MODELING OF WAX PRECIPITATION

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MODELING OF WAX PRECIPITATION

A

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ABSTRACT

Due to increasing oil demand, oil companies are moving into deep water and arctic environments for oil production. In these regions, due to lower temperature, wax starts depositing when the temperature in wellbore falls below Wax Appearance Temperature (WAT). This leads to reduced production rates and larger pressure drops. Wax problems in production wells are very costly due to production down time and removal of wax. Therefore, it is necessary to develop the solution to overcome wax deposition. Wax precipitation is one of the most important phenomena in wax deposition, and hence, it needs to be modeled. There are various models present in literature. The purpose of this study is to compare two major classes of wax precipitation models. Won's model which considers the wax phase as a non-ideal solution and Pedersen's model which considers the wax phase as an ideal-solution were compared. Comparison indicated that Pedersen's model gives better results but the assumption of wax phase as an ideal solution is not realistic. Hence, Won's model was modified to consider different precipitation characteristics of the different constituents in the hydrocarbon fraction. The results obtained from the modified Won's model were compared with existing models and it was found that predictions from the modified model are encouraging.

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Disclaimer

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Chapter 1
Introduction

Since the industrial revolution, demand for energy has been constantly increasing. Currently oil is the main source of energy throughout the world. **Figure 1.1** shows the demand and supply of the crude oil in the world.

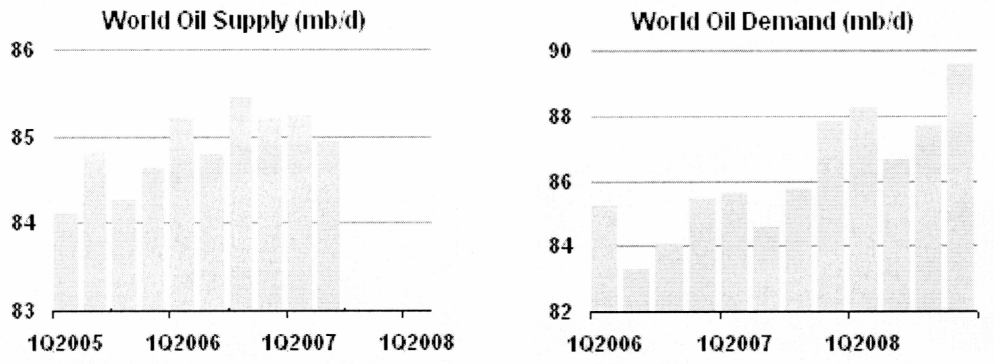

Figure 1.1 Demand and supply of oil in the world (Oil Market Report, 2007)

From **Figure 1.1**, it can be seen that the demand for oil has been constantly increasing. It can also be observed that oil companies are struggling to meet the ever increasing demand for oil. With rapid development in highly populated China and India, the demand for oil is going to increase at an alarming rate due to huge transportation demands in those large countries. Since oil production started in the early 1900s, most oil fields have reached the mature stage and oil production has been on decline. As a result, oil companies are exploring fields situated in deeper water or in arctic environments. In these regions, the wellbore temperature is very low. Oil generally has n-paraffins as constituents. When the wellbore temperature falls below what is known as the Wax Appearance Temperature (WAT), wax deposition occurs on the walls of the well. Wax deposits restrict the oil flow from the bottomhole to wellhead. This means the production of oil is reduced. Also due to wax deposition in the wellbore, the pressure drop increases, thereby decreasing the amount of oil that can be produced, as the bottomhole pressure is increased. **Figure 1.2** shows a typical case of wax deposition in wellbore. Production losses and restarting of operations associated with wax deposition cost millions of dollars (Venkatesan and Creek, 2007).

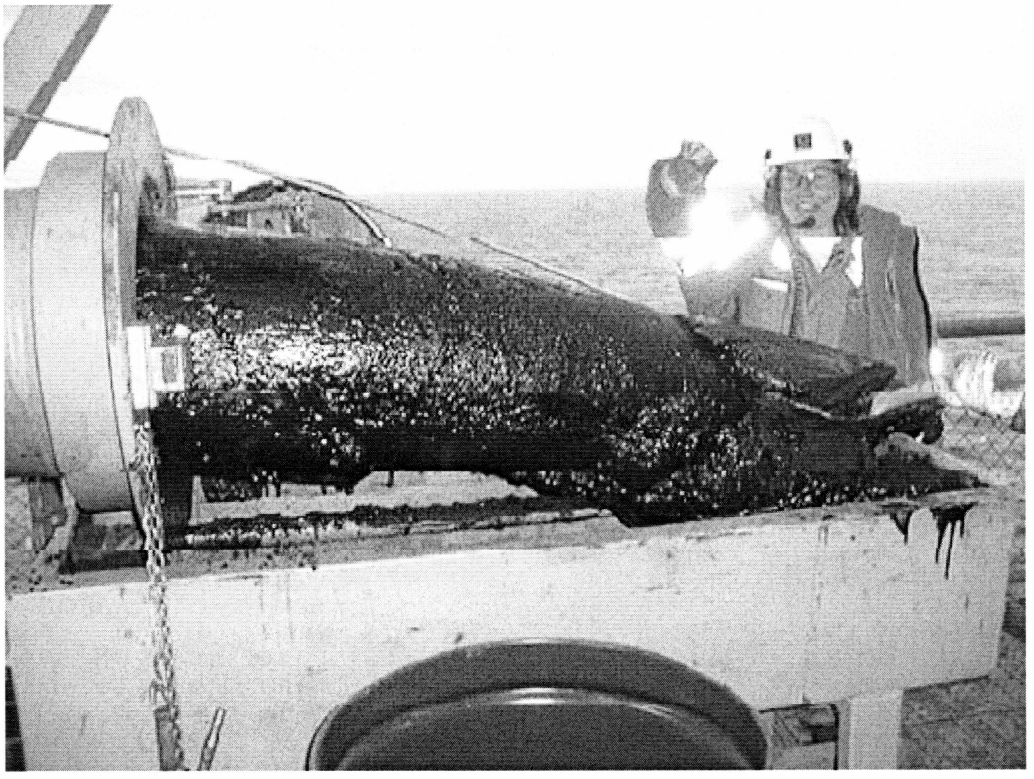

Figure 1.2 Wax plug in wellbore on platform C in North Sea (Labes-Carrier et al., 2002)

Hence, control of wax deposition is essential. To address the issue of wax deposition, three important phenomena have to be considered: Wax precipitation, Dynamic wax deposition, and Heat transfer from the wellbore. Wax plug, which is obtained from wax deposition, is a gel that contains solid wax crystals and trapped liquid (Venkatesan and Creek, 2007). Wax precipitation is a thermodynamic phenomenon and will lead to deposition of solid wax crystals. Dynamic wax deposition is the phenomenon in which a gel is formed with wax crystals and liquid. Heat transfer is another important facet as it decides whether the temperature of the wellbore will fall below the WAT or not.

Wax precipitation should be described accurately in order to develop the solutions to control the wax deposition in wellbore. The work done in this thesis mainly involves description of wax precipitation behavior through thermodynamic models.

Chapter 2
Literature Review

2.1 Overview of Wax

When temperature is reduced, most oils show a tendency for solid precipitation. The solid deposit is called as wax. Wax precipitation causes operational problems due to plugging of the wellbore or transportation lines.

It has been found that wax particles are essentially normal paraffins and slightly branched paraffins. Occurrence of napthenes with long paraffinic chains is rare. Structures of typical wax forming components are shown in **Figure 2.1**.

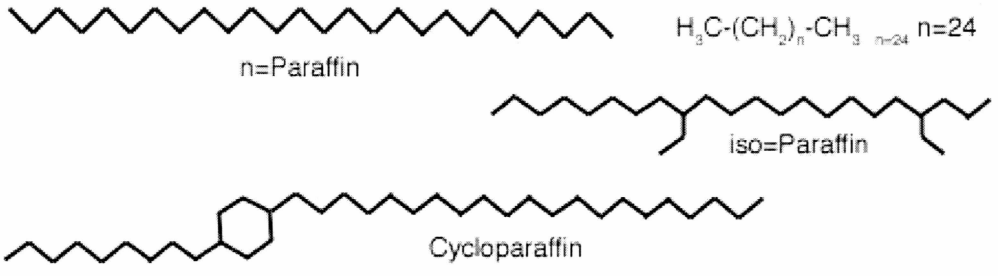

Figure 2.1 Structure of various types of constituents in hydrocarbon fraction (International Group Inc, 2007)

Pedersen and Christensen (2007) have mentioned that compounds heavier than C_{50} are rarely present in the wax phase. When the molecular weight of plus fraction is high, generally the degree of branching in the components present is high and these components have less chance of entering into a solid phase. In lighter C_{7+} fractions, the components are generally n-paraffins with a lower degree of branching. But their presence in wax is limited due to very low melting temperatures of these components. Hence it is found that the wax phase is generally dominated by C_{20}-C_{50} components.

2.2 Concerns with Wax Deposition

As discussed earlier, wax starts precipitating when the temperature of the system is lowered. This wax precipitation is a precursor to wax deposition. Precipitation and deposition should not be confused. Precipitation is a necessary phenomenon as it is a thermodynamic activity. When temperature is reduced below the WAT, the wax should

precipitate. But wax deposition is a much more complex phenomenon. When an aqueous phase is present with oil, which would be the case in the production well, the wax will deposit on the wall of wellbore. Also there will be formation of wax particles which will stay suspended in the solution. This leads to formation of gel which contains wax crystals and trapped liquid. This phenomenon is called wax deposition. This leads to plugging of pipelines as well as wellbores. This causes a higher pressure drop in the pipeline while transporting the oil. In production wells, due to wax deposition, the amount of energy required to lift the oil from bottomhole to wellhead increases, hence the bottomhole pressures have to be kept significantly higher than in the case without wax deposition. This reduces the amount of oil that is produced from the formation due to lower pressure difference between bottomhole and formation. Also as oil developments are moving into deeper water and arctic environments, the chances are that the wellbore temperature will fall well below WAT and may reach a temperature which is known as the Pour Point Temperature (PPT). At the pour point, no movement of oil is possible because of highly dense wax deposition throughout the cross-section of the pipe. This is the extreme case and the wax needs to be removed from the wellbore manually. This leads to shutdown of the well and restarting the well takes a huge amount of work and results in economic losses (Venkatesan and Creek, 2007). Gluyas and Underhill (2003) have reported that the Staffa field had to be abandoned due to a severe case of wax deposition and remedial treatments failing to take care of the wax deposition problem. These lead to losses of hundreds of millions of dollars. Therefore, there is lot of interest within the oil industry to develop solutions to control wax deposition in the wellbores and pipelines.

2.3 Need for Modeling Wax Precipitation

For developing wax deposition control techniques, the wax deposition phenomenon should be simulated on a computer because studying effects at the field scale is not feasible. For developing wax deposition simulator, three phenomena should be considered: 1) Wax precipitation, 2) Dynamic wax deposition, and 3) Heat transfer from wellbore.

Wax precipitation would describe the amount of wax formed at a given pressure and temperature condition. This is done by thermodynamically modeling wax

precipitation. This does not take into account any effect of flow rate or other dynamic factors.

Dynamic wax deposition describes the formation of gel and the amount of wax deposited on pipe walls. This takes into account the effect of shear rate, flow rate, water cut etc. This requires knowledge of wax precipitation. It is obtained by thermodynamic modeling as discussed earlier (Ahn et al., 2005).

One of the most important parameters controlling wax deposition is the temperature of wellbore. If the temperature is above the WAT, then wax will not precipitate. The temperature of the wellbore is controlled by heat transfer from the wellbore to surroundings.

These three phenomena should be modeled with mathematical models and should be programmed and combined to actually simulate the conditions in the wellbore and wax deposition in it.

Hence, it is necessary to thermodynamically describe the wax precipitation. That is the focus of this study. The next section reviews various thermodynamic models present for describing wax precipitation.

2.4 Overview of Thermodynamic Models for Wax Precipitation

There are many models present in literature which describe precipitation of wax from oil. They can be broadly classified into two categories:1) those which consider the solid phase as a single phase and 2) those which consider the wax phase as a mixture multiple solid phases. Some models consider the solid phase as a mixture of multiple independent pure solid phases. The rest of the models consider the solid phase as a single phase. The second category can be divided into two further sub-categories. The first sub-category considers the solid phase as a non-ideal mixture, whereas the second sub-category considers the solid phase as an ideal mixture. Various models present in literature are divided into these categories as shown in Figure 2.2.

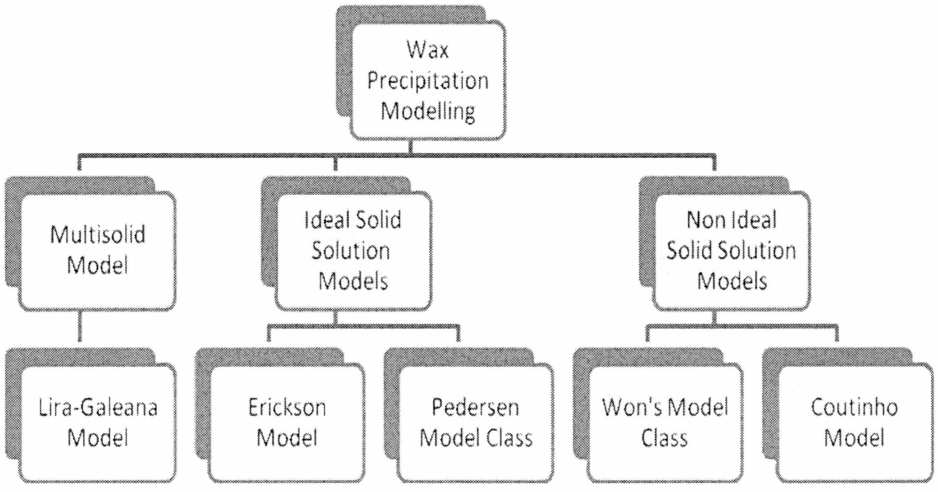

Figure 2.2 Classification of wax precipitation models

The first main category is one which considers the solid phase as a mixture number of a independent pure solid phases. This was developed by Lira-Galeana et al. (1996).

2.4.1 Lira-Galeana Model

This model assumes that wax consists of multiple solid phases and each solid phase is described as a pure component that does not mix with other solid phases. The liquid phase is considered as a non-ideal solution and its behavior is described by the Equation of State (EOS). This model is also known as the Multi-Solid Model. The model assumes that a component may exist in pure solid form when the fugacity of the component in the liquid phase mixture is equal to or greater than the solid state fugacity of the pure component. The solid state fugacity of a pure component is found by relating the chemical potential of a component in solid state with chemical potential of a component in liquid state in sub-cooled condition. The model actually fits the experimental data very well, but Pedersen and Michelsen (1997) pointed out that the predictions from the model change when the plus factor characterization procedure is changed, and it is contradictory to the principles of plus factor characterization.

The next main category is one in which the solid phase is considered to be one phase and behaving as an ideal-solution. Erickson's, Pedersen et al.'s model (1991) and its modified version fall in this category.

2.4.2 Erickson's Model

This model is a modification of Won's model but considers the solid phase as an ideal solution. The activity coefficient of the solid phase is considered to be unity. But this model requires experimental determination of amounts of n-paraffinic, iso-paraffinic and naphthenic part of each component through mass spectroscopy (Erickson et al, 1993). This involves huge efforts on experimental part and is rarely done. This model has not been used much.

2.4.3 Pedersen's Model and its Modified Versions

Pedersen (1995) developed a model in which it was assumed that only part of heavy hydrocarbon fractions can potentially enter into the wax phase. The authors developed a numerical scheme which let them split each hydrocarbon fraction into wax forming and non-wax forming fractions. The authors assumed the solid phase to be an ideal solution in equilibrium with the liquid phase. The liquid phase is assumed to be a non-ideal solution and is described by any EOS. Ronningsen et al. (1997) provided modification of a model in which they introduced a term to account for the effect of pressure. This model is used in PVTSim® which is commercial PVT simulator for the prediction of wax deposition and used by many oil companies (www.calsep.com). Due to use of EOS and tunable parameters, the model becomes very calculation intensive.

The next main category of thermodynamic models is one which considers the solid phase to be a non-ideal solution. Won's model, Pedersen's model and Coutinho's model fall in this category.

2.4.4 Won's Model

This model was the first one to consider the solid phase to be a non-ideal solution. Both liquid and solid phases were considered as non-ideal solutions, and non-ideality of both

phases was described by the Regular Solution theory. This model assumed that all components present can form wax (Won, 1986).

Pedersen et al. (1991) modified Won's original model by introducing a large number of tunable parameters to match the experimental data. But this makes the model also very calculation intensive.

Computer Modeling Group's (CMG) PVT simulator WINPROP® uses modified version of Won's model but the information regarding it is proprietary and is not published (WINPROP user manual). WINPROP® is used by a large number of oil companies for studying wax deposition.

2.4.5 Coutinho's Model

This model considers both solid and liquid phases to be non-ideal solutions. The non-ideality is described by activity coefficients. The activity coefficients are obtained by the predictive UNIQUAC model with use of the predictive free energy model. This model gives pretty good predictions (Coutinho et al., 2001).

2.5 Selection of Model for Current Study

A detailed comparative study of all wax models has not been done. Multi-solid model's limitation has been inconsistency in results after use of a different plus fraction characterization scheme. Pedersen's model and Won's model are used by various commercial software companies such as CMG WINPROP ®, PVTSim® for a description of wax precipitation. Pedersen's model is calculation intensive. One of the aims of current study is to compare these two classes of models. Pedersen's model considers the solid phase to be an ideal solution and it is not what is observed in most cases. The program developed in this study is going to be used in a wellbore simulator which simulates the conditions in wellbore including wax deposition and heat transfer. Due to a large amount of calculations involved in the overall project, it is advisable to have a wax precipitation model which is less calculation intensive. So the other aim is to develop a new model or modify an existing model so the model becomes closer to actual thermodynamic behavior and less calculation intensive.

Chapter 3

Objective of Study

In order to control the wax deposition in the wellbore, the wax precipitation must be modeled. Existing established thermodynamic models can be divided into two categories: a) those who consider the solid phase as a non-ideal solution b) those who consider the solid phase as ideal solution. The purpose of the current work is to compare these two categories of thermodynamic models and find out advantages and shortcomings of each type of model. This is done by programming these models and comparing the predictions with experimental data. Also based on conclusions obtained, modify the existing model to depict actual behavior of wax and if possible make the model less calculation intensive. And then, compare the results from the modified model with the predictions from existing model.

Chapter 4

Thermodynamic Modeling of Wax Precipitation

4.1 Two Phase Flash Calculations (Riazi, 2005)

Aforementioned, wax precipitation may occur from the liquid phase as the temperature is lowered. To calculate the temperature at which the first crystal of wax will be precipitated and to predict how much wax will be precipitated, flash calculations must be performed. In flash calculations, a feed of known composition is taken and flashed at given pressure and temperature conditions. The task is to estimate the amount of solid and liquid fractions and composition of each stream.

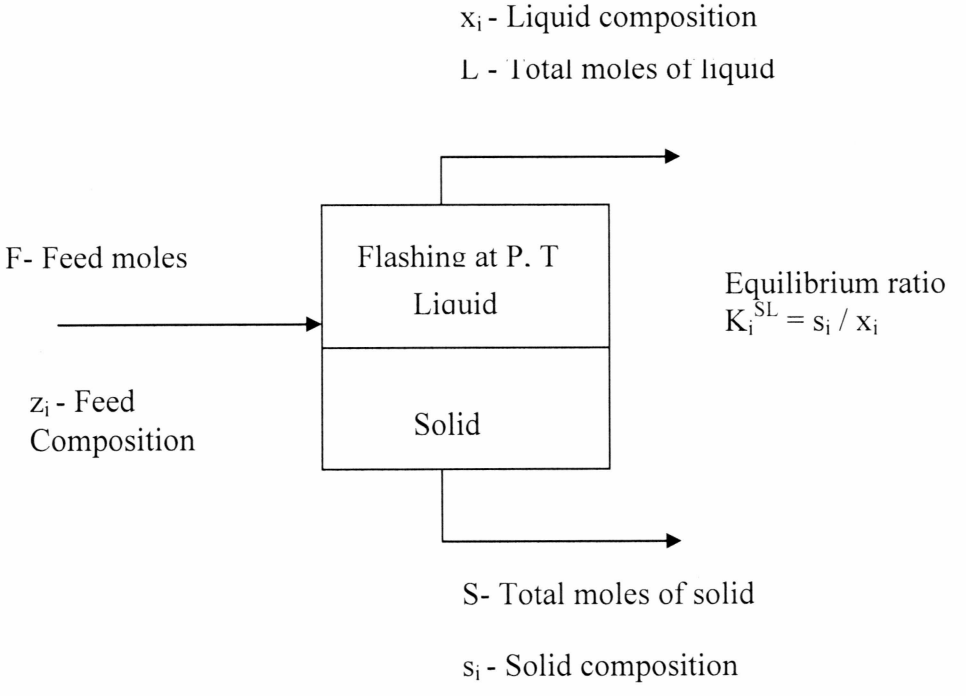

Figure 4.1: Schematic diagram of flash calculation

In figure 4.1, F moles of feed steam with overall composition, z_i is flashed at pressure, P and temperature, T. Flashing leads to formation of a solid stream (S moles at a composition, s_i) and a liquid stream (L moles at a composition, x_i)

Applying overall material balance,

$$F = L + S \tag{4.1}$$

Material balance applied to a particular component i can be expressed as

$$F \cdot z_i = L \cdot x_i + S \cdot s_i \tag{4.2}$$

Since the solid and liquid leaving the flash vessel are in equilibrium, it can be written that

$$s_i = K_i^{SL} \cdot x_i \tag{4.3}$$

Where K_i^{SL} : Equilibrium ratio of mole fraction of component i in solid and liquid phases at T and P

Putting L= F-S and from Equation (4.3), Equation (4.2) becomes

$$F \cdot z_i = (F - S) \cdot x_i + S \cdot K_i^{SL} \cdot x_i \tag{4.4}$$

Solving for x_i, Equation (14) can be written as

$$x_i = \frac{z_i}{1 + \frac{S}{F}\left(K_i^{SL} - 1\right)} \tag{4.5}$$

s_i can be expressed as

$$s_i = \frac{K_i^{SL} z_i}{1 + \frac{S}{F}\left(K_i^{SL} - 1\right)} \tag{4.6}$$

In addition, for both solid and liquid stream, $\sum s_i = \sum x_i = 1$ or $\sum (s_i - x_i) = 0$ must be always satisfied. Therefore, from Equations (4.5), (4.6) and the above criterion, the following objective function of S/F can be obtained:

$$f(S/F) = \sum \frac{\left(K_i^{SL} - 1\right) z_i}{1 + \frac{S}{F}\left(K_i^{SL} - 1\right)} = 0 \tag{4.7}$$

Equation (4.7) is also referred to as the Rachford-Rice equation. For flash calculations, feed moles (F), feed composition (z_i), pressure (P) and temperature (T) are known. Unknowns are solid moles (S), liquid moles (L), solid phase composition (s_i) and liquid phase composition (x_i). As shown in Equations (4.1),(4.5), (4.6) and (4.7), if the value of K_i^{SL} is known, the value of solid mole fraction S/F can be calculated from Equation (4.7) and based on that, all the other unknown variables can be determined. Hence, to do the flash calculations, the value of the equilibrium ratio of the mole fraction of the component in the solid phase to that in the liquid phase should be known. Therefore as

explained earlier in the literature survey, many authors have suggested various models to predict K_i^{SL}. In this chapter, Won's and Pedersen's models are discussed in detail.

4.2 Won's Model

Won first presented the model to predict wax precipitation (Won, 1985). But in this study, the modified version of Won's model is used.

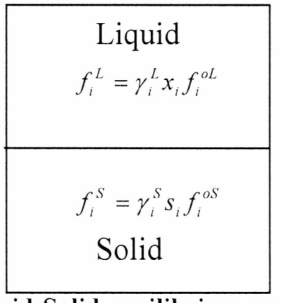

Figure 4.2 Liquid-Solid equilibrium model by Won

4.2.1 Assumptions of Model

Following are the assumptions made in Won's model (Won, 1986).

- The solid phase is a single, homogeneous solution which is in equilibrium with the liquid solution.
- Almost all components contained in the reservoir fluid may potentially enter into the wax phase.
- Heat capacity change of fusion is assumed to be negligible.
- Volume change during fusion was also neglected.
- The solid phase is assumed to behave non-ideally.

4.2.2 Won's Model Description (Won, 1986)

The model was based on the thermodynamic criterion that, at equilibrium, the fugacity of a component i in the solid phase (wax phase) should be equal to the fugacity of the same component in the liquid phase (oil phase). It can be expressed as following:

$$f_i^L = f_i^S \tag{4.8}$$

Where f_i^L = fugacity of a component i in the liquid phase mixture

f_i^S = fugacity of a component i in the solid phase mixture

The liquid phase fugacity of component i in the mixture can be expressed as

$$f_i^L = \gamma_i^L x_i f_i^{oL} \tag{4.9}$$

Where γ_i^L is the activity coefficient of component i in liquid phase. The activity coefficient is generally a function of composition of the phase.

x_i is the mole fraction of component i in the liquid phase.

f_i^{oL} is the standard state fugacity of component i in the liquid phase. It can also be described as the liquid phase fugacity of component i in its pure form.

The solid phase fugacity of component i in the mixture can be expressed as

$$f_i^S = \gamma_i^S s_i f_i^{oS} \tag{4.10}$$

Where γ_i^S is the activity coefficient of component i in the solid phase. s_i is the mole fraction of component i in the solid phase and f_i^{oS} is the standard state fugacity of component i in the solid phase. It can also be described as the solid phase fugacity of component i in its pure form.

From Equations (4.8), (4.9) and (4.10), we get,

$$\gamma_i^L x_i f_i^{oL} = \gamma_i^S s_i f_i^{oS} \tag{4.11}$$

From Equation (4.3), $K_i^{SL} = s_i / x_i$ and rearranging Equation (4.11),

$$K_i^{SL} = \frac{s_i}{x_i} = \frac{\gamma_i^L f_i^{oL}}{\gamma_i^S f_i^{oS}} \tag{4.12}$$

Currently, there is no equation of state that can describe the volumetric behavior of a solid. But by relating the chemical potential of the solid phase to that of the liquid phase, the ratio of f_i^{oL} to f_i^{oS} can be expressed as

$$K_i^{SL} = \frac{s_i}{x_i} = \left(\frac{\gamma_i^L}{\gamma_i^S}\right) \exp\left[\frac{\Delta H^f}{RT}\left(1 - \frac{T}{T^f}\right) + \frac{\Delta C_P}{R}\left(1 - \frac{T^f}{T} + \ln\frac{T^f}{T}\right) + \int_0^P \frac{\Delta V}{RT} dP\right]_i \tag{4.13}$$

Where T^f, ΔH^f, ΔC_P and ΔV are fusion temperature, heat of fusion, heat capacity change of fusion and volume change of fusion, respectively. P & T are the pressure and temperature at which flashing is being carried out. The derivation is explained in detail in Appendix A.

Won also presented the co-relation to calculate the heat of fusion (ΔH^f) and the temperature of fusion (T^f) as

$$\Delta H^f = 0.1426 \cdot MW_i \cdot T_i^f \tag{4.14}$$

Where MW_i is the molecular weight of the component i and T_i^f can be obtained from

$$T_i^f = 374.5 + 0.02617 \cdot MW_i - 20172 / MW_i \tag{4.15}$$

As explained in section 4.2.1, the second and third terms in Equation (4.13) are assumed to be zero. If the solid phase is assumed to be an ideal mixture, then the ratio of activity coefficients becomes 1. But in the actual wax phase, the mixture is found to be behaving non-ideally. So, Won (1986) assumed the solid phase to be a non-ideal mixture. Hence, the ratio of activity coefficients can not be assumed as 1. In Won's model, he used the regular solution theory to estimate the ratio of activity coefficients.

The activity coefficient for component i (for both liquid and solid phases) can be calculated using the regular solution theory as,

$$\ln \gamma_i = \frac{v_i(\bar{\delta} - \delta_i)^2}{RT} \tag{4.16}$$

Where, v_i is the molar volume, δ_i is the solubility parameter and $\bar{\delta}$ is the average solubility parameter of the mixture. The average solubility parameter can be estimated as:

$$\bar{\delta} = \sum \varphi_i \delta_i \tag{4.17}$$

Where φ_i is the volume fraction of component i and can be obtained for both liquid and solid phases from the following relationships:

$$\varphi_i^L = \frac{x_i v_i}{\sum x_i v_i} \text{ and } \varphi_i^S = \frac{s_i v_i}{\sum s_i v_i} \tag{4.18}$$

The solubility parameter for component i in the liquid phase mixture can be estimated as

$$\delta_i^L = \left(\frac{\Delta H^V - RT}{V} \right)_i^{0.5} \Bigg|_{25^0 C} \tag{4.19}$$

Where ΔH^V the heat of vaporization at 25°C

The solubility parameter for component i in the solid solution can be estimated as

$$\delta_i^S = \left(\frac{\Delta H^V + \Delta H^f - RT}{V} \right)_{i,S}^{0.5} \Bigg|_{25^0 C} \tag{4.20}$$

All the properties in Equation (4.18) are at 25^0C.

δ_i^L and δ_i^S are given by Won for components upto C_{40}. They are presented in **Table 4.1**.

In the current work, the co-relations given by Pedersen et al. (1991) have been used for estimating the solubility parameters of the components in the solid and liquid phases as they give better results.

$$\delta_i^L = 7.41 + a_1(\ln C_N - \ln 7) \tag{4.21}$$

$$\delta_i^S = 8.50 + a_2(\ln C_N - \ln 7) \tag{4.22}$$

Where C_N is the carbon number of the component, a_1 and a_2 are equal to 0.5914 $(cal/cm^3)^{0.5}$ and 5.763 $(cal/cm^3)^{0.5}$, respectively.

For calculating the average solubility parameter and the activity coefficient, the molar volume is required. Won presented the correlation for calculating the molar volume as

$$v_i = MW_i / d_{25}^L \tag{4.23}$$

$$d_{25}^L = 0.8155 + 0.6272 \cdot 10^{-4} \cdot MW_i - 13.06 / MW_i \tag{4.24}$$

Won assumed that the molar volumes of component i in solid and liquid phases are equal. Therefore,

$$v_i^L = v_i^S \tag{4.25}$$

Using (4.23), (4.24) and (4.18), the volume fraction factor (ϕ_i) can be calculated. The solubility parameters can be obtained from Equations (4.21) and (4.22). Using the solubility parameters (δ) and the volume fraction factors (φ), the average solubility parameter can be estimated with Equation (4.17). With the knowledge of molar volume, solubility parameter (for both liquid and solid phases) and average solubility parameter, the activity coefficients for the components in both liquid and solid phases can be calculated from Equation (4.16). After applying Equation (4.16) to both liquid and solid phases, the ratio of activity coefficients can be expressed as

$$\frac{\gamma_i^L}{\gamma_i^S} = \exp\left[\frac{v_i}{RT}\left((\bar{\delta} - \delta_i)_L^2 - (\bar{\delta} - \delta_i)_S^2\right)\right] \tag{4.26}$$

Table 4.1 Solubility parameters for components up to C40 (Won, 1986)

	T^f	Δh^f	δ^L	δ^S
	k	cal/gmol	(cal/cc)^0.5	(cal/cc)^0.5
CO2	216	0	7.12	7.12
C1	90	0	5.68	5.68
C2	101	385	6.6	6.6
C3	86	0	6.65	6.65
C4	138	0	6.65	6.65
C5	97	996	7.02	7.62
C6	143	1750	7.25	8.13
C7	179	2510	7.41	8.5
C8	201	2070	7.53	8.78
C9	221	3270	7.63	9
C10	237	4030	7.71	9.17
C11	250	4800	7.78	9.32
C12	261	5560	7.83	9.44
C13	270	6330	7.88	9.55
C14	278	7100	7.92	9.64
C15	285	7870	7.96	9.72
C16	291	8640	7.99	9.9
C17	297	9410	8.02	9.86
C18	302	10200	8.05	9.92
C19	306	11000	8.07	9.97
C20	311	11700	8.09	10
C21	314	12500	8.11	10.1
C22	318	13300	8.13	10.1
C23	321	14900	8.15	10.1
C24	324	15600	8.17	10.2
C25	327	16400	8.18	10.2
C26	329	17200	8.2	10.3
C27	332	18000	8.21	10.3
C28	334	18800	8.22	10.3
C29	336	19000	8.24	10.3
C30	338	20400	8.25	10.4
C31	340	21200	8.26	10.4
C32	342	22000	8.27	10.4
C33	343	22800	8.28	10.4
C34	345	23600	8.29	10.4
C35	346	24400	8.3	10.5
C36	348	25200	8.31	10.5
C37	349	26000	8.32	10.5
C38	351	26800	8.33	10.5
C39	352	27600	8.34	10.5
C40	353	28400	8.35	10.6

From Equation (4.26) and (4.13), K_i^{SL} can be expressed as

$$K_i^{SL} = \frac{s_i}{x_i} = \exp\left[\frac{\Delta H^f}{RT}\left(1-\frac{T}{T^f}\right)+\frac{v_i}{RT}\left((\bar{\delta}-\delta_i)_L^2-(\bar{\delta}-\delta_i)_S^2\right)\right] \tag{4.27}$$

As explained in section 4.1, with the knowledge of K_i^{SL}, the Rachford-Rice Equation can be solved to obtain the amount of wax precipitated (S/F). But, it should be noted that for calculating K_i^{SL}, the compositions of the liquid (x_i) and solid streams (s_i) are required, and before attempting to solve the Rachford-Rice equation, these values are not known. So, it is an open ended problem. The work-around procedure for this problem will be explained in the next chapter.

4.3 Pedersen's Model

One of the main drawbacks with Won's model as reported in literature is that it overestimates the amount of wax precipitated (Fredenslund et al., 1988). Pedersen and Christensen (2007) attributed the problem to assigning the melting properties of n-paraffins to all the constituents of a hydrocarbon pseudo-component. As seen from Equation (4.14) and (4.15), Won has assigned the melting properties of the wax forming components to the non-wax forming components, too. For example, consider oil dominated by C_{10} component. From Won's model, all constituents in the oil (paraffins, iso-paraffins, aromatics, naphthenes, whichever of them are present) will be assigned the melting properties of paraffins. So, if the sample is cooled to a temperature below the melting point of C_{10}, then the model will predict that almost all of the oil constituents will be converted into wax. The solid phase will include the aromatics and naphthenes which have less of a tendency to go into solid phase. In general, the potential wax forming components constitute about 15% of oil's weight. So the predictions from Won's model are not consistent with the experimental data. Therefore, it is necessary to distinguish between the potentially wax forming and non-wax forming compounds (Pedersen and Christensen, 2007).

The experimental techniques such as Gas Chromatography (GC) can identify the hydrocarbon components with less than 7 carbon atoms. But as the carbon number goes up, various types of compounds such as n-paraffins, naphthenes, aromatics are

represented together in one single carbon number fraction. The composition analysis does not describe how much of n-paraffin is present in e.g. C_{20} fraction. In general, the n-paraffins are expected to enter into the wax phase. The presence of branched paraffins and naphthenes is not very common in the solid phase (wax phase). Aromatics are not generally present in the wax phase. Only a part of each C_7^+ fraction contributes to the wax formation. This generally is the n-paraffin fraction. Therefore it is essential to know how much of n-paraffin is present in each carbon number fraction. The amount can be found out from PNA analyses but it is rarely done due to the complexity and huge amount of efforts involved. Hence, Pedersen (1995) developed a theoretical scheme to find out the amount of wax forming components contained in as single carbon number fraction.

According to the model, the mole fraction of potentially wax forming part, z_i^S, of a pseudo-component i, having a total mole fraction, z_i^{old}, is given by

$$z_i^S = z_i^{old}\left[1-(A+B\cdot M_i)\cdot\left(\frac{\rho_i-\rho_i^p}{\rho_i^p}\right)^C\right] \tag{4.28}$$

Where, M_i is the molecular weight of pseudo-component i, ρ_i is the density of pseudo component i at the standard conditions and ρ_i^P is density of the n-paraffin with the molecular weight M_i at the atmospheric pressure and 15°C. ρ_i^P can be obtained from

$$\rho_i^p = 0.3915 + 0.0675\cdot\ln M_i \tag{4.29}$$

A, B and C are the constants which are found by fitting the predictions with the experimental data. Pedersen gave the values of A, B and C which were fitted to many oil samples. They are given in table 4.2.

Table 4.2 Constants in Equations 4.28

A	0.8824
B	$5.353*10^{-4}$
C	0.1144

The non-wax forming part can be obtained from

$$z_i^{no-S} = z_i^{old} - z_i^S \tag{4.30}$$

Where, z_i^{no-S} represents the non-wax forming part of the pseudo-component i. In general, z_i^S is lower than z_i^{old}. If z_i^S equals z_i^{old}, that means all the constituents in pseudo-component i can potentially enter into wax phase. As each component is split into the wax forming and non-wax forming components, the number of components one has to work with get doubled.

4.3.1 Assumptions of Pedersen's Model

- All constituents of a pseudo-component can not enter into the wax phase.
- Only C_{7+} can potentially form wax.
- The solid phase is a single, homogeneous solution in equilibrium with the liquid solution.
- The solid phase is assumed to behave ideally.
- The equilibrium ratio, K_i^{SL}, the ratio between the mole fractions of component i in the solid and liquid phases, is assumed to be 0 for the non-wax forming parts of all pseudocomponents.

4.3.2 Pedersen's Model Description (Pedersen, 1995)

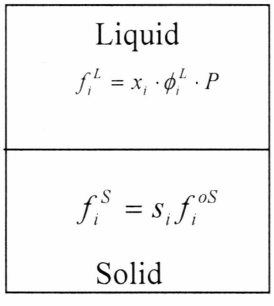

Figure 4.3 Liquid-Solid model proposed by Pedersen

As shown in **Figure 4.3**, a component i in the liquid phase is in equilibrium with the same component i in the solid phase. The basic criterion for equilibrium is same as that for Won's model as described in section 4.3.2. At equilibrium, the fugacity of a

component i in the liquid mixture, f_i^L, should be equal to the fugacity of the same component i in the solid phase, f_i^S. Therefore,

$$f_i^L = f_i^S \tag{4.31}$$

The fugacity of component i in the liquid phase mixture can be described as:

$$f_i^L = x_i \phi_i^L P \tag{4.32}$$

Where x_i is the mole fraction of component i in the liquid phase, ϕ_i^L is the fugacity coefficient of i in the liquid phase and P is the system pressure. The fugacity coefficient of component i in the liquid phase mixture can be obtained from any Equation of State (EOS) like Peng-Robinson EOS (PR-EOS) as,

$$\ln(\phi_i^L) = \frac{b_i}{b_m}(Z_L - 1) - \ln(Z_L - B_m) - \frac{A_m}{B(\delta_2 - \delta_1)}\left[\frac{2\psi_i}{\psi} - \frac{b_i}{b_m}\right]\ln\left[\frac{Z_L + \delta_2 B_m}{Z_L + \delta_1 B_m}\right] \tag{4.33}$$

Where b_i, A_m, B_m, b_m, ψ_i and ψ are the parameters for PR-EOS. Z_L is the compressibility factor for a component i in the liquid mixture at the system pressure and temperature. The calculation procedures of these parameters are described in Appendix B. δ_1 and δ_2 equal to $1+\sqrt{2}$ and $1-\sqrt{2}$ respectively.

As the wax phase is assumed to an ideal solution, the fugacity of component i, f_i^S in the solid phase mixture can be described as,

$$f_i^S = s_i f_i^{oS} \tag{4.34}$$

Where, f_i^{oS} is the fugacity of pure component i in the solid phase and it can be expressed as:

$$f_i^{oS} = f_i^{oL} \exp\left(\frac{-\Delta H_i^f}{RT}\left[1 - \frac{T}{T_i^f}\right]\right) \tag{4.35}$$

Where f_i^{oL} is the fugacity of pure component i in the liquid phase at the system pressure, P and temperature T. T_i^f and ΔH_i^f are fusion temperature, heat of fusion of pseudo-component i, respectively. They are given by,

$$\Delta H^f = 0.1426 \cdot MW_i \cdot T_i^f \tag{4.36}$$

Where MW_i is the molecular weight of component i and T_i^f can be obtained from,

$$T_i^f = 374.5 + 0.02617 \cdot MW_i - 20172 / MW_i \tag{4.37}$$

f_i^{oL} is expressed as,

$$f_i^{oL} = \phi_i^{oL} \cdot P \tag{4.38}$$

Where ϕ_i^{oL} is the fugacity coefficient for pure component i in the liquid phase and can be obtained from application of PR-EOS to single component as,

$$\ln\left(\phi_i^{oL}\right) = Z_L^{pure} - 1 - \ln(Z_L^{pure} - B_i^{pure}) + \frac{A_i^{pure}}{2\sqrt{2}B_i^{pure}} \ln\left[\frac{Z_L^{pure} + (1-\sqrt{2})B_i^{pure}}{Z_L^{pure} + (1+\sqrt{2})B_i^{pure}}\right] \tag{4.39}$$

A_i^{pure} and B_i^{pure} are PR EOS parameters for a single component i and Z_L^{pure} is the compressibility factor of pure component i in the liquid phase. Calculations of these parameters are described in Appendix B.

From Equations (4.34), (4.35) and (4.38), the fugacity of component i in the solid phase mixture can be expressed as

$$f_i^S = s_i \exp\left(\frac{-\Delta H_i^f}{RT}\left[1 - \frac{T}{T_i^f}\right]\right)\phi_i^{oL} \cdot P \tag{4.40}$$

From (4.31), (4.32) and (4.40), it can be written that,

$$x_i \phi_i^L P = s_i \exp\left(\frac{-\Delta H_i^f}{RT}\left[1 - \frac{T}{T_i^f}\right]\right)\phi_i^{oL} \cdot P \tag{4.41}$$

It should be noted that there is a difference between ϕ_i^L and ϕ_i^{oL}. ϕ_i^L is the fugacity coefficient of a component i in the liquid phase mixture (obtained by Equation (4.33))and ϕ_i^{oL} is the fugacity coefficient of a pure component i in the liquid phase (obtained by Equation (4.39)). Rearranging Equation (4.41) and noting that $K_i^{SL} = s_i / x_i$,

$$K_i^{SL} = \frac{s_i}{x_i} = \frac{\phi_i^L}{\exp\left(\frac{-\Delta H_i^f}{RT}\left[1 - \frac{T}{T_i^f}\right]\right)\phi_i^{oL}} \tag{4.42}$$

As seen from section 4.1, the Rachford-Rice equation can be solved to obtain the liquid and solid stream compositions and the amount of wax precipitated if the values of

K_i^{SL} are known. The values of K_i^{SL} can be obtained from Equation (4.42). But for finding the value of ϕ_i^{oL}, the liquid stream composition should be known, so this is, again, an open ended problem. The solution to this problem is explained in the next chapter.

Also for calculating ϕ_i^{L} and ϕ_i^{oL} from PR EOS, the critical properties (P_c, T_c) of the pseudo-components should be known. The critical pressure of a n-paraffin is lower than that for an aromatic with same molecular weight. As discussed earlier, the n-paraffins go into the wax phase where as the aromatics do not generally form wax. Therefore, the wax forming part of the pseudo-component (mainly consisting of n-paraffins) should have a lower P_c than the non-wax forming part (mainly consisting of naphthenes, aromatics). So the values of P_c for the wax forming and non-wax forming components are obtained from the following co-relations:

$$P_{ci}^{S} = P_{ci}\left(\frac{\rho_i^{p}}{\rho_i}\right)^{3.46} \tag{4.43}$$

$$\text{And } \frac{1}{P_{ci}} = \frac{\left(\frac{z_i^{tot} - z_i^{s}}{z_i^{tot}}\right)^2}{P_{ci}^{no-S}} + \frac{\left(\frac{z_i^{s}}{z_i^{tot}}\right)^2}{P_{ci}^{S}} + \frac{2\left(\frac{z_i^{tot} - z_i^{s}}{z_i^{tot}}\right)\cdot\left(\frac{z_i^{s}}{z_i^{tot}}\right)}{\sqrt{P_{ci}^{no-S}}\cdot\sqrt{P_{ci}^{S}}} \tag{4.44}$$

Where, P_{ci}^{S} and P_{ci}^{no-S} are the critical pressures of the wax forming and non-wax forming part of the pseudo-component i and P_{ci} is the critical pressure of pseudo-component i before it is split into the wax forming and non-wax forming parts using Equation 4.28. z_i^{total} represents the mole fraction of the pseudo-component i in the feed stream in **Figure 4.1**. z_i^{S} and z_i^{no-S} represent the wax forming and non-wax forming part of that pseudo component and $z_i^{old} = z_i^{S} + z_i^{no-S}$. Therefore the feed stream to the flash vessel in **Figure 4.1** contains twice the number of components than those initially, since each single carbon number fraction is split into two parts. For example, consider a C_{20} component with mole fraction z_{C20} in oil. After splitting, the feed stream to the flash vessel in **Figure 4.1** will contain two pseudo-components C_{20}^{S} and C_{20}^{no-S} with mole fractions z_{C20}^{S} and z_{C20}^{no-S}, of which the former can enter into the wax phase where as the

latter will always stay in the liquid phase. The wax forming and non-wax forming parts are treated as different components (The values of K_i^{SL} for the non-wax forming components are taken as 0 for all calculations).These z's should not be confused with Z's in Equation (4.33) and (4.39), small letter z's represent the mole fractions of component in the feed stream to the flash vessel where as capital letter Z's represent the compressibility factors of the components.

Ronningsen et al. (1997) introduced a correction factor for describing the solid phase fugacity of component i at high pressures as,

$$f_i^S = s_i \exp\left(\frac{-\Delta H_i^f}{RT}\left[1-\frac{T}{T_i^f}\right]+\frac{\Delta V_i(P-P_{ref})}{RT}\right)\phi_i^{oL}\cdot P \tag{4.45}$$

where, ΔV_i is the volume change associated with the solidification process. They suggested that it should taken as -10% of the molar volume of pseudo-component i in the liquid phase. P_{ref} is taken as 14.7 psia as the melting properties are generally available at the atmospheric pressure. Using Equation (4.45), the expression for K_i^{SL} is modified to,

$$K_i^{SL} = \frac{s_i}{x_i} = \frac{\phi_i^L}{\exp\left(\frac{-\Delta H_i^f}{RT}\left[1-\frac{T}{T_i^f}\right]+\frac{\Delta V_i(P-P_{ref})}{RT}\right)\phi_i^{oL}} \tag{4.46}$$

Both Won's model and Pedersen's liquid-solid models, deal with wax precipitation from the liquid phase. This case is generally valid at lower pressures where the components which may enter into the vapor phase have already vaporized. But at higher pressures, the vapor phase influences the wax precipitation. For this, three phase equilibrium containing vapor phase should be described. This is done in following section.

4.4 Three Phase Flash Calculations (Won, 1986)

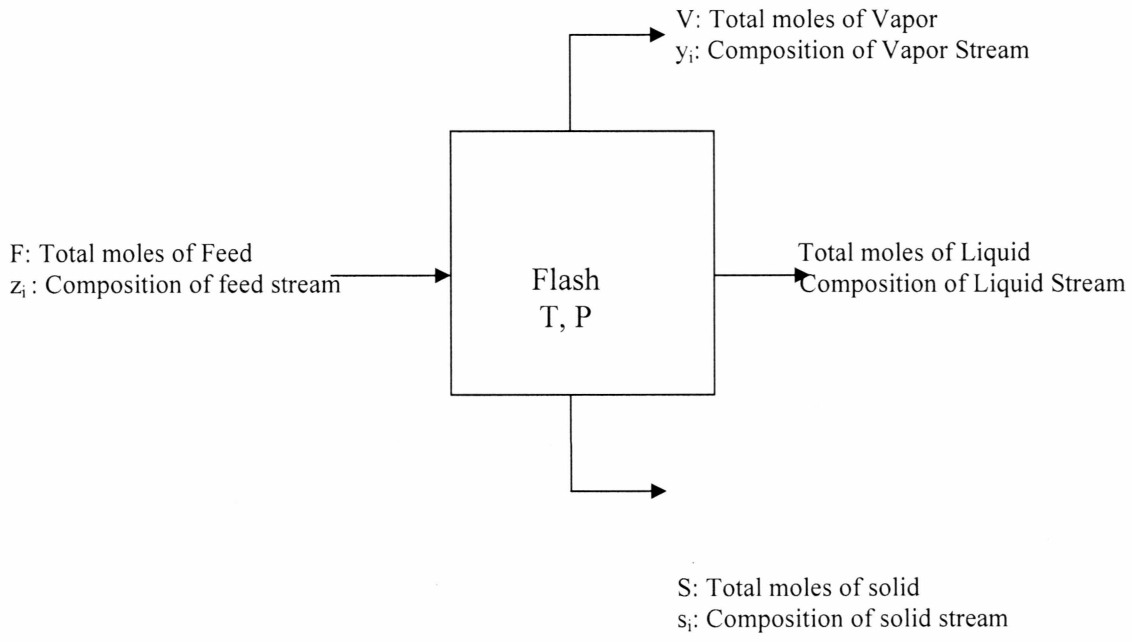

Figure 4.4 Three phase flash

As explained earlier, to find out the amount of wax precipitated, flash calculations need to be performed. At higher pressures, the three phase flash calculations need to be performed as the vapor phase comes into the picture along with the liquid and solid phases. This is explained in **Figure 4.4. A** feed of F moles with known composition, z_i, is flashed in a flash vessel (with known pressure P and temperature T) and three streams are formed: a liquid stream of L moles with an overall composition as x_i, a vapor stream of V moles with an overall composition y_i and a solid stream of S moles with an overall composition s_i.

The overall material balance can be written as,

$$F = V + L + S \tag{4.47}$$

The component balance yields,

$$F \cdot z_i = V \cdot y_i + L \cdot x_i + S \cdot s_i \tag{4.48}$$

As the solid and liquid phases are in equilibrium in the flash vessel, it can be written that

$$s_i = K_i^{SL} \cdot x_i \tag{4.49}$$

Where K_i^{SL} : Equilibrium ratio of the mole fractions of component i in the solid and liquid phases at T and P

Also, as the vapor and liquid phases are in equilibrium,

$$y_i = K_i^{VL} \cdot x_i \tag{4.50}$$

Where K_i^{VL} : Equilibrium ratio of the mole fractions of component i in the vapor and liquid phases at T and P

Substituting s_i and y_i from Equation (4.49) and (4.50) and L = F- V-S and rearranging for x_i, Equation (4.48) can be written as,

$$x_i = \frac{F \cdot z_i}{V \cdot K_i^{VL} + (F - V - S) + S \cdot K_i^{SL}} \tag{4.51}$$

Dividing F and rearranging, x_i can be expressed as,

$$x_i = \frac{z_i}{1 + \frac{V}{F} \cdot (K_i^{VL} - 1) + \frac{S}{F} \cdot (K_i^{SL} - 1)} \tag{4.52}$$

Substituting value of x_i in Equations (4.49) and (4.50),

$$s_i = \frac{K_i^{SL} \cdot z_i}{1 + \frac{V}{F} \cdot (K_i^{VL} - 1) + \frac{S}{F} \cdot (K_i^{SL} - 1)} \tag{4.53}$$

$$y_i = \frac{K_i^{VL} \cdot z_i}{1 + \frac{V}{F} \cdot (K_i^{VL} - 1) + \frac{S}{F} \cdot (K_i^{SL} - 1)} \tag{4.54}$$

For both solid and liquid streams, $\sum s_i = \sum x_i = 1$ or $\sum (s_i - x_i) = 0$ must be always satisfied. Also for both vapor and liquid stream, $\sum y_i = \sum x_i = 1$ or $\sum (y_i - x_i) = 0$ must be always satisfied.

$$f^{SL}\left(\frac{V}{F}, \frac{S}{F}\right) = \sum (s_i - x_i) = \sum \frac{(K_i^{SL} - 1) \cdot z_i}{1 + \frac{V}{F} \cdot (K_i^{VL} - 1) + \frac{S}{F} \cdot (K_i^{SL} - 1)} = 0 \tag{4.55}$$

$$f^{VL}\left(\frac{V}{F},\frac{S}{F}\right)=\sum(y_i-x_i)=\sum\frac{(K_i^{VL}-1)\cdot z_i}{1+\frac{V}{F}\cdot(K_i^{VL}-1)+\frac{S}{F}\cdot(K_i^{SL}-1)}=0 \qquad (4.56)$$

Equations (4.55) and (4.56) represent the modified Rachford-Rice method for the three phase flash involving vapor, liquid and solid phases. In these equations, z_i is known. V/F and S/F are the fractions that need to be found out as S/F represents the mole fraction of wax precipitated. If values of K_i^{VL} and K_i^{SL} are known, then these equations can be solved to obtain V/F and S/F and by Equations (4.52), (4.53) and (4.54), the compositions of each stream can be found out. Won's model (1986) described the method to predict K_i^{VL} and K_i^{SL} for three phases. This model is described in the next section. The solution for the Rachford-Rice problem will be explained in the next chapter.

4.5 Three Phase Modeling

This model is presented in the same paper by Won (1986) in which he proposed the two phase model. The assumptions for this model are essentially the same as that for the two phase model as described in section 4.2.1.

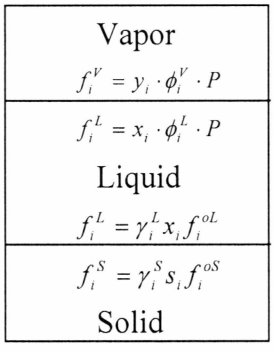

Figure 4.5 Vapor-liquid-solid equilibrium model by Won

As shown in **Figure 4.5,** the solid phase is in equilibrium with the liquid and gas phases. All the phases are considered to be non-ideal mixtures. At equilibrium, the fugacity of each component in all the phases should be equal. Therefore,

$$f_i^S = f_i^L = f_i^V \qquad (4.57)$$

Where, f_i^S, f_i^L and f_i^V represent the fugacities of component i in the solid , liquid and vapor phases respectively. This equilibrium can be considered as two separate

equilibriums as $f_i^S = f_i^L$ and $f_i^L = f_i^V$. The first one considers the equilibrium between the liquid and solid phases and the latter one considers the equilibrium between the liquid and vapor phases.

As both liquid and solid phases are considered as non-ideal mixtures, as explained in section 4.2.2,

$$f_i^L = \gamma_i^L x_i f_i^{oL} \tag{4.58}$$

$$f_i^S = \gamma_i^S s_i f_i^{oS} \tag{4.59}$$

Equating the fugacities and applying the Regular Solution Theory as explained in section 4.2.2, $K_i^{SL} = s_i/x_i$ is obtained as,

$$K_i^{SL} = \frac{s_i}{x_i} = \exp\left[\frac{\Delta H^f}{RT}\left(1-\frac{T}{T^f}\right)+\frac{v_i}{RT}\left((\bar{\delta}-\delta_i)_L^2-(\bar{\delta}-\delta_i)_S^2\right)\right] \tag{4.60}$$

which is exactly as same Equation (4.27). T_i^f and ΔH_i^f are the fusion temperature and the heat of fusion and can be obtained from Equations (4.14) and (4.15). δ_i^L and δ_i^S are the solubility parameters for the liquid and solid phases respectively and can be obtained from Equations (4.21) and (4.22). $\bar{\delta}$ is the average solubility parameter of the mixture and is obtained from Equation (4.17). It requires the average volume fraction φ_i which is obtained by Equations (4.18) and (4.23)-(4.25). Thus knowing the values of all the parameters in Equation (4.60), K_i^{SL} can be calculated.

As both the vapor and liquid phases are assumed to behave non-ideally,

$$f_i^V = y_i \cdot \phi_i^V \cdot P \tag{4.61}$$

$$f_i^L = x_i \cdot \phi_i^L \cdot P \tag{4.62}$$

Where, y_i and x_i are the mole fractions of component i in the vapor and liquid phases, respectively. ϕ_i^V and ϕ_i^L are the fugacity coefficients of component i in the vapor and liquid phases. These ϕ's should not be confused with the φ's in Equation (4.17) and (4.18). The former are the fugacity coefficients and the latter ones are the volume fractions of each component in the various phases. ϕ_i^V can be calculated from PR EOS.

$$\ln(\phi_i^V) = \frac{b_i}{b_m}(Z_V - 1) - \ln(Z_V - B_m) - \frac{A_m}{B(\delta_2 - \delta_1)}\left[\frac{2\psi_i}{\psi} - \frac{b_i}{b_m}\right]\ln\left[\frac{Z_V + \delta_2 B_m}{Z_V + \delta_1 B_m}\right] \qquad (4.63)$$

Where b_i, A_m, B_m, b_m, ψ_i and ψ are the parameters for PR-EOS. Z_V is the compressibility factor for component i in the vapor mixture at the system pressure and temperature. Calculation procedures of these parameters are described in Appendix B. δ_1 and δ_2 equal to $1+\sqrt{2}$ and $1-\sqrt{2}$ respectively. ϕ_i^L is obtained from Equation (4.33). Equating Equations (4.61) and (4.62), and noting $K_i^{VL} = y_i/x_i$

$$K_i^{VL} = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} \qquad (4.64)$$

Thus, K_i^{SL} and K_i^{VL} can be obtained and as explained in section 4.5, the Rachford-Rice equation for the three phase problem can be solved to obtain the amount of wax, liquid and vapor phases formed and the composition of each stream. But again, the problem is the same that for the calculation of both K_i^{SL} and K_i^{VL}, x_i, y_i and s_i should be known. But for the first iteration, they are not known. The solution procedure is explained in next chapter.

Chapter 5

Development of Algorithm

5.1 Two Phase Flash Calculations

To find out the amount of wax formed and the amount of wax precipitated, flash calculations have to be performed first. As explained in section 4.1, the Rachford-Rice equation needs to be solved for this purpose. For two phase flash calculations, the Rachford-Rice equation is expressed as,

$$f(S/F) = \sum \frac{\left(K_i^{SL} - 1\right) z_i}{1 + \frac{S}{F}\left(K_i^{SL} - 1\right)} = 0 \tag{5.1}$$

In Equation (5.1), S/F is the value that one is interested in determining, as it represents the amount of wax precipitated. Oil may contain up to 200 components; therefore, a direct solution to Equation (5.1) is very difficult. A numerical method has to be used to solve the equation. K_i^{SL} has to be calculated from either Won's model or Pedersen's model, but these models require the compositions of the solid and liquid phases. Since the compositions of solid and liquid stream are unknown, the values of K_i^{SL} have to be guessed in order to find S/F and the compositions of each stream. The compositions then should be used to find the correct values of K_i^{SL} from Won's or Pedersen's model. This will be explained in detail in the next section. For this section, it is assumed that the correct guess values of K_i^{SL} are available.

For solving Equation (5.1), Newton's method is used. The initial guess value of S/F is needed. Due to the large number of components involved and non-linearity of the equation, the nature of flash calculation is such that the convergence of the solution depends largely on the initial guess value of S/F. Therefore, Riazi (2005) suggested the following formula to calculate the initial guess value of S/F:

$$(S/F)^{initial} = \frac{\sum\left[z_i \cdot \left(K_i^{SL} - 1\right)\right]}{\sum\left[z_i \cdot \left(K_i^{SL} - 1\right)\right] - \sum\left[\frac{z_i \cdot \left(K_i^{SL} - 1\right)}{K_i^{SL}}\right]} \tag{5.2}$$

Then the value of $(S/F)^{initial}$ is substituted in Equation (5.1) to calculate the value of $f(S/F)$. If it is smaller than a preset tolerance criterion (ε), then the value of S/F is the correct one. For this study, a tolerance criterion of 10^{-10} was used. If the value of $f(S/F)$ is larger than ε, then the new value of (S/F) is determined by Newton's method:

$$(S/F)^{new} = (S/F) - \frac{f(S/F)}{f'(S/F)} \tag{5.3}$$

where $f'(S/F)$ is the first order derivative of $f(S/F)$ with respect to (S/F). It is obtained as,

$$f'(S/F) = -\sum_{i}^{N} \frac{z_i \cdot (K_i^{SL} - 1)^2}{[(S/F) \cdot (K_i^{SL} - 1) + 1]^2} \tag{5.4}$$

Therefore, the procedure to solve the Rachford-Rice equation for a two phase flash problem is given below.

1. The feed composition (z_i), initial guess values of K_i^{SL}, pressure (P) and temperature (T) are known.
2. Find out the initial guess value of (S/F), $(S/F)^{initial}$, from Equation (5.2).
3. Substitute $(S/F)^{initial}$ in Equation (5.1) to evaluate $f(S/F)$.
4. If $f(S/F) < \varepsilon$, then the value of (S/F) is correct, and the compositions of solid and liquid streams are determined from Equations (4.5) and (4.6).
5. If $f(S/F) > \varepsilon$, then find $f'(S/F)$ from Equation (5.4)
6. Calculate the new value of (S/F) from Equation (5.3) and the value obtained from step 5.
7. Substitute (S/F) obtained from step 6 in Equation (5.1) to evaluate $f(S/F)$.
8. Repeat steps 4-7 until the ($f(S/F) < \varepsilon$) criterion is satisfied.
9. From the correct value of (S/F), calculate the solid and liquid stream compositions.

It should be noted that the correct value of (S/F) is obtained from the assumed values of K_i^{SL}, and may not correspond to the actual K_i^{SL} values. The actual equilibrium ratio values should be obtained from Won's model or Pedersen's model. The procedure to obtain those values will be explained in later sections of this chapter.

5.2 Initial Guess Values of K_i^{SL}

As discussed earlier, to solve the Rachford-Rice equation, the values of K_i^{SL} are required. These values can be obtained from Won's model or Pedersen's model, but the models require the compositions of liquid and solid streams, which are not known initially; thus K_i^{SL} values have to be guessed. Due to the complex nature of the Rachford-Rice equation, the solution will not converge, however, unless proper values of K_i^{SL} are used. The same problem is faced when the Rachford-Rice equation is used for the vapor-liquid flash calculations. For the vapor-liquid flash calculations, the initial guess values of equilibrium ratios are obtained by Wilson's co-relation. It is given as,

$$K_i^{VL} = \frac{y_i}{x_i} = \frac{P_{ci}}{P} \exp\left[5.37 \cdot (1+\omega_i)\left(1-\frac{T_{ci}}{T}\right)\right] \tag{5.5}$$

where, P_{ci} , T_{ci} and ω_i are the critical pressure, critical temperature, and the acentric factor of component i, respectively. P and T are the pressure and temperature values at which the flash calculations are carried out. y_i and x_i represent the mole fractions of component i in the vapor and liquid phases, respectively. As the hydrocarbon fraction becomes heavier (i.e., when the carbon number of a fraction increases), the tendency of the fraction to go into the vapor phase decreases. Therefore, the value of K_i^{VL} decreases. An exactly opposite behavior is observed when the solid phase precipitation is considered. The heavier fractions have a higher tendency to go into the solid phase; therefore, the value of K_i^{SL} (which is the ratio of mole fractions of component i in the solid and liquid phases) increases. Hence, Mei et al. (1999) suggested using the reciprocal of K_i^{VL} for calculating the initial guess values of K_i^{SL} as:

$$K_i^{SL_{initial}} = \frac{s_i}{x_i} = \frac{1}{K_i^{VL_{initial}}} = \frac{1}{\frac{P_{ci}}{P} \exp\left[5.37 \cdot (1+\omega_i)\left(1-\frac{T_{ci}}{T}\right)\right]} \tag{5.6}$$

Thus, using the initial guess values of K_i^{SL}, the Rachford-Rice equation can be solved using the procedure explained in section 5.1, and the composition of solid and

liquid phases can be obtained. Using the compositions, the correct values of K_i^{SL} are obtained from Won's or Pedersen's model.

5.3 Two Phase Flash Calculations Using Won's Model

Using the initial guess values of K_i^{SL}, the amount of wax precipitated (S/F) and the compositions of solid (s_i) and liquid streams (x_i) can be calculated. The values do not correspond to reality, however, as the calculations have no thermodynamic base. Won's model gives the method to calculate the values of K_i^{SL} using thermodynamics.

An algorithm for estimating the amount of wax precipitated and the compositions of solid and liquid phases by Won's model is developed and described below.

1. The feed composition (z_i), pressure (P) and temperature (T) are known.
2. Find out the initial guess values of K_i^{SL} using Equation (5.6). Solve the Rachford-Rice equation using the procedure explained in section 5.1 to find out S/F, s_i and x_i, which are compositions of solid and liquid streams, respectively.
3. Calculate δ_i^L and δ_i^S using Equations (4.21) and (4.22) for all components.
4. Estimate the molar volume of each component in solid (v_i^S) and liquid phases (v_i^L) from Equations (4.23) through (4.25).
5. Find out the volume fractions of each component in solid (φ_i^S) and liquid phases (φ_i^L) using Equation (4.18).
6. Calculate $\bar{\delta}$, the average solubility parameter of the mixture, for both the liquid and solid phases by appropriately putting the volume fraction and the solubility parameters of component phase using Equation (4.17).
7. Find out T_i^f and ΔH_i^f, the fusion temperature and the heat of fusion, from Equations (4.14) and (4.15) for each component.
8. Using the terms obtained in the above steps, find out K_i^{SL} for each component using Equation (4.27).

9. Solve the Rachford-Rice equation using the procedure explained in section 5.1 and the newly obtained K_i^{SL} values, to obtain the solid mole fraction (S/F), the compositions of wax (s_i) and liquid phases (x_i).
10. Repeat steps 3-9, till constant values of the solid mole fraction (S/F) are obtained.

A program based on the above-described algorithm was developed in MATLAB. The results obtained are presented in the next chapter.

5.4 Two Phase Flash Calculations Using Pedersen's Model

Pedersen's model gives another method to calculate K_i^{SL} based on thermodynamics. An algorithm of estimating the amount of wax precipitated and the compositions of solid and liquid phases based on Pedersen's model is developed and described below.

1. The feed composition (z_i), pressure (P), and temperature (T) values are known. For C_{7+} components, $z_i^{old} = z_i$.
2. Calculate the density of n-paraffin ρ_i^P using Equation (4.29) for each C_{7+} component.
3. Estimate the wax forming fraction of each C_{7+} component (z_i^S) using Equation (4.28) and the values of constants given in Table 4.2.
4. Calculate the non-wax forming fraction of each C_{7+} component (z_i^{no-S}) using Equation (4.30) and the values obtained in step 3. The wax forming fraction and non-wax forming fraction are treated as two different components. These components form the new feed to the flash vessel. The C_{7+} components get doubled in this new feed due to the division into these fractions.
5. Obtain initial guess values of K_i^{SL} using Equation (5.6) for the wax forming fractions. For the non-wax forming components and components C_1-C_7, the values of K_i^{SL} are assumed to be zero.
6. Solve the Rachford-Rice equation using the procedure explained in section 5.1 to find out S/F, s_i and x_i, which are the compositions of solid and liquid streams.

7. The wax forming and non-wax forming components are assigned the critical properties using Equations (4.43) and (4.44).
8. Calculate the fugacity of each component in the liquid phase, ϕ_i^L, using Equation (4.33) and the procedure explained in Appendix B.
9. Calculate the liquid phase fugacity of each pure C_{7+} component, ϕ_i^{oL} using Equation (4.39) and the procedure explained in Appendix B.
10. The fusion temperature (T_i^f) and the heat of fusion (ΔH_i^f) of each pseudo-component i are obtained from Equations (4.36) and (4.37), respectively.
11. Knowing all the terms in Equation (4.42), the K_i^{SL} values are calculated. At higher pressures, use Equation (4.46) instead of Equation (4.42). V_i required for the calculations is obtained from PR EOS.
12. Again for the non-wax forming fractions, the K_i^{SL} s are assumed to be 0.
13. Solve the Rachford-Rice equation using the procedure explained in section 5.1 and these newly obtained K_i^{SL} values to find out the solid mole fraction (S/F) and compositions of the wax (s_i) and liquid phases (x_i).
14. Repeat steps 7-13, till constant values of solid mole fraction (S/F) are obtained.

A program based on the above described algorithm was developed in MATLAB. The results obtained are presented in the next chapter.

5.5 Three Phase Flash Calculations

At higher pressures, the vapor phase also enters the picture. For finding the amount of wax and vapor phases formed and the compositions of wax, vapor and liquid streams, the Rachford-Rice equation modified for three phases has to be solved as described in section 4.4.

The Rachford-Rice equation for the three phase flash calculations is,

$$f^{SL}\left(\frac{V}{F},\frac{S}{F}\right)=f^{SL}=\sum(s_i-x_i)=\sum\frac{(K_i^{SL}-1)\cdot z_i}{1+\frac{V}{F}\cdot(K_i^{VL}-1)+\frac{S}{F}\cdot(K_i^{SL}-1)}=0 \qquad (5.7)$$

$$f^{VL}\left(\frac{V}{F},\frac{S}{F}\right)=f^{VL}=\sum(y_i-x_i)=\sum\frac{(K_i^{VL}-1)\cdot z_i}{1+\frac{V}{F}\cdot(K_i^{VL}-1)+\frac{S}{F}\cdot(K_i^{SL}-1)}=0 \qquad (5.8)$$

In Equations (5.7) and (5.8), the values of (V/F) and (S/F) are unknown and are our area of interest, as (S/F) represents the mole fraction of wax formed. The values of K_i^{SL} and K_i^{VL} are determined from the model explained in section 4.5. The model requires the composition of each stream and it is not known initially. Therefore, the initial values of K_i^{SL} and K_i^{VL} have to be guessed. The initial guess values of K_i^{SL} and K_i^{VL} can be estimated from Equations (5.5) and (5.6). From Equation (5.8), it can be seen that these equations are simultaneous, non-linear equations. Also, as many components are involved, a direct solution for this problem is not possible. Therefore, the multivariate Newton's method is applied for finding out the values of S/F and V/F (King, 1971).

The methods for estimating initial guesses for multivariate Newton's method are very complicated and were not used. The program for solving Rachford-Rice equation was written. The initial values of (V/F) were assumed to be in the range of 0.85-0.90, whereas values (S/F) were assumed to be in the range of 0.01-0.05. These values did not introduce any convergence problems, for the data sets used in this study. These values are substituted in Equations (5.7) and (5.8), and the values of $f^{SL}\left(\frac{V}{F},\frac{S}{F}\right)$ and $f^{VL}\left(\frac{V}{F},\frac{S}{F}\right)$ were calculated. If these values are smaller than a preset tolerance criterion (ε), then the values of (S/F) and (V/F) are correct. For the current study, a tolerance criterion of 10^{-5} was used. If values are larger than ε, then the new values of (S/F) and (V/F) is determined by multivariate Newton's method as,

$$(V/F)_{j+1}=(V/F)_j+\frac{\left(f^{SL}{}_j\cdot\left.\frac{\partial f^{VL}}{\partial(S/F)}\right|_j-f^{VL}{}_j\cdot\left.\frac{\partial f^{SL}}{\partial(S/F)}\right|_j\right)}{\left(\left.\frac{\partial f^{VL}}{\partial(V/F)}\right|_j\cdot\left.\frac{\partial f^{SL}}{\partial(S/F)}\right|_j-\left.\frac{\partial f^{VL}}{\partial(S/F)}\right|_j\cdot\left.\frac{\partial f^{SL}}{\partial(V/F)}\right|_j\right)} \qquad (5.9)$$

$$(S/F)_{j+1} = (S/F)_j + \frac{\left(f^{SL}{}_j \cdot \left.\frac{\partial f^{VL}}{\partial (V/F)}\right|_j - f^{VL}{}_j \cdot \left.\frac{\partial f^{SL}}{\partial (V/F)}\right|_j \right)}{\left(\left.\frac{\partial f^{VL}}{\partial (S/F)}\right|_j \cdot \left.\frac{\partial f^{SL}}{\partial (V/F)}\right|_j - \left.\frac{\partial f^{VL}}{\partial (V/F)}\right|_j \cdot \left.\frac{\partial f^{SL}}{\partial (S/F)}\right|_j \right)} \tag{5.10}$$

where, j indicates the iteration number. $\left.\frac{\partial f^{VL}}{\partial (S/F)}\right|_j$ and $\left.\frac{\partial f^{VL}}{\partial (V/F)}\right|_j$ are the values of the partial derivatives of $f^{VL}\left(\frac{V}{F}, \frac{S}{F}\right)$ when differentiated with respect to (S/F) and (V/F) respectively while keeping other variables constant, and evaluated by substituting values of (S/F) and (V/F) in j^{th} iteration. Those partial derivatives are expressed as,

$$\left.\frac{\partial f^{VL}}{\partial (V/F)}\right| = -\sum z_i \cdot \left(\frac{(K_i^{VL} - 1)}{1 + \frac{V}{F} \cdot (K_i^{VL} - 1) + \frac{S}{F} \cdot (K_i^{SL} - 1)} \right)^2 \tag{5.11}$$

$$\left.\frac{\partial f^{VL}}{\partial (S/F)}\right| = -\sum z_i \cdot \left(\frac{(K_i^{VL} - 1)}{1 + \frac{V}{F} \cdot (K_i^{VL} - 1) + \frac{S}{F} \cdot (K_i^{SL} - 1)} \right) \cdot \left(\frac{(K_i^{SL} - 1)}{1 + \frac{V}{F} \cdot (K_i^{VL} - 1) + \frac{S}{F} \cdot (K_i^{SL} - 1)} \right) \tag{5.12}$$

Similarly,

$\left.\frac{\partial f^{SL}}{\partial (S/F)}\right|_j$ and $\left.\frac{\partial f^{SL}}{\partial (V/F)}\right|_j$ are the values of the partial derivatives of $f^{SL}\left(\frac{V}{F}, \frac{S}{F}\right)$ when differentiated with respect to (S/F) and (V/F), respectively, while keeping other variables constant, and evaluated by substituting values of (S/F) and (V/F) in j^{th} iteration. Those partial derivatives are expressed as,

$$\left.\frac{\partial f^{SL}}{\partial (S/F)}\right| = -\sum z_i \cdot \left(\frac{(K_i^{SL} - 1)}{1 + \frac{V}{F} \cdot (K_i^{VL} - 1) + \frac{S}{F} \cdot (K_i^{SL} - 1)} \right)^2 \tag{5.13}$$

$$\left.\frac{\partial f^{SL}}{\partial (V/F)}\right| = -\sum z_i \cdot \left(\frac{(K_i^{VL}-1)}{1+\frac{V}{F}\cdot(K_i^{VL}-1)+\frac{S}{F}\cdot(K_i^{SL}-1)} \right) \cdot \left(\frac{(K_i^{SL}-1)}{1+\frac{V}{F}\cdot(K_i^{VL}-1)+\frac{S}{F}\cdot(K_i^{SL}-1)} \right) \tag{5.14}$$

Therefore, the procedure to solve the Rachford-Rice equation for the three phase flash problem can be summarized as

1. The feed composition (z_i), initial guess values of K_i^{SL} and K_i^{VL}, pressure (P) and temperature (T) are known.
2. Use the initial guesses of (S/F) and (V/F) in the range mentioned earlier.
3. Calculate the values of f^{SL} and f^{VL} from Equations (5.7) and (5.8)
4. If $f^{SL} < \varepsilon$ and $f^{VL} < \varepsilon$, then the values of (S/F) and (V/F) are correct, and the compositions of vapor, solid and liquid streams are determined from Equations (4.52) through (4.54).
5. If $f^{SL} > \varepsilon$ or $f^{VL} > \varepsilon$, then calculate the values of $\left.\frac{\partial f^{SL}}{\partial (S/F)}\right|$ and $\left.\frac{\partial f^{SL}}{\partial (V/F)}\right|$ from Equations (5.13) and (5.14). Also, calculate the values of $\left.\frac{\partial f^{VL}}{\partial (S/F)}\right|$ and $\left.\frac{\partial f^{VL}}{\partial (V/F)}\right|$ from Equations (5.11) and (5.12).
6. Obtain the new values of (V/F) and (S/F) from Equations (5.9) and (5.10) using the values obtained in step 3 and 5.
7. Substitute the new values of (V/F) and (S/F) obtained from step 6 into Equations (5.7) and (5.8).
8. Repeat steps 4-7 till ($f^{SL} < \varepsilon$ and $f^{VL} < \varepsilon$) criterion is satisfied.
9. From the correct values of (V/F) and (S/F), calculate the vapor, liquid and solid stream compositions.

It should be noted, that the correct values of (V/F) and (S/F) are obtained from the assumed values of K_i^{VL} and K_i^{SL}; thus they may not correspond to the actual equilibrium

ratio values. These equilibrium ratio values should be obtained from Won's model for three phase flash calculations.

5.5.1 Three Phase Equilibrium Calculations

Won's model gives a method to calculate K_i^{SL} and K_i^{VL} based on thermodynamics. An algorithm of estimating the amount of wax precipitated and the compositions of vapor, liquid and solid phases based on Won's three phase model is developed and described below.

1. The feed composition (z_i), pressure (P) and temperature (T) are known.
2. Find out the initial guess values of K_i^{SL} and K_i^{VL} from Equations (5.5) and (5.6). Solve the Rachford-Rice equation using the procedure explained in section 5.5 to obtain (S/F) and (V/F) and y_i, s_i and x_i which are the compositions of vapor, solid and liquid streams from Equations (4.52) through (4.54).
3. For calculation of K_i^{SL}
    a. Calculate δ_i^L and δ_i^S using Equations (4.21) and (4.22) for all the components.
    b. Estimate the molar volume of each component in the solid (v_i^S) and liquid phases (v_i^L) from Equations (4.23) through (4.25).
    c. Find out the volume fractions of each component in the solid (φ_i^S) and liquid phase (φ_i^L) using Equation (4.18).
    d. Calculate $\overline{\delta}$, the average solubility parameter of the mixture, for both liquid and solid phases by appropriately substituting the volume fraction and solubility parameters of each component using Equation (4.17).
    e. Find out T_i^f and ΔH_i^f, the fusion temperature and the heat of fusion, from Equations (4.14) and (4.15) for each component.
    f. Using the terms obtained in the above steps, find out the K_i^{SL} values for each component using Equation (4.27).
4. For calculation of K_i^{VL}

a. Calculate the fugacity of each component in the liquid phase, ϕ_i^L using Equation (4.33) and the procedure explained in Appendix B.
b. Calculate the fugacity of each component in vapor phase, ϕ_i^V using Equation (4.63) and the procedure explained in Appendix B.
c. Using the terms obtained in the above steps, estimate K_i^{VL} for each component using Equation (4.64).

5. Solve the Rachford-Rice equation using the procedure explained in section 5.5 and these newly obtained K_i^{SL} and K_i^{VL} values to calculate the solid mole fraction (S/F), the vapor mole fraction (V/F) and the compositions of vapor (y_i), wax (s_i) and liquid phases (x_i) from Equations (4.52) through (4.54).
6. Repeat steps 3-5, till the constant values solid (S/F) and vapor mole fractions (V/F) are obtained.

This algorithm allows us to predict the amount of wax precipitated and the amount of vapor phase formed at a given pressure and temperature. A program based on the above described algorithm was developed, and results obtained from it are presented in the next chapter.

Chapter 6

Predictions and Comparisons

6.1 Predictions from Won's model

Dauphin et al. (1999) published data for wax precipitation from the liquid phase, which have become the standard for testing the wax precipitation models. **Table 6.1** gives the composition of a system used by Dauphin et al.

Table 6.1 Composition of oil system A

Component	Mole Fraction
C10	0.80065
C18	0.029981
C19	0.025723
C20	0.022065
C21	0.018946
C22	0.016246
C23	0.013939
C24	0.01196
C25	0.01026
C26	0.008812
C27	0.007555
C28	0.006513
C29	0.005561
C30	0.004769
C31	0.004101
C32	0.00351
C33	0.003024
C34	0.002589
C35	0.001889
C36	0.001904

The composition in **Table 6.1** was used as feed composition (z_i). Next, flash calculations were carried out using the procedure explained in section 5.1. Won's model was used to predict K_i^{SL} values. Then, flash calculations were repeated until constant values of the solid mole fractions were obtained. The calculation procedure is explained in detail in

section 5.3. Then the solid mole fraction was converted into the weight percent. **Figure 6.1** presents a comparison of the results obtained from Won's model with the experimental data.

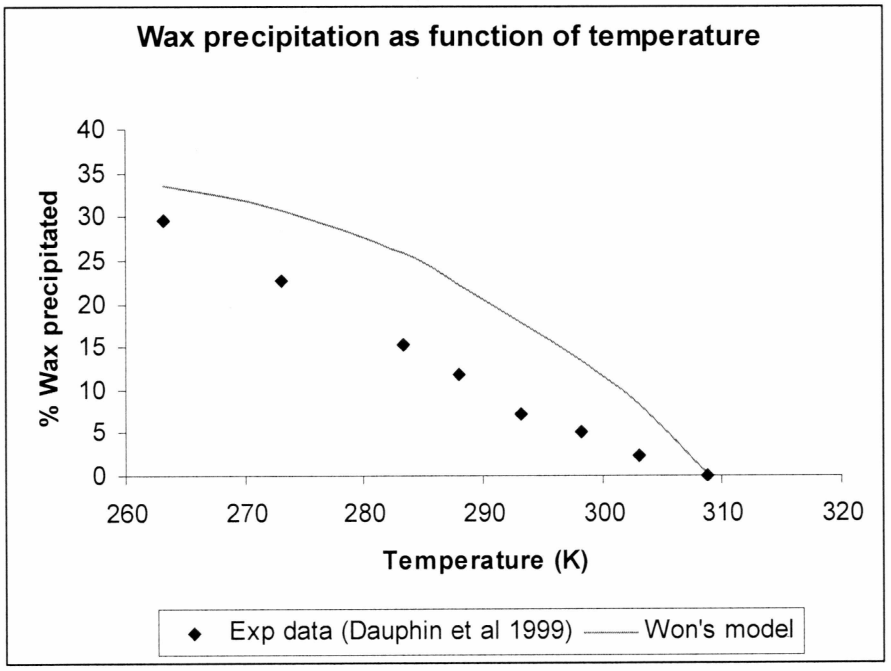

Figure 6.1 % wax precipitated as function of temperature for system A

It can be seen from **Figure 6.1** that, as the temperature is reduced, the amount of wax precipitated increases. This is consistent with the experimental observation. It can also be seen that Won's model overestimates the amount of wax precipitated at a given temperature, but the wax appearance temperature (WAT) prediction is close to the experimental value. The WAT of system A was found from the experiments to be 308.75K. As the WAT is the temperature at which wax starts precipitating, it can be taken as the temperature at which the 0% of wax precipitation curve meets the temperature line. It is estimated as 308.90K from Won's model. So the prediction is quite close.

The predictions from Won's model were compared with commercial computer software to learn the difference in predictions. The composition of system A was used as a feed to Computer Modeling Group's PVT simulator WINPROP®, but, the program failed to execute for the given composition. Therefore, the same composition was used in

PVTPROP's PROTROLEUM® software for the predictions. The comparison is shown in **Figure 6.2.**

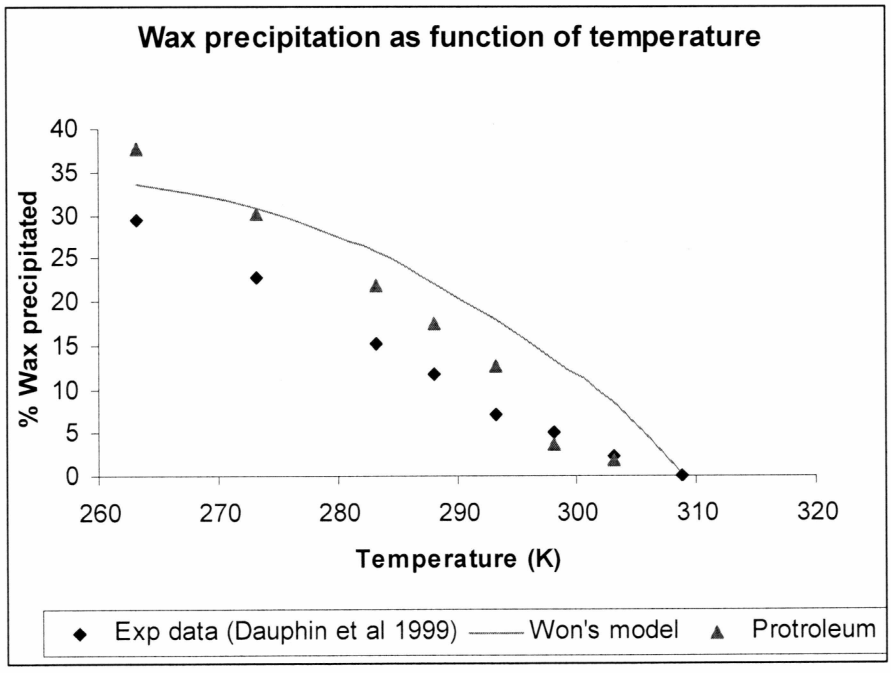

Figure 6.2 % wax precipitated as a function of temperature for system A: Comparison with other software

It can be seen that predictions from the Protroelum®'s wax module show a different behavior. At higher temperatures, the predictions are lower than the experimental values, whereas the predictions are significantly higher at lower temperatures. Protroleum® uses the polymer solution theory model (Zhou et al., 1995). The WAT predicted using Protroleum® is around 304.55K, so the WAT prediction is better using Won's model than that by Protroleum® software.

The reason why Won's model overestimates the amount of wax precipitated can be attributed to the use of melting properties of n-paraffins to the whole carbon number fraction. This essentially means that all the components in a single carbon number fraction are n-paraffins and can precipitate as wax. This is not actually the case. Pedersen (1995) has mentioned that stable oil contains around 15% paraffinic compounds. Therefore, the amount of wax precipitated is generally higher for Won's model.

The model was tested for another mixture, system B. The composition of system B is shown in **Table 6.2.**

Table 6.2 Composition of system B

Component	Mole fraction
C10	0.800033
C18	0.033915
C19	0.029102
C20	0.024961
C21	0.021427
C22	0.018372
C23	0.015766
C24	0.013528
C25	0.011604
C26	0
C27	0
C28	0
C29	0.006288
C30	0.005405
C31	0.004631
C32	0.003972
C33	0.003411
C34	0.002922
C35	0.002508
C36	0.002153

The composition for system B was used in the program for Won's model to predict the % of wax deposited as a function of temperature. As expected, as the temperature is reduced more and more wax starts precipitating. **Figure 6.3** gives the comparison of results obtained from the model and experimental data. Also, the predictions are compared with Protroleum®'s wax module. Again, CMG's Winprop® failed to execute for the given composition.

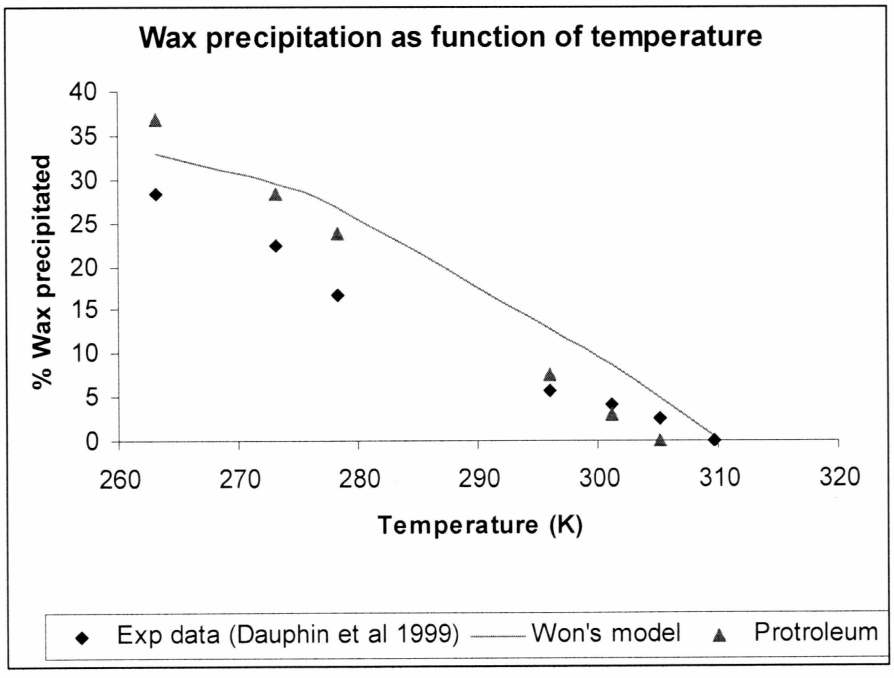

Figure 6.3 % wax precipitated as function of temperature for system B

From **Figure 6.3**, it can be seen that the predictions from Won's model are higher than the experimental values. Protroleum® gives better results, but overestimates at lower temperatures. The WAT predicted from Won's model is 310.42K, while that from Protroleum® is 305.1K. The experimental value of WAT for system B is 309.65K. Hence, the WAT predicted from Won's model is closer than that from Protroleum®. The reason for the overestimation of wax precipitated is the same as described earlier.

The model was tested for the third sample, system C. Composition of the sample given in **Table 6.3** was used as feed composition. The amount of wax precipitated as a function of temperature was predicted using Won's model and Protroleum® software. The results are compared with the experimental data in **Figure 6.4**.

From **Figure 6.4**, it can be seen that, again, Won's model predicts higher wax precipitation than the experimental values. Also, the predictions are higher from the Protroleum® software at lower temperatures. The WATs predicted from Won's model and Protroleum® are 311.2K and 304.75K, respectively. The experimental value of WAT is 310.37K. As observed in earlier cases, the WAT predictions from Won's model are much closer to the experimental values.

Table 6.3 Composition of system C

Component	Mole fraction
C10	0.800033
C18	0.037241
C19	0.031958
C20	0.027418
C21	0.023527
C22	0.020185
C23	0.017317
C24	0.014858
C25	0
C26	0
C27	0
C28	0
C29	0
C30	0.00593
C31	0.005086
C32	0.00437
C33	0.003745
C34	0.003209
C35	0.002754
C36	0.002368

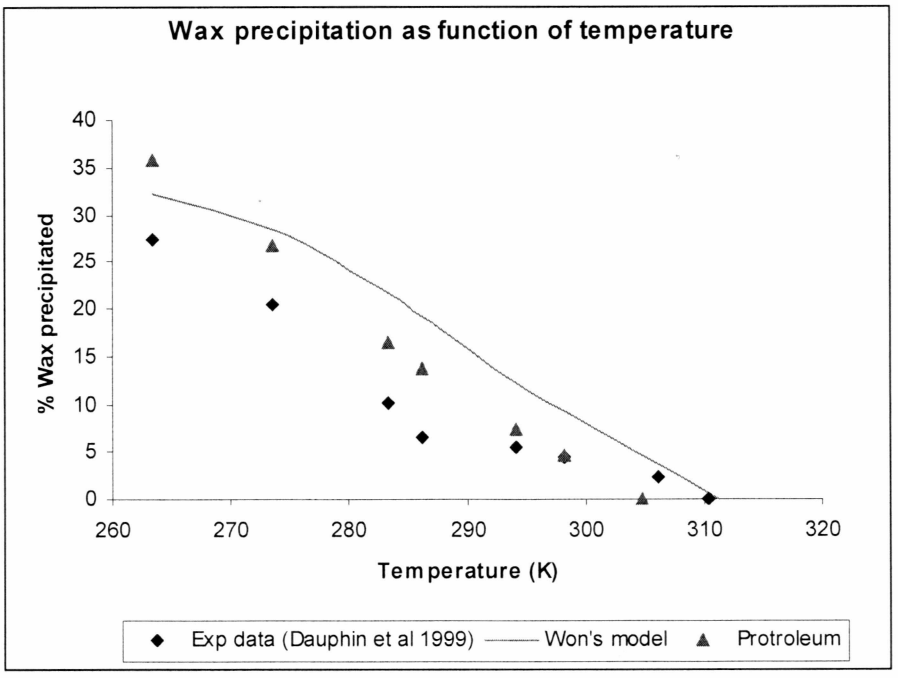

Figure 6.4 % wax precipitated as function of temperature for system C

A summary of the WAT predictions is given in Table 6.4.

Table 6.4 Summary of WAT predictions

	System A	System B	System C
WAT experimental (K)	308.75	309.65	310.37
WAT from Won's model (K)	308.9	310.42	311.2
WAT from Protroleum (K)	304.55	305.1	304.75
Average Absolute Deviation (K)	0.15	0.77	0.83

From **Table 6.4** it can be seen that the average absolute deviation for the WAT prediction is very low. Won's model predicts the WATs reasonably even though it overestimates the amount of wax precipitated. Therefore, Won's model is still used in industry.

From system A to system C, the composition changes in that the mole fractions of intermediate components are lowered. The melting properties assigned by Won's model are such that heavier components have a higher tendency of going into wax phase. Therefore, the heavier components will have larger mole fractions in the wax phase. As the composition changes from system A to C, the volume fraction of heavier components also increases in the solid phase; thus equilibrium ratio values become higher for system C than those for system A at the same temperature. Hence, the amount of wax precipitated becomes higher at a given temperature for system C, and the WAT also increases accordingly. The same trend is observed here.

Even though solid-liquid equilibrium data given by Dauphin et al. (1999) are considered standard for wax models, the Won's model is checked with a real reservoir fluid system. Composition of oil used is given in **Table 6.5**. The composition given is only up to C_{30+} components. Generally, the wax forming components are within the range of C_{15}-C_{50}. Therefore, to study the actual behavior, the C_{30+} components need to be split to C_{80} using any plus factor characterization scheme. The model then becomes very calculation intensive due to the large number of components involved and due to the complex nature of flash calculations. It is advised that the characterized components should be lumped together to a suitable number of components to simulate the process. Pedersen's lumping scheme was used for lumping. The composition after lumping is given in **Table 6.6,** as given by Pedersen et al. (1991).

Table 6.5 Composition of oil 1 (Pedersen et al., 1991)

Component	Mole%	mol wt	density
C1	1.139	16.043	0.3
C2	0.507	30.07	0.356
C3	0.481	44.097	0.507
i-C4	0.563	58.124	0.563
C4	0.634	58.124	0.584
i-C5	1.113	72.151	0.625
C5	0.515	72.151	0.631
C6	2.003	86	0.69
C7	5.478	90.9	0.749
C8	8.756	105	0.768
C9	7.222	117.7	0.793
C10	5.414	132	0.808
C11	5.323	148	0.815
C12	4.571	159	0.836
C13	5.289	172	0.85
C14	4.72	185	0.861
C15	4.445	197	0.873
C16	3.559	209	0.882
C17	3.642	227	0.873
C18	3.104	243	0.875
C19	2.717	254	0.885
C20	2.597	262	0.903
C21	1.936	281	0.898
C22	2.039	293	0.899
C23	1.661	307	0.899
C24	1.616	320	0.9
C25	1.421	333	0.905
C26	1.233	346	0.907
C27	1.426	361	0.911
C28	1.343	374	0.915
C29	1.3	381	0.92
C30+	13.334	624	0.953

Table 6.6 Composition after lumping

Component	mole %	MW
C1	1.128	16
C2	0.502	30.1
C3	0.476	44.1
i-C4	0.557	58.1
C4	628	58.1
i-C5	1.102	72.1
C5	0.51	72.1
C6	1.983	86.2
C7	5.424	90.9
C8	8.669	105
C9-C10	7.15	117.7
C11-C13	20.392	152.4
C14-C15	9.074	190.8
C16-C19	10.206	225.6
C20-C23	9.197	270.4
C24-C28	7.284	331.9
C29-C37	5.266	406.9
C38-C48	4.644	529
C49-C65	3.344	685.9
C65+	2.465	921

Using the composition given in **Table 6.5** as feed, the results obtained from Won's model are shown in **Figure 6.5**.

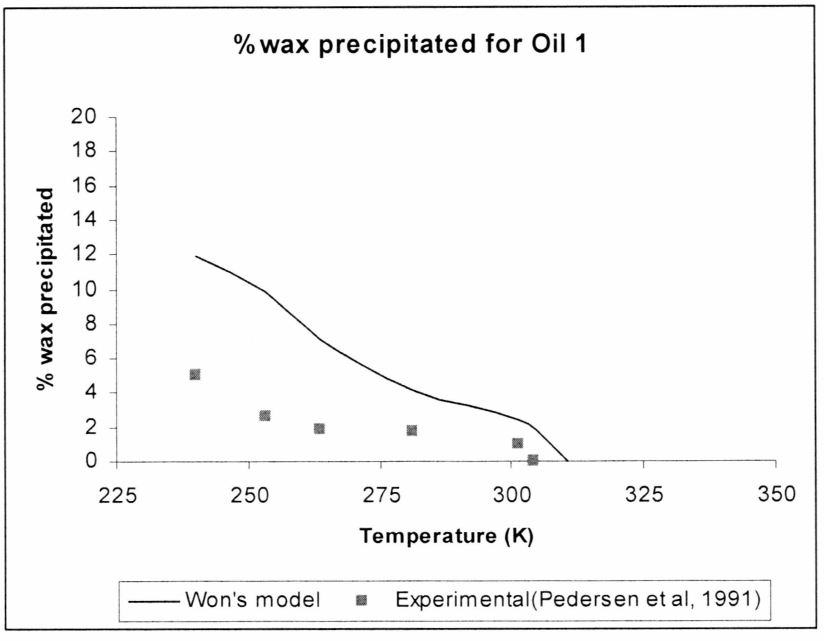

Figure 6.5 % wax precipitated as function of temperature for oil 1

From **Figure 6.5**, it can be seen that, as in earlier cases, Won's model over-predicts the amount of wax precipitated. The WAT determined experimentally is 304.16K, while that

from Won's model is 310.68K. There is a deviation of about 6.52K. This can also be attributed to the assigning of melting properties of n-parafffins to all components in a single carbon number fraction.

6.2 Predictions from Pedersen's Model

Pedersen's model assumption distinguishes between n-paraffinic compounds and other components in hydrocarbon families. This scenario is much closer to reality.The model was tested against the solid-liquid experimental data published by Dauphin et al. (1999), as it has become the standard for wax modeling. The composition given in **Table 6.1** was used as the feed composition for the flash calculations. The procedure explained in section 5.4 was used to predict the amount of wax precipitated at a given temperature. The predictions are compared with experimental data, as well as the predictions obtained from Won's model. The results are shown in **Figure 6.6**.

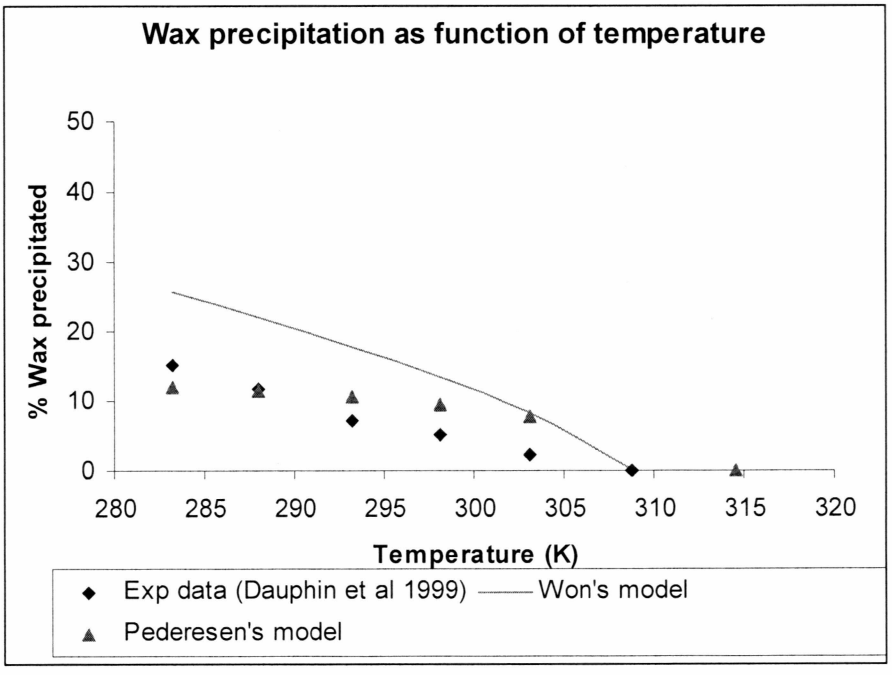

Figure 6.6 % wax precipitated as function of temperature for system A

From **Figure 6.6,** it can be seen that predictions for the amount of wax precipitated from Pedersen's model are much closer to the experimental values than those from Won's model. This can be attributed to the concept of distinguishing between n-paraffins and other components of carbon fraction. In Won's model, the assignment of melting

properties of n-paraffins to whole carbon fraction means that the whole carbon fraction is n-paraffinic and can form wax. Hence, the predictions are higher for Won's model. Pedersen's model separates n-paraffins from other components with the distribution explained in Equation (4.28). A, B, and C are the constants which are obtained by tuning them with experimental data. For tuning, the Levenberg-Marquardt optimization routine in MATLAB was used. It uses the least-squares method to fit the data. Optimum values obtained are shown in **Table 6.7**.

Table 6.7 Optimum values of A, B and C in Equation (4.28)

A	0.5903
B	$5.70*10^{-4}$
C	0.1354

The WAT obtained from Pedersen's model is 314.6K whereas that from Won's model is 308.90K. The experimental value of the WAT of 308.75K is close to the prediction from Won's model. This error can be attributed to the assumption of ideality in a solid phase. The experimental data has indicated that the solid phase generally behaves as a non-ideal solution.

The model is tested with another data set from Dauphin's data. The composition is given in **Table 6.2**. This composition of system B was used as composition of feed stream to flash vessel. The A, B and C values are the values obtained by optimizing the data for all the samples; therefore A, B, and C, given in **Table 6.7,** were used. Predictions from Pedersen's model are given in **Figure 6.7** as a function of temperature. The results are compared with the experimental data as well as the predictions from Won's model.From **Figure 6.7,** it can be see that, again, the predictions for the amount of wax precipitated from Pedersen's model are closer to the experimental values than those from Won's model. The reason is the same as that in the earlier case. The WAT predicted from Pedersen's model is 315.2K, while that from experiments is 309.65K. The prediction from Won's model (310.4K) is closer to the experimental value.

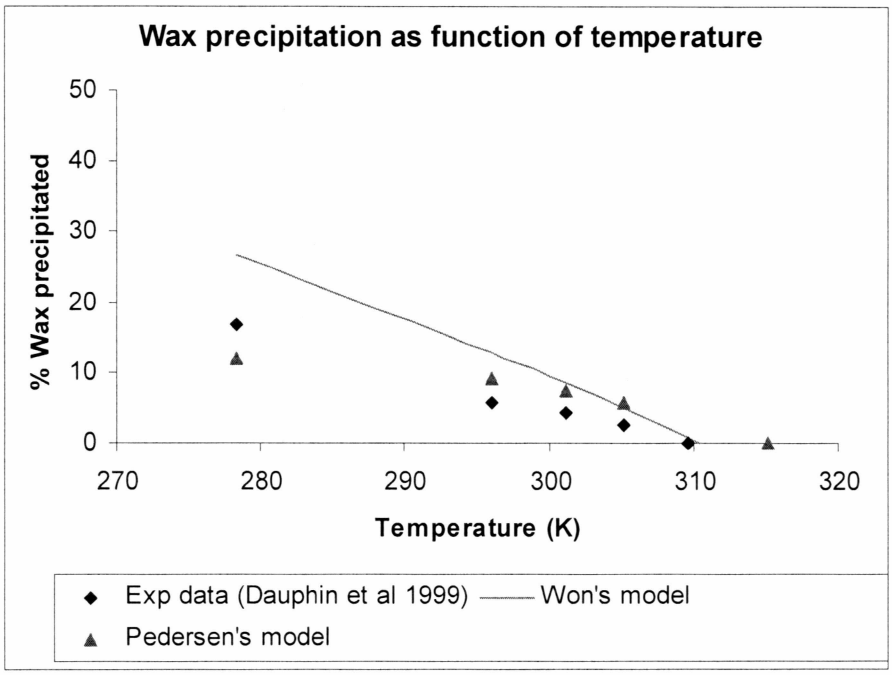

Figure 6.7 % wax precipitated as function of temperature for system B

Pedersen's model was tested against another sample data from Dauphin. The composition is given in **Table 6.3**. The values for A, B and C, given in **Table 6.7,** were used in the procedure explained in section 5.4. The predictions were compared with experimental data and predictions from Won's model in Figure 6.8. The trend is similar to those seen in earlier cases. The predictions from Pedersen's model are closer to experimental data than those from Won's model. This is due to the splitting of a carbon fraction into the wax forming and non-wax forming parts. Yet again, the WAT predicted for system C using Pedersen's model is 315.6K. It is considerably different from the experimental value of 310.37K. The prediction of Won's model is much closer. This deviation can be attributed to the assumption of the solid phase behaving as an ideal solution.

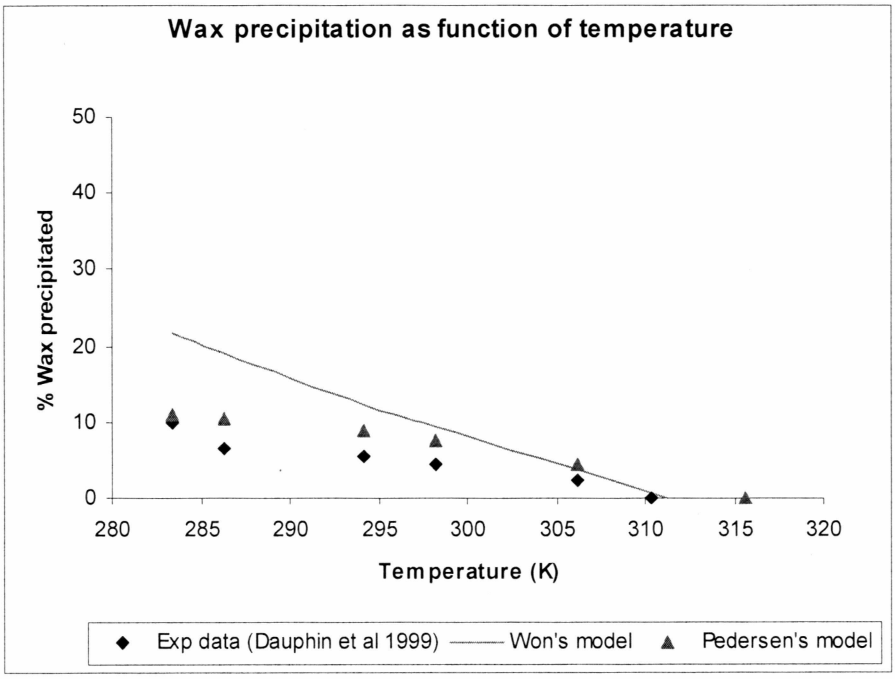

Figure 6.8 % wax precipitated as function of temperature for system C

The model also was checked for real reservoir fluid. For this, the composition of oil given in **Table 6.5** was used as the feed composition. As seen earlier, the composition up to C_{30} is not sufficient to describe the behavior of wax; therefore, the C_{30+} fraction needs to be split into higher carbon number fractions. As the number of components increase, however, the flash calculations become very unstable. Therefore, to get the actual description and to the reduce number of components; the components are lumped together using Pedersen's scheme. The composition after lumping is shown in **Table 6.6**. The results obtained from the model are shown in **Figure 6.9**. These results were compared with the experimental data and were compared with the predictions from Won's model. It can be seen that the predictions from Pedersen's model are lower than those from Won's model and closer to the experimental values. This is due to the splitting of carbon fraction into wax forming and non-wax forming components, but the WAT predicted from Pedersen's model is 311.2K and that from Won's model is 310.68K, while the experimental value is 304.68K. Again, the WAT prediction is closer with Won's model. This can be attributed to the assumption of the solid behaving as an ideal solution, as it is not what is expected in reality.

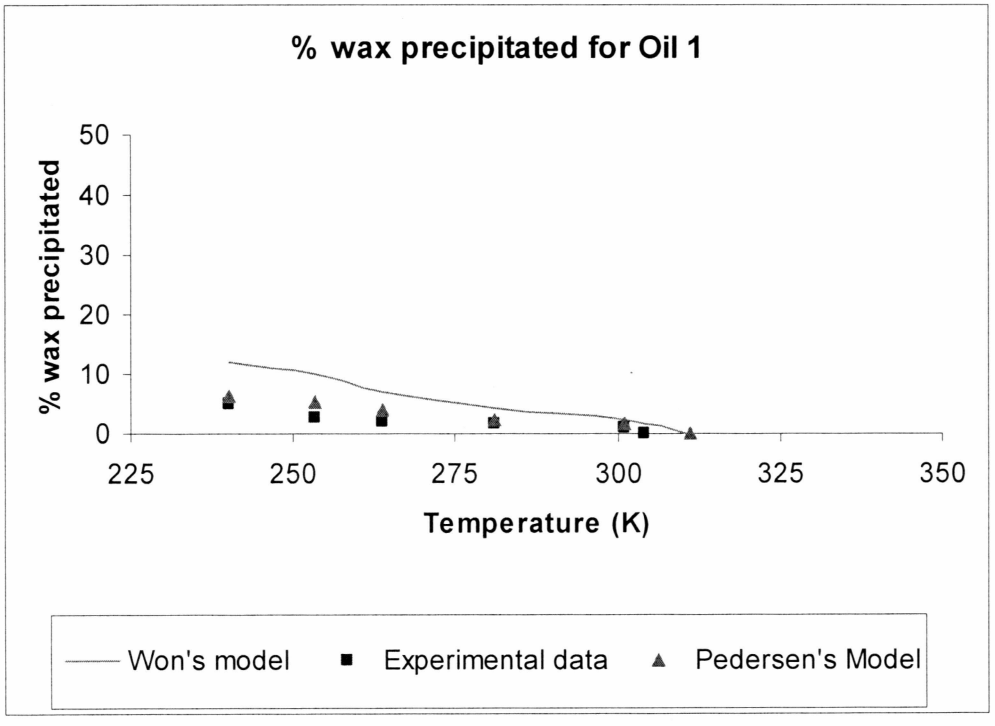

Figure 6.9 % wax precipitated as function of temperature for oil 1

6.3 Predictions from Three Phase Flash Calculations

As discussed earlier, at higher pressures the vapor phase will come into the picture. For this condition, the three phase flash calculations need to be performed. Sections 4.4 and 4.5 explain the three phase modeling. The composition of the oil used is given in **Table 6.8**.

The experimental data for three phase solid-liquid-vapor equilibrium is scarce; therefore, predictions from the developed program are compared with predictions given by Won (1986) in **Figure 6.10**. From this figure, it can be seen that predictions from the developed program are in close agreement with predictions from Won's model. This is because the program is based on Won's model. The deviation can be due to the use of different EOS for describing vapor-liquid equilibrium. The PR EOS was used in this study while in Won's paper, the SRK EOS was used.

Table 6.8 Composition of oil used for three phase calculations (Won, 1986)

Component	Mole %	Component	Mole %
CO2	9.16	C21	0.037
C1	68.8	C22	0.031
C2	8.43	C23	0.026
C3	5.11	C24	0.022
C4	5.11	C25	0.018
C5	1.05	C26	0.015
C6	0.63	C27	0.012
C7	0.83	C28	0.01
C8	0.95	C29	0.0086
C9	0.52	C30	0.0071
C10	0.26	C31	0.0059
C11	0.2	C32	0.0049
C12	0.17	C33	0.0041
C13	0.16	C34	0.0034
C14	0.15	C35	0.0028
C15	0.11	C36	0.0024
C16	0.086	C37	0.002
C17	0.078	C38	0.0016
C18	0.068	C39	0.0014
C19	0.054	C40	0.0011
C20	0.045		

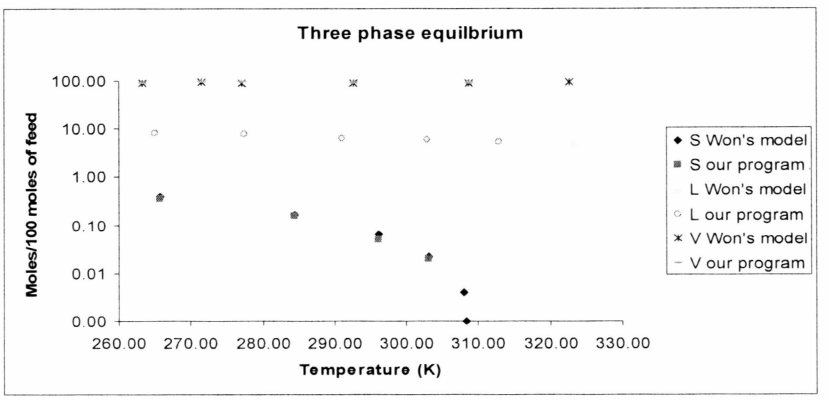

Figure 6.10 Three phase equilibrium calculations

6.4 Summary of comparisons

- Won's model overestimates the amount of wax precipitated at a given temperature, but the WAT predicted by Won's model are in agreement with the experimental data.
- The reason for overestimation of wax precipitated is the model's inability to distinguish between wax forming and non-wax forming components.
- Predictions from Pedersen's model for the amount of wax formed are lower than those from Won's model and closer to the experimental values. This is due to the model being able to distinguish between n-paraffinic (wax forming components) and other components in carbon fraction (non-wax forming components).
- The WAT predicted by Pedersen's model are much higher than those by Won's model. This can be attributed to the assumption in Pedersen's model that the solid phase behaves as an ideal solution, as it is contradictory to the experimental observation.

Chapter 7

Modification of Won's Model

There is growing evidence which suggest that only compounds with long n-alkyl chains form a wax phase. These components with long n-alkyl changes are also known as n-paraffins (Coutinho et al., 2001). The other components present in oil, such as branched paraffins and naphthenes, generally do not enter into the wax phase. As explained in section 4.3, it is very difficult to distinguish between n-paraffins and other components experimentally, as it requires a huge amount of work on the experimental part and is not generally done. Pedersen (1995), as explained earlier, devised an easy numerical model to distinguish between wax forming and non-wax forming components. In the proposed modification of Won's model, this concept of splitting a carbon fraction into the wax forming and non-wax forming components is used.

Also, most mixtures behave non-ideally in the solution (Prausnitz, 1969). Therefore, the assumption of the solid phase behaving ideally does not really depict the actual scenario. For that reason, the assumption of the solid phase behaving non-ideally, which was made in Won's model, is retained in this modification.

The melting properties given in Won's model were actually for n-paraffins, but were used for the whole fraction of a pseudo-component. In this modification, there will be a distinction between the wax forming and non-wax forming components. The melting properties will only be assigned to wax forming components. Non-wax forming components will not be present in the solid phase and will contribute only in the liquid phase.

The presence of C_1- C_7 components in the wax phase is rare. If they are present, it is often argued that, during experiments, these components get trapped in the wax phase and are not actually present in the wax phase as solids. In this modification, therefore, it is assumed that only C_{7+} components can form wax.

7.1 Assumptions of Modified Model

- The solid phase is a single, homogeneous solution, which is in equilibrium with the liquid solution.

- The solid phase is assumed to be behaving non-ideally.
- Only C_{7+} components can form wax.
- Only part of a pseudo-component can potentially enter into the wax phase.
- The heat capacity change of fusion is assumed to be negligible.
- The equilibrium ratio, K_i^{SL}, the ratio between mole fraction of component i in solid phase and liquid phase, is assumed to be 0 for non-wax forming parts of all pseudo-components.

7.2 Modified Won's model

According to the modified Won's model, the mole fraction of the potentially wax forming component, z_i^S, of a pseudo-component i, having a total mole fraction z_i^{old} is given by ,similar to Pedersen's model (1995),

$$z_i^S = z_i^{old}\left[1-\left(A+B\cdot M_i\right)\cdot\left(\frac{\rho_i-\rho_i^p}{\rho_i^p}\right)^C\right] \tag{7.1}$$

where M_i is the molecular weight of pseudo-component i, ρ_i is the density of the pseudo component at standard conditions and ρ_i^P is the density of n-paraffin with molecular weight M_i at atmospheric pressure and 15^0C. ρ_i^P can be obtained from

$$\rho_i^p = 0.3915 + 0.0675\cdot\ln M_i \tag{7.2}$$

The values of A, B, and C are constants which are determined from the predictions tuning with the experimental data. The non-wax forming part (z_i^{no-S}) can be obtained from

$$z_i^{no-S} = z_i^{old} - z_i^S \tag{7.3}$$

From the above equations, all C_{7+} components are split into two parts: wax forming part (z_i^S) and non-wax forming parts (z_i^{no-S}). These two parts are treated as two different components. Therefore, the number of components are doubled C_{7+} onwards. The non-wax forming part does not come into picture when the solid phase is being considered,

but the wax-forming part is in all calculations corresponding to the liquid phase, as it is a component that *may* potentially enter into wax phase.

Thermodynamic criterion is the same in Won's model, which is at equilibrium the fugacity of a component i in solid phase (wax phase) should be equal to the fugacity of the same component in the liquid phase (oil phase). Therefore,

$$f_i^L = f_i^S \tag{7.4}$$

Where f_i^L = fugacity of a component i in the liquid phase mixture.

f_i^S = fugacity of a component i in the solid phase mixture.

The liquid phase fugacity of component i in the mixture can be expressed as

$$f_i^L = \gamma_i^L x_i f_i^{oL} \tag{7.5}$$

where γ_i^L is the activity coefficient of component i in liquid phase, x_i is the mole fraction of component i in liquid phase mixture, and f_i^{oL} is the standard state fugacity of component i in liquid phase. It can also be described as the liquid phase fugacity of component i in its pure form.

The solid phase fugacity of component i in the mixture can be expressed as

$$f_i^S = \gamma_i^S s_i f_i^{oS} \tag{7.6}$$

where γ_i^S is the activity coefficient of component i in solid phase. s_i is the mole fraction of component i in solid phase, and f_i^{oS} is the solid phase fugacity of component i in its pure form.

From Equations (7.4), (7.5) and (7.6)

$$\gamma_i^L x_i f_i^{oL} = \gamma_i^S s_i f_i^{oS} \tag{7.7}$$

As $K_i^{SL} = s_i / x_i$, rearranging Equation (7.7),

$$K_i^{SL} = \frac{s_i}{x_i} = \frac{\gamma_i^L f_i^{oL}}{\gamma_i^S f_i^{oS}} \tag{7.8}$$

Currently, there is no equation of state that can describe the volumetric behavior of a solid. As explained in Appendix A, however, by relating the chemical potential of the solid phase to that of the liquid phase, the ratio of f_i^{oL} to f_i^{oS} can be expressed as:

$$\frac{f_i^{oL}}{f_i^{oS}} = \exp\left[\frac{\Delta H^f}{RT}\left(1-\frac{T}{T^f}\right)+\frac{\Delta C_P}{R}\left(1-\frac{T^f}{T}+\ln\frac{T^f}{T}\right)+\int_0^P\frac{\Delta V}{RT}dP\right]_i \tag{7.9}$$

where $T^f, \Delta H^f$, ΔC_P and ΔV are fusion temperature, heat of fusion, heat capacity change during fusion and volume change of fusion, respectively. P & T are the pressure and temperature, respectively at which flashing is being carried out. Therefore, from Equations (7.8) and (7.9),

$$K_i^{SL} = \frac{s_i}{x_i} = \left(\frac{\gamma_i^L}{\gamma_i^S}\right)\exp\left[\frac{\Delta H^f}{RT}\left(1-\frac{T}{T^f}\right)+\frac{\Delta C_P}{R}\left(1-\frac{T^f}{T}+\ln\frac{T^f}{T}\right)+\int_0^P\frac{\Delta V}{RT}dP\right]_i \tag{7.10}$$

Co-relations given by Won were used to calculate the heat of fusion (ΔH^f) and temperature of fusion (T^f) of the wax forming components as

$$\Delta H_i^f = 0.1426 \cdot MW_i \cdot T_i^f \tag{7.11}$$

where MW_i is the molecular weight of the component, and T_i^f can be obtained from

$$T_i^f = 374.5 + 0.02617 \cdot MW_i - 20172/MW_i \tag{7.12}$$

As explained in section 7.1, the second term is assumed to be zero. Ronningsen et al. (1997) suggested that volume change during solidification should be taken as -10% of the molar volume of the pseudo-component i in a liquid phase. P_{ref} is taken as 14.7 psia, as the melting properties are generally available at atmospheric pressure. The molar volume of a component in liquid phase can be obtained from Won (1986):

$$v_i^L = MW_i \Big/ d_{25}^L \tag{7.13}$$

$$d_{25}^L = 0.8155 + 0.6272 \cdot 10^{-4} \cdot MW_i - 13.06/MW_i \tag{7.14}$$

and therefore, the molar volume of component i solid is obtained by $v_i^S = 0.9 * v_i^L$.

The solid phase is assumed to be a non-ideal mixture. Hence, the ratio of activity coefficients cannot be equated to 1. Similar to Won's model (1986), the use of regular solution theory to estimate the ratio of activity coefficients (for both liquid and solid phases) yields:

$$\ln\gamma_i = \frac{v_i(\bar{\delta}-\delta_i)^2}{RT} \tag{7.15}$$

where v_i is the molar volume, δ_i is the solubility parameter, and $\bar{\delta}$ is the average solubility parameter of the mixture. The average solubility parameter can be estimated as:

$$\bar{\delta} = \sum \varphi_i \delta_i \tag{7.16}$$

where φ_i is the volume fraction of component i, and it can be obtained for both liquid and solid phases from the following relationships:

$$\varphi_i^L = \frac{x_i v_i}{\sum x_i v_i} \text{ and } \varphi_i^S = \frac{s_i v_i}{\sum s_i v_i} \tag{7.17}$$

The molar volumes for solid and liquid phases are obtained from Equations (7.13) and (7.14). The solubility parameters for the components in the liquid and solid phases are obtained by co-relations given by Pedersen et al. (1991):

$$\delta_i^L = 7.41 + a_1(\ln C_N - \ln 7) \tag{7.18}$$

$$\delta_i^S = 8.50 + a_2(\ln C_N - \ln 7) \tag{7.19}$$

where, C_N is the carbon number of the component, and a_1 and a_2 are equal to 0.5914 $(cal/cm^3)^{0.5}$ and 5.763 $(cal/cm^3)^{0.5}$, respectively.

Thus from Equations (7.13-7.14) and (7.16-7.19), all of the parameters required in Equation (7.15) can be obtained, and the activity coefficients for both liquid and solid phases can be calculated. Applying Equation (7.15) to both liquid and solid phases, the ratio of activity coefficients can be expressed as

$$\frac{\gamma_i^L}{\gamma_i^S} = \exp\left[\frac{v_i}{RT}\left((\bar{\delta} - \delta_i)_L^2 - (\bar{\delta} - \delta_i)_S^2\right)\right] \tag{7.20}$$

From Equation (7.10), (7.20) and neglecting the change in heat capacity after solidification, K_i^{SL} can be expressed as

$$K_i^{SL} = \frac{s_i}{x_i} = \exp\left[\frac{\Delta H^f}{RT}\left(1 - \frac{T}{T^f}\right) + \frac{v_i}{RT}\left((\bar{\delta} - \delta_i)_L^2 - (\bar{\delta} - \delta_i)_S^2\right) + \frac{\Delta v^{fusion} \cdot (P - P_{ref})}{RT}\right] \tag{7.21}$$

After obtaining K_i^{SL} values, the Rachford-Rice equation can be used to find the amount of wax precipitated at any given condition. The material balance equations remain the same as explained in section 4.1. The detailed procedure is explained in the next section.

7.3 Procedure for Using Modified Won's Model

1. The feed composition (z_i), pressure (P) and temperature (T) are known initially. For C_{7+} components, $z_i^{old} = z_i$.
2. Estimate the density of n-paraffin ρ_i^P using Equation (4.29) for each C_{7+} component.
3. Obtain the wax forming fraction of each C_{7+} component (z_i^S) using (7.2)
4. Calculate the non-wax forming fraction of each C_{7+} component (z_i^{no-S}) using (7.3) and the values obtained in step 3. From here on, the wax forming fraction and non-wax forming fractions are treated as two different components. These components now form the new feed to the flash vessel. The C_{7+} components get doubled in this new feed due to the division into these fractions.
5. Determine the initial guess values of K_i^{SL} using Equation (5.6) for the wax forming fractions. For the non-wax forming components and components C_1-C_7, K_i^{SL} are taken to be zero.
6. Solve the Rachford-Rice equation by using the procedure explained in section 5.1 to find out S/F, s_i and x_i, which are the compositions of solid and liquid streams. Due to the assumption made in step 5, the liquid stream will contain C_1-C_7, the non-wax forming part of the pseudo-component and a fraction of the potentially wax-forming part of pseudo-component. The solid stream will only contain the wax-forming part of pseudo-components.
7. Calculate δ_i^L and δ_i^S using Equations (7.18) and (7.19) for all of the components.
8. Estimate the molar volume of each component in the solid (v_i^S) and liquid phases (v_i^L) from Equations (7.13)-(7.14).
9. Determine the volume fractions of each component in the solid (φ_i^S) and liquid phase (φ_i^L) using Equation (7.17).

10. Calculate $\overline{\delta}$, the average solubility parameter of the mixture, for both liquid and solid phases by appropriately substituting the volume fraction and solubility parameters of each phase in Equation (7.16).
11. Find out T_i^f and ΔH_i^f, the fusion temperatures and heat of fusion, from Equations (4.14) and (4.15), for each component.
12. Using the terms obtained in the above steps, find out K_i^{SL} for each component using Equation (7.21). Again, K_i^{SL} for the non-wax forming fraction of component and C_1-C_7 are taken as 0.
13. Solve the Rachford-Rice equation by using the procedure explained in section 5.1 and using these newly obtained K_i^{SL} values to determine the solid mole fraction (S/F), the compositions of wax (s_i) and liquid phases (x_i).
14. Repeat steps 3-13, till constant values of the solid mole fraction (S/F) are obtained.

A program based on the above described algorithm was developed in MATLAB. The results obtained are presented in the next chapter.

7.4 Results and Discussion

Modified Won's model distinguishes between the wax forming and non-wax forming components of a hydrocarbon pseudo-component. The solid phase is assumed to be a non-ideal solution. The Regular Solution Theory is used to describe the non-ideality of both phases.

A program was developed in MATLAB using the procedure explained in section 7.3. The model was tested against the data published by Dauphin et al., (1999). The composition given in **Table 6.1** was used as the feed composition for flash calculations. The program was run for various temperatures to find out the amount of wax precipitated at those conditions. The results from the program are shown and compared with the experimental data in **Figure 7.1**.

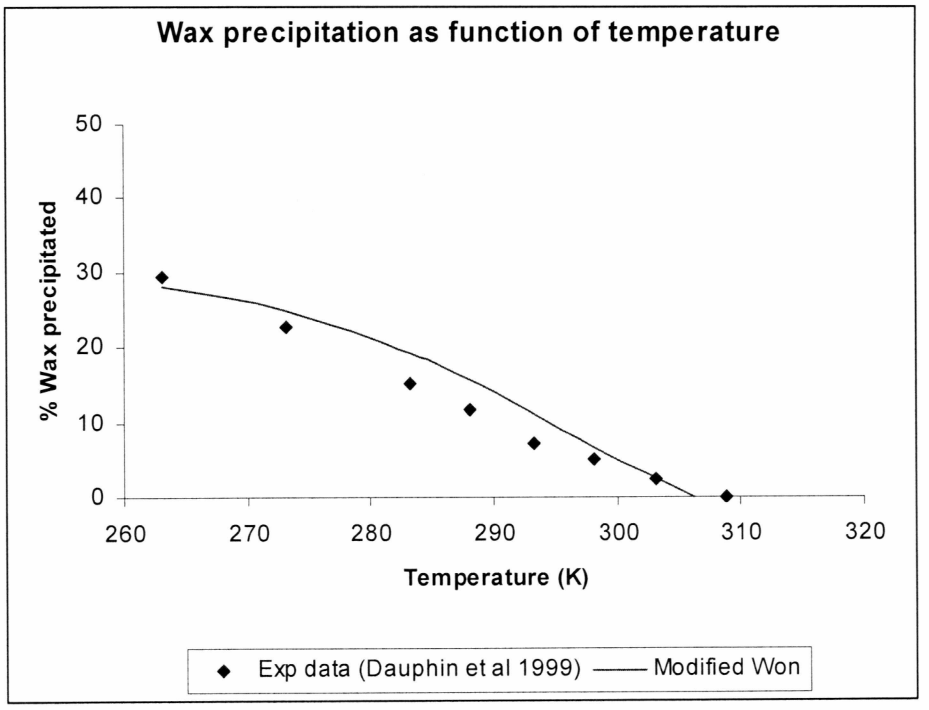

Figure 7.1 % wax precipitated as function of temperature for system A

From **Figure 7.1,** it can be seen that the predictions from the modified Won's model are within reasonable accuracy. The general trend is also captured properly. The WAT predicted from the modified model is 306.2K whereas that which was experimentally determined is 308.75K.

Figure 7.2 shows the comparison of predictions from the modified model versus predictions from the other models.

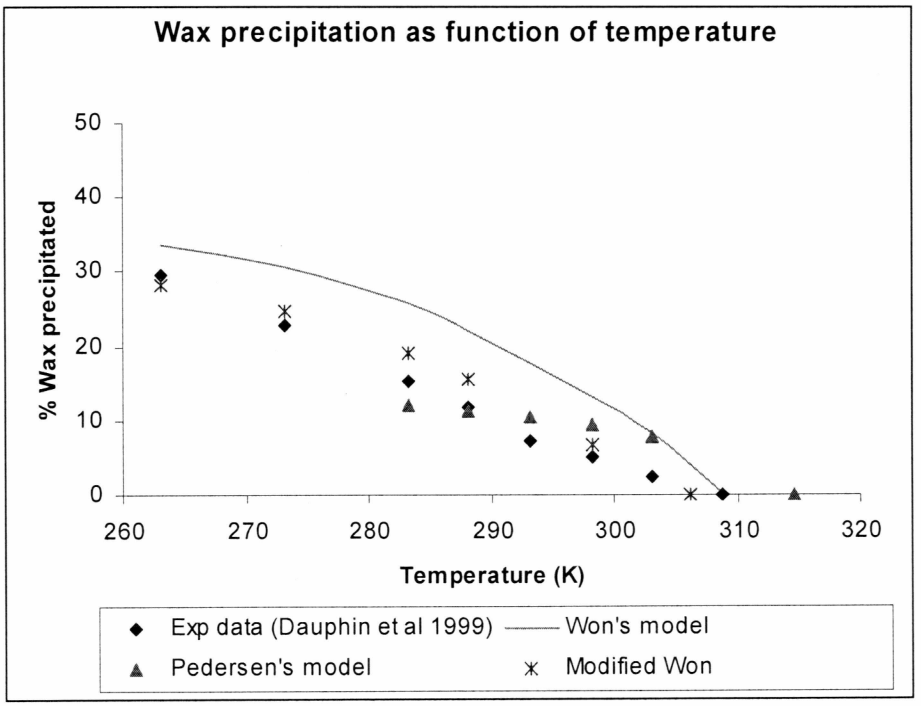

Figure 7.2 % wax precipitated as function of temperature for system A

From **Figure 7.2**, it can be seen that the predictions from the modified Won's model are much closer to the experimental data than those from other models. But the WAT predicted from the original Won's model is much closer to the experimental value than the modified Won's model or Pedersen's model. It should be noted that the modified Won's model has tunable parameters A, B and C, which can be tuned to match the experimental data. Also, it should be understood that Pedersen's model has these tunable parameters, but Pedersen's model is very calculation intensive and due to the complex nature of flash calculations, convergence is not always achieved. Thus, tuning is much more difficult in the case of Pedersen's model. In current study, emphasis was given to match the amount of wax precipitated at various temperatures. The values of A, B and C were obtained to be 0.15, 0, and 0, respectively. Deviation in the WAT prediction is within the acceptable range as other models in literature have reported deviations of up to 15°C. Predictions are better for the modified model compared to Won's model because the modified model distinguishes between n-paraffinic components and other components of hydrocarbon fraction. The melting properties of n-paraffins are assigned only to the wax forming part of carbon fraction. Thus, predictions from the modified

model are lower than the original model and are closer to the experimental value. Pedersen's model assumes the solid phase to be an ideal phase. It is proven that most mixtures behave non-ideally (Prausnitz, 1969); therefore the description of the solid phase as a non-ideal solution in the modified model might be the reason why the modified model's predictions are better. Also, in Won's model, the change in volume during solidification is neglected and such behavior is not observed experimentally. The modified model accounts for the change in the volume when a component in the liquid state is converted into the solid state. All these factors lead to better predictions from the modified Won's model.

The composition given in **Table 6.2** was used as the feed composition for flash calculations. At various temperatures, the predictions for the amount of wax precipitated are obtained from the program. The comparison of predictions from the program and the experimental data is shown in **Figure 7.3**.

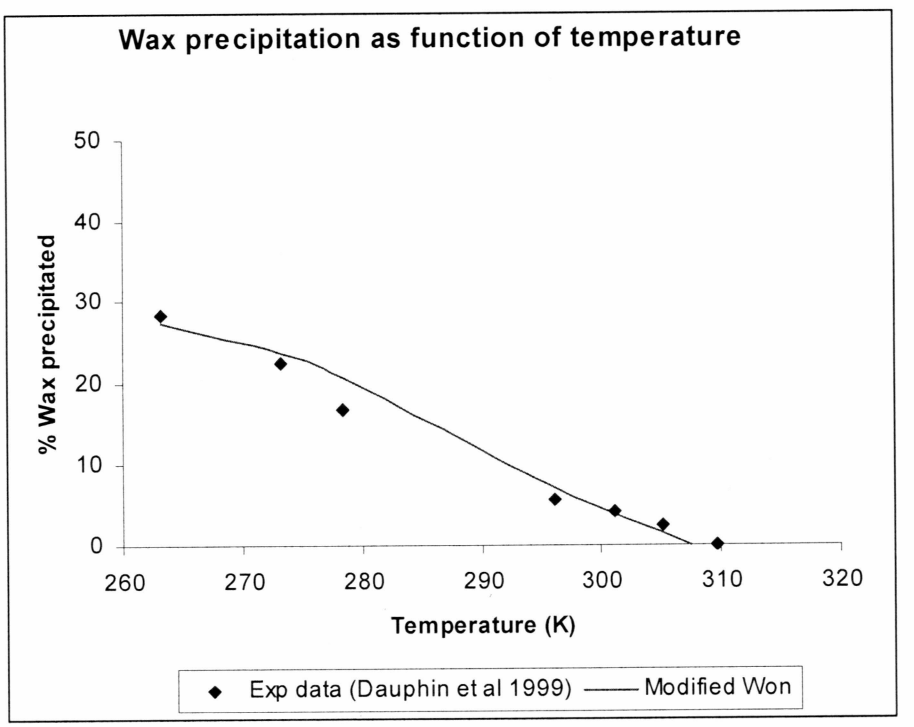

Figure 7.3 % wax precipitated as a function of temperature for system B

From **Figure 7.3**, it can be observed that predictions from the modified Won's model are quite close to experimental values. The WAT predicted from the modified Won's model is 307.4K, while that determined from experiments is 309.65K. The error is within

acceptable limits when compared with deviations in WAT predictions, as reported in literature.

Figure 7.4 shows the comparison predictions from Won's model with predictions from other models.

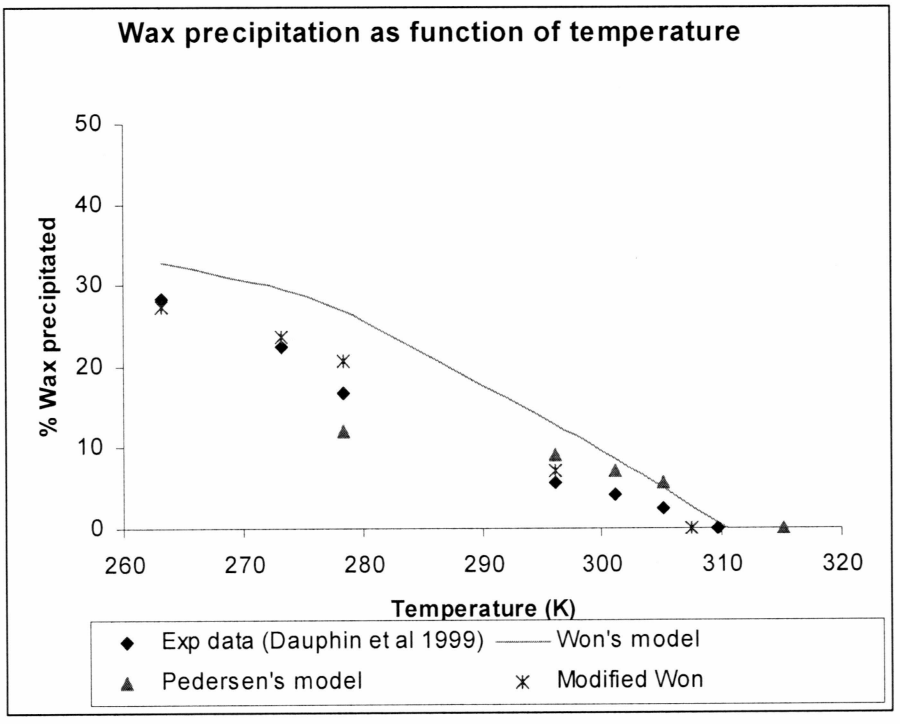

Figure 7.4 % wax precipitated as function of temperature for system B

It can be seen once again that the modified Won's model gives better predictions for the amount of wax precipitated at a given temperature than from other models. The reason is the distinction between the wax forming and non-wax forming components, accounting for volume change during the solidification process and the assumption of the solid phase as a non-ideal solution. Again, the WAT predictions are better with the original Won's model. The modified Won's model neglects the difference in heat capacities between solid and liquid states of a component while relating the fugacity of the component in solid phase to fugacity of the component in sub-cooled liquid state at same conditions. This may be the reason why there is a deviation in the WAT from the modified Won's model.

The composition of system C, as given in **Table 6.3**, was used as a feed to the flash vessel. The amounts of wax precipitated at various temperatures were obtained

using the program for the modified Won's model. The predictions were compared with the experimental data in **Figure 7.5**.

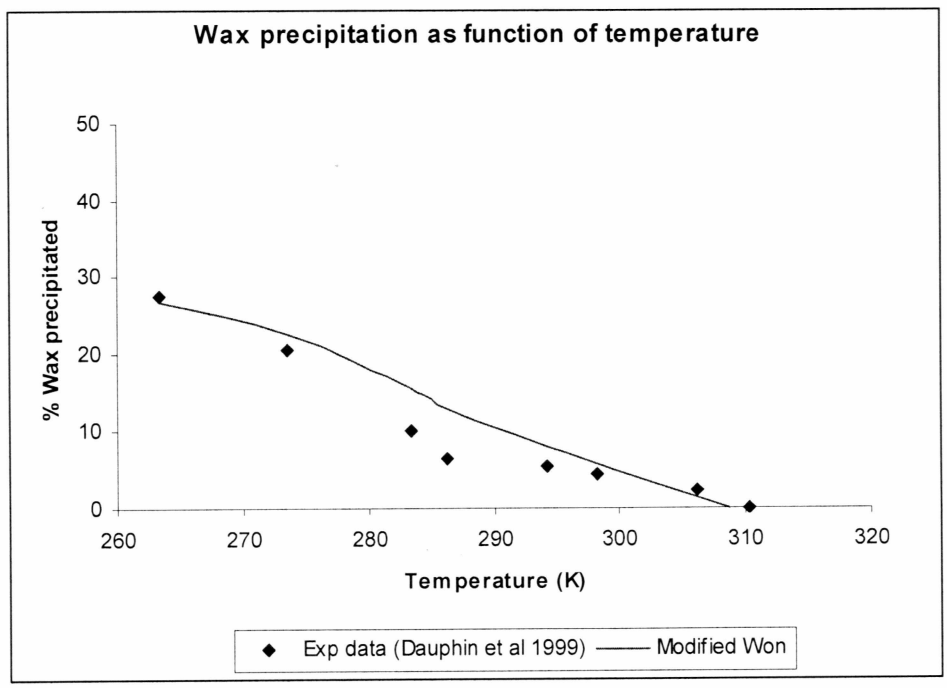

Figure 7.5 % wax precipitated as function of temperature for system C

It can be seen from **Figure 7.5**, that the predictions from the modified model are in agreement with the experimental data. In the region of 280-295K, the model overpredicts the amount of wax precipitated. It should be noted that the model does not describe what type of crystal wax forms. Wax crystals exhibit many kinds of solid habits such as orthorhombic, triclinic etc. The thermophysical properties, such as heat of fusion and fusion temperature, are dependent on the solid habit of the crystal. The properties used in the modified model are reported just for n-paraffins; it is not mentioned which solid habits exhibit those properties. Therefore, the properties used in the modified Won's model may not depict actual properties of wax crystals. That could be the reason why the model does not describe the behavior exactly.

Figure 7.6 shows the comparison of predictions from the modified model with other models. It can be seen that, again, overall predictions are better with the modified model. The reason is the same as seen in earlier cases. The WAT prediction of 308.72K is within the acceptable range of the experimental value of 310.37K. But, again, the WAT prediction from the original Won's model is much better.

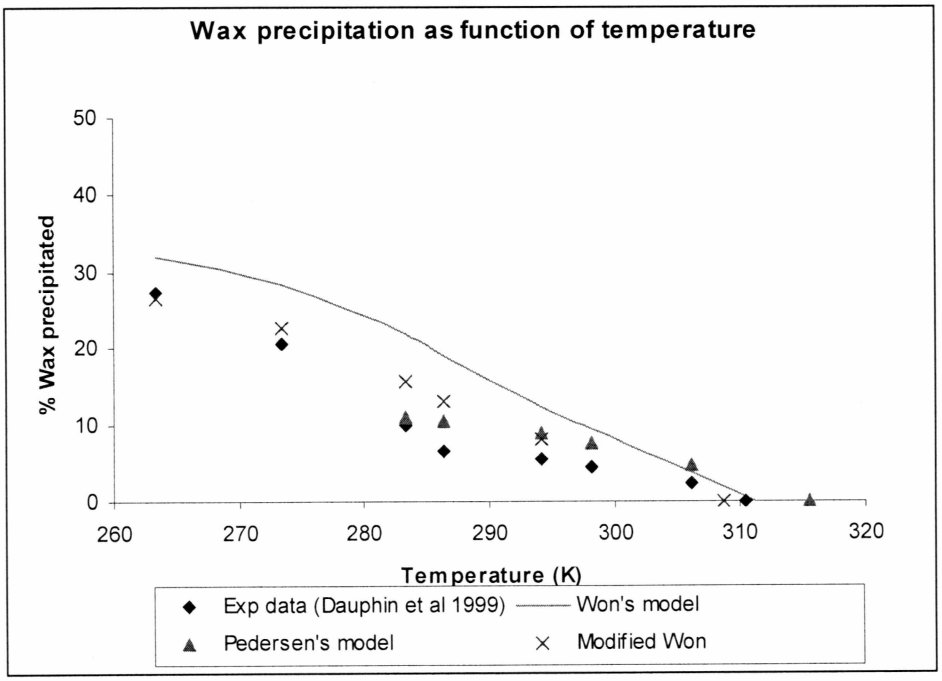

Figure 7.6 % wax precipitated as function of temperature for system C

The model was tested against a real reservoir fluid. The composition of the oil is given in **Table 6.5**. As explained earlier, to get the actual behavior of the oil, the plus fraction must be split into higher carbon number fractions by a plus factor characterization scheme. Due to the large number of components involved and the complexity of flash calculations, however, the convergence is not always achieved. Hence, it is suggested that the components should be lumped. The lumped composition is given in **Table 6.6**. This composition becomes the feed for flash calculations.

The predictions obtained from the modified model are compared with predictions from other models in **Figure 7.7**. The predictions from Pedersen's model and the modified Won's model are very close and lower than predictions form Won's model. This is expected because, in the modified model, the number of components which can form wax are lower than those in the original Won's model. This is due to the distinction made between n-paraffins and other models in the modified model as well as Pedersen's model. The WAT prediction of 308.32K from the modified model is lower than predictions from the Pedersen's model and the original Won's model as seen in all of the previous cases. In this case, however, the original Won's model severely overpredicts the amount of wax precipitated, and hence, the WAT is also higher for the original Won's

model. Thus, the WAT prediction from the modified Won's model is closer to the experimental value.

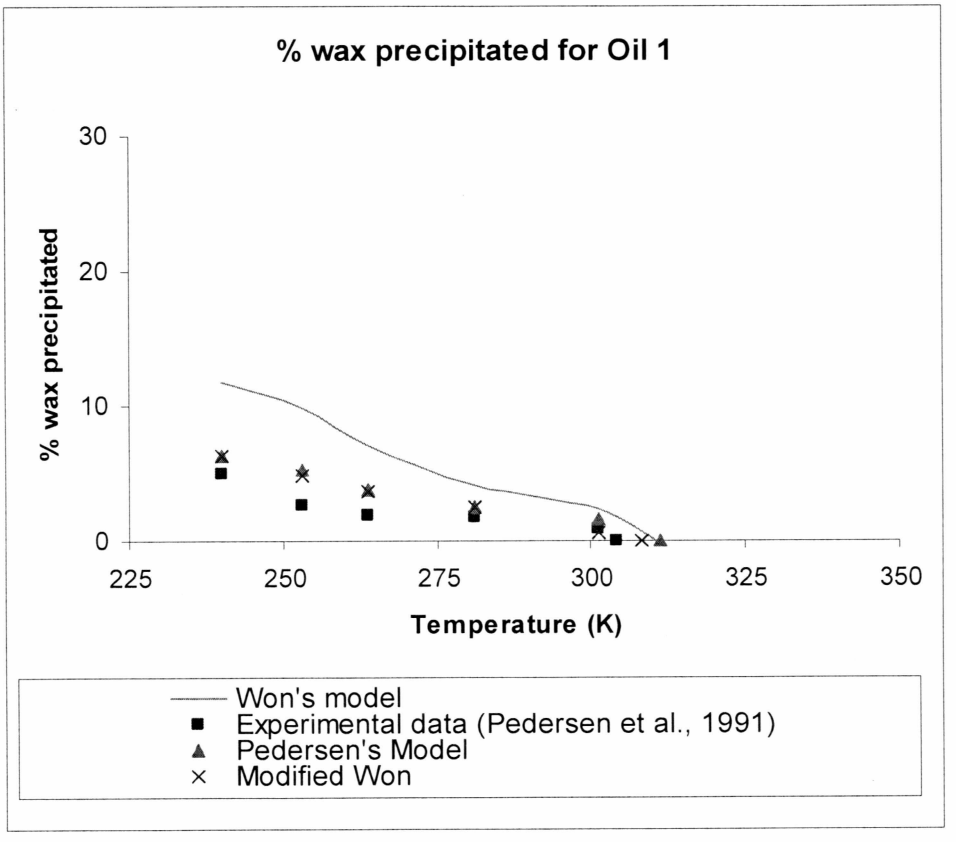

Figure 7.7 % wax precipitated as function of temperature for Oil 1

Chapter 8

Conclusions and Recommendations

8.1 Conclusions

Based on the results obtained in the study, the following conclusions were drawn:

- The comparison of Won's model and Pedersen's model showed that Won's model overestimates the amount of wax precipitated, but predicts the WAT in better way than Pedersen's model. Predictions for the amount of wax precipitated by Pedersen's model are superior to those from Won's model.
- The reason for overestimation of the amount of wax precipitated using Won's model was due to the model not being able to distinguish between wax forming and non-wax forming components in a carbon fraction.
- Limitations of Pedersen's predictions were due to the description of the wax phase as an ideal solution.
- Won's model was then modified to distinguish between the wax forming and non-wax forming components. Also, a provision was made to account for change in the volume when a component in the liquid state transforms into a solid state.
- A comparison of the modified Won's model and the other models indicated that overall predictions from the modified model are better. WAT predictions, though, are superior from the original Won's model.
- The reason for better predictions from the modified Won's model is more accurate description of the phases due to consideration of non-ideality, distinction between the wax forming and non-wax forming components, and accounting for the change in volume during the solidification process.
- Another advantage of the modified model is that it is less calculation intensive, hence easy to tune to experimental results when compared to Pedersen's model.
- The inability of the modified model to account for change in heat capacity during the solidification process and to accurately describe the thermo-physical properties corresponding to solid habits of the wax crystals was the main reason for deviation between the experimental and predicted data.

8.2 Recommendations for Future Work

- More research should be done to study the behavior of wax crystals. Accurate description of wax crystals and their thermo-physical (heat of fusion, temperature of fusion) properties would lead to better predictions from thermodynamic models.
- The model should be modified to account for change in heat capacity during the solidification process while describing the fugacity of solid with the fugacity of liquid in the sub-cooled state.
- A more advanced flash calculation procedure, such as simulated annealing or genetic algorithm, should be used for flash calculations, as the flash calculations often lead to convergence problems and are highly dependent on initial guess value.
- A more powerful optimization routine should be used for tuning the results from the model to the experimental data.

Nomenclature

a_1, a_2 Constants in Equations (4.21) and (4.22)

A Constant

A_m PR EOS parameter for mixture

A_i^{pure} PR EOS parameter for single component i

b PR EOS parameter of a component

b_m PR EOS parameter of a mixture

B Constant

B_m PR EOS parameter for mixture

B_i^{pure} PR EOS parameter for single component i

C Constant

d_{25}^{L} Density of a component in liquid phase at 25^0C

f_i^L Fugacity of component i in liquid phase mixture

f_i^S Fugacity of component i in solid phase mixture

f_i^V Fugacity of component i in vapor phase mixture

f_i^{oL} Fugacity of pure component i in liquid phase

f_i^{oS} Fugacity of pure component i in solid phase

F Total moles of feed

K_i^{SL} Equilibrium ratio between mole fractions of component i in solid and liquid phases

K_i^{VL} Equilibrium ratio between mole fractions of component i in vapor and liquid phases

L Total moles of liquid stream

MW_i Molecular weight of component i

P_{ci}^{S} Critical pressure of wax forming part of component i

P_{ci}^{no-S} Critical pressure of non-wax forming part of component i

R Universal gas constant

s_i Molar composition of solid stream

S	Total moles of solid stream
T_i^f	Temperature of fusion of component i
v_i^L	Molar volume of component i in liquid state
v_i^S	Molar volume of component i in solid state
V	Total moles of vapor stream
x_i	Molar composition of liquid stream
y_i	Molar composition of vapor stream
z_i	Molar composition of feed
z_i^S	Mole fraction of wax forming part of component i in feed
z_i^{no-S}	Mole fraction of non-wax forming part of component i in feed
z_i^{old}	Mole fraction of component i in feed before splitting into wax forming and non-wax forming parts
Z_i^L	Compressibility factor of component i in liquid phase mixture
Z_i^{pure}	Compressibility factor of pure component i in liquid phase
Z_i^V	Compressibility factor of component i in vapor phase mixture
ΔC_P	Heat capacity difference between liquid and solid state of a component
$\overline{\delta}$	Average solubility parameter of a mixture
δ_i^L	Solubility parameter of component i in liquid phase
δ_i^S	Solubility parameter of component i in solid phase
ε	criterion for convergence
γ_i^L	Activity coefficient of component i in liquid phase mixture
γ_i^S	Activity coefficient of component i in solid phase mixture
ΔH^F	Enthalpy of fusion
ΔH^V	Heat of vaporization
φ_i	Volume fraction of component i in corresponding phase
ϕ_i^L	Fugacity coefficient of component i in liquid phase mixture
ϕ_i^V	Fugacity coefficient of component i in vapor phase mixture

ϕ_i^{oL} Fugacity coefficient of pure component i in liquid phase

ϕ_i^{oS} Fugacity coefficient of pure component i in solid phase

ρ_i Density of component i at standard conditions

ρ_i^P Density of paraffinic component i at standard conditions

ψ_i PR EOS parameter of component i

ψ PR EOS parameter of mixture

ω Acentric factor of a component

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Appendix A
Solid State Fugacity Calculations

The standard state fugacities at temperature T and pressure P of component i in the liquid and wax phases can be expressed as,

$$\Delta G = RT \ln\left(f^{oS} / f^{oL}\right) \tag{A-I}$$

where ΔG is the change in the molar Gibbs free energy is associated with the transition of component i from liquid to solid form at temperature T and pressure P. Change in Gibb's free energy can be expressed as,

$$\Delta G = \Delta H - T\Delta S \tag{A-II}$$

Change in enthalpy (ΔH) can be expressed as,

$$\Delta H = -\Delta H^{f} + \int_{T}^{T^{f}} (C_P^L - C_P^S) dT \tag{A-III}$$

And change in entropy (ΔS) can be expressed as,

$$\Delta S = \frac{-\Delta H^{f}}{T^{f}} + \int_{T}^{T^{f}} \frac{(C_P^L - C_P^S)}{T} dT \tag{A-IV}$$

Using Equations (A-I)-(A-IV), and calculating the fugacity of pure component in liquid phase from EOS, fugacity of pure component in solid phase can be calculated (Pedersen et al, 1991).

Appendix B

Liquid and Vapor Fugacity Calculations (Dandekar, 2006)

It is convenient to do the fugacity calculations in the terms of fugacity coefficient Φ, which is the ratio of fugacity to the system pressure. Fugacity coefficient as given by PR EOS is

$$\ln\phi = Z - 1 - \ln(Z - B) + \frac{A}{2\sqrt{2}B} \cdot \ln\left[\frac{Z + (1-\sqrt{2})B}{Z + (1+\sqrt{2})B}\right] \qquad \text{(B-I)}$$

In these equations, Z is the compressibility factor. The A and B are given by following equations.

$$A = \frac{a\alpha P}{(RT)^2} \quad \text{and} \quad B = \frac{bP}{RT} \qquad \text{(B-II)}$$

and a and b are given by following equations

$$a = \Omega_a \frac{R^2 T_C{}^2}{P_c} \quad \text{and} \quad b = \Omega_b \frac{RT_C}{P_c} \quad \text{where } \Omega_a = 0.45724 \text{ and } \Omega_b = 0.07780 \qquad \text{(B-III)}$$

α is given by

$$\alpha = [1 + m(1 - T_r^{0.5})]^2 \qquad \text{(B-IV)}$$

where, T_r is the reduced temperature and m is given for PR EOS respectively as follows

$$m = 0.48 + 1.574\omega - 0.176\omega^2 \text{ for SRK} \qquad \text{(B-V)}$$

and $m = 0.379642 + 1.48503\omega - 0.1644\omega^2 + 0.016667\omega^3$ for PR (B-VI)

ω is the acentric factor. It was introduced to account for the deviation from the corresponding states principle.

It should be noted that Equation B-I is for pure components.

Extension of EOS models to mixtures

All EOS models are developed for pure components and are extended to mixtures by employing mixing rules. These mixing rules are simply the means of calculating the mixture parameters equivalent to those of pure components. The mixture parameters are given by,

$$(a\alpha)_m = \sum_{i=1}^{n}\sum_{j=1}^{n} y_i y_j (a_i a_j \alpha_i \alpha_j)^{0.5}(1 - k_{ij}) \qquad \text{(B-VII)}$$

and $b_m = \sum_{i=1}^{n} y_i b_i$ (B-VIII)

where, $(a\alpha)_m$ represents the product of constant a and α for a given mixture, y_i and y_j are the mole fraction of component i and j in the mixture, a_i and a_j the constant a for component i an j the mixture, α_i *and* α_j the parameter α for component i and j in the mixture, k_{ij} or k_{ji} the binary interaction parameter, b_m a constant b for the mixture; and b_i a constant b for component i in the mixture. The binary interaction parameter (BIP) is an empirically determined correction factor that characterizes the binary formed by components i and j in the mixture. The fugacity of component in mixture in liquid phase or vapor phase is found out by following equation.

$$\ln(\phi_i^V) = \frac{b_i}{b_m}(Z_V - 1) - \ln(Z_V - B) - \frac{A}{B(\delta_2 - \delta_1)}\left[\frac{2\psi_i}{\psi} - \frac{b_i}{b_m}\right]\ln\left[\frac{Z_V + \delta_2 B}{Z_V + \delta_1 B}\right] \quad \text{(B-IX)}$$

A and B are found out from Equation (B-II), aα and b_m obtained from Equations (B-VII) and (B-VIII) should be used. $\delta_1 = 1 + \sqrt{2}$ and $\delta_2 = 1 + \sqrt{2}$ for PR EOS and ψ_i and ψ are given by,

$$\psi_i = \sum_{j=1}^{n}[y_j(a_i a_j \alpha_i \alpha_j)^{0.5}(1 - k_{ij})] \quad \text{(B-X)}$$

$$\psi = \sum_{i=1}^{n}\sum_{j=1}^{n}[y_i y_j(a_i a_j \alpha_i \alpha_j)^{0.5}(1 - k_{ij})] \quad \text{(B-XI)}$$

Z_L which is found out from cubic equation of state can be substituted in Equation (B-IX) and the liquid phase fugacity coefficient can be found out.