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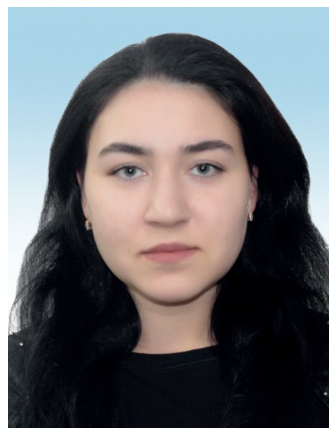
MODIFYING TEMPERATURE CORRELATIONS IN MELTING PROPERTIES CALCULATIONS FOR ACCURATE PREDICTION OF WAX DEPOSITION



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The formation of paraffin deposits is a common problem faced by oil production companies, as it complicates the production and transportation of hydrocarbons. Paraffins are a mixture of saturated hydrocarbons (alkanes) contained in oil in a dissolved or, depending on temperature, crystalline state. Paraffins in the form of crystals can be released from oil if its temperature drops below a certain value - the temperature at which paraffins begin to crystallize. The crystallization temperature of paraffins depends on the chemical composition of the oil and the molecular weight of the paraffins dissolved in it.

Thermodynamic modeling plays an important role in preventing wax formation.

The article analyzes modifications of temperature correlations (melting point and pour point) included in the calculations of fusion properties. Temperature correlation data is used in thermodynamic prediction models of wax precipitation. Two correlations were taken for the study: Won's (1986) correlation and Nichita's (2001) correlation, and by modifying them, new correlations were obtained that give more accurate results with the experimental data. For the experiment, 3 samples with calculated molecular weights were taken from field X.

As a result, the modified correlation for determining the melting point gives an accuracy of calculation results compared to the correlation of Won (1986) by 5%. The modified correlation for determining the solid-state transition temperature gives an accuracy of the calculation results compared to the Nichita (2001) correlation by 17.5% for the X field.

These results provide valuable information for the practical application of modified theoretical temperature correlations, which will make it possible to more accurately characterize the behavior of the oil mixture, increase the accuracy of calculations, and improve the predictive model of wax deposition for various oils.

KEYWORDS: *paraffin, phase behavior, melting point, pour point, molecular weight.*

ПАРАФИН ТҰНУЫН ДӘЛ БОЛЖАУ ҮШІН БАЛҚУ ҚАСИЕТТЕРІН ЕСЕПТЕУДЕГІ ТЕМПЕРАТУРАЛЫҚ КОРРЕЛЯЦИЯЛАРДЫ ӨЗГЕРТУ

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Парафин кен орындарының пайда болуы мұнай өндіруші кәсіпорындарда кездесетін ортақ мәселе, өйткені бұл көмірсутектерді өндіру мен тасымалдауды қиындатады. Парафиндер – мұнайдың құрамында еріген немесе температураға байланысты кристалдық күйдегі қаныққан көмірсутектердің (алкандардың) қоспасы. Кристалл түріндегі парафиндер мұнайдан бөлінуі

мүмкін, егер оның температурасы белгілі бір мәннен – парафиндердің кристалдана бастайтын температурасынан төмен түссе. Парафиндердің кристалдану температурасы мұнайдың химиялық құрамына және онда еріген парафиндердің молекулалық массасына байланысты.

Парафиннің пайда болуының алдын алуда термодинамикалық модельдеу маңызды рөл атқарады.

Мақалада балку қасиеттерінің есептеулеріне енгізілген температуралық корреляциялардың (балку температурасы мен қатаю температурасы) модификациялары талданады. Температуралық корреляция деректері парафин шөгінділерінің термодинамикалық болжау үлгілерінде қолданылады. Қолданыстағы теориялық температуралық корреляцияларды өзгерту мұнай қоспасының сипатын дәлірек сипаттауға, температураға тәуелділіктерді есептеудің дәлдігін арттыруға және әртүрлі мұнайлар үшін парафинді тұндырудың болжамды моделін жақсартуға мүмкіндік береді.

ТҮЙІН СӨЗДЕР: парафин, фазалық әрекет, балку температурасы, құю температурасы, молекулалық салмақ.

МОДИФИКАЦИЯ КОРРЕЛЯЦИЙ ТЕМПЕРАТУР В РАСЧЕТАХ СВОЙСТВ ПЛАВЛЕНИЯ ДЛЯ ТОЧНОГО ПРОГНОЗИРОВАНИЯ ОТЛОЖЕНИЯ ПАРАФИНА

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Образование парафиновых отложений является распространенной проблемой, с которой сталкиваются нефтедобывающие компании, так как это приводит к осложнению добычи и транспортировки углеводородов. Парафины – это смесь предельных углеводородов (алканов), содержащихся в нефти в растворенном или, в зависимости от температуры, кристаллическом состоянии. Парафины в виде кристаллов могут выделяться из нефти, если ее температура опускается ниже определенного значения – температуры начала кристаллизации парафинов. Температура кристаллизации парафинов зависит от химического состава нефти и молекулярной массы растворенных в ней парафинов.

Термодинамическое моделирование играет важную роль в предотвращении образования парафина.

В статье производится анализ модификаций корреляций температур (температуры плавления и температуры застывания), заложенных в расчеты свойств плавления. Данные корреляции температур используются в термодинамических прогнозных моделях парафиновых отложений.

Для исследования были взяты две корреляции: корреляция Вона (1986) и корреляция Ничита (2001), и путем их модификации были получены новые корреляции, которые дают более точные результаты с экспериментальными данными. Для эксперимента брали по 3 пробы с рассчитанными молекулярными массами с месторождения X.

В результате, модифицированная корреляция для определения температуры плавления дает точность результатов расчетов по сравнению с корреляцией Вона (1986) на 5 %. Модифицированная корреляция для определения температуры твердотельного перехода дает точность результатов расчетов по сравнению с корреляцией Никиты (2001) на 17,5 % для месторождения X.

Эти результаты дают ценную информацию для практического применения модифицированных теоретических корреляций температур, что позволит более точно охарактеризовать поведение нефтяной смеси, повысить точность расчетов и улучшить прогнозную модель отложения парафина для различных нефтей.

КЛЮЧЕВЫЕ СЛОВА: парафин, фазовое поведение, температура плавления, температура застывания, молекулярная масса.

I ntroduction. Paraffins are the one primary type of solids which present flow assurance problem. Wax deposition is the big issue for production where significant drops in temperature are expected. The high intensity of formation of paraffin deposits in fields with complex geological and physical development conditions leads to a significant decrease in operating efficiency.

During production and transportation, changes in thermobaric conditions occur, which leads to the formation of deposits of heavy oil components at any point in the field development.

Modifications to existing correlations that describe calculations of fusion properties in thermodynamic models will allow an accurate description of fluid properties and improve the accuracy of the predictive wax deposition model.

Materials and methods. Paraffin crystallization and paraffin deposition are a common type of complications that arise during oil production and transportation. This problem is especially relevant when developing fields with highly paraffinic oils.

Oil is considered as a multicomponent mixture of hydrocarbons [1].

The condition for phase equilibrium in a multicomponent system, as is known, is the equality of the partial thermodynamic Gibbs potentials ϕ of each component in all phases. However, due to the presence of arbitrary constants in the expressions for internal energy and entropy, for solving practical problems it is often more convenient to use another thermodynamic function instead of ϕ , called fugacity f [2].

Paraffins are a mixture of saturated hydrocarbons (alkanes) contained in oil in a dissolved or, depending on temperature, crystalline state. The composition of petroleum paraffins includes normal alkanes C_{16} - C_{40} (known as paraffins), iso-paraffin hydrocarbons and naphthenic hydrocarbons C_{30} - C_{80} . Paraffins in the form of crystals can be released from oil if its temperature drops below a certain threshold - the temperature of the onset of crystallization of paraffins [3]. Paraffin crystallization temperature depends on the chemical composition of the oil and the molecular weight of the paraffins dissolved in it. Waxes can be deposited anywhere in oilfield systems. Deposition of paraffins in pipelines leads to a decrease in their throughput and an increase in pressure drop [4].

The two main forms of wax-liquid equilibrium calculations are the solid solution (Won, 1986) or the multisolid assumption, where pure solids are immiscible (Lira-Galeana, Firoozabadi, & Prausnitz, 1996) [5].

Using the thermodynamic phase equilibrium method is one way, and another is using the ideal solution theory for a binary mixture (solid and liquid).

The crystallization temperature prediction steps in many studies are based on thermodynamic phase equilibrium relationships. The main parameters in these methods are fugacity and fugacity coefficient [6]. These indicators must be adjusted to predict the crystallization point.

When analyzing the deposition process, the main variables are the solution temperature and the melting point of the wax.

The studied modification of the thermodynamic paraffin forecasting model and the planned implementation of the correlation are the main analytical solution for predicting the crystallization temperature of paraffin for various oils.

When implementing this correlation, parameters such as mass fractions, molecular weights, and melting temperatures of the solution components are analyzed.

The initial data for developing the topic include the following factors. Lira-Galeana et al. (1996) [5-6] were the first research group to propose a multisolid model to predict wax deposition in a hydrocarbon mixture. The proposed method is based on the assumption that pure solid components don't mix after wax precipitation and takes into account the role of phase stability analysis, which identifies pseudo or pure components that precipitate as pure solids. To calculate the fugacity of components in liquid phases, the Peng-Robinson equation of state was used. The authors modified the melting point proposed by Won (1986) [7]. The enthalpy of fusion of paraffinic hydrocarbons proposed by Won (1986) was modified due to an overestimation of the amount of wax below the cloud point. Experiments and analytical calculations were carried out on both binary and multicomponent mixtures. The binary mixture results showed an improvement in analytical results after including a term for the heat capacity of fusion.

There are various modified thermodynamic models created to calculate the amount of precipitated wax in a hydrocarbon mixture and analyze the cloud point of the mixture. These thermodynamic models were divided into two assumptions: solid solution (SS) and multi-solid solution (MSS). The solid solution (SS) model is characterized by the miscibility of solid components in a mixture of hydrocarbons, where most of the components form a single amorphous solid phase (Won 1986, 1989, Hansen 1988) [8]. Another "multi-solid" (MS) model describes multiple crystalline solid phases, where each crystalline solid phase is represented by a component of the system [9].

Won (1986) used a new modified solubility parameter in his model. Based on the iso-fugacity relationship between different phases, the solid-liquid equilibrium coefficient, K_i^{SL} :

$$K_i^{SL} = \frac{S_i}{X_i} = \left(\frac{\gamma_i^L}{\gamma_i^S}\right) \exp\left(\frac{\Delta H^f}{RT}\left(1 - \frac{T}{T^f}\right) + \frac{\Delta C_p}{R}\left(1 - \frac{T^f}{T} + \ln \frac{T^f}{T}\right) + \int_o^P \frac{\Delta V}{RT} dP\right)_i \quad (1)$$

where, S_i and X_i denote the mole fractions of component i in the solid and liquid phases, respectively, γ_i^L are the activity coefficients, T^f is the melting temperature, ΔH^f is the heat of fusion, ΔC_p is the change in the heat capacity of fusion, and ΔV is the change of the volume.

A modified model was used to estimate activity coefficients in both, liquid and solid phases.

Then Won (1989) modified his earlier model by adding a combinatorial Flory-Huggins term to calculate liquid phase activity coefficients, and introduced a new thermodynamic correlation to predict the cloud point and composition of the precipitated wax phase over

a wide temperature range (210 to 320 K). Despite the inaccuracies, this model gave high-quality results depending on temperature with an accuracy of ± 3 K.

When setting up the model, consider a system of N_s precipitating components, and N components. The phase equilibrium equation has the form N equation of vapor-liquid iso-fugacity [10].

Melting point is the temperature of a crystalline solid at which it transitions to the liquid state. At its melting point, a substance can be in either a liquid or a solid state. The calculation was modified from Won's (1986) correlation to determine the melting point of alkanes.

The next parameter of the fusion property is the temperature of the solid-state transition (solidification), T_i^r .

Pour point T_i^r is the lowest temperature at which oil and petroleum products are mobile. For oil and petroleum products, the pour point depends on the amount of paraffin.

For the analysis, a modification of the Nichita et al. (2001) correlation was made to determine the solid-state transition (solidification) temperature of alkanes [11].

Also, the main parameters of the fusion property include the enthalpy of melting, the enthalpy of transition to the solid state, and the heat capacity of melting.

The melting enthalpy (Δh_i^f) is calculated from various correlations in which the coefficient is modified. One of the more well-known correlations is calculated using the Lira-Galeana formula (1996):

$$\Delta h_i^f = 0.05276 M_i T_i^f \quad (2)$$

The constant 0.05276 represents the average slope when the entropy of fusion ($\Delta h_i^f / T_i^f$) is plotted as a function of the molecular weight of the paraffinic hydrocarbons [12].

Enthalpy of transition to a solid state (Δh_i^r) is a thermodynamic designation for the amount of heat released that accompanies the transition between states.

Heat capacity of fusion (ΔC_{pi}) is a property that describes how much thermal energy is required to raise the temperature of a given system.

Results and discussions. Won's (1986) correlation was chosen as the generally accepted one for determining the melting point of each individual component using the molecular weights of the components.

$$T_i^f = 374,5 + 0,02617 * M_i - 20172/M_i \quad (3)$$

To carry out a modification of the correlation, it is necessary to carry out a calculation to determine the results of the melting temperatures of each component, then to increase the accuracy of the model calculations, the Python programming language is used by determining the correlation coefficients.

Analyzing the calculation results, the modified correlation is represented by the formula

$$T_i^f = 101,82154 + 0,02617 * M_i - \frac{20172}{M_i} \quad (4)$$

Based on the molecular weight of the components and the calculated melting point, we can construct a dependence graph for the components $C_6H_{14} - C_{36+}$.

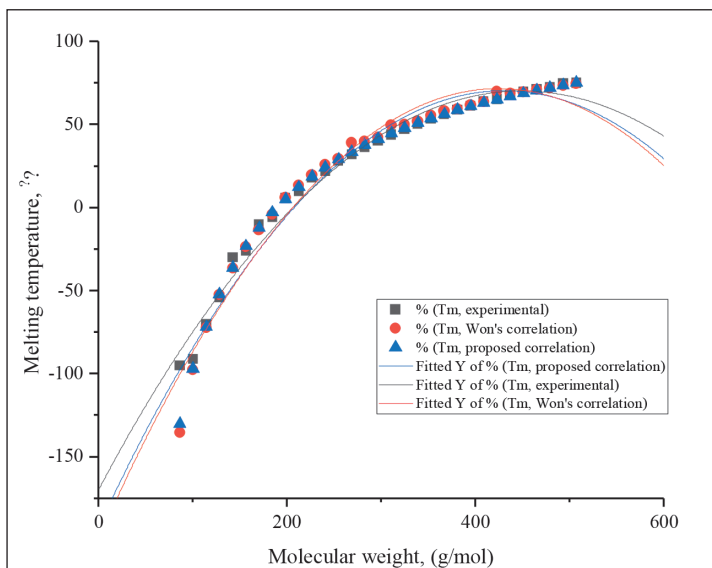


Figure 1 - Melting temperature (°C) versus molecular weight (g/mol)

Other known modifications of correlations for a mixture of hydrocarbons were analyzed, where the melting temperature of the mixture was calculated. The molecular weight of the mixture was calculated in two steps, the first for components C₃ - C₆, and the second for components C₇₊. The molecular weights of components C₃ to C₆ were calculated using Kay's mixing rules:

$$M_{wi} = \sum_{i=1}^n m_i M_i \tag{5}$$

The molecular weight of components from C₇₊ was calculated using the rules of exponential distribution – Lohrenz-Bray-Clark (LBC) correlation:

$$M_{Cn+} = \sum_{i=n}^{\infty} \frac{z_i M_i}{z_{Cn+}} \tag{6}$$

The calculation results for one field (X) are presented in Table 1.

Table 1 – Calculation results

Sample №	Field	Molecular weight from C3 to C6, g/mol	Molecular weight from C7+, g/mol	Final molecular weight, g/mol
1.1	X	47,43	341,76	388,907
1.2		48,525	339,901	388,426
1.3.		53,188	344,09	397,279

Using the Won correlation (1986) with the obtained molecular masses, we calculate the melting point temperature:

$$T_i^f = 102,333 + 0,02617 * M_i - 20172/M_i \tag{7}$$

With known values of molecular weight, melting temperature (Won correlation), experimental melting temperature, and melting temperature calculated using formula (7) the convergence of results can be compared using a graph of molecular weight versus temperature.

As a result, the correlation provides an accuracy of 5% over the Won (1986) correlation for Field X. The calculation results for field (X) are presented in *Table 2*.

Table 2 – Calculation results

№ Sample	Field	Final molecular weight, g/mol	Melting point, Won's correlation (1986)	Meting point (experimental)	Melting point (correlation)
1.1	X	388,907	59,809	62	60,642
1.2		388,426	59,732	61	60,565
1.3.		397,279	61,121	62	61,954

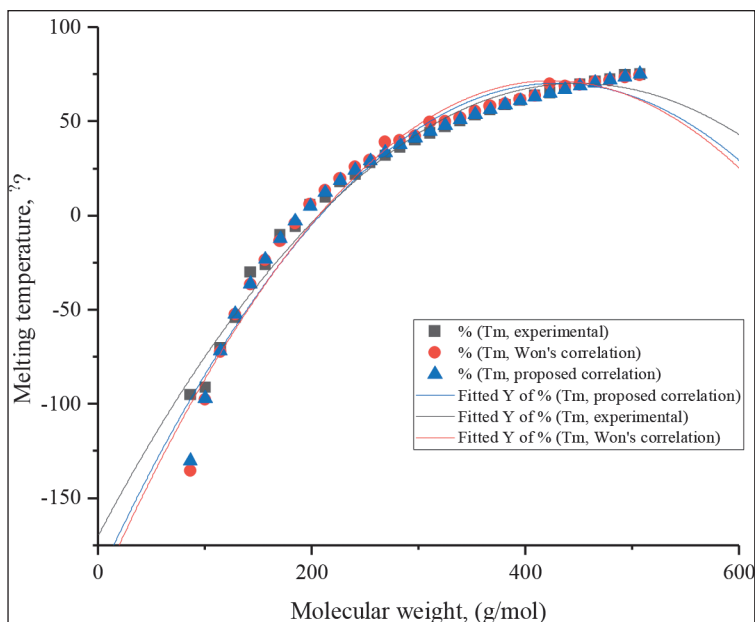


Figure 2 - Melting temperature (°C) versus molecular weight (g/mol)

Modification of Nichita's (2001) correlation to determine the solid-state transition (solidification) temperature:

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

Based on the data, a calculation was made, also using Python software, and a correlation coefficient was determined for increased accuracy of calculations with minimal error. The correlation value is presented by a formula, as well as a graph comparing correlation and experimental temperatures.

$$T_{i1}^{tr} = 95.666 + 0.003609M_i - \frac{20879.6}{M_i} \quad (9)$$

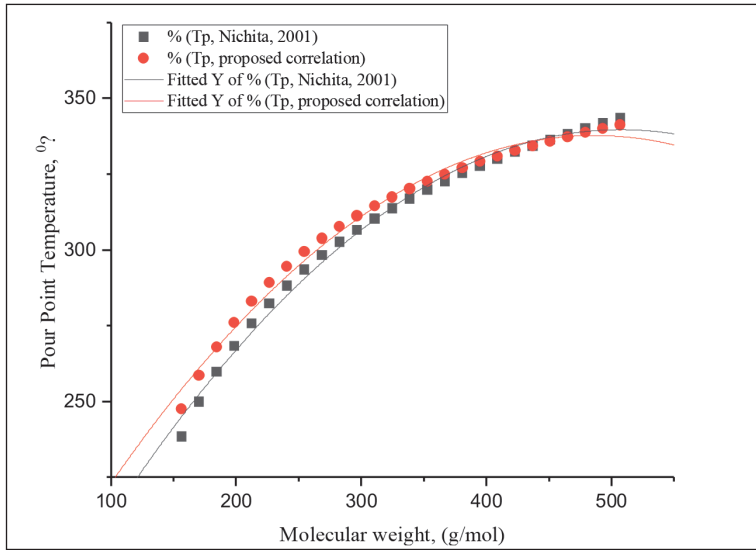


Figure 3 – Pour Point temperature (°C) versus molecular weight (g/mol)

Taking into account the molecular weight of the mixture, which was also calculated to correlate the melting point, we obtain a modified solidification correlation for the mixture using the example of a field X:

$$T_{i1}^{tr} = 71.3333 + 0.003609M_i - \frac{20879.6}{M_i} \quad (10)$$

The correlation gives an accuracy of calculation results compared to the Nichita (2001) correlation by 17.5% for the X field. The calculation results for field (X) are presented in Table 3.

Table 3 – Calculation results

Nº Sample	Field	Final molecular weight, g/mol	Pour point by correlation Nichita (2001)	Pour point (experimental)	Pour point (correlation)
1.1	X	388,907	53,74705	19	19,22572
1.2		388,426	53,66321	20	19,20629
1.3.		397,279	55,18054	20	19,55657

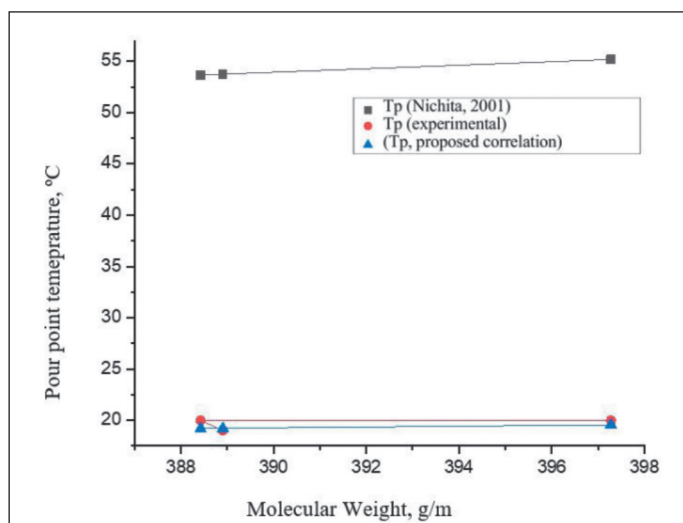



Figure 4 – Pour Point temperature (°C) versus molecular weight (g/mol)

Conclusion. Melting and pour points are one of the most important operational characteristics of oils, condensates and products of their field preparation and processing, which are taken into account when designing and operating field collection and transport systems and installations for stabilization and primary processing of hydrocarbon raw materials. This direction is relevant due to the laboriousness of direct experimental determination of the indicated indicators for flows of hydrocarbon mixtures during project development. Therefore, it is necessary to predict the melting and pour temperatures.

In the course of writing the article, a review of the scientific research literature was carried out, the main correlations used in calculating the properties of fluids were studied, the errors of the calculation results were analyzed, and the correlations of the melting and solidification properties of oil were improved in order to increase the accuracy of the models. 

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