Deposition of wax on the pipe walls is one of the complex flow assurance problems that causes a decrease and complete blockage of oil production rates by reducing the cross-sectional area of flow in the pipelines. In addition, surface facilities require higher energy consumption and failure of facilities due to wax plugging.

Effective design of oil recovery processes requires an adequate prediction of the thermodynamic conditions in which wax can precipitate from crude oil, depending on the pressure, temperature, and composition of the oil.

In this paper, the modified melting and pour point temperatures were presented based on the fluid description. Other fusion properties such as the enthalpy of fusion, the solid-state transition enthalpies, and the heat capacity of fusion have been calculated to modify the multi-solid model for predicting wax deposition.

The proposed modified equations for melting and pour point temperatures were showing reliable agreement with experimental data based on SARA analysis and demonstrated more accurate results compare to literature data.

In order to justify the proposed model, the comparative approach has been implemented between literature, experimental, and data obtained based on proposed solutions.

The detailed description of the Republic of Kazakhstan's (RoK) oil fields, components from C1 up to C^{36+} has been used during this research and the most crucial components which tend to form wax precipitation from $C_{15}H_{32}$ to $C_{20}H_{42}$ were plotted, which showed an increasing accuracy of 11 % for melting point temperature and 7 % for pour point temperature compared to literature data.

As a result, the proposed modified solutions for fusion properties demonstrated good agreement with literature and obtained results of modifications can be used for further research on Multi solid model of wax precipitation

Keywords: fusion properties, melting point temperature, solid state temperature, wax deposition

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THE IMPLEMENTATION OF FUSION PROPERTIES CALCULATION TO PREDICT WAX DEPOSITION

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1. Introduction

The prevention of wax formation by forecasting it is possible location in the petroleum industry poses a substantial and complex challenge. It is imperative to gain a comprehensive comprehension of the behavior of waxy solid phases to effectively address this issue. The ability to predict the circumstances in which wax will appear at certain melting and solid-state temperatures is crucial for evaluating the risks of deposition and devising appropriate preventive and remedial measures. Furthermore, the careful consideration of fusion properties, such as melting and solid-state temperatures, holds significant significance in this context. Doing so enhances our ability to manage the formation and potential impacts of waxy deposits during exploitation, transportation, and refining processes, thus minimizing costs and avoiding detrimental economic outcomes.

The fusion properties of n-alkanes with an odd and even number of carbon atoms are different. This difference is mainly caused by the steric effects of the rearrangement of atoms in molecules. The n-alkane molecules tend to rotate about their longitudinal axes at temperatures below their melting points and undergo solid state transitions caused by the onset of free rotation in the lattice structure.

The proposed procedure differs in the way they formulate the melting point and solid-state parameters. There are several factors that have hindered the development and application of rigorous theories for the thermodynamic prediction of paraffin equilibrium over a wide range of conditions. For example, current analytical limitations in the characterization of the heavy fraction of crude oil, as well as the unavailability of vapor-liquid-solid equilibrium (VLS) data over wide pressure and temperature ranges are some of the limitations.

Although recent experimental methods for measuring wax crystallization by spectrometry and microscopy are currently available, it has not yet been possible to develop an accurate, predictive computational tool for thermodynamic prediction of oil and wax equilibrium with direct applications in the design and development, and optimization of the reservoir/oil well/ production facilities system.

Therefore, research on the development of accurate determination of fusion properties is essential to eliminate the

following issues: lack of a reliable model to predict WAT for RoK's crude oil.

2. Literature review of wax modeling and problem statement

Nowadays, much attention has been paid to the wax deposition in the pipeline transportation of waxy crude oil. In the research [1], the experimental work done on the wax deposition in a waxy crude oil, considering the impact of the dispersion degree of asphalting was summarized. The extensive analysis conducted in a comprehensive review [2] primarily aimed to pinpoint challenges that have a negative impact on the anticipated stable offshore oil production. These challenges encompassed factors such as diminished flow efficiency, heightened pumping expenses, and the development of wax gels. Moreover, the researchers presented solutions in the form of pour point depressants, which were innovatively designed and adjusted to fulfill the requirements for addressing wax-related issues. The research outlined in the study [3] defined a range of approaches, both theoretically conceptualized and practically implemented, to mitigate the occurrence and accumulation of waxes. Notably, among the array of strategies, the modification of the pour point temperature has emerged as an expedient technique for anticipatory management of wax deposition tendencies.

Numerous research papers [4–7] have addressed the thermodynamic modeling of wax formation. However, the outcomes of these models, concerning the prediction of wax formation, do not align well with experimental findings. The amount of precipitated wax and cloud point temperatures of oils are often overestimated by these models. The prevailing approach in these models is to utilize solid solution theory, which assumes that the precipitated wax behaves as a solid solution, where all components dissolve into each other, forming a single solid phase.

In the paper [4] employed an Equation of State (EOS) to analyze vapor-liquid equilibria, and to account for non-ideal behavior in both the liquid and solid solution phases, a modified regular solution model was adopted. However, for the sake of simplicity, they did not consider the impact of the difference in heat capacity between the solid and liquid phases on the fugacity.

The research [5] utilized polymer-solution theory [7] to characterize the non- ideal behavior within the liquid phase. Additionally, they made the assumption that the activity coefficient of solid components is equal to one (unity). Also, to enhance the accuracy of predictions, the researchers conducted a comprehensive characterization of the C_{7+} fraction, utilizing 160 pseudo components, and adjusted the activity coefficients to very small values (on the order of 10^{-10}) in comparison to those calculated using the previous model [1]. The experimental findings demonstrated reasonably good agreement (within ±2 K).

The study of regular solution [6] made several modifications to their previous model, resulting in improved results compared to their earlier models. These modifications involved incorporating an extended regular-solution approach to estimate activity coefficients within the liquid phase. Additionally, they assumed an ideal solid phase for heavier hydrocarbon components and considered the influence of heat capacity on the ratio.

In the work [7] introduced modifications to previous model [4] by incorporating the solubility parameter, where each of the liquid and solid phases involved an adjustable parameter. They also integrated the paraffinic/naphthenic/aromatic (PNA) split for each pseudo component of the C_{7+}. Additionally, the melting enthalpy of P, N, and A was adjusted using a single parameter, and the impact of the heat-capacity difference on the fugacity ratio was considered in their refined model.

This recent model exhibits reduced error compared to previous works. However, similar to the other models, it still tends to overestimate the amount of wax deposition, particularly in cases where the value is high.

At this point, another approach involves employing an Equation of State (EOS) to represent the behavior of all phases in equilibrium has been implemented to the industry. Specifically, the EOS is directly applied to model vapor-liquid equilibria, while the non-ideal characteristics of the solid phase are indirectly described using the fugacity ratio derived from the EOS.

This technique has been utilized in various papers [8–11], however the lack of experimental data and precise calculation of fusion properties based on specific conditions of certain region could be the limitation and increase the average deviation error (ADE).

The fundamental paper [8] introduced a multi-solid model to predict wax deposition in hydrocarbon mixtures. The proposed method operates under the assumption that pure solid components do not mix following wax deposition and incorporates phase stability analysis to identify pseudo or pure components that precipitate as pure solids. The authors utilized the Peng-Robinson equation of state (EoS) to calculate the volatility of components in liquid phases. They modified the melting point suggested by the regular model [6], where the temperature dependence of the equation reflects the average melting point of heavy naphthenic and aromatic hydrocarbons with carbon atom numbers exceeding 30. Furthermore, they made adjustments to the enthalpy of melting of paraffinic hydrocarbons proposed by solid-state solutions [6] due to an overestimation of paraffin content below the cloud point. Experimental measurements and analytical calculations were conducted on both binary and multicomponent mixtures. The results of the binary mixture analysis demonstrated improved accuracy after incorporating the heat capacity of the fusion term. The multicomponent mixture was represented by eight samples of crude oil, and the experimental findings regarding wax deposition characteristics aligned with the results obtained from the analytical model. Additionally, the proposed method successfully reproduced the observed behavior of discontinuous deposits in real oil systems [8].

In the research [9], the modification of multi-solid approach by separating each undefined component in normal paraffin (N), naphthenic and iso-paraffin (P), and aromatics (A) was implemented. This method was followed by emphasizing the impact of pressure for predicting wax deposition.

In the paper [10], an extensive investigation into wax precipitation in gas condensate fluids was conducted using a thermodynamic model. The study revealed that the precipitated wax phase can demonstrate retrograde behavior analogous to that observed in gas condensates. Specifically, as the pressure decreases at a constant temperature, the amount of precipitated wax may initially increase, then decrease,

and subsequently increase once more. However, the detailed characteristic of pressure and temperature is necessary to apply given approach. The researchers introduced novel correlations for fusion enthalpy and transition temperature. They incorporated a solid-solid phase transition term into the equation for the solid-to-liquid fugacity ratio of pure components. Furthermore, the Peng and Robinson (PR) EOS was utilized in their model for vapor-liquid equilibrium (VLE) calculations.

The recent study [11] presents a comprehensive thermodynamic framework that has been formulated to compute the cloud point, amount, and composition of wax precipitates across a broad temperature range. The model integrates the principles of ideal solution and multiple solid phase formation and relies on the application of cubic equations of state.

Currently, this model holds widespread usage within the field of wax deposition research.

The critical parameters provide crucial information for further calculation of fusion properties and were determined using equations from the book [12].

In the study [13], two correlations were introduced for fusion properties based on PNA approach and four ternary systems were utilized to validate the new developed thermodynamic model.

Recent techniques for developing new thermodynamic models for forecasting a wax deposition include PC-SAFT, UNIQUAC, and other methods.

In the research [14], a new UNIQUAC based predictive local composition model was compared against predictive Wilson and predictive modified UNIQUAC on their abilities to predict wax formation, however the investigation [15] developed the new correlations to calculate the volume parameter, *c*, taking into account SRK EOS and the heat of vaporization in UNIQUAC equation.

In the comprehensive review [16] stated that more mechanistically rigorous wax deposition models and experimental data are still needed to improve the forecast of wax appearance, while the critical review [17] emphasize the lack of data on the aspect ratio of wax crystals in the deposit is common in mass transfer-based models as a fitting-tool to "correct" the predictions of wax appearance models.

The recent approach based on the software [18] aimed to determine wax deposition by applying Aspen HYSYS, however this software does not accurately allow esteeming wax precipitation curve, nor the Wax Appearance Temperature, given the oil properties.

A robust technique is imperative to thermodynamically model the phase behavior of wax within crude oils, exemplified by the application of perturbed-chain statistical associating fluid theory (PC-SAFT). Within the context of the study [19], a novel methodology was introduced. This approach hinged on leveraging the wax appearance temperature exhibited by crude oil, offering a means to predict and derive the requisite PC-SAFT parameters for precise thermodynamic simulation of wax crystallization within crude oil matrices.

Further research studies [20, 21] involve the PC-SAFT equation of state for modeling of liquid phase behavior and the multi-solid framework to describe solid phase for predicting wax deposition.

In terms of experimental procedures, the research [22] stated that the flow loop was utilized to examine the deposition behavior of a waxy condensate with the bulk temperatures equal or lower than the coolant temperatures, under which conditions wax deposition is not supposed to occur. As a result, it has been demonstrated that molecular diffusion alone is not sufficient to describe wax deposition, and further accurate description of fusion properties is necessary.

The manuscript [23] evaluated different techniques that have been adopted to estimate and predict the wax thickness deposited either using conventional techniques or using numerical models validated experimentally. Regardless of the approach, the detailed description of fusion properties remains the crucial step for predict wax deposition.

Another complex approach presented in the paper [24]. The cloud point and wax precipitation characteristics of the crude oil were obtained using the differential scanning calorimetry (DSC) thermal analysis method. Then, the wax deposition rate of the pipeline was predicted by two methods: OLGA software and wax deposition kinetic model. Consequently, accurate description is key step for obtaining a reliable data and compare it with experimental.

In the study [25], a cold finger experimental device was constructed, and eight groups of experimental scenarios under cold flow conditions were performed in accordance with field conditions. The effects of deposition time and cold and hot bath temperatures on wax deposition were investigated. The authors emphasized the necessity of having the critical and fusion properties for validating experimental data.

The findings indicate that the newly proposed model exhibits superior performance compared to the conventional solution model when calculating wax precipitation in complex systems but has lack of agreement with experimental data.

All this allows to assert that it is expedient to conduct a study on accurate determination of fusion properties that can severely affect for further prediction of wax deposition suitable for RoK's hydrocarbon oil.

3. The aim and objectives of the study

The aim of the study is to develop the modification of fusion properties equations that can be implemented for forecasting the wax deposition, correlated with the composition of RoK's oil and pressure and temperature conditions [26]. It allows to minimize the cost expenditures during planning and design the surface facilities and prevent pipe blockage during the transportation.

To achieve this aim, the following objectives are accomplished:

– to conduct of SARA analysis to provide a detailed description of the range of components from C_1 to C_{36+};

– to determine the fusion properties, the melting-point temperature, the solid-state transition temperatures, the enthalpy of fusion, the solid-state transition enthalpies, and the heat capacity of fusion has been calculated;

– to obtain the proposed equation, the melting point temperature and the pour point temperature correlations were modified for certain RoK's crude;

– to perform a numerical calculation of the proposed model by using Python programming language.

4. Materials and methods of research

The object of this study is a fusion properties such as melting point and pour point temperatures that can facilitate further prediction of wax deposition.

The main hypothesis of the study is a modification possibility of fusion properties equations for implementing in multi-solid model to forecast wax deposition. As a result, the proposed solutions can be represented as a numerical simulator to determine the wax precipitation to prevent a pipe blockage.

During the research the following assumptions were made:

1. The crude oil samples have been collected from two different oil fields, however have identical fluid characteristics.

2. The obtaining description of fluid component was done by SARA analysis using gas chromatograph, assumed no need to validate by DSC or other PVT tests.

3. In order to simplify the calculation procedures, the essential calculations were made within C_{15} to C_{20} components, due to the fact that these components tend to form wax in pipelines.

In the current research, two crude oil samples were supplied from Uzen and Zhetybay fields in RoK. These samples were subjected to SARA analysis, which helped to determine the composition of oil components ranging from C_1 to C_{36+}. Additionally, the tests on the physical and chemical properties of surface samples of the oil to facilitate the calculation of the multi-solid model were conducted and presented in Table 1.

The critical temperature of n-alkanes as a function of the boiling point T_{bi}, R given below:

$$T_c^0 = T_b \begin{pmatrix} 0.533272 + 0.191017\times10^{-3}T_b + \\ +0.779681\times10^{-7}T_b^2 - \\ -0.284376\times10^{-10}T_b^3 + \\ +0.959468\times10^{28}/T_b^{13} \end{pmatrix}^{-1}. \quad (1)$$

The critical pressure of *n*-alkanes:

$$P_c^0 = \begin{pmatrix} 3.83354 + 1.19629\alpha^{1/2} + 34.8888\alpha + \\ +36.1952\alpha^2 + 104.193\alpha^4 \end{pmatrix}^2. \quad (2)$$

The boiling point is calculated as:

$$T_b = \exp\begin{pmatrix} 5.71419 + 2.715790 - 0.2865900^2 - \\ -39.8544/\theta - 0.122488/\theta^2 \end{pmatrix} - \\ -24.7522\theta + 35.3155\theta^2. \quad (3)$$

Molecular weight function:

$$\theta = \ln MW^0. \quad (4)$$

Lower boiling point:

$$\alpha = 1 - T_b/T_c^0. \quad (5)$$

The critical volume:

$$V_c^0 = \left[1 - \begin{pmatrix} 0.419869 - 0.505839\alpha - \\ -1.56436\alpha^3 - 9481.70\alpha^{14} \end{pmatrix}\right]^{-8}. \quad (6)$$

Melting points, pour points and their modifications.

Won's correlation [3] was chosen as the generally accepted one for determining the melting point of each component using the molecular weights of the components:

$$T_i^f = 374{,}5 + 0{,}02617 * M_i - 20172/M_i. \quad (7)$$

The algorithm of modification the correlation is provided below:

1. Based on the results of the experiment (Table 1), calculations were made to determine the results of the melting points of each component.

2. The program was written in the Python programming language to determine the correlation coefficients in order to improve the accuracy of calculations.

3. The calculation results were tested using the modified correlation.

Modification of the Nichita (2001) correlation to determine the solid-state transition (pour point) temperature.

Nichita (2001) modified the equation as follows:

$$T_{i1}^{tr} = 366.39775 + 0.003609M_i - \frac{20879.6}{M_i}. \quad (8)$$

The algorithm of modification the correlation is provided below:

1. The calculations have been made to determine the pour point for each component based on the data in Table 1.

2. The program was written in the Python programming language to determine the correlation coefficients in order to improve the accuracy of calculations.

3. The calculation results were tested using the modified correlation.

Melting point for mixture.

The molecular weight of the mixture was calculated in 2 steps, the first for components from C_3 to C_6, and the second for components C_{7+}.

The molecular weight of the components from C_3 to C_6 was calculated according to mixing rules:

$$M_{wi} = \sum_{i=1}^{n} m_i M_i. \quad (9)$$

The molecular weight of the components from C_{7+} was calculated according to the rules of exponential distribution, namely The Lohrenz-Bray-Clark (LBC) correlation [22]:

$$M_{Cn+} = \sum_{i=n}^{\infty} z_i M_i / z_{Cn+}. \quad (10)$$

The obtained results of critical parameters then will be utilized to determine the fusion properties. In addition, several parameters are directly using for multi-solid model to predict wax deposition.

5. Results of fusion properties modifications

5. 1. The results of SARA analysis

The data of RoK's oil fields were obtained and utilized for determining the fusion properties. Table 1 indicated the SARA analysis that was implemented to provide a detailed description for range of components from C_1 to C_{36+}.

The results of SARA analysis provide a detailed description of samples, and was made by gas chromatography approach. The values of molecular weight can be applied for further calculation of fusion properties.

Table 1

Detailed composition of sample (Uzen oil field)

Component	Nomenclature	Weight, %
Propan	C_3	0.000
Isobutane	i-C_4	0.072
Butane	C_4	0.000
Isopentane	i-C_5	0.251
Pentane	C_5	0.419
2-methylheptane	C_6H_{14}	0.000
Isohexane	i-C_6	0.137
Hexane	C_6	0.984
Methylcyclopentane	C_6H_{12}	0.211
Benzene	C_6H_6	0.206
Cyclohexane	C_6H_{12}	0.006
Heptane	C_7	1.560
Methylcyclohexane	C_7H_{14}	0.632
Toluene	C_7H_8	0.195
Octane	C_8	2.346
Ethylbenzene	C_8H_{10}	0.146
m p - Xylene	C_8H_{10}	0.156
o- Xylene	C_8H_{10}	0.054
Nonane	C_9	2.502
Trimethylbenzenes	C_9H_{12}	0.186
Decane	C_{10}	2.666
Undecane	C_{11}	2.605
Dodecane	C_{12}	2.649
Tridecane	C_{13}	3.072
Tetradecane	C_{14}	2.914
Pentadecane	C_{15}	3.439
Hexadecane	C_{16}	2.878
Heptadecane	C_{17}	2.791
Octadecane	C_{18}	2.833
Nonadecane	C_{19}	2.707
Eicosane	C_{20}	2.465
Heneicosane	C_{21}	2.456
Docosane	C_{22}	2.107
Tricosane	C_{23}	2.861
Tetracosane	C_{24}	2.574
Pentacosane	C_{25}	2.718
Hexacosane	C_{26}	2.882
Heptacosane	C_{27}	3.084
Octacosane	C_{28}	2.925
Nonacosane	C_{29}	3.272
Triacontane	C_{30}	3.308
Hentriacontane	C_{31}	3.216
Dotriacontane	C_{32}	3.099
Tritriacontane	C_{33}	2.856
Tetratriacontane	C_{34}	2.397
Pentatriacontane	C_{35}	2.655
Hexatriacontane	C_{36+}	16.504
Overall	C_{1e} to C_{36+}	100.000

5. 2. The values of critical parameters for fusion properties calculation

Based on samples composition, the critical parameters based on eq. (1) and (2) have been calculated. Table 2 indicated the detailed description of critical parameters.

Table 2

The results of critical parameters of component for C7—C36

Component	Mole fraction, Z_{cn}	Molecular weight, M_w, g/mol	Critical temperature, T_c, K	Critical pressure, P_c, MPa
Heptane	0.222125641	94	642.1377145	2.660247011
Octane	0.17143654	108	663.0170572	2.395102473
Nonane	0.132314699	122	682.429072	2.174872927
Decane	0.102120468	136	700.6390911	1.988558059
Undecane	0.078816563	150	717.8421369	1.828582633
Dodecane	0.060830613	164	734.1863416	1.689535127
Tridecane	0.046949059	178	749.7872435	1.567432645
Tetradecane	0.036235278	192	764.7369485	1.459270229
Pentadecane	0.027966383	206	779.1102394	1.362732803
Hexadecane	0.02158445	220	792.9687869	1.276004529
Heptadecan,	0.016658876	234	806.3641357	1.197638844
Octadecane	0.012857318	248	819.3398726	1.126467572
Nonadecane	0.009923277	262	831.9332351	1.061535934
Eicosane	0.007658784	276	844.1763263	1.002055163
Geneicosan	0.005911048	290	856.0970473	0.947367356
Docosane	0.004562146	304	867.7198242	0.896918982
Tricosane	0.003521064	318	879.066181	0.850240653
Tetracosane	0.002717557	332	890.1551974	0.806931471
Pentacosane	0.00209741	346	901.0038778	0.766646781
Hexacosane	0.001618781	360	911.6274528	0.729088488
Heptacosane	0.001249375	374	922.0396254	0.693997329
Octacosane	0.000964267	388	932.2527764	0.661146648
Nonacosane	0.000744221	402	942.2781354	0.630337345
Triacontane	0.00057439	416	952.1259239	0.601393743
Hentriacontane	0.000443314	430	961.8054773	0.574160188
Dotriacontane	0.00034215	444	971.325348	0.548498224
Tritriacontane	0.000264071	458	980.6933937	0.524284244
Tetratriacontane	0.00020381	472	989.9168539	0.501407515
Pentatriacontane	0.000157301	486	999.002415	0.479768516
Hexatriacontane	0.000121405	500	1007.956268	0.459277527

The obtained critical parameters in Table 2 will be utilized for further calculation of fusion properties such as melting point and pour point temperatures. Further, this data can have used for software to simulate the possible location of wax precipitation.

5. 3. The modified equations of melting and pour point temperatures

Based on the extensive research, the modified correlation (2021) for the Uzen oil field presented below:

$$T_i^f = 101{,}82154 + 0{,}02617 * M_i - 20172 / M_i. \quad (11)$$

The Fig. 1 described the dependence of the melting point T_m on the molecular weight of the M_{wi} component constructed for components from hexane C_6 to hexatriacontane C_{36+} for the Uzen field in RoK.

The absolute average deviation was calculated for these components using the following equation:

$$\mathrm{AAD} = \frac{1}{n}\sum_{i=1}^{n}\left|x_i - m(X)\right|. \quad (12)$$

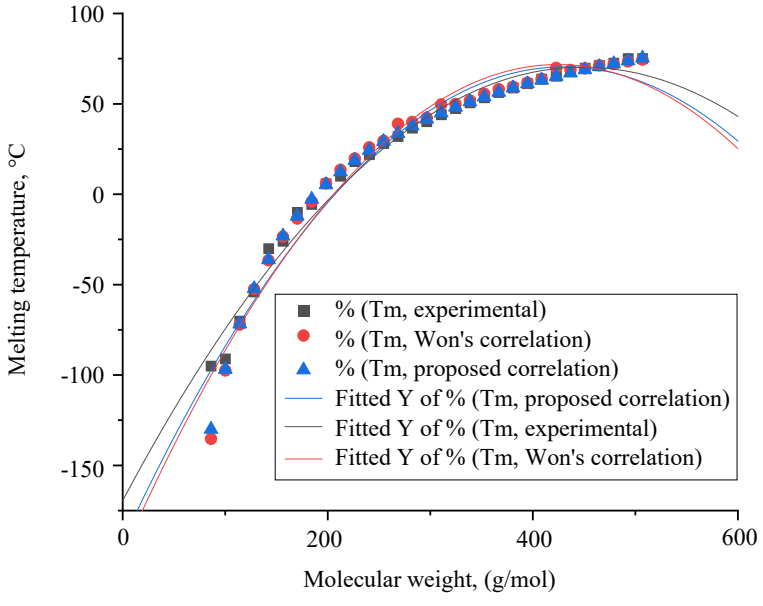

Fig. 1. The melting point temperature from hexane C_6 to hexatriacontane C_{36+}

As a result, the proposed correlation provides the accuracy of the calculation results in comparison with the correlation of Won's correlation [3] by 7 % for the Uzen field (RoK).

Further, it was experimentally established that the precipitated paraffin contains only heavy hydrocarbons from C_{15} to C_{20} and above.

To obtain more precise results for the components from pentadecane $C_{15}H_{32}$ to eicosane $C_{20}H_{42}$, the correlation (11) was recalculated using the Python programming language and a Fig. 2 was constructed that showed the accuracy of the results for 6 components compared to Won's correlation [3] correlation by 11 %:

$$T_i^f = 99{,}833 + 0{,}02617 * M_i - 20172 / M_i. \quad (13)$$

Therefore, the modified correlation (2021) for the Uzen field is provided:

$$T_i^f = 102{,}333 + 0{,}02617 * M_i - 20172 / M_i. \quad (14)$$

The calculation results based on proposed equation are presented in Tables 3, 4.

After modifying the melting temperature, the same procedure is applied to modify the pour point temperature. The proposed correlation is provided below:

$$T_{i1}^{tr} = 95.666 + 0.003609 M_i - \frac{20879.6}{M_i}. \quad (15)$$

Fig. 3 demonstrate the pour point temperature for components from hexane C_6 to C_{36+}, to verify the proposed correlation the calculated values were compared with data available in literature.

Fig. 4 provide the comparison between experimental data, data from literature and data based on proposed solution of pour point temperature of precipitated paraffin contains only heavy hydrocarbons from C_{15} to C_{20} and above.

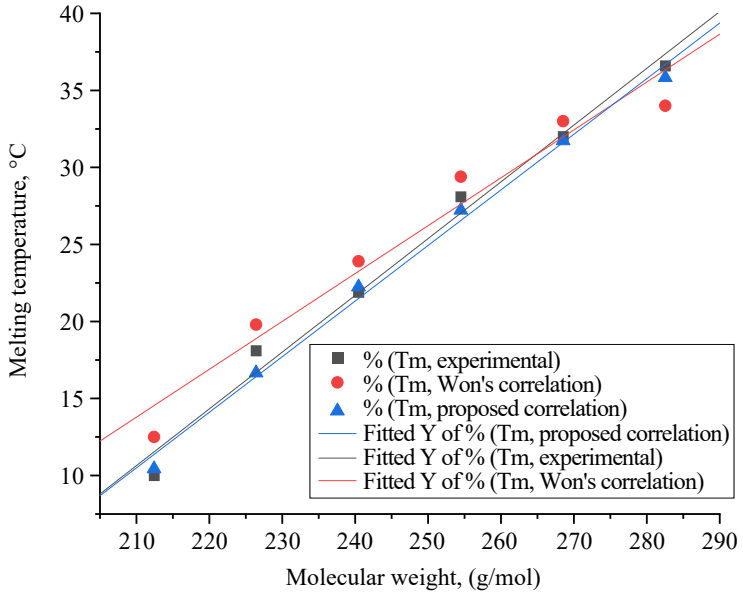

Fig. 2. The melting point temperature for 6 components from Uzen and Zhetybai fields (RoK)

Table 3

Melting point modification results from pentadecane to eicosane

Components	Mol. Weight	Molar mass	Experimental (literary) data, °C	Results based on Won' correlation, °C	Results based on modified correlation (2021), °C
Pentadecane, C_{15}	3.439	212.42	10	12.5	10.43
Hexadecane, C_{16}	2.878	226.41	18.1	19.8	16.66
Heptadecan, C_{17}	2.791	240.471	21.9	23.90775	22.24
Octadecan, C_{18}	2.833	254.494	28.1	29.4	27.23
Nonadecan, C_{19}	2.707	268.518	32	33	31.73
Eicosane, C_{20}	3.439	212.42	36.6	34	35.83

Table 4

The results of pour point modification from tridecane to heptadecane

Components	Molecular Weight, g/mol	Molar mass	Pour point (Nichita, 2001), °C	Pour point (experimental values), °C	Pour point (correlation, 2001), °C
Tridecane, C_{13}	3.072	184.37	–13.1934	–15	–16.91
Tetradecane, C_{14}	2.914	198.39	–4.6846	–9	–8.86
Pentadecane, C_{15}	3.439	212.42	2.7729	–1	–1.86
Hexadecane. C_{16}	2.878	226.41	9.3512	5.5	4.26
Heptadecan, C_{17}	2.791	240.471	15.2509	10.4	9.70

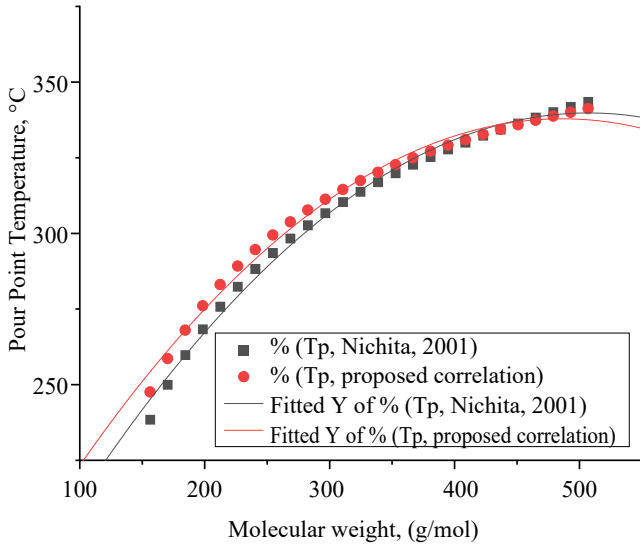

Fig. 3. The pour point temperature from hexane C_6 to hexatriacontane C_{36+}

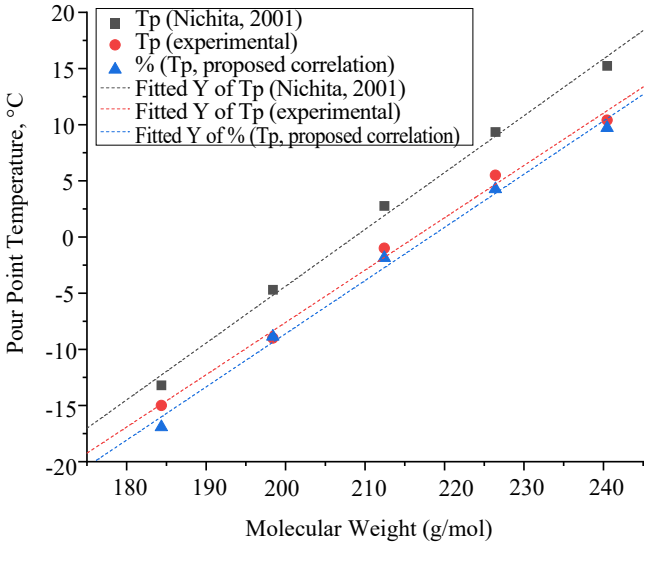

Fig. 4. The pour point for components from C_{15} to C_{20}

The modified correlation of the pour point for the mixture is provided:

$$T_{i1}^{tr} = 71.3333 + 0.003609M_i - \frac{20879.6}{M_i}. \quad (16)$$

According to the results of the absolute average deviation, the efficiency of using the proposed correlation for measuring the pour point was 7 % compared to the Nichita [7].

5. 4. Numerical solution based on Python Language

In order to provide more robust model and eliminate possible errors the proposed equations for melting and pour point temperatures were coded utilizing Python programming language.

The information below provides the code for modification of melting point temperature:

```
n=int(input("number of exp: "))
B=0.02617
C=20172
list=[]
i=1
while(i<=n):
        print("Exp num", i)
        Ti_exp=float(input("Ti_exp="))
        Tif=float(input("Tif="))
        Mi=float(input("Mi="))
        A=Ti_exp–B*Mi + (C/Mi)
        list.append(A)
        print("A=", A)
        i+=1
print(*list)
sa=0
for x in list:
        sa=sa+int(x)
print(sa/len(list))
Number of experiments: 30
Experiment number: 1
Ti_exp=-91
Tif=–97.1951
Mi=100.2
A=107.69513126946107
.....
Experiment number: 30
Ti_exp=75.08
Tif=70.97838
Mi=506.973
A=101.60161778473818
```

$$T_i^f = 99{,}833 + 0{,}02617 * M_i - 20172 / M_i.$$

The information below provides the code for modification of pour point temperature:

```
n=int(input("number of exp: "))
B=0.003609
C=20879.6
list=[]
i=1
while(i<=n):
        print("Num of exp", i)
        Tpp_exp=float(input("Tpp_exp="))
        Tipp=float(input("Tipp="))
        Mi=float(input("Mi="))
        A=Tpp_exp–B*Mi + (C/Mi)
        list.append(A)
        print("A=", A)
        i+=1
print(*list)
sa=0
for x in list:
 sa=sa+int(x)
print(sa/len(list)).
```

6. Discussion of modified equations for fusion properties

Based on the data extracted from Fig. 1, 2, the proposed solutions for predicting melting point temperatures demonstrate a higher level of agreement, to be precise 11 %, with experimental data compared to the calculated values, as per the correlation established by Won [6]. Fig. 3, 4 demonstrate the increasing accuracy of pour point temperature for 7 % compare to Nichita' correlation as confirmed by the Average Absolute Deviation (AAD) analysis. The obtained more precise result based on the oil samples of RoK's field, and modifications of fusion properties particularly made for RoK's region. These figures followed by the Table 3 and 4, were detailed description of results provided.

However, it is essential to acknowledge certain limitations within the scope of this research. One notable constraint is the limited number of oil fields considered in the study.

To enhance the reliability and precision of the multi-solid model for predicting wax deposition, it is crucial to expand the dataset by including more field data from various sources. In terms of drawback, several software can model the wax deposition, but the commercial price is unaffordable to ordinary companies. By doing so, a more robust foundation for the prediction methodology can be established, and potential issues related to the coding procedure can be mitigated, thereby bolstering the overall reliability of the findings.

For further development, the authors suggested to add more dataset to eliminate errors in calculation of fusion properties. In addition, the experimental study based on flow loop techniques could provide the determination of wax location.

7. Conclusions

1. During this research, the crucial parameters for modification were obtained by SARA analysis. Gas chromatograph technique has been used to provide a detailed description of fluid components range from C_1 to C_{36+} for further calculation of fusion properties.

2. A values of critical parameters based on the detailed description of fluid samples have been determined to apply in modification procedure of melting and pour point temperatures.

3. The modified equations of melting and pour point temperatures were introduced by using equations in papers [6, 10] and adapting them based on RoK's oil fields. As a result, the modified equations demonstrated reliable results compare to experimental data. These equations are lately can be used in Multi-solid model to forecast the wax precipitation to prevent the pipelines from blockage.

4. To implement a numerical solution, the researchers employed the Python programming language to code the modified equations. The results of this research exhibit a high level of concurrence with experimental data and frequently outperform the results obtained from previous models.

Conflict of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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Data availability

The data will be provided upon reasonable request.

References

1. Lei, Y., Han, S., Zhang, J. (2016). Effect of the dispersion degree of asphaltene on wax deposition in crude oil under static conditions. Fuel Processing Technology, 146, 20–28. doi: https://doi.org/10.1016/j.fuproc.2016.02.005
2. Hao, L. Z. et al. (2019). A Review of the Mechanism and Role of Wax Inhibitors in the Wax Deposition and Precipitation. Pertanika Journal of Science & Technology 27 (1). URL: http://www.pertanika.upm.edu.my/resources/files/Pertanika%20PAPERS/JST%20Vol.%2027%20(1)%20Jan.%202019/29%20JST-1110-2018.pdf
3. Lim, Z. H., Al Salim, H. S., Ridzuan, N., Nguele, R., Sasaki, K. (2018). Effect of surfactants and their blend with silica nanoparticles on wax deposition in a Malaysian crude oil. Petroleum Science, 15 (3), 577–590. doi: https://doi.org/10.1007/s12182-018-0241-2
4. Won, K. W. (1986). Thermodynamics for solid solution-liquid-vapor equilibria: wax phase formation from heavy hydrocarbon mixtures. Fluid Phase Equilibria, 30, 265–279. doi: https://doi.org/10.1016/0378-3812(86)80061-9
5. Hansen, J. H., Fredenslund, Aa., Pedersen, K. S., R nningsen, H. P. (1988). A thermodynamic model for predicting wax formation in crude oils. AIChE Journal, 34 (12), 1937–1942. doi: https://doi.org/10.1002/aic.690341202
6. Won, K. W. (1989). Thermodynamic calculation of cloud point temperatures and wax phase compositions of refined hydrocarbon mixtures. Fluid Phase Equilibria, 53, 377–396. doi: https://doi.org/10.1016/0378-3812(89)80104-9
7. Schou Pedersen, K., Skovborg, P., Roenningsen, H. P. (1991). Wax precipitation from North Sea crude oils. 4. Thermodynamic modeling. Energy & Fuels, 5 (6), 924–932. doi: https://doi.org/10.1021/ef00030a022
8. Lira-Galeana, C., Firoozabadi, A., Prausnitz, J. M. (1996). Thermodynamics of wax precipitation in petroleum mixtures. AIChE Journal, 42 (1), 239–248. doi: https://doi.org/10.1002/aic.690420120
9. Pan, H., Firoozabadi, A., Fotland, P. (1997). Pressure and Composition Effect on Wax Precipitation: Experimental Data and Model Results. SPE Production & Facilities, 12 (04), 250–258. doi: https://doi.org/10.2118/36740-pa
10. Nichita, D. V., Goual, L., Firoozabadi, A. (2001). Wax Precipitation in Gas Condensate Mixtures. SPE Production & Facilities, 16 (04), 250–259. doi: https://doi.org/10.2118/74686-pa
11. Escobar-Remolina, J. C. M. (2006). Prediction of characteristics of wax precipitation in synthetic mixtures and fluids of petroleum: A new model. Fluid Phase Equilibria, 240 (2), 197–203. doi: https://doi.org/10.1016/j.fluid.2005.12.033
12. Riazi, M. (Ed.) (2005). Characterization and Properties of Petroleum Fractions. ASTM International. doi: https://doi.org/10.1520/mnl50_1st-eb
13. Mansourpoor, M., Azin, R., Osfouri, S., Izadpanah, A. A. (2018). Study of wax disappearance temperature using multi-solid thermodynamic model. Journal of Petroleum Exploration and Production Technology, 9 (1), 437–448. doi: https://doi.org/10.1007/s13202-018-0480-1
14. Chen, W., Zhao, Z., Zhang, X., Wang, L. (2007). Thermodynamic phase equilibria of wax precipitation in crude oils. Fluid Phase Equilibria, 255 (1), 31–36. doi: https://doi.org/10.1016/j.fluid.2007.03.015
15. Coutinho, J. A. P., Mirante, F., Pauly, J. (2006). A new predictive UNIQUAC for modeling of wax formation in hydrocarbon fluids. Fluid Phase Equilibria, 247 (1-2), 8–17. doi: https://doi.org/10.1021/ie980340h
16. Soedarmo, A. A., Daraboina, N., Sarica, C. (2017). Validation of wax deposition models with recent laboratory scale flow loop experimental data. Journal of Petroleum Science and Engineering, 149, 351–366. doi: https://doi.org/10.1016/j.petrol.2016.10.017
17. van der Geest, C., Melchuna, A., Bizarre, L., Bannwart, A. C., Guersoni, V. C. B. (2021). Critical review on wax deposition in single-phase flow. Fuel, 293, 120358. doi: https://doi.org/10.1016/j.fuel.2021.120358
18. Sousa, A. M., Matos, H. A., Pereira, M. J. (2019). Modelling Paraffin Wax Deposition Using Aspen HYSYS and MATLAB. 29th European Symposium on Computer Aided Process Engineering, 973–978. doi: https://doi.org/10.1016/b978-0-12-818634-3.50163-6
19. Jafari Behbahani, T. (2016). Experimental study and a proposed new approach for thermodynamic modeling of wax precipitation in crude oil using a PC-SAFT model. Petroleum Science, 13 (1), 155–166. doi: https://doi.org/10.1007/s12182-015-0071-4
20. Asbaghi, E. V., Assareh, M. (2021). Application of a sequential multi-solid-liquid equilibrium approach using PC-SAFT for accurate estimation of wax formation. Fuel, 284, 119010. doi: https://doi.org/10.1016/j.fuel.2020.119010

21. Asbaghi, E. V., Nazari, F., Assareh, M., Nezhad, M. M. (2022). Toward an efficient wax precipitation model: Application of multi-solid framework and PC-SAFT with focus on heavy end characterization for different crude types. Fuel, 310, 122205. doi: https://doi.org/10.1016/j.fuel.2021.122205
22. Yang, J., Lu, Y., Daraboina, N., Sarica, C. (2020). Wax deposition mechanisms: Is the current description sufficient? Fuel, 275, 117937. doi: https://doi.org/10.1016/j.fuel.2020.117937
23. Alnaimat, F., Ziauddin, M. (2020). Wax deposition and prediction in petroleum pipelines. Journal of Petroleum Science and Engineering, 184, 106385. doi: https://doi.org/10.1016/j.petrol.2019.106385
24. Yao, B., Zhao, D., Zhang, Z., Huang, C. (2021). Safety Study on Wax Deposition in Crude Oil Pipeline. Processes, 9 (9), 1572. doi: https://doi.org/10.3390/pr9091572
25. Hu, Z., Meng, D., Liu, Y., Dai, Z., Jiang, N., Zhuang, Z. (2019). Study of wax deposition law by cold finger device. Petroleum Science and Technology, 37 (15), 1846–1853. doi: https://doi.org/10.1080/10916466.2019.1613431
26. Yang, T., Fevang, Ø., Christoffersen, K., Ivarrud, E. (2007). LBC Viscosity Modeling of Gas Condensate to Heavy Oil. All Days. doi: https://doi.org/10.2118/109892-ms