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DETERMINING FUSION PROPERTIES OF KAZAKHSTANI OIL USING GAS CHROMATOGRAPHY, DSC AND PPT



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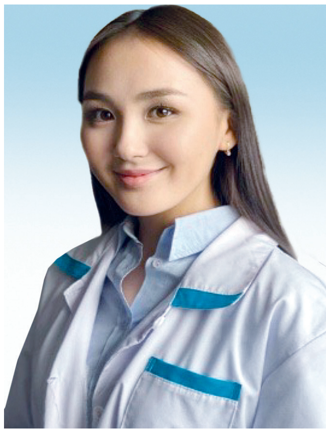

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This research focuses on investigating the melting behavior of crude oil extracted from five specific fields located in Kazakhstan. Understanding the crude oil's melting point and the temperature at which it transitions to a solid state is crucial for predicting wax precipitation, a significant concern during oil transportation and storage.

The study employs various laboratory instruments to achieve this goal. These instruments include gas chromatograph for analyzing the oil's composition, differential scanning calorimeter (DSC) for measuring the heat flow associated with phase changes during temperature variations and pour point tester for determining the lowest temperature at which the oil can still flow.

By utilizing this comprehensive approach, the researchers aim to establish new correlations between the crude oil's properties and its melting point and solid-state transition temperature. These newly developed correlations are expected to demonstrate a closer alignment with the actual melting points of various hydrocarbon components within the crude oil compared to the standard correlations currently employed by most prediction models. This improved accuracy could lead to more reliable wax precipitation predictions, ultimately benefiting oil production, transportation, and storage operations in Kazakhstan.

Obtained experimental results provide valuable insights into the melting properties of the analyzed crude oil samples.This observation indicates that this particular oil is less viscous, as it solidifies at a relatively positive temperature. Furthermore, by incorporating these findings along with the oil's molecular weight, researchers can potentially establish a correlation specific to Field A oil for predicting wax deposition.

KEY WORDS: *fusion properties, melting temperature, solid state transition temperature.*

ГАЗ ХРОМАТОГРАФИЯСЫН, ДСК ЖӘНЕ ҚНС ҚОЛДАНА ОТЫРЫП, ҚАЗАҚСТАНДЫҚ МҰНАЙДЫН ТЕРМОЯДРОЛЫҚ ҚАСИЕТТЕРІН АНЫҚТАУ

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Бұл зерттеу Қазақстанда орналасқан бес кен орнында өндірілген шикі мұнайдың балқуын зерттеугеарналған. Шикі мұнайдың балқу температурасын және оның қатты күйге түсетін температурасын түсіну парафиннің түсуін болжау үшін өте маңызды, бұл мұнайды тасымалдау мен сақтаудың маңызды мәселесі.

Осы мақсатқа жету үшін зерттеу әртүрлі зертханалық құралдарды пайдаланады. Олардың ішінде мұнай құрамын талдауға арналған газ хроматографы, температураның ауытқуындағы фазалардың өзгеруіне байланысты жылу ағынын өлшеуге арналған дифференциалды сканерлеу калориметрі (ДСК) және мұнай әлі де ағып кетуі мүмкін ең төменг ітемпературана анықтау үшін қатаю температурасын сынаушы бар.

Осы кешенді тәсілді қолдана отырып, зерттеушілер шикі мұнайдың қасиеттері мен оның балқу температурасы мен қатты күйге өту температурасы арасында жаңа корреляциялар орнатуға ниетті. Бұл жаңа корреляциялар қазіргі уақытта болжау модельдерінің көпшілігінде қолданылатын стандарты корреляциялармен салыстырғанда мұнайдың әртүрлі көмірсутек компоненттерінің нақты балқу температураларына дәлірек сәйкес келеді деп күтілуде. Дәлдіктің мұндай артуы парафинді жауын-шашынның неғұрлым сенімді болжамдарына әкелуі мүмкін, бұл, сайып келгенде, Қазақстанда мұнай өндіруге, тасымалдауға және сақтауға жағымды әсер етеді.

Алынған эксперименттік нәтижелер талданатын шикі мұнай үлгілерінің балқу қасиеттері туралы құнды түсінік береді. Бұл бақылау берілген мұнайдың тұтқырлығы аз екенін көрсетеді, өйткені ол салыстырмалы түрде оң температурада қатып қалады. Сонымен қатар, осы деректерді мұнайдың молекулалық салмағымен бірге зерттеушілер парафиннің тұнбасын болжау үшін А кен орнының мұнайына корреляция орната алады.

ТҮЙІН СӨЗДЕР: *термоядролық қасиеттері, балқу температурасы, қатты күйге өту температурасы*

ОПРЕДЕЛЕНИЕ СВОЙСТВ ПЛАВЛЕНИЯ КАЗАХСТАНСКОЙ НЕФТИ С ПОМОЩЬЮ ГАЗОВОЙ ХРОМАТОГРАФИИ, ДСК И ТТС

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Данное исследование посвящено изучению плавления сырой нефти, добытой на пяти месторождениях, расположенных в Казахстане. Понимание температуры плавления сырой нефти и температуры, при которой она переходит в твердое состояние, имеет решающее значение для прогнозирования выпадения парафина, что является серьезной проблемой при транспортировке и хранении нефти.

Для достижения этой цели в исследовании используются различные лабораторные приборы. Среди них газовый хроматограф для анализа состава нефти, дифференциальный сканирующий калориметр (ДСК) для измерения теплового потока, связанного с изменением фаз при колебаниях температуры, и тестер температуры застывания для определения самой низкой температуры, при которой нефть еще может течь.

Используя этот комплексный подход, исследователи намерены установить новые корреляции между свойствами сырой нефти и ее температурой плавления и температурой перехода в твердое состояние. Ожидается, что эти новые корреляции будут более точно соответствовать фактическим температурам плавления различных углеводородных компонентов нефти по сравнению со стандартными корреляциями, используемыми в настоящее время в большинстве моделей прогнозирования. Такое повышение точности может привести к более надежным прогнозам выпадения парафиновых осадков, что в конечном итоге благоприятно скажется на добыче, транспортировке и хранении нефти в Казахстане.

Полученные экспериментальные результаты дают ценное представление о свойствах плавления анализируемых образцов сырой нефти. Это наблюдение указывает на то, что данная нефть является менее вязкой, поскольку застывает при относительно положительной температуре. Более того, используя эти данные вместе с молекулярным весом нефти, исследователи могут установить корреляцию для нефти месторождения А для прогнозирования осаждения парафина.

КЛЮЧЕВЫЕ СЛОВА: *свойства плавления, температура плавления, температура перехода в твердое состояние*

Introduction. Crude oil is a complex mixture of several hydrocarbon and non-hydrocarboncomponents. Typically, the hydrocarbon components consist of asphaltenes, resins, aromatics naphthenes and paraffins. These hydrocarbon components are frequentlyremain stable in the crude system until a distortion in the equilibrium state occurs. Change in pressure, temperature and oil composition are the mandatory factors thatdrive disequilibrium, hence instability of a crude oil system.

Most crude oil in Kazakhstan contains heavy hydrocarbons that precipitate as paraffin (wax) solids at low temperature. Paraffin is a heavy component of crude oil that precipitates as a solid phase below the pour point. Deposition of precipitatedparaffin on pipe walls is one of the challenging flow assurance problems that causesreduced and complete blockage of oil flow rates by reducing the cross-sectional flowarea in pipelines. In addition, onshore facilities require higher energy consumptionandequipment failure due to paraffin plugs. Wax deposition also increases the viscosity ofthe oil mixture, resulting in higher energy requirements for crude oil transportation.

Numerous approaches have been developed to predict and prevent the above-mentioned flow problems in both science and industry. Most of them are based onprediction of melting point temperature and solid-state transition temperature.Currently, there are two types of models that can be used to calculate waxdeposition.One model assumes that the precipitated paraffin is a solid solution. Theother assumes that the separated phase consists of multiple solid phases.The studies were carried out by statistical analysis and data preparation usingfields data from the deposits. The melting point temperature and solid-state transitiontemperature were calculated from the results of the analysis.

Materials and methods. Starting from melting point temperature, Won (1986) [1] in paper presented a method for thermodynamic prediction of vapor-liquid-solid paraffin phase equilibria. Then proposed equation to calculate melting point temperature according to the molecular weight.

$$T_i^f = 374.5 + 0.02617 * MW_i - 20172/MW_i \tag{1}$$

where: MW – molar mass.

The subsequent correlations are modifications of Won's equation. Nichita et al. (2001) [2] correlation one of the crucial equations of wax modeling. Researchers found that the precipitated paraffin phase can exhibit retrogradephenomena like those in gascondensates. As a result of pressure reduction (at constanttemperature), the amountof precipitated paraffin can first increase, then decrease,andthen increase again.

They obtained a new correlation to determine solid state transition temperature:

$$T_i^{tr} = 366.39775 + 0.03609M_i - 2.08796 \times 10^4/M_i \tag{2}$$

While Xue et al. (2019) [3] studied a thermodynamic model for four phases involving vapor, liquid, wax-rich and asphaltene-rich which is developed to predict the cloudand the amount of wax and asphaltenes precipitation at different temperatures. A scientist used Won's melting point temperature correlation which is depends on value of molar mass:

$$T_i^f = 374.5 + 0.02617M_i - \frac{20172}{M_i}, \; M_i \leq 450 \tag{3}$$

$$T_i^f = 411.4 - \frac{32326}{M_i}, \; M_i > 450 \tag{4}$$

Escobar Remolina (2006) [4] predicted characteristics of wax precipitation in synthetic mixtures and fluids of petroleum by creation of new model. They derived Won's melting point temperature by adding mathematical exponent, which is required for the calculation of the fugacity of the pure solid:

$$T_i^f = 370.12 + 0.002403M_i - \frac{15760.33}{M_i} - 139.67\exp(-0.008546M_i) \tag{5}$$

In Mansourpoor (2018) [5] study, an multi-solid thermodynamic model was developed for wax disappearance temperature (WDT) prediction at low pressures. Phase behavior of liquid was described by using Peng-Robinson equation of state [6]. Paraffinic-naphthenic-aromatic (PNA) analysis was applied to divide each component into its paraffinic-naphthenic and aromatic sub-fractions. In addition, two correlations for fusion properties of mentioned sub-fractions were developed to better estimation of solid-phase behavior.

The PNA analysis was performed using Riazi (2005) [7] method. PNA analysis separates each component into paraffinic (P), naphthenic (N), and aromatic (A) species. Where each property was estimated by this equation:

$$\theta = x_p\theta_p + x_N\theta_N + x_A\theta_A \tag{6}$$

Where: θ – property; x_p, x_N and x_A are composition of the P, N and A species, respectively. Experimental data of Himran et al. (1994) [8] for fusion temperature of normal paraffins, and experimental fusion temperature data of naphthenic and aromatic hydrocarbons (API, R 1964) [9] were utilized to derive a correlation in the following form:

$$T^f = a - b * \exp\,(c - d * MW^e) \qquad (7)$$

Where: MW – molecular weight; a,b,c,d and e are constants for PN and A species.

Table 1 – **Constants for PN and A species**

Species	a	b	c	d	e
PN species	392,008	1,00	7,18704	0,34752	0,036808
A species	367,994605	1,084989	6,340110	0,037477	0,714217

The new developed correlation has no adjustable parameter in estimating fusion enthalpy of PN species based on average properties of these sub-fractions. The correlation is as follows:

$$\Delta h_i^f = 0.08476 MW_i T_i^f \qquad (8)$$

Experimental Procedures. To obtain accurate wax modeling prediction three laboratory equipment are used. They are gas chromatography, differential scanning calorimeter (DSC) and pour point tester (PPT). Experiment was obtained at laboratory and oil fluid sample from West Kazakhstan was analyzed.

The sample was predicted several times by a gas chromatograph, which breaks down the oil into its individual components. For their calculation the worldwide standard ASTM D2887 was used. The implementation of gas chromatography was necessary to further calculate the molar weight of each component using Kay's mixing rule. Consequently, calculating the fusion properties such as melting temperature and solid state transition temperature for each component of the Kazakhstani oil.

Kay's rule (1936) is as follows:

$$\theta = \sum_{i=1}^{N} z_i \theta_i \qquad (9)$$

As an example of calculation, consider the calculation procedure for field A.

By applying Kay's rule, the molecular weight for the mixture can be calculated using Eq.6:

$$\theta = \sum_{i=1}^{N} z_i \theta_i$$

$$MW = \sum_{i=1}^{N} z_i MW_i = 0{,}79 + 5{,}83 + 7{,}42 + \cdots + 4{,}11 = 218{,}43 \qquad (10)$$

Knowing the molecular weight, it becomes possible to calculate the fusion properties using the equations of Won (1986) [1] and Nichita (2001) [2]:

$$T_i^f = 374{,}5 + 0{,}02617 * MW_i - \frac{20172}{MW_i} = 374{,}5 + 0{,}02617 * 218{,}43 - -\frac{20172}{218{,}43} = 287{,}86\ °K = 14{,}71\ °C \qquad (11)$$

$$T_i^{tr} = 366{,}39775 + 0{,}03609 M_i - 2{,}08796 \times \frac{10^4}{M_i} = 366{,}39775 + +0{,}03609 * 218{,}43 - \frac{20879{,}6}{218{,}43} = 278{,}69\ °K = 5{,}54\ °C \qquad (12)$$

In addition, DSC which due to heat flux determines the melting temperature and PPT due to gradual cooling system determines the solid state transition temperature is important to analyze in a neater way.

Results and discussions. The accurate prediction of paraffin, or wax, deposition within pipelines is crucial for ensuring efficient and uninterrupted flow. To achieve this goal, a thorough understanding of the oil's fusion properties, particularly melting temperature and solid-state transition temperature, is mandatory. These properties dictate the oil's behavior at varying temperatures and its susceptibility to wax formation. When the temperature falls below a critical threshold, the waxy components within the oil begin to solidify and precipitate. This phenomenon, known as wax deposition, presents a significant challenge in pipeline operations. As these wax crystals accumulate on the pipe's inner walls, they progressively reduce the available cross-sectional area, hindering fluid flow and potentially leading to complete blockage. *Table 1* showcases the results obtained through Differential Scanning Calorimetry (DSC) and Pressure Pour Point (PPT) testing for field A oil, located in West Kazakhstan. This data provides valuable insights into the fusion properties of this specific oil, paving the way for a more accurate assessment of potential wax deposition issues.

Table 1 – **Experimental Values obtained using DSC and PPT**

Sample origin (Field)	Melting temperature [°C]	Solid-state transition temperature [°C]
A	+11	+4

The data presented in the table reveals a fascinating phase transition for the fluid in question. At a temperature of 11°C, the fluid undergoes a transformation from a solid state to a liquid state. Conversely, the temperature at which the transition from liquid to solid occurs is a significantly lower 4 °C. This observation signifies a key characteristic of the oil: it has a relatively low viscosity, as evidenced by its ability to solidify at a temperature above freezing.

Leveraging the current findings and the known molecular weight of the oil, we can potentially establish a correlation for field A oil. This correlation would allow us to predict wax deposition with greater accuracy, a valuable tool in various industrial applications.

Conclusion. In conclusion, this study employed oil samples from Kazakhstan to gain a comprehensive understanding of their fusion properties, specifically focusing on melting point and solid-state transition temperature. To achieve this, a meticulous approach was undertaken. First, it was crucial to obtain detailed data on the oil's compositional makeup. This critical step was accomplished by utilizing a gas chromatograph, adhering to the globally recognized standard ASTM D2887. This analytical technique enabled the identification and quantification of each individual component within the oil. Subsequently, the molecular weights of these waxy components were meticulously calculated using Kay's mixing rule. Finally, the melting and solid-state transition temperatures were determined using specialized equipment such as Differential Scanning Calorimetry (DSC) and Pressure Pour Point tester (PPT). By meticulously investigating these key parameters, we can establish a robust predictive model for wax precipitation within the oil. This model will not only enhance our understanding of the oil's behavior at varying temperatures but also serve as a valuable tool for various industrial applications.

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