

Software and Modeling Development for Wax Deposition Phenomenon

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## Abstract

Wax deposition is an inevitable phenomenon in subsea pipelines where surrounding temperature is well below the Wax Appearance Temperature (WAT). Formation of waxy deposit is extremely problematic because it can result in reduction of cross-sectional area of pipe, potential blockage of production stream, elevated pressure-drop, increased risk of production shutdowns, etc. Therefore, it is crucial to have a reliable model to predict various characteristic of wax deposition for optimum treatment planning. In this study, we have developed two software which account for important aspects of wax deposition. Through our first software (SP-Wax), thermodynamic properties of waxy solutions are predicted and validated by extensive experimental data. In our second software (SP-Depo), we developed a new wax deposition model to predict deposit's thickness, solid wax fraction and carbon number distribution under single-phase turbulent flow. Within both software, core calculation is coded in C++ and the OpenMp parallel programming technique is incorporated to improve the performance. Also, a C# Windows Forms user interface is created for maximum reusability for technical and non-technical users.

SP-Wax is our first software to predict different SLE thermodynamic characteristics of the paraffinic solutions. In SP-Wax, solid solubility, precipitation curve, Wax Appearance Temperature (WAT), equilibrium constant, relative concentration gradient, liquid and solid phase compositions are predicted as a function of temperature. SP-Wax predictions are validated by experimental data of five binary and seven multicomponent systems. Using SP-Wax, the aging concept in wax deposition phenomenon is verified thermodynamically and a new CCN determination method was introduced. Through further investigation, it is also shown that SP-Wax thermodynamic software can be used as a quick tool to predict the deposit's solid phase carbon number distribution in pipes.

For our second software (SP-Depo), a new thermodynamically-coupled wax deposition model was developed and verified by data from 12 flow-loop experiments. Through our new model, deposit's thickness, solid wax fraction and Carbon Number Distribution (CND) are predicted. Moreover, the effect of shear stress on solid phase average carbon number (ACN) was elucidated using SP-Depo predictions and experimental ACN data.

SP-Depo software is coded in an object-oriented format (containing more than 40 classes and 350 methods) and incorporates the SP-Wax thermodynamic model for the solid phase composition prediction. In SP-Depo, Levenberg-Marquardt optimization tool is coded to tune the model using the fitting parameters.

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## **Chapter 1**

### **Introduction**

Energy is an important element for economic development. When energy is not adequately supplied, it can hinder the economic growth [1]. Although the universal demand for energy continuously increases, fossil fuel remains the main source of energy. In recent years, on average, the daily oil production rate has been above ninety million barrels per day. By considering the remained conventional oil reserves of 1.64 trillion barrels [2] and assuming that the oil production rate stays constant, oil can be produced for approximately 50 more years. These numbers show the limitation of current conventional oil reserves. That is why new efforts should be made to look into harsher and more difficult environments to find other potential oil reserves. Seventy percent of our planet's surface is covered by the ocean and, there is a great possibility to find new hydrocarbon reserves in the middle of the ocean hundred miles away from the shoreline. In such conditions, the transportation of oil becomes a critical issue. Scales and flow assurance problems are among the main challenges during the transportation of oil. In the subsea condition, the hydrocarbon is exposed to a very cold environment ( $T = 4^{\circ}\text{C}$ ) where wax molecules start precipitating out of oil and stick to the inner wall of the pipe. Accordingly, periodic remedial actions are needed to maintain the production by discharging the deposit from the pipeline. Therefore, a complete understanding of the paraffin deposition phenomenon is crucial in planning effective treatments in the most optimal and cost-efficient way possible. In one instance , due to paraffin deposition problem and flow assurance mismanagement, the financial loss was reported to be as high as \$100 million while the main part of it was due to production shutdown for several days [3]. There are two general approaches in treating wax deposition problem. The first method is to mechanically remove the deposit from the inner surface of the pipe using a device called "pig". The pig is placed inside the pipe and is moved by the production stream to scratch the deposit. The second treatment method is to use appropriate chemicals to prevent the deposition growth or to remove the waxy deposits chemically. Some of the common treating chemical products are solvents, paraffin inhibitors and dispersants [4].

Both mentioned remedial methods are expensive and require detailed planning. Aside from the operating costs associated with pigging and chemical treatment, deferring production is extremely costly [5] which leads to the loss of tens of millions of dollars. Lu [5] investigated the cost of pigging with different frequencies for a twenty-nine km long line. Seven days pigging frequency led to twenty-five million dollars while pigging every ninety days costed less than five million dollars per year. This emphasizes the importance of flow assurance management and planning.

There are two equally important aspects associated with wax deposition phenomenon. The first one is related to the thermodynamics of paraffin and the second aspect is to address the hydrodynamic, heat transfer and mass transfer of the flow during the deposition phenomenon. In my Ph.D., both aspects have thoroughly been investigated and two modeling software (SP-Wax and SP-Depo) have been developed for further influential contribution.

In general, wax deposition can be characterized by thickness, solid wax fraction and carbon number distribution. For an optimal paraffin deposition treatment design, the mentioned characteristics need to be predicted accurately by a reliable wax deposition model [6]–[8]. The available wax deposition models usually consider wax as a single-component [3], [9]–[12] however, there are several n-alkane components that individually contribute to the deposition with different wax mass flux rates [6], [13]. The popular single-component modeling approach has some major flaws which are listed below.

Firstly, crude oil usually contains a wide range of n-alkane components starting from C5 to C<sub>60+</sub> with different melting temperatures. Although, some n-alkane components could precipitate at a certain temperature, they might remain dissolved at another temperature. Therefore, it is impossible to refer to a certain range of carbon number components as wax at different temperatures. Therefore, the definition of wax from the single-component modeling approach is inconsistent.

Second, in wax deposition models, solubility of wax is an important parameter which is required in the calculations. In the single-component approach, only one lumped solubility curve is used, and it is assumed to be constant during the wax deposition phenomenon.

However, due to inconsistent wax mass flux rate of different carbon number components, the lumped solubility also changes as precipitation occurs. In the single-component approach, this important effect is not considered and could lead to errors.

Lastly, In the single-component approach, the deposit's solid phase Carbon Number Distribution (CND) cannot be predicted. CND prediction plays an important role in treatment planning.

In this study, our main objective was to develop a compositional wax deposition model to predict the deposit's solid phase composition in addition to thickness and solid wax fraction in paraffin deposition phenomenon. For this purpose, we needed to develop two reliable models for thermodynamic and wax deposition predictions. SP-Wax is our first software which is developed based on the thermodynamic model of Coutinho et al. [14]–[21] and other literature [22], [23], [32]–[35], [24]–[31]. For our second simulation tool, we developed SP-Depo software with a new thermodynamically-coupled wax deposition model to predict the composition of the waxy deposits along with other deposition characteristics. In our model, the depositable carbon number components are determined at given surrounding temperature, then, they are grouped into one pseudo-single-component for the wax deposition calculation. The depositable carbon number components are referred to those n-alkanes that participate in deposition process at certain flow conditions. In this study, we have developed a consistent thermodynamic methodology to determine the minimum depositable carbon number component as a function of temperature. Next, the thermodynamic properties of the pseudo-single-component will be calculated based on the properties of all carbon numbers. By choosing this approach, unlike Zheng et al. [6], we only need to solve the PDE (for calculation of concentration profile) once, which results in performance enhancement and improved simulation speed.

## 1.1 Background

The primary deposition characteristics, which are responsible in determining the frequency of wax deposition treatments, are thickness, solid wax fraction [8] and deposit's solid phase carbon number distribution (CND) [9]. A systematic modeling procedure based on heat and mass transport needs to be developed to approximate the mentioned properties [3], [9].

Among the three deposit's properties, carbon number distribution of the deposit is exclusively related to the thermodynamics of wax. Coutinho proposed a thermodynamic model which can deal with the nonideality of waxy solutions [20]. The model only uses the properties of pure components and can predict the phase behavior of liquid and solid as well as their compositions. He validated his model with various experimental data. Coutinho's model [14]–[21] was a huge improvement since, unlike the other models, it was capable of dealing with more than one solid phase in waxy solutions. This used to be the primary limitations of SLE modeling approaches. For liquid phase non-ideality, it is proven that ideal and regular solution models, Flory-Huggins activity coefficient approach and improved UNIFAC do not work in paraffinic systems [21]. Instead, Coutinho et al. [21] showed that the improved Entropic free-volume and Flory free-volume models are suitable for accounting liquid phase non-ideality in paraffin systems.

On the other hand, for wax deposition phenomenon in pipe, some conditions need to be satisfied for n-alkanes to precipitate and form a stable deposit. For example, heavy components should be present in the oil sample [36] and the ambient temperature should be less than WAT for wax molecules to precipitate out of the oil. Finally, the wax crystals need to have an adequate attraction to stick to the wall and within their networks.

Mechanisms that are likely to be involved in paraffin deposition process include molecular diffusion, gravity settlement, co-crystallization of n-alkanes, Brownian diffusion, aging, shear or turbulent effect, shear dispersion [37], [38]. Molecular diffusion mechanism is characterized by radial concentration gradient inside the pipe. Many studies have suggested that the molecular diffusion is the dominant driving force for wax deposition [3], [39]–[41]. Also it is suggested that the Brownian diffusion mechanism can safely be neglected since it is a very slow process [40]. For shear dispersion effect, it is believed that the suspended precipitated wax particles might settle down toward the pipe's wall due to the differences in fluid particle velocities. However, it is not considered to be very significant [39]. Gravity settling is another process which causes the particles to settle due to their higher density than liquid.

Increase in solidified wax content of the deposit with time is called aging and it is related to the hardness of the deposit [3]. Shear effect is included in several wax deposition models [10], [13], [42] to account for additional wax mass flux and deposition thickness reduction [3], [42]–[44]. The other requirement of wax crystal formation is co-crystallization process which includes bounding of several n-alkanes. This implies that thicker deposits are not, necessarily, expected when more soluble wax is present in the system [45]. In the next chapter, a brief review about the history of wax deposition research is included

## Chapter 2

### Literature Review

For investigating the physics behind the wax deposition phenomenon, it is necessary to analyze the thermodynamics of paraffin in equilibrium condition as well as the wax deposition models in flowing conditions. Accordingly, complete literature reviews about both aspects are presented in this chapter.

#### 2.1 Thermodynamics of paraffin

Normal and slightly branched alkanes are considered as wax particles. These components are predominantly present in carbon number range of  $C_{20} - C_{50}$  [37]. Due to higher degree of branching, heavier carbon number components (larger than  $C_{50}$ ) are not usually considered as wax. In paraffinic solutions, accounting for solid and liquid phase's non-idealities are in great importance. Won [46] was the first researcher who related the fugacity terms using the activity coefficients of each carbon number in both phases. He incorporated the regular solution theory to express activity coefficients. In his modeling, the pressure effect on fugacities was neglected and the specific heat capacity of each component for two phases were assumed to be the same ( $\Delta C_p = 0$ ). He later found his first assumption to be invalid and considered the specific heat transfer coefficient differences in his new approach [47]. Won's model did not use an independent expression for describing each phase's fugacity. Won's method was further analyzed by Pederson for WAT calculation of several oil samples and it was discovered that the model is largely overpredicting the WAT [35]. The observed behavior was an indication of less thermodynamic favorability of solid phase in compare to what was predicted by the model. Accordingly, further attempts were carried to make the solid phase less thermodynamically favorable in compare to the liquid phase. This objective was followed by Hansen et al. [48]. In their modeling, polymer solution theory was used to calculate the liquid phase activity coefficient term while the solid phase was assumed to be ideal ( $\gamma_s = 1.0$ ). Pedersen et al. [49] made several suggestions which caused the solid phase's fugacity coefficients to increase. Their model was similar to Won's method however, iso-alkanes were also considered as participants in precipitation. The resulted lower heat of melting was the main cause of increase in solid phase fugacities. Ruffier et al. [50] proposed a

thermodynamically consistent methodology to calculate the solid phase activity coefficients independent of the liquid phase. Erickson et al. [51] emphasized the importance of distinguishing between components which are responsible for wax formation and those which are not. Therefore, more realistic melting temperature and heat of fusion values were chosen to use in the governing equations. The enthalpy of fusion was the main factor to determine the tendency of a compound to precipitate below its melting temperature. Increase in  $\Delta H^f$  affects the fugacity of the solid phase to rise exponentially. Rønningsen et al. [52] modified the wax formation model which was proposed by Pederson. The new model assumed that just C7 + normal alkanes contribute to the wax formation. The following formula was used to determine the mole fraction of wax forming compounds for a specific carbon number,

$$Z_i^s = Z_i^{tot} \left( 1 - (A + B * M_i) \left( \frac{\rho_i - \rho_i^p}{\rho_i^p} \right)^c \right) \quad (2-1)$$

where  $M_i$ ,  $\rho_i$ ,  $\rho_i^p$  and  $Z_i^{tot}$  are molecular weight, average density, density of a normal paraffin of the same molecular weight as  $i^{\text{th}}$  carbon number fraction, and total mole fraction of  $i^{\text{th}}$  carbon number fraction, respectively. A, B and C are fitting parameters which are adjusted based on the experimental data.

Won [46] calculated the liquid phase fugacity from Soave–Redlich–Kwong equation as follows:

$$f_i^{\circ L} = \phi_i^{\circ L}(P)P \quad (2-2)$$

where  $\phi_i^{\circ L}$  is the fugacity coefficient of pure component i in a liquid phase.

For C7 + fraction, the EOS inputs ( $\omega$ ,  $T_c$  and  $P_c$ ) can be calculated using proposed procedure by Pederson [36]. For the critical pressure of C20 +, separate correlations were proposed for participating and non-participating components. Rønningsen et al. [52] showed the importance of such distinction in critical pressure parameter formulas for n-alkanes and non-wax-forming components to match the experimental data. The WAT experiments were conducted using NMR spectroscopy. Several experimental studies were

conducted by Hansen et al. [53] and it was revealed that the solidified paraffin contains more than one phase. A model, later, was proposed based on a multi-solid phase assumption. The solid phase was assumed to contain several pseudo-components where each one consists of either one single pure component or multiple carbon number compounds [54]. After grouping, each pseudo-component's pure solid fugacity was compared to its  $f_i^v$  and  $f_i^L$  and if  $f_i^{\circ s}$  was the lowest, the corresponding pseudo-component was considered to be in the solid phase. However, this method is, massively, dependent on grouping variations. Ideally, it is expected that grouping should be done to a level where further subgrouping does not make much difference on the results. However, such behavior was not seen in the proposed model of Lira-Galeana et al. [54]. Further modification of multi-solid phase modeling approach was done by Pan et al. [55] although the existence of a robust pseudo-component grouping procedure remained unfulfilled.

For the solid phase, predictive Wilson methodology and ideal solution models are proven to be appropriate for accounting the non-ideality of solid and liquid phases, respectively [56]. For liquid phase molar volume, the modified Racket equation [57] was used. On the other hand, Won [46], [47] and Nichita's correlations [58] were chosen for melting temperature and molar volume of the solid phase, respectively. An extended UNIQUAC model was applied for the solid phase by Coutinho et al. [20] for non-ideal solid-liquid equilibria. In another study, Coutinho et al. [59] presented a work of wax precipitation prediction in jet and diesel fuels. In that work, modified UNIFAC and UNIQUAC equations were used for liquid and solid phases, respectively. Vafaie et al. [60] used the previously described multi-solid phase model developed by Lira-Galeanaetal while Peng–Robinson EOS was applied for liquid and gas phases. Different activity coefficient models were studied by Esmaeilzadeh et al. [61] and it was reported that the predictive Wilson method is suitable for describing a non-ideal solid phase. Ji et al. [62] predicted WDT in binary and multicomponent systems using UNIQUAC model. In their study, initially, they predicted the thermodynamic characteristics of n-alkanes to calculate different parameters in the fugacity equation. In our study, we developed a predictive thermodynamic software primarily based on the Coutinho model to estimate various SLE characteristics of paraffinic solutions [14]–[21].

## 2.2 Wax deposition phenomenon in pipelines

In the previous section, the thermodynamic aspect of wax deposition was investigated in the solid-liquid equilibrium condition. However, wax deposition occurs in the pipeline and in the flowing condition. Therefore, it is crucial to simulate the hydrodynamic, heat-transfer and mass-transfer of the flow within the modeling of wax deposition phenomenon. In the following section, an overview about the history of the wax deposition research is provided.

During transportation, paraffin components are responsible for the formation of waxy deposits on the inner side of the pipe when they are exposed to a cold environment. In the reservoir condition, due to high temperature and pressure, the solubility of paraffin is high enough to be fully dissolved in the crude oil. However, when crude oil reaches to the subsea pipeline, it will be exposed to a cold environment (around 4°C) where heavy organic components precipitate out of the solution (due to limited solubility) and stick to the wall. There are several proposed mechanisms for wax deposition occurrence. Burger et al. [40] analyzed the wax deposition in the Trans Alaska Pipeline and concluded that molecular diffusion, Brownian diffusion and shear dispersion are the primary mechanisms in the formation of waxy deposits. They concluded that molecular diffusion and shear dispersion are dominantly responsible for the deposition at higher and lower temperatures, respectively. Singh et al. [3] later showed that the only responsible mechanism is the molecular diffusion for the deposition of waxy components. Singh et al. [3] conducted experiments with different operating conditions to quantify the effect of other potential responsible mechanisms. Among all, only the shear effect was appeared to have some minor impacts on the deposition even though, the Reynolds number was within the range of the laminar flow. Singh et al. [3] also showed that the deposit's solid fraction increases with time through a counter-diffusion process where carbon number components larger than Critical Carbon Number (CCN) diffuse toward the deposit and smaller n-alkanes move away from it. This process was verified thermodynamically by Shahdi and Panacharoensawad [63]. In the pipe, there is a radial temperature gradient within the flowing fluid where the highest temperature is at the center (e.g., Figure 2-1). Paraffin concentration is a great function of temperature which expectedly varies in the radial direction along with the temperature change. In Figure 2-2, an example of a concentration

profile is presented which is approximated by SP-Depo software. Notably, heavy n-alkanes have higher concentrations at the bulk in compare to the deposit's interface. Such concentration gradient derives heavy paraffin components to move toward the waxy deposit from the center of the pipe. Within the deposit, a similar concentration gradient exists where concentration is lower near the wall. Such gradient results in further diffusion of heavy n-alkanes toward the wall where they will be solidified. Along this process, due to an existing temperature gradient within the deposit, some n-alkanes start solidifying before reaching to the wall. This results in a complicated morphological structure of waxy deposits [64].

Convective wax mass flux due to the existence of concentration gradient has been addressed differently in the literature. The following three wax mass flux theories are mainly used in wax deposition models:

- A. No precipitation at the bulk – Singh et al. [3]
- B. Instantaneous precipitation (solubility method) – Venkatesan [11]
- C. Partial precipitation – Lee [12]

Scenario “A” assumes that waxy components will not precipitation until they reach to the deposit's interface [3]. This model was proposed by Singh et al. [3] and it is found to be the upper limit for wax mass flux. For the scenario “B” (also known as solubility method), an instantaneous precipitation is considered which is merely dictated by the temperature profile [11]. Venkatesan [11] showed that the solubility method provides a lower bound for wax mass flux. In 2008, Lee [12] proposed a new wax mass flux model (scenario C) by assuming partial precipitation. Resulted wax mass flux from scenario “C” lays between no precipitation and solubility method cases.

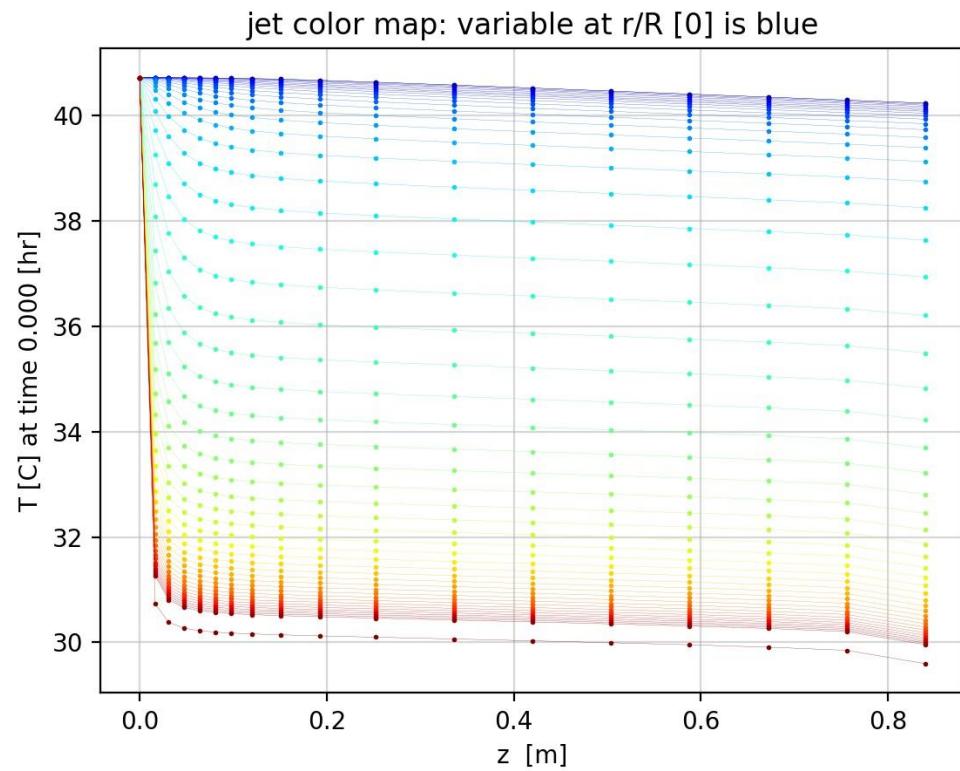


Figure 2-1: SP-Depo predicted temperature profile in the pipe at  $t=0$  for test #28 [10]

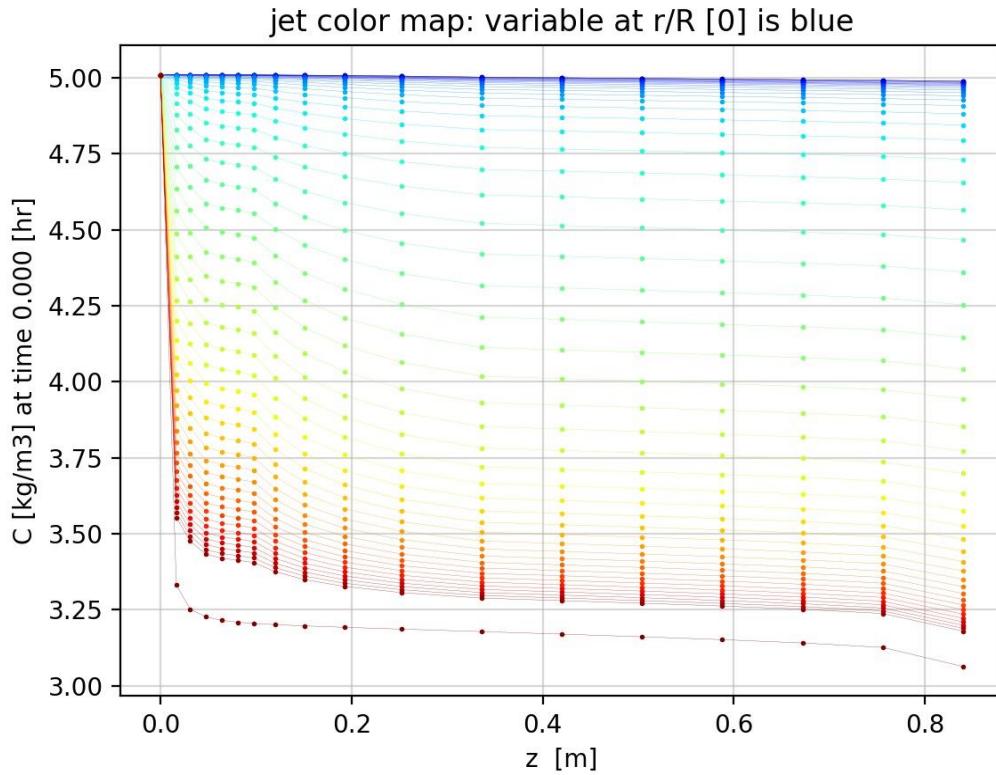


Figure 2-2: SP-Depo predicted concentration profile in the pipe at  $t=0$  for test #28 [10] with minimum depositable carbon number of  $C_{30}H_{62}$

Further attempts were taken to develop a mathematical model for predicting the deposit's thickness, solid wax fraction and solid phase carbon number distribution. Previously, the existing wax deposition models assumed a constant value for solid wax fraction and used the deposit's oil content as an adjustment parameter to tune the model. This approach was disproven by several experimental studies [3], [5], [10], [12], [65]. Increase in solid wax fraction is very important because it increases the deposit's thermal conductivity and decreases wax molecular diffusivity. Singh et al. [3] developed a mass transfer model to account for the growth and aging process of wax deposition phenomenon under the laminar flow. In that study, decoupled correlations for heat and mass transfer calculations were used and satisfactory results were obtained. Singh et al. method is based on the first wax mass flux scenario "A" where no precipitation in the bulk was assumed. Although scenario "A" worked adequately well for the laminar flow, it was not well-adopted for the case where turbulent flow was present. Venkatesan and Fogler [42] showed that precipitation is

significant in turbulent flow condition and cannot be neglected. In that study, it was shown that even though the precipitated particles do not directly contribute to the deposition, the paraffin solubility decreases due to decreased dissolved mass. Accordingly, a new concentration profile will be formed similar to Figure 2-2. The resulted concentration gradient contributes to the molecular diffusion in wax deposition phenomenon. Lee [12] further compared the two wax mass flux scenarios and showed that, in reality, true wax mass flux falls between scenario “A” and “B” in the turbulent flow conditions. In his modeling, he accounted for the kinetics of the paraffin precipitation in the oil phase. From SP-Depo software, the following graph (Figure 2-3) was generated which perfectly illustrates all three scenarios for wax mass flux where the light blue curve represents the upper bound or the maximum theoretical limit for the wax mass flux (scenario A) and the black line represents the scenario B where the lowest wax mass flux is expected.

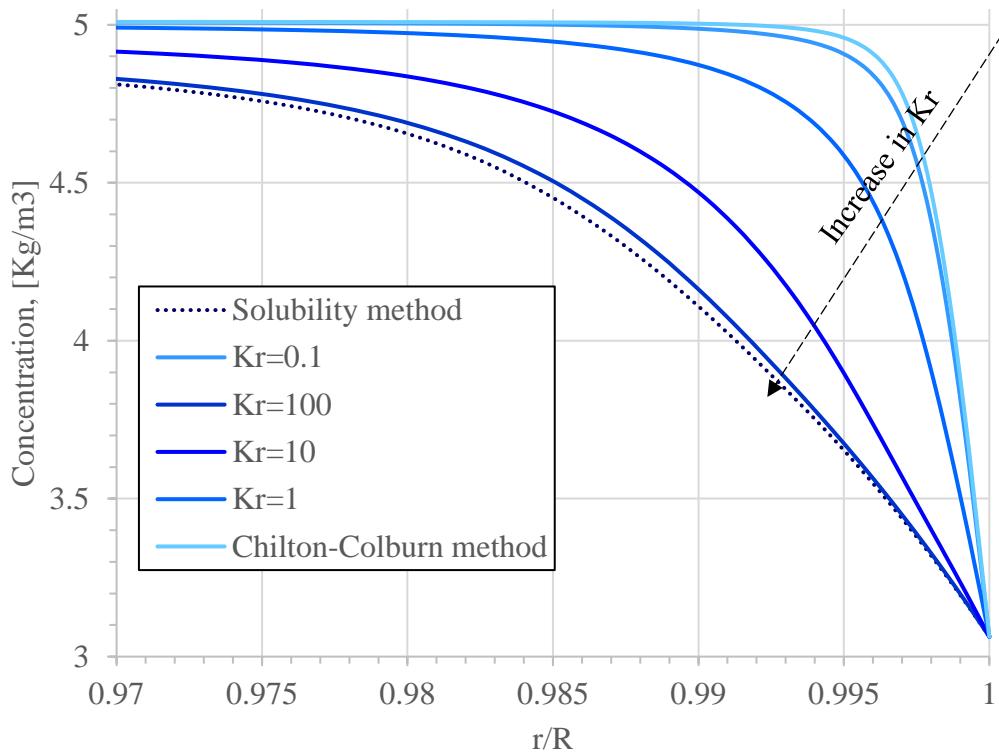


Figure 2-3: SP-Depo simulation: Chilton-Colburn analogy (scenario A), partial precipitation (C) and the solubility method (scenario B) for wax mass flux consideration in wax deposition modeling

In the previously mentioned models, the impact of shear effect was not included. Panacharoensawad [10] proposed a new wax deposition model which considers scenario "A" for wax mass flux. He then introduced two fitting parameters to include the shear effect and the initial deposit's growth in the modeling. In that study, the model successfully predicted different characteristics of the wax deposition phenomenon under single-phase and two-phase water-in-oil flow conditions. Later on, panacharoensawad et al. [9] broadened the application of the previously developed wax deposition model to two-phase gas-oil slug flow conditions. In SP-Depo, user can choose any of the above wax deposition models.

Up to this point, all proposed wax deposition models were only capable of estimating the deposit's thickness ( $\delta$ ) and the solid wax fraction ( $\bar{F}_w$ ). In 2013, Zheng et al. [6] solved the transport equations for different carbon number components separately rather than treating the paraffin as a single-component. In this modeling approach, he accounted for each component's mass flux individually and was able to predict the deposit's solid phase carbon number distribution. Zheng et al. [6] used Coutinho's thermodynamic model to predict SLE properties of waxy components including their solubilities. In the proposed model, the concentration profile was determined for all carbon number components. Zheng et al. study [6] was a pioneering study in estimation of deposit's CND however, there are some issues associated with their proposed model which are elaborated in the next paragraph.

Zheng et al. model [6] requires concentration profile calculation of all carbon number components. This modeling approach results in a very slow simulation run-time which is nearly impractical to be implemented in multi-mile subsea pipelines. In SP-Depo, we found that concentration profile calculation is one of the slowest steps in wax deposition calculation even though it is solved for only one lumped component. Secondly, in Zheng et al. model [6], no selective depletion is considered for oil composition update in wax deposition modeling. In long subsea pipelines, due to varying wax mass flux rates of different participating carbon numbers, n-alkane composition of oil changes along the pipe. Such change of n-alkane composition should be considered in the wax deposition calculation to correctly predict deposit's thickness, solid wax fraction and other deposit's

characteristics. Thirdly, the used temperature for deposit's solid phase composition estimation requires more investigation. In Zheng et al. study, there is not a clear explanation for using the appropriate temperature for solid phase composition prediction to account for the complex morphological structure of the deposit. Lastly, in Zheng et al. model [6], no shear effect investigation was included even though, the importance of shear stress effect on wax deposition occurrence has been well-proven.

In our study, we address most of the above issues and introduce a new thermodynamically-coupled wax deposition model (SP-Compo). In our developed model, concentration,  $dC/dT$  and molecular diffusivity of all depositable carbon number components are predicted individually from SP-Wax thermodynamic model [63]. Then, these values will be used to calculate total concentration,  $dC/dT$  and molecular diffusivity for one pseudo single component which will be used in the wax deposition calculation. Since SP-Wax thermodynamic model takes about 0.2 - 0.5 seconds to run at each temperature, it was not practical to directly call SP-Wax to obtain these parameters. Instead, we fitted sets of regression equations to the thermodynamic data and used them for the required parameters. After knowing the required parameters, wax deposition model from Panacharoenawad [10] is used to predict deposit's thickness, solid wax fraction and carbon number distribution.

## Chapter 3

### Theoretical Framework

In this chapter, the theoretical framework and technical aspects of our two developed software (SP-Wax and SP-Depo) will be thoroughly presented.

#### 3.1 SP-Wax thermodynamic model

In this section the mathematical framework of the developed thermodynamic model in SP-Wax is presented. SP-Wax is based on the thermodynamic model of Coutinho et al. [14]–[21] and other literature [22], [23], [32]–[35], [24]–[31]. Form SP-Wax, solidified weight fraction values ( $S_f \left[ \frac{w}{w} \right]$ ) at different temperatures are calculated and plotted. The generated curve from the plotted  $S_F$  values is called precipitation curve and it varies with n-alkane composition. Therefore, n-alkane composition of the system ( $z_i$ ) should be provided by the user. Please note that SP-Wax can only predict characteristics of the n-alkane system. Therefore, composition of the total fluid is not required. User should only provide the weight percentage of n-alkanes in the total fluid ( $W_{NA}$ ) in addition to n-alkane composition. For example, if in one-kilogram solution, there is 250 grams of soluble wax,  $W_{NA}$  will be 0.25.

SP-Wax can predict SLE thermodynamic properties of the solution at any temperature below WAT. However, convergence problem might be encountered near WAT. To overcome this problem, a set of initial values for equilibrium constants are generated at various temperatures. These  $K$  values are then used as initial guesses for equilibrium constant parameters when SP-Wax is called. By this solution, the mentioned convergence problem has been eliminated.

In SP-Wax, Coutinho thermodynamic model was chosen because it can express liquid and solid non-ideality accurately. In SP-Wax, governing equations [29] are solved for non-ideal paraffinic solutions and different SLE characteristics are reported. The following governing equation relates each carbon number component's equilibrium constant ( $K_i$ ) to its thermophysical properties using activity coefficients ( $\gamma_i^L, \gamma_i^S$ ).

$$K_i = \frac{\gamma_i^L}{\gamma_i^S} \exp \left( \frac{\Delta H_i^f}{RT_i^f} \left( \frac{T_i^f}{T} - 1 \right) + \frac{\Delta H_i^{tr}}{RT_i^{tr}} \left( \frac{T_i^{tr}}{T} - 1 \right) - \frac{\Delta_s^l C_{p_i}}{R} \right. \\ \left. * \left( \frac{T_i^f}{T} - \ln \left( \frac{T_i^f}{T} \right) - 1 \right) \right) \quad (3-1)$$

where  $\Delta H_i^f$ ,  $T_i^f$ ,  $\Delta H_i^{tr}$ ,  $T_i^{tr}$  and  $\Delta_s^l C_{p_i}$  are thermophysical properties which are expressed through empirical correlations (discussed later). Newly calculated  $K$  values are then compared to the previous equilibrium constants ( $K_i^C$ ) through the following relation. If the calculated error is not less than a certain threshold, the calculation continues. The error is calculated as:

$$\epsilon = \frac{\sum |K_i^C - K_i|}{\sum K_i^C} \quad (3-2)$$

The mole fraction of the precipitated phase in n-alkane system ( $n_S$ ) is determined from the following equation as follows:

$$\sum_{i=1}^{i=N} \left( z_i * \frac{K_i - 1}{1 + n_s * (K_i - 1)} \right) = 0 \quad (3-3)$$

Finally, liquid and solid phase composition ( $x_i^L, x_i^S$ ) are calculated from

$$x_{m,i}^L = \frac{z_i}{1 + n_s * (K_i - 1)} \quad (3-4)$$

$$x_{m,i}^S = \frac{z_i * K_i}{1 + n_s * (K_i - 1)} \quad (3-5)$$

### 3.1.1 Liquid phase non-ideality

In SP-Wax, liquid phase non-ideality [21] is expressed by:

$$\ln \gamma_i^L = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} \quad (3-6)$$

where  $\phi_i$  is the composition fraction and is defined as,

$$\phi_i = \frac{x_i S_i}{\sum x_j S_j} \quad (3-7)$$

The main difference between all models is the way element "S" has been defined. In SP-Wax Entropic Free-Volume model has been used and "S" is expressed as:

$$S_i(\text{Entropic}) = (V_{m,i} - V_{w,i})^{2/3} \quad (3-8)$$

### 3.1.2 Solid phase non-ideality

In SP-Wax, solid phase activity coefficients are calculated using Wilson method [16] (shown below).

$$\ln(\gamma_i^s) = -\ln(\sum_j \Lambda_{ij} x_j) + 1 - \sum_j \frac{\Lambda_{ji} x_j}{\sum_k \Lambda_{jk} x_k} \quad (3-9)$$

where

$$\Lambda_{ij} = \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \quad (3-10)$$

$$\Lambda_{ij} = \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \quad (3-11)$$

$$\lambda_{ii} = -\frac{1}{3}(\Delta H_i^{\text{sub}} - RT) \quad (3-12)$$

$$\Delta^{\text{sub}}H = \Delta^{\text{vap}}H + \Delta^{\text{f}}H + \Delta^{\text{tr}}H \quad (3-13)$$

$$\lambda_{ij} = \alpha_{ij} \min(\lambda_{ii}, \lambda_{jj}) \quad (3-14)$$

$\alpha_{ij}$  is a correction factor that has been expressed differently in the literature. In this study, we analyzed different correlations for  $\alpha_{ij}$  and proposed Eq. 3-15. The correction factor is only used in multicomponent systems. In binary systems, no correction factor was required, and model is purely predictive.

$$\alpha_{ij} = 1 - a \cdot |\Delta H_i^{\text{sub}} - \Delta H_j^{\text{sub}}| \quad (3-15)$$

where "a" is an adjustment coefficient.

We compared experimental data of seven multicomponent systems and adjusted "a" for all of them. For three oil systems where n-alkane weight fraction was less than 0.15, "a" was adjusted to be  $3 * 10^{-6}$ . However, for the case where only n-alkanes were present ( $WF = 1$ ), very small "a" (close to zero) was needed. So, we suggest using "a" coefficients as follows:

$$\text{If } W_f \cong 1, \quad 0 \leq a < 8 \times 10^{-7} \quad (3-16)$$

$$\text{If } 0.15 < W_f < 1, \quad 8 \times 10^{-7} \leq a < 3 \times 10^{-6} \quad (3-17)$$

$$\text{If } W_f \leq 0.15, \quad a = 3 \times 10^{-6} \quad (3-18)$$

Please note that the mentioned recommendations are based on analyzing seven multicomponent systems through various parameters including precipitation curve, solid phase composition and Critical Carbon Number (CCN). For each oil composition, all parameters were optimally predicted with one adjustment parameter at various conditions. Our work is amongt the few studies that verified Coutinho's model by analyzing different paraffin related parameters against the experimental data. (not just by precipitation data points).

The following derivation is used to calculate the solidified wax fraction in precipitation curve formation

$$S_f \text{ (Solidified wax weight fraction)} \left[ \frac{\text{weight of solid phase}}{\text{weight of total fluid}} \right] = \quad (3-19)$$

$$\Sigma x_i^s Mw_i \left[ \frac{\text{weight of solid phase}}{1 \text{ mole of solid phase}} \right] * n_s \left[ \frac{\text{mole of solid phase}}{1 \text{ mole of total n - alkanes}} \right]$$

$$* \frac{1}{\Sigma z_i Mw_i} \left[ \frac{1 \text{ mole of total n - alkanes}}{\text{wieght of nalkanes}} \right] * W_{NA} \left[ \frac{\text{weight of nalkanes}}{\text{weight of total fluid}} \right]$$

In the calculation of activity coefficients of liquid and solid phases, thermophysical properties, molar volumes and Van der Waals volumes are required. In the following

section, we present the correlations which have been used in our thermodynamic software for the required parameters.

One of the main findings of our study was to validate the aging process in wax deposition phenomenon using the thermodynamic model. For this purpose, we introduce a new parameter which represents the relative concentration of carbon number component in the n-alkane system ( $C_i^{NA}$ ). In other word, if only the n-alkane system is considered within the oil sample, the relative concentration of each carbon number component will be expressed by  $C_i^{NA}$ . Although, the relative concentration parameter does not represent the actual concentration, it is a very helpful parameter to determine CCN and verify the aging process. Please note that in SP-Depo, actual concentrations of different carbon numbers are calculated and presented in the next chapter of this dissertation.

$$C_{i,NA} = \frac{m_{i,NA}}{V_{NA}} \quad (3-20)$$

Where

$$V^{NA} = \sum_{i=1}^{i=N} (V_{i,NA}) \quad (3-21)$$

where  $V_i^{NA}$  is calculated from DIPPR and GCVOL models

### 3.1.3 Thermophysical properties

Heat and temperature of fusion are expressed through the following equations [19]. Among all the thermophysical properties, melting temperature has the highest impact on the final thermodynamic results.

$$T_i^f [K] = 421.6 - (421.6 + 1935991) \exp(-7.8945(CN - 1)^{0.07194}) \quad (3-22)$$

$$\Delta_{fus}H_i \left[ \frac{KJ}{mol} \right] = 0.00355CN^3 - 0.2376CN^2 + 7.4CN - 34.814 \quad (3-23)$$

Similarly, heat and temperature of solid phase transition [19] are expressed as:

$$T^{tr}[K] = 420.42 - (420.42 + 134364) \exp(-4.344(CN + 6.592))^{0.14627} \quad (3-24)$$

$$\Delta^{tr}H = \Delta^{tr}H - \Delta^f H \quad (3-25)$$

$$\Delta^{\text{tot}}H_i \left[ \frac{\text{KJ}}{\text{mol}} \right] = 3.7791CN - 12.654 \quad (3-26)$$

Heat of vaporization is another required thermophysical property which is calculated from Extension of Pitzer CSP models [28] as:

$$\Delta^{vap}H \left[ \frac{KJ}{mole} \right] = \Delta^{vap}H^* * RT_c \quad (3-27)$$

$$\Delta^{vap}H^* = \Delta^{vap}H^{*(0)} + \omega\Delta^{vap}H^{*(1)} + \omega^2\Delta^{vap}H^{*(2)} \quad (3-28)$$

$$\omega = 0.0520750 + 0.0448946n - 0.000185397n^2 \quad (3-29)$$

$$\Delta^{vap}H^{*(J)} = b_1^{(J)}x^{0.3333} + b_2^{(J)}x^{0.8333} + b_3^{(J)}x^{1.2083} + b_4^{(J)}x + b_5^{(J)}x^2 + b_6^{(J)}x^3 \quad (3-30)$$

$$x = 1 - T_r \quad (3-31)$$

$$\ln(959.98 - T_c) = 6.81536 - 0.211145n_c^{\frac{2}{3}} \quad (3-32)$$

where corresponding coefficients are expressed in Table 3-1.

Table 3-1: Coefficient table of Extension of Pitzer CSP models [28]

	$\Delta H_v^{*(0)}$	$\Delta H_v^{*(1)}$	$\Delta H_v^{*(2)}$
b1	5.2804	0.80022	7.2543
b2	12.865	273.23	-346.45
b3	1.171	465.08	-610.48
b4	-13.116	-638.51	839.89
b5	0.4858	-145.12	160.05
b6	-1.088	74.049	-50.711

### 3.1.4 Molar volume

In our study, the molar volume term is very important because it is used in both thermodynamic and wax deposition models for liquid phase non-ideality and molecular diffusivity calculations. In SP-Wax, for liquid phase activity coefficient calculation, molar volumes of all carbon number components are required. For this purpose, we used DIPPR

correlations [32] and GCVOL group contribution method [34]. Molar volumes for  $7 \leq CN \leq 20$  are calculated from DIPPR Correlations as:

$$V_{m,i} \left[ \frac{m^3}{Kmol} \right] = \left( \frac{A}{B^{(1+(1-\frac{T}{C})^D)}} \right)^{-1} \quad (3-33)$$

where A, B, C and D are sets of coefficients which are unique for each carbon number component (shown in Table 3-2).

Table 3-2: Coefficients of DIPPR correlations for molar volume calculation

DIPPR	A	B	C	D
<b>C7</b>	0.6034	0.2602	540.26	0.2791
<b>C8</b>	0.50864	0.25476	568.83	0.2694
<b>C9</b>	0.46554	0.25556	595.65	0.2857
<b>C10</b>	0.4129	0.2524	618.45	0.2857
<b>C11</b>	0.37012	0.24999	638.76	0.2857
<b>C12</b>	0.346	0.2518	658.2	0.2896
<b>C13</b>	0.3228	0.2504	675.8	0.312
<b>C14</b>	0.30382	0.25588	692.4	0.273
<b>C15</b>	0.28834	0.25375	706.8	0.31579
<b>C16</b>	0.27356	0.25442	720.6	0.3238
<b>C17</b>	0.25217	0.25316	733.37	0.3052
<b>C18</b>	0.2413	0.25763	745.26	0.274
<b>C19</b>	0.22147	0.25012	755.93	0.3065
<b>C20</b>	0.20966	0.24934	767.04	0.3088

For other carbon numbers ( $C_n < 7$  &  $C_n > 20$ ), molar volume is calculated from GCVOL group contribution method [34] as:

$$V_{m,i} \left[ \frac{m^3}{mole} \right] = \frac{\sum n_i \Delta v_i}{10^6} \quad (3-34)$$

$$\Delta v_i \left[ \frac{cm^3}{mole} \right] = A_i + B_i^T + C_i T^2 \quad (3-35)$$

Table 3-3: GCVOL Coefficients

Component	A $\left[ \frac{cm^3}{mole} \right]$	B $\left[ \frac{cm^3}{mole \cdot k} \right]$	C
CH2	12.52	$12.94 * 10^{-3}$	0
CH3	18.96	$45.58 * 10^{-3}$	0

### 3.1.5 Van der Waals volume

Another volume term which is needed in the calculation of liquid phase non-ideality is the Van der Waals volume. Bondi [33] used the group contribution method for  $V_w$  calculation.

$$V_{w,i} \left[ \frac{m^3}{mole} \right] = \frac{\sum n_i \Delta v_i}{10^6} \quad (3-36)$$

Table 3-4: Van der Waals volume

Comp	$\Delta v_i \left[ \frac{cm^3}{mole} \right]$
CH2	10.23
CH3	13.67

Now that all required parameters are available, the equations from Eq. 3-1 to Eq. 3-5 are solved iteratively till the desired accuracy is reached. In the next chapter, the implementation details for SP-Wax are provided.

## 3.2 SP-Depo wax deposition modeling software

In SP-Depo software, two general calculation options are included. The first option requires the user to provide equations for concentration and  $\frac{\partial C}{\partial T}$  considering only one component which is referred as wax. In addition, the molecular diffusivity ( $D_{wo}$ ) is considered by only one value. In this method, the thermodynamic model is not

incorporated, and it is referred to “conventional method” in this document. This method only provides predictions about the deposit’s thickness and solid wax fraction.

The second method, which is one of the main contributions of our study, employs a new thermodynamically-coupled model to predict wax deposition characteristics. This method uses SP-Wax thermodynamic tool for calculation of concentration,  $D_{wo}$  and  $\frac{\partial C}{\partial T}$  during the wax deposition calculation. In our newly proposed modeling approach, we have used Panacharoensawad [10] governing equations where no precipitation wax mass flux scenario and  $k_\alpha = 1$  are assumed. By using this calculation option, deposit’s solid phase composition will be predicted. Our new wax deposition model is referred to as “SP-Compo model” in this dissertation. In addition, SP-Depo is developed for single-phase turbulent flow with counter-current coolant flow condition.

### 3.2.1 Minimum depositable carbon number concept

In SP-Compo model, concentration,  $\partial C / \partial T$  and diffusivity terms are calculated based on depositable carbon number components’ thermodynamic properties. So, one of the challenges we encountered was to propose a reliable method to determine the depositable carbon numbers in wax deposition process. In this section, we introduce a new thermodynamic method to calculate the depositable carbon number range for different temperatures.

There is not a clear definition for the word “wax” in the literature. In the wax deposition research, wax usually refers to those n-alkane components that contribute to the deposition. For example, even though Heptane ( $C_7H_{16}$ ) is present in the oil sample but, it is not considered as wax because it does not contribute to the deposition. This definition is also inconsistent because there are some carbon number components that participate in deposition process at only a certain range of temperatures. In other word, at different temperatures, the range of precipitable carbon number components also changes.

We previously mentioned that the main deriving mechanism for deposition is the radial concentration gradient (or  $\partial C / \partial T$ ). Accordingly, in this study, we define the depositable wax content as a group of carbon number components with positive  $\partial C / \partial T$  at the deposit’s

interface temperature. In Figure 3-1,  $\partial C / \partial T$  versus carbon number is plotted for different temperatures and it is suggested that carbon numbers with only positive  $\partial C / \partial T$  will diffuse toward the deposit. To be more elaborate, for example, if the deposit's interface temperature is at  $T=10.5^{\circ}\text{C}$ , only carbon number components larger than C21 will diffuse toward the deposit (C21 is annotated by X in the graph). Since the interface temperature increases with time, the minimum depositable (MinC) carbon number shifts toward the larger n-alkanes too. In the second graph (Figure 3-2), MinC is plotted against temperature till WAT. In Figure 3-2, it can be seen that MinC stays constant for a certain range of temperature. However, this range shrinks as temperature increases toward WAT.

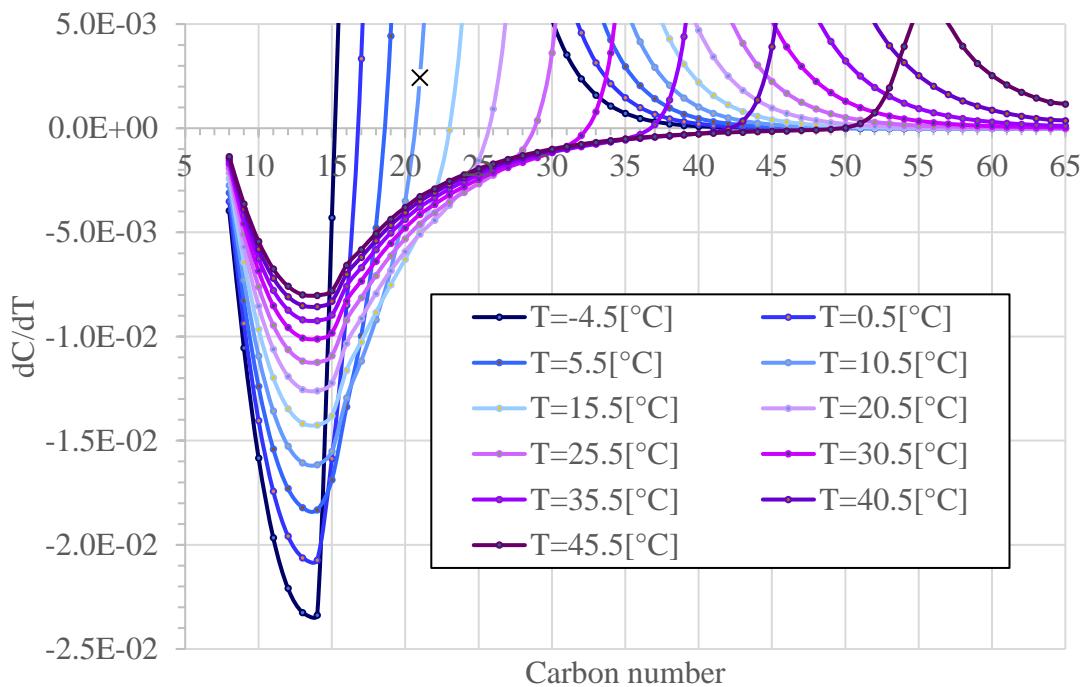


Figure 3-1: SP-Depo simulation: thermodynamically calculated  $\frac{\partial C}{\partial T}$  versus carbon number for different temperatures. Smoothened input South Pelto composition have been used. X is the smallest depositable carbon number component at  $T = 10.5^{\circ}\text{C}$

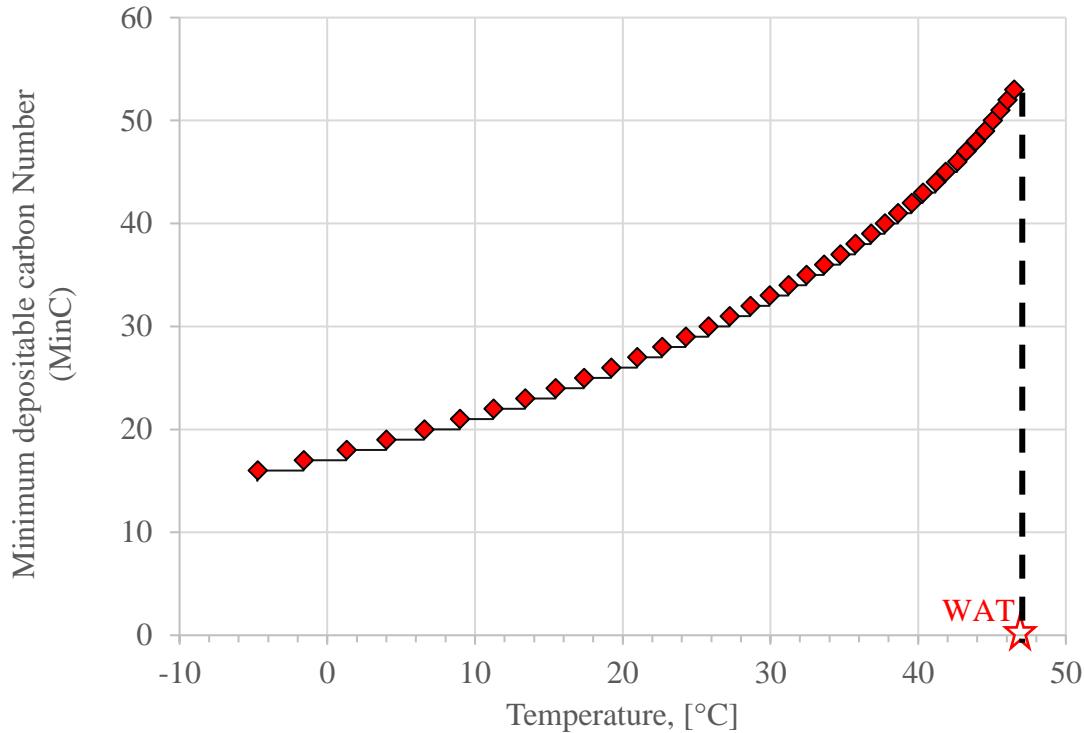


Figure 3-2: Minimum depositable carbon number versus temperature based on smoothed input South Pelto oil composition. The red points represent the lowest temperatures where MinC is shifted and the solid lines show the MinC within a temperature range.

### 3.2.2 Thermodynamically calculated parameters

Concentration gradient near the deposit is the primary driving mechanism for wax particles to move toward the deposit. Therefore, it is very important to calculate the concentration accurately. In our model, we use SP-Wax thermodynamic model to calculate the concentration of each depositable carbon number component. Unfortunately, concentration is not directly reported by the thermodynamic models. Therefore, we derived the following relations for concentration calculation using SP-Wax.

In the following derivation, it is assumed that the temperature is below WAT and some part of the paraffinic components are in the solid phase.  $\tilde{m}_i$  is the dissolved amount of  $i^{\text{th}}$  carbon number n-alkane in the liquid phase per unit-mass of oil and it is calculated as:

$$\tilde{m}_i = x_{w,i}^L \times W_f \times f_{NA}^L \quad (3-37)$$

where  $f_{NA}^L$  is the weight fraction of dissolved n-alkanes in liquid phase over the total amount of n-alkanes in the system and it is calculated as:

$$f_{NA}^L = \frac{\sum z_{m,i} \times Mw_i - \sum n_s \times x_{m,i}^S \times Mw_i}{\sum z_{m,i} \times Mw_i} \quad (3-38)$$

Another parameter in Eq. 3-37 is  $x_{w,i}^L$  which represents the weight composition of n-alkanes in liquid phase. In SP-Wax, mole composition of n-alkanes liquid phase ( $x_{m,i}^L$ ) is calculated through Eq. 3-4. The following equation is used to convert the composition to weight fraction ( $x_{w,i}^L$ ) based on the molecular weight of each carbon number.

$$x_{w,i}^L = \frac{x_{m,i}^L \times Mw_i}{\sum_i x_{m,i}^L \times Mw_i} \quad (3-39)$$

The term “oil” means solid+ liquid which accounts for both n-alkanes and non n-alkanes. Now that the dissolved mass of each n-alkane component is known, we need to know the volume of the oil sample for concentration calculation.

In our model, the user should provide an equation for the oil density for temperatures above WAT. To be more elaborate, the density change due to volume expansion is required for the case where no dissolution of n-alkanes from the solid phase occurs. In Rittirong [38] and Panacharoenawad [10] studies, oil densities and simple fitted equations are reported for temperatures above WAT.  $\Phi_L$  is defined as the volume per unit mass of oil through Eq. 3-40.

$$\Phi_L = \Phi_{exp} - \frac{f_{NA}^S}{\rho_{Wax}} \quad (3-40)$$

where  $f_{NA,S}$  is the weight fraction of the solidified wax particles over one unit mass of oil as:

$$f_{NA}^S = W_f \times \frac{n_s \times \sum x_{m,i}^S \times Mw_i}{\sum z_{m,i} \times Mw_i} \quad (3-41)$$

Now that  $\tilde{m}_i$  and  $\phi_L$  are known, one can calculate the actual concentration of  $i^{\text{th}}$  carbon number component in the system from the following equation.

$$C_i \left[ \frac{\text{kg NA}_{i,L}}{m_L^3} \right] = \frac{\tilde{m}_i}{\phi_L} \quad (3-42)$$

Please refer to the nomenclature section for each parameter’s definition and unit. In our proposed model, we considered the depositable carbon number components as one

pseudo-single-component and calculated the corresponding concentration as the summation of all depositable component's concentrations (shown below).

$$C = C_{MinC} + C_{MinC+1} + \dots + C_N \quad (3-43)$$

And similarly, for  $\frac{\partial C}{\partial T}$ ,

$$\frac{\partial C}{\partial T} = \frac{\partial}{\partial T} (C_{MinC} + C_{MinC+1} + \dots + C_N) \quad (3-44)$$

Or

$$\frac{\partial C}{\partial z} = \frac{\partial C_{MinC}}{\partial T} + \frac{\partial C_{MinC+1}}{\partial T} + \dots + \frac{\partial C_N}{\partial T} \quad (3-45)$$

We also calculate n-alkane molecular diffusivities ( $D_{wo,i}$ ) using SP-Wax thermodynamic model. Hayduk-Minhas diffusivity equation [66] (shown below) is used in SP-Depo.

$$D_{wo,i} = 13.3 \times 10^{-12} \times \frac{(T + 273.15)^{1.47} (\mu \times 1000)^\gamma}{V_{m,i}^{0.71}} \quad (3-46)$$

where,

$$\gamma = \frac{10.2}{V_{m,i}} - 0.791 \quad (3-47)$$

$V_{m,i}$  is the molar volume of  $i^{\text{th}}$  carbon number component which is calculated from DIPPR correlations [32] and the group contribution method (GCVOL) [34] (as suggested by Coutinho et al. [14]). In Figure 3-3, molecular diffusivity of different carbon number components is plotted at three different temperatures. As expected, molecular diffusivity increases with temperature.

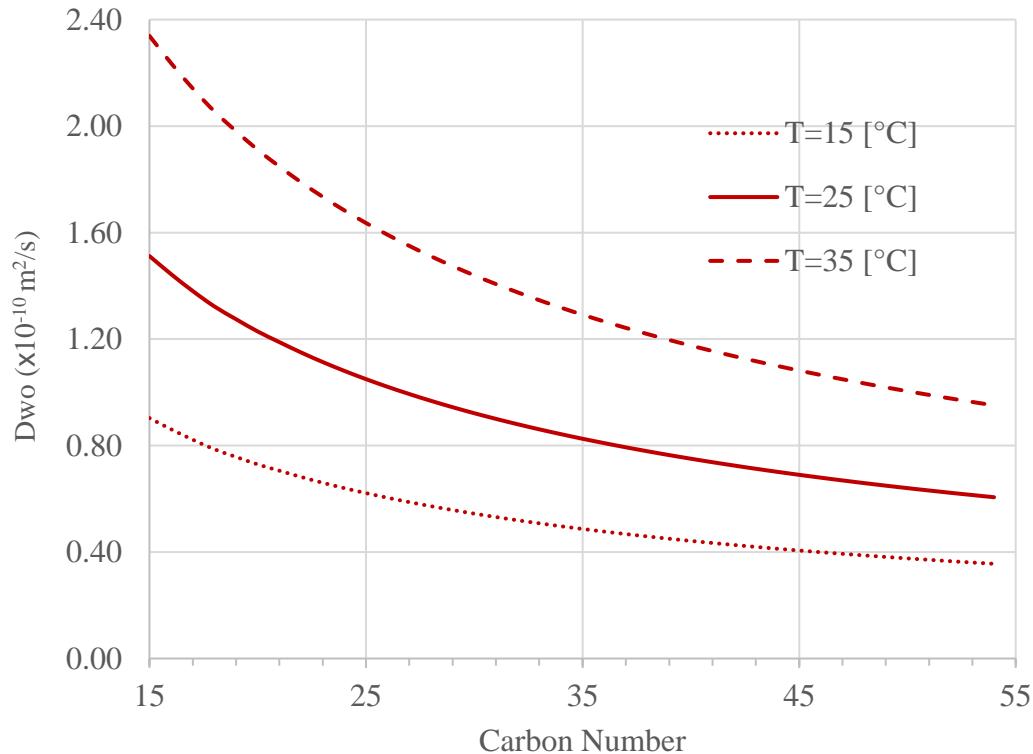


Figure 3-3: Diffusivity versus carbon number at three different temperatures

By knowing the diffusivities of all carbon number components, average diffusivity of the pseudo-single-component is calculated using the volume fraction of each depositable n-alkane as:

$$\bar{D}_{wo} = \sum D_{wo,i} \Phi_i \quad (3-48)$$

where  $\Phi_i$  is the volume fraction of  $i^{\text{th}}$  n-alkane among depositable carbon number components

$$\sum \Phi_i = 1.0 \quad (3-49)$$

### 3.2.3 Wax deposition theory

In this section, wax deposition and supplementary transport equations which are used in SP-Depo will thoroughly be elaborated.

When deposit is formed, the solid phase mass can be expressed as:

$$Mass_{sol} = \pi(R^2 - r_i^2)L_{pipe}\rho_{dep}\bar{F}_w \quad (3-50)$$

where,  $Mass_{sol}$ ,  $R$ ,  $r_i$ ,  $L_{pipe}$  and  $\bar{F}_w$  are the precipitated mass, pipe's radius, effective pipe's radius, pipe's length and average deposit's solid wax fraction, respectively. Then, wax mass rate of change can be expressed as:

$$\frac{dMass_{sol}}{dt} = \underbrace{\frac{\partial Mass_{sol}}{\partial \bar{F}_w} \frac{d\bar{F}_w}{dt}}_{1} + \underbrace{\frac{\partial Mass_{sol}}{\partial r_i} \frac{dr_i}{dt}}_{2} \quad (3-51)$$

where,

$$\left(\frac{\partial Mass_{sol}}{\partial \bar{F}_w}\right)_{r_i} \frac{d\bar{F}_w}{dt} = \pi(R^2 - r_i^2)L_{pipe}\rho_{oil} \frac{d\bar{F}_w}{dt} \quad (3-52)$$

and,

$$\frac{\partial Mass_{sol}}{\partial r_i} \frac{dr_i}{dt} = -2\pi r_i L_{pipe}\rho_{dep}\bar{F}_w \frac{dr_i}{dt} \quad (3-53)$$

In Eq. 3-51, the first term represents the rate of wax mass increase because of the increase in solid wax fraction (aging process) and the second term represents the contribution of thickness growth (buildup term) to the rate of wax mass increase. Both of these contributions are explained in the following sections.

### 3.2.4 Aging term

The first term (aging term) is only dependent on the wax mass flux going into the deposit and can be expressed as:

$$\left.\frac{\partial Mass_{sol}}{\partial \bar{F}_w}\right|_{r_i} \frac{d\bar{F}_w}{dt} = \left(-\bar{D}_e \left.\frac{\partial C}{\partial r}\right|_{r_i^+}\right) 2\pi r_i L_{pipe} = \pi(R^2 - r_i^2)L_{pipe}\rho_{oil} \frac{d\bar{F}_w}{dt} \quad (3-54)$$

where  $\bar{D}_e \left[ \frac{m^2}{s} \right]$  and  $\frac{\partial C}{\partial r} \Big|_{r_i^+}$  are effective wax diffusivity in the deposit and concentration gradient in radial direction at deposit's interface location (in the deposit side), respectively. By simple mathematical manipulation, the above relation becomes:

$$\frac{d\bar{F}_w}{dt} = \frac{2r_i \underbrace{\left( -\bar{D}_e \frac{\partial C}{\partial r} \Big|_{r_i^+} \right)}_{J_{aging}}}{(R^2 - r_i^2)\rho_o} \quad (3-55)$$

Effective diffusivity term ( $\bar{D}_e$ ) is calculated from the following formula [67]:

$$\bar{D}_e = \frac{\bar{D}_{wo}}{1 + \alpha^2 \bar{F}_w^2 / (1 - \bar{F}_w)} \quad (3-56)$$

This equation was not originally developed for wax deposition however, Singh et al. [3] showed that it can be adopted to represent the effective diffusivity of wax components through a 3D network of wax crystals. Singh et al. [3] suggested that the wax crystal aspect ratio ( $\alpha$ ) increases linearly as wax fraction increases:

$$\alpha = 1 + k_\alpha \bar{F}_w \quad (3-57)$$

where  $k_\alpha$  is an adjustment parameter. From another study, Lee [12] suggested another relation for  $\alpha$  with a new fitting parameter “A” as follows:

$$\alpha = 1 + \sqrt{\frac{\bar{F}_w - \bar{F}_{w0}}{A}} \quad (3-58)$$

Please note that both crystal aspect ratio formulas (Eq. 3-57 and Eq. 3-58) are included in SP-Depo and can be chosen by the user. However, in SP-Compo model, Eq.3-57 is used and  $k_\alpha$  is set to be one as suggested by Panacharoenawad [10].

### 3.2.5 Buildup term

In this section, the buildup term which is related to the increase in deposit's thickness will be presented. From the following equation, it is believed that the difference between the

total incoming wax mass flux and the wax mass flux associated with the aging process accounts for the buildup term as shown:

$$-2\pi r_i L_{pipe} \bar{F}_w \rho_{oil} \frac{dr_i}{dt} = 2\pi r_i L_{pipe} \underbrace{[J_{M,Total} - J_{M,Aging}]}_{J_{buildup}} \quad (3-59)$$

where  $J_{M,Total}$  is the convective wax mass flux in the oil side from the bulk to the deposit's interface  $\left(-\bar{D}_e \frac{\partial C}{\partial r}\Big|_{r_i^+}\right)$  and  $J_{M,Aging}$  is related to the diffusive mass flux of waxy components into the deposit side from the interface to the pipe's wall  $\left(-\bar{D}_{wo} \frac{\partial C}{\partial r}\Big|_{r_i^-}\right)$ . From the following schematic,  $J_{M,Total}$  and  $J_{M,Aging}$  are illustrated in the wax deposition process.

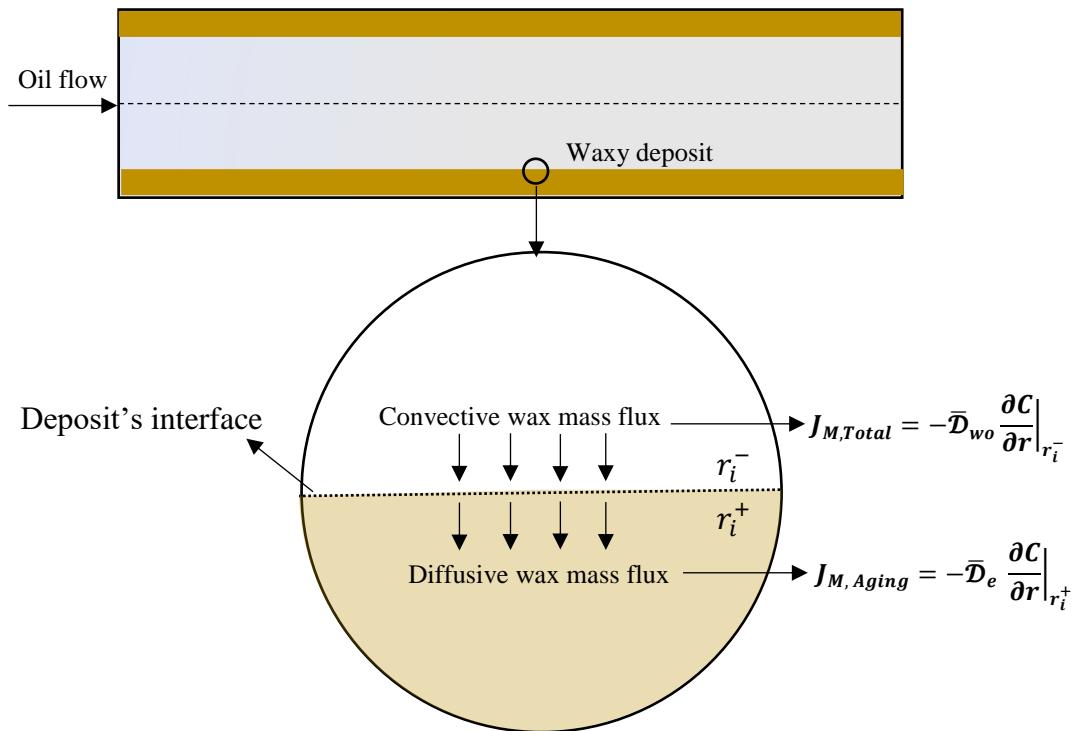


Figure 3-4: Incoming and diffusive wax mass flux at the waxy deposit's interface

The total incoming wax mass flux can be approximated by:

$$q_{M,IN} \equiv k_l(C_b - C(r_i)) = -\bar{\mathcal{D}}_{wo} \frac{\partial C}{\partial r} \Big|_{r_i^-} \quad (3-60)$$

As previously discussed, the concentration profile can be calculated using three wax mass flux scenarios. In the partial precipitation model [12], the proposed approach includes the precipitation rate parameter ( $k_r$ ) which could vary from 0 to infinity and should be adjusted by the user. When  $k_r$  approaches to infinity, a minimum value for the wax mass flux is provided which is the same as wax mass flux calculated from the solubility method. However, studies have shown that the wax mass flux could be less than the solubility method [10]. This behavior is observed because of shear effect which is ignored by the three mentioned wax mass flux models. Moreover, in partial precipitation wax mass flux model, the precipitation rate ( $k_r$ ) range is very wide which could not be easily adjusted.

In Panacharoensawad wax deposition model [10], the above issues are solved. In his modeling approach, the effect of shear stress is included through the maximum tolerable shear stress parameter which increases linearly with  $\bar{F}_w$ . When shear stress reaches to the maximum tolerable value, the buildup term becomes zero and the deposit's thickness does not increase. On the other side, Panacharoensawad model assumed that the deposit can grow freely when there is no shear effect (oil velocity = 0). The following equations accounts for the above assumptions [10]. The maximum allowable shear stress is:

$$\tau_{max} = \tau_{ini} * MSR_1 * \bar{F}_w + \tau_{ini} \quad (3-61)$$

where  $\tau_{max}$  is related to the wax mass flux parameters through the following relation:

$$J = J_{Max} \frac{\tau_{max} - \tau}{\tau_{max}} = J_{Max} SR_1 \quad (3-62)$$

$J$  and  $J_{Max}$  are actual and maximum buildup wax mass flux terms, respectively. Through the following equations, deposit's solid fraction and thickness increase rates are expressed [10].  $SR_1$ , and  $SR_2$  are employed to adjust the growth and aging equations in wax deposition governing equations [10].

$$\frac{d\bar{F}_w}{dt} = \frac{2r_i \left( -\bar{\mathcal{D}}_e \frac{\partial C}{\partial T} \frac{\partial T}{\partial r} \Big|_{r_i^+} \right)}{\rho_{Dep} (R^2 - r_i^2)} SR_2 \quad (3-63)$$

and

$$\frac{dr_i}{dt} = \frac{-1}{F_w \rho} \left[ \left( -\bar{\mathcal{D}}_{wo} \frac{\partial C}{\partial r} \Big|_{r_i^-} \right) - \left( -\bar{\mathcal{D}}_e \frac{\partial C}{\partial r} \Big|_{r_i^+} \right) SR_2 \right] SR_1 \quad (3-64)$$

where  $SR_2$  is defined as:

$$SR_2 = MSR_2 \frac{\tau - \tau_0}{\tau_0}; 0 \leq SR_2 \leq 1 \quad (3-65)$$

Through  $SR_1$  and  $SR_2$  multipliers, the initial deposition formation and the deposit's growth rate are addressed [10]. In Eq. 3-63 and Eq. 3-64,  $\frac{\partial T}{\partial r} \Big|_{r_i^+}$ ,  $\frac{\partial C}{\partial T} \Big|_{r_i^+}$  and  $\frac{\partial C}{\partial r} \Big|_{r_i^-}$  are calculated after solving for temperature and concentration profiles. Temperature and concentration profile calculations are explained in the next chapter.

Eq. 3-63 and 3-64 are solved using the Dormand-Prince ODE solving method [68] which uses adaptive time steps. Dormand-Prince has also been used for non-uniform discretization. In addition, Levenberg–Marquardt optimization tool [69] has been coded in SP-Depo for fitting parameter adjustment (e.g.,  $MSR_1$  and  $MSR_2$ ).

### 3.2.6 Laminar Flow Formulation

The above formulation is specifically developed for the turbulent flow condition which is included in the SP-Depo software. However, we also investigated the wax deposition process under the laminar flow through a separate paper [70]. In that paper, we simulated a wax deposition predictor in C++ under the laminar flow. The results were confirmed by data of more than twenty-five flow-loop experiments [3]. Please note that the presented methodology is only included in our paper [70] (not in SP-Depo software).

For wax deposition in laminar flow, no precipitation scenario for wax mass flux is chosen [3]. Wax deposition equations under laminar flow are similar to the equations related to

the turbulent flow case (explained above). However, there are slight differences which are elaborated in this section.

For heat and mass transfer coefficient calculations, Chilton–Colburn analogy has been used where Hausen empirical Nusselt number correlation [71] is used for long pipes as shown:

$$Nu_p = 3.66 + 1.7813 \times 10^{-3} \frac{G_{z,p}^{5/3}}{(1 + 0.04G_{z,p}^{2/3})^2} \quad (3-66)$$

and for short lab-scale pipes, Seider and Tate correlation [72] is suggested as follows:

$$Nu_p = 1.24G_{z,p}^{1/3} \quad (3-67)$$

where subscript "p" can be replaced by "mass" and "heat" for mass transfer and heat transfer coefficient calculations, respectively. Finally, Graetz number can be calculated as:

$$G_{z,heat} = \frac{Re \times Pr \times 2R}{z} \quad (3-68)$$

$$G_{z,heat} = \frac{Re \times Sc \times 2R}{z} \quad (3-69)$$

Then, heat and mass transfer coefficients are calculated as:

$$Nu_{heat} = \frac{hD}{k} = -\frac{D}{T_b - T_i} \frac{\partial T}{\partial r} \Big|_{r=r_i^-} \quad (3-70)$$

$$Nu_{mass} = \frac{k_l D}{\bar{D}_{wo}} = -\frac{D}{C_b - C_i} \frac{\partial C}{\partial r} \Big|_{r=r_i^-} \quad (3-71)$$

So, the first term in Eq. 3-64 will be changed to:

$$-\bar{D}_{wo} \frac{\partial C}{\partial r} \Big|_{r_i^-} = k_l(C_b - C_i) \quad (3-72)$$

where  $C_b$  and  $C_i$  are solubility terms at the bulk and at the deposit's interface, respectively.

Eq. 3-72 considers instantaneous precipitation and it is another representation of the no precipitation wax mass flux scenario which is explained in Chapter 1. Furthermore, aspect ratio of the wax crystals in the deposit ( $\alpha$ ) is calculated using Eq. 3-57 where it is linearly correlated to the solidified wax fraction.

To correctly account for the mass balance, it is important to consider the axial depletion which is presented by the following relation:

$$\frac{dC}{dz} = -k_l(C_{b_0} - C_i) * 2\pi r_i * \frac{\rho_L}{w_h} \quad (3-73)$$

We solved the governing ODEs ( $\frac{dr_i}{dt}$  and  $\frac{d\bar{F}_w}{dt}$ ) using RK45 and solved Eq. 3-73 in each half/full time step of RK45. By applying this method, we made sure that the updated  $C_b$  is considered in our calculations. Eq. 3-73 was solved using RK4 method.

In order to tune the prediction to match the experimental data, the fitting parameter ( $k_\alpha$ ) was adjusted. Since one of the objectives of our paper was to understand the potential effects of different factors on  $k_\alpha$ , Levenberg–Marquardt tool was used for fitting parameter adjustment.

## Chapter 4

### Software Development and Implementation

In this section, calculation procedure and software's structure of our two software will be thoroughly explained. SP-Wax is our first software which is simulated to predict different SLE characteristics of waxy solutions. For our second software, SP-Depo is developed to model wax deposition phenomenon in pipe. In SP-Depo, a new thermodynamically-coupled wax deposition model is developed to predict deposit's solid phase carbon number distribution in addition to thickness and solid wax fraction. For both software, the simulation results are verified by extensive experimental data.

#### 4.1 SP-Wax software

The open-source software (SP-Wax) for the solid–liquid equilibrium (SLE) calculation of paraffin is presented. Paraffin modeling is important to many industries and engineering applications. SP-Wax provides reliable predictions for phase behavior of paraffinic solutions, which is crucial for petroleum industry. The Coutinho et al. thermodynamic model was primarily used and coded in SP-Wax. The developed simulation was validated by experimental data of binary and multicomponent systems. Solid phase compositions were successfully estimated, and aging process of wax deposition problem was analyzed. Within the software, core calculations were coded in C++ and OpenMP parallel programming technique was incorporated to improve the performance. A C# Windows Forms user interface was created to ensure the reusability of the software for both technical and non-technical users. The following flow chart represent the programming structure of SP-Wax.

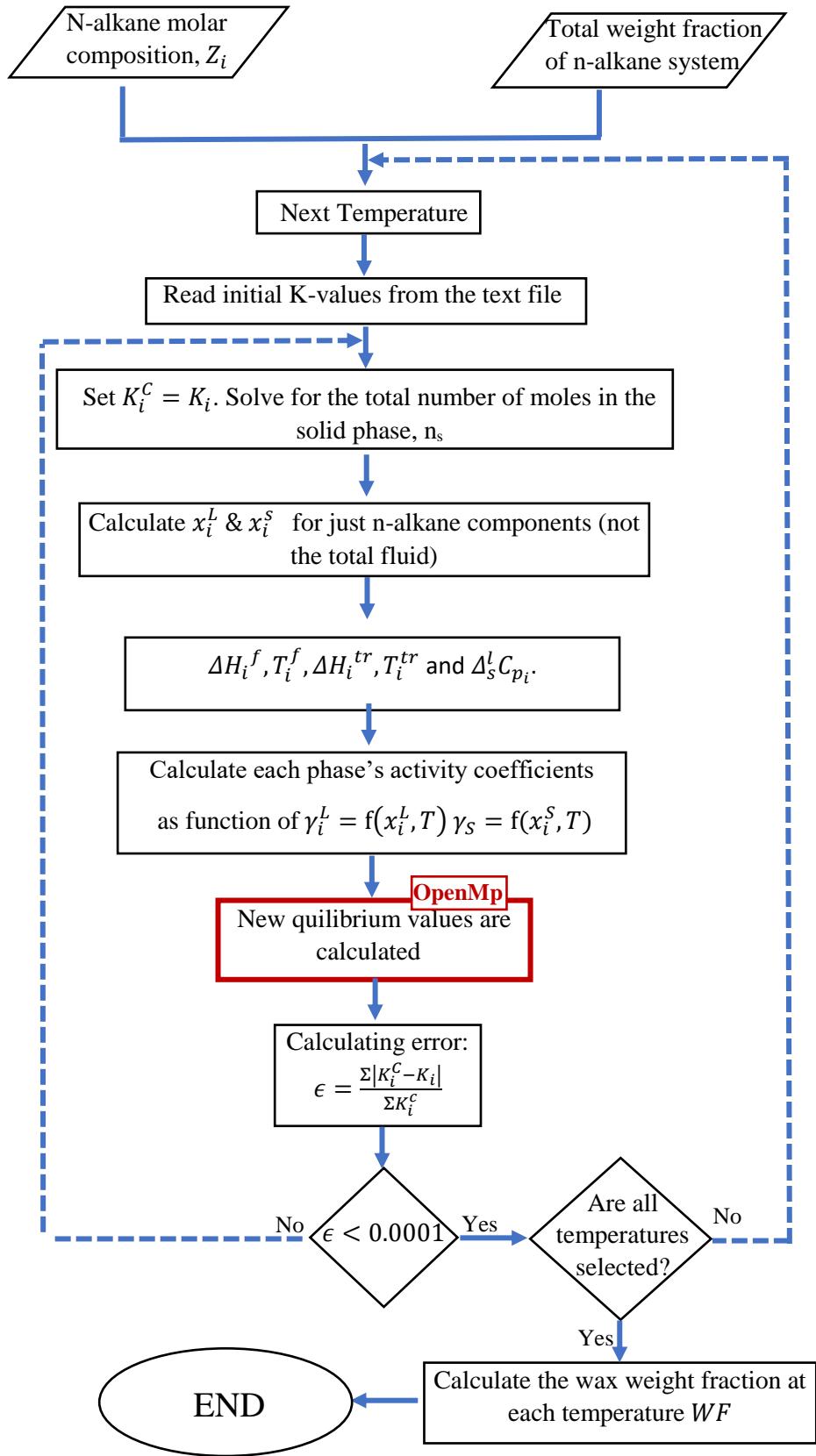


Figure 4-1:SP-Wax flowchart for calculation of the precipitation curve

We initially tried to code the SP-Wax in MATLAB however, speed was a big problem for the calculation of solid phase activity coefficients. Therefore, we switched to C++ programming language and incorporated OpenMp parallel tool to optimize the performance even more. Successfully, we were able to decrease the run-time from fifty seconds to less than one second for each temperature point. The simulation run-time was very important because the thermodynamic model was planned to be used in SP-Compo model in SP-Depo software. Additionally, we further decreased the run-time by excluding those carbon number components with much lower melting temperatures from the calculation. The following graph shows the run-time of the simulation for South Pelto oil sample with 60 n-alkane components. Please note that SP-Wax incorporates 8 threads because it uses OpenMp parallel programming technique.

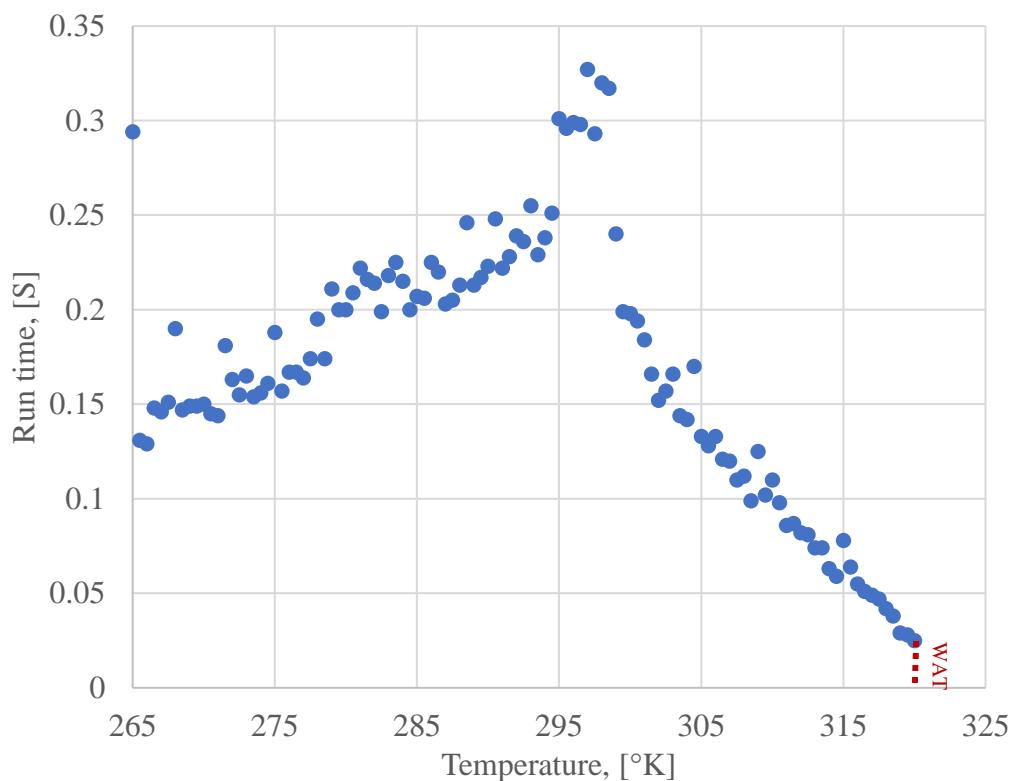


Figure 4-2: SP-Wax run-time at different temperatures

SP-Wax's functionality is divided into four categories including 1) Thermodynamics of binary systems 2) Precipitation curve 3) Single-temperature SLE modeling 4) Critical Carbon Number (CCN) estimation. Last three categories are for multicomponent systems.

There are unique cpp and exe files for each of the mentioned functionalities. In the following picture, all source and executable files of SP-Wax are shown.

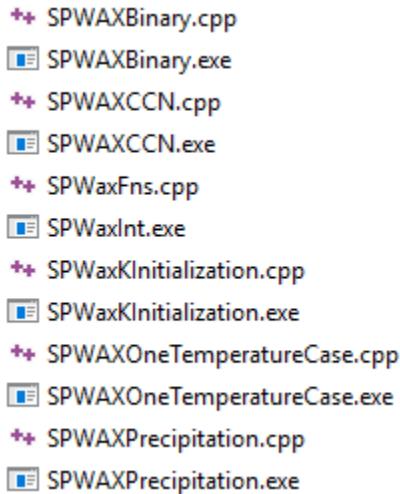


Figure 4-3: Source and executable files in SP-Wax (Computations of SLE model)

In the following section, the shown cpp and executable files are explained.

#### 4.1.1 **SPWaxInt.exe**

This exe file is for the GUI and should be clicked first by the user. Communication between C++ and C# is mainly done through the text files. The user provides required inputs in Windows Form interface and, C# generates set of text files which contain the inserted inputs. When “Run Simulation” button is clicked in GUI, corresponding C++ executable file will run. The C++ exe-file requires set of input files which have already been created by C#. When C++ exe-file runs successfully, the outputs are created and reported to text files in the same directory. The user, then, can plot the data in the GUI for different parameters. For data visualization, C# reads the newly created output text files (generated by C++ exe files) and plots the output data.

#### 4.1.2 **SPWaxFn**

The required functions are included in SPWaxFn which will be called by other cpp files as illustrated in Figure 4-4.

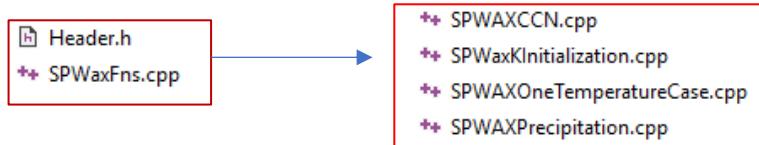


Figure 4-4: The header and cpp files in SP-Wax software

Multicomponent system source files use the same functions which are defined and listed in “SPWaxFn.cpp” and “Header.h.” In SPWaxFn.cpp, more than seventy-five lines of comments are included in different sections to elaborate all variables and functions. The included functions in SPWaxFn.h are listed in Figure 4-5. Some of the functions are explained in the following section as a guide for future developers.

```

double TempFusYang(int CN);
double HeatFusYang(int CN);
double HeatFus(int CN);
double HeatTrans(int CN);
double HeatVap(double T, int CN);
double TempFus(int CN);
double TempTrans(int CN);
double *ArrayRetA();
double *ArrayRetB();
double *ArrayRetC();
double *ArrayRetD();
double Vm(double T, int CN);
double Vw(int CN);
double LambdaCorr3(int CN1, int CN2, double T, double CF);
double LambdaCorr1(int CN1, int CN2, double T, double CF);
double LambdaCorr2(int CN1, int CN2, double T, double CF);
double GammaSolid(int CN1, double X_S[], int MinC, int MaxC, double T, double CF);
double GammaSolMes(int MinC, int CN1, int CompNum, int CarbonNum[], double X_S[], double T, double CF);
double GammaLiqMesFFV(int MinC, int NumOfCN1, int CN1, int CompNum, int CarbonNum[], double X_L[], double T);
double GammaLiqMesEFV(int MinC, int NumOfCN1, int CN1, int CompNum, int CarbonNum[], double X_L[], double T);
double objFunc(double nS, int CompNum, double Z[], double K[]);
double objFuncDer(double nS, int CompNum, double Z[], double K[]);
double Fsolve(double nS, int CompNum, double Z[], double K[]);
  
```

Figure 4-5: Function in SP-Wax software

In this section, all function in Figure 4-5 will be explained. In `Vm(double T, int CN)`, molar volumes are calculated by DIPPR correlations [32] and GCVOL method[34]. By `*ArrayRetA()`, `*ArrayRetB()`, `*ArrayRetC()` and `*ArrayRetD()`, coefficients of DIPPR molar volume correlations [32] are read from DIPP.txt which are

used in SP-Wax. `Vw(int CN)` contains Van der Waal volume which is calculated from group contribution method proposed by Bondi [33].

Major binary interaction energy parameters in Wilson equation ( $\Lambda_{ij}$ ) are calculated in `LambdaCorr3(int CN1, int CN2, double T, double CF)` which is proposed by Coutinho et al. [14] and it is used in SP-Depo. Since  $\Lambda_{ij}$  is defined differently in the literature, we included two more models through `LambdaCorr1` [18] and `LambdaCorr2` [27].

For heat and temperature of fusion, correlations from Coutinho et al. [19] and Yang et al. [27] are included. These functions are represented through `HeatFus(int CN)`, `TempFus(int CN)`, `HeatFusYang(int CN)` and `double TempFusYang(int CN)`. In SP-Depo, proposed correlations from Coutinho et al. is used. We found that Yang et al. [27] correlations are also accurate in expressing heat and temperature of fusion when compared to experimental data. Coutinho et al.[19] also provided correlations for temperature and enthalpy of solid phase transition which are included in `HeatTrans(int CN)` and `TempTrans(int CN)`. Last thermodynamic property is heat of vaporization which is calculated from Extension of Pitzer CSP models [28] and represented through `HeatVap(double T, int CN)`. Since, there are uncertainties among experimental enthalpies of vaporization from different sources, available correlations carry the mentioned uncertainties too. In this study, we compared the predictions from CSP model with two sets of experimental vaporization enthalpy data at  $T = 25^{\circ}\text{C}$  and satisfactory results were observed.

For solid phase activity coefficient, two functions are created for Wilson model. `GammaSolMes` (shown below) is used in SP-Wax.

```

/*
Non-ideality of solid phase (activity coefficients, Gamma_Solid)
Wilson methodology
This function is primarily used for binary systems and has also been verified for multicomponent systems
*/
double GammaSolMes(int MinC, int CN1, int CompNum, int CarbonNum[], double Xs[], double T, double CF)
{
    double SumE = 0;
    double Sum1 = 0;
    double Sum2 = 0;
    for (int CN2 = MinC; CN2 < (CompNum + 1); CN2++)
    {
        SumE = SumE + LambdaCorr3(CN1, CarbonNum[CN2], T, CF)*Xs[CN2]; //checkt eh CN2-1
    }

    Sum1 = 0;
    for (int CN3 = MinC; CN3 < (CompNum + 1); CN3++)
    {
        double Sum2 = 0;
        for (int CN4 = MinC; CN4 < (CompNum + 1); CN4++)
        {
            Sum2 = Sum2 + LambdaCorr3(CarbonNum[CN3], CarbonNum[CN4], T, CF)*Xs[CN4];
        }
        Sum1 = Sum1 + LambdaCorr3(CarbonNum[CN3], CN1, T, CF)*Xs[CN3] / Sum2;
    }
    return(exp(-log(SumE) + 1 - Sum1));
}

```

Figure 4-6: Solid phase activity coefficient function used in SP-Wax

where some parameters are defined as:

- MinC:** Minimum carbon number to be included in the SLE calculation
- CN1:** Desired carbon number that activity coefficient is calculated for
- CompNum:** Total number of n-alkane components
- CarbonNum[]:** Returns carbon number
- Xs[]:** Solid-phase composition
- T:** Temperature
- CF:** Correction factor

- o **GammaLiqMesFFV** (liquid phase activity coefficients)

For liquid phase activity coefficient calculation, We analyzed several models and found that Flory-free volume [24] and Entropic free-volume [23] models are the best candidates to be included in SP-Wax. Both models are coded and included in **GammaLiqMesFFV**, **GammaLiqMesEFV**. Although both models are good candidates, **GammaLiqMesEFV** function has been used to express the liquid phase activity coefficients in SP-Wax. Function input variables for **GammaLiqMesEFV** are very similar to the solid phase activity coefficient function (**GammaSolMes**) which was explained previously.

#### 4.1.3 SPWaxBinary (.exe & .cpp)

SP-Wax is designed to work for binary and multicomponent systems. SPWaxBinary.cpp and SPWaxBinary.exe are the only source and executable files for the binary system case. The user provides the required inputs and C# creates several text files which are needed for C++ executable files. The main output from binary n-alkane system is to obtain Wax Appearance Temperature (WAT) for different solute mole fraction values. For example, the created input text files are shown in the following picture.

**1** **2**

SoluteFractionFile.txt - Notepad	BinaryInfo.txt - Notepad	
File Edit Format View H File Edit Format View	File Edit Format View	
0.308	7	1- Mole fraction of solute in the solution
0.268	23	a. For different solute mole fractions, solubilities and, therefore, WAT will be different. So, it is important to provide Solute mole fractions from which WATs are required.
0.252		2- Carbon number of solvent and solute respectively. In this example, they are: $C_7H_{16}$ and $C_{23}H_{48}$
0.235		
0.2		
1		

Figure 4-7: The created input files for the binary system option

SP-Wax reads one value of solute mole fraction and calculates mole of the solid phase ( $n_s$ ) at different temperatures till it reaches to a high enough temperature where no more solidified particle is formed ( $n_s = 0$ ). The corresponding temperature will be saved, and it will be reported as WAT for that specific solute mole fraction. Then, the next value of solute mole fraction is read, and the same procedure is followed. At the end, all saved WATs will be reported to “OutPutBinary.txt”. Please remember that DIPR.txt should be present in the same directory as SPWaxBinary.exe.

This source code is designed to estimate the smallest temperature at which all solute components are dissolved in liquid phase. This temperature is referred Wax Appearance Temperature (WAT). Required functions and main calculation are included in SPWaxBinary.cpp. All functions are identical to those that are used in multicomponent system functions that are listed in SP-WaxFn.cpp except two functions that are specifically

defined for binary system case including “**BinarySys**” and “**BinarySysDer**”. “**BinarySys**” calculates solid mole fraction ( $n_s$ ) based on given temperature and solute mole fraction. “**BinarySysDer**” calculates the derivative of “**BinarySys**” based on Temperature. Please refer to SPWaxBinary.cpp for more information about all other functions.

In the main section (“int main”), the general goal is to find the temperature that results in zero solid particles for function “**BinarySys**”. Newton Raphson was chosen to find the root which requires an initial value. There were two main difficulties that needed to be resolved. The first one was the initial value for  $T$  in root finding algorithm. The second problem was encountered when too high initial temperature beyond WAT was selected which resulted in the failure of the program. We found that if a relatively close  $T$  is chosen for an initial guess, such convergence problems will be vanished. So, in the main body, we followed a step-by-step procedure to find a good initial value for temperature for Newton Raphson method to find WAT. The numerical method was validated by fifty experimentally measured WAT data points. In the following picture, first two while-loops are used to find proper initial value for temperature and the third while-loop is used to find WAT.

```

/*The temperature that does not result in nan value is detected here
in this while loop*/
while (isnan(BinarySys(FracParam[j], T)))
{
    T = T + step1;
    a = BinarySys(FracParam[j], T);
}

/*A new temperature step is used to move forward
to find WAT (by two following while loops)*/
step = 1;
a = BinarySys(FracParam[j], T);
while (abs(BinarySys(FracParam[j], T)) > 0.0001)
{
    T = T + step;
    a = BinarySys(FracParam[j], T);
    if (BinarySys(FracParam[j], T) < 0 || isnan(BinarySys(FracParam[j], T))) {
        T = T - step;
        break;
    }
}

a = BinarySys(FracParam[j], T);
while (abs(err) > pow(10, -9))
{
    T = T - BinarySys(FracParam[j], T) / BinarySysDer(FracParam[j], T);
    err = BinarySys(FracParam[j], T);
}

```

Figure 4-8: A snapshot of SPWaxbinary.cpp

#### 4.1.4 SPWaxKInitialization (.exe & .cpp)

In the development process of the SP-Wax software, we found that convergence problem could be encountered in higher temperatures (close to WAT). The problem was because of the initial guesses of equilibrium constants. We solved this problem by generating sets of initial k-values at various temperatures which will be called when SP-Wax is executed. These initial k-values are generated by SPWaxKInitialization.cpp. In this C++ source file, sets of K values are generated which will be used by other executable files in SP-Wax.

SPWaxKInitialization.cpp is a C++ source file that takes input information of the oil sample (from GeneralInput.txt) and calculates the equilibrium constant values at every half-temperature ( $\Delta T = 0.5^{\circ}\text{K}$ ) ranging from  $280.15^{\circ}\text{K}$  to WAT. The calculated K values are reported in “KInitialVal.txt”. For this source file, initial values for equilibrium constants are also needed for  $T = 280.15^{\circ}\text{K}$ . There is a text file (“KInput.txt”) which

includes 62 K values for  $C_1$  to  $C_{62}$  which are used in this source file as initial values of equilibrium constant at  $T = 280.15^{\circ}K$ . The initial equilibrium constants are not only temperature dependent. They are also dependent on oil composition. In other words, for each oil composition, new equilibrium constants need to be calculated which will be used throughout other SP-Wax functionalities.

In order to run SPWaxKInitialization.exe, following files (shown below) should be present in the same directory.

-  [Data.txt](#) → Oil composition
-  [DIPP.txt](#) → DIPPR molar volume coefficients
-  [GeneralInputs.txt](#) → Inputs (provided in C# by the user)
-  [KInput.txt](#) → Initial K values at 280.15K
-  [SPWaxKInitialization.exe](#)

When SPWaxKInitialization.exe is ran, following two text files are generated:

-  [KInitialVal.txt](#)
-  [NumLine.txt](#)

where “KInitialVal.txt” is k-values for every half temperature starting from  $280^{\circ}K$  to WAT and “NumLine.txt” is a text file that contains total number of temperature points.

#### 4.1.5 SPWaxPrecipitation (.exe & .cpp)

This option is developed to predict the precipitation curve and Wax Appearance Temperature (WAT) of the provided oil composition for the desired temperature range. When user provides the required input parameters, C# produces text files that contain input data for C++ exe files. The following picture is an example of created input text files for SPWaxPrecipitation.exe.

GeneralInputs.txt - Notepad		PrecipitationCurveWAT.txt - Notepad	
File	Edit	Format	View
1 14.77	5 100		
2 0.000003	6 280		
3 10	7 0.5		
4 62	8 0.0001		
	9 0.001		

1- Wax content in total fluid  
2- Coefficient Adjustment  
3- Minimum  $C_n$  to be included  
4- Total number of n-alkanes  
5- Number of points in curve  
6- Starting temperature  
7- Temperature interval  
8- Acceptable error  
9- Acceptable error

Figure 4-9: General required inputs for the multicomponent system option

Now that inputs are provided, the simulation can run to calculate the precipitation curve and WAT. However, these data are not enough to run the simulator. The following graph shows the required files which should be present in the same directory for SP-Wax to run:

- 📄 Data.txt → Coefficients of DIPPR for molar volumes
- 📄 DIPP.txt → N-alkane mole composition
- 📄 GeneralInputs.txt → Inputs (provided in C# by the user)
- 📄 KInitialVal.txt → Initial K values generated by SPWaxKInitialization.exe
- 📄 NumLine.txt → Number of temperature points in KInitialVal.txt
- 📄 PrecipitationCurveWAT.txt → More inputs for precipitation curve prediction (in C# by SPWAXPrecipitation.exe)

The outputs are stored in following text files:

- WAT.txt (Wax Appearance Temperature is stored as second number)
- Wax weight fraction.txt (solid phase fraction values)
- SolidWComposition.txt (solid phase compositions of the temperature range)

For precipitation and WAT calculations, SP-WaxFn.cpp and Header.h are required to access the required functions in the main source file. In SPWaxPrecipitation.cpp, a major for-loop is used to iterate the desired temperatures. Inside the mentioned for-loop, SLE characteristics are calculated and saved to arrays. However, if temperature passes WAT, the program detects it and moves back to find WAT with the desired accuracy. Since, the program performs fast in higher temperatures, this method is a safe way to avoid any convergence problem.

#### 4.1.6 SPWaxOneTemperatureCase (.exe & .cpp)

This option of the SP-Wax allows users to obtain different SLE characteristics of a multicomponent system at any temperature. The user should provide the desired temperature in GUI which will be written to a text file and accessed by SPWaxOneTemperatureCase.exe. The following data files are required to be in the same directory for one temperature case SLE calculation.

-  **Data.txt** → N-alkane mole composition
-  **DIPP.txt** → Coefficients of DIPPR for molar volumes
-  **GeneralInputs.txt** → Inputs (provided in C# by the user)
-  **KInitialVal.txt** → Initial K values generated by SPWaxKInitialization.exe
-  **NumLine.txt** → Number of temperature points in KInitialVal.txt
-  **SPWAXOneTemperatureCase.exe**
-  **TempCase.txt** → Desired temperature °K

When SPWaxOneTemperatureCase.exe is run successfully, the results are reported into the following text files. In SP-Wax, a combo-box is included which lets the user choose the desired parameter to plot.

- Wax weight fraction.txt (Solid wax fraction in total fluid)
- Concentration.txt (Relative concentration of n-alkanes in the paraffin system)
- DissolvedMass.txt (mass of n-alkanes that are dissolved in the liquid phase)
- K\_values.txt (equilibrium constant from the last iteration)
- LiquidMoleComposition.txt (normalized mole composition of n-alkanes in the liquid phase)
- LiquidWComposition.txt (normalized weight composition of n-alkanes in the liquid phase)
- SolidMoleComposition.txt (normalized mole composition of n-alkanes in the solid phase)
- SolidWCompositionOnetemp.txt (normalized weight composition of n-alkanes in the solid phase)

#### 4.1.7 SPWaxCCN (.exe & .cpp)

Aging is one of the most important concepts in wax deposition phenomenon. In SP-Wax, a new parameter is defined which represents the relative concentration of a specific n-alkane. The relative concentration parameter is used to predict Critical Carbon Number (CCN) in wax deposition occurrence.

Waxy deposits are in contact with the bulk fluid and pipe's wall with corresponding temperatures of  $T_{int}$  and  $T_{wall}$ . In SP-Wax, relative concentrations of all n-alkanes at  $T_{int}$  are subtracted from relative concentrations of all n-alkanes at  $T_{wall}$ . The smallest carbon number with positive relative concentration gradient value is considered to be Critical Carbon Number (CCN).

For CCN determination in SP-Wax, C# asks for two temperature values which are corresponded to  $T_{int}$  and  $T_{wall}$  in GUI. The two temperatures are then written to a text file which is called "TempCaseCCN.txt". After running SPWaxCCN.exe, the predicted relative concentration gradient values for different carbon numbers are reported to a text file which is called "ConcentrationGradient.txt". The following picture shows the required files that need to be in the same directory to run "SPWaxCCN.exe"

- 📄 Data.txt → N-alkane mole composition
- 📄 DIPPR.txt → Coefficients of DIPPR for molar volumes
- 📄 GeneralInputs.txt → Inputs (provided in C# by the user)
- 📄 KInitialVal.txt → Initial K values generated by SPWaxKInitialization.exe
- 📄 NumLine.txt → Number of temperature points in KInitialVal.txt
- 💻 SPWAXCCN.exe
- 📄 TempCaseCCN.txt →  $T_{int}$  and  $T_{wall}$  for Relative concentration calculation

In SPWaxCCN.cpp, relative concentrations of all n-alkanes at two given temperatures ( $T_{wall}$  and  $T_{int}$ ) are calculated and, then, subtracted from each other. Resulted relative concentration gradient values will be exported to a text file which is called "ConcentrationGradient.txt". The following picture is a snapshot of SP-Wax graphical user interface.

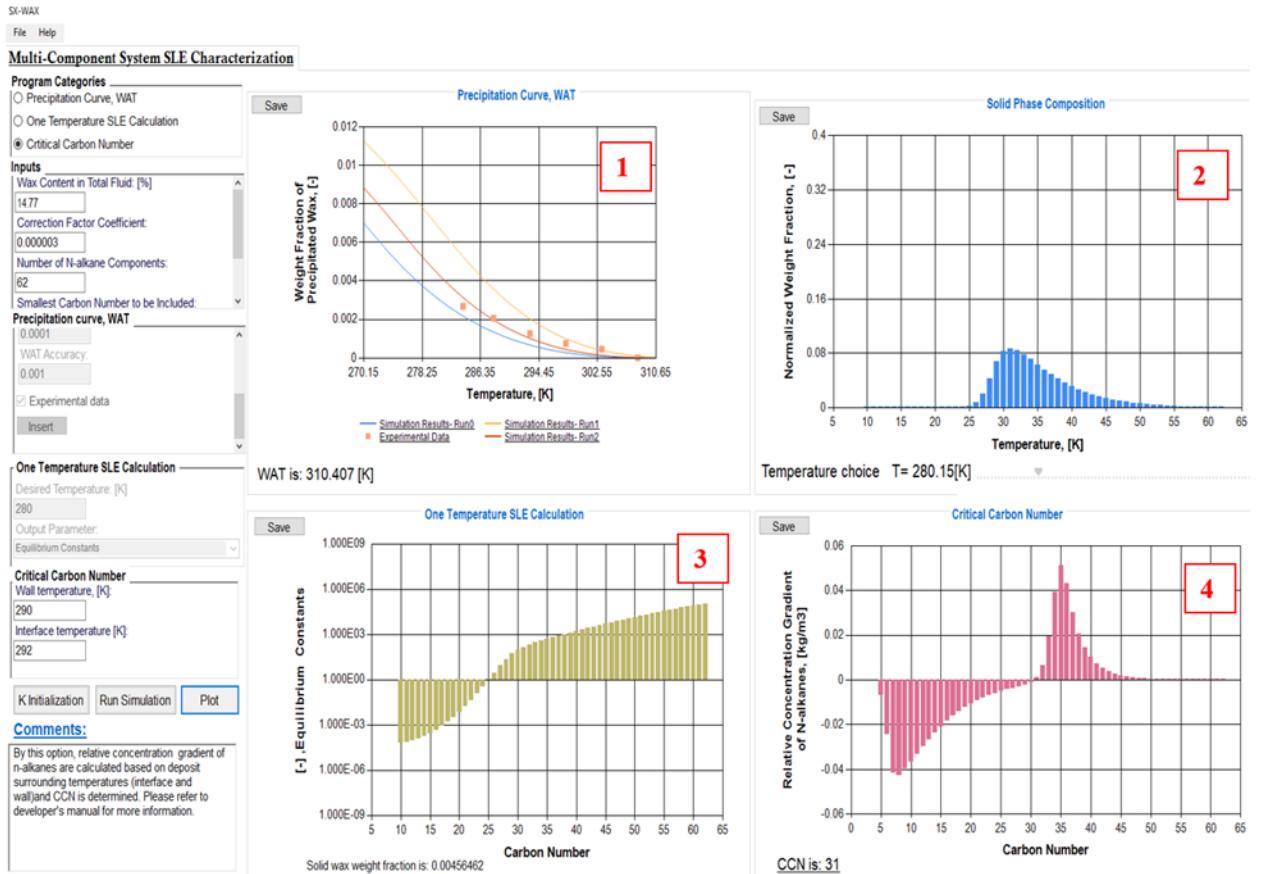


Figure 4-10: SP-Wax interface for multicomponent systems with various functionalities. The inputs are given through different textboxes on the left of the screen and the plots are created. In [1] the predicted and experimental precipitation curves can be plotted, in [2] the solid phase composition can be plotted for the given temperature range using a trackbar, in [3] different SLE characteristics can be plotted (as desired) for the provided temperature point and, in [4] the relative concentration gradient is plotted for CCN determination

## 4.2 SP-Depo software

Before going through the details about the computation procedure of SP-Depo, our software's structure will be discussed. In this section, a detailed description about different parts of SP-Depo's code is presented. In SP-Depo, the core scientific calculation is coded in C++ through more than 12,500 lines of code in an object-oriented programming style. C++ was chosen because it is one of the fastest programming languages available. To further optimize SP-Depo's performance, we have used OpenMp parallel programming technique which employs the maximum capacity of all processors. In Figure 4-11, it can

be seen that almost 100% of all processors have been used periodically due to applied parallelism.

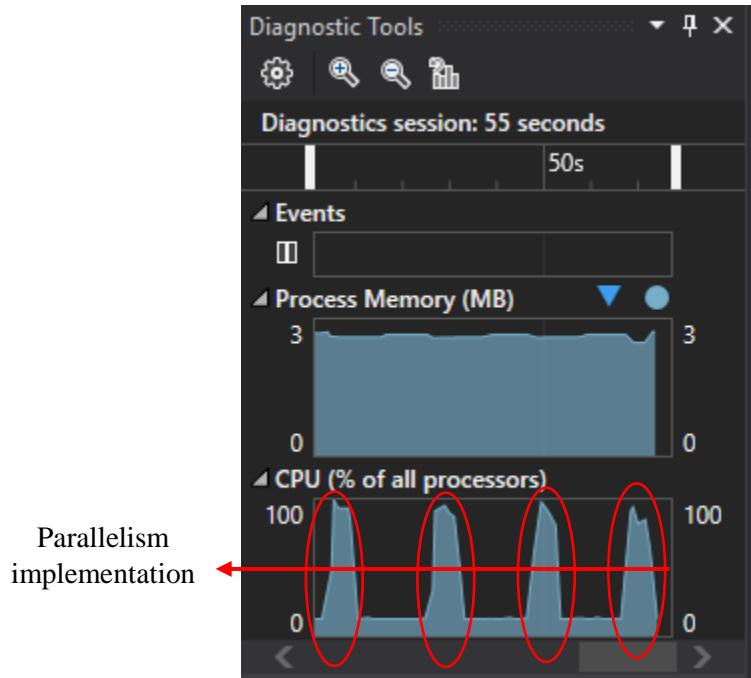


Figure 4-11: An example of SP-Depo's diagnostic session during LM run.

On the other side, a C# Windows Forms Graphical User Interface (GUI) has been developed for a guaranteed practicality for technical and non-technical users. SP-Depo is the world's first compositional wax deposition software with many unique functionalities that cannot be found in any commercialized wax deposition software. In SP-Depo, several equations are solved analytically using various advanced numerical methods which have been coded through separate functions in the software. Some of the applied numerical techniques are: Newton-Raphson and bisection root-finding algorithms, PDE solving methods (e.g., backward Finite Difference Method, FDM), various matrix operations, ODE solving methods (e.g., Dorman Prince), integration techniques, a modified regression method and Levenberg-Marquardt optimization algorithm. In the following sections, the program's structure in C++ will be discussed since It contains the scientific computation related to wax deposition modeling

The following graph shows a quick map of SP-Depo's header files in C++. Each header file (.h) is exclusively described later in this document.

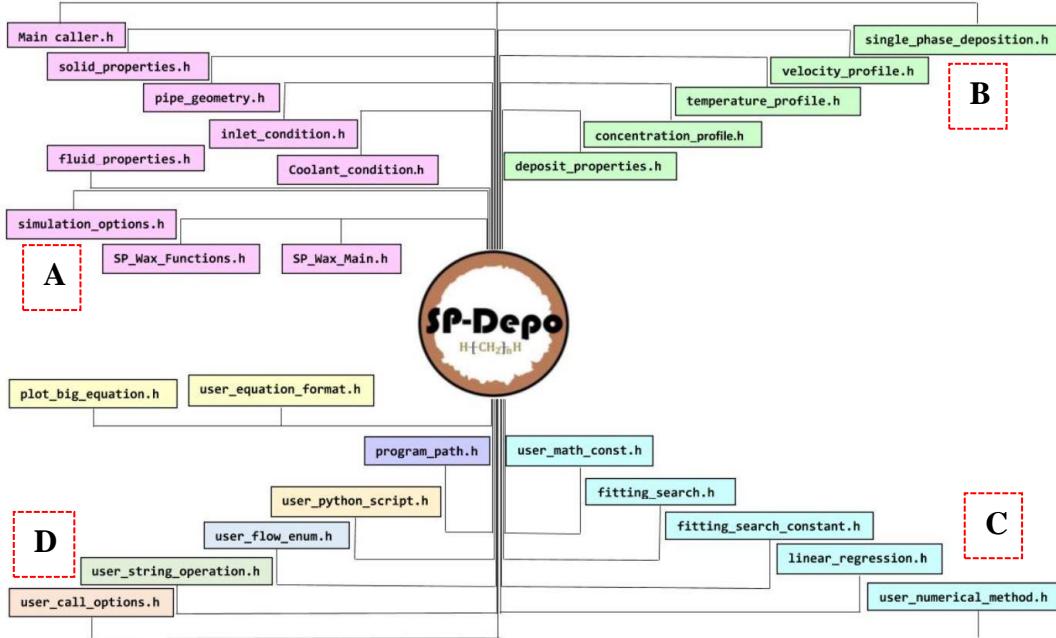


Figure 4-12: C++ header-files of SP-Depo

In the above graph, the header-files in section “A” represents those files that mostly contain the input information and are called repeatedly throughout the program. In section “B”, wax deposition and transport equations are solved by direct communications with classes in section “A” and “C”. In section “C”, all numerical methods are included which are responsible in calculation of different parameters in section “B”. In the last group (“D”), other files are included which are mostly responsible in data visualization, program’s directory, etc.

#### 4.2.1 Primary programming path

In SP-Depo, the input files are read, many parameters are calculated using the transport equations and the two governing wax deposition ODEs (Eq.3-63 & 3-64) are solved numerically for full prediction of deposition profile. The primary path for wax deposition calculation can be illustrated through five steps (shown below) within SP-Depo’s code. The order of the following steps is as if someone debugs the program from the outmost layer and proceeds into the most inner layer. The annotated symbols show the most important executable methods which use the functions from the inner layer classes.

- **Step 1**

**SPDepo.cpp** is where the entry point of the program exists (`int wmain(int argc, TCHAR **argv)`). Based on the argument input, the correct section of the code is executed. For this example, the “deposition single\_phase” argument case is illustrated where the wax deposition prediction is performed with given fitting parameters. Through “**Deposition1PMain.Run(program\_path)**”, the program runs the wax deposition model.

```

SPDepo.cpp
case spdepo::usr::kMainArgv2::deposition: {
    spdepo::usr::kMainArgv3 argv3;
    argv3 =
spdepo::usr::string_to_kmainarg3.at(argv[3]);
    switch (argv3) {

case(spdepo::usr::kMainArgv3::single_phase): {
    spdepo::Main1PhaseDeposition
    Deposition1PMain;

Deposition1PMain.Run(program_path); 
-----
    break;
}
}
    std::system("pause");
    return 0;
    break;
}

```

Figure 4-13: SP-Depo.cpp and Deposition1PMain.Run(program\_path)

- **Step 2**

Within `void Main1PhaseDeposition::Run(ProgramPath p_path)`, all required object members of `deposition1` are initialized through different methods in `read_input` using the input files which are produced by C# GUI. With all provided input information, the calculation method will be called through `deposition1.Calculate()` where the governing ODEs are solved numerically.

```


main_caller.cpp
void Main1PhaseDeposition::Run(ProgramPath p_path)
    ReadInput read_input;
    SPWax00::Thermo thermo_local;
    read_input.SetPath(p_path);
    Fluid oil = read_input.ReadLiquid1P();
    Solid pipe_material;
    PipeGeometry pipe;
    read_input.ReadPipe1P(&pipe, &pipe_material);
    InletCondition inlet = read_input.ReadInlet1P();
    CoolantCondition coolant_inlet;
    Fluid coolant_fluid;
    SimulationOptions sim_option;
    read_input.ReadCoolant1P(&coolant_inlet,
        &coolant_fluid, &pipe, &sim_option);
    read_input.ReadSimulationOption(&sim_option, coolant_inlet);
    Solid wax;
    wax.SetConstantProperties("wax", -950, -2000, 0.25);
    sim_option.SetWaxMaterialProperties(wax);
    SinglePhaseDeposition deposition1;
    deposition1.SetAll(sim_option,
        oil, coolant_fluid, inlet, coolant_inlet, pipe,
        pipe_material);
    thermo_local = read_input.ReadThermo1P(); //Added
    deposition1.SetThermo(thermo_local); //Added
    deposition1.SetProgramPath(p_path);

deposition1.Calculate(); 
deposition1.SimplePostCalculation();

```

Figure 4-14: main\_caller.cpp and deposition1.Calculate()

- **Step 3**

Within **deposition1.Calculate()**, the two governing ODEs (Eq.3-63 & 3-64) of the wax deposition theory are solved using the Dorman-Prince method. Among function inputs of Dorman-Prince method (**usr::DormandPrinceMany**), **WrapSolve1P** is the function that calculates the right-hand sides of the wax deposition governing equations and returns them into a vector. The size of the returning vector is twice the number of axial

sections. For example, if the pipe is discretized into 17 axial sections, the size of the returning vector will be 34. The first and second half of the returning vector will be associated with  $\frac{dr}{dt}$  and  $\frac{dF}{dt}$ , respectively.

The Dormand-Prince ODE solving method is coded in user\_numerical\_method.cpp. In this cpp file, various numerical methods are manually coded as general functions which are utilized in different sections of SP-Depo. When the Dormand-Prince method (shown below) is executed, pipe's effective radius, solid wax fraction and solid phase carbon number distribution of each axial section in the pipe will be predicted for different times.



```

single_phase_deposition.cpp
void SinglePhaseDeposition::Calculate() {
    Initialize();
    std::vector<double> ri;
    std::vector<double> fw;
    std::vector<double> ri_fw;
    std::vector<double> eps_vec;
    std::vector<double> eps_fw_vec;
    long num_fn_call;
    CoreDepositionEquation DepEq;
    Storage_fit_eqs Storage_;
    ri = deposit_profile_.GetRiVec();
    fw = deposit_profile_.GetFwVec();
    DepEq.SetThermo(thermo_local, Is_Lm);
    DepEq.SetStorage(Storage_);
    DepEq.SetAll1Phase(*this);
    ptr_wrap = &DepEq;
    ptr_spdep = this; //compo_model
    ri_fw = ri;
    eps_vec.assign(ri.size(), 1.0e-4);
    eps_fw_vec.assign(fw.size(), 1.0e-3);
    ri_fw.insert(ri_fw.end(), fw.begin(), fw.end());
    eps_vec.insert(eps_vec.end(), eps_fw_vec.begin(),
    eps_fw_vec.end());
    //Time-loop is already in DormandPrinceMany
    ans_ri_fw_.clear();
    info_history.clear();
    if(DepEq.sim_dep_options_.GetPrecipitationCurveModel() ==
        usr::
            kPrecipitationCurveModel::user_defined){
        usr::DormandPrinceMany(WrapSolve1P, ri_fw.size(),
            &num_fn_call, &ans_t_, &ans_ri_fw_, ri_fw, 0.0,
            sim_dep_options_.GetDepositionDuration(),
            1, eps_vec, 100, 100, 3, 7000.0, 0.1, true, false, false);
    }
}

```



Figure 4-15: single\_phase\_deposition.h and Dorman-Prince method

- **Step 4**

As previously mentioned, `WrapSolve1P` returns a vector that contains the values of  $\frac{dr}{dt}$  and  $\frac{dF}{dt}$  for different sections of the pipe. Through the following structure, the `Solve1P(ri, fw)` was wrapped to be used as an input function in the `DormandPrinceMany` method.

```
single_phase_deposition.cpp

std::vector<double> WrapSolve1P(double t,
    const std::vector<double>& ri_fw_vec_vec)
{
    //ri_fw_vec_vec = {ri[0], ..., ri[N],
    fw[0], ..., fw[N]}
    int n_zsec = ptr_wrap->n_zsec_;
    std::vector<double>
    ri(ri_fw_vec_vec.begin(),
        ri_fw_vec_vec.begin() + n_zsec);
    std::vector<double>
    fw(ri_fw_vec_vec.begin() + n_zsec,
        ri_fw_vec_vec.end());
    return ptr_wrap->Solve1P(ri, fw); 
```

Figure 4-16: Main method to calculate the RHS of the governing ODEs

- **Step 5**

**Solve1P(ri, fw)** is the most important method in SP-Depo as it calculates temperature and concentration profile and reports the RHS of the two wax deposition governing equations (Eq. 3-63 and Eq.3-64). For SP-Compo model, there is one overloading function of **Solve1P** where each section's average temperature is also reported.



```

single_phase_deposition.cpp

std::vector<double> CoreDepositionEquation::Solve1P(
    const std::vector<double>& ri,
    const std::vector<double>& fw) {

&

    std::vector<double>
CoreDepositionEquation::Solve1P(
    const std::vector<double>& ri,
    const std::vector<double>& fw,
    std::vector<std::vector<double>>& TempInfo) {

```

Figure 4-17: Two functions for calculation of ODEs

In the header-file map (Figure 4-12), the header-files in section “A” will thoroughly be explained in this section. Section “A” represents those files that mostly contain the input information and are called repeatedly throughout the program. For example, there are several class members in simulation\_options.h which will be initialized by information from the input files. Later, those variables will be used in class methods of section “B”. In addition, we will discuss the theories associated with each calculation step within each header file. The following picture shows the header files associated with section “A”.

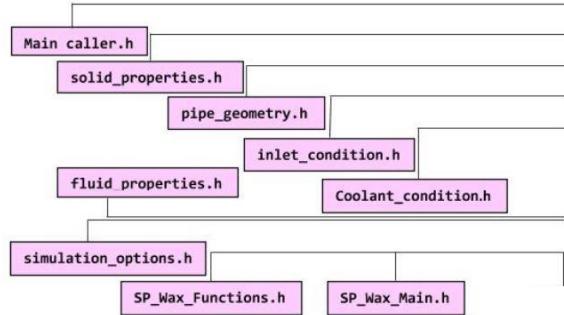


Figure 4-18: Input calling header-files (section “A”)

In the following sections, each header file in section “A” will thoroughly be explained.

#### 4.2.2 **Main\_caller.h** and **Main\_caller.cpp**

Through **Main\_caller.h** and **Main\_caller.cpp**, the input files are read from the files which are produced by C# and then are assigned to the several class methods. The input files (produced by C#) are listed as shown in the picture.

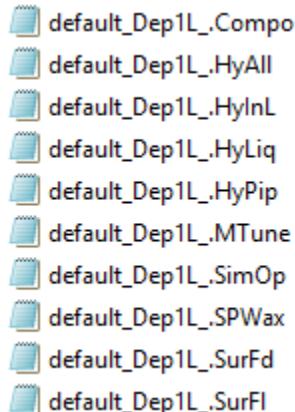


Figure 4-19: Created input files by C# which will be used by CPP files based on the provided input information by the user.

`default_Dep1L.Compo` represent the input n-alkane composition of the oil. `default_Dep1L.HyAll` includes all the input files for Load operation in C#. `default_Dep1L.HyInL` contains information about the inlet condition. `default_Dep1L.HyLiq` contains information about the rheological properties of the oil including viscosity, density, specific heat capacity, thermal conductivity, etc. `default_Dep1L.HyPipe` has the pipe's properties. `default_Dep1L.MTune` includes the required information for LM including the experimental data. `default_Dep1L.SimOp` contains the calculation options for wax

deposition modeling including time of the experiment. Also, msr1 and msr2 should be specified in `default_Dep1L.SimOp`. `default_Dep1L.SPWax` contains the required input information for the SP-Wax thermodynamic model. `default_Dep1L.SurFl` includes information about the surrounding (e.g., coolant temperature, flow direction, coolant flow rate, etc). All the above input files are reflected through several tabs in the interface of SP-Depo as shown in Figure 4-20.

In some of the input tabs, the user is required to provide equations for certain parameters rather than just constant values. For example, fluid properties change with temperature and they need to be provided as equations. Later in this chapter, a complete manual will be presented about how to provide equations for some of the inputs. The associated header file is `User_equation_format.h`.

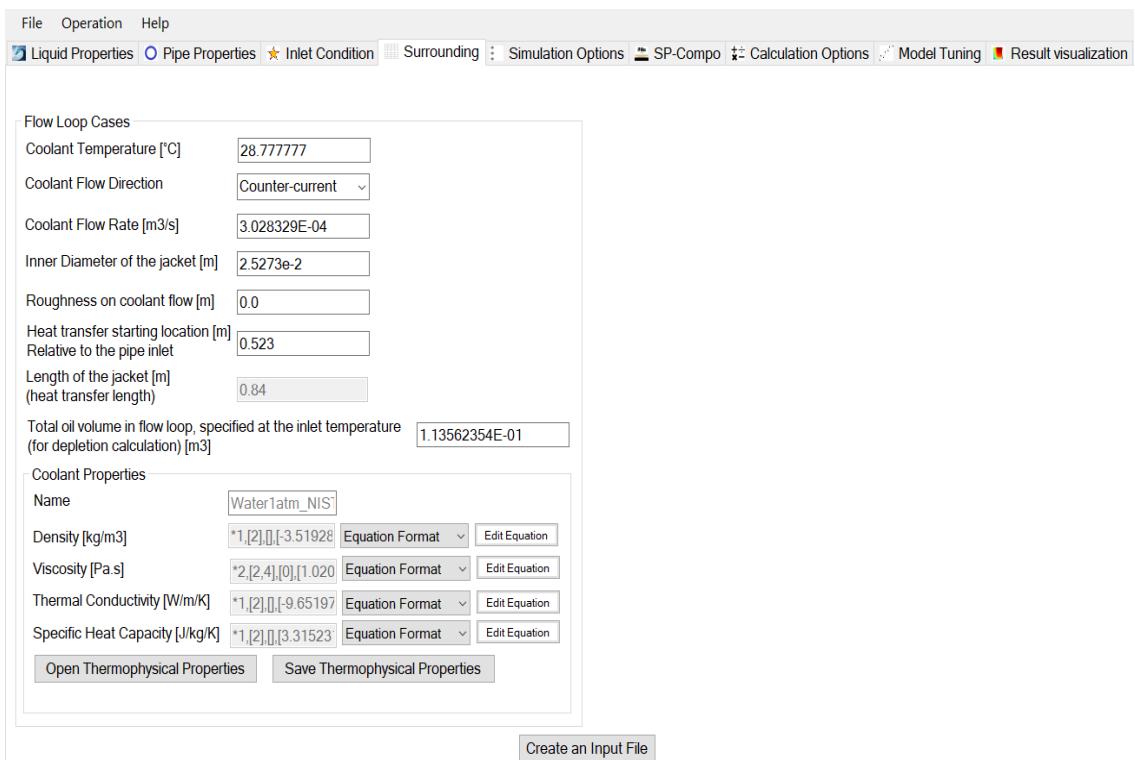


Figure 4-20: A screenshot of SP-Depo user-interface. Different tabs acquire different input information

Please note that each of the tabs are defined as separate classes in our code. In `Main_caller.h & cpp`, there are several functions that are responsible for reading the input information and assigning them into the objects with the same class types.

#### 4.2.3 **Solid\_properties.h** and **Solid\_properties.cpp**

In these header and cpp files, the properties of the pipe are assigned to the “solid” object in Main\_caller.h which will be passed to more inner layers of the program for the calculations in section “B” in Figure 4-12.

#### 4.2.4 **pipe\_geometry.h** and **pipe\_geometry.cpp**

In this header and cpp files, pipe and flow geometries are calculated and assigned to member variables. Some of these properties are: pipe’s cross sectional area, annulus flow cross sectional area, inner diameter, outer diameter, inner diameter of the jacketed pipe, hydraulic diameter of the jacketed pipe, pipe roughness, annulus/jacketed pipe roughness, annulus/jacketed pipe roughness, pipe total length. The following picture is a screenshot of the tab which takes the pipe’s input information.

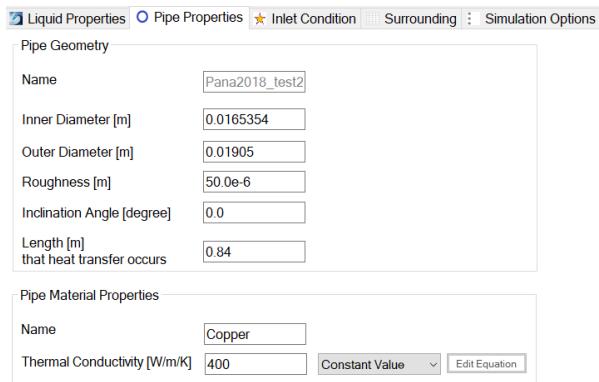


Figure 4-21: Pipe’s input properties.

#### 4.2.5 **inlet\_condition.h** and **inlet\_condition.cpp**

In these files, the inlet conditions including the oil initial velocity and inlet temperature are assigned to the associate member variables.

#### 4.2.6 **coolant\_condition.h** and **coolant\_condition.cpp**

In these files, coolant properties are assigned to the class member variables. Some of the inputs are: coolant’s inlet temperature, volumetric flow rate and jacket’s flow type (only counter-current flow is included).

#### 4.2.7 fluid\_properties.h and fluid\_properties.cpp

Fluid properties usually change with temperature. So, in our simulation, fluid properties need to be provided in the equation format as a function of temperature. In fluid\_properties.cpp, fluid property equations are converted to readable functions and accessed by other objects. The following picture shows the user-interface section where fluid property equations should be provided.

When “Edit Equation” button is clicked, the user is directed to another window where equations can be inserted for various liquid properties. Please refer to “user\_equation\_format.h & cpp” section for an instruction about inserting the equations.

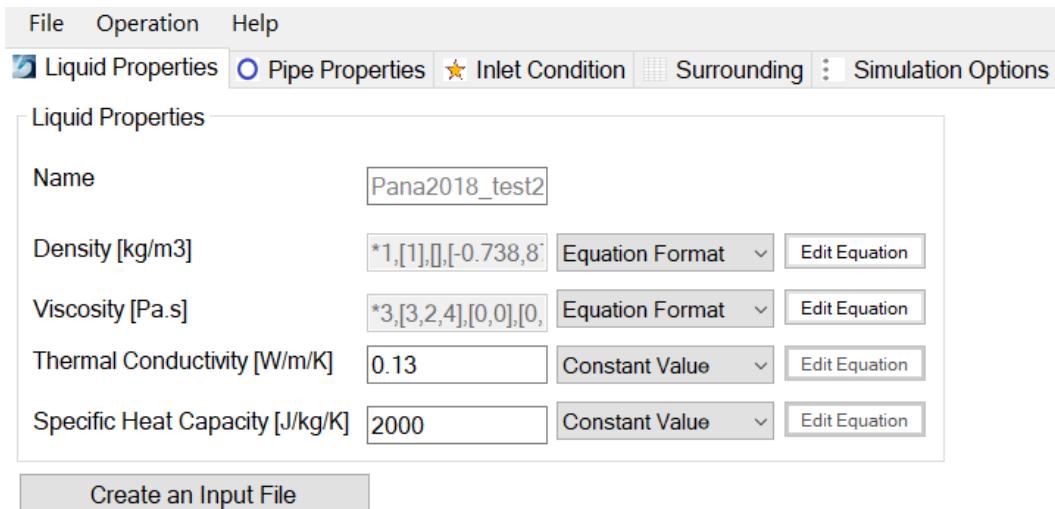


Figure 4-22: “Liquid properties” section of SP-Depo which takes the equations of rheological properties of the oil phase

#### 4.2.8 simulation\_options.h and simulation\_options.cpp

Through this class, member variables which are specified by the user will be assigned accordingly. As mentioned, in SP-Depo, we made it possible for users to choose different wax deposition models. Some of the included wax mass flux models are: no precipitation method (Singh et al. [3]), solubility method (Venkatesan [11]), and partial precipitation model (Lee [12]). In simulation\_options header and cpp files, the chosen model options with their corresponding fitting parameters, which have been specified by the user, will be captured and assigned to the right member variables. The following picture shows the

corresponding simulation-option tab in SP-Depo's GUI. The two precipitation curve models (conventional and SP-Compo) can be chosen in this tab.

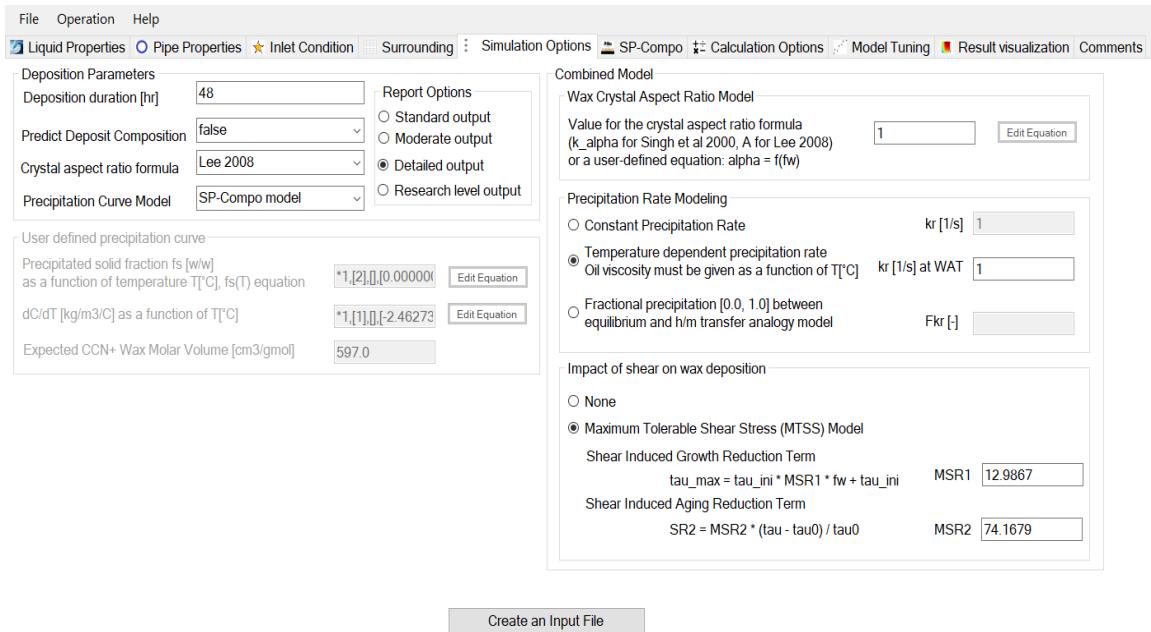


Figure 4-23: Simulation Option section in SP-Depo GUI

#### 4.2.9 SP\_Wax\_Functions.h and SP\_Wax\_Functions.cpp

In our new proposed model, we included SP-Wax thermodynamic model in the wax deposition modeling calculation. For this purpose, SP-Wax thermodynamic software was recoded to an object oriented programming style and was added to SP-Depo software. SP-Wax thermodynamic model is represented through two header files (`SP_Wax_Functions.h` and `SP-Wax_Main.h`). `SP_Wax_Functions.h` includes the functions which are used by `SP-Wax_Main.h`. The following picture is a screenshot of SP-Depo GUI's SP-Wax tab.

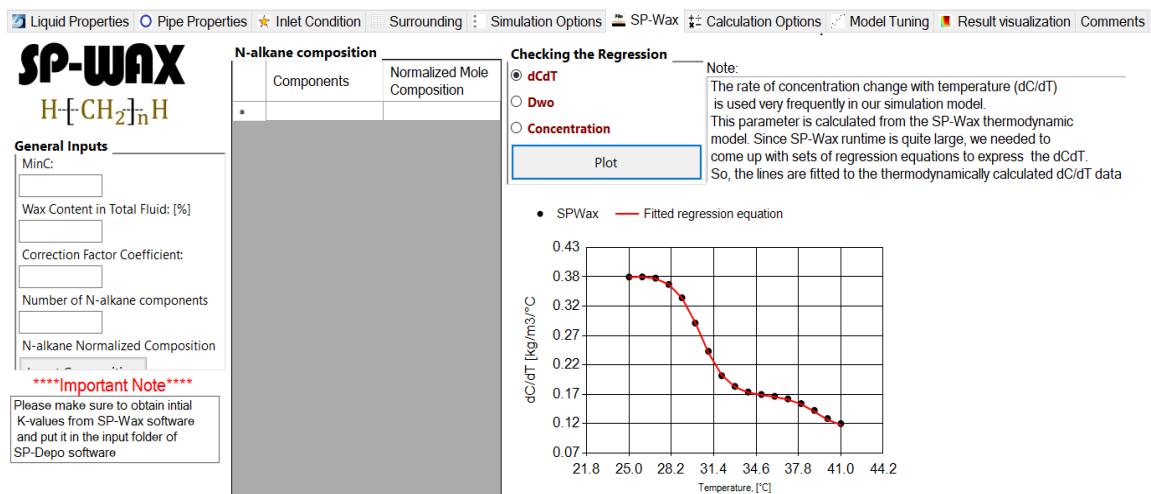


Figure 4-24: SP-Wax thermodynamic model tab in SP-Depo GUI

#### 4.2.10 SP\_Wax\_Main.h and SP\_Wax\_Main.cpp

In these files, the SP-Wax thermodynamic model is included. Some of the outputs include solid wax fraction, solid phase and liquid phase compositions, equilibrium constants, each component's concentration, etc.

In the header-file map, the section “B” includes the files that are responsible in solving wax deposition and transport equations. The main wax deposition governing equations are solved in `single_phase_deposition.cpp` where nearly all other inner-layer objects in section “A” and “C” and some parts of section “D” are called.

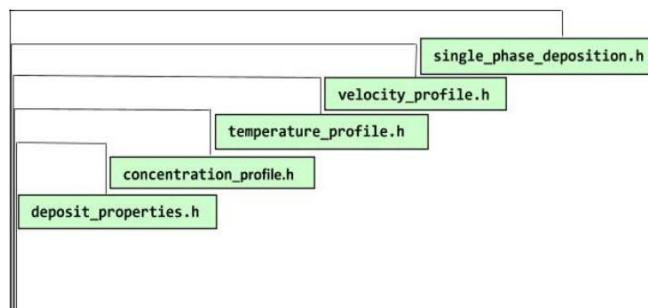


Figure 4-25: SP-Depo header-files about wax deposition and transport equations

In the following section, the header-files associated with the wax deposition and transport equations in section “B” are explained.

#### 4.2.11 deposit\_properties.h and deposit\_properties.cpp

In this section, deposit's properties (thermal conductivity, total solid mass, etc.) are calculated through different class methods. Within the traditional modeling approach, molecular diffusivity ( $D_{wo}$ ), precipitation curve and  $\frac{\partial C}{\partial T}$  are also considered here.

Accordingly, in the traditional modeling approach, effective diffusivity ( $D_e$ ) is calculated based on the solid wax fraction and  $D_{wo}$ . Please note that the above parameters associated with SP-Comp model are calculated in different places (e.g., concentration\_profile.cpp).

#### 4.2.12 temperature\_profile.h and temperature\_profile.cpp

As mentioned, in SP-Depo, the counter-current pipe-in-pipe heat exchange flow-loop is considered for heat transfer calculation in pipe. Basically, the deposit's interface temperature and the oil temperature near the waxy deposit are the two most important temperature values which should be known for wax deposition model calculation. In SP-Depo, we used the approach in Panacharoensawad [10] for temperature profile calculation in pipe. The boundary condition in radial temperature profile calculation was considered from the heat balance equation. Nusselt number in coolant is calculated from:

$$Nu_c = \frac{(f/2) Re_c Pr_c 0.75 \beta^{-0.17} x_1 k_2}{k_1 + 12.7 \sqrt{\frac{f}{2}} (Pr_c^{\frac{2}{3}} - 1)} \quad (4-1)$$

$$k_1 = 1.07 + \frac{900}{Re_c} - \frac{0.63}{1 + 10 Pr_c} \quad (4-2)$$

$$k_2 = \left( \frac{Pr_c^{bulk}}{Pr_c^{wall}} \right)^{0.11} \quad (4-3)$$

$$x_1 = \left( 1 + \frac{D_c}{L_c - z} \right)^{\frac{2}{3}} \quad (4-4)$$

where Reynold's number ( $Re_c$ ), Prandtl number ( $Pr_c$ ) and heat transfer coefficient ( $h_c$ ) are calculated as:

$$Re_c = \frac{\rho_c V_c D_c^{hydraulic}}{\mu_c} \quad (4-5)$$

$$Pr_c = \frac{\mu_c C_{p,c}}{k_c} \quad (4-6)$$

$$h_c = \frac{Nu_c k_c}{D_c^{hydraulic}} \quad (4-7)$$

In the oil side and for turbulent flow, the velocity profile is calculated from as:

$$V^+ = \begin{cases} y^+ & y^+ \leq 5 \\ 5 \ln(y^+) - 3.05 & 5 \leq y^+ \leq 30 \\ 2.5 \ln(y^+) + 5.5 & 30 \leq y^+ \end{cases} \quad (4-8)$$

$$h_c = \frac{Nu_c k_c}{D_c^{hydraulic}} \quad (4-9)$$

$$y^+ = \frac{y}{\nu} \sqrt{\frac{\tau_w}{\rho_{oil}}} = \left(1 - \frac{r}{R}\right) \frac{Re}{2} \sqrt{\frac{f}{2}} \quad (4-10)$$

$$V^+ = \frac{V}{V^*} = \frac{V}{V_{av}} \sqrt{\frac{2}{f}} \quad (4-11)$$

$$\tau_w = \frac{1}{2} f \rho_{oil} V_{av}^2 \quad (4-12)$$

where average velocity is calculated as:

$$V_{av} = \frac{\dot{m}_{oil}}{\rho_{oil} \pi r_{i,ave}^2} \quad (4-13)$$

Then temperature profile will be determined using the following heat transfer equation as:

$$V_z \frac{\partial T}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r(\varepsilon_H + \alpha_H) \frac{\partial T}{\partial r} \right] \quad (4-14)$$

Please note that the heat of crystallization is not considered in the calculations. In the above equation, heat transfer eddy diffusivity ( $\varepsilon_H$ ) can be calculated as:

$$\frac{\varepsilon_H}{\alpha_H} \equiv \frac{Pr}{Pr_T} \frac{\varepsilon}{\nu}; \quad Pr_T = 0.85 + \frac{0.015}{Pr} \quad (4-15)$$

And finally,  $\frac{\varepsilon}{\nu}$  is calculated as:

$$\frac{\varepsilon}{\nu} = \begin{cases} (0.4y^+)^2 \left[ 1 - \exp\left(-\frac{y^+}{26}\right) \right]^2 \left| \frac{dV^+}{dy^+} \right| & y^+ \leq 80 \\ \frac{0.4y^+}{6} \left[ 1 + \frac{r}{R} \right] \left[ 1 + 2 \left( \frac{r}{R} \right)^2 \right] & y^+ > 80 \end{cases} \quad (4-16)$$

The equation 4-14 is solved using backward finite difference method [10]. The two boundary conditions are:

at  $r = 0$  or at the center of the pipe: (4-17)

$$\frac{\partial T}{\partial r} \Big|_{r=0} = 0$$

And, at the deposit interface in the oil side:

$$\frac{\partial T}{\partial r} \Big|_{r_i^-} = \frac{T_{i,N} - T_{i,N-1}}{r_N - r_{N-1}} = -\frac{(T_{i,N} - T_C)}{r_l k_{oil} \Omega_\Sigma} \quad (4-18)$$

where N represent the point at the deposit interface

In SP-Depo, by considering the mentioned boundary conditions, the PDE is solved as [10]:

$$\begin{bmatrix} 1 & -1 & 0 & \dots & 0 & 0 & 0 \\ C_2^T & A_2^T & B_2^T & \dots & 0 & 0 & 0 \\ 0 & C_3^T & A_3^T & \dots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & A_{N-2}^T & B_{N-2}^T & 0 \\ 0 & 0 & 0 & \dots & C_{N-1}^T & A_{N-1}^T & B_{N-1}^T \\ 0 & 0 & 0 & \dots & 0 & \frac{r_N k_{mix}}{\Delta r_N} & -\left(\frac{r_N k_{mix}}{\Delta r_N} + \frac{1}{\Omega_\Sigma}\right) \end{bmatrix} \begin{bmatrix} T_{i,1} \\ T_{i,2} \\ T_{i,3} \\ \vdots \\ T_{i,N-2} \\ T_{i,N-1} \\ T_{i,N} \end{bmatrix} = \begin{bmatrix} 0 \\ D_2^T \\ D_3^T \\ \vdots \\ D_{N-2}^T \\ D_{N-1}^T \\ \frac{-T_c}{\Omega_\Sigma} \end{bmatrix}$$

where

$$A_j^T = \frac{V_{z,ij}}{\Delta z_i} + \frac{1}{r_j(\Delta r_{j+1} + \Delta r_j)} \left[ \frac{[r(\varepsilon_H + \alpha_H)]_{j+1} + [r(\varepsilon_H + \alpha_H)]_j}{\Delta r_{j+1}} + \frac{[r(\varepsilon_H + \alpha_H)]_j + [r(\varepsilon_H + \alpha_H)]_{j-1}}{\Delta r_j} \right] \quad (4-19)$$

$$B_j^T = \frac{-1}{r_j(\Delta r_{j+1} + \Delta r_j)} \left[ \frac{[r(\varepsilon_H + \alpha_H)]_{j+1} + [r(\varepsilon_H + \alpha_H)]_j}{\Delta r_{j+1}} \right] \quad (4-20)$$

$$C_j^T = \frac{-1}{r_j(\Delta r_{j+1} + \Delta r_j)} \left[ \frac{[r(\varepsilon_H + \alpha_H)]_j + [r(\varepsilon_H + \alpha_H)]_{j-1}}{\Delta r_j} \right] \quad (4-21)$$

$$D_j^T = \frac{V_{z,ij} T_{i-1,j}}{\Delta z_i} \quad (4-22)$$

After calculating the radial temperature profile, the important term  $\frac{\partial T}{\partial r}\Big|_{r_i^-}$  is determined which will be directly used in the wax deposition model. Then, the other important term which is the temperature gradient at the interface but in the deposit side  $\left(\frac{\partial T}{\partial r}\Big|_{r_i^+}\right)$  is calculated as:

$$\frac{\partial T}{\partial r}\Big|_{r_i^+} = \frac{k_{oil}}{k_{dep}} \frac{\partial T}{\partial r}\Big|_{r_i^-} \quad (4-23)$$

Please note that the radial discretization is non-uniform and is calculated based on the one-seventh power-law velocity profile equation as follows:

$$\frac{v_{av}}{v_{max}} = f(r) = (1 - r_{ratio})^{1/7} \quad (4-24)$$

In SP-Depo, the derivative  $\left(\frac{df}{dr_{ratio}}\right)$  will be calculated and, will be provided to the Dormand-Prince ODE solving function. This adaptive method then gives a non-uniform discretization which be considered in the calculation. The derivative is as follows:

$$\frac{df}{dr_{ratio}} = -\frac{1}{7}(1 - r_{ratio})^{-\frac{6}{7}} \quad (4-25)$$

The following graph shows the temperature profile at early time.

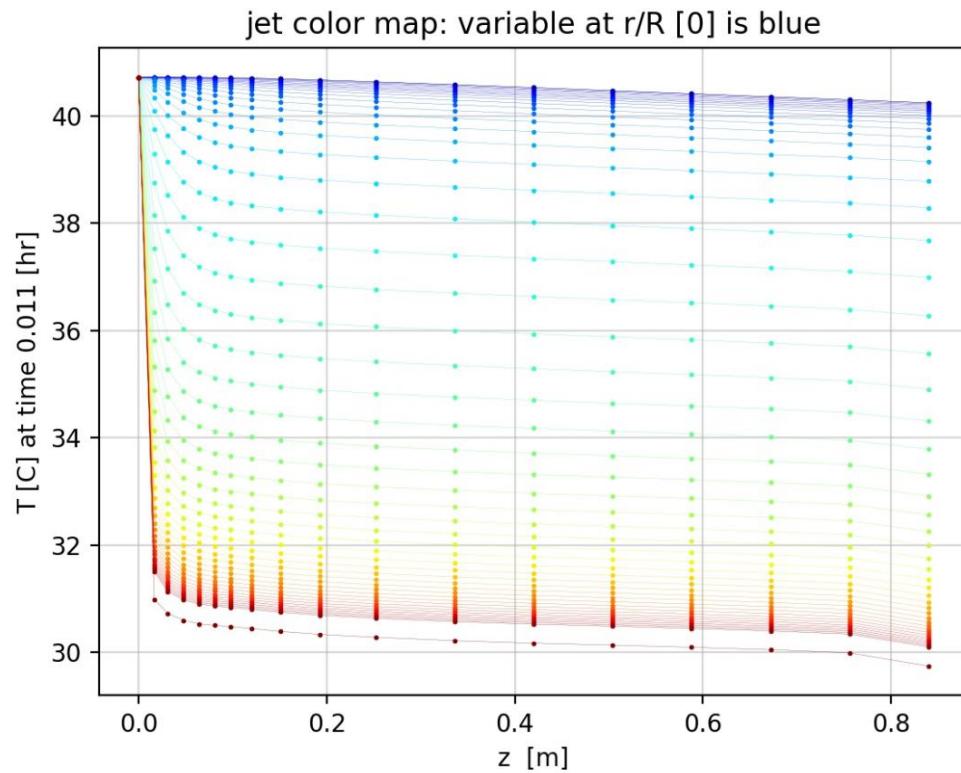


Figure 4-26: Radial temperature profile in the pipe for different axial locations

In the wax deposition calculation, the deposit's interface temperature is very important. Therefore, in the two following graphs, the deposit's interface temperature is plotted versus time and location.

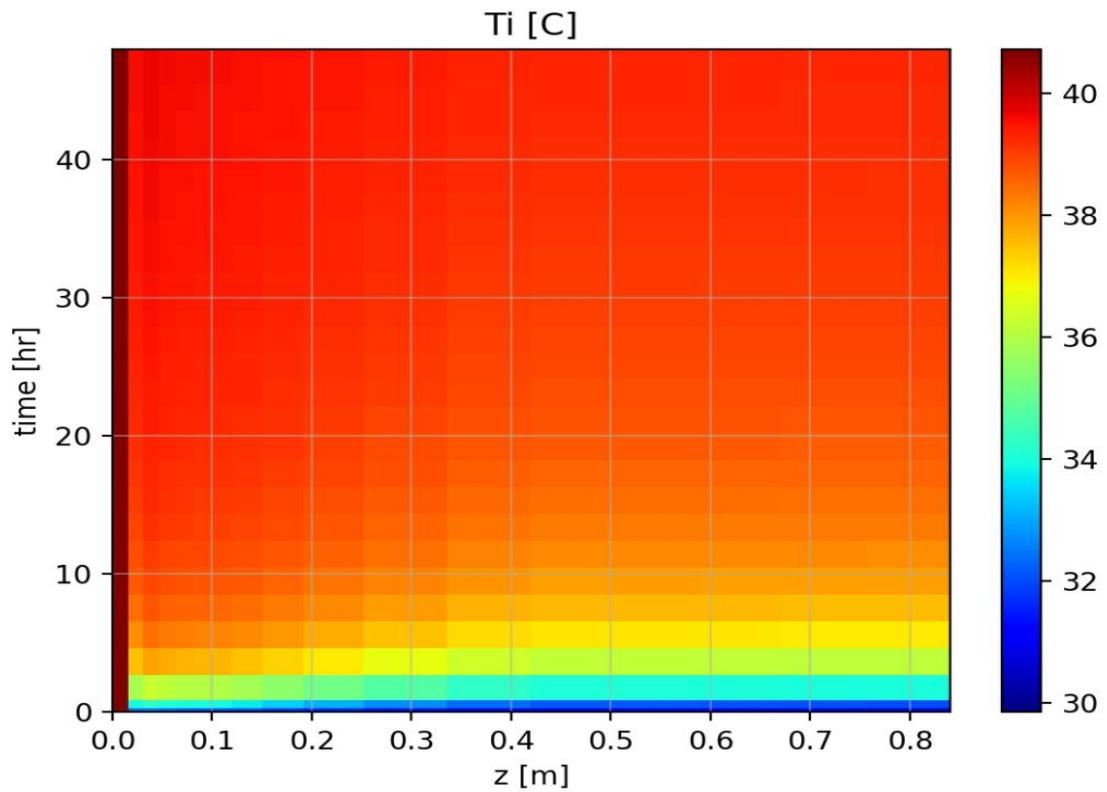


Figure 4-27: Deposit's interface temperature color map for different time and axial locations

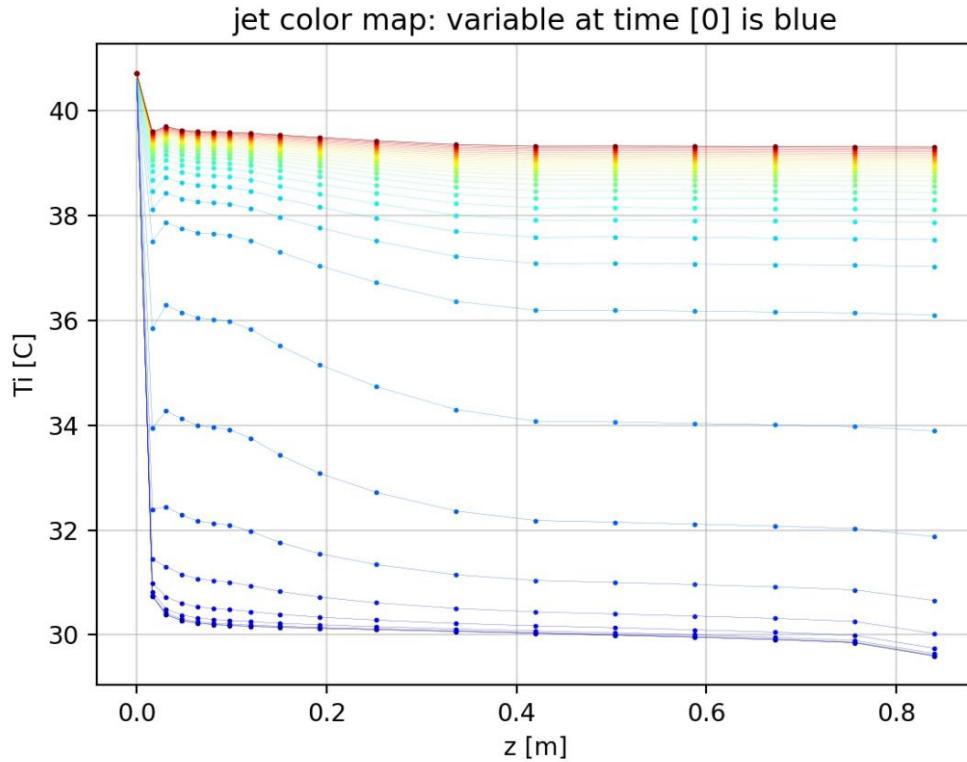


Figure 4-28: Deposit's interface temperature axial profile

#### 4.2.13 velocity\_profile.h and velocity\_profile.cpp

Turbulent flow is known to be characterized by chaotic fluctuations in pressure and velocity. A set of equations are solved in SP-Depo to estimate the velocity profile of the turbulent flow in pipe. These equations are expressed in Temperature\_profile.h & cpp section. However, we will repeat them in this section too.

$$V^+ = \begin{cases} y^+ & y^+ \leq 5 \\ 5 \ln(y^+) - 3.05 & 5 \leq y^+ \leq 30 \\ 2.5 \ln(y^+) + 5.5 & 30 \leq y^+ \end{cases} \quad (4-26)$$

$$y^+ = \frac{y}{\nu} \sqrt{\frac{\tau_w}{\rho_{oil}}} = \left(1 - \frac{r}{R}\right) \frac{Re}{2} \sqrt{\frac{f}{2}} \quad (4-27)$$

$$V^+ = \frac{V}{V^*} = \frac{V}{V_{av}} \sqrt{\frac{2}{f}} \quad (4-28)$$

$$\tau_w = \frac{1}{2} f \rho_{oil} V_{av}^2 \quad (4-29)$$

where average velocity is calculated as:

$$V_{av} = \frac{\dot{m}_{oil}}{\rho_{oil} \pi r_{i,ave}^2} \quad (4-30)$$

Velocity profile is crucial, because it is needed for radial temperature profile calculation.

#### 4.2.14 `concentraion_profile.h` and `concentration_profile.cpp`

As mentioned, SP-Depo has two primary calculation options for wax deposition calculation (traditional and SP-Compo). Concentration,  $\frac{\partial C}{\partial T}$ , and actual molecular diffusivities are calculated and reported by `Get_dCdT_thermo`, `Get_C_thermo` and `Diff_thermo`. All these parameters are calculated from the SP-Wax thermodynamic model.

For concentration profile calculation, the following governing equation is solved numerically.

$$V_z \frac{\partial C}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r(\varepsilon_M + D_{wo}) \frac{\partial C}{\partial r} \right] - k_r(C - C(T)) \quad (4-31)$$

$$\frac{\varepsilon_M}{D_{wo}} \equiv \frac{Sc}{Sc_T} \frac{\varepsilon}{\nu}; \quad Sc_T = 0.85 + \frac{0.015}{Sc} \quad (4-32)$$

This equation has been reported by Lee-2008 and  $k_r$  is the precipitation rate which is treated as a fitting parameter. As previously mentioned, the suggested model by Panacharoensawad 2012 puts  $k_r = 0$  for no precipitation wax mass flux case.

Similar to temperature profile calculation, the governing PDE is solved numerically using the backward finite difference method. The boundary conditions are:

$$\text{At } r = 0, \frac{\partial C}{\partial r} = 0 \quad (4-33)$$

$$\text{At } r = r_i, C = C(T_i) \quad (4-34)$$

By knowing the concentration profile, the total wax mass flux can be calculated as:

$$J_{total} = -D_{wo} \frac{C_N - C_{N-1}}{r_N - r_{N-1}} \quad (4-35)$$

Then, in SP-Compo model, the concentration profile for the grouped component will be estimated. A partial differential equation for concentration profile has been solved using the finite element method (FEM).

As previously stated, the above parameters are calculated for all individual carbon numbers and they are used to calculate the concentration,  $\frac{\partial C}{\partial T}$  and molecular diffusivity for the grouped component in SP-Compo wax deposition model. `Get_dCdT_fit_eqns` and

`DwoFit` are the methods to create the fitted regression equations for the thermodynamic parameters. Within these two methods, the SP-Wax thermodynamic model is called for a specific range of temperature and the produced data are saved into vectors. Then, the regression equations are fitted to the previously generated data (by SP-Wax). So, in `Get_C_thermo`, `Get_dCdT_thermo` and `Diff_thermo`, the thermodynamic properties are calculated using the fitted equations (NOT the thermodynamic model). In this way, the run-time was improved considerably. In Figure 4-29, classes and methods that are included in `concentration_profile.h` are shown.

```

Class: spdepo::mass_calculation::RadialCProfile
Methods: void SetAllContinue, void SetAll, void ThermoSetAll,
           void Solve, void StandardOutput, void ZDepositGrouping,
           void GroupTCProfileCalculation, int SectionToGroupNumber,
           void PlotDefaultCProfile, void PlotDefaultTPProfile,
           void PlotPColorGraph, void HeatBalanceVerification
           void InitializeCompositionalModel, void
           UpdateInletComposition,
           void Get_dCdT_fit_eqns, double Get_C_thermo,
           double Get_dCdT_thermo, double Diff_thermo, int MinC_cal,
           void DwoFit, double DVPlusByDYPlus, void CheckRadialHeat,
           void CheckAxialHeat

```

Figure 4-29: Class, and methods which are included in `concentration_profile.h`

#### 4.2.15 `single_phase_deposition.h` and `single_phase_deposition.cpp`

Inarguably, `single_pase_deposition.h` & `cpp` contain the most important components of the SP-Depo software. The governing equations of wax deposition modeling ( $f = \frac{dF_w}{dt}$ ,  $g = \frac{dr_i}{dt}$ ) are solved using numerus objects from nearly all classes. For further model improvement, future developers are advised to give extra attention to these files.

In the wax deposition calculation, there are many numerical methods which should be employed repeatedly. Therefore, we separately defined these numerical techniques and included them in separate header and `cpp` files. In this section, the classes and methods of each header-file are listed. Please note that the coded numerical methods are double-checked by known-solution scenarios in EXCEL.

#### 4.2.16 **fitting\_search.h** and **fitting\_search.cpp**

In these files, parameters related to LM optimization algorithm are defined which are called when fitting parameters are being estimated.

#### 4.2.17 **linear\_regression.h** and **linear\_regression.cpp**

The thermodynamic model takes about 0.5-1 seconds to run and to calculate various thermodynamic properties of the system at one temperature. In the wax deposition model, concentration,  $\frac{\partial C}{\partial T}$  and diffusivity (which are calculated from the thermodynamic model) should be accessed many times and it is not feasible to call the thermodynamic model every time the mentioned parameters are required in SP-Depo. Therefore, we developed a unique regression model to represent the thermodynamic data. Since we adopted a modified regression model, it will be illustrated by an example and different graphs.

In this section, a regression model is coded to estimate solubilities and  $\left(\frac{\partial C}{\partial T}\right)_i$  points. After analyzing the shape of the data points, we found that the data can be fitted by polynomial equations through three zones. In the following graph, three polynomial equations are fitted to a sample set of  $\frac{\partial C}{\partial T}$  data points for  $C_{46}H_{94}$ . The data points are divided into three sections. First, the maximum point is found, and a three-degree polynomial is fitted to the data from the beginning to the point right before the maximum. For the second zone, a two-degree polynomial is fitted to three data points including the maximum and neighboring data points. Finally, for the last zone, a three-degree polynomial is fitted starting from one data point after the maximum till the last data point. For the following case, the average  $R^2$  for all three zones for this specific example is  $R^2 = 0.998$ . In the next graph,  $\frac{dC}{dT}$  curves for different carbon number are then shown.

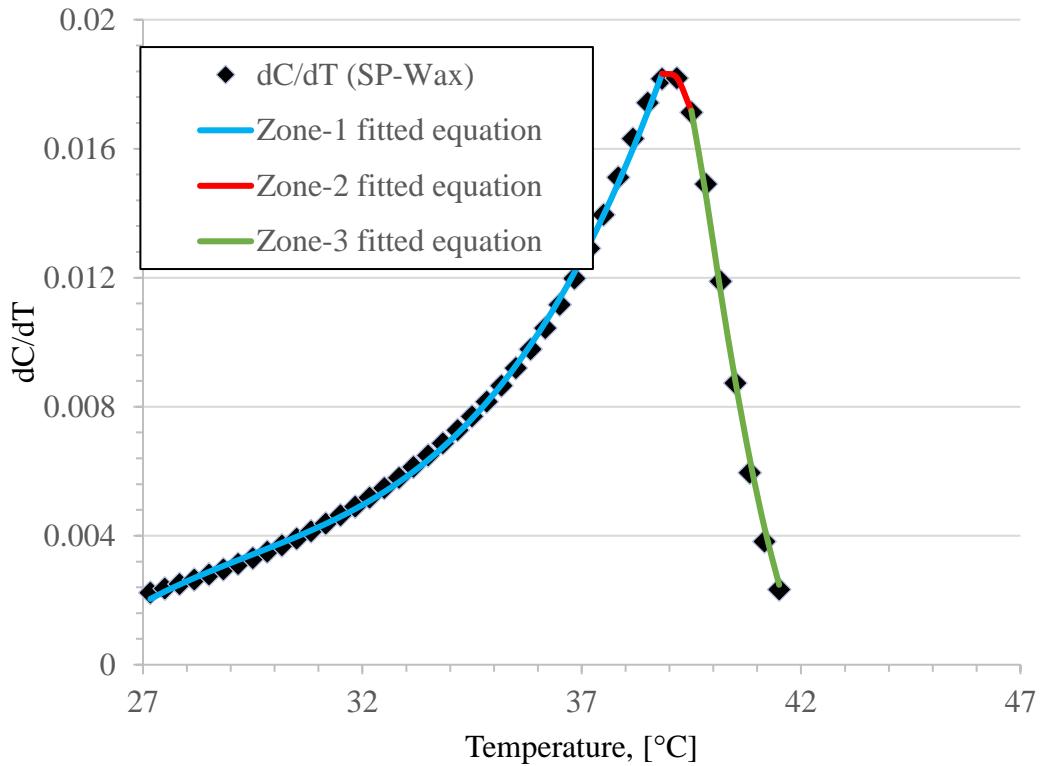


Figure 4-30:  $\frac{dc}{dt}$  versus temperature for  $C_{46}H_{94}$ . The data points are generated by the SP-Wax thermodynamic model and the solid lines are generated by the fitted three-zone regression equations.

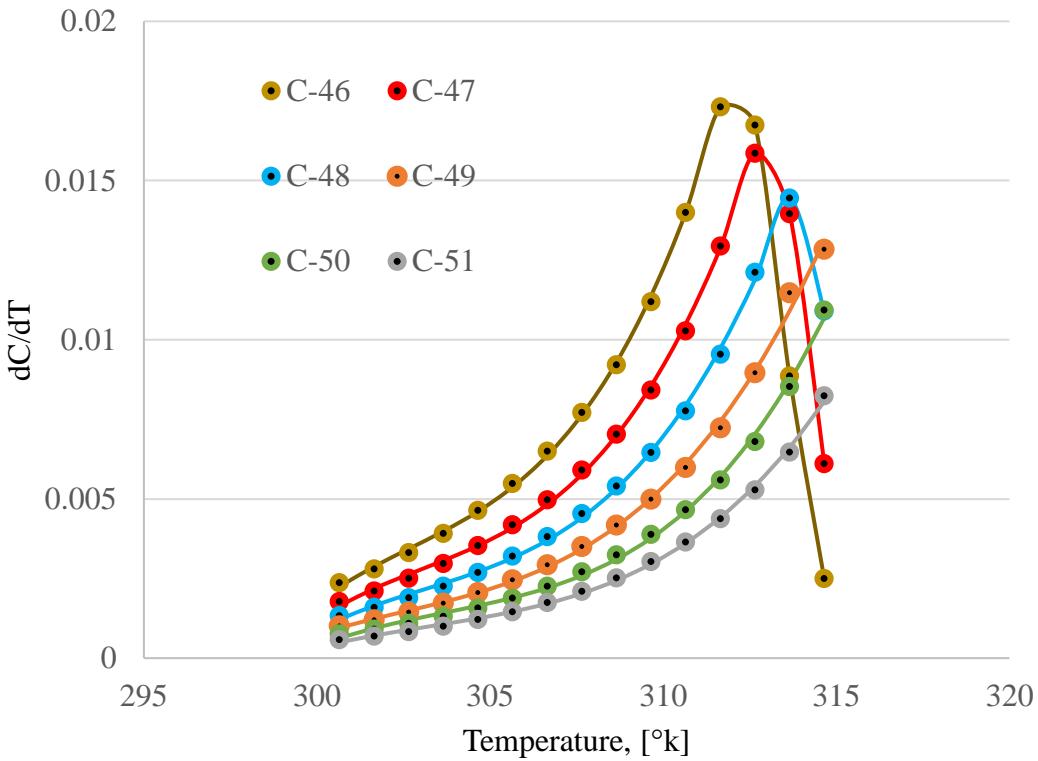


Figure 4-31: SP-Depo simulation:  $dC/dT$  curves for carbon numbers C 46-51

In addition, since the performance of our software is massively dependent on the accuracy of the fitted regression equations, we made it possible for the user to check the fitted equations in the GUI. The following three graphs show the total concentration,  $\frac{dc}{dt}$  and  $\bar{D}_{wo}$  with the fitted equations.

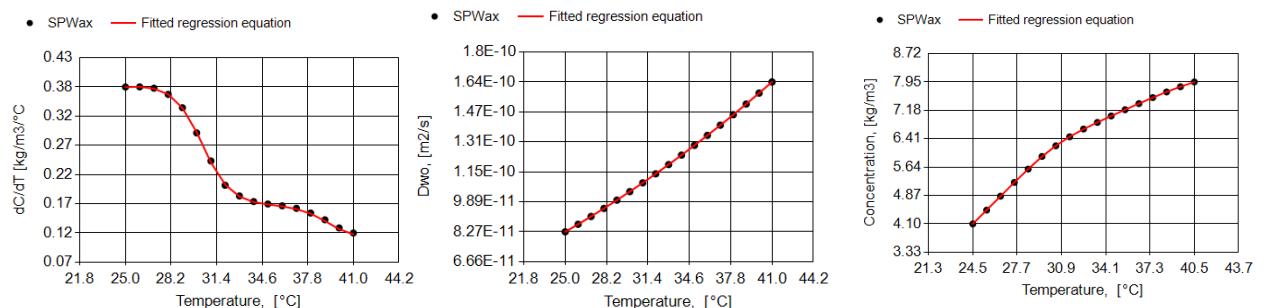


Figure 4-32: Concentration,  $\frac{dc}{dt}$  and  $\bar{D}_{wo}$  versus temperature. The data points are generated by the SP-Wax thermodynamic model and the lines are from the fitted regression equations.

```

Class: spdepo::usr::Polynomial
Methods: double operator(),double operator_combined
Class: spdepo::usr::LinearRegressionEqFit
Methods: void SetAll, void calculate, Polynomial GetPoly()
    std::vector<std::vector<double>> MatMult,
    std::vector<std::vector<double>> MatTrans,
    std::vector<double> GaussianEliminationWithBackSubstitution,

```

Figure 4-33: Class, and methods which are included in linear\_regression.h

#### 4.2.18 user\_numerical\_method.h and user\_numerical\_method.cpp

user\_numerical\_method.cpp consists of more than 1800 lines of code with many numerical methods including: Bisection method, Newton-Raphson method, combined root finding method (Bisection and Newton-Raphson) , trigonal Thomas matrix , matrix multiplication, Dorman-Prince 1D and more than 1D, Simpson 1/3 integration method, Gaussian Elimination with Back-Substitution, Levenberg-Marquardt optimization algorithm, matrix transpose, interpolation. Please note that the above numerical methods are coded in a way that takes the function as their inputs. In this way, these methods will be reusable and can be used whenever needed.

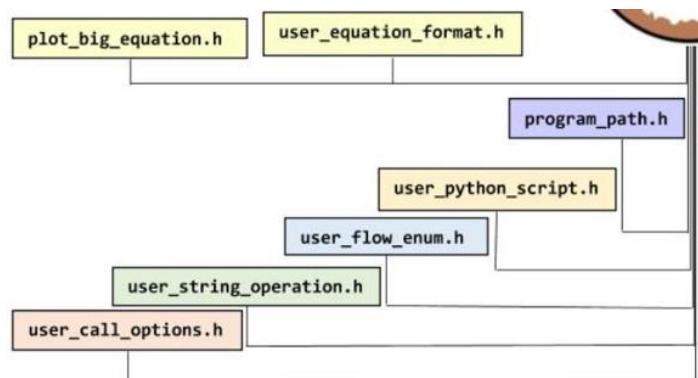


Figure 4-34: Header files in section "D"

The above header files are primarily related to enum classes and the software's structure of the SP-Depo code. Please note that python is used for data visualization with high quality graphs.

#### 4.2.19 `user_equation_format.h` and `user_equation_format.cpp`

As previously shown, some of the input parameters are needed with equation format. For example, oil density is greatly dependent on the temperature and should be expressed through an equation. We made it possible for the user to insert equations for these parameters. The following graph shows the main window of SP-Depo which requires the user to provide the input information. In the “Liquid Properties” tab, equations are required for the fluid properties.

Liquid Properties			
Name	Pana2018_test2		
Density [kg/m <sup>3</sup> ]	*1,[1],[],[-0.738,8]	Equation Format	Edit Equation
Viscosity [Pa.s]	*3,[3,2,4],[0,0],[0,	Equation Format	Edit Equation
Thermal Conductivity [W/m/K]	0.13	Constant Value	Edit Equation
Specific Heat Capacity [J/kg/K]	2000	Constant Value	Edit Equation
Create an Input File			

Figure 4-35: Liquid Properties input tab in SP-Depo

If user clicks “Edit Equation” button, the following window will be opened. Through the newly opened window, the user can choose the correct equation type and coefficients. One can click “Help” for the complete manual guidance where “Equation Description” and “Big Equation Creation Guidelines” will be accessed (Figure 4-37 and Figure 4-38)

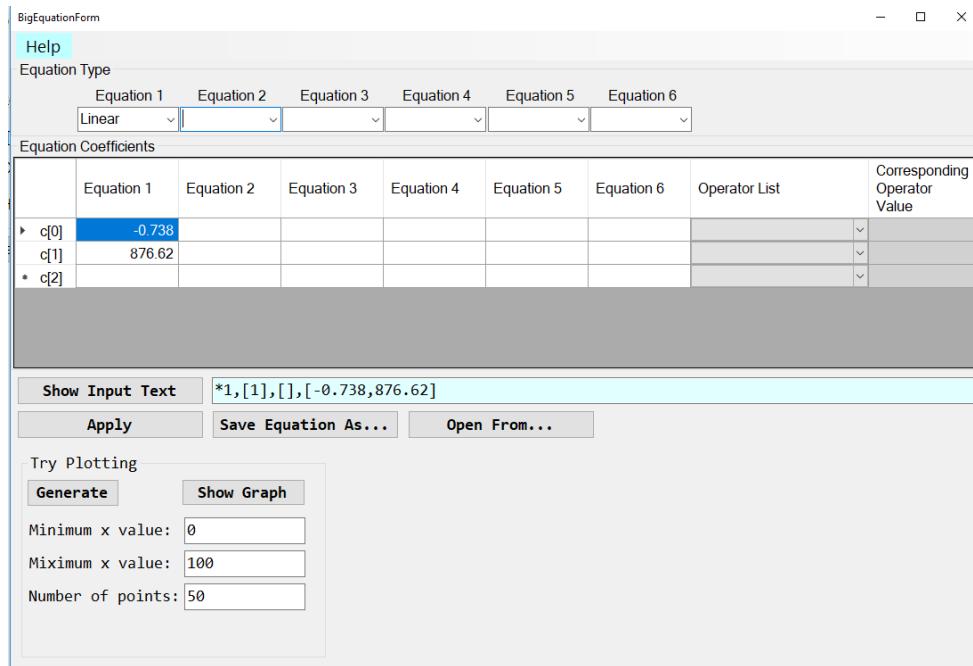


Figure 4-36: Equation insertion tab where user can provide the equation for non-constant variables including the fluid properties

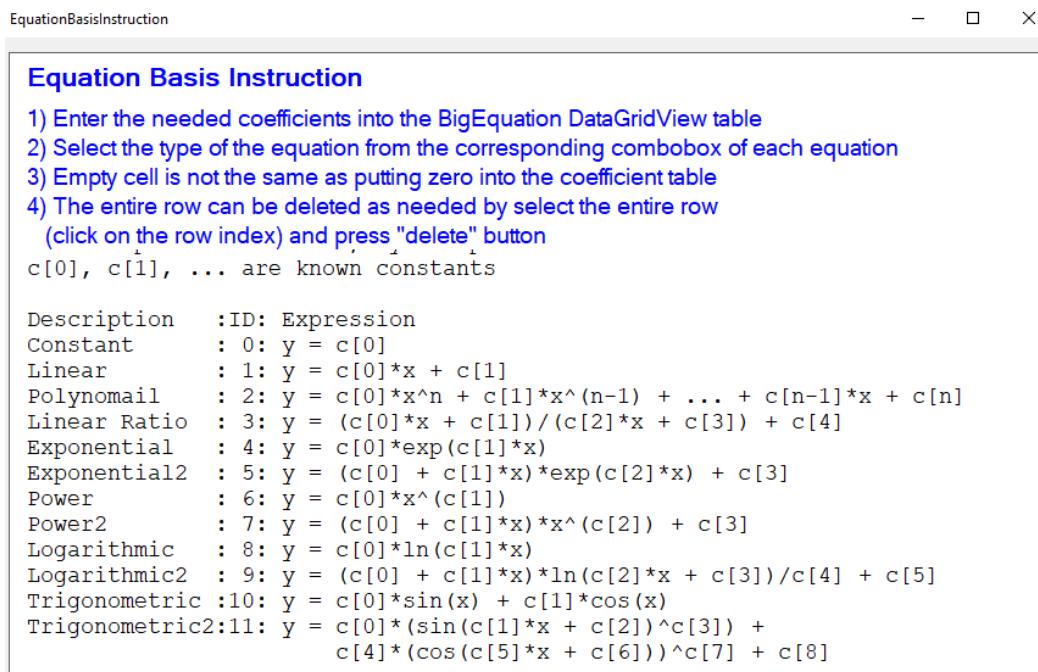


Figure 4-37: Equation Description manual

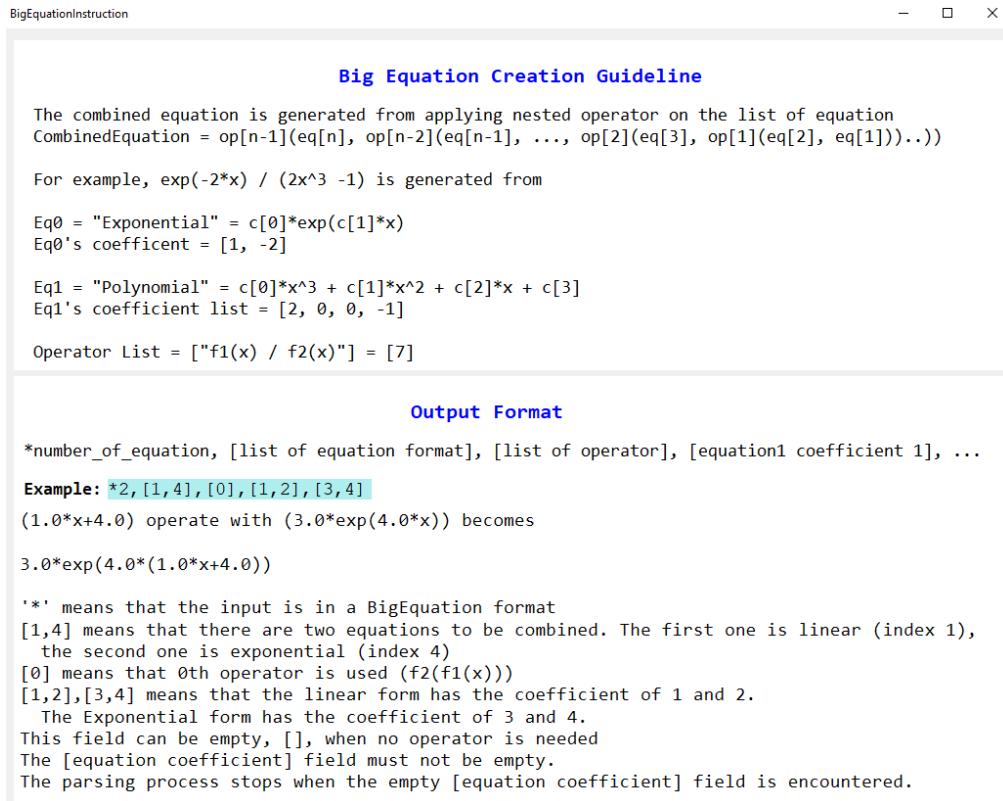


Figure 4-38: Big Equation Creation Guidelines

In Figure 4-38, the number corresponding to the operator list can be set in “Operator List” (Figure 4-36). In the following figure, the available operators are shown.

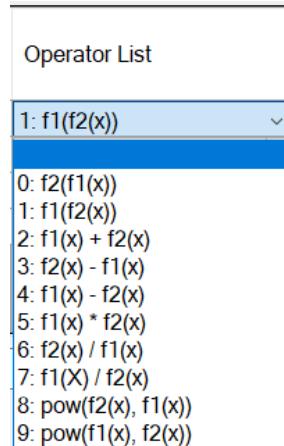


Figure 4-39: Operator List assignment

Our proposed equation insertion method covers nearly every typical equation format. The following picture shows the available equation types which can be used by the user.

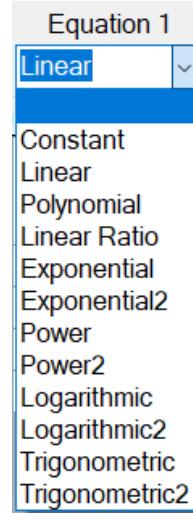


Figure 4-40: Available equation types

## Chapter 5

### Results and discussion

To verify our two developed software, we used experimental data from different resources and compared them to our simulation results. For SP-Wax, our software's performance and accuracy have been validated by experimental data of five binary and seven multicomponent systems. For SP-Depo, we used the data from twelve flow-loop experiments for our model and software verification.

#### 5.1 SP-Wax thermodynamic model and software

In SP-Wax thermodynamic model, empirical correlations are used for some of the thermophysical properties. We initially compare these correlations to available thermophysical experimental data. Then, we present some of the thermodynamic experimental data which have been used in our model verification.

##### 5.1.1 Validation of empirical correlations

Several empirical correlations are used to express many parameters including thermophysical properties, molar volume, etc. In our study, we rechecked the accuracy of those correlations by comparing them to the experimental data and other correlations. For the first parameter, we checked the DIPPR and GCVOL methods for molar volume calculation. Validity of both methods have been verified using experimental data. The two following graphs show the comparison between DIPPR and GCVOL molar volume models and experimental data [30] at two temperature points. From the following plots, it is shown that both models successfully tracked the experimental data.

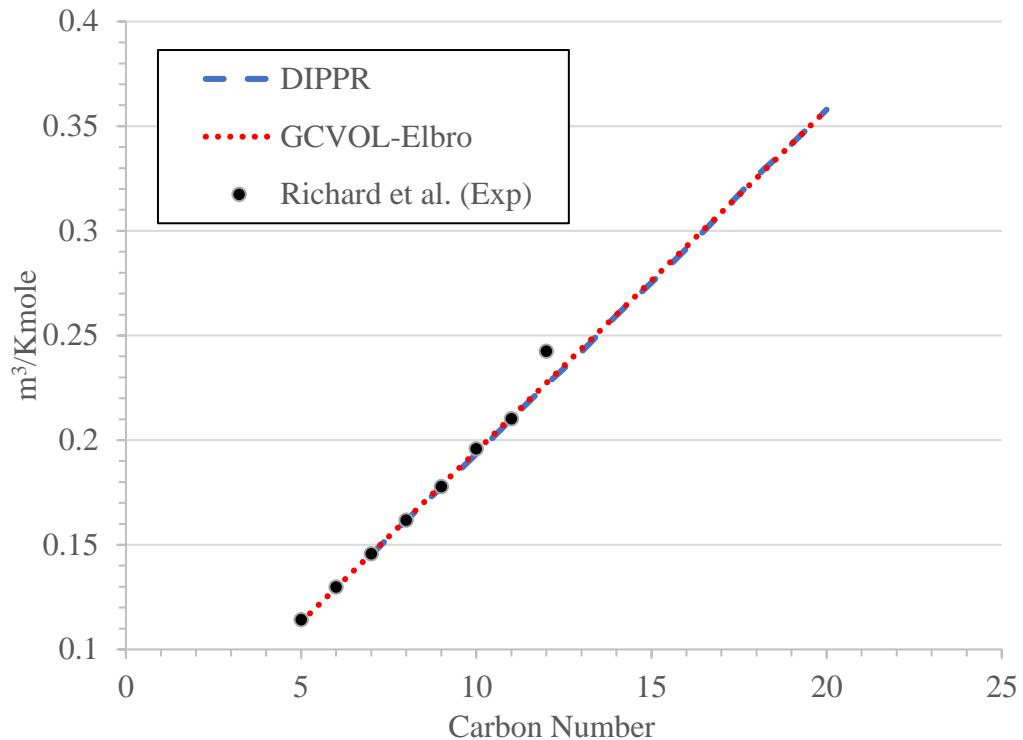


Figure 5-1: Molar volume comparison between experimental data [30] and correlations from DIPPR and GCVOL models at  $T=288.15^\circ\text{K}$

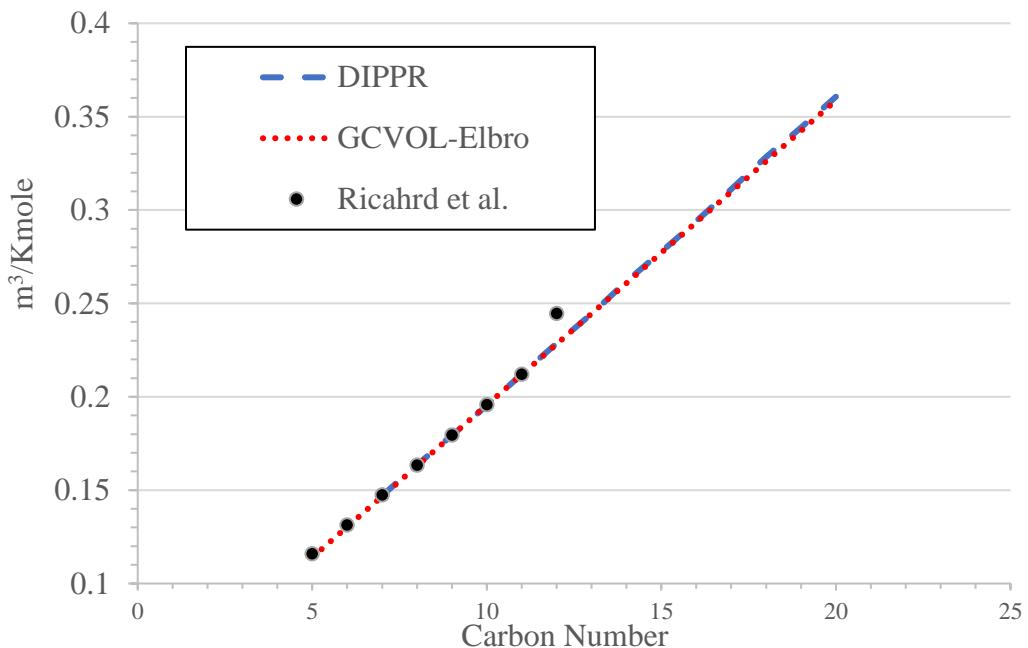


Figure 5-2: Molar volume comparison between experimental data [30] and correlations from DIPPR and GCVOL models at  $T=298.15^\circ\text{K}$

For the next step, the correlations for thermophysical properties are evaluated. In SP-Wax, enthalpy and temperature of fusion are correlated using Coutinho's formulas. In the two following graphs, results from the correlations are compared to the experimental data reported by Broadhurst [31]. Fusion temperature is accurate with only 1% uncertainty while Coutinho model does not represents very good accuracy in estimation of fusion enthalpy for even carbon numbers ranging from 9 to 20.

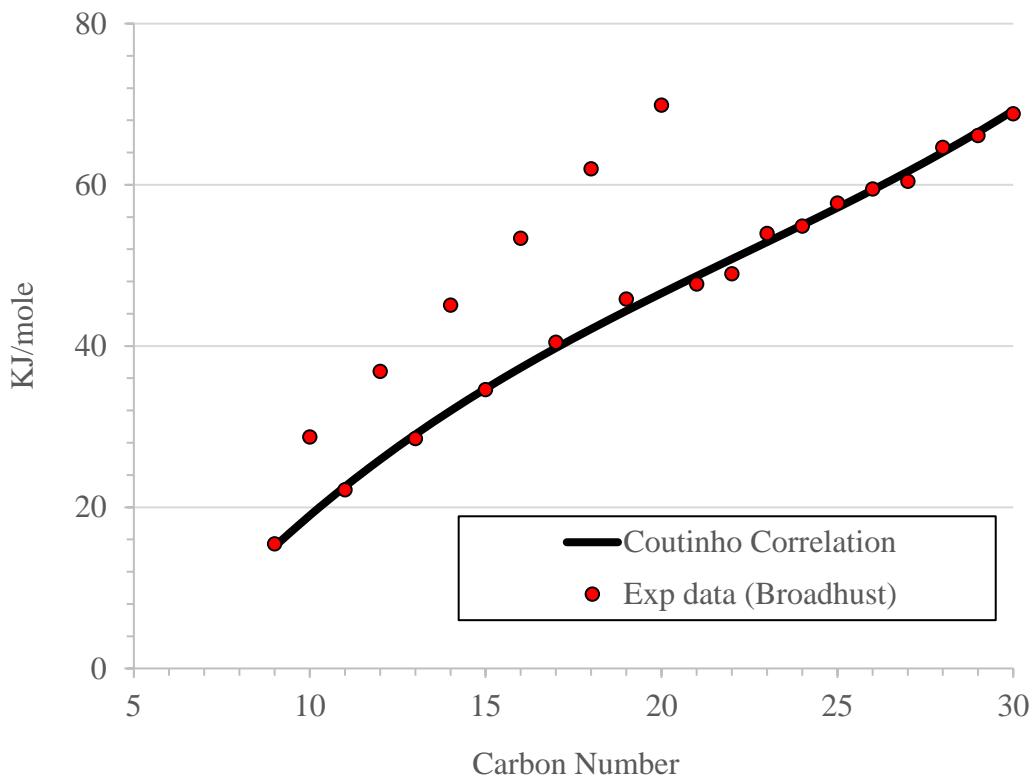


Figure 5-3: SP-Wax Enthalpy of fusion prediction using Coutinho et al. model correlation versus experimental data of Broadhurst [31]

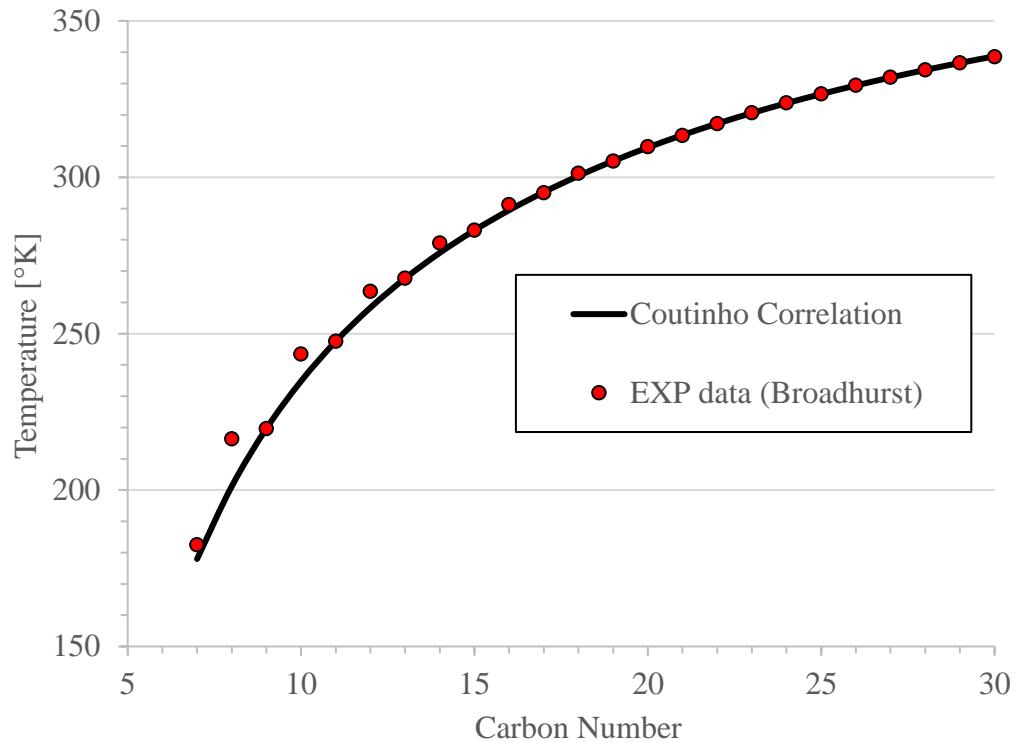


Figure 5-4: SP-Wax Temperature of fusion prediction using Coutinho et al. model correlation versus experimental data of Broadhurst [31]

Similarly the enthalpy and temperature of solid phase transition correlations which are used in SP-Wax were compared to the experimental data reported by Broadhurst [31].

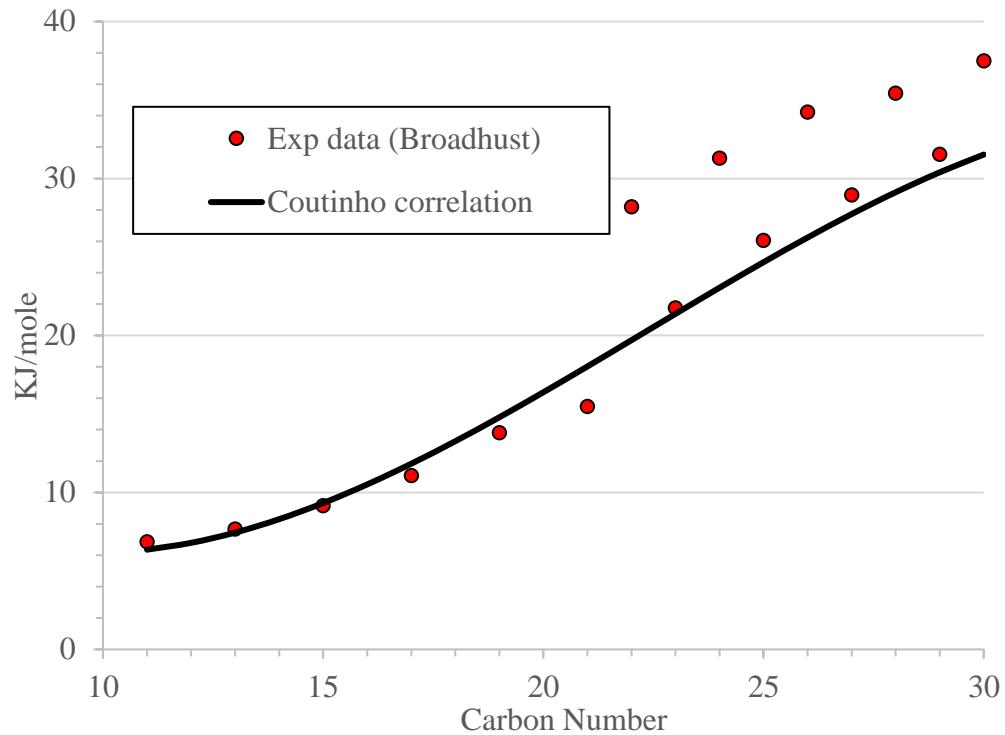


Figure 5-5: SP-Wax Enthalpy of solid phase transition prediction using Coutinho et al. model correlation versus experimental data of Broadhurst [31]

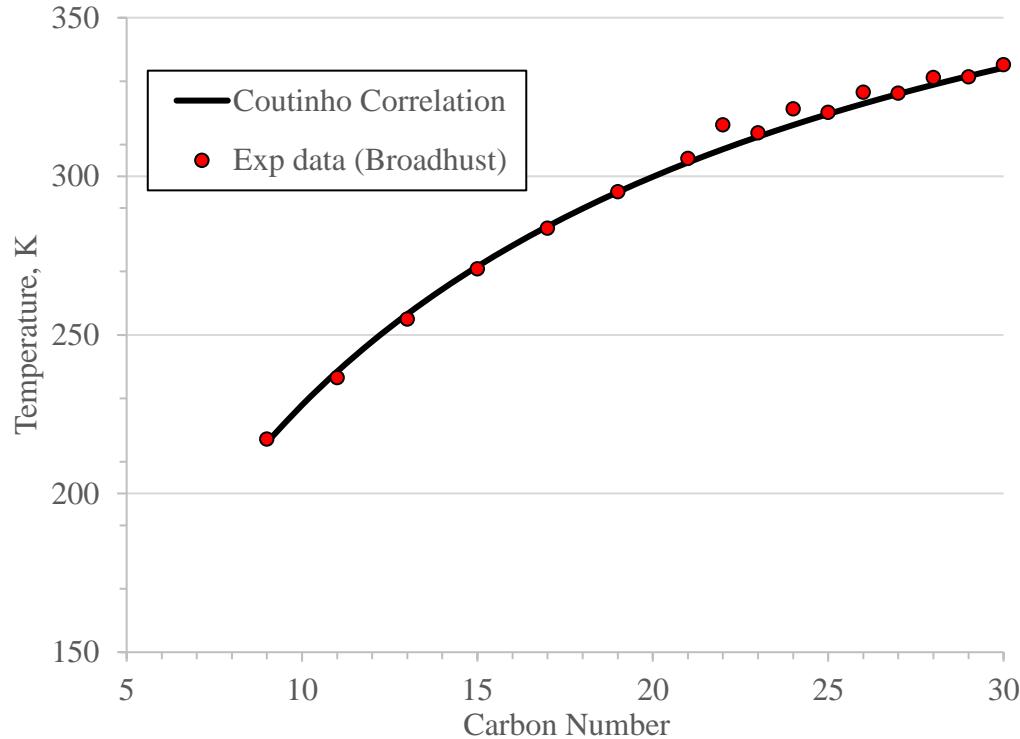


Figure 5-6: SP-Wax Temperature of solid phase transition prediction using Coutinho et al. model correlation versus experimental data of Broadhurst [31]

The next investigated parameter is the heat of vaporization. Heat of vaporization is needed to calculated heat of sublimation in solid phase activity coefficient modeling. Extension of Pitzer CSP models [28] have been used and compared to experimental data. In the following graph, Pitzer CSP predictions are plotted against experimental data at 25° C .[73], [74]. Our proposed correlation successfully predicts the experimental data.

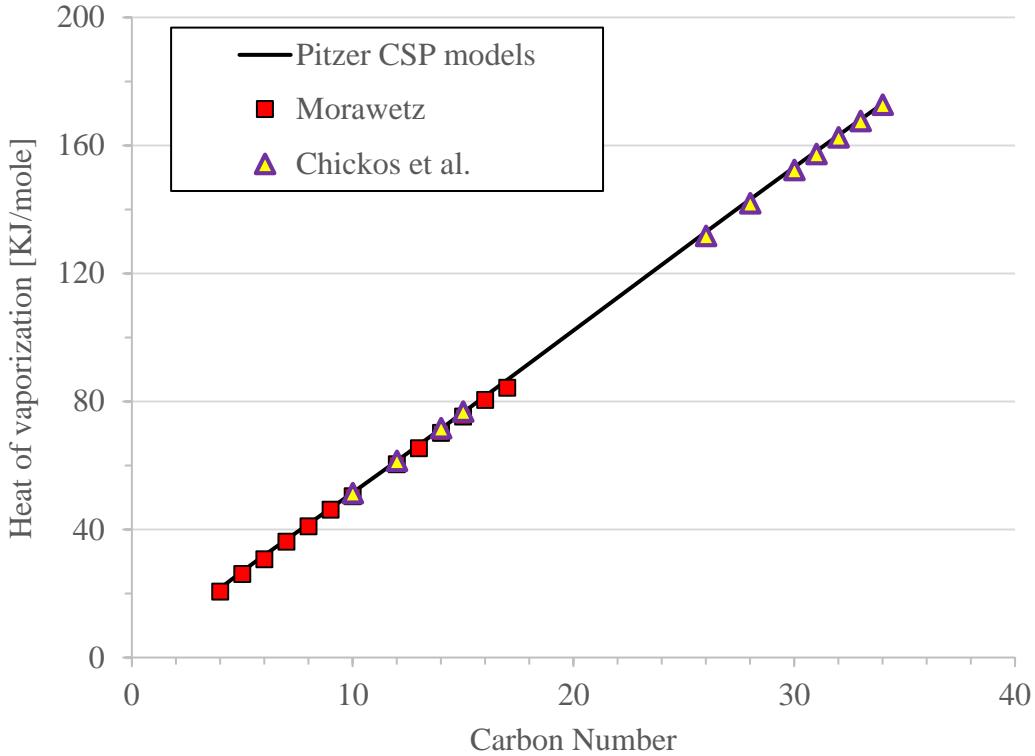


Figure 5-7: CSP model prediction of vaporization enthalpy for different carbon numbers at T=25°C versus experimental data (Morawetz and Chickos et al. [73], [74]).

### 5.1.2 Experimental dataset

For the next step, we needed to find reliable source of experimental data to verify our developed model. In this section, we provide a brief overview of the experimental data which have been used for our model verification. We compared the results obtained from SP-Wax to experimental data of five binary and seven multicomponent systems. Various experimentally measured properties from different sources are tabulated. We have referred to these experiments multiple times and it is beneficial to present them exclusively in one section. In binary systems, SP-Wax performance was verified by forty-nine experimentally measured WAT data points from five different systems. In multicomponent systems, various aspects of SP-Wax were verified through experimental data of seven different oil compositions including nineteen precipitation points, one-hundred and forty-seven solid phase composition data and five CCN values. South Pelto [10] and Garden Banks [38] are two oil samples which have been used in our study for verification purposes. For both oil samples, input composition and other input data are available. In addition, different types

of experimentally measured data have been reported including, precipitation data, solid phase CND, CCN and WAT. The two mentioned oil samples are evaluated through series of flowing experiments by Panacharoenawad and Rittirong. Please note that, HTGC method has been used to measure the composition of the deposit which contains solid wax particles and the trapped oil. This is why the measured composition needed to be subtracted by the liquid phase composition to obtain solid phase CND. The following table contains the experimental WAT data of the binary system.

Table 5-1: Binary system experimental data [26][75]

	Temperature, [°C]	solute mole fraction in liquid phase		Temperature, [°C]	solute mole fraction in liquid phase
n-C <sub>28</sub> in n-C <sub>7</sub>	22.9	1.56E-02	n-C <sub>32</sub> in n-C <sub>7</sub>	16.1	1.37E-03
	23.75	1.74E-02		17.9	1.83E-03
	24.3	2.04E-02		19.6	2.30E-03
	24.55	2.06E-02		20.7	2.76E-03
	26.2	2.57E-02		22.1	3.43E-03
	29.15	3.76E-02		22.7	3.69E-03
	35.2	7.74E-02		24.3	4.79E-03
	38.8	1.14E-01		25.2	5.54E-03
	44.15	4.69E-01		26.55	6.82E-03
	42.65	3.91E-01		27.9	8.05E-03
	42.25	3.76E-01		28.4	8.61E-03
	41.05	3.56E-01	n-C <sub>36</sub> in n-C <sub>7</sub>	18.1	3.29E-04
	37.75	2.57E-01		19	3.56E-04
	37.25	2.23E-01		19.25	3.75E-04
	28.25	1.04E-01		20.3	4.31E-04
	27.55	9.80E-02		22.1	5.98E-04
n-C <sub>25</sub> in n-C <sub>7</sub>	32.05	2.68E-01		22.9	6.70E-04
	31.35	2.52E-01		23.25	7.54E-04
	31.15	2.35E-01		24.4	9.18E-04
	28.15	2.00E-01		25.8	1.16E-03
	27.75	1.71E-01		27.1	1.42E-03
	25.65	1.42E-01		29.25	2.11E-03
	24.05	1.17E-01		31.4	2.64E-03
	21.05	9.30E-02		32.65	3.25E-03
	19.45	7.20E-02		34.1	4.04E-03
	13.35	5.20E-02			

Since our thermodynamic simulation is only a function of temperature, we needed to have accurate temperature information. In Rittirong and Panacharoenawad studies, different temperatures have been calculated using the experimental thickness and wax fraction data. Bulk, wall and interface temperatures are presented in the following table from both studies.

Table 5-2: Supplementary data from Garden Banks and South Pelto oil case experiments [10] [38]

<b>Oil Type</b>	<b>South Pelto</b>	<b>South Pelto</b>	<b>South Pelto</b>	<b>Garden Banks</b>	<b>Garden Banks</b>
<b>Test #</b>	27	28	29	AR-21	AR-7
<b>T<sub>b</sub> [C]</b>	40.55	40.48	40.33	25.08	26.02
<b>T<sub>w</sub> [C]</b>	29.54	29.30	29.53	16.80	16.47
<b>T<sub>i</sub> [C]</b>	37.51	35.99	34.00	18.01	19.73

Precipitation data of three oil samples are available and will be used for verification purposes of our thermodynamic model.

Table 5-3: Experimental precipitation data for Garden Banks [38], Fleming et al. [25], and Zheng et al. [6]

<b>System</b>	<b>T[°C]</b>	<b>Precipitated weight fraction</b>
<b>Garden Banks</b>	10.75	2.69E-03
	15.00	2.06E-03
	20.04	1.27E-03
	25.03	7.64E-04
	30.01	4.65E-04
	35.00	0
	-10.01	3.08E-01
	-0.01	2.46E-01
	9.99	1.64E-01
	14.85	1.22E-01
<b>Fleming et al.</b>	19.85	8.14E-02
	24.92	4.64E-02
	29.93	1.84E-02
	34.35	0
	5.00	1.70E+00
	10.00	1.35E+00
	15.00	1.03E+00
	20.00	7.48E-01
	25.00	5.10E-01
	30.00	3.26E-01
<b>Zheng et al.</b>	35.00	1.47E-01

Please refer to Rittirong for details about testing conditions. In addition, compositional input data of n-alkanes for South Pelto and Garden Banks are plotted in the next graph. For smoother CND plots, exponentially fitted lines (with  $R^2 > 0.98$ ) have been used for composition. The effect was on precipitation curve was checked and it is small when fitted data were used for composition instead of actual input composition data. From the following graph, the composition data of heavier components are extrapolated. Please note that such extrapolation is somewhat subjective.

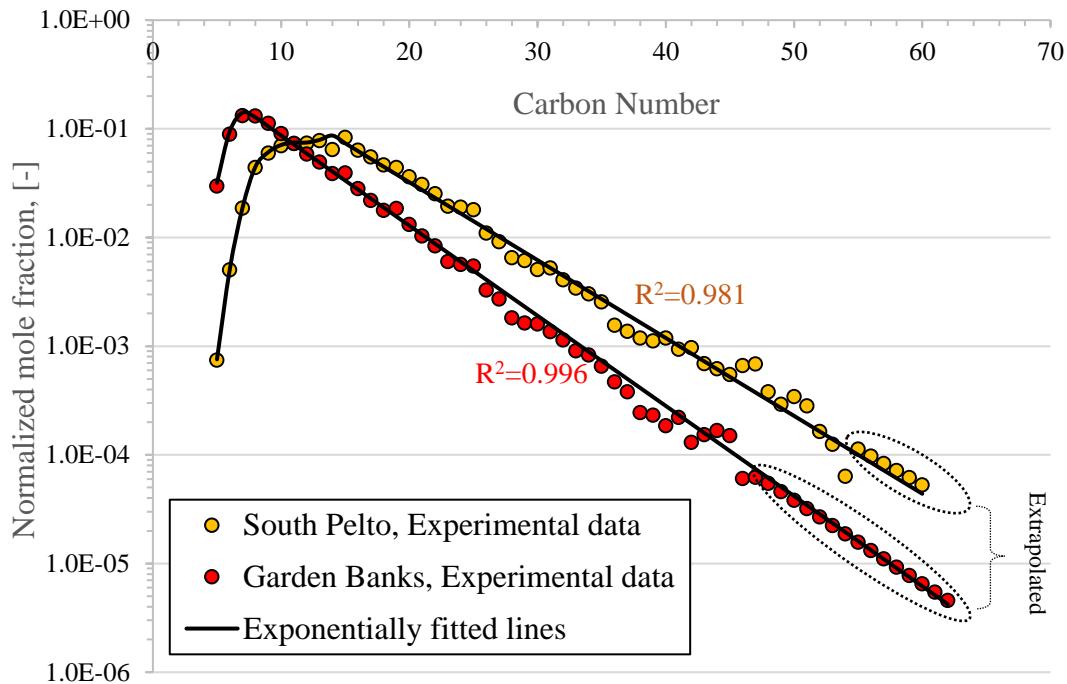


Figure 5-8: Compositional input data of n-alkanes for oil cases of Garden Banks and South Pelto and exponentially fitted lines

### 5.1.3 Binary System Model Validation

SP-Wax predictions have been validated by experimental data of five binary systems. The dissolved solute mole fractions at various WAT values from SP-Wax were compared to the literature data [26][75] and satisfactory agreement was obtained as shown in. The dissolved solute mole fraction decreases as either the temperature decreases (or  $1000/T$  increases) or the n-alkane chain length becomes longer, as expected.

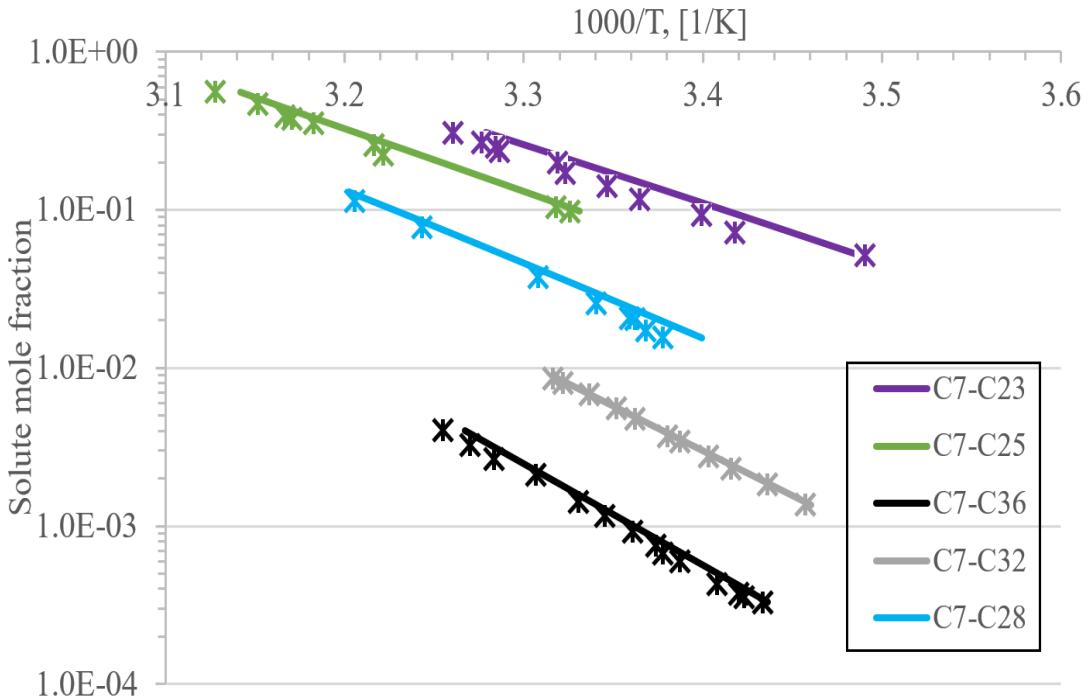


Figure 5-9: SP-Wax predictions and experimental data [26], [75] ( $\text{x}$  symbol) of solid solubilities for five binary system at 1 bar (Table 5-1)

#### 5.1.4 Multicomponent System Model Validation

One important aspect of a reliable thermodynamic model is its accuracy to predict the mass of precipitated paraffin in different temperatures (precipitation curve). Experimental precipitation data [6], [25], [38] were used to validate SP-Wax software. Fleming et al. [25] reported the experimental and predicted precipitation data points. Their prediction was based on Coutinho et al.'s model [20] using UNIQUAC approach for solid phase non-ideality. For another case, Rittirong [38] reported experimental precipitation data along with simulation results from TUWAX and PVTsim thermodynamic software. Notably, SP-Wax is far more accurate than all other simulation results. Zheng et al.'s [6] precipitation data are from the direct centrifugal technique. The direct technique is subject to less uncertainty because it does not need to calculate the precipitated amount based on the estimated enthalpy of crystallization of wax [76]. Zheng et al.'s [6] input composition for n-alkanes were reported graphically from C15 to C36. In our study, we extrapolated the composition for the wider range of carbon numbers, however, the extrapolation is somewhat subjective, and it is not unique. SP-Wax predictions of precipitation curve are in very good agreement with all three experimental data sets. SP-Wax prediction is almost

identical to Fleming et al.'s prediction. Both studies use Coutinho thermodynamic model. However, Fleming used UNIQUAC to express solid phase's activity coefficients and SP-Wax used the Wilson method. As per Coutinho's comparison, both methods should result in similar predictions which is true in our analyzed case. This is another indication of the validity of our developed thermodynamic software.

For Fleming et al. [25], the precipitation curves with three different values of adjustment parameter " $a$ " ( $0, 3 \times 10^{-7}$  and  $8 \times 10^{-7}$ ) were calculated and shown in Figure 4(a). In their case, only n-alkane components were present ( $W_f = 1$ ) and very small adjustment was needed. Among the three curves, the best fit resulted from  $a = 3 \times 10^{-7}$  with  $R^2 = 0.997$ . For oil cases of Zheng et al. [6] and Rittirong [38], the optimum adjustment coefficient was chosen to be  $a = 3 \times 10^{-6}$  with  $R^2$  of 0.95 and 0.96, respectively.

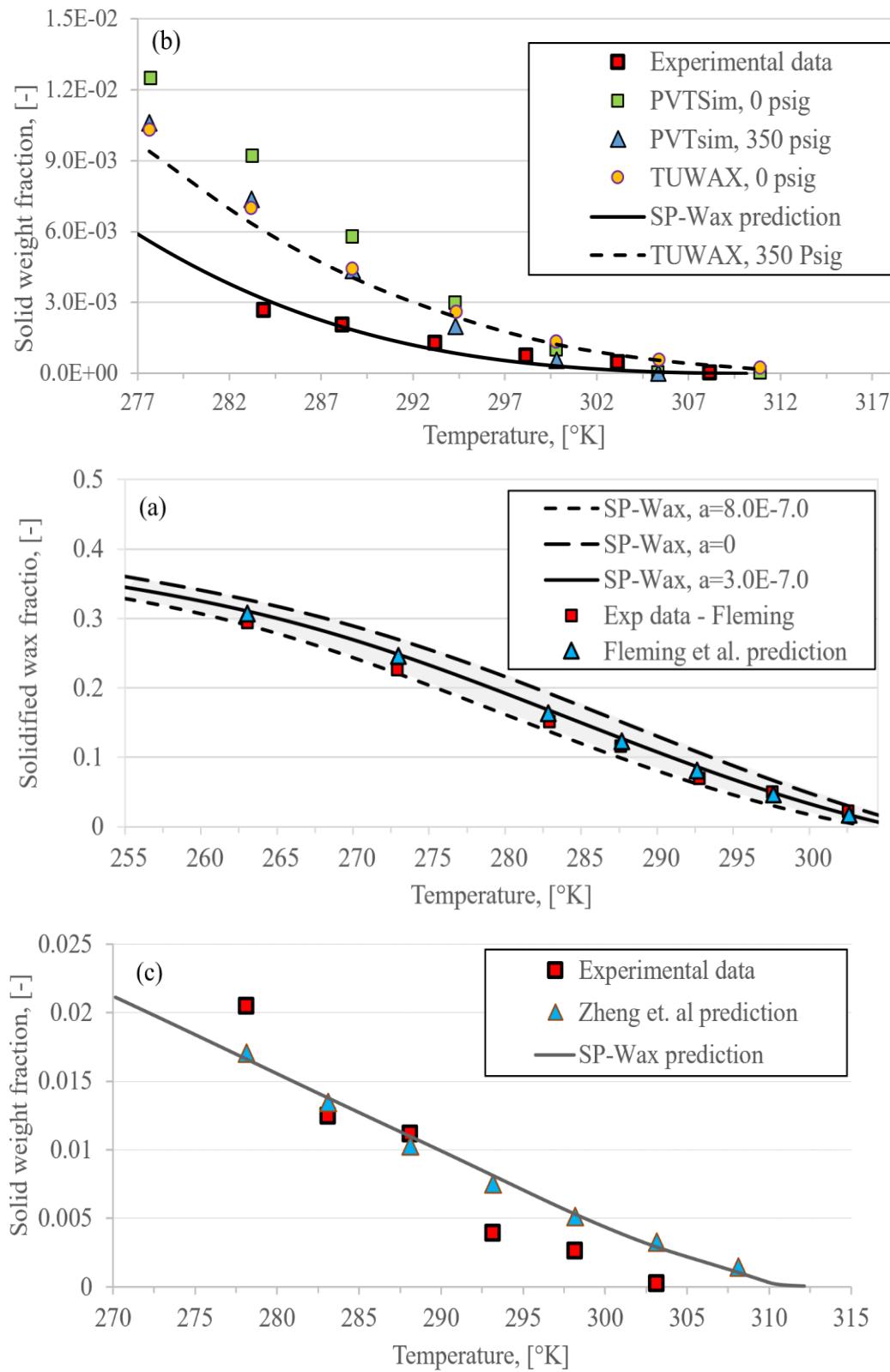


Figure 5-10: SP-Wax precipitation curve validation against Fleming et al.(a) [25], Rittirong(b) [38], and Zheng et al.(c) [6].

In addition to Figure 5-10, we compared SP-Wax predictions to experimental precipitation data of three more multicomponent systems from Dauphin et al. [77]. Notably, SP-Wax successfully predicts the experimental precipitation data.

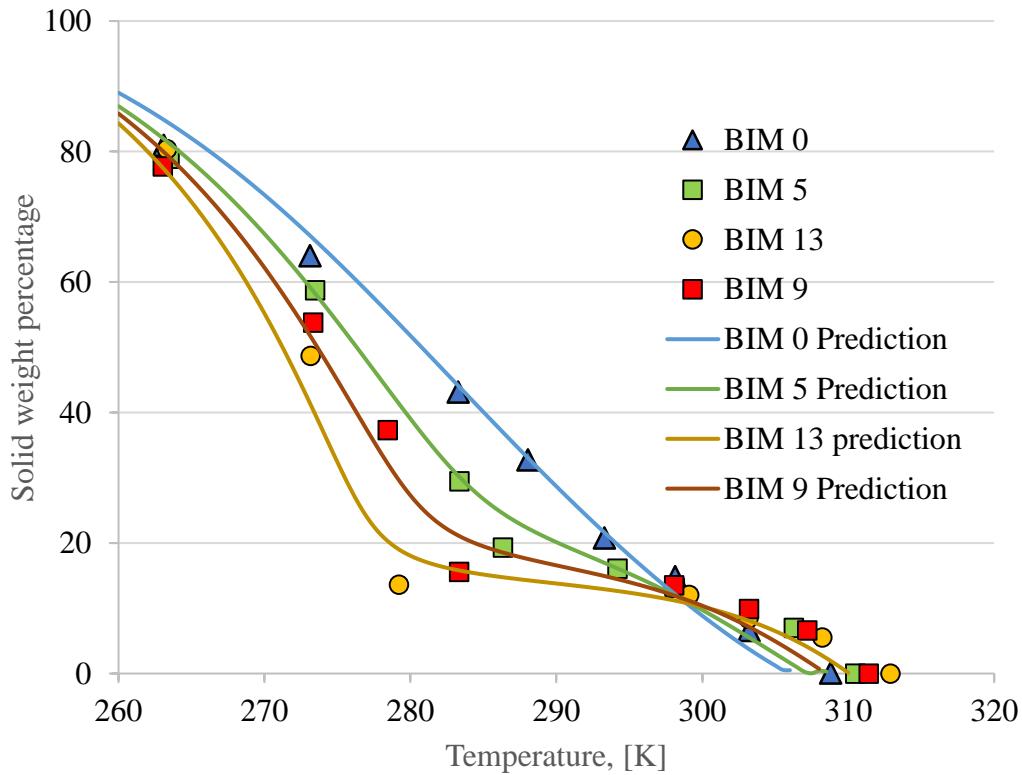


Figure 5-11: SP-Wax predictions versus precipitation data of Dauphin et al. [77]

Corresponding correction factor coefficient for each oil case is presented in the following table.

Table 5-4: Correction factor coefficients of different oil systems from Dauphin et al. [77]

Case	a
Bim 5	4.0E-07
Bim 0	4.0E-07
Bim 9	3.0E-07
Bim 13	2.0E-07

In addition to the precipitation curve prediction which is used in the pseudo-single-wax-phase modeling approach [3], [11], [12], [78], the solid phase composition information is

also important for a compositional-based model [6] and for analyzing the CCN of wax deposit for both single-phase [78] and multiphase cases [43], [65]. SP-Wax's ability to predict solid phase composition was validated through five sets of experimental CND data from Rittirong [38] and Panacharoensawad's [10] single phase wax deposition test results. The following graph shows the SP-Wax predictions against experimental solid phase CND data. SP-Wax predictions are in good agreement with experimental data for all cases. The slight overestimation is expected because, SP-Wax takes only the final-time temperature which is always higher than the average temperature over the time of the experiment.

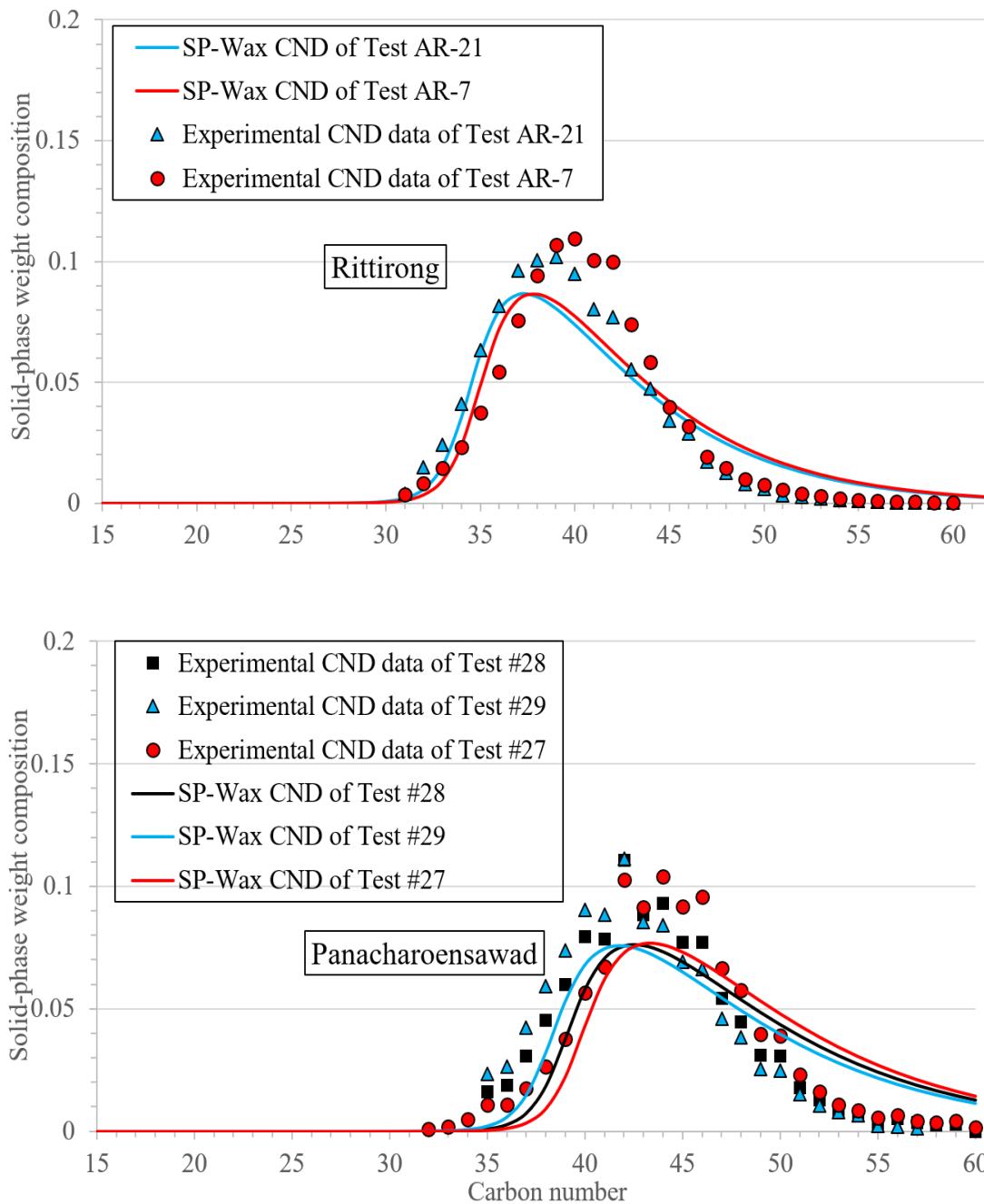


Figure 5-12: Solid phase CND data of paraffin deposit. SP-Wax predictions versus CND experimental data of Ritirrong [38] and Panacharoensawad [10] at average deposit temperature  $T_{avg} = 0.5(T_{int} + T_{wall})$  at the end of each test

### 5.1.5 Thermodynamic Verification of CCN and Aging Process

Lastly, the relative concentration gradient from SP-Wax is used to estimate the CCN in five different tests. In our analysis, the pre-calculated deposit's temperatures, which were reported in the literature [10], [38], were used to calculate the relative concentration gradient for CCN estimation. The relative concentration gradient is defined as the ratio of the dissolved mass of  $i^{\text{th}}$  carbon number over the volume of all n-alkanes in liquid phase (in  $\text{m}^3$ ). In SP-Wax, CCN is estimated by determining the smallest carbon number with positive relative concentration gradient. We note that the CCN estimation typically requires significant overhead calculations as part of wax deposition modeling. However, this thermodynamic property (CCN) can be estimated as a function of deposit's temperature. Since the deposit's temperature can be determined using experimental measurements at the final time (the time at which the composition was determined by HTGC), CCN can be predicted by SP-Wax. CCN is closely related to the aging concept where lighter n-alkanes diffuse out of the deposit and heavier n-alkanes ( $>\text{CCN}$ ) diffuse toward the well through a counter-diffusion process due to concentration gradient. In our study, we verified this phenomenon thermodynamically. In Figure 5-13, within the red highlight carbon number range, it can be seen that the relative concentration of lighter n-alkanes ( $<\text{CCN}$ ) are higher at wall temperature in compare to the deposit's temperature. This implies that the existing concentration gradient derives the light n-alkanes diffuse out of the deposit. On contrary, the heavier n-alkanes ( $\text{CCN}<$ ) will diffuse toward the wall due to concentration gradient from paraffin deposit to the pipe's wall.

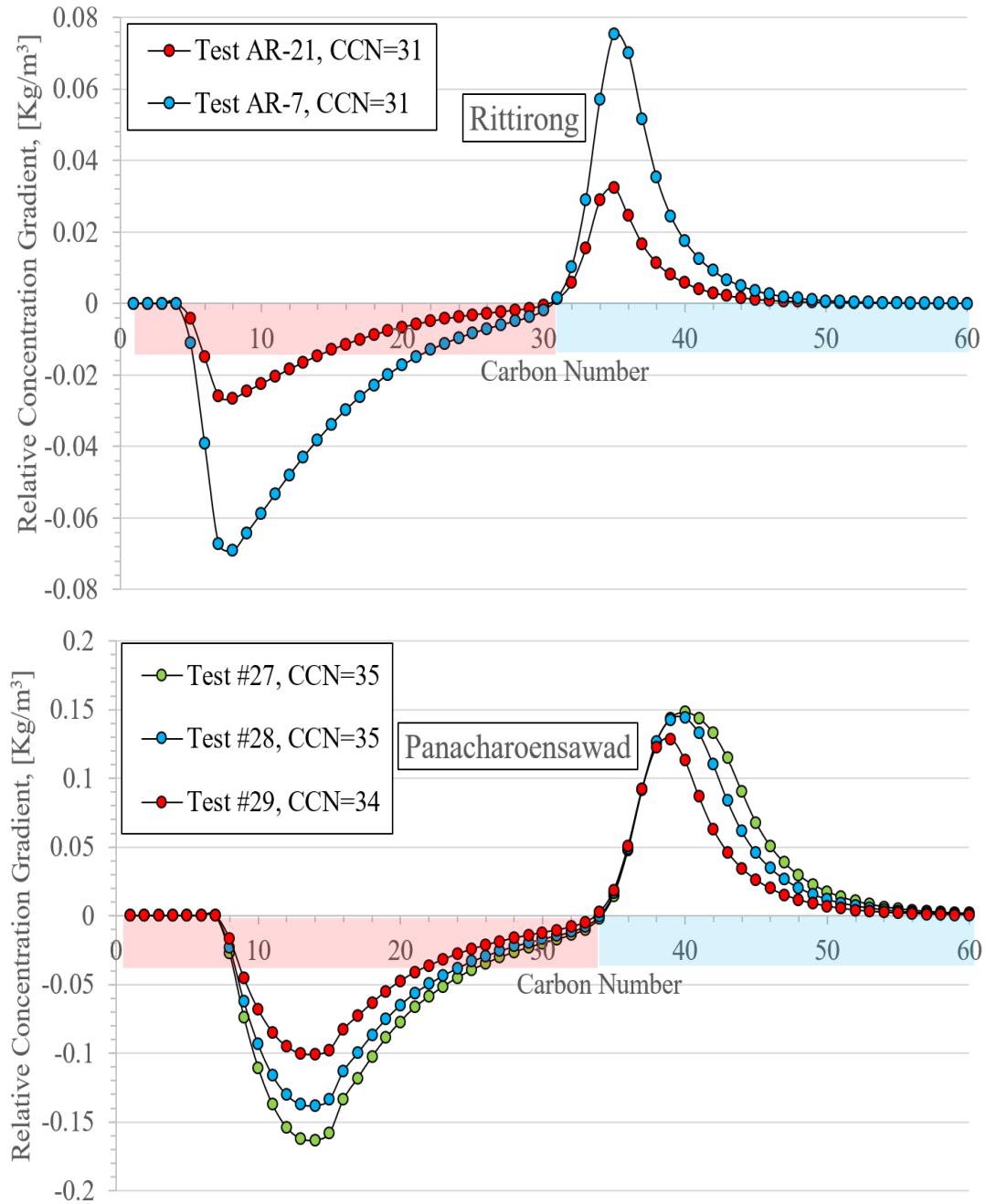


Figure 5-13: SP-Wax relative concentration gradient predictions for five tests of Ritirong [38] and Panacharoensawad [10]. Associated CCN values are annotated in the graph for each test. Blue and red highlighted sections are referred to carbon number components that diffuse in and out of the deposit, respectively.

The numerical values of solid phase Average Carbon Number (ACN), mode and CCN predictions with test temperature values used in SP-Wax simulation are shown in the following table. In addition to the comparison in the above graphical form, the numerical

value shown below confirm the match of SP-Wax to the literature data.

Table 5-5: Temperatures data at the end of experiments for five tests plus experimental data [10], [38] and predictions of Average Carbon Number (ACN), Mode, and Critical Carbon Number (CCN). South Pelto and Garden Banks are the names of oil samples that have been used by Panacharoensawad [10] and Ritirong [38], respectively.

Oil Type	South Pelto	South Pelto	South Pelto	Garden Banks	Garden Banks	Mean Absolute Relative percentage error %*
<b>Test #</b>	27	28	29	AR-21	AR-7	
<b>T<sub>b</sub> [C]</b>	40.6	40.5	40.3	25.1	26.0	
<b>T<sub>w</sub> [C]</b>	29.5	29.3	29.5	16.8	16.5	
<b>T<sub>i</sub> [C]</b>	37.5	36.0	34.0	18.0	19.7	
<b>ACN (Exp)</b>	44.8	43.6	42.8	40.5	39.6	
<b>ACN (Pred)</b>	47.3	46.6	45.9	41.9	41.4	5.49
<b>Mode (Exp)</b>	44	42	42	40	39	
<b>Mode (Pred)</b>	43	43	42	38	37	2.96
<b>CCN (Exp)</b>	35	35	35	30	30	
<b>CCN (Pred)</b>	35	35	34	31	31	1.90
<b>Correction Factor Coefficient</b>	3.0E-06					

\* Mean relative percentage error % is defined as  $\frac{1}{NN} \sum_{ii=1}^{NN} \left| \frac{y_{Sim,ii} - y_{Exp,ii}}{y_{Exp,ii}} \right| 100\%.$

Table 5-5 contains the relative error of the model for solid solubilities of binary systems and precipitation curves of multicomponent systems. The relative error formula which is used in Table 5-5 is as follows:

$$\text{Estimated relative error} = \frac{\frac{1}{NN} \sum_{ii=1}^{NN} \left| y_{Sim,ii} - y_{Exp,ii} \right|}{\frac{1}{NN} \sum_{ii=1}^{NN} \left| y_{Exp,ii} \right|} 100 \quad (5-1)$$

where, NN,  $y_{sim}$  and  $y_{Exp}$  are the total number of cases, simulated and experimental sample parameters, respectively

Table 5-5 shows that the model has the average estimated relative error of about 22% and 3.7% for the case of multicomponent precipitation curve and the binary system WAT, respectively. SP-Wax requires accurate input n-alkane compositions. In multicomponent systems, the accumulative error of input compositions is higher than in binary systems,

simply because more components are present. In some multicomponent cases, such as in Zheng et al. [6], the n-alkane input composition data are incomplete and the extrapolation of the n-alkane composition is needed. This contributes to the model prediction's uncertainty.

Table 5-6: Estimated relative error of the SP-Wax prediction for precipitation curves of multicomponent systems.

Case	System	Estimated Relative error [%]
Rittirong	Multicomponent	20.0
Zheng et al.	Multicomponent	28.7
Fleming et al.	Multicomponent	17.1

Furthermore, the average absolute errors of WAT prediction for the binary systems are calculated and shown in Table 3. The results show that SP-Wax can successfully predict the solid solubility of binary systems.

Table 5-7: Temperature differences between predicted and experimental WAT parameter of five binary systems.

System	Average temperature difference [°C]
C7-C23	1.83
C7-C25	1.10
C7-36	0.74
C7-C32	0.22
C7-C28	1.28

## 5.2 Wax Deposition in Laminar Flow

We developed a C++ simulation to predict different characteristics of wax deposition phenomenon under laminar flow [70]. We, then, compared our simulated results to the experimental data reported by Singh et al. [3]. Table 5-8 represents the operating conditions of the investigated experimental data [3].

Table 5-8: Operating conditions of Singh et al. wax deposition tests [3]

<b>Data Source</b>	<b>Case#</b>	<b><math>ID_{pipe}</math></b>	<b><math>\mu_{oil}</math></b>	<b><math>\rho_{oil}</math></b>	<b><math>T_{bulk}</math></b>	<b><math>t_{test}</math></b>	<b><math>T_{ambient}</math></b>	<b><math>Q</math></b>
		[cm]	[pa.s]	$\left[\frac{kg}{m^3}\right]$	[°C]	[day]	[°C]	$\left[\frac{gal}{s}\right]$
Singh et al. (Laminar flow)	1	1.44	0.0087	838.5	22.2	5.0	8.3	1.0
	2						8.3	2.5
	3						8.9	4.0
	4						7.2	1.0
	5						4.4	1.0

Through our developed simulation, we predicted the deposit's thickness and solid wax fraction for all five cases. In Figure 5-14, the simulated results are plotted against the experiment data for deposit's thickness versus solid wax fraction. The predictions show great accuracy as they successfully track the experimental data for all five flow conditions.

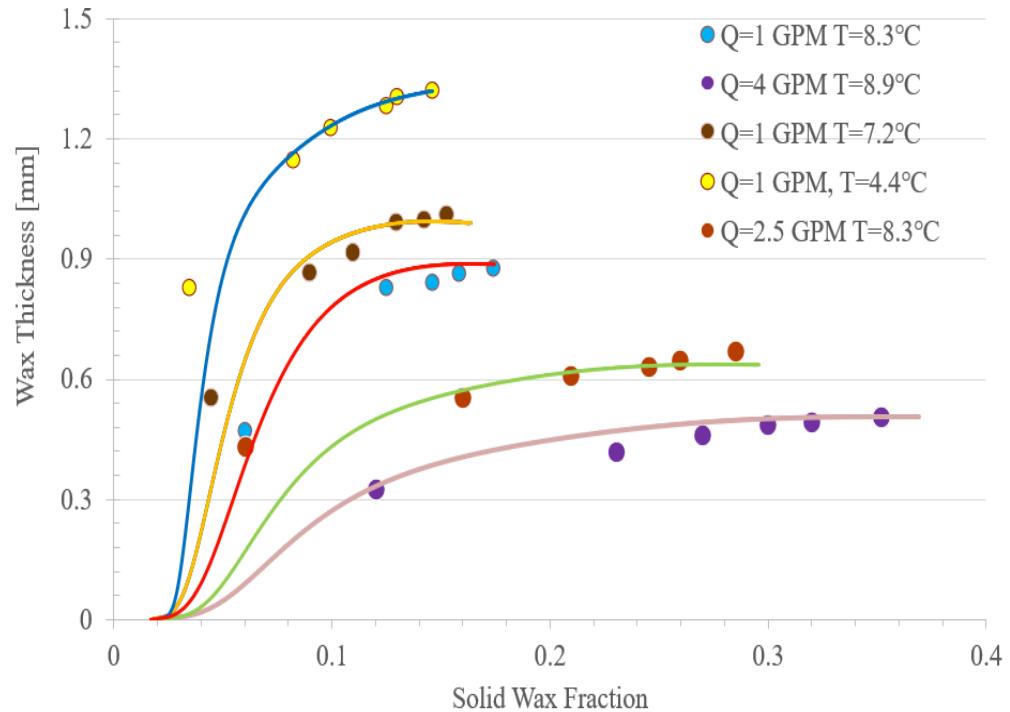


Figure 5-14: Deposit's thickness versus solid wax fraction. Points represent the experimental data and the solid lines are created by our developed simulation

In our modeling approach, we updated the bulk concentration axially using Eq. 3-73 and

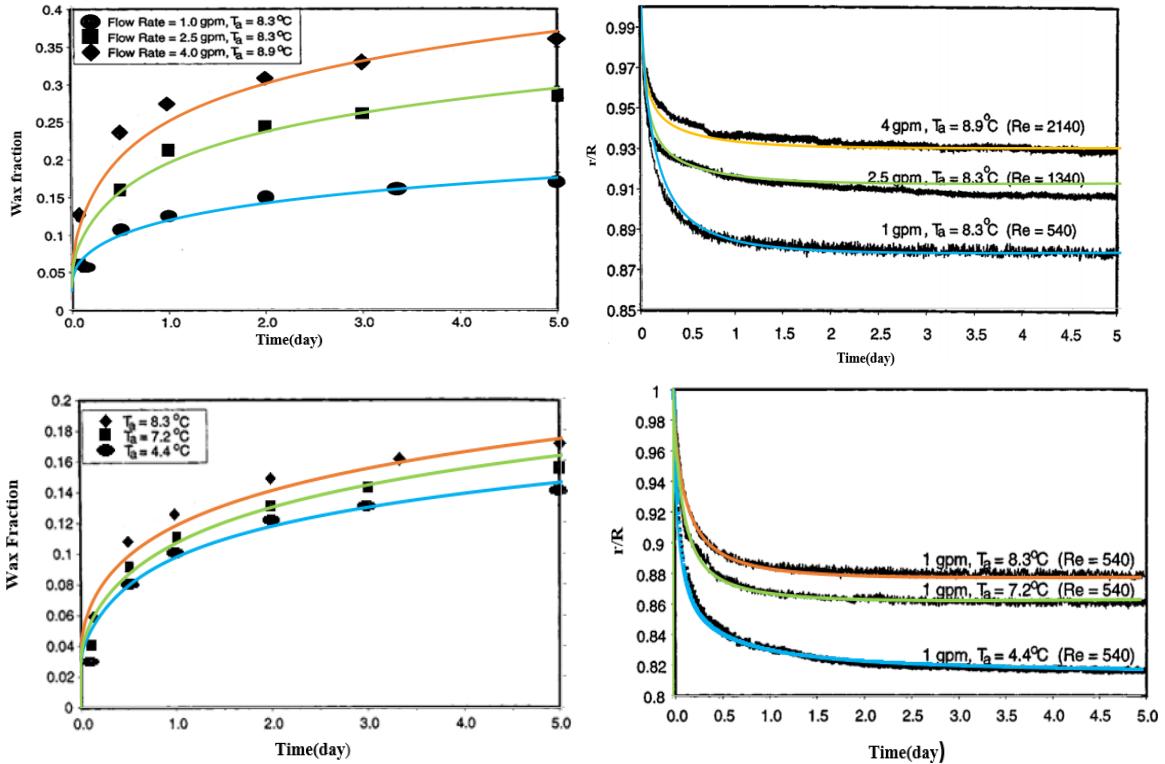


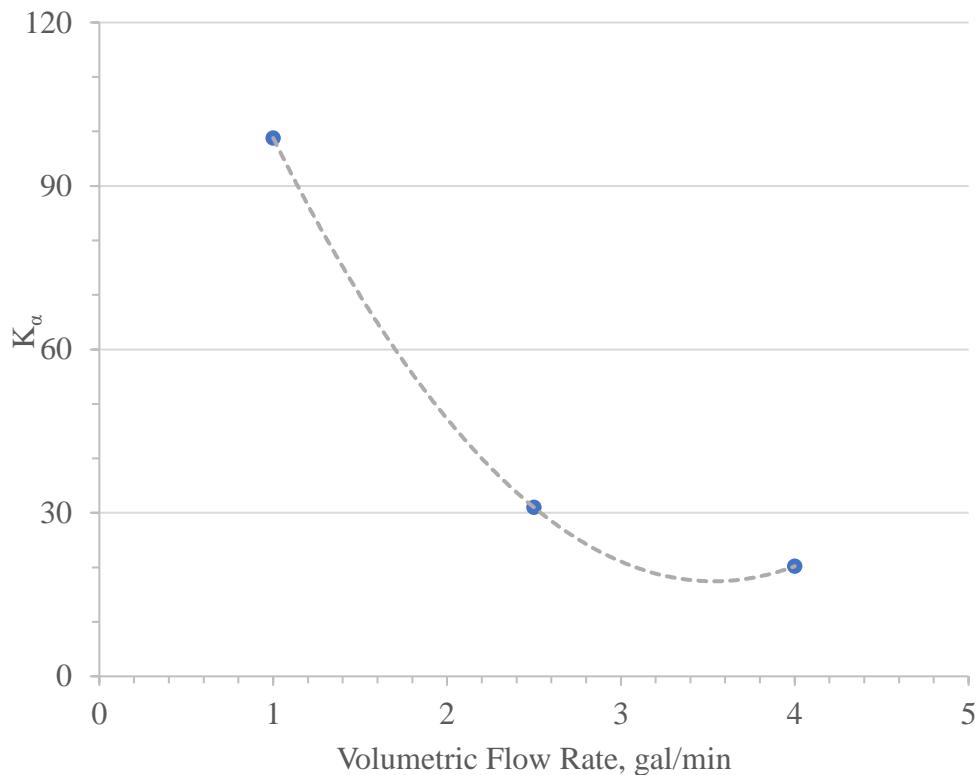
Figure 5-15: Simulation results versus experimental data for solid wax fraction and effective pipe's radius parameters. Colored lines are generated by our simulation and the rest are experimental data [3].

included it in the RK45 steps. This approach resulted in a slightly more accurate predictions in compare to Singh et al. predictions [3]. We also analyzed the crystal aspect ratio parameter (Eq. 3-57) based on the fitted  $k_\alpha$  values. The following table contains the adjusted  $k_\alpha$  values which are reported by the Levenberg-Marquardt optimization tool.

Table 5-9:  $k_\alpha$  values for different testing flow conditions

$T_{ambient}$ °C	Q gal/min	$K_\alpha$
8.3	1.0	98.8
8.3	2.5	31
8.9	4.0	20.2
7.2	1.0	107
4.4	1.0	146.3

From Table 5-9, it can be noticed that “ $\alpha$ ” decreases as flow rate increases. Assuming the same ambient temperature, the isolated effect of flow rate has been illustrated in Figure 5-16. Additionally, by assuming constant flow rate,  $k_\alpha$  increases as temperature decreases (Figure 5-17).

Figure 5-16: LM adjusted  $k_\alpha$  versus volumetric flow rate

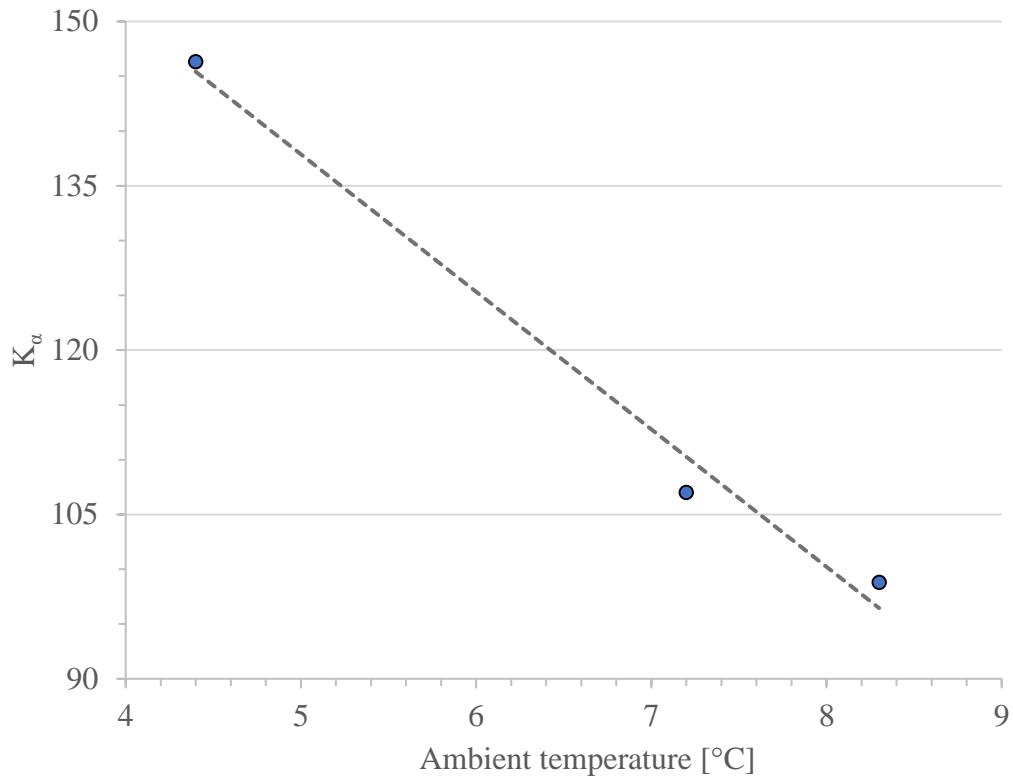


Figure 5-17:  $k_\alpha$  versus ambient temperature for  $Q_{oil} = 1 \text{ gal}/\text{min}$

Finally, we derived the wax crystal aspect ratio values from the  $\bar{F}_w$  predictions and plotted them versus solid wax fraction. Notably, the slopes are very similar to those reported in Table 5-9.

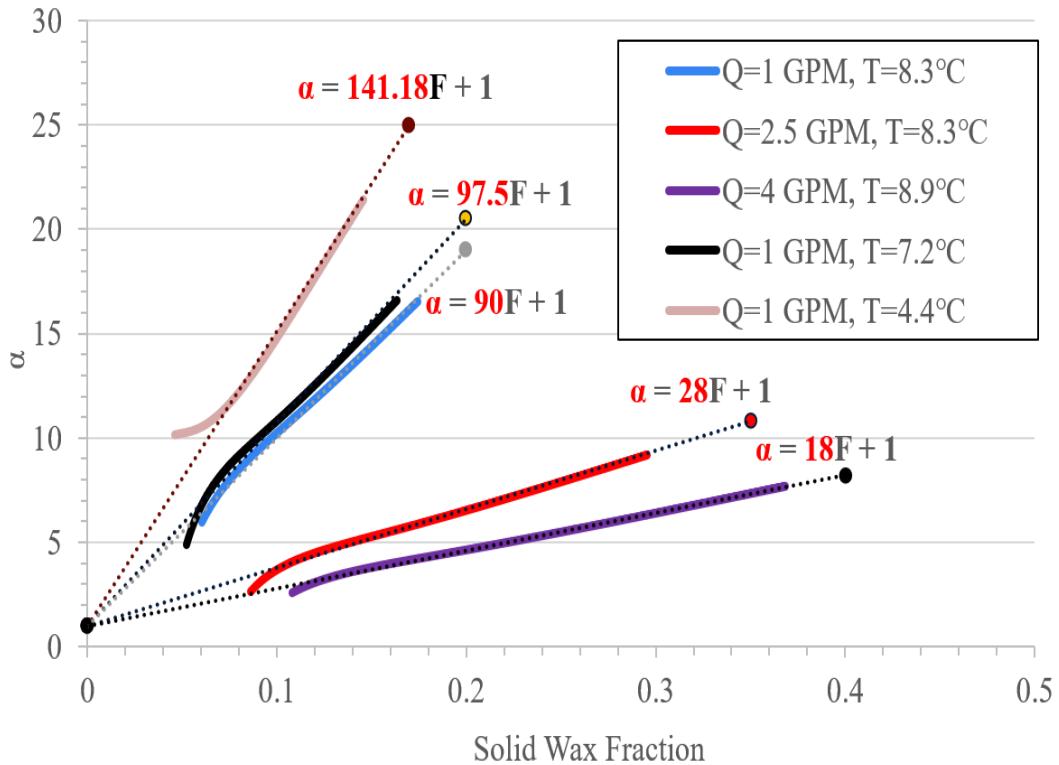


Figure 5-18: Derived crystal aspect ratio versus solid wax fraction for five operating conditions

### 5.3 SP-Depo Wax Deposition Model and Software

In this section, SP-Depo's accuracy will be verified by data from flow-loop experiments reported by Pancharoensawad [10]. Therefore, when we refer to a test number or a test condition, it is from Pancharoensawad dissertation [10] where all digitized data are available. The data types associated with each flow-loop experiment include deposit's thickness, solid wax fraction and deposit's solid phase carbon number distribution. In the following table, test conditions is presented [10].

Table 5-10: Test conditions of the used experiments [10]

Test #	Oil Velocity [m/s]	time [hr]	T <sub>h,inlet</sub> [°F]	Q <sub>c</sub> [gpm]	T <sub>C,inlet</sub> [°F]
36	2.25	48	107.1	4.4	83.8
24	2.24	48	105.3	4.8	82.9
25	2.24	32	105.8	4.8	82.9
26	2.25	16.4	106.3	4.8	82.8
27	2.24	4	105.5	4.8	82.8
32	1.83	48	105.5	4.4	83.1
18	1.83	48	104.9	4.7	83.2
31	1.83	32	104.5	4.4	83.3
20	1.83	32	105.4	4.7	83.1
19	1.83	16	105.5	4.7	83.1
30	1.83	16	104.9	4.4	83.1
28	1.83	4	105.4	4.4	83
21	1.19	48	105.2	4.8	84.3
23	1.19	32	104.8	4.7	84.1
22	1.19	16	105.1	4.7	84.2
29	1.19	4	105	4.4	84

For n-alkanes composition, there are three reported compositions in Panacharoensawad [10] from different sources as shown below. We use the composition from Bruno (2006) in our study.

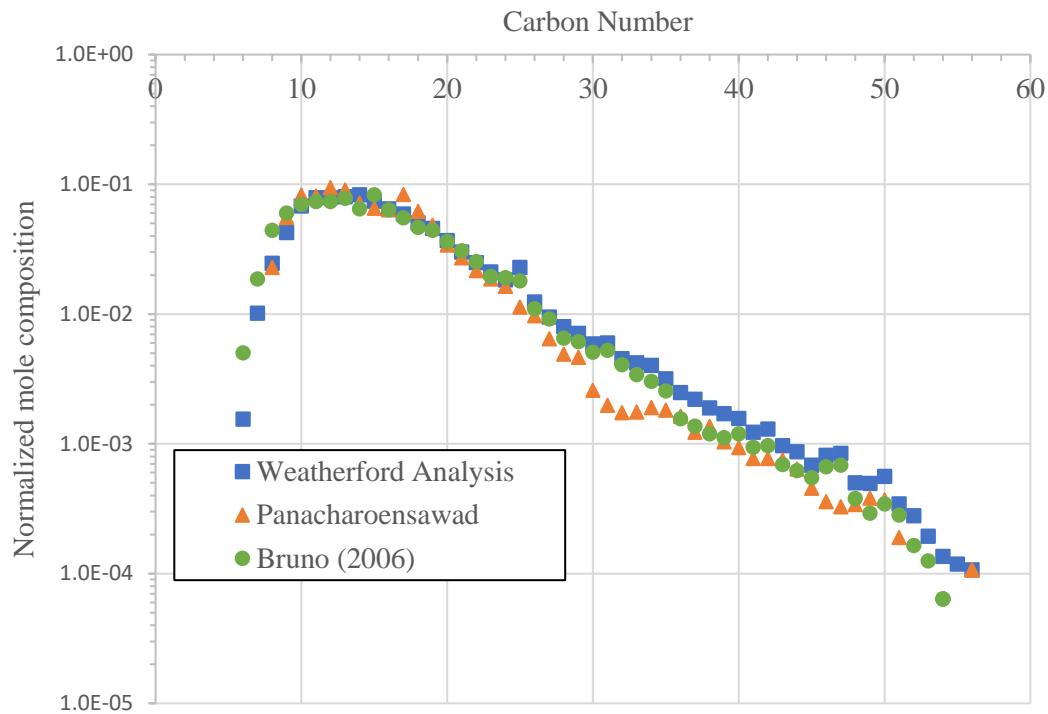


Figure 5-19: Normalized mole composition of South Pelto oil (used in Panacharoensawad [10])

In Table 5-11, the experimental thickness, solid wax fraction and solid phase average carbon number data are presented.

Table 5-11: Experimental data of deposit's thickness,  $F_w$  and ACN

Test #	Thickness [mm]	$F_w$ [%]	ACN
24	0.79	24.8	46.2
36	0.8	28.6	46.3
25	0.74	23.2	46.3
26	0.66	19.8	46.1
27	0.39	10.8	44.6
18	1.03	23	45.3
32	1.15	22	45.7
20	1.16	18.3	45.6
31	1.14	18.1	45.4
19	0.92	12.6	44.8
30	1	14.1	45.2
28	0.28	8.1	43.6
21	1.19	12	44.3
23	0.96	12.1	44
22	0.61	9.1	43.4
29	0.22	6.1	42.8

### 5.3.1 Minimum depositable carbon number (MinC)

As we discussed in chapter three, concentration,  $\frac{\partial C}{\partial T}$  and  $D_{wo}$  are calculated from SP-Wax thermodynamic model. Therefore, all required inputs (*Figure 4-9*) for SP-Wax are also needed for SP-Depo. In our SP-Wax thermodynamic model, the user should provide a value for the correction factor coefficient for Eq. 3-15 based on the experimental precipitation data for each n-alkane composition. Although, the precipitation data are not available for the South Pelto oil case, we used the deposit's solid phase CND to determine the correction factor coefficient for Weatherford and Bruno n-alkane compositions as follow:

$$a = \begin{cases} 3 \times 10^{-6} & \text{Weatherford n - alkane composition} \\ 2 \times 10^{-6} & \text{Bruno n - alkane composition} \end{cases} \quad (5-2)$$

Another important input parameter of SP-Wax thermodynamic model is the minimum carbon number or MinC. MinC is defined to be the smallest carbon number which

contributes to the deposition which is very similar to CCN. For MinC determination, the user should refer to Figure 3-2 and choose the minimum depositable carbon number based on the lowest operating temperature which usually is the coolant temperature. In our dataset [10], the coolant temperature is constant for more than sixteen single-phase flow-loop experiments and based on raw HTGC data of the deposit's composition, CCN is approximated to be 33 which is very similar to our simulation prediction of  $CN = 33$ .

Expectedly, deposit mostly contains oil with smaller fraction of the solidified phase. Therefore, raw HTGC data should show two carbon number distributions for both liquid and solid phases (Figure 5-20). It is almost impossible to know what the exact composition of each phase is using the HTGC data. However, it is possible to approximate each phase's composition. One method is to assume that carbon numbers before  $CN = 33$  are only in liquid phase and heavier n-alkanes are both in both phases. This assumption seems reasonable because our thermodynamic model also shows that it is nearly impossible for carbon numbers smaller than  $CN = 33$  precipitate at coolant temperature (Figure 5-21).

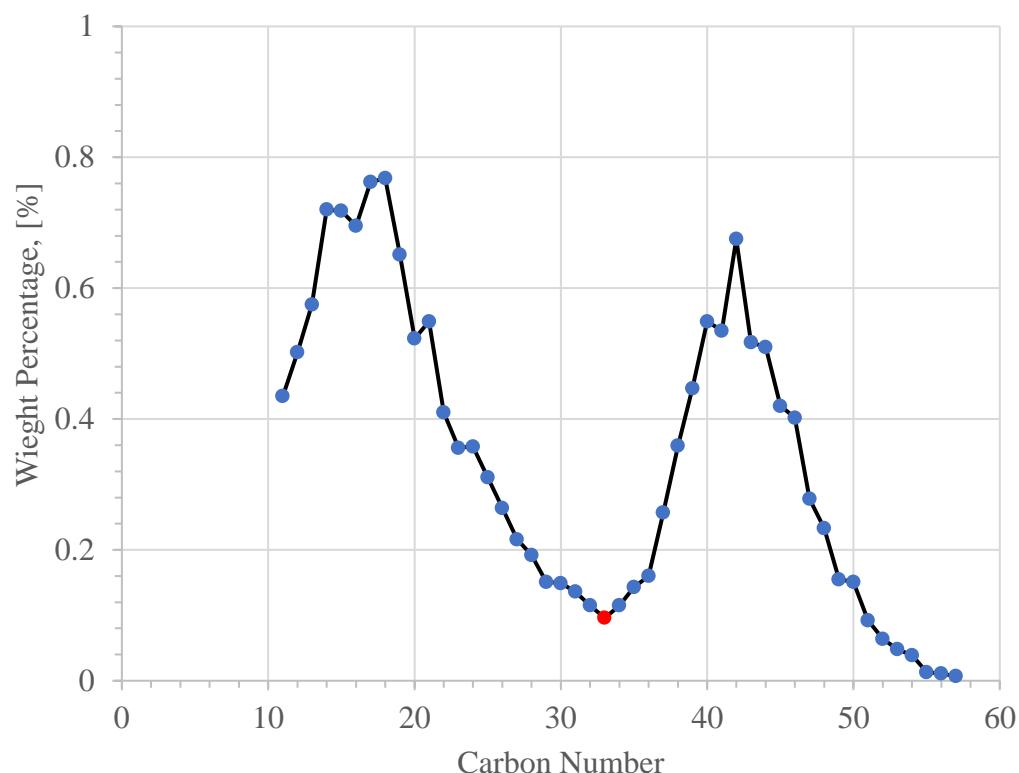


Figure 5-20: Deposit's raw HTGC data for Test #29 where  $CCN=33$  is determined by red

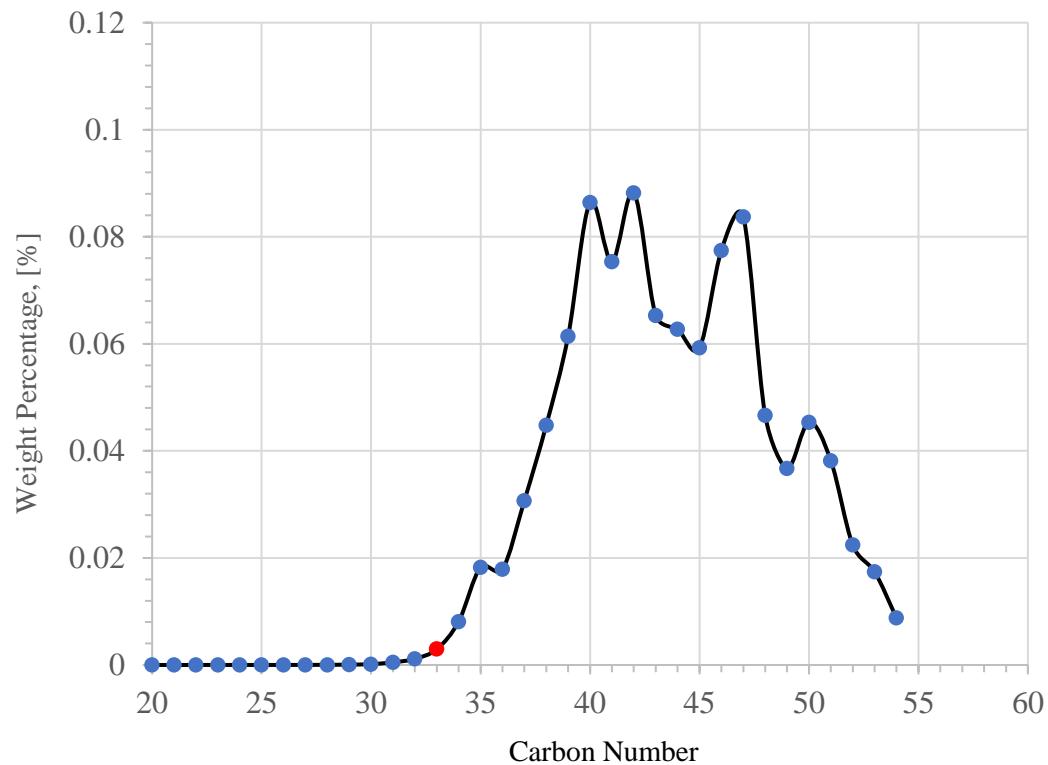


Figure 5-21: SP-Wax simulation: deposit's solid phase CND at coolant temperature ( $T=28.77^{\circ}\text{C}$ )

So, by accepting the above assumption, if we subtract the oil composition from the deposit's composition, the solid phase composition can be approximated. In Figure 5-22, the data for  $\text{CN} > 33$  were extrapolated using the equation which was resulted from fitted regression to data from  $\text{CN} = 27$  to 33.

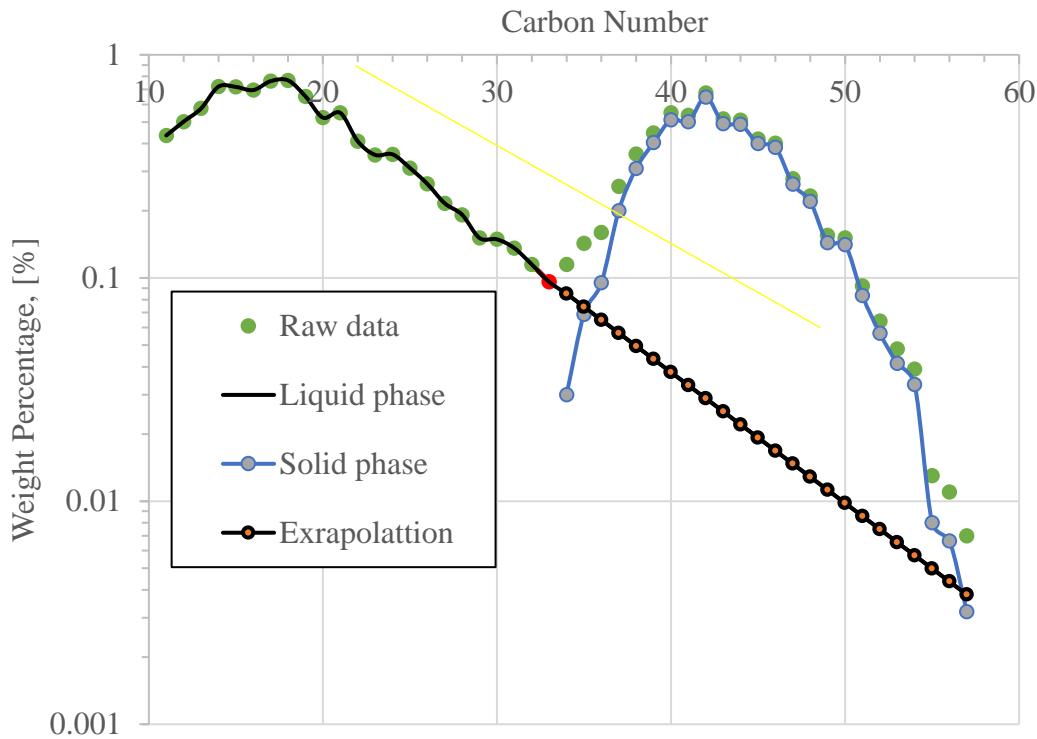


Figure 5-22: HTGC data with separated liquid and solid compositions.

Therefore, our developed method for determination of minimum depositable carbon number (MinC) is consistent with the experimental data.

### 5.3.2 Thickness and solid wax fraction predictions

After knowing the MinC, all required inputs are enough to run the wax deposition model. However, it is crucial to recheck the fitted regression equations to the thermodynamic data. In SP-Depo, we made it possible for the user to check fitted lines to concentration,  $\frac{\partial C}{\partial T}$  and  $D_{wo}$ . The following graphs, shows that all thermodynamic parameters are well represented by the fitted curves.

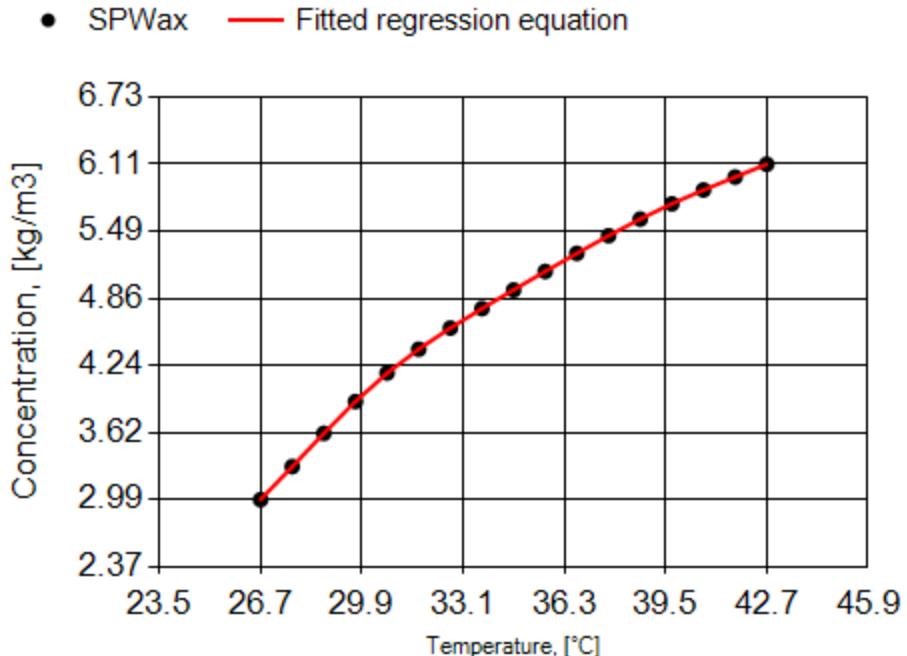


Figure 5-23: Concentration calculated from the SP-Wax thermodynamic model with fitted regression curve for South Pelto oil case

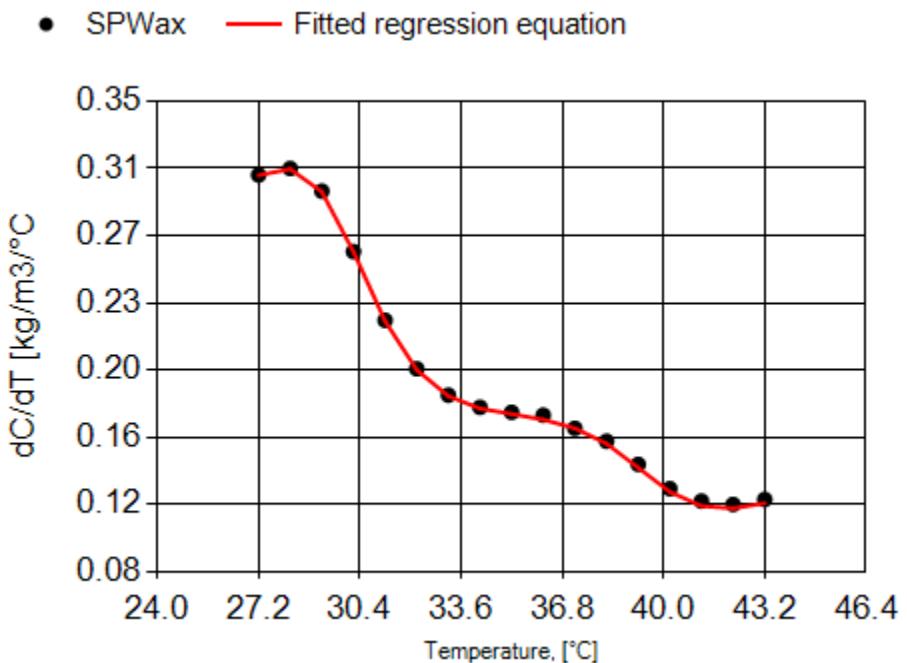


Figure 5-24:  $\frac{\partial C}{\partial T}$  calculated from the SP-Wax thermodynamic model with fitted regression curve for South Pelto oil case

- SPWax    — Fitted regression equation

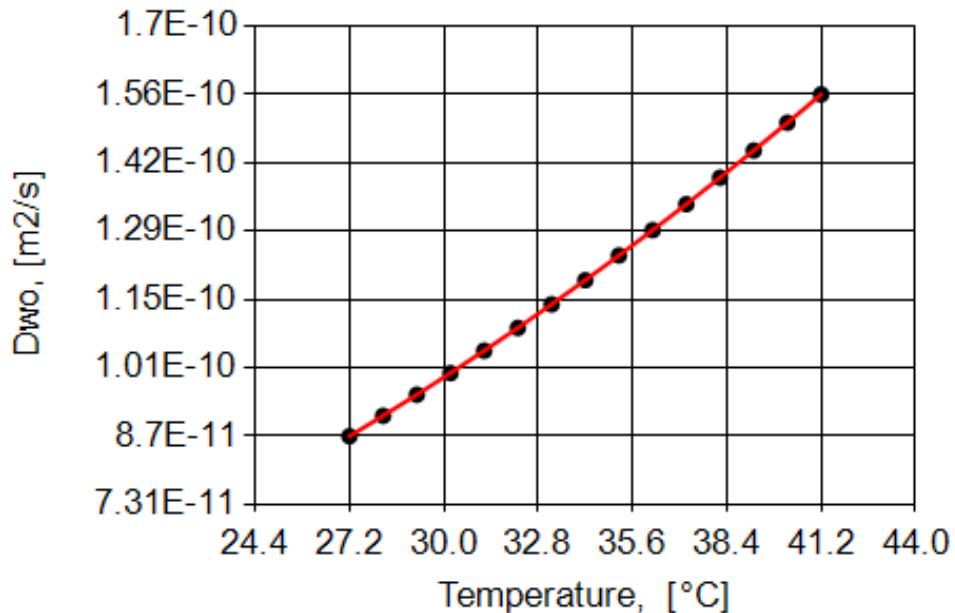


Figure 5-25:  $D_{wo}$  calculated from the SP-Wax thermodynamic model with fitted regression curve for South Pelto oil case

So, after reassuring about the thermodynamic model and the fitted regression equations, the software can be run. In SP-Depo, deposit's thickness, solid wax fraction and solid phase CND are predicted for each axial section. In the two following graphs, SP-Depo predicted thickness and  $F_w$  profiles are plotted using SP-Comp wax deposition model.

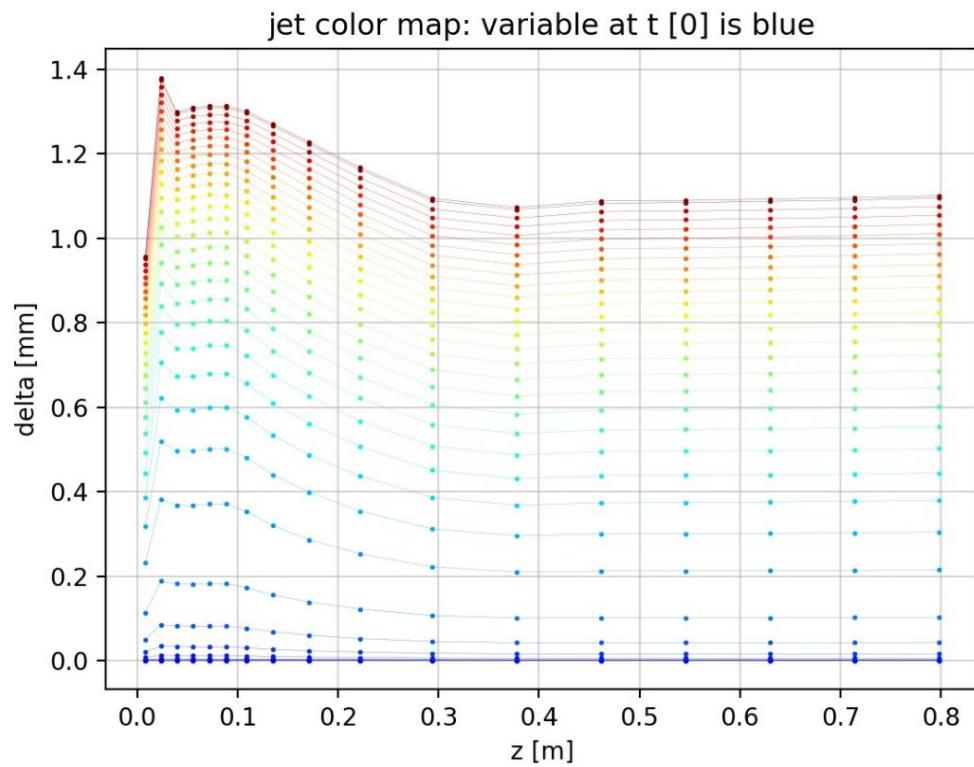


Figure 5-26: Deposit's thickness axial profile for Test #21 ( $V_{oil} = 1.19 \text{ m/s}$ )

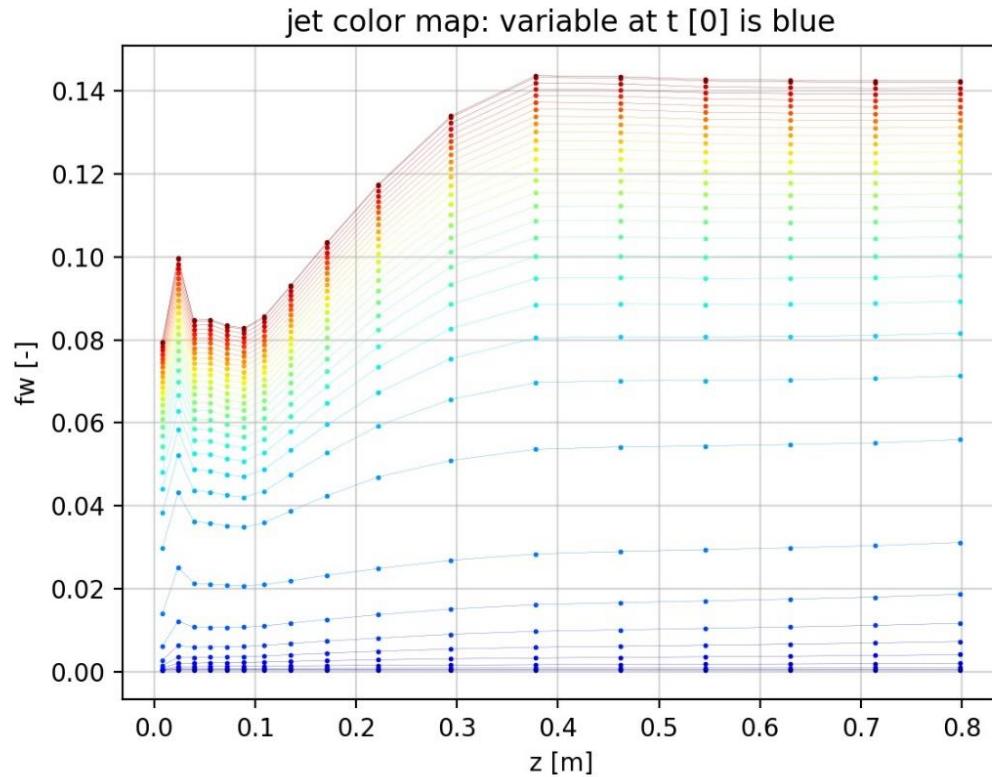


Figure 5-27: Deposit's solid wax fraction axial profile for Test #21 ( $V_{oil} = 1.19 \text{ m/s}$ )

And average deposit's thickness and solid wax fraction have been plotted against the experimental data in Figure 5-28, Figure 5-29 and Figure 5-30. Notably, SP-Depo successfully predicts thickness and solid phase wax fraction for all three flow conditions using SP-Compo wax deposition model. In SP-Depo, Dormand-Prince ODE solving method has been used which incorporates adaptive step size when rate of change is high. In the three following graphs, denser discretization is chosen at earlier times due to higher rate of change.

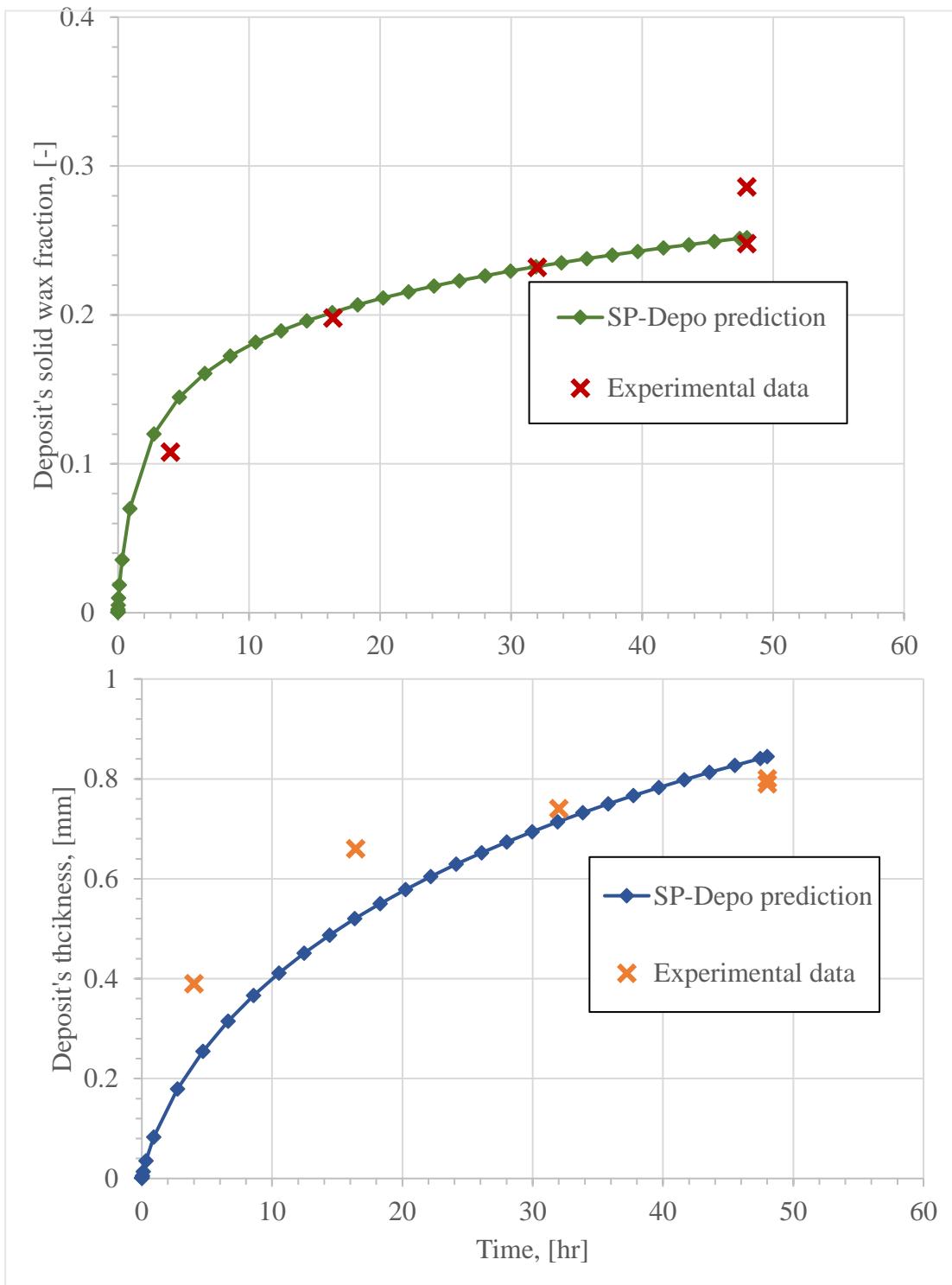


Figure 5-28: Average deposit's and solid wax fraction predictions versus experimental data for  $V_{oil} = 2.24 \text{ m/s}$

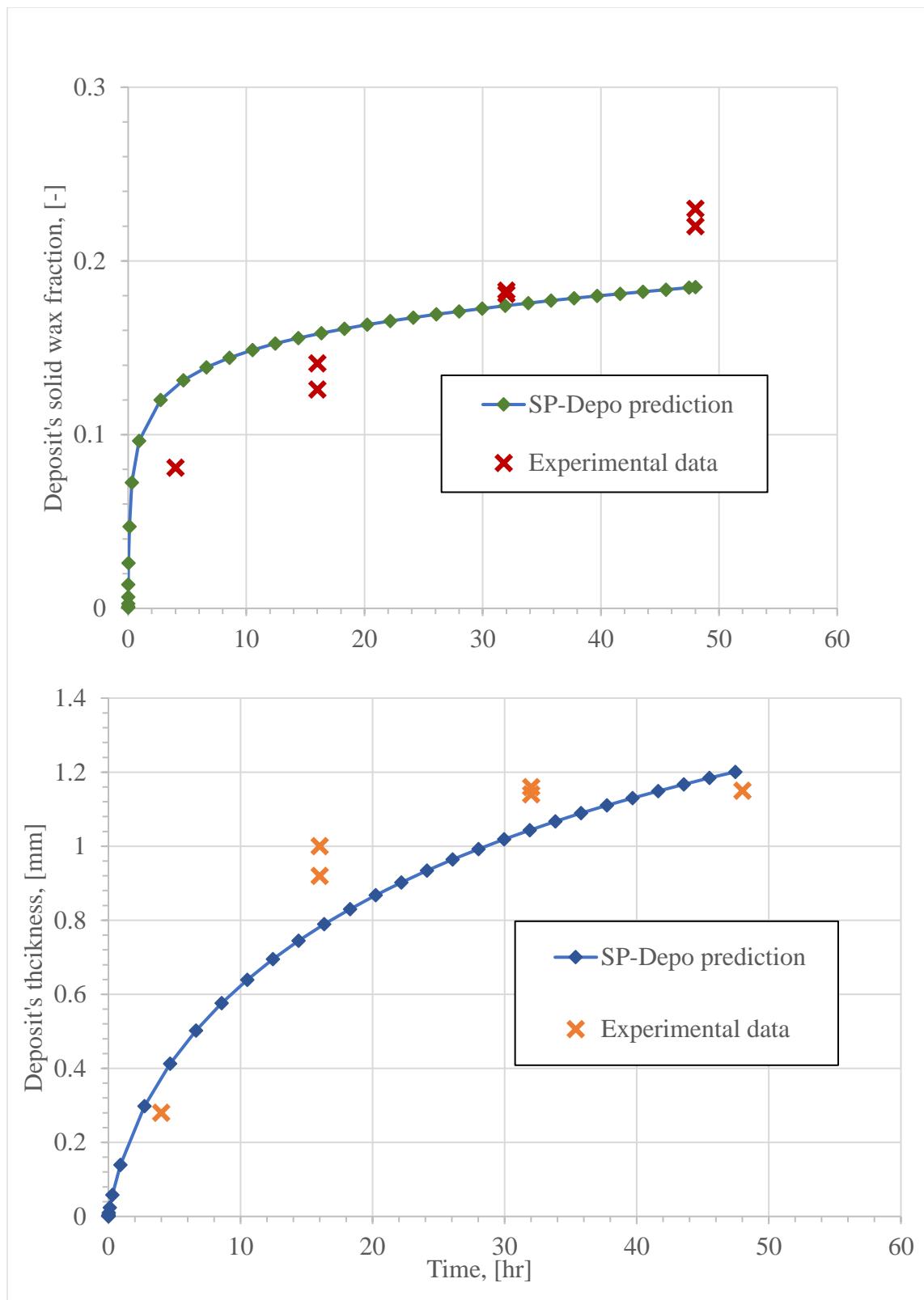


Figure 5-29: Average deposit's and solid wax fraction predictions versus experimental data for  $V_{oil} = 1.83 \text{ m/s}$

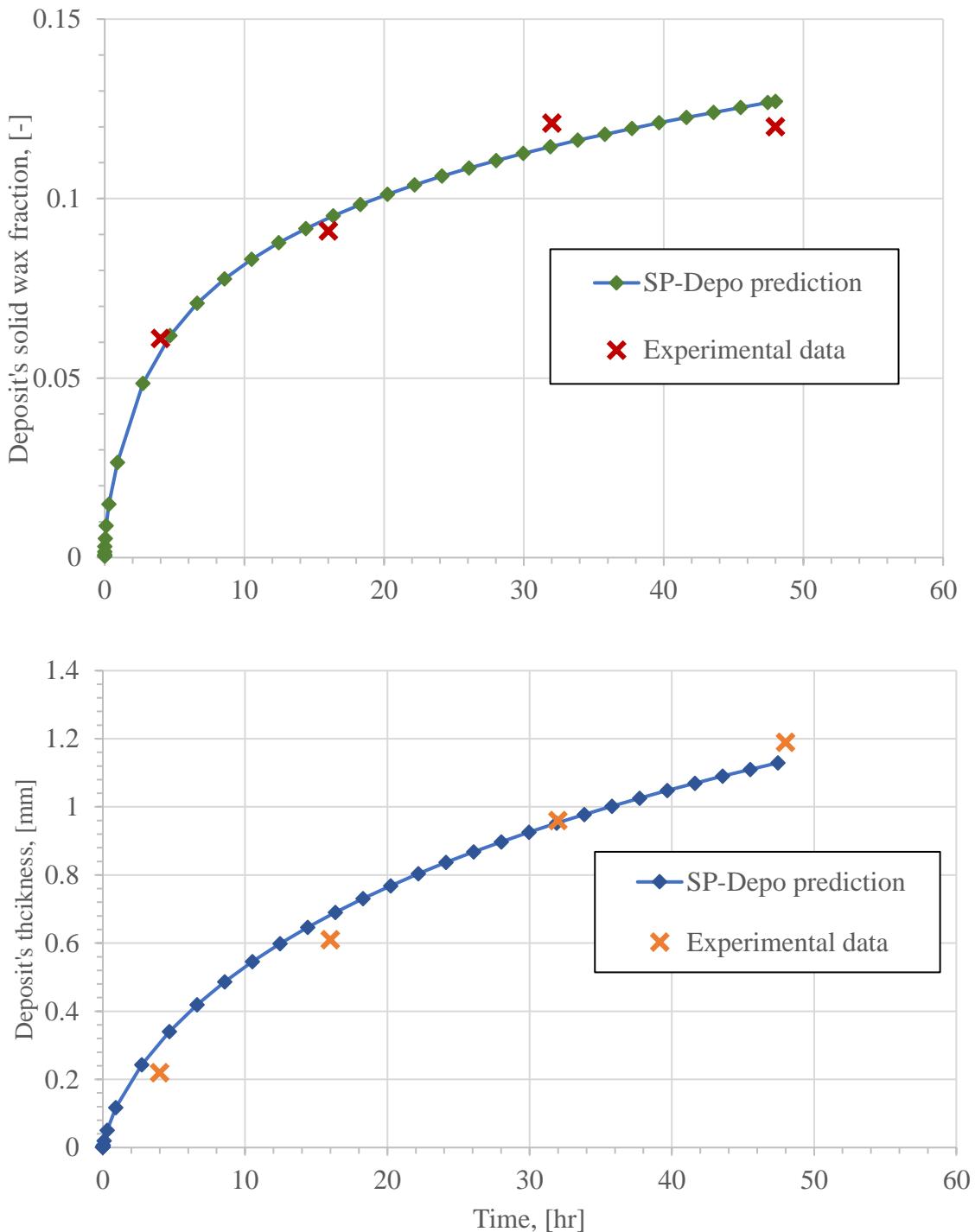


Figure 5-30: Average deposit's thickness and solid wax fraction predictions versus experimental data for  $V_{oil} = 1.19 \text{ m/s}$

In SP-Compo wax deposition model, the governing equations from Panacharoensawad [10] have been used where no precipitation curve and  $k_\alpha = 1$  have been assumed. Moreover, *msr1* and *msr2* fitting parameters were adjusted using Levenberg-Marquardt non-linear optimization tool which are coded in SP-Depo (Table 5-12).

Table 5-12: Determined fitting parameters in Eq.3-63 and Eq.3-64 by LM algorithm in SP-Depo

$V_{oil}$ [m/s]	msr1	msr2
1.19	15.53	12.25
1.83	13.30	90.86
2.24	5.34	26.36

### 5.3.3 Deposit's solid phase composition

Carbon number distribution of the deposit is crucial for pigging frequency planning and chemical treatment design. Longer chain n-alkanes form stronger deposits which are harder to be removed from the pipe. So, it is important for a wax deposition software to predict deposit's solid phase composition. Fortunately, SP-Compo model predicts the deposit's solid phase average carbon number (ACN) and carbon number distribution (CND) in addition to thickness and solid wax fraction parameters. In SP-Depo software, the temperature terms ( $T_{wh}$ ,  $T_{dep}$  and  $T_i$ ) are calculated based on the estimated deposit's thickness and solid wax fraction. Then, the thermodynamic model is used to predict solid phase CNDs at the mentioned temperatures.

Waxy deposits can be characterized by three temperatures including interface temperature ( $T_i$ ), average deposit temperature ( $T_{dep}$ ) and pipe wall temperature ( $T_{wh}$ ).

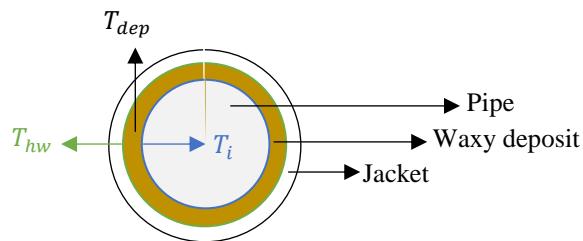


Figure 5-31: The deposit's surrounding temperatures

Right after the start of the experiment, a layer of waxy deposit is formed which mostly contains oil which is trapped in a 3D network of solidified wax molecules. In time, the oil content decreases and solid wax fraction increases through a counter-diffusion process (Figure 5-13). Also,

Due to concentration gradient within the deposit, some of the dissolved wax molecules (larger than CCN) move from the interface to the pipe's wall where much lower temperature exists. Even though it is nearly impossible to quantify such movement of wax molecules in the deposit, it is almost certain that the solidified molecules were precipitated at a temperature between  $T_{wh}$  and  $T_i$ . In Figure 5-32 and Figure 5-33, the predicted wall and interface temperatures are plotted. The temperature difference between the pipe's wall and the deposit's interface increases and reaches up to  $\Delta T \cong 9^\circ\text{C}$ .

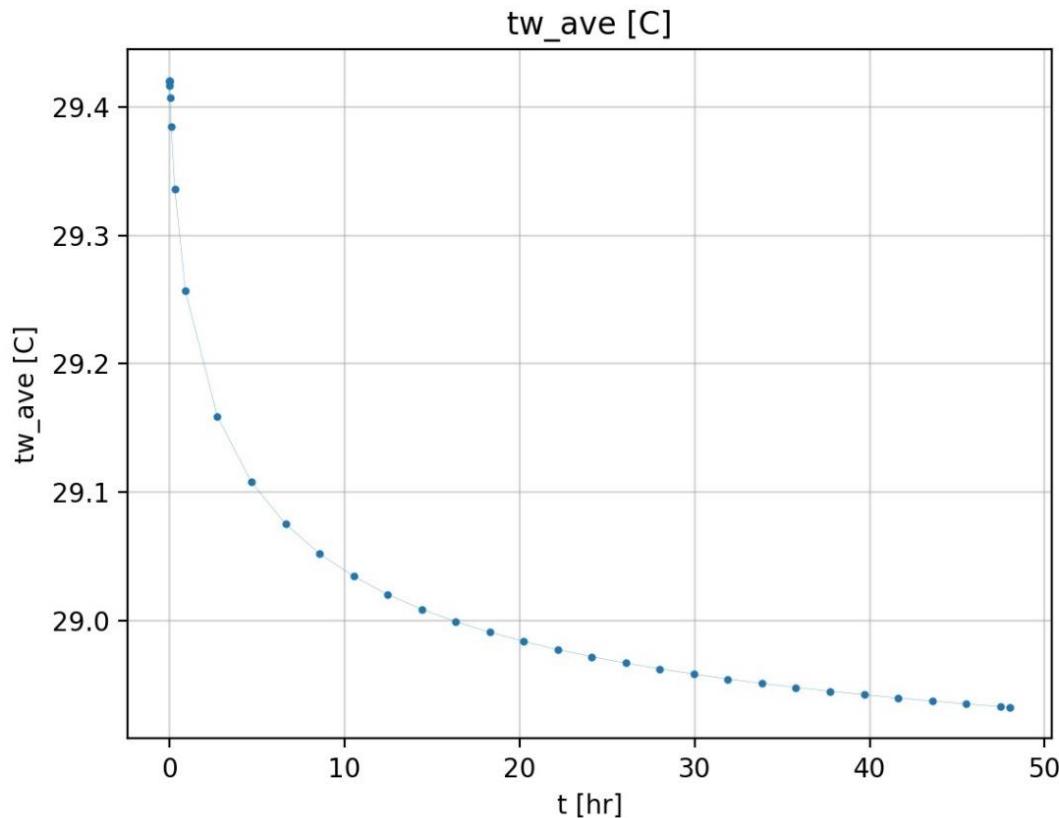


Figure 5-32: Pipe's inner wall temperature ( $T_{wh}$ ) for Test #21

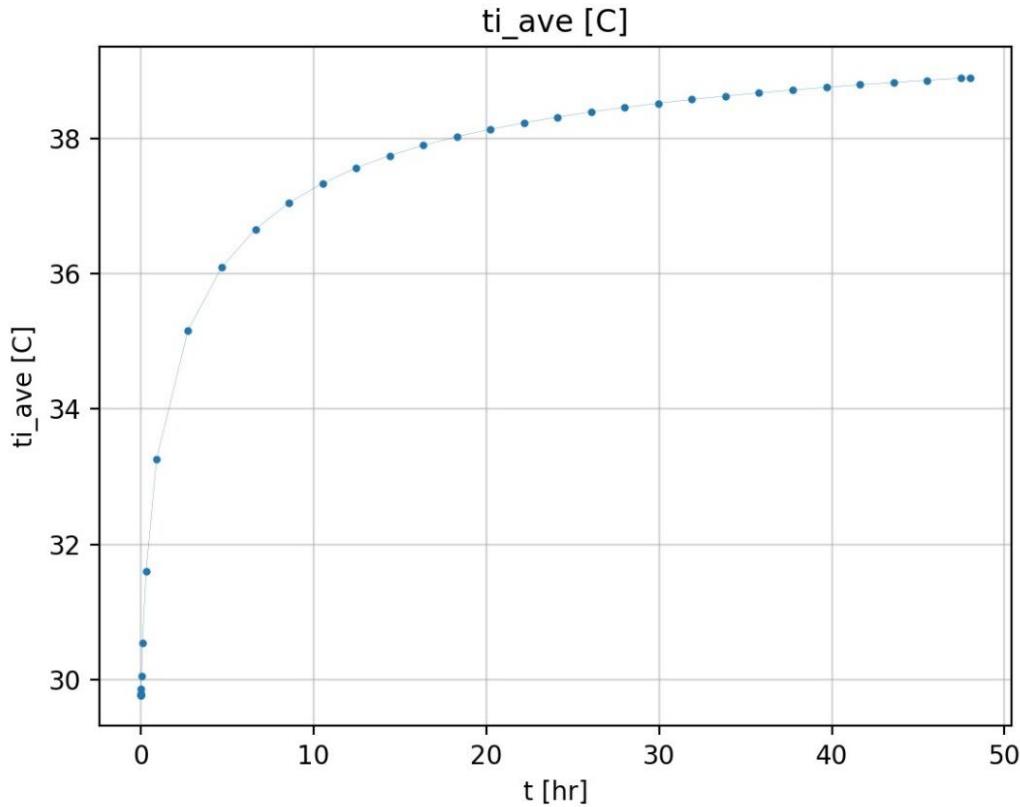


Figure 5-33: The deposit's interface temperature ( $T_i$ ) for Test #21

Consequently, the deposit's solid phase carbon number distribution (CND) should also lay between the predicted CNDs at  $T_{wh}$  and  $T_i$ . In the following graph, the predicted ACN profile for test #21 is shown. Near inlet, ACN is predicted to be higher which is consistent with experimental data reported by Panacharoensawad [10]. He showed that experimental ACN is correlated with the local heat transfer coefficient where it is the highest near the inlet.

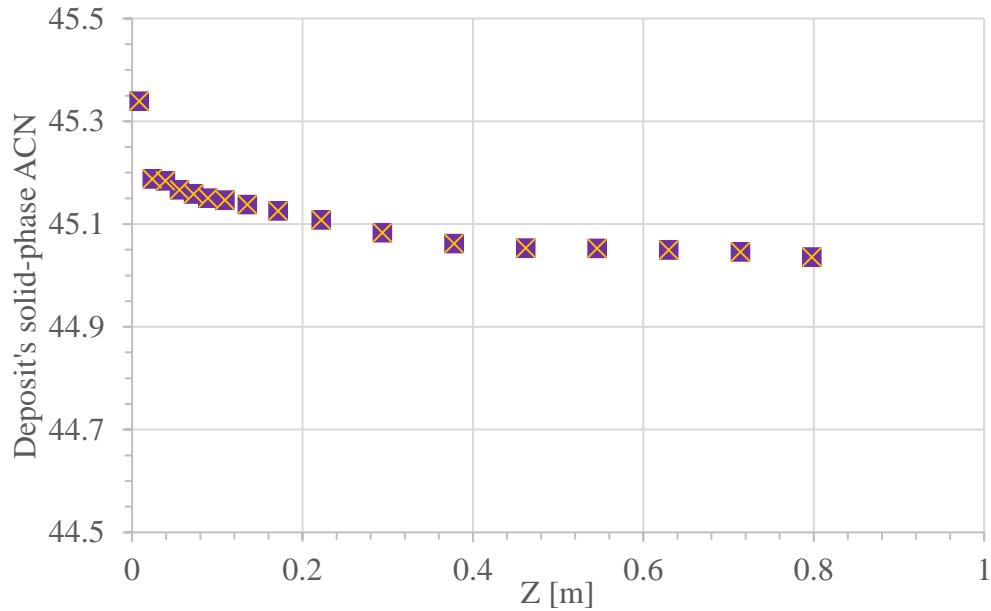


Figure 5-34: Predicted solid phase ACN in axial direction for test #21

In the following graph, experimental solid phase CND are plotted versus SP-Depo predictions at  $T_{wh}$ ,  $T_i$  and  $T_{dep} = \frac{T_i + T_{wh}}{2}$ , for Test #32. In Figure 5-35, predicted CNDs at  $T_{wh}$  and  $T_i$  are considered as the lower and upper bounds for CND prediction, respectively. Furthermore, in, predictions for solid phase average carbon number (ACN) at  $T_{wh}$ ,  $T_i$  and  $T_{dep}$  are plotted against the experimental data. In Figure 5-36, it is shown that the experimental ACN data are bounded within the two limiting ACN predictions which are predicted at deposit's interface and inner pipe's wall temperature. Please note that the same fitting parameters (*Table 5-12: Determined fitting parameters in Eq.3-63 and Eq.3-64 by LM algorithm in SP-Depo*), which are determined previously using thickness and solid wax fraction data, are used for solid phase composition predictions.

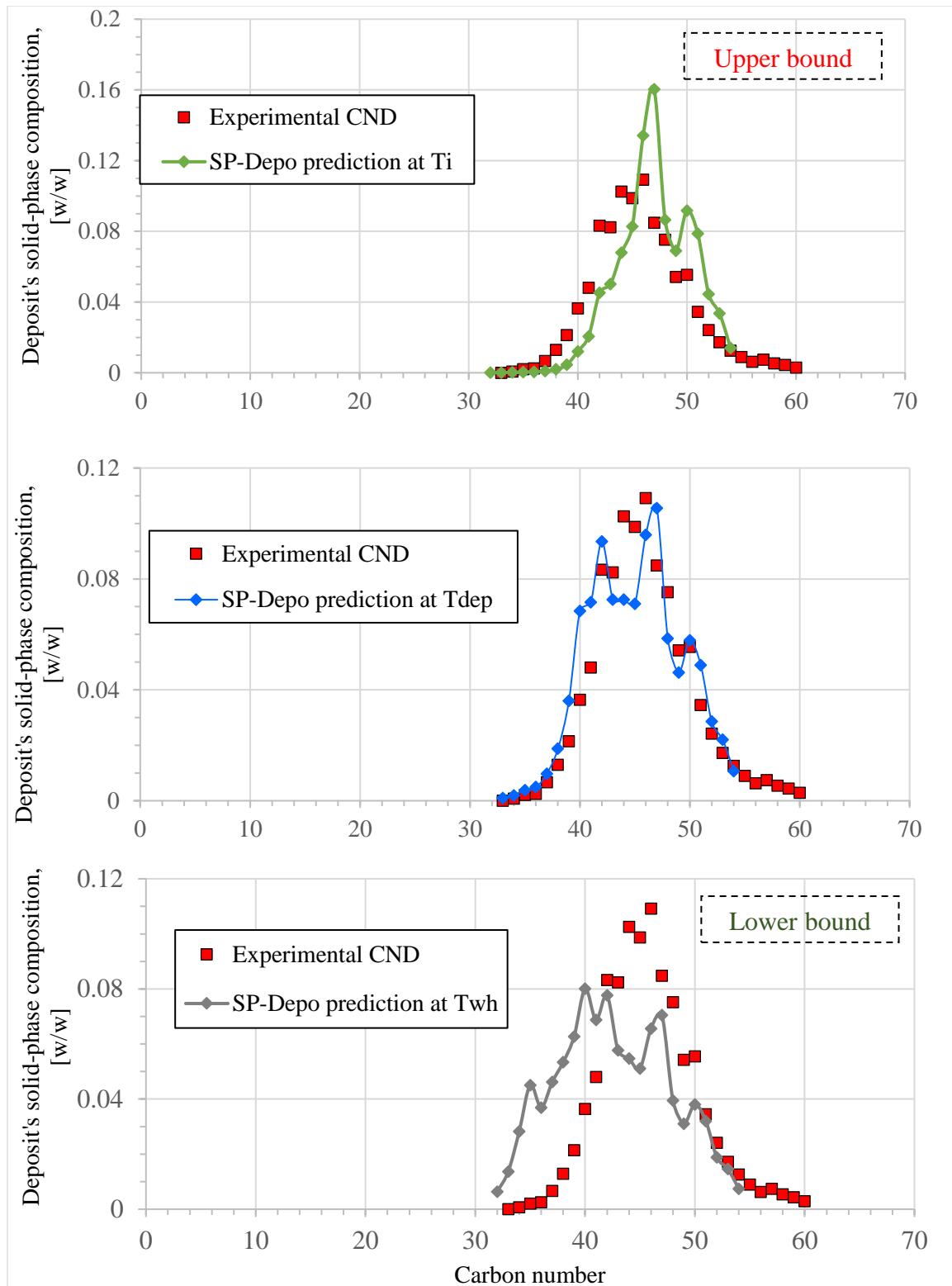


Figure 5-35: Experimental CND versus SP-Depo predictions at interface, average and wall temperatures, respectively for Test #32.

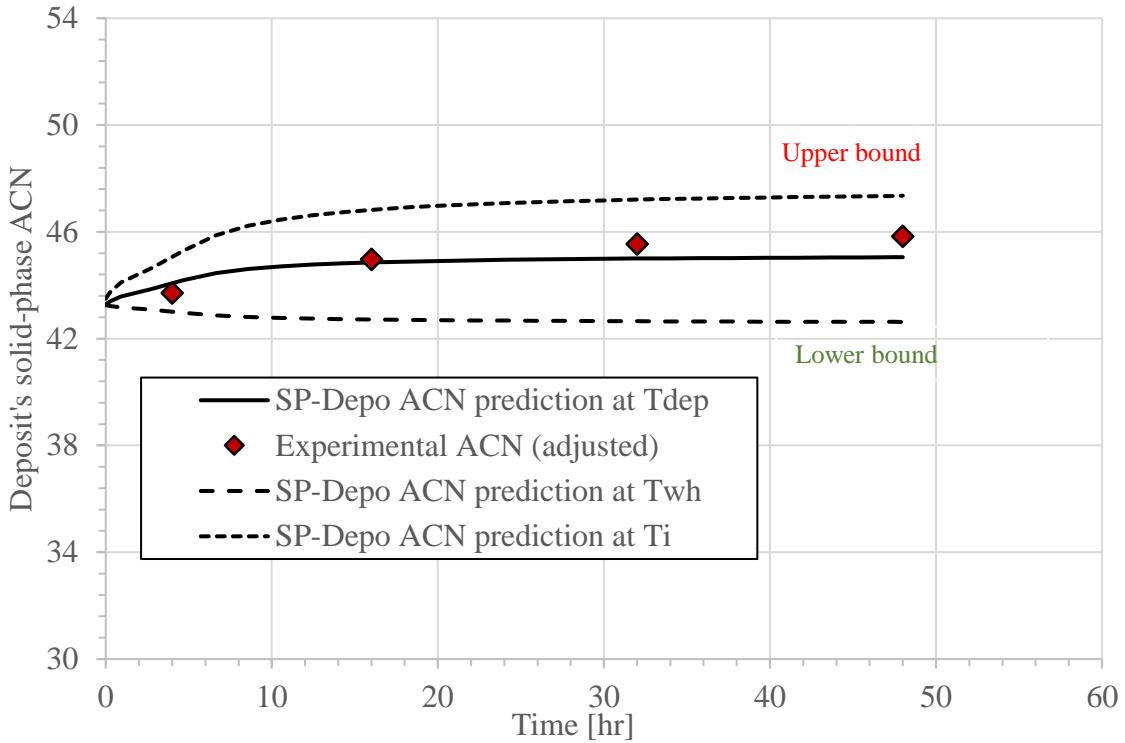


Figure 5-36: ACN prediction at  $T_{wh}$ ,  $T_{dep}$  and  $T_i$  versus experimental data. ACN was adjusted and updated after subtracting the oil composition from the raw HTGC data for  $V_{oil} = 1.83 \text{ m/s}$

- **Effect of shear stress on ACN prediction**

In the deposit, the lighter wax crystals are likely to break by the shear force which is exerted by the high velocity flow. Panacharoensawad [10] showed that the experimental solid phase ACN increases with initial shear stress. In our study, we estimated the solid phase ACN for three oil velocities (Table 5-10) and investigated the effect of shear stress on the carbon number distribution of the solidified phase using SP-Depo. We previously showed that SP-Depo accurately predict the thickness and solid wax fraction for the three flowing conditions through Figure 5-28 to Figure 5-30 using the adjusted fitting parameters shown in Table 5-12. By using the same fitting parameters, we plotted the predicted ACN versus the experimental data and showed that the average carbon number of the solidified phase increases with shear stress.

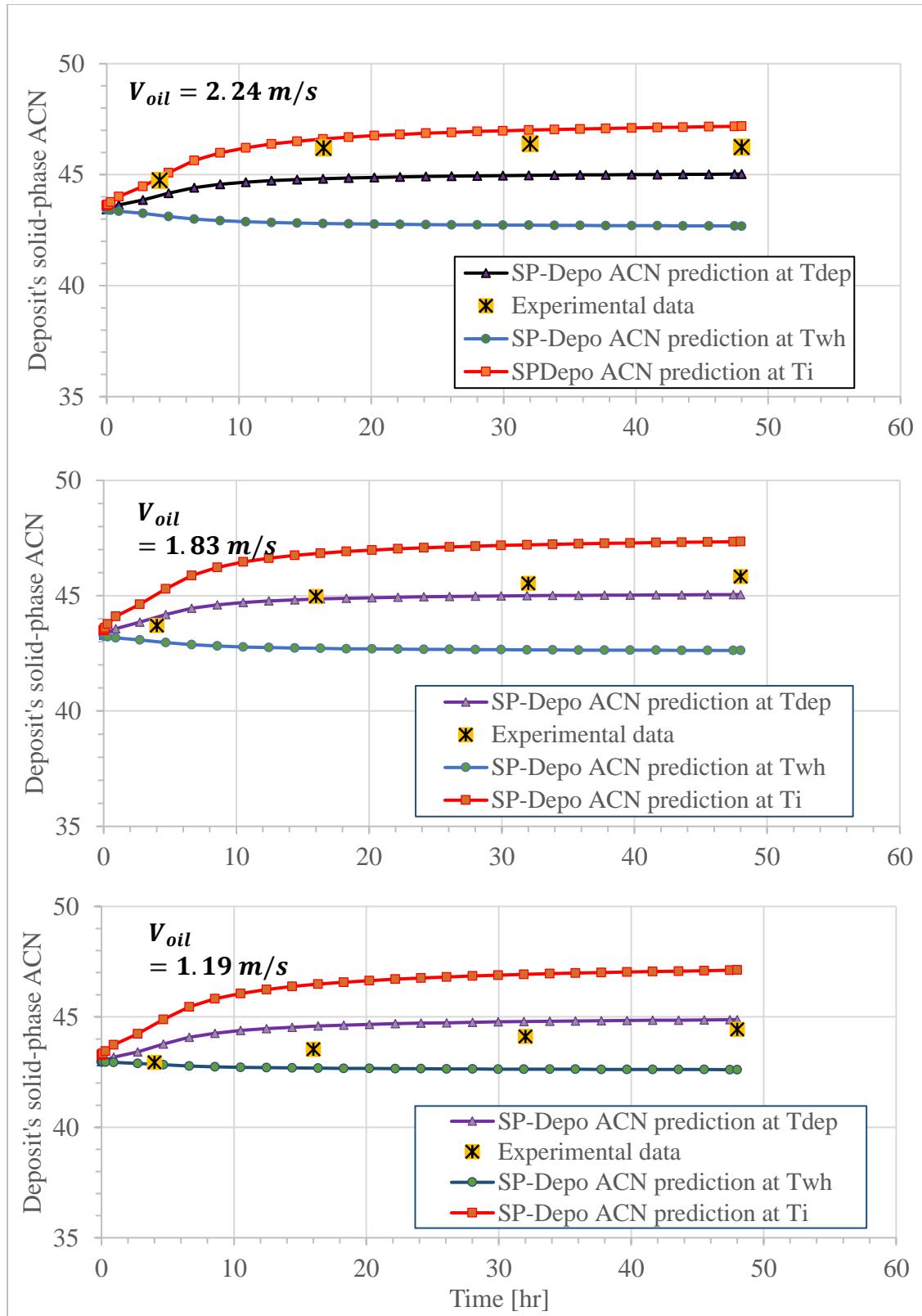


Figure 5-37: Predicted and experimental ACN for three oil velocities

In Figure 5-37, at the lower velocity ( $V_{oil} = 1.19 \text{ m/s}$ ), the experimental ACN data are close to the lower bound prediction which gradually approach toward the upper limit as velocity increases. This behavior is mainly due to the shear effect which results in the breakage and removal of lighter n-alkane crystals. The following schematic illustrates the effect of shear stress on the deposit.

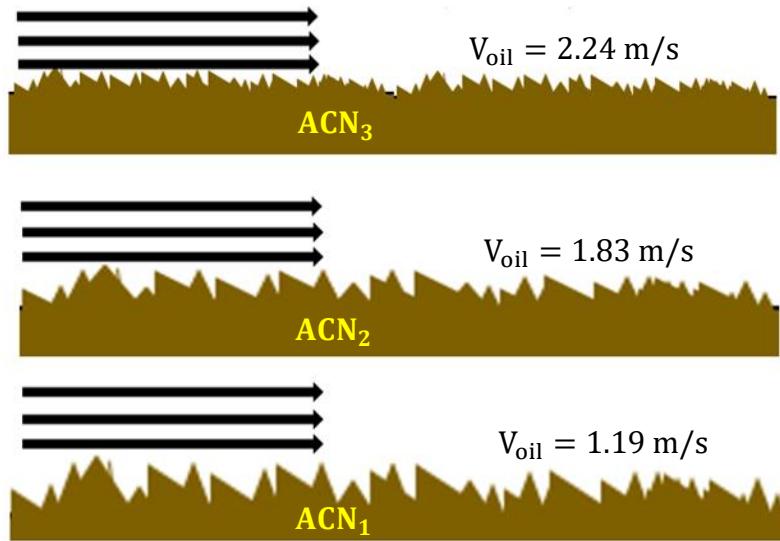


Figure 5-38: Effect of shear stress on the deposit. As oil velocity increases, shorter n-alkanes will be removed by the flow because of their low yield stress and ACN will increase ( $ACN_3 > ACN_2 > ACN_1$ ).

In Figure 5-39, total solid mass is plotted versus time for different grouped components where groups C43-C46, C39-C42 and C47-C50 contain highest amount of solid wax in the deposit, respectively.

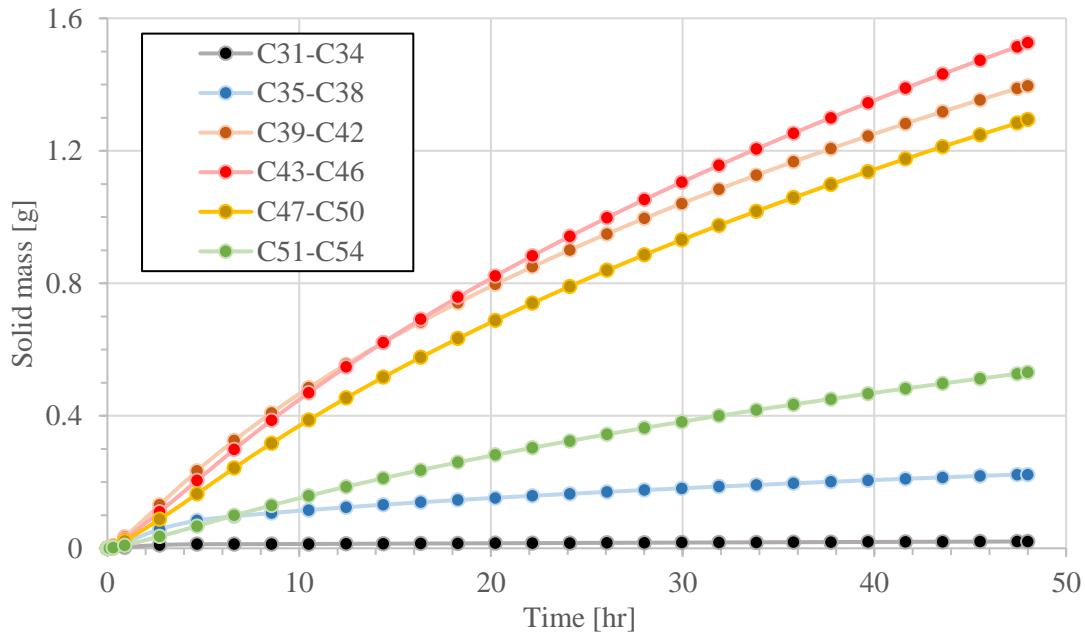


Figure 5-39: solid mass of grouped components versus time.

### 5.3.4 Sensitivity analysis

In this section, different input n-alkane compositions will be used, and the results will be shown. Then, different scenarios for longer and bigger pipes will be presented to investigate the applicability of SP-Depo for longer pipes and different conditions. For South Pelto showed three n-alkane compositions for

#### Effect of input n-alkane composition

SP-Depo is greatly dependent on the n-alkane composition of the oil which should be provided as an input for SP-Compo wax deposition model. Panacharoensawad [10] provided three n-alkane compositions for South Pelto oil which has been used in his experiments (Figure 5-19). So far, we have used the n-alkane composition reported by Bruno (2006) in our illustrative examples. Now, we will use the Weatherford n-alkane compositions and compare the results through the following graphs.

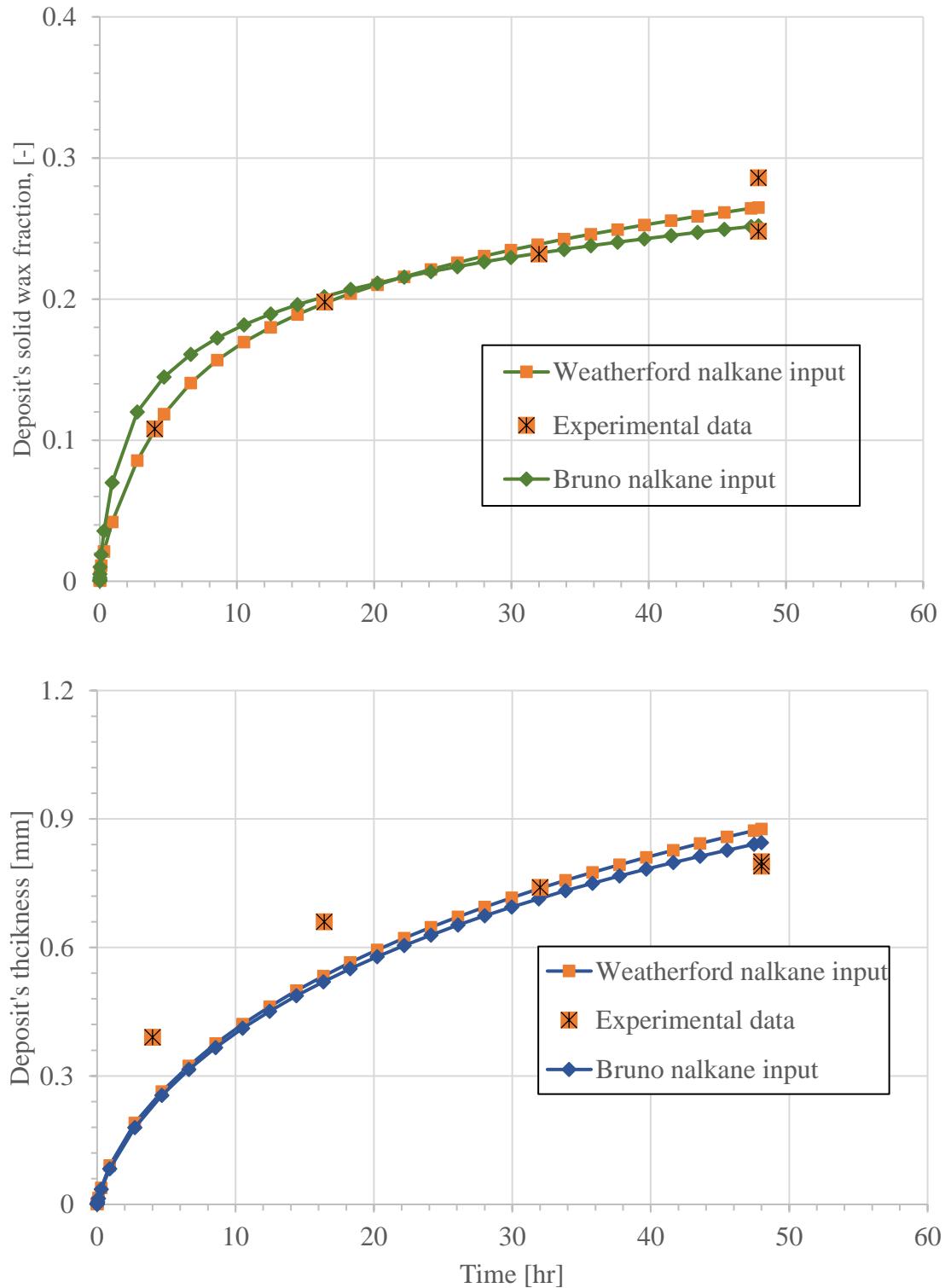


Figure 5-40: Average deposit's and solid wax fraction predictions from Bruno and Weatherford n-alkane compositions for  $V_{oil} = 2.24 \text{ m/s}$

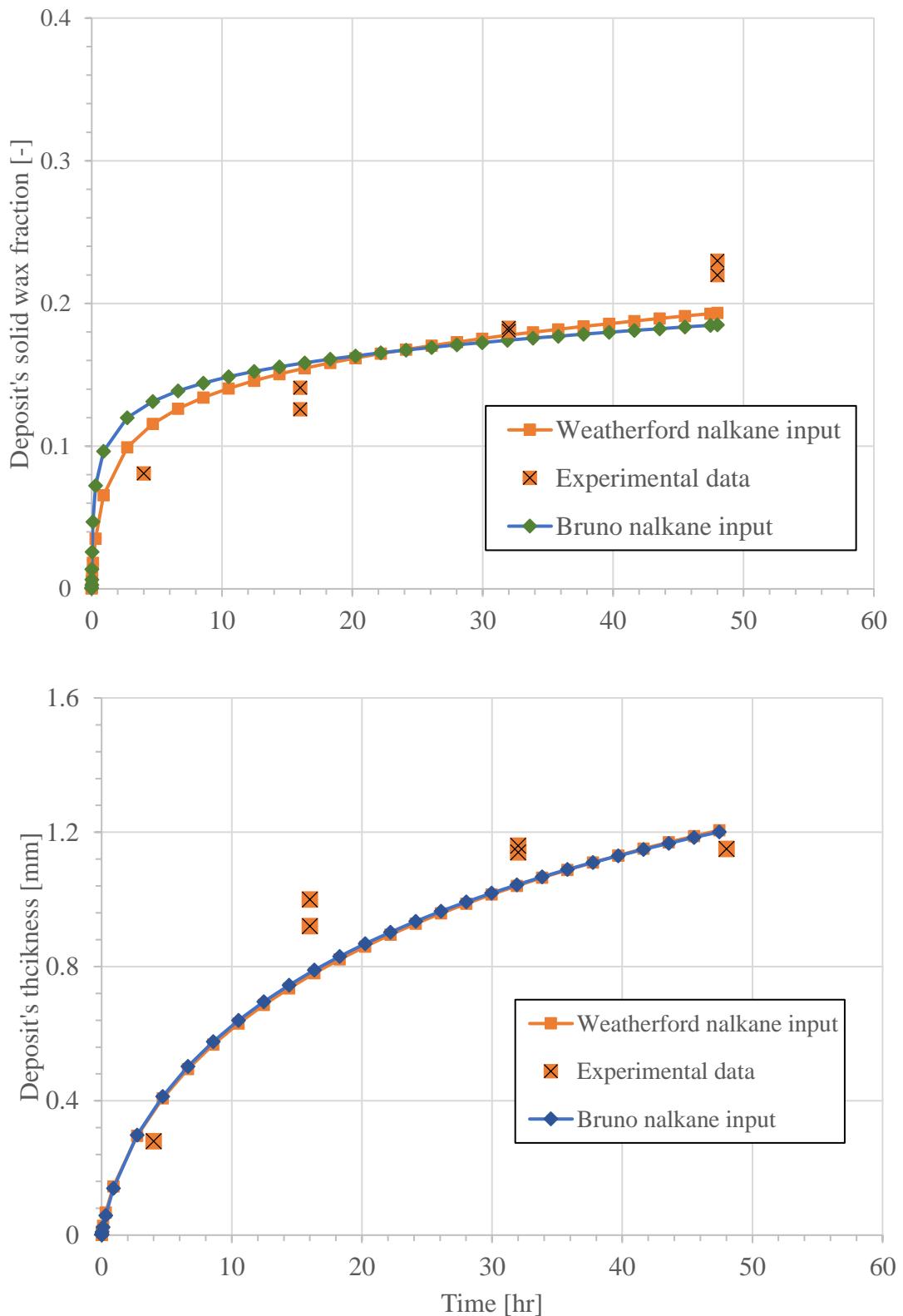


Figure 5-41: Average deposit's and solid wax fraction predictions from Bruno and Weatherford n-alkane compositions for  $V_{oil} = 1.83 \text{ m/s}$

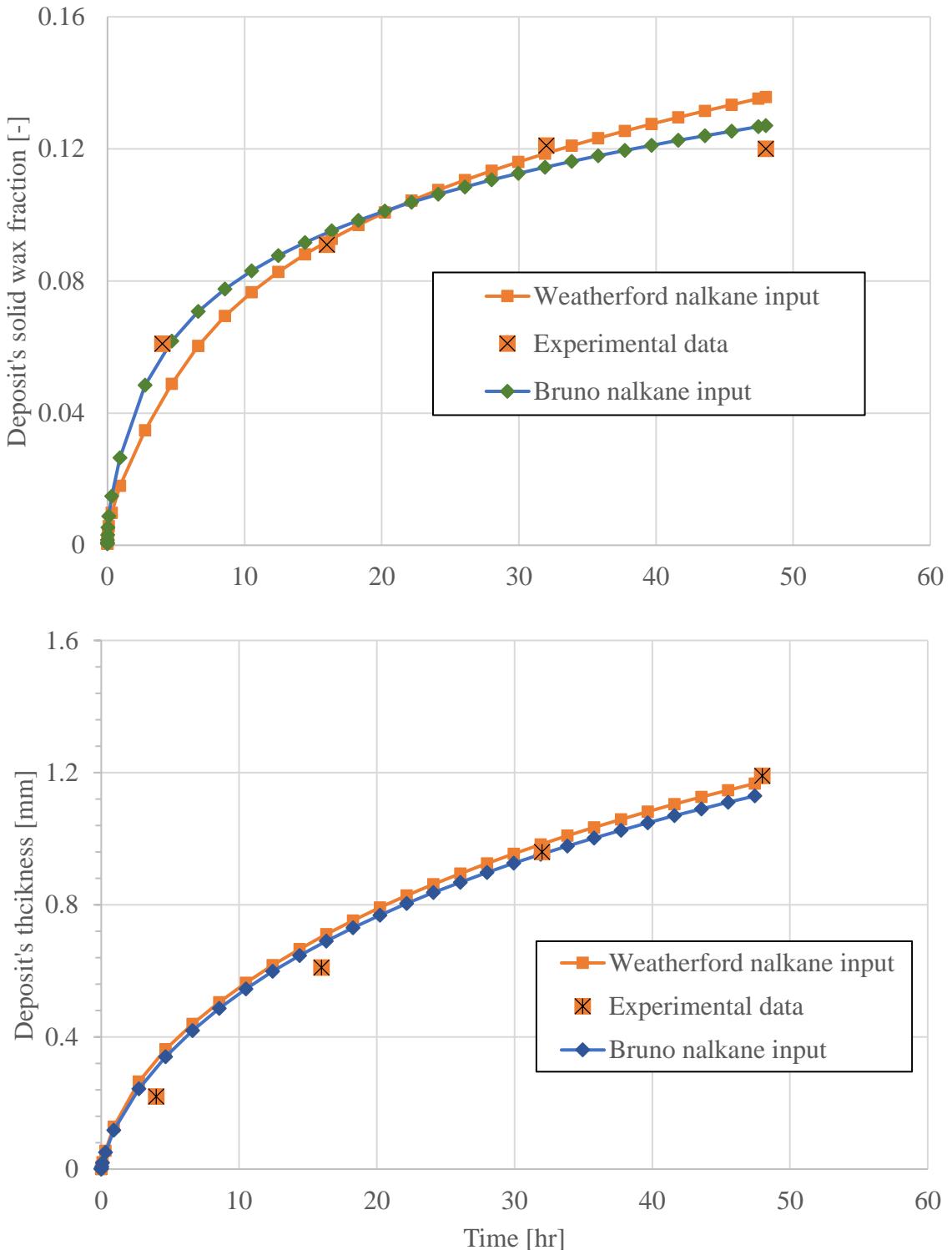


Figure 5-42: Average deposit's and solid wax fraction predictions from Bruno and Weatherford n-alkane compositions for  $V_{oil} = 1.19 \text{ m/s}$

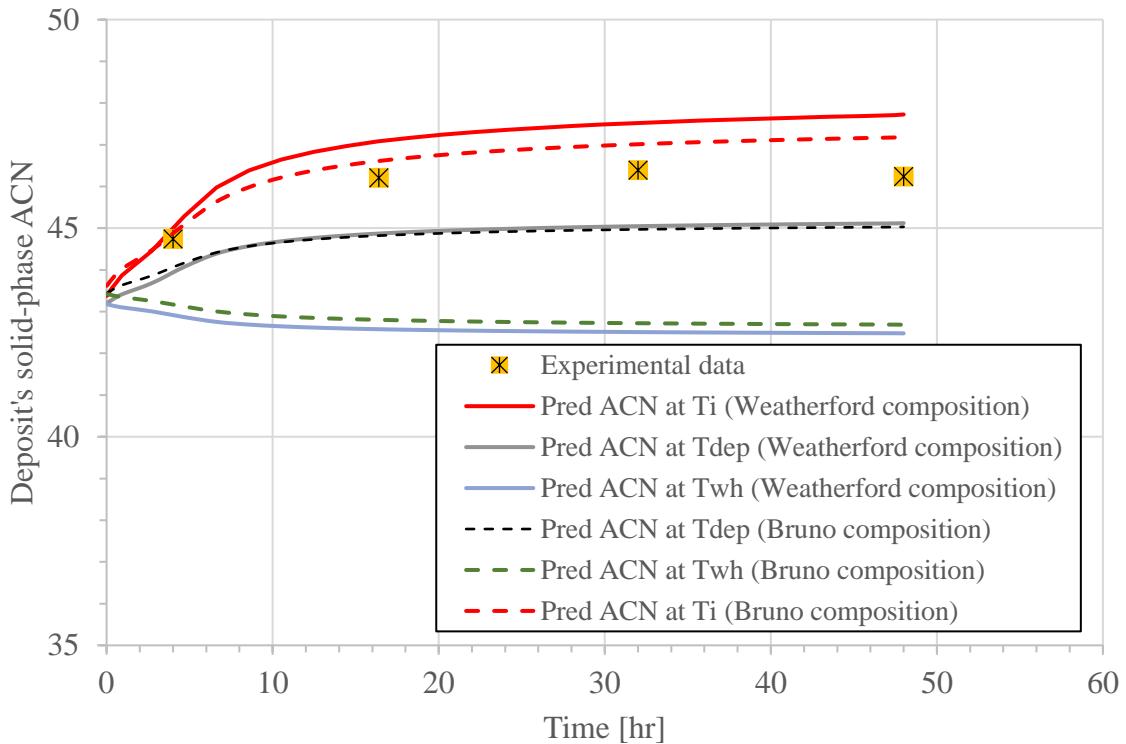


Figure 5-43: ACN predictions using Bruno and Weatherford n-alkane compositions

And the adjusted fitting parameters for both oil compositions are presented in the following table:

Table 5-13: Adjusted msr1 and msr2 for two n-alkane compositions

$V_{oil}$ [m/s]	Weatherford n-alkane composition		Bruno n-alkane composition	
	msr1	msr2	msr1	msr2
1.19	12.29	5.33	15.53	12.25
1.83	9.43	22.48	13.30	90.86
2.24	4.19	9.80	5.34	26.36

The above graphs show how n-alkane composition variation could result in different predictions in different wax deposition characteristics. Therefore, it is suggested to use accurate n-alkane composition data for SP-Depo software.

### Different operating conditions (pipe's diameter and length)

Although SP-Depo is verified by the experimental data of a lab-scale pipeline, it is important to show its applicability in different operating conditions. Ambient temperature, pipe's radius, oil velocity and pipe's length are the parameters whose effects will be investigated in this section. Some of the larger pipes similar in the field. In this section, we will run SP-Depo for different operating conditions and compare the results.

#### Pipe's Diameter Change Analysis Case Analysis

In this case, we want to explore the effect of pipe's diameter on the wax deposition prediction. In Table 5-14, the original and modified input parameters are included while the fitting parameters stay constant. In Figure 5-44, one can notice that increase in pipe's diameter result in slight decrease in deposit's thickness and solid wax fraction while deposit's solid phase carbon number composition remains almost unchanged.

Table 5-14: Original and new testing conditions for case 1. Every other parameter is the same

Parameters	Original	Changed
$V_{oil}$ [m/s]	2.24	
$d_{in,pipe}$ [Inch]	0.651	1.3
$d_{out,pipe}$ [Inch]	0.75	1.5
$d_{in,cool}$ [Inch]	1	2

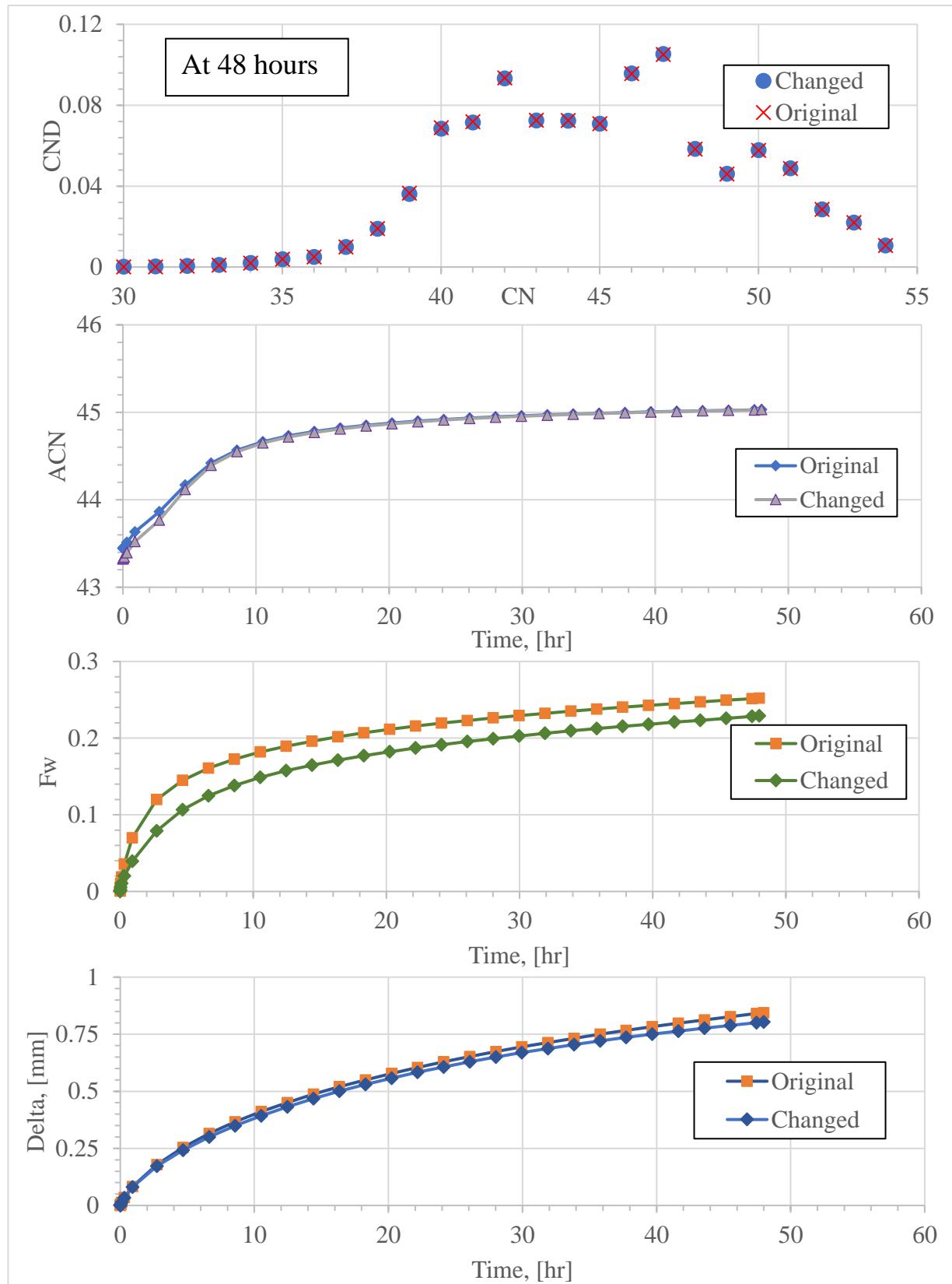


Figure 5-44: Simulation result comparison for case 1 sensitivity analysis with pipe's size variation

### Ambient Temperature Change Case Analysis

Surrounding temperature is one of the most important parameters which could affect the wax deposition process massively. As ambient temperature decreases, more carbon number components will precipitate out of the solution and contribute to the deposition. Therefore, we investigated the effect of ambient temperature on different characteristics of the waxy deposit. In Figure 5-45, lowered ambient temperature resulted in more deposition as deposit's thickness and solid wax fraction are increased considerably. On the contrary, ACN is decreased since more lighter n-alkanes deposited due to the low coolant temperature.

Table 5-15: Original and new testing conditions for case 2. Other parameters are the same

Parameters	Original	Changed
$v_{oil}$ [m/s]	2.24	
$T_{ambient}$ [°C]	28.78	20

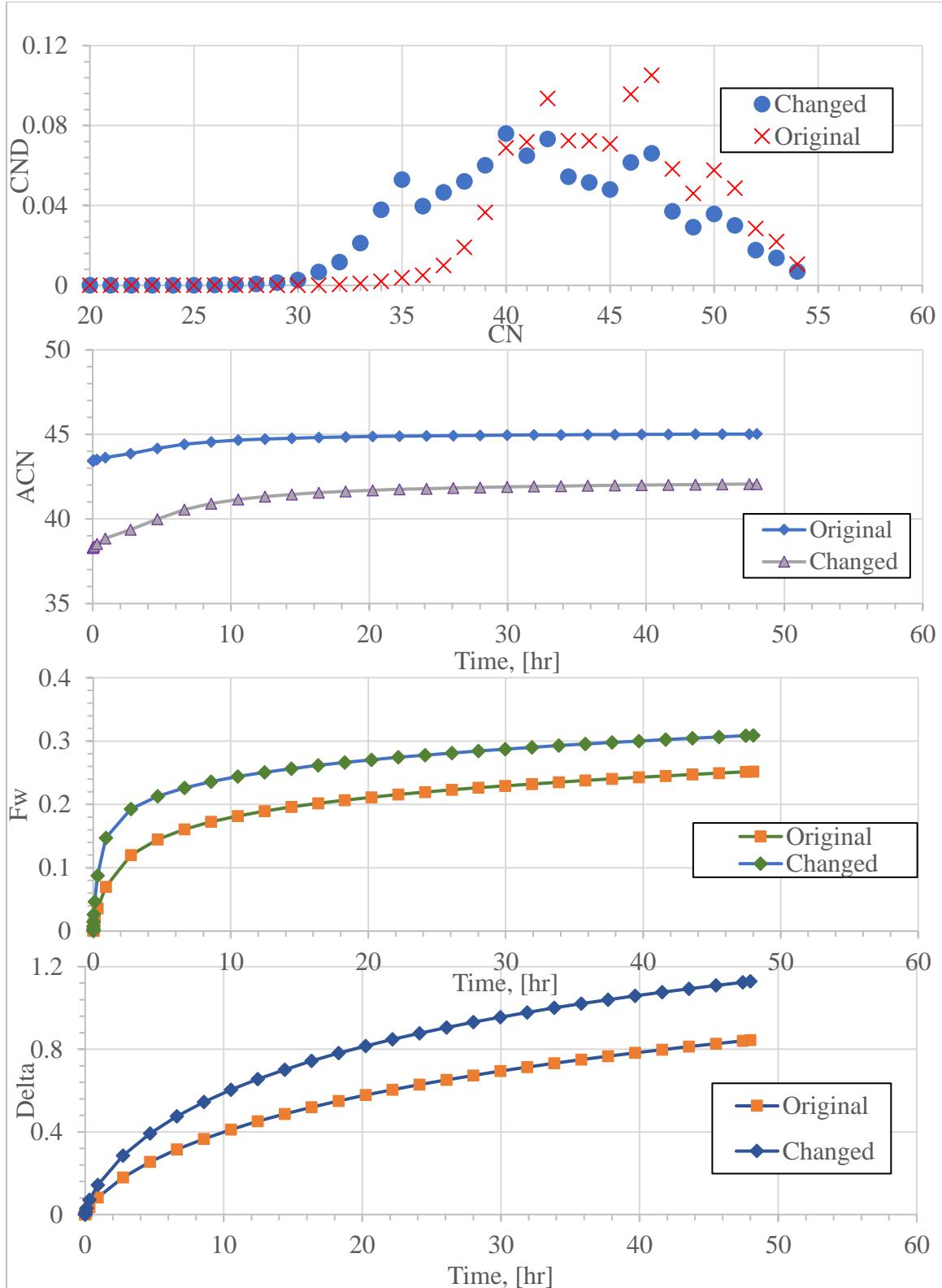


Figure 5-45: Simulation result comparison for case 2 sensitivity analysis with ambient temperature variation

## Upscaled Case Analysis

In this case, we consider a larger and longer pipe for our case analysis. As we discussed previously, it is important to show that SP-Depo works in other operating conditions too. In the previous cases, we changed only one parameter (pipe's dimeter and ambient temperature) and showed the simulation results. However, in this sensitivity analysis case, pipe's dimeter, ambient temperature, pipe's length and coolant flow rate will vary and the results are illustrated.

Table 5-16: Original and changed parameters for upscaled sensitivity case analysis

Parameters	Original	Changed
$V_{oil}$ [m/s]	2.24	
$d_{in,pipe}$ [Inch]	0.65	5.21
$d_{out,pipe}$ [Inch]	0.75	6
$d_{in,cool}$ [Inch]	1	7.95
$T_{ambient}$ [°C]	28.78	4
$Q_{coolant}$ [ $\frac{gal}{s}$ ]	0.08	264.2
Pipe's Length,[m]	0.84	100.84

From Table 5-16, Pipe's dimeters are increased by eight times, the ambient temperature has been decreased to subsea conditions (4°C), coolant flow rate is increased considerably to make the inner pipe's wall temperature constant. Due to the importance of this sensitivity analysis case, we will include the plots of various parameters without comparing it to a base case.

Please note that in SP-Depo, heat transfer calculations are based on the counter-current pipe-in-pipe flow condition and it is different than subsea condition. However, the coolant flow rate has been increased considerably to make the inner pipe's wall temperature constant. In the following graph, wall temperature ( $T_{wh}$ ) is plotted versus z and times,

respectively. As expected, high coolant flow rate has resulted in almost constant wall temperature.

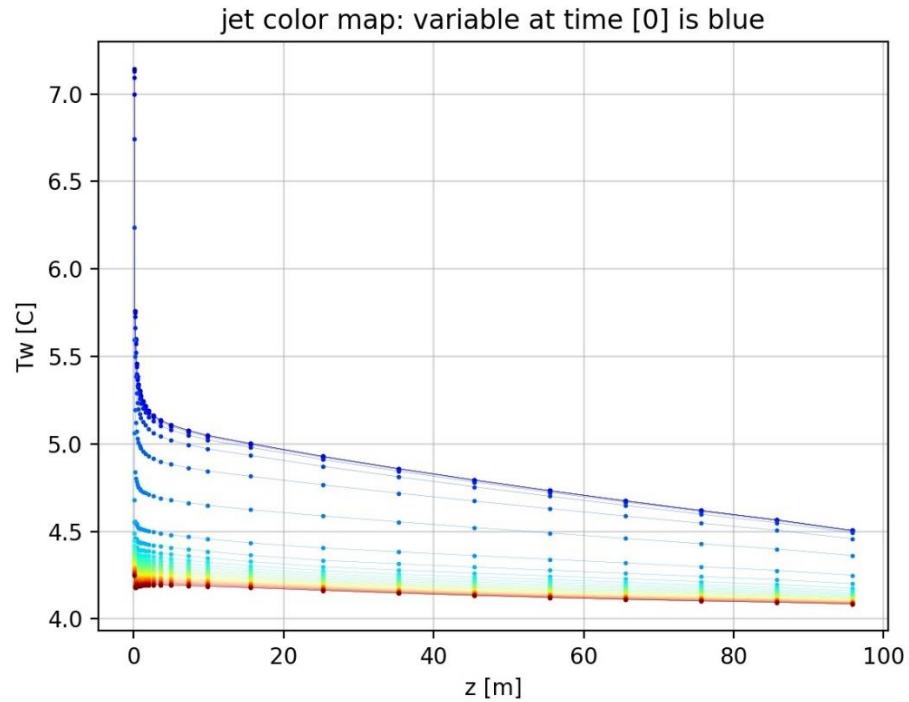


Figure 5-46: Inner pipe's wall temperature versus axial sections

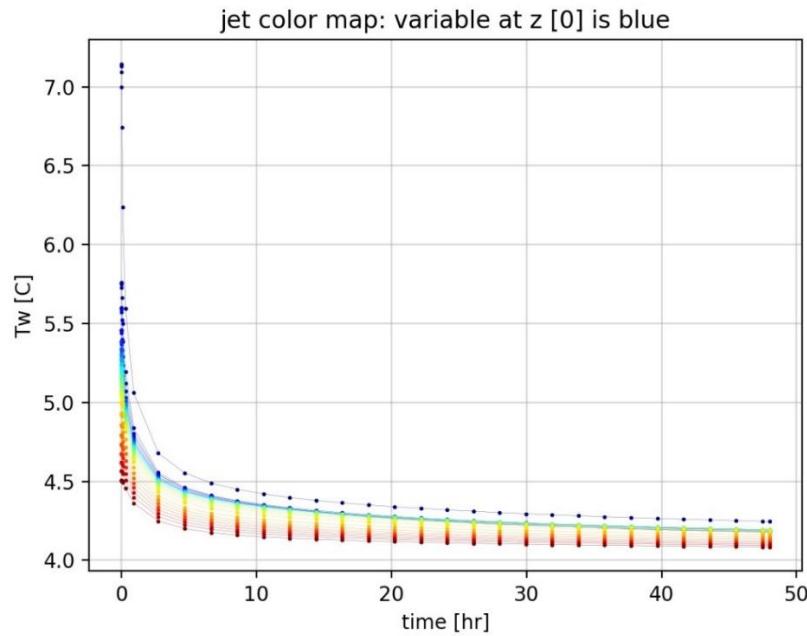


Figure 5-47: Pipe's inner wall temperature versus time

Then, the following graphs show the interface temperature ( $T_i$ ). Even though  $T_i$  drops axially at early times, it does not vary at final time steps.

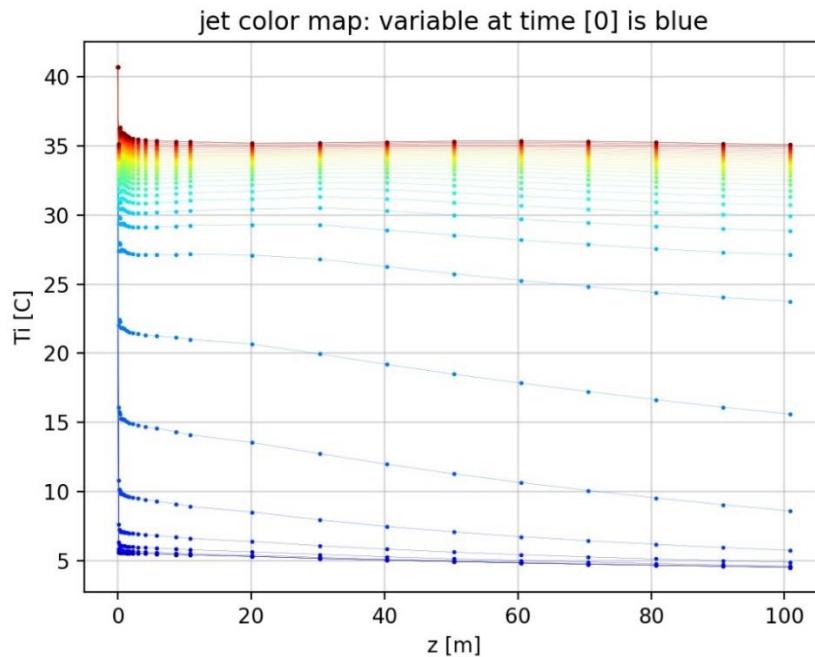


Figure 5-48: Deposit's interface temperature versus axial locations for different times

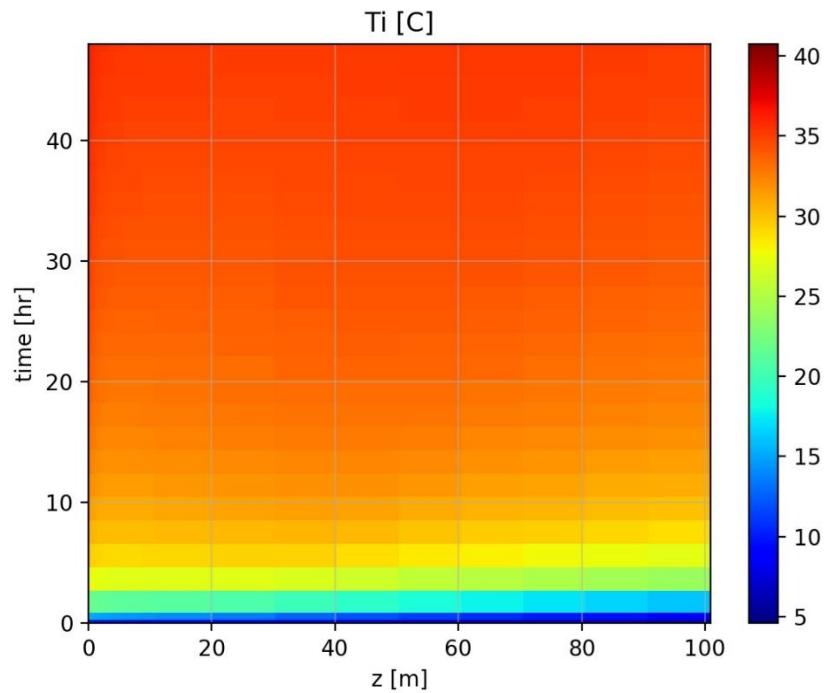


Figure 5-49: Deposit's interface temperature map (z vs time)

The final temperature parameter is the radial temperature profile which is illustrated through graphs at  $t = 0$  [hr] and  $t = 48$  [hr].

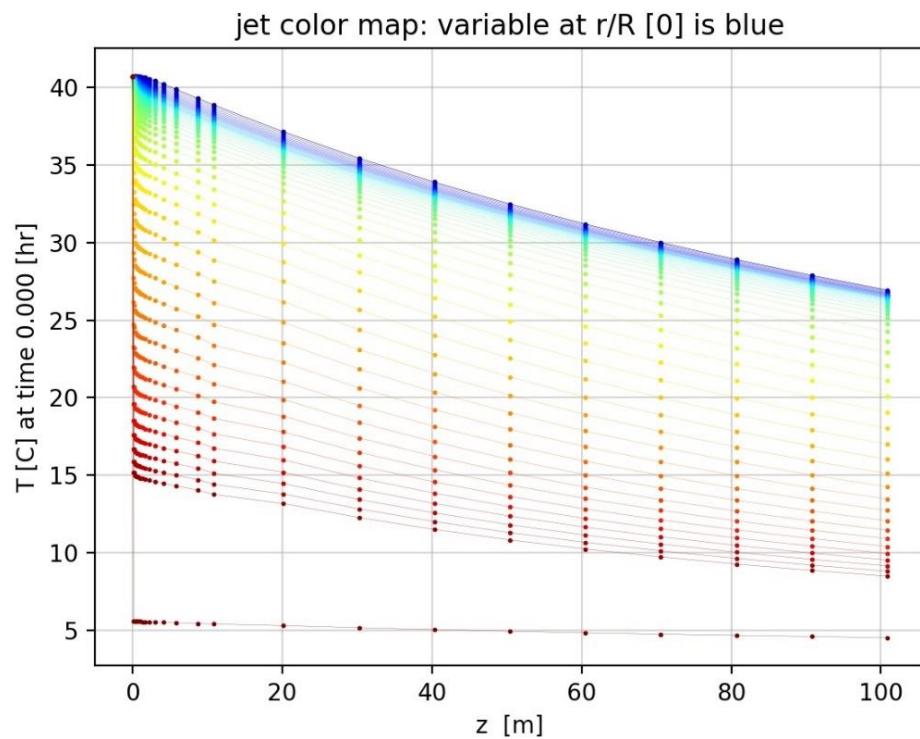


Figure 5-50: Radial temperature profile within the pipe at  $t = 0 [hr]$

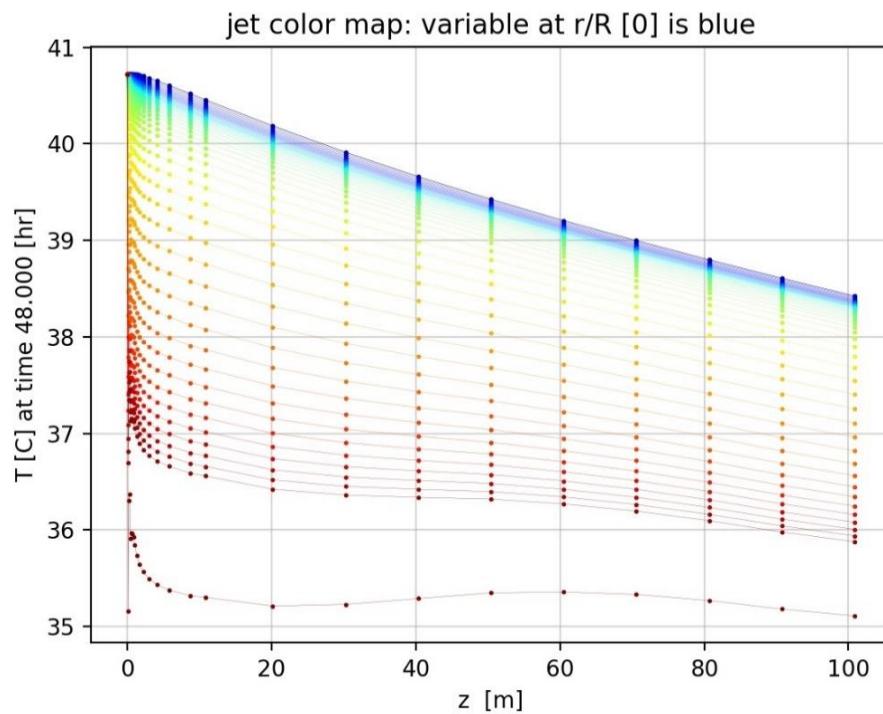


Figure 5-51: Radial temperature profile within the pipe at  $t = 48 [hr]$

The next graphs are the radial concentration profile at  $t = 0 [hr]$  and  $t = 48 [hr]$ . Concentration gradient near the deposit's interface is the main driving force in wax deposition phenomenon.

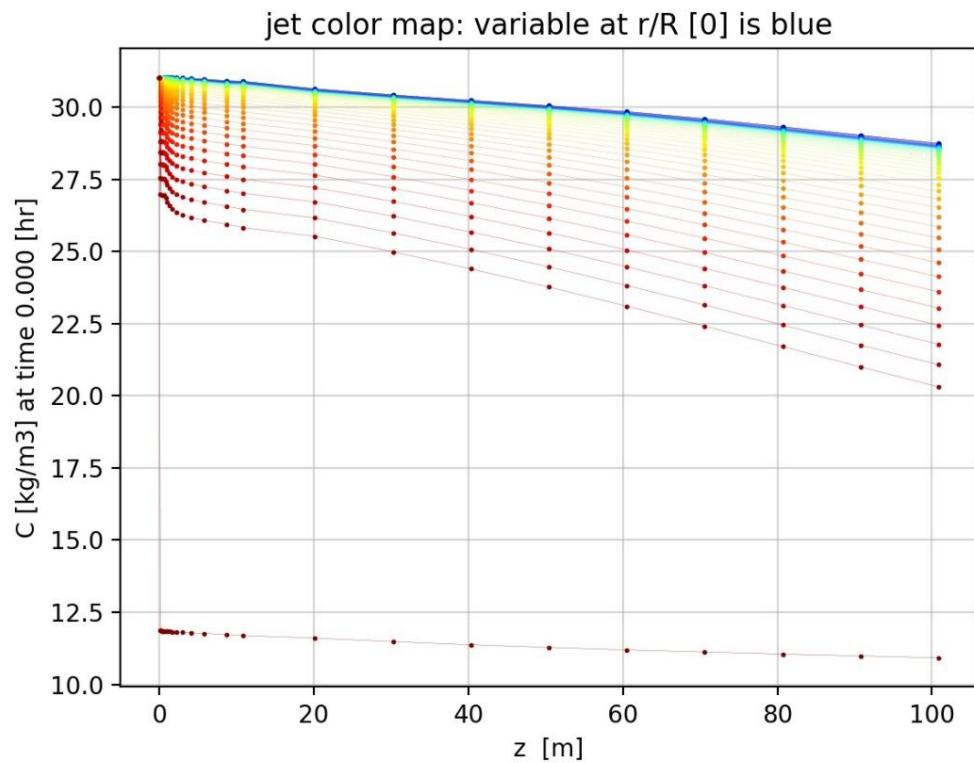


Figure 5-52: Radial concentration profile within the pipe at  $t = 0$  [hr]

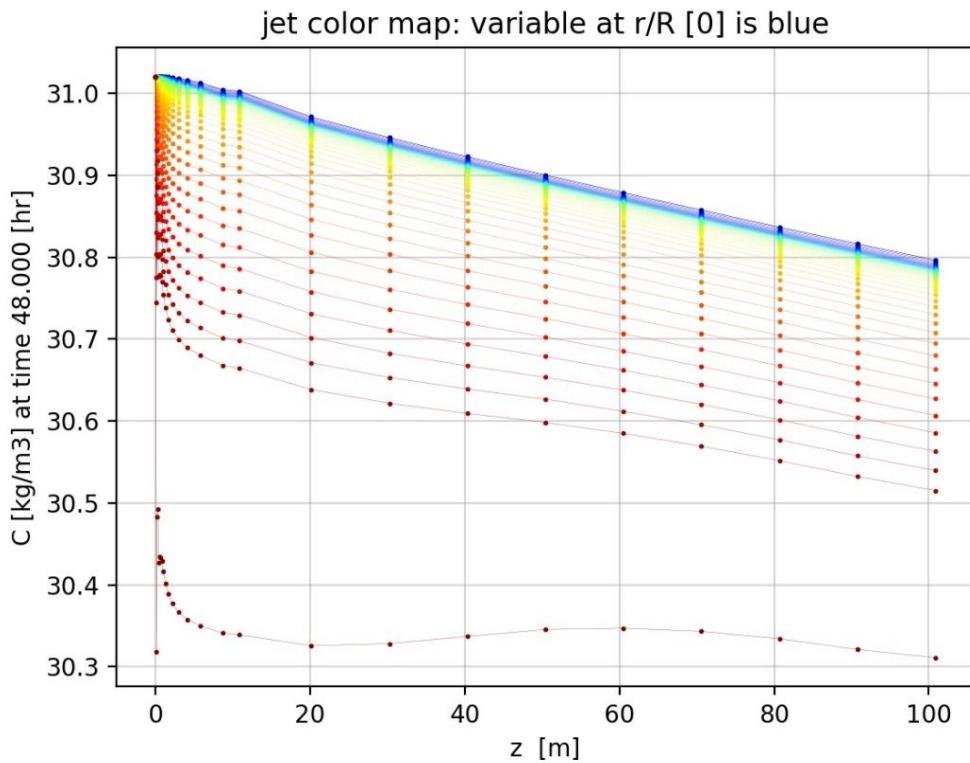


Figure 5-53: Radial temperature profile within the pipe at  $t = 48 [hr]$

After presenting the temperature and concentration profiles, we will include the solid wax fraction and deposit's thickness plots. The following plot shows the solid wax fraction profile.

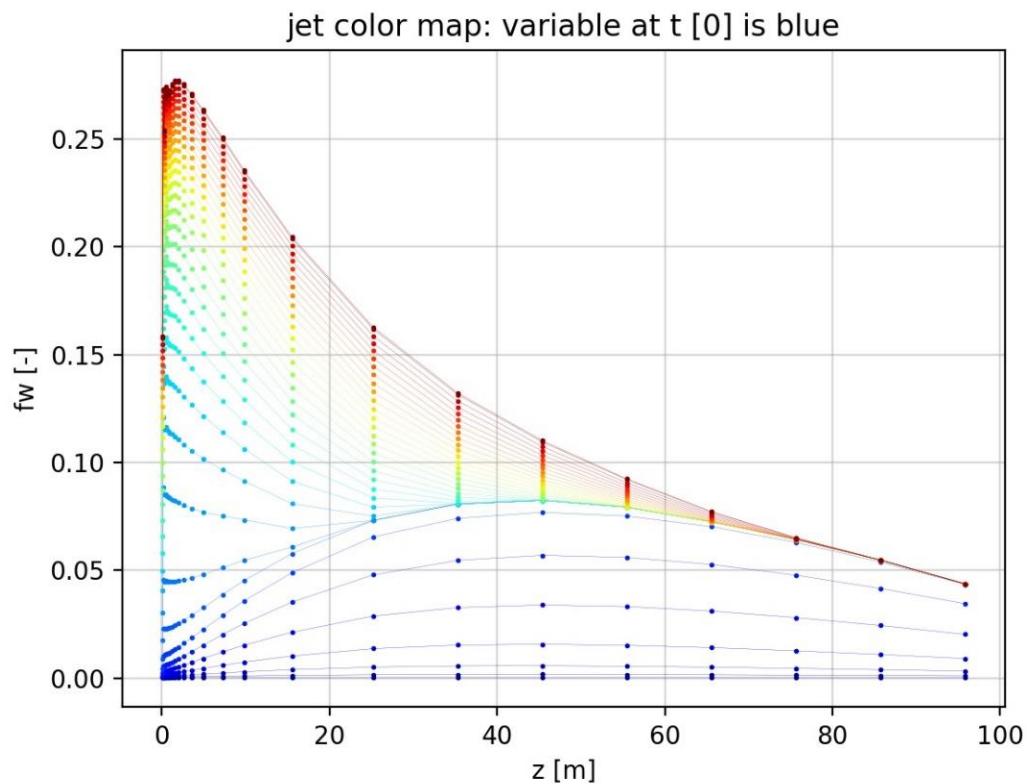


Figure 5-54: Axial solid wax fraction profile for different times

In the next figure, color map for solid wax fraction is plotted as a function of time and axial location

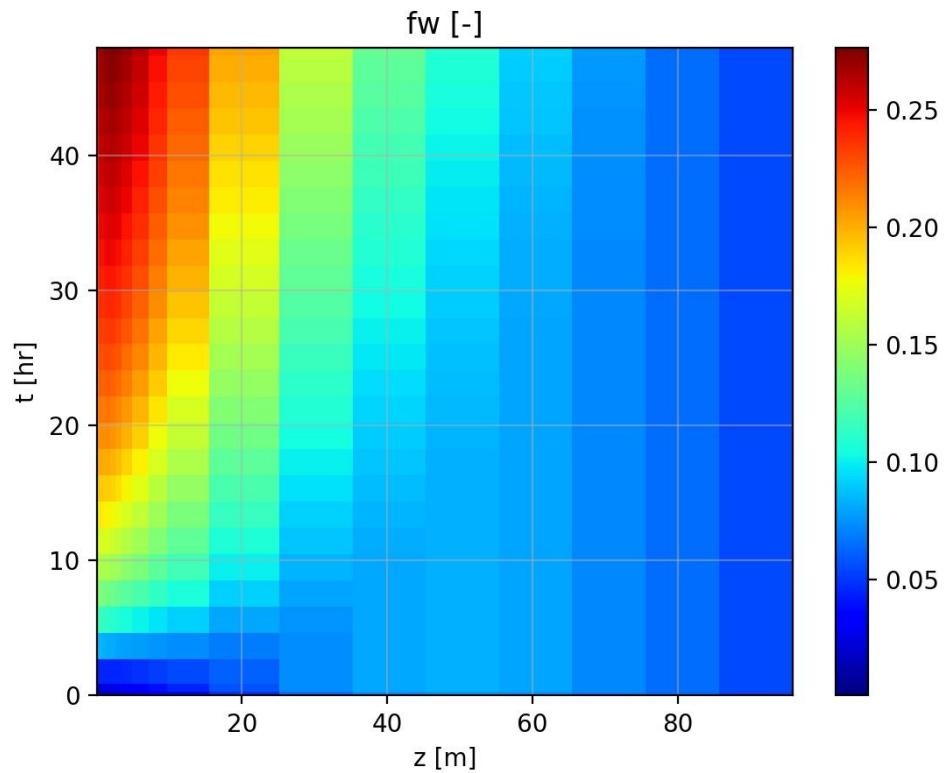


Figure 5-55: Solid wax fraction map (z vs time)

Finally, average solid wax fraction versus time is plotted as shown below.

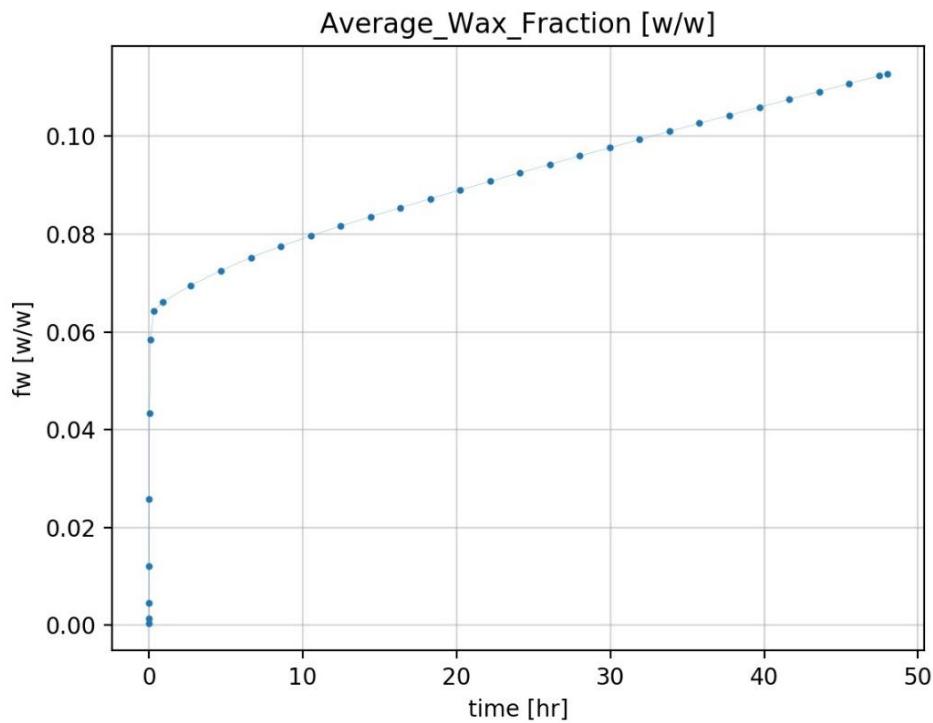


Figure 5-56: Average solid wax fraction versus time

Thickness ( $\delta$ ) profile, color map and average thickness are plotted in the next following plots.

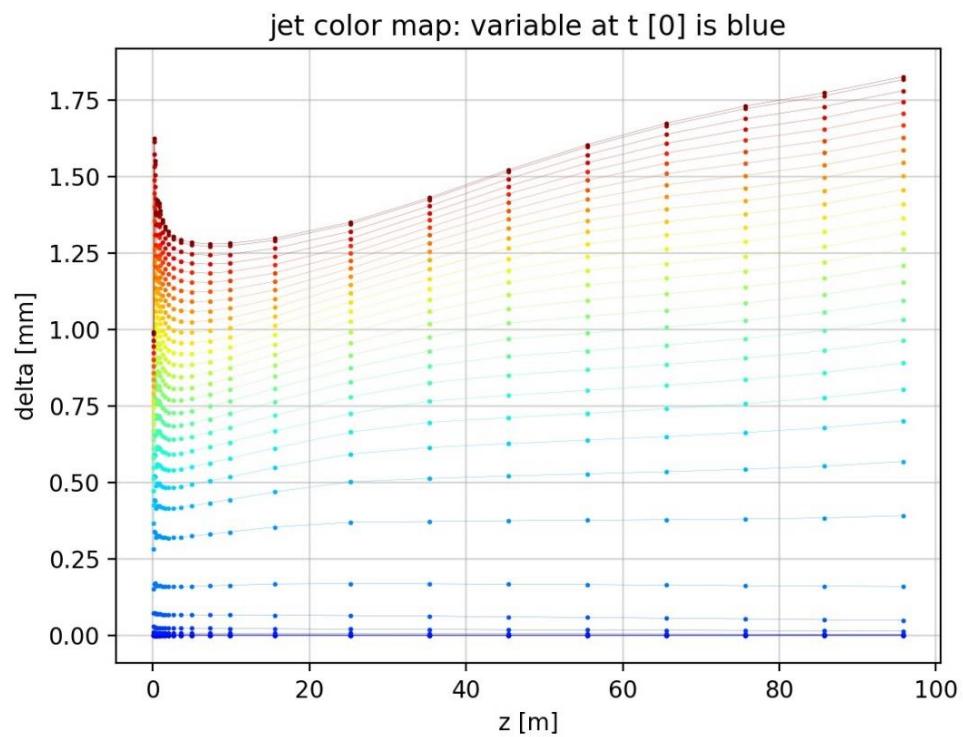


Figure 5-57: Axial deposit's thickness profile for different times

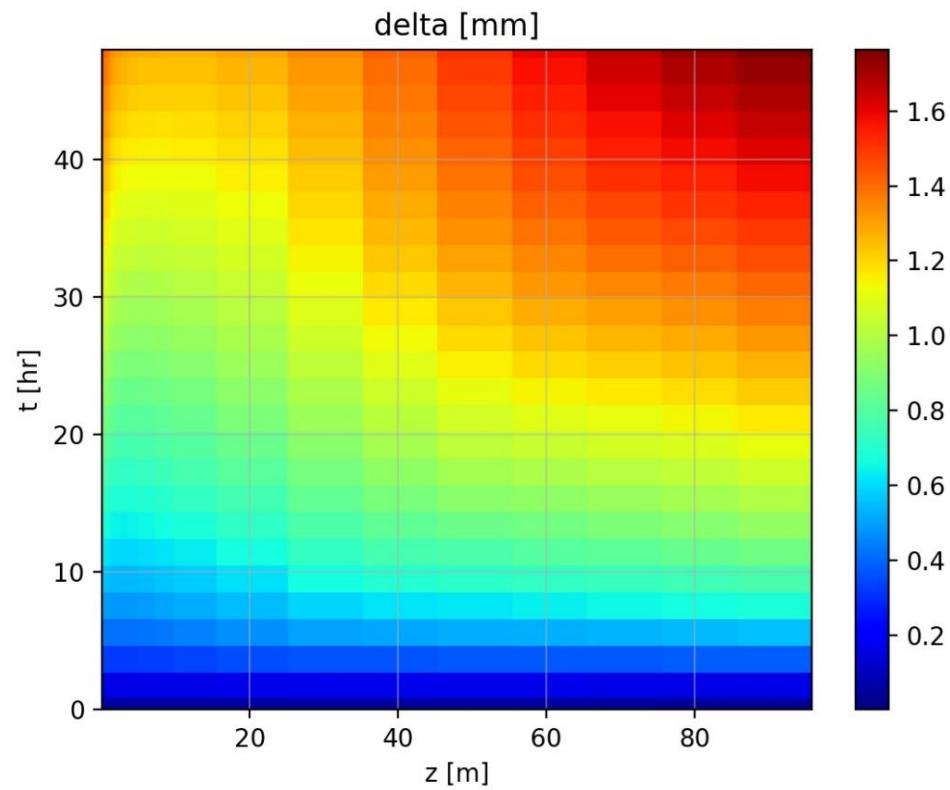


Figure 5-58: Deposit's thickness map (z vs time)

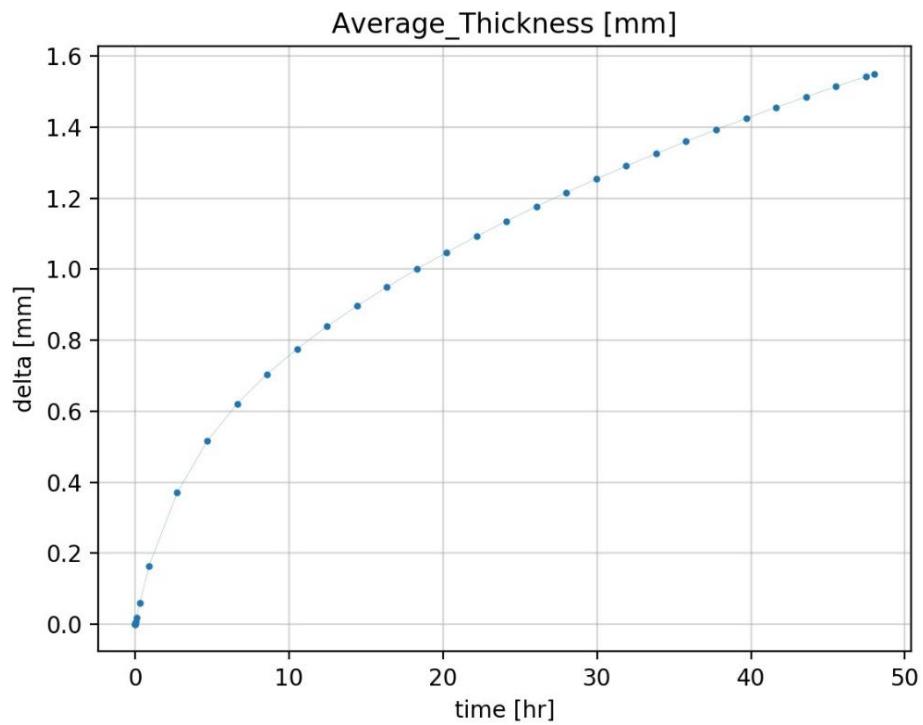


Figure 5-59: Average deposit's thickness versus time

Finally, the following graphs show ACN and CND of the deposit's solidified phase.

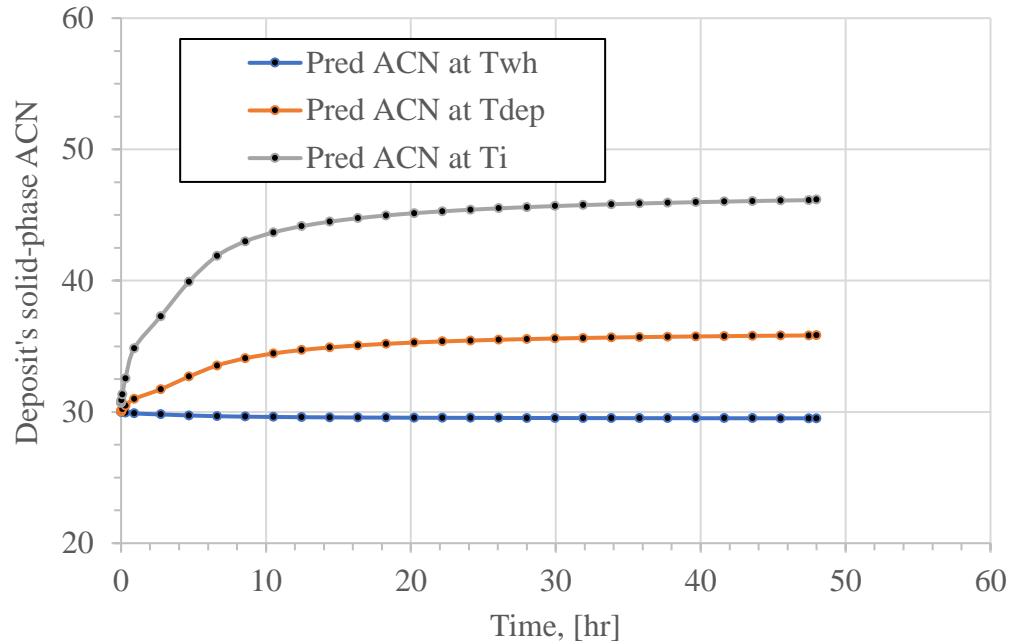


Figure 5-60: Deposit's solid phase ACN versus time at wall, deposit and interface temperature

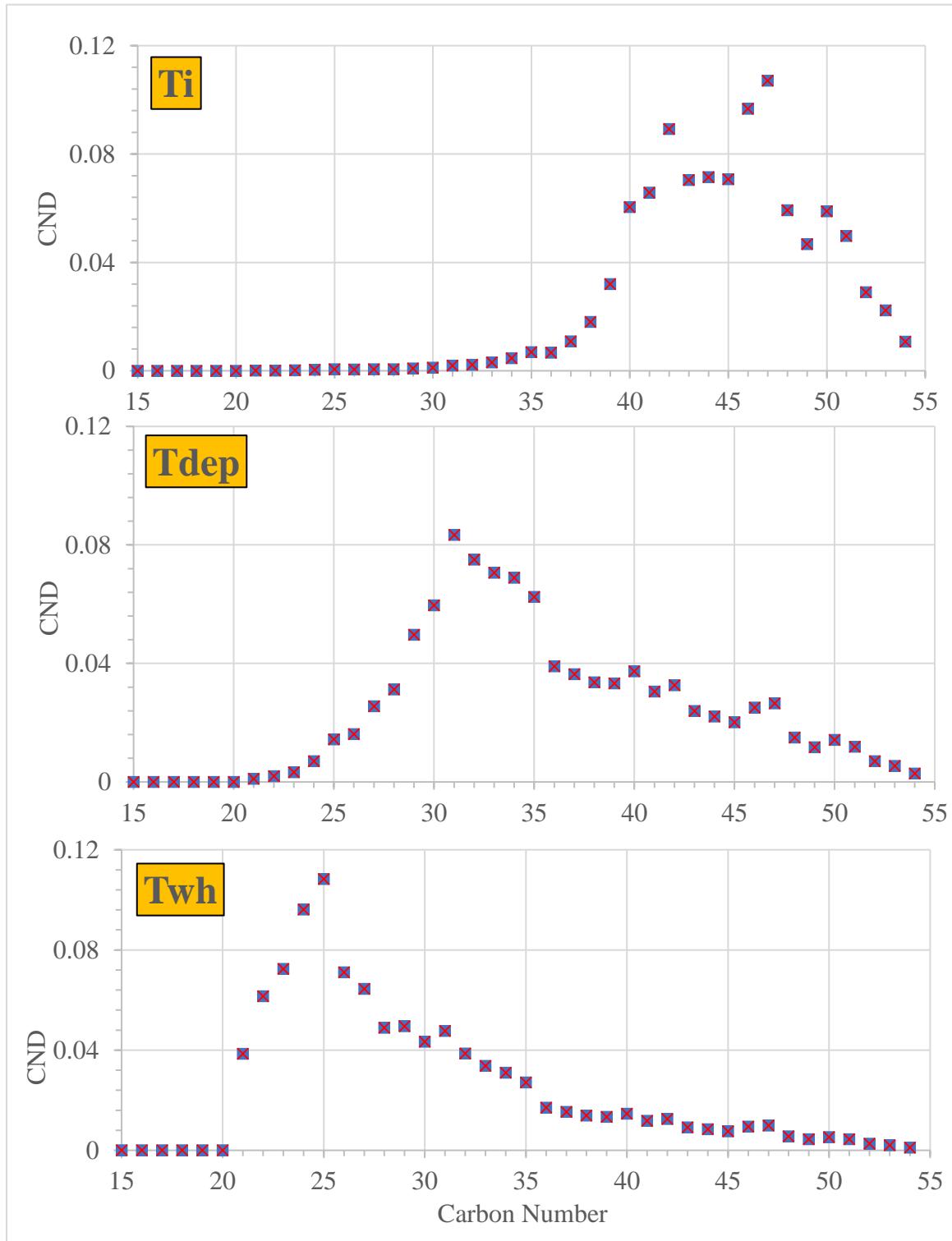


Figure 5-61: Deposit's solid phase carbon number distribution at wall, deposit and interface temperatures

## Chapter 6

### Conclusions

In wax deposition phenomenon, carbon number distribution (CND) of the deposit is a crucial factor to optimally design the pigging frequency and to correctly select the inhibiting chemicals. Despite its importance, wax deposit's composition prediction remains one of the missing pieces of nearly all commercialized wax deposition software (e.g., OLGA and LedaFlow). In our study, we solved this problem by developing a new wax deposition software (SP-Depo) to predict the deposit's solid phase CND in addition to thickness and solid wax fraction. In SP-Depo, a new thermodynamically-coupled wax deposition model has been used which is exclusively developed for this study. For verification purposes, SP-Depo's simulation results were plotted against data from more than 12 flow-loop experiments. In all cases, SP-Depo's predictions were successfully matched with the experimental data. We also introduced a limiting prediction bound for solid phase ACN and showed that experimental data will lay within this bound. In addition, we used our newly developed software to elucidate the effect of shear stress on deposit's solid phase carbon number distribution (CND) and average carbon number (ACN). After comparing our simulation results to the experimental ACN data, it was found that short n-alkanes are more likely to be removed from the deposit due to their low yield stress as shear stress increases. On the contrary, in lower flow rates, experimental ACN data approached to the lower bound prediction.

Furthermore, we developed SP-Wax software which is used to predict various SLE characteristics of paraffin in binary and multicomponent systems. For the first time, a simplified CCN estimation method has been proposed via the use of SP-Wax thermodynamic simulation without the need to fully solve the whole wax deposition equations. In SP-Wax, the SLE thermodynamic model from Coutinho and co-workers [14]–[21] and other literature [22], [23], [32]–[35], [24]–[31] were simulated and verified by experimental data of five binary and seven multicomponent systems. In SP-Wax, a novel numerical technique has been invented to solve the convergence problem near WAT. In both of our developed software, scientific modeling is coded through more than 17,000 lines of code in C++ and C# GUI (with more than 16,000 lines of code) has been used to

make a user-friendly interface for technical and non-technical users. Performance was our top priority in our developed software. Therefore, we implemented OpenMp parallel programming technique to minimize the run-time. Moreover, in SP-Depo, fluid-flow transport equations are solved using various numerical methods (e.g., Dorman Prince ODE solving method, Backward Finite Difference Method for solving PDEs, linear regression and Levenberg-Marquardt optimization algorithm).

Finally, we included three sensitivity analysis cases with varying operating conditions to make sure that SP-Depo works in different cases too. Even though we used experimental data from a lab-scale flow-loop for validation purposes, a hypothetical upscaled case was analyzed with one-hundred meter 5" pipe at subsea temperature of 4°C. SP-Depo predicted different wax deposition characteristics without any problem. Nevertheless, reliable field data are required to further develop SP-Depo for multi-mile subsea pipelines.

## Nomenclature

### *Variables*

$a$	Correction factor coefficient
$C_p$	Specific heat capacity, $\left[\frac{J}{^{\circ}K}\right]$
$D$	Diameter, [m]
$D_{wo}$	Molecular diffusivity of wax in oil, $\left[\frac{m^2}{s}\right]$
$D_e$	Effective diffusivity of wax in oil, $\left[\frac{m^2}{s}\right]$
$C$	Concentration, $\left[\frac{kg}{m^3}\right]$
$CN$	Carbon Number
$F_w$	Solid wax fraction, $\left[\frac{w}{w}\right]$
$f$	Friction factor, [-]
$f$	Fugacity, [psia]
$f_{NA}^L$	Ratio of n-alkane mass in liquid phase over total n-alkane mass in liquid and in solid phases, $\left[\frac{kg\ NA_L}{kg\ NA_{(S+L)}}\right]$
$f_{NA}^S$	Ratio of n-alkane mass in solid phase over total n-alkane mass in liquid and in solid phases, $\left[\frac{kg\ NA_s}{kg\ NA_{(S+L)}}\right]$
$G_z$	Graetz number, [-]
$h$	Heat transfer coefficient, $\left[\frac{W}{m^2 K}\right]$
$\Delta H$	Enthalpy, $\left[\frac{J}{mol}\right]$
$J$	Wax mass flux, $\left[\frac{kg}{m^2 s}\right]$
$K$	Equilibrium constant, [-]
$k$	Thermal conductivity, $\left[\frac{W}{m\ ^{\circ}K}\right]$
$K^C$	Equilibrium constant from previous iteration, [-]
$k_l$	Convective mass transfer coefficient, $\left[\frac{W}{m\ K}\right]$

$k_r$	Precipitation rate in Lee model
$k_\alpha$	Fitting parameter in wax crystal aspect ratio formula from Singh model, [-]
$L$	Length, [m]
$\dot{m}$	Mass flow rate, $\left[\frac{kg}{s}\right]$
$\tilde{m}$	Ratio of n-alkane mass in liquid phase over one-unit mass of oil, $\left[\frac{kg\ NA_{i,L}}{kg\ oil}\right]$
$MSR_1, MSR_2$	Fitting parameters from Panacharoensawad model
$MW$	Molecular weight, $\left[\frac{kg}{mole}\right]$
$N$	Number of carbon number components
$NN$	Total number of cases used to calculate the mean absolute relative error.
$n_s$	Solid mole fraction in n-alkane system (or [mole of solidified n-alkanes] / [total moles of all n-alkanes]), [-]
$R$	Pipe's radius, [m]
$r_i$	Effective pipe's radius, [m]
$Sc$	Schmidt number
$S_f$	Solidified weight fraction (from the thermodynamic model) $\left[\frac{w}{w}\right]$
$SR_1, SR_2$	Shear effect multiplier (Panacharoensawad model)
$T$	Temperature, [ $^{\circ}C$ ], [ $^{\circ}K$ ]
$t$	time, [s], [hr]
$T_c$	Critical temperature, [ $^{\circ}K$ ]
$V$	Volume, [ $m^3$ ]
$V$	Velocity, $\left[\frac{m}{s}\right]$
$V_z$	Axial velocity, $\left[\frac{m}{s}\right]$
$W_f$	Mass of total n-alkanes in one-unit mass of oil, $\left[\frac{kg\ NA_{(S+L)}}{kg\ oil}\right]$
$x_{m,i}^S$	mole fraction of i <sup>th</sup> component in solid phase and in n-alkane system, $\left[\frac{mole\ NA_{i,S}}{mole\ NA_S}\right]$
$x_{m,i}^L$	mole fraction of i <sup>th</sup> component in liquid phase and in n-alkane system, $\left[\frac{mole\ NA_{i,L}}{mole\ NA_L}\right]$
$x_{w,i}^L$	weight fraction of i <sup>th</sup> component in liquid phase and in n-alkane system, $\left[\frac{kg\ NA_{i,L}}{kg\ NA_L}\right]$
$y$	Sample parameter in relative error equation

$z_i$	Input mole composition of n-alkanes ( $\sum z_i = 1$ ), $\left[ \frac{\text{mole NA}_{i,(S+L)}}{\text{mole NA}_{(S+L)}} \right]$
$z$	Axial location, [m]
$\Delta_s^l C_{p_i}$	Difference between specific heat capacity of $i^{th}$ component in liquid and in solid phase

### Greek letters

$\alpha$	Aspect ration of wax crystal, [-]
$\alpha$	Thermal diffusivity, $\left[ \frac{m^2}{s} \right]$
$\alpha$	Correction factor, [-]
$\gamma$	Activity coefficient, [-]
$\epsilon$	Relative error, [-]
$\varepsilon$	Eddy diffusivity
$\Lambda$	Major binary interaction energy parameter in Wilson equation, [-]
$\rho$	Density, $\left[ \frac{kg}{m^3} \right]$
$\lambda$	Minor binary interaction energy parameter, $\left[ \frac{J}{mol} \right]$
$\mu$	Viscosity, [cp]
$\nu$	Volume fraction for n-alkanes in total fluid, [-]
$\xi$	Volume fraction, [-]
$\Phi$	Volume over one-mass of oil, $\left[ \frac{m^3}{\text{kg oil}} \right]$
$\phi$	Composition fraction, [-]
$\phi_i^L$	Fugacity coefficient of $i^{th}$ pure component in the liquid phase
$\gamma_i^{comb}$	Combinatorial contribution in liquid phase non-ideality
$\tau_{max}, \tau_{ini}$	Maximum and initial shear stresses, [Pa]
$\tau_w$	Wall shear stress, [Pa]
$\Omega$	Heat resistance, $\left[ \frac{m^{\circ}K}{W} \right]$

### *Subscripts*

<i>b</i>	Bulk
<i>c</i>	Coolant
<i>dep</i>	Deposit
<i>exp</i>	Experimental
<i>i</i>	<i>i</i> <sup>th</sup> carbon number
<i>i</i>	Interface
<i>ii</i>	<i>ii</i> <sup>th</sup> cases used in the mean absolute relative error calculation.
<i>int</i>	Interface
<i>j</i>	<i>j</i> <sup>th</sup> carbon number
<i>k</i>	<i>k</i> <sup>th</sup> carbon number
<i>l</i>	Long
<i>m</i>	Mole
<i>MinC</i>	Minimum depositable carbon number
<i>N</i>	Last section or component
<i>NA</i>	Normal n-alkane
<i>s</i>	Short
<i>sol</i>	Solidified
<i>Sim</i>	Simulation
<i>w</i>	Weight
<i>VDW</i>	Van der Waals

### *Superscripts*

<i>f</i>	Fusion
<i>L</i>	Liquid
<i>S</i>	Solid
<i>Sub</i>	Sublimation
<i>tot</i>	Total
<i>tr</i>	Solid phase transition
<i>vap</i>	Vaporization

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