against pressure. Figure 4.16 shows the graph Wax Appearance Temperature (WAT) predicted by using Chung Modified method against pressure. Lastly, figure 4.17 shows the graph Wax Appearance Temperature (WAT) predicted by using Pederson Wax method against pressure. All of the graph shows that as the pressure increase, the wax appearance temperature predicted decrease.

From all the graph shown above, every wax method prediction resulted in decrease of wax appearance temperature prediction as the pressure increase. This is an error since studies shows that supposedly, as the pressure increases, the WAT also increases slightly. This is a simple thermodynamic effect. The error in the graph plotting might because of the wrong setting of the software.

Comparison of Wax Apperance Temperature Predicted

Table 4.1 : Wax Appearance Temperature predicted by PIPEsim Software

Pressure	Shell Temperature (^{o}F)	British Petroleum (BP) Temperature (^{o}F)	Schlumberger DBR Temperature (^{o}F)
1450	103	104	116

Table 4.2 : Predicted Wax Apperance Temperature by PVTP software

Pressure (psia)	Won Original Temp. (deg F)	Won with Sol Params Temp. (deg F)	Chung Original Temp. (deg F)	Chung Modified Temp. (deg F)	Pedersen Wax Temp. (deg F)
14.5000	111.77	109.702	112.246	105.425	105.647
373.375	110.602	108.547	111.078	102.995	104.519
732.250	110.239	108.185	110.709	102.236	104.163
1091.13	109.991	107.936	110.461	101.726	103.921
1450.00	109.803	107.748	110.273	101.336	103.74

The wax appearance temperature that was obtained experimentally by using viscosity method and differential scanning calorimetry (DSC). The WAT is obtained was 36^0C (96.8^0F). This value was then compared with the value predicted by both PIPEsim and PVTP software.

Table 4.3 shows that every method in PIPEsim software overestimates the prediction of wax appearance temperature (WAT). However, by using Shell method, the WAT predicted gives the lowest error percentage by only 6.4%. The British Petroleum (BP) method shows the error percentage of 7.4% and lastly the Schlumberger DBR method with error percentage of 19.8%.

Table 4.3 : Error Percentage of Predicted Wax Appearance Temperature by PIPEsim

Methods	Wax Appearance Temperature obtained experimentally(^{0}F)	Wax Appearance Temperature Predicted (^{0}F) @ 1450psia	Error Percentage (%)
Shell	96.8	103	6.4
British Petroleum (BP)	96.8	104	7.4
Schlumberger DBR	96.8	116	19.8

Table 4.4 : Error Percentage of Predicted Wax Appearance Temperature by PVTP

Methods	WAT obtained experimentally (^{0}F)	WAT Predicted (^{0}F) @ 1450psia	Error Percentage (%)
Won Original	96.8	109.8	13.4
Won with Sol Parameter	96.8	107.748	11.3
Chung Original	96.8	110.273	13.9
Chung Modified	96.8	101.336	4.6
Pederson Wax	96.8	103.74	7.1

Table 4.4 also shows that every method in PVTP software overestimates the prediction of wax appearance temperature (WAT). However, by using Chung Modified method, the WAT predicted gives the lowest error percentage by only

4.6%. The Pederson Wax method shows the error percentage of 7.1%, Won with Solubility method withe error percentage of 11.3%, Won Original method with 13.4% and lastly the Chung Original method with error percentage of 13.9%.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

Conclusion :

The project which derived from a problem statement in which to study the simulation software and wax depositional model has successfully done. All the objectives listed for this project have been achieved by using the simulation software available in the laboratory such as PIPEsim Simulation software and Petroleum Experts PVT-P software.

There are still several other simulation software that can be used in predicting wax deposition in pipelines and flowlines such as PVTsim and OLGA. Unfortunately, these software are not available in UTP resulting incapability to be used in this projects.

By using PIPEsim software, wax predictions are done by using three methods. The methods are Shell method, British Petroleum method and Schlumberger DBR method. From the simulation results obtained, Shell method turns out to be the most realiable method to predict wax appearance temperature (WAT) as it gives the lowest error percentage of 6.4% compared to other methods. British Petroleum (BP) method is the second place in the list with error percentage of 7.4% and Schlumberger DBR method is the least reliable in predicting wax deposition with error percentage of 19.8%.

By using Petroleum Experts PVT-P software, wax predictions are done by using five wax models. The models are Won Original, Won with Solubility Parameter, Chung Original, Chung Modified and Pedersen Wax. The most reliable model in predicting wax by using this software is Chung Modified with an error percentage of 4.6%, followed by Pedersen Wax model with an error of 7.1%, Won with solubility

parameter with 11.3%, Won Original with 13.4% and last but not least, Chung Original with error percentage of 13.9%.

Recommendation :

In order to make significant progress towards more reliable wax deposition prediction tools, there are multiple approaches that can be done in future :

- Continue effort on generation of deposition data in multiphase system
- Collection of good field data for model validation
- Increased effort on developing understanding in the basic phenomena underlaying wax deposition processes in flowing system.

APPENDIX 1 : GANTT CHART

Task	Final Year Project 1													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Topic selection	■	■												
Prelim Research		■	■	■	■									
Collecting reference		■	■	■	■	■								
Preparation for proposal defence				■	■	■								
Submission of proposal defence							■							
Prepare methodology			■	■	■	■	■	■						
Finalize the methodology								■						
Prepare the equipment to be used						■	■	■						
Preliminary results									■	■	■			
Preparation for interim report									■	■	■	■		
Submission of Interim Draft Report													■	
Submission of Interim Report														■

■	Process
■	Key Milestone

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