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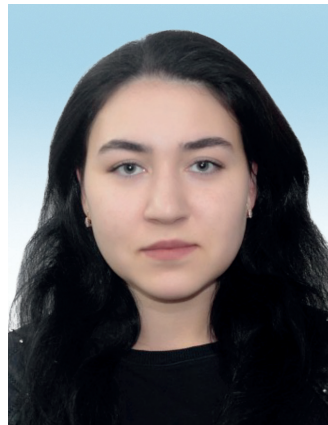
ANALYSIS OF EXISTING CALCULATION METHODS FOR PREDICTING PARAFFIN PRECIPITATION AND DETERMINATION OF CRITICAL PARAMETERS



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The problem of wax deposition is a common and important problem in the petroleum industry, especially during the production, transportation and refining of crude oil. This problem is related to changes in temperature and pressure, crude oil composition, and flow conditions. Research in the petroleum industry is actively focused on developing improved models and correlations to accurately predict wax deposition.

The authors of the paper consider approaches based on thermodynamic principles to develop a model capable of predicting the conditions under which wax deposition occurs. The model takes into account the chemical and physical interactions in the system, and also includes parameters determined from laboratory experiments and data on the characteristics of crude oil.

This article presents an analysis of scientific research literature and publications on calculation methods for predicting paraffin precipitation, and a comparative analysis of existing current correlations is carried out. Also shown is the calculation of the critical parameters (PVT) from the obtained data, which is the first step towards a model for calculating the precipitated wax.

KEYWORDS: paraffin, critical parameters, molecular weight, correlations

ПАРАФИН ТҮЗІЛУІН БОЛЖАУ ЖӘНЕ КРИТИКАЛЫҚ ПАРАМЕТРЛЕРДІ АНЫҚТАУ ҮШІН ҚОЛДАНЫСТАҒЫ ЕСЕПТЕУ ӘДІСТЕРІН ТАЛДАУ

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Парафин тұну мәселесі мұнай өнеркәсібінде, әсіресе шикі мұнайды өндіруде, тасымалдауда және өңдеуде жиі кездесетін және маңызды мәселе болып табылады. Бұл мәселе температура мен қысымның, шикі мұнай құрамының және ағынның жағдайының өзгеруіне байланысты. Мұнай өнер кәсібіндегі зерттеулер парафин тұнуын дәл болжау үшін жетілдірілген модельдер мен корреляцияларды әзірлеуге белсенді бағытталған. Жұмыстың авторлары парафин тұну жағдайларын болжай алатын модельді әзірлеу үшін термодинамикалық принциптерге негізделген тәсілдерді қарастырады. Модель жүйедегі химиялық және физикалық әрекеттесуді ескереді, сонымен қатар зертханалық тәжірибелер мен шикі мұнайдың сипаттамалары туралы мәліметтерде наықталған параметрлерді қамтиды.

Бұл мақалада парафин түзілуін болжау үшін есептеу әдістері бойынша ғылыми-зерттеу әдебиеттері мен жарияланымдарға талдау жасалған және қолданыстағы корреляци-

яға салыстырмалы талдау жасалған. Алынған деректерден критикалық параметрлерді (PVT) есептеуде көрсетілген, бұл парафин тұнуын есептеу моделіне алғашқы қадам болып табылады.

ТҮЙІН СӨЗДЕР: парафин, критикалық параметрлер, молекулалық салмақ, корреляция.

АНАЛИЗ СУЩЕСТВУЮЩИХ МЕТОДИК ВЕДЕНИЯ РАСЧЕТОВ ДЛЯ ПРОГНОЗИРОВАНИЯ ВЫПАДЕНИЯ ПАРАФИНА И ОПРЕДЕЛЕНИЕ КРИТИЧЕСКИХ ПАРАМЕТРОВ

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Проблема выпадения парафина является распространенной и важной задачей в нефтяной промышленности, особенно при добыче, транспортировке и переработке сырой нефти. Данная проблема связана с изменением температуры и давления, с составом сырой нефти, условиями потока. Исследования в нефтяной промышленности активно направлены на разработку улучшенных моделей, корреляций для точного прогнозирования выпадения парафина.

Авторы статьи рассматривают подходы, основанные на термодинамических принципах, для разработки модели, способной предсказать условия, при которых происходит выпадение парафина. Модель учитывает химические и физические взаимодействия в системе, а также включает параметры, определенные на основе лабораторных экспериментов и данных о характеристиках сырой нефти.

В данной статье представлен анализ научно-исследовательской литературы и публикаций по методикам ведения расчетов для прогнозирования выпадения парафина, проведен сопоставительный анализ по существующим актуальным корреляциям. Также показан расчет критических параметров (PVT) по полученным данным, который является первым шагом на пути к модели расчета осажденного парафина.

КЛЮЧЕВЫЕ СЛОВА: парафин, критические параметры, молекулярная масса, корреляции.

I ntroduction. Crystallization and deposition of paraffins during the production, transportation and use of crude oil and refined petroleum products are one of the causes of economic losses in the oil industry, namely reduction in production, shutdown of wells, and blockage of pipelines.

To predict the formation of paraffin in a fluid, it is necessary to develop a thermodynamic model through experimental tests and adjustments to existing models. This theoretical solution, which can work under given environmental conditions, use data on the composition of the liquid in the analysis, will become an important tool in solving the issue of paraffin formation.

Materials and methods. These models have been developed by other researchers and are used in the petroleum industry. Currently, when describing and calculating models for predicting paraffin formation in hydrocarbon liquids, based on the correlation of authors who have studied this area. These models include: the model of Won (1986), Pedersen et al. (1991), Lira-Galeana et al., Hansen et al. (1989).

Hansen et al.'s (1988) model describes a group contribution approach for modeling the interaction parameter χ_{ij} . This correlation has up to 160 pseudocomponents was used in the calculations, the calculated cloud temperatures in most cases within +4 K coincided with the measured ones[1].

In the model of Pedersen et al. (1991), the following general relationships were proposed for the solubility parameters in the liquid and solid phases [2].

This model showed a more accurate calculation of the paraffin and naphthenic parts of the C7+ fraction.

In the Coutinho J.A.P. (1998) model, group values for estimating the structural parameters “r” and “q” are obtained by simply dividing the initial results r and q by r and q for 10 methylene units. The model performs better than the model (Wilson 1964) that predicts the phase behavior of complex hydrocarbon mixtures in both aliphatic and aromatic solvents. [3]

Model Zuo et al. (2001) proposed an equation for the fugacity coefficient of the i-th component in the solid phase, which shows a better understanding of the phase behavior [4]:

$$\varphi_i^S = \varphi_{pure,i}^{OL} \gamma_i^S \exp \left[-\frac{\Delta H_i^f}{RT} \left(1 - \frac{T}{T_i^f} \right) \right] \times \exp \left[- \left(\int_{P_i^f}^P \frac{v_i^L - v_i^S}{RT} dP \right) \right] \quad (1)$$

Coutinho J.A.P. et al (2002) proposed a correlation for the melting point and melting point enthalpy[5]:

$$T_m = 421.63 - 1936112.63 \exp(-7.8945(N - 1)^{0.07194}) \quad (2)$$

where N is the carbon number.

In addition, Coutinho J.A.P. et al. presented an alternative equation for the wax phase based on the UNIQUAC equation.

With this correlation, more accurate results were obtained compared to the model (Wilson 1964) and the wax was not considered as a single solid solution.

Research by Hong-Yan J. et al. (2003) showed a new correlation between “r” and “q” values.

Melting temperatures under elevated pressure conditions were also realized:

$$T_{f(P)} = T_{f(P=0.1MPa)} + 0.2 \times (P - 0.1) \quad (3)$$

Correlations were developed to calculate heat capacity as a function of temperature and carbon number using measured data for n-paraffins. The accuracy of the cloud point prediction depends largely on the reliability of the melting property and heat capacity values.

In the work of Jean-Marc Sansot et al. (2005), the parameters are replaced by single average parameter ξ .

Description of solid-liquid boundaries for synthetic complex paraffin mixtures and for real petroleum liquids.

The calculation of wax deposits is more accurate than other local models, especially for complex crude oil systems.

C. Lira-Galeana et al. (1996) authors proposed a procedure for assessing the thermodynamic behavior during wax deposition, called the multi-solid solution model. Currently, this model is one of the widely used methods in this field [6].

H. Pan et al. (1997) proposed a correlation to estimate the enthalpy of fusion of aromatic substances. This correlation also can describe P_{ci} for hydrocarbon with molecular weight greater than 300 g/mol. According to the results of this study, the precipitated paraffin does not contain aromatic hydrocarbons. First, normal paraffins with the same number of carbon atoms as naphthene are precipitated.

Nichita et al. (2001) proposed a new correlation for the temperature of the first solid-state transition [7]:

$$T_{i1}^{tr} = 366.39775 + 0.03609M_i - 2.08796 \times 10^4/M_i \quad (4)$$

Moreover, the authors proposed correlations for the enthalpies of fusion and solid-phase transition of normal alkanes.

Based on the results of correlations for synthetic mixtures, a good estimate of the cloud point was observed within the Multisolid model, but the solid model overestimated it; at the same time, the amount of paraffin was underestimated by the multisolid model and overestimated by the solid state model. For natural mixtures, the amount of precipitated wax was overestimated by the solid state model.

A. R. Solaimani Nazar et al. (2007) proposed a relationship for estimating the heat of fusion for components of normal alkanes [8].

In addition, the correlation is proposed to estimate the binary interaction coefficients between two normal alkanes:

$$k_{ij} = f1 + f2 \times \ln(Mw_i) + f3 \times \frac{\ln(Mw_i)}{Mw_i^2} \quad (5)$$

The proposed approach makes it possible to describe the phase equilibria of various mixtures of paraffins in a very wide temperature range.

In M. Mansourpour et al.'s (2018) model, two correlations were introduced for merging properties:

$$T^f = a - b \times \exp(c - d \times MW^e) \quad (6)$$

The results show that the melting point and melting enthalpy of the components are the most important parameters in predicting cloud point. The proposed thermodynamic model predicts cloud point well in multicomponent systems, as well as in ternary mixtures.

Researcher J. C. M. Escobar-Remolina (2005) developed a solid fraction equation that directly calculates the amount of precipitated fraction when the value is greater than zero, and not precipitated when it is zero:

$$s_i = z_i - x_i^l \left(\frac{\varphi_i^l}{\varphi_i} \right) \quad (i = 1, 2, \dots, N) \quad (7)$$

R. Dalirsefat et al. (2007) worked with the enthalpy of fusion relation, where the enthalpy of fusion depends on the melting temperature, molecular weight for a particular component.

The modifications significantly improved cloud point prediction compared to the Lear-Galeana et al. and Pederson et al. models.

Results and discussions. To calculate the multi-solid solution model, it is necessary to analyze the physicochemical properties of surface oil. To begin with, critical parameters are determined, which include the critical temperature of n-alkanes. For evaluating lighter hydrocarbon component properties Twu correlation have been used. Mixtures with defined components comprise of substances with a known boiling point [9]. The critical properties (T_c and P_c) and either the boiling point of acentric factor, w , are needed to describe pure components by an EOS. The equation of state contains a structure parameter which acts as a third parameter in addition to molecular size and energy parameters. The size parameter can be calculated from the critical volume, the energy parameter from the critical temperature, and the structure parameter from the normal boiling-point temperature. Furthermore, the generalized equation of state for normal alkanes can be reduced to a function only of normal boiling-point temperature. [10]:

$$T_c^0 = T_b(0.533272 + 0.191017 \times 10^{-3}T_b + 0.779681 \times 10^{-7}T_b^2 - 0.284376 \times 10^{-10}T_b^3 + 0.959468 \times 10^{28}/T_b^{13})^{-1} \quad (8)$$

From the formula we see that the critical temperature is represented as a function of the boiling point T_b :

$$T_b = \exp(5.71419 + 2.71579\theta - 0.286590\theta^2 - 39.8544/\theta - 0.122488/\theta^2) - 24.7522\theta + 35.3155\theta^2 \quad (9)$$

where θ – molecular weight function

$$\theta = \ln MW^0$$

The next important critical parameters are pressure and volume:

$$P_c^0 = (3.83354 + 1.19629\alpha^{1/2} + 34.8888\alpha + 36.1952\alpha^2 + 104.193\alpha^4)^2 \quad (10)$$

$$V_c^0 = [1 - (0.419869 - 0.505839\alpha - 1.56436\alpha^3 - 9481.70\alpha^{14})]^{-8} \quad (11)$$

The research analyzed a sample from the X field. Based on laboratory experiments, the component composition of the oil was determined and their molecular weights were determined. Using the necessary data, critical parameters were calculated: critical temperature, critical pressure and critical volume.

Table 1 – Calculation result

Components	Mw, g/mol	Tc, K	Pc, MPa	Vc, m3/kmol
CH4	16,04	347,8125	809,41257	1,562810039
C2H6	30,07	540,4186	715,46113	2,279623964
C3H8	44,1	667,1174	617,99933	3,228557558
C4H10	58,12	764,6047	544,93719	4,126250357
C5H12	72,15	844,7391	486,649	5,009166502
C6H14	86,18	912,9805	438,55384	5,896046281
C7H16	100,21	972,3948	398,02166	6,795930242
C8H18	114,23	1024,857	363,39853	7,71118468
C9H20	128,2	1071,553	333,5918	8,638720962
C10H22	142,29	1113,957	307,41512	9,587713827
C11H24	156,31	1152,191	284,58703	10,54232068
C12H26	170,33	1187,043	264,45493	11,50379667

Table 1 – Calculation result

C13H28	184,37	1219,009	246,58306	12,47011106
C14H30	198,39	1248,372	230,68703	13,43531165
C15H32	212,42	1275,507	216,45489	14,3985754
C16H34	226,41	1300,586	203,70425	15,35395699
C17H36	240,471	1324,022	192,14705	16,30684183
C18H38	254,494	1345,818	181,7163	17,24798918
C19H40	268,518	1366,204	172,24252	18,17854492
C20H42	282,5475	1385,327	163,60754	19,09758086
C21H44	296,57	1403,293	155,72005	20,00331633
C22H46	310,61	1420,24	148,48202	20,89657685
C23H48	289,5	1394,371	159,60956	19,5483096
C24H50	338,654	1451,338	135,71652	22,63802257
C25H52	352,691	1465,684	130,05524	23,48763344
C26H54	366,718	1479,297	124,81697	24,32174003
C27H56	380,745	1492,248	119,95551	25,14092423
C28H58	394,772	1504,587	115,43399	25,94523893
C29H60	408,799	1516,363	111,21996	26,73480406
C30H62	422,826	1527,617	107,28474	27,50979418
C31H64	436,853	1538,388	103,60292	28,27042782
C32H66	450,88	1548,711	100,15196	29,01695848
C33H68	464,907	1558,617	96,911775	29,74966694
C34H70	478,934	1568,134	93,864422	30,46885477
C35H72	492,961	1577,289	90,993855	31,17483887
C36+	506,988	1586,105	88,285676	31,86794691

Models describing the solid-liquid equilibrium (SLE) of wax in oil are needed to predict when and under what conditions wax will precipitate from crude oil. Calculating the percentage of wax crystallization involves determining the fraction or percentage of wax that has crystallized from the liquid phase. This calculation is often important in the oil and gas industry, especially in understanding and managing flow assurance problems in pipelines [11]. The percentage of crystallization can be estimated from experimental data or modeled using thermodynamic principles.

The Multisolid model is based on the precipitation of certain heavy components of crude oil with average properties assigned to each fraction.


At the beginning of deposition, an unstable solid solution appears in which the components are temporarily mixed in all proportions. However, after a characteristic time, separation of the solid solution leads to a final stable state containing pure hydrocarbon components. Precipitated paraffin is a mass of pure hydrocarbon components containing precipitating components that are immiscible with each other.

The amount of precipitated paraffin as a percentage of the oil is calculated as [12]:

$$\text{wax wt\% in oil} = 100 \times \frac{\sum_{i=1}^N M_i n_i^s}{F \sum_{i=1}^N z_i M_i} \quad (12)$$

where F is the total number of moles of the original oil and the number of moles of component i precipitated as a solid. M_i is the molecular weight of component i , z_i is mole fraction.

Calculation of critical parameters is one of the first step in calculating the thermodynamic model of paraffin deposits. The article presents an analysis of a sample from X field, with a known compositional composition, as well as molecular weights. Given the known data, the critical parameters were calculated. Temperature and molecular weight are interrelated and this is observed in correlations. To calculate the critical boiling point, it was necessary to calculate the molecular weight function, since the boiling point depends on this variable.

Conclusion. As a result of the paper, an analysis of scientific research works was carried out that considered paraffin deposition models. Correlations of existing models were compared. Based on the analysis of a sample from the field, the component composition of the oil was determined. In this article, the first stage of finding a thermodynamic model was carried out, this was finding the critical parameters. These include: critical temperature, critical pressure and critical volume. 

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