COMPOSITIONAL MODELING OF WAX FORMATION IN PETROLEUM MIXTURES

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Abstract   Heavy organics deposition is a common problem in oil industry, especially in oil production, transportation and processing. Wax or solid paraffin series are examples of heavy organics that deposit. Precipitation and crystallization of wax causes major difficulties in different processes. Based on multi-solid theory, a basic model is modified in this paper for wax precipitation in different oils. Four oil samples with paraffin/naphthene/aromatic (PNA) analysis are used. Two-parameter gamma function is used for molecular weight distribution of C7+ fraction. Since all samples in original multi-solid model were dead oil with vapor phase being ignored, the pressure and composition effects on wax precipitation were, therefore, impossible (existence of vapor phase). When considering vapor phase in this work, the proposed modification (i.e. solution method) is well able to predict pressure and composition (addition of different solvents) effects on wax appearance point (WAP). The results obtained agree very well with the experimental and previous investigator's results.

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چکـیده   رسوب اجزای آلی موجود در نفت، یکی از مشکلات رایج صنعت نفت است. این مساله خصوصاً در فرایـندهای تولـید، انـتقال و پردازش نفت خام پیش می آید. رسوبات پارافینی جامد مانند واکسها از جمله این رسـوبات آلی می باشند. تبلور و رسوب واکسها مشکلات متعددی از جمله رسوب در خطوط لوله انتقال نفت، مخـازن، چاههـا و تجهـیزات پـردازش و فرآوری نفت را بدنبال دارد. در اینجا، بر اساس تئوری جامد چندگانه (چـند جامده)، یک مدل پایه ای اصلاح شده برای پیش بینی رسوب واکس در ترکیبات نفتی ارائه می گردد که قادر است میزان و نقطه شروع رسوب را در نفتهای مختلف پیش بینی کند. داده های مورد استفاده برای این کار شـامل داده هـای چهـار نمونـه نفتی است که از مراجع مختلف جمع آوری شده است. به منظور تعیین خواص شـبه اجـزاهای جـز سنگین این چهار نمونه نفتی، آنالیز پارافین/نفتن/آروماتیکی بکار برده می شود. برای تعیین توزیـع وزن مولکولی و مولی جزء تابع توزیع دو پارامتری گاما بکار برده شد. نمونه های مورد استفاده درمدل اولـیه چـند جـامده همگـی نفت مرده بودند و از اینرو برای مدل سازی آنها میزان فاز بخار ناچیز در نظر گرفته شـد. بنابرایـن بررسـی اثر فشار و ترکیب نفتی بر رسوب واکس با استفاده از مدل اولیه چند جامده امکان پذیر نـبود (بدلیل ایجاد فاز بخار در اثر این تغییرات). در این تحقیق با در نظر گرفتن فاز بخار، روش حل پیشنهادی قـادر خواهـد بود اثر فشار و ترکیب نفتی بر رسوب واکس را بخوبی پیش بینی کند. نتایج بدست آمده با نتایج حاصل از تحقیقات دیگر و نتایج تجربی تطبیق خوبی دارد.

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INTRODUCTION

Precipitation and crystallization of a solid phase is highly undesirable in the oil wells, oil pipelines and process equipments. Solid paraffin, or wax, is an example of such solid phases. The main consequences of wax formation are choking of flow lines, the increase of pressure drop and the decrease or the stoppage of oil recovery from oil reservoirs.

Thermodynamics modeling of wax formation has been treated in a number of papers [1,4].

Results of these models for prediction of wax formation are not in good agreement with experimental findings. These models overestimate the amount of precipitated wax and cloud temperatures of the oils. Most of these models use solid solution theory, which assumes that the precipitated wax is a solid solution, where all the components dissolve in each other and form a single solid phase.

Won [1] used an EOS for vapor-liquid equilibrium and for estimating non-idealities of the liquid and solid solution, a modified regular solution model was used; however, the effect of heat capacity difference of solid and liquid (ΔCp_i) on the (f^s / f^l) was neglected for simplicity.

Hansen et al. [2] used the polymer-solution theory of Flory [5] for describing non-idealities in the liquid phase, and assumed activity coefficient of solid components equal to unity.

Won [3] modified their previous model by the following items and obtained the better results compared to the their previous models. These modifications use, an extended regular-solution for activity coefficients in the liquid phase, assumes an ideal solid phase for heavier hydrocarbon components and includes the heat capacity effect on the ratio (f^s / f^l).

Pedersen et al. [4] modified Won's model [1] by using solubility parameter with an adjustable parameter for each of the liquid and solid phases, incorporating the paraffinic/naphthenic/aromatic (PNA) split for each pseudo-component of the C_{7+}, modifying the melting-enthalpy of the P, N and A by means of one adjustable parameter and incorporating the effect of the heat-capacity difference on the (f^s / f^l).

This recent model has less error relative to the other works; but, like the other one, this model overestimated amount of wax deposition in high value.

Pedersen [6], proposed that only a portion of C_{7+} fraction of an oil may coexist in solid-liquid equilibrium and assumed the wax to be an ideal solid solution. Results of this model were better than the previous models, but like the other models, this model, also, overestimated amount of wax deposition.

Using calorimetric and microscopy experiments on solid precipitated from binary normal-alkane mixture, Dorset [7] found that the precipitated wax phase is unstable and segregates into two solid phases. He also, found that segregated solid phases are pure hydrocarbon components.

Recent studies and researches [8-10] on kinetics of the phase segregation by spectroscopy and calorimetric and electron diffusion have shown that the rate of phase segregation is very sensitive to the chain-length difference between precipitating hydrocarbon components. For crude oil, these experiments have been rarely performed; however, phase transition of precipitated wax has been observed (Hansen et al., [11]). In this article, considering these research studies and experiments, a new and effective algorithm for prediction of wax precipitation, based on multi-solid phase model (C. Lira-Galeana, A. Firoozabadi and J. M. Prausnitz [12]) will be presented.

Performed studies (Pedersen et al. [13] and Ronningsen et al. [14]) show that precipitated wax consists primarily of normal paraffin series, iso-paraffin series and naphthene series; however, the aromatics are often not included because they do not precipitate. Therefore assuming average properties (considering P, N and A in one group) for undefined hydrocarbons (pseudo-compotes) is not right.

In this work, the average properties method was applied for the first three oil samples and for other oil samples, the PNA analysis method for evaluating properties of heavy components was used. The results of this research show fewer errors relative to previous works.

MODIFICATION OF MULTI-SOLID (MULTI-SOLID-WAX) PHASE MODEL

Wax deposition is often described as paraffin deposition. This is because of two main reasons, first, paraffin series are the major components in wax deposition and their values are greater than the values of other components in solid, and the second, paraffin series are the first components that precipitate (when wax formation occurs). In order to predict the limits of pressure, temperature and composition in which wax or paraffin precipitate, we have used a modified thermodynamic model based on multi-solid model, with a proposed solution method on it. Multi-solid model [12] is based on precipitation of certain heavy components

Vapor Phase
Liquid Phase
Solid Phase 1
Solid Phase 2
Solid Phase i

Figure 1. Multisolid Phase for Wax.Precipitation.

of crude oil with average properties assigned to each fraction.

Researches performed on a number of North Sea crude oil mixtures show that under the cloud point temperature of different crude oils, phase transition will occur. Similar studies performed in the years 1990 to 1994, on demixing kinetic of hydrocarbon mixtures, under cloud point temperature [7-10] show that at the beginning of precipitation, there is an unstable solid solution, where the components are temporarily miscible in all proportion.

However, after a characteristic time, spontaneous demixing of solid solution lead to the final stable state, which contains pure hydrocarbon components. Namely precipitated wax is a mass of pure hydrocarbon components that contains mutually immiscible precipitating components. Figure 1 depicts this model.

The number and the nature of precipitating components are obtained from a phase stability analysis, as follows:

$$f_i(P,T,Z_i) - f_{i,pure}^l(P,T) \geq 0.0 \qquad (1)$$

The component that fulfills this expression will precipitate. This equation is easily derived from Equation 5 of Michelen [15]. The Peng-Robinson EOS [16] is used for describing vapor-liquid phase behavior.

Proposed algorithm is illustrated in Appendix I (Figure 7). It is assumed that depending on temperature and pressure, there are a vapor, a liquid and several solid phases. Based on this algorithm, computer program converges fast and gives accurate results.

THE PHASE EQUILIBRIUM EQUATIONS AND THEIR RELATED CORRELATIONS IN THIS WORK

At constant temperature and pressure, the equilibrium equation for precipitating i-component is:

$$f_i^v = f_i^l = f_{i,pure}^s \qquad (2)$$

where f_i is the fugacity of component i; v is vapor phase, l is liquid phase and s is solid phase. For non-precipitating components:

$$f_i^l = f_i^v \qquad (3)$$

In order to calculate fugacity of each component in pure solid state, the following equation is used [17]:

$$Ln(\frac{f^s}{f^l}) = -\frac{\Delta h_i^f}{RT}(1. - \frac{T}{T_i^f}) + \frac{1}{R}\int_{T_i^f}^{T}\frac{\Delta Cp_i}{T}dT - \frac{1}{RT}\int_{T_i^f}^{T}\Delta Cp_i dT \qquad (4)$$

where superscript ^{f}, indicates fusion, Δh_i^f is the molar enthalpy of fusion, T_i^f is fusion temperature, ΔC_P is heat capacity of fusion and T is system temperature.

Fugacity of each component in pure liquid state is obtained from the following equation:

$$f_{i,pure}^l = \phi_{i,pure}^l P \qquad (5)$$

where ϕ_i^l may be found by using a cubic EOS (Robinson et al. [16] in this work) on i component at the temperature and pressure of system and p is the system pressure.

For the first series of samples, binary interaction coefficient is calculated from the following equation (Lira-Galeana et al. [12]):

$$k_{ij}^{EOS} = 1.0 - \frac{2v_{ci}^{1/6}v_{cj}^{1/6}}{v_{ci}^{1/3} + v_{cj}^{1/3}} \qquad (6)$$

where v_c is critical volume. For the other samples, where the PNA analysis method is used, the following equation (Pan et al. [18]) is applied:

$$k_{C1j} = 0.0289 + 1.633 10^{-4} Mt_j \qquad (7)$$

where Mt is molecular weight and k_{C1-j} is methane-hydrocarbon binary parameter. In this samples the k_{ij} value for the other hydrocarbon-hydrocarbon is zero.

THE NEEDED EQUATIONS FOR CALCULATING PURE SOLID FUGACITY

Melting-Point Temperature (T_i^f) For normal alkanes [18]:

$$T_i^f = 374.5 + 0.02617 Mt_i - 20172 / Mt_i \qquad (8)$$

For other components (aromatics and naphthene series), (Lira-Galeana et al. [12]):

$$T_i^f = 333.5 - 419 Exp(-0.00855 Mt_i) \qquad (9)$$

Enthalpy of Fusion (Δh_i^f) (Pan et al. [17])
For normal alkanes:

$$\Delta h_i^f = 0.1426 Mt_i T_i^f \qquad (10)$$

For other components (aromatics and naphthene series), (Lira-Galeana et al. [12]):

$$\Delta h_i^f = 0.05276 Mt_i T_i^f \qquad (11)$$

Heat Capacity of Fusion (ΔCp) For all components (Pan et al. [18]):

$$\Delta Cp_i = 0.3033 Mt_i - 4.635 10^{-4} Mt_i T_i^f \qquad (12)$$

CRITICAL PROPERTIES AND ACENTRIC FACTOR

For evaluating lighter hydrocarbon component properties, Riazi and Al-Sahhaf [19] recent work and Twu [20] correlation have been used. However, critical pressure for components with molecular weight higher than 300 gr/mol is

TABLE 1. The Values of the Parameters A, B and C in Equation 13.

Parameter	Paraffins	Naphthens	Aromatics
A	0.6799	2.588	4.85
B	-22.18	-27/629	-42.93
C	0.00284	0.0045	0.00561

calculated from Equation 8 of Pan et al. [18]:

$$Pc_i = A - B \exp(-CMt_i) \qquad (13)$$

where the constants A, B, and C are presented in Table 1.

Critical temperature for all heavy hydrocarbon components (aromatics naphtens, paraffins) is calculated from Riazi and Al-Sahhaf [19] correlations. The following correlations [19] is used for evaluating acentric factor of aromatic components:

$$Ln(\omega_i) = -36.1544 + 30.94 Mt_i^{0.026261} \qquad (Mt_i \le 800) \qquad (14)$$

For $Mt_i > 800$ the value ω_i will be assumed equal to 2; however, acentric factor for paraffin and naphthene series are being calculated from Riazi and Al-Sahhaf [19] correlations.

Crude Oil Systems and Related Data Table 3 contains final (modified) data of composition of four oil mixtures. For these oil mixtures, we use the PNA analysis method to evaluate properties of heavy components or pseudo-components.

PRESSURE AND OIL COMPOSITION EFFECT ON WAX APPEARANCE POINT TEMPERATURE

Pressure Effect Experimental data show that wax appearance point (WAP) temperature raises with increase of pressure. The calculations performed in this work also show that by increasing of pressure, wax precipitation temperature will increase (Figures 5 and 6). It is contended in this article that increase of pressure will decrease solubility of precipitating

Oil 1			Oil 2			Oil 3			Oil 4		
Comp.	Mol Frac	Mw	Comp.	Mol Frac	Mw	Comp.	Mol Frac	Mw	Comp.	Mol Frac	Mw
P-C50	40.	72.00	P-CP1	4.4627	167.0	P-CP1	3.5922	157.0	P-CP1	5.7265	164.0
P-C10	5.0	144.0	N-CP1	6.4827	160.0	N-CP1	4.7712	157.0	N-CP1	7.3568	164.0
N-C10	5.0	142.0	A-CP1	15.126	160.0	A-CP1	4.7712	157.0	A-CP1	9.6703	164.0
A-C10	5.0	136.0	P-CP2	2.9096	237.0	P-CP2	2.7858	201.0	P-CP2	2.9853	234.0
P-C15	5.0	212.0	N-CP2	3.8428	233.0	N-CP2	4.5495	201.0	N-CP2	5.2281	234.0
N-C15	5.0	210.0	A-CP2	8.9664	233.0	A-CP2	4.5495	201.0	A-CP2	7.2834	234.0
A-C15	5.0	204.0	P-CP3	1.5446	307.0	P-CP3	1.8055	252.0	P-CP3	1.3769	305.0
P-C20	2.0	284.0	N-CP3	2.1514	302.0	N-CP3	2.9829	252.0	N-CP3	2.0712	305.0
N-C20	3.0	282.0	A-CP3	5.0199	302.0	A-CP3	4.4744	252.0	A-CP3	6.1298	305.0
A-C20	2.0	276.0	P-CP4	0.7856	375.0	P-CP4	1.2238	300.0	P-CP4	0.6310	374.0
P-C25	1.0	352.0	N-CP4	1.3890	372.0	N-CP4	2.9018	300.0	N-CP4	1.5455	374.0
N-C25	3.5	350.0	A-CP4	3.2409	372.0	A-CP4	4.3527	300.0	A-CP4	3.8695	374.0
A-C25	2.5	344.0	P-CP5	0.3528	449.0	P-CP5	0.3674	563.0	P-CP5	0.2621	445.0
P-C30	1.0	424.0	N-CP5	1.4348	440.0	N-CP5	2.5116	563.0	N-CP5	1.0180	445.0
N-C30	2.0	422.0	A-C$_{30+}$	1.4348	440.0	A-CP5	5.1937	563.0	A-C$_{30+}$	2.3772	445.0
A-C30	2.0	416.0	P-C$_{35+}$	0.1377	511.0	P-CP6	0.0581	654.0	P-C$_{35+}$	0.1101	514.0
P-C35	1.0	492.0	N-C$_{35+}$	1.5694	512.0	N-CP6	1.0319	654.0	N-C$_{35+}$	0.1271	514.0
N-C35	2.5	490.0	A-C$_{35+}$	0.0174	512.0	A-CP6	1.6277	654.0	A-C$_{35+}$	2.1982	514.0
A-C35	1.5	484.0	P-C$_{40+}$	0.0468	590.0	P-CP7	0.0736	666.0	P-CP1$_+$	0.0016	644.0
P-C40	0.5	562.0	N-C$_{40+}$	1.1964	587.0	N-CP7	1.0099	666.0	N-CP1$_+$	0.0185	644.0
N-C40	1.0	560.0	A-C$_{40+}$	0.0491	587.0	A-CP7	2.8634	666.0	A-CP1$_+$	2.1278	644.0
A-C40	1.5	554.0	P-C$_{46+}$	0.0259	713.0	N-CP8	0.8611	744.0	A-CP2$_+$	2.6341	912.0
P-C45	0.5	632.0	N-CP1$_+$	0.3143	724.0	A-CP8	2.1707	744.0			
N-C45	1.0	630.0	A-CP1$_+$	1.8285	724.0						
A-C45	1.5	624.0	N-CP2$_+$	0.2257	901.0						
			A-CP2$_+$	1.3396	901.0						

components in liquid phase, therefore solid phases will appear sooner (at higher temperatures). The following equation is a theoretical explanation for this fact:

$$x_i = F(T) \exp\left[-\frac{P(V_i^l - V_i^s)}{RT} \right] \qquad (15)$$

This correlation is an approximation of the solubility of the first precipitating component (a heavy normal paraffin) (Hansen and Ronningsen, [2]) at solid wax appearance point temperature. Liquid molar volume is a weak function of pressure and the change of the solid volume with pressure is also negligible. Therefore, it can be concluded from the above equation that increases in pressure decreases the solubility of the precipitated component in the liquid phase.

COMPOSITION EFFECT

Light components in oil mixtures act as a solvent. These solvents dissolve heavy components in themselves; consequently, inhibit heavy component precipitation at low temperatures. In other words, these light components cause decreasing of WAP
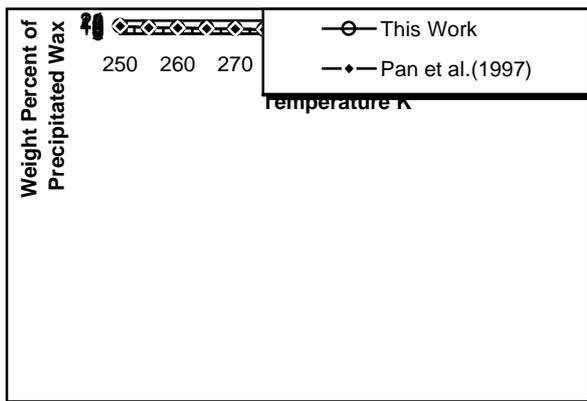
Figure 2. Weight percent of precipitated solid wax for oil 1.
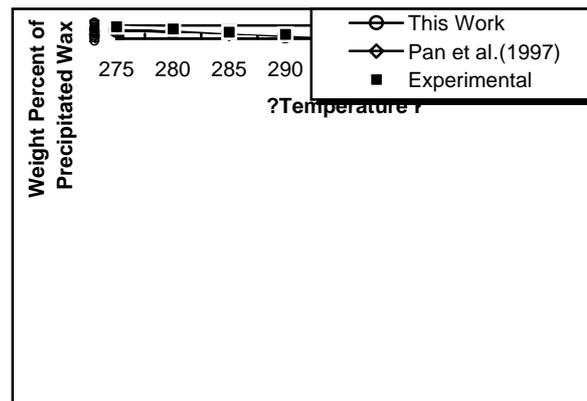
Figure 3. Weight percent of precipitated solid wax for oil 2.

in petroleum mixtures. Results of this work also indicate this light component effect that have been depicted in Figure 6.

RESULTS AND DISCUSSION

Figures 2, 3 and 4 show results using our proposed method (modification of multi-solid model for wax formation). For calculating the properties of light components (paraffin, naphthene or aromatics) in these oil samples, Riazi and Al-Sahhaf [19] correlations were used. In these samples, by using two parameters gamma-distribution function [21], heavy component (C_{7+}) splits into lighter components, and then these lighter components are grouped into a lesser number of pseudo components (where each one is composed of some components). Then by utilizing the properties of these pseudo components each heavy component splits into three groups (paraffinic, naphtenic, aromatic).

Figure 2 indicates the predicted results of this work and the results of Pan et. al. [18]. Oil 1, which its calculation results are shown in Figure 2, is synthetic oil. Almost in all temperature ranges, both calculation results are the same.

Results predicted for oil 2 (Figure 3) and oil 3 (Figure 4), are as good as those for the other oils. As it can be observed in Figures 2, 3, and 4, the results obtained from the present work in comparison with previous work (Lira-Galeana et al. [12] and Pan et al. [18]) can be said to be more accurate and acceptable.

As was stated before, increasing pressure in oil with fixed composition leads to increasing of solid wax appearance point temperature. Results of other investigations for oils 2, 3 and 4 (Pan et al. [18]) are also included in Figure 5 for comparison purposes. Presence of light components in oil mixtures causes decreasing in WAP as it has been depicted in Figure 6, for oil 1.

Results of WAP calculation at high pressures, for petroleum mixtures, are presented in Table 3. As can be observed the results of the present work (for wax appearance point temperature and the amount of precipitated wax for a wide range of temperatures) are in good agreement with results presented by other works [12,18].

CONCLUSION

The major aim for performing this research was to develop a thermodynamic-computerized model for predicting WAP and amount of precipitated wax in petroleum mixtures.

As expressed in the introduction, almost all of the previous models for predicting wax formation overestimate the amount of solid wax and all of them use solid solution theory. However, overestimations of the results obtained by multi-solid model are very smaller than that of other models. In multi-solid model [12], the amount of vapor phase in samples (dead oils) was ignored and therefore calculations were based on liquid–solid(s) equilibrium. By considering vapor phase in
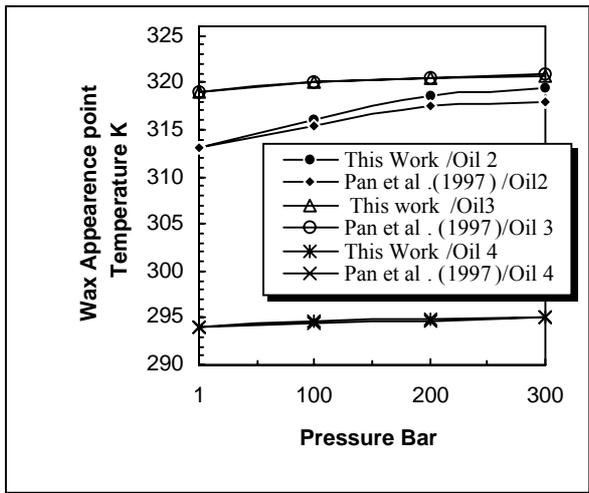
Figure 4. Weight percent of precipitated solid wax for oil 3.
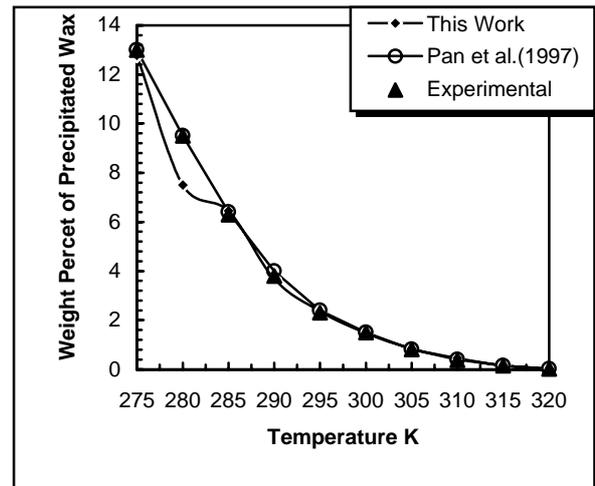
Figure 5. Pressure effect on wax appearance point temperature (Oils 2,3 and 4).

phase equilibrium, we modified multi-solid model, and based on this modification we proposed a new and effective solution method for this modification, and finally our obtained results were comparable with experimental data.

The main conclusions obtained from this work are as follows:

1. Normal paraffin series are the first components that precipitate as solid phase, when temperature decreases. Normal paraffin, iso-paraffin and naphthene will then precipitate in the process. Aromatics usually remain in liquid phase. Analysis of the precipitated wax shows that the main percentage of the precipitation is normal paraffin. This finding is supported by experimental work and laboratory observation.

2. By considering the significant difference in the properties of paraffin, naphthene and aromatics of a heavy component, PNA analysis for wax precipitation is recommended, rather than average properties method, in which properties of a heavy fraction is average of paraffin, naphthene and aromatic properties of that component.

3. Because of considering vapor phase in this study, this work will be able to predict pressure and composition effect on WAP and amount of precipitated wax.

4. Increase of pressure in oil with constant composition leads to increases in WAP. Results obtained and depicted in Figure 5, for three oil sample cases and in Figure 6 for one sample case are in support of this claim.

5. Increase of light component concentration or adding these light components to the oil, leads to decrease of WAP. These results are depicted in Figure 6 (this figure is showing both pressure and composition effects on WAP).

NOMENCLATURE

A	Aromatics
N	Naphthenes
P	Paraffins
Pc_i	Critical Pressure
Tc_i	Temperature
ω_i	Acentric Factor
Δh_i^f	Enthalpy of Fusion (cal/mol)
f_i	Fugacity of i
v (V)	Vapor
l (L)	Liquid
s (S)	Solid
Mt_i	Molecular Weight gr/ mol
k_{ij}	Binary Interaction Coefficient
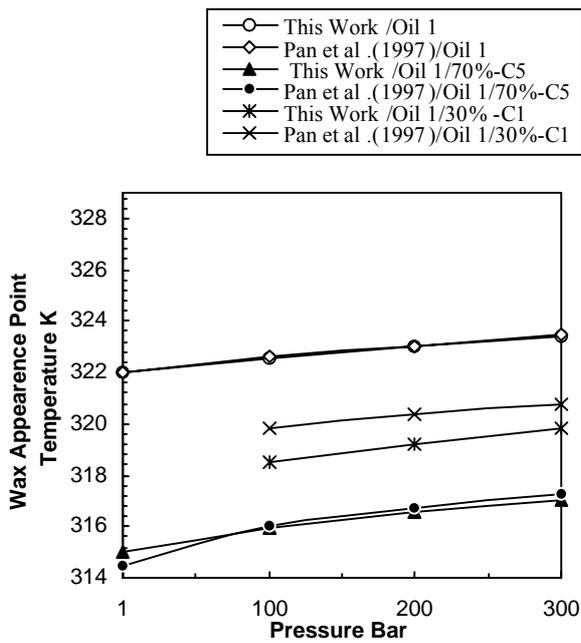
Figure 6. Pressure and oil composition effect on wax appearance point temperature.

Z $_i$ Mole fraction in feed
nc (NC)   Number of Carbon atoms
WAP   Wax appearance point temperature
ϕ_i Fugacity coefficient of i components
VSE   Vapor-Solid Equilibrium
LSE   Liquid-Solid Equilibrium

APPENDIX I

PROCEDURE AND PROPOSED SOLUTION METHOD ALGORITHM

Figure 7 shows our proposed solution method algorithm for solving modified multi-solid phase model.

In this work, five subroutines have been used. The first subroutine contains a calculating program for evaluating average properties (Tc, Pc, ..., when average properties method are used). The second subroutine calculates the properties of heavy components from raw input data (when PNA analysis method is used). Box 1 of flow chart depicts output of these two subroutines. As mentioned before many correlations are used for

calculating properties of light and heavy components. The third subroutine is for calculating the number and the nature of precipitating components in pure solid phases (at any temperature and pressure). In this subprogram we check phase stability analysis for all components. The stability equation is (Box 2 of flow chart show this section):

$$f_i(P,T,Z_i) - f^d_{i,pure}(P,T) \geq 0.0 \qquad (16)$$

phases based on Peng-Robinson EOS. This
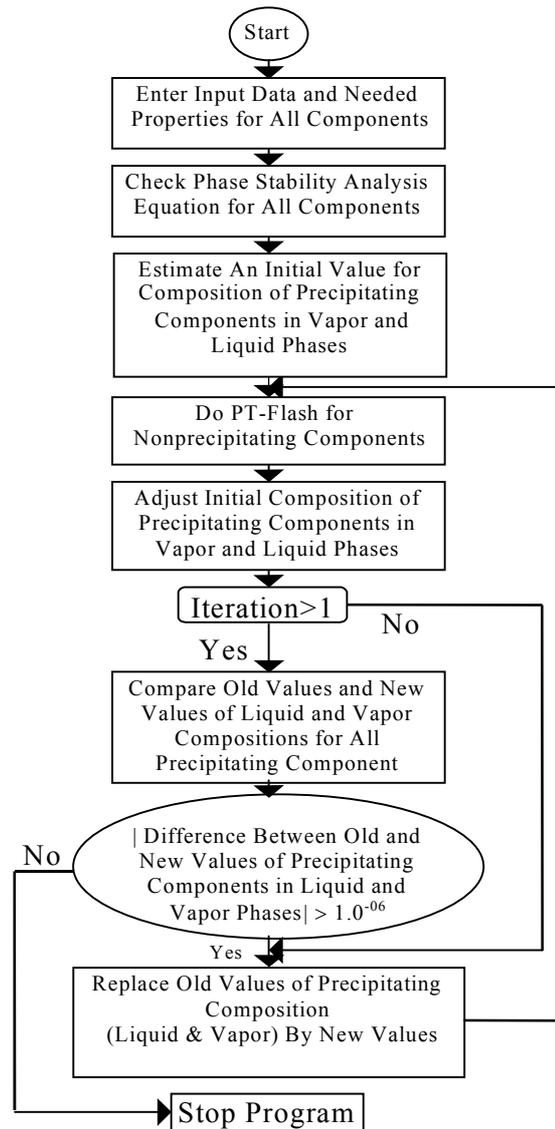
Figure 7. Proposed algorithm in this work.

**TABLE 3. Pressure and Oil Composition Effect on WAP for Oils 1, 2, 3 and 4
(This Work and Pan et al. [18].**

Pressure Bar	Method	Oil 1	Oil 1 C1 ↓30%	Oil 1 C1 ↓70%	Oil 2	Oil 3	Oil 4
1.0	This Work	322.0	—	315.0	312.5	317.65	293.1
1.0	Pan et al., (1997)	322.0	—	314.5	312.8	319.0	293.8
100.0	This Work	322.55	318.5	315.94	315.98	318.4	293.63
100.0	Pan et al., (1997)	322.6	319.8	316.0	316.0	320.0	294.5
200.0	This Work	323.0	319.2	316.55	318.4	318.75	294.0
200.0	Pan et al., (1997)	323.0	320.4	316.7	318.0	320.5	294.8
300.0	This Work	323.44	319.8	317.0	319.8	319.5	294.2
300.0	Pan et al., (1997)	323.5	320.8	317.4	320.0	320.8	295.0

The fourth subroutine is used for calculating fugacity of each component in liquid and vapor subprogram is very important and applicable in main program, and finally in accuracy of obtained results. The first application based on this subprogram is estimation of initial values for compositions of precipitating components in vapor and solid phases.

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