

Calculation of wax appearance temperature directly from hydrocarbon compositions of crude oil



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ABSTRACT

The purpose of this research is to develop a correlation in order to calculate the wax appearance temperature directly from hydrocarbon compositions of crude oil. Different methods have been used to measure wax appearance temperature including experimental instruments and thermodynamic models. A lot of empirical correlations have been used to calculate the physical properties of crude oil. However, there are no correlations for calculating the wax appearance temperature of the crude oils based on hydrocarbon compositions of crude oil. Calculation of the wax appearance temperature has become crucial in the study of wax crystallisation to prevent any congealing of the crude oil in production facilities and transportation pipelines. In this study, new correlations based on the hydrocarbon compositions of crude oil are developed to calculate the wax appearance temperature. The DataFit® scientific software's multiple nonlinear regression analysis tools are used as a platform to develop a novel correlation to calculate the wax appearance temperature. Two correlations are developed. The accuracy and reliability of these correlations were verified experimentally and thermodynamically by different thermodynamic models. The R^2 and AAD% for these correlations (Eqs. 4 and 5) are 0.973, 0.999, 0.0170 and 0.00028 respectively. It can be concluded that the correlation equations are acting better than the thermodynamic wax model in predicting the wax appearance temperature of the crude oils. However, this correlation does not have the capability of thermodynamic wax models in prediction of the phase equilibriums at any temperatures and pressures and are subject to availability of the hydrocarbon composition range as indicated.

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1. Introduction

Formation and deposition of paraffin wax on the inner wall of production facilities and transportation pipelines continues to be a critical operational problem faced by the oil industry (Alcazar-Vara and Buenroostro-Gonzalez, 2013; Jafari Ansaroudi et al., 2013; Chala et al., 2014; Coto et al., 2014; Elhaddad et al., 2015; Zhang, 2014; Quan et al., 2015). Petroleum industries worldwide have been threatened by the risk of wax crystallisation and deposition which leads to

tremendous economic losses due to the chemicals, well shut-in, choking of the flowlines, reduced production, less utilization of capacity, increased manpower attention and extra horse-power requirement. For deep-water oilfields, the problem is more pronounced and crucial due to the cold water subsea environments (Matzain et al., 2002). Therefore, oilfield operators have invested in technical and economic solutions to rectify such problems.

An important parameter is called wax appearance temperature (WAT) which is the temperature that the first wax crystal appears (Sanjay et al., 1995) and crude oil compositions, temperature and pressure are the major parameters of the wax crystallizations. Different methods have been used to measure WAT (Claudy et al., 1988; Kruka et al., 1995; Letoffe et al., 1995; Japper-Jaafar et al., 2016). In order to prevent any congealing of the crude oil in the pipeline, it is a high importance to have the accurate instruments

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measuring WAT, thermodynamic wax models or a correlation to assess wax crystallisation.

Scholars have developed several thermodynamic models to predict WAT. A lot of empirical correlations have been used to calculate the physical properties of the crude oil. However, there are no correlations for calculating the WAT of the crude oils based on the hydrocarbon compositions of crude oil. The developed model could assist with the calculation of WAT at any given temperature or pressure of the sample. It is especially useful for crude oils consisting of normal, branched and cyclic alkanes as the current prediction models for these waxy crude oils are not available. The goal of this study is to develop a correlation in order to calculate the WAT.

2. Methodology

2.1. Development of novel correlation to predict the wax appearance temperature

In order to develop correlations, various types of crude oils such as waxy oil, biodegraded, paraffinic oil, naphthenic oil, light and heavy oil are utilized from the literature (Hansen et al., 1988; Schou Pedersen et al., 1991; Pan et al., 1997; Queimada et al., 2001; Pedersen and Rønningsen, 2003; Escobar-Remolina, 2006; Alghanduri et al., 2010). A novel correlation is developed by the DataFit® scientific software's multiple nonlinear regression analysis tools. The National Institute of Standards and Technology (NIST) is used as the statistical reference dataset which defining the accuracy of the DataFit®.

2.2. Model variables

Table 1 presents the input (Independent) and output (Dependent) variables defining the different compositions of hydrocarbon components of crude oil utilized to calculate WAT. The output (target) variables in this work were produced by experimental WAT values and other studies in developing the model.

Table 1: Correlation parameters

Carbon no. (wt%)		Variables
(X1)	H/C no. < C ₁₀	Independent- (X)
(X2) or (X1)	H/C no. C ₁₀ -C ₁₅	Independent- (X)
(X3) or (X2)	H/C no. C ₁₆ -C ₂₀	Independent- (X)
(X4) or (X3)	H/C no. C ₂₁ -C ₃₀₊	Independent- (X)
(Y)	WAT (K)	Dependent

Multiple regression analysis has been used to estimate WAT. Observed data were used to model an equation by fitting the two or more input variables and a target variable (DeCoursey, 2003). The dependent variable (Y) is linked through the independent (input) variables (X).

Three statistical criteria have been used to evaluate the performance of the equations. These are the standard error of estimate (SEE), the coefficient of multiple determination (R²) and average absolute error (AAE).

The accuracy of predictions is defined by SEE. A small SEE value is desirable. The lowest value of zero

for SEE indicates that there is no variation corresponding to the computed line and the correlation is perfect. The SEE can be stated as:

$$SEE = \sqrt{\frac{\sum_{i=1}^n (Y_e - Y_p)^2}{n-p}} \quad (1)$$

where in the regression model, *p* denotes the number of parameters.

The R-squared (R²) is used as a statistical measure to show how close the data are to the fitted regression line. The R-squared can be expressed as:

$$R^2 = \frac{\sum_{i=1}^n (Y_p - \bar{Y})^2}{\sum_{i=1}^n (Y_a - \bar{Y})^2} \quad (2)$$

where \bar{Y} and Y_a represent the arithmetic mean of the observed data and actual data point, respectively.

In statistics, how close the original data to forecasts or predictions are expressed by AAE. A value close to zero is desirable. AAE is defined as:

$$AAE = \frac{1}{n} \sum_{i=1}^n |Y_e - Y_p| \quad (3)$$

where Y_p and Y_e denote predicted values and experimental data point, respectively. *n* is considered as the number of data points (DeCoursey, 2003).

The compositions of the hydrocarbon component of the crude oils were categorized into four variables. The hydrocarbon composition range greater than C₁₆ and less than C₁₆ to determine a correlation did not lead to a suitable correlation via trial and error and therefore, these correlations were decided to be deleted.

3. Results and discussions

3.1. Correlation to predict the WAT of crude oils

The goal of this research is to establish a correlation to calculate the WAT of crude oils based on the compositions of the hydrocarbon component. This shall assistance to deliver a new insight on measuring WAT by utilizing different compositions of the crude oils.

3.2. Hydrocarbon composition range of less than C₁₀, between C₁₀ to C₁₅, C₁₆-C₂₀, and C₂₁-C₃₀₊

The data is pertaining to the model variables for hydrocarbon composition range of less than C₁₀, between C₁₀ to C₁₅, C₁₆-C₂₀, and C₂₁-C₃₀₊ are given in Table 2. The database of the DataFit® scientific software constitutes the source of the equations. Eq. (4) yields the highest coefficient (R² =0.973) and lowest AAE (0.441) and SEE (1.404) indicating the best possible fit for the WAT prediction. The regression coefficient values from the regression analysis lead to the equation for WAT estimation which is expressed as:

$$WAT = 6.808X_1 + 0.366X_2 + 3.381X_3 + 3.028X_4 \quad (4)$$

The ultimate model equation structure could be formed by replacing the model variables for

hydrocarbon composition range of less than C₁₀, between C₁₀ to C₁₅, C₁₆-C₂₀ and C₂₁-C₃₀₊ into Eq. (4).

According to the error performance analysis of the regression modelling in Eq. (4), and Fig. 1 for all the samples, the model remarkably predicts the WAT of the crude oils based on the different composition of hydrocarbon components. Therefore, it could be justly argued that the developed model might be utilized for WAT estimation of the crude oils. This new method and approach for determining the WAT is subjected to the availability of the four hydrocarbon composition ranges denoted as X₁, X₂, X₃, and X₄.

3.3. Hydrocarbon composition range of C₁₀ to C₁₅, C₁₆-C₂₀, and C₂₁-C₃₀₊

Data pertains to the model variables for hydrocarbon composition range of C₁₀ to C₁₅, C₁₆-C₂₀, and C₂₁-C₃₀₊ are given in Table 3. In Table 3, the hydrocarbon compositions data from Alghanduri et al. (2010) work is used to calculate the WAT based on the thermodynamic model using Multiflash software. Eq. (5) yields the highest coefficient, R² (0.999) and lowest AAE (0.001) and SEE (0.002). The regression coefficient values from the regression analysis lead to the equation for WAT estimation:

$$WAT = 1.017X_1 + 0.075X_2 + 1.611X_3 + 213.586 \quad (5)$$

The ultimate model equation structure could be formed by replacing the model variables with hydrocarbon composition range of C₁₀ to C₁₅, C₁₆-C₂₀, and C₂₁-C₃₀₊ into Eq. (5).

Based on the error performance results of the regression modelling for the considered model (Eq. 5)

and Fig. 2 for all the samples, the model excellently predicts the WAT of the crude oils based on a different composition of hydrocarbon components. It can then be said that the developed model can be certainly used for estimating the WAT values of waxy crude oils. Similar to the observations discussed in 3.2., this new method and approach for determining the WAT is subject to availability of the three hydrocarbon composition ranges denoted as X₁, X₂, and X₃.

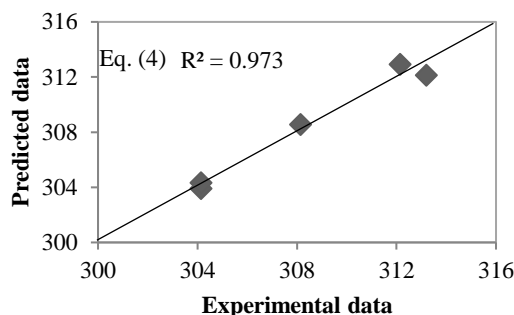


Fig. 1: Experimental data versus predicted data for Eq. (4)

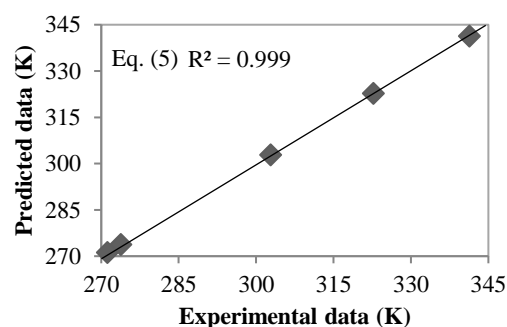


Fig. 2: Experimental data versus predicted data for Eq. (5)

Table 2: Data pertaining to the model variables and the experimental WAT compared with the calculated value with their thermodynamic models (literature) and correlation based on Eq. (4)

H/C no. C ₁₀ -C ₁₅	H/C no. C ₁₆ -C ₂₀	H/C no. C ₂₁ -C ₃₀₊	H/C no. C ₂₁ -C ₃₀₊	WAT _{exp} (K)	WAT _{Pri} (K)		Models AD%		carbon ranges	
					Eq. (4)*	Lit.	Eq. (4)*	Lit.		
X ₁	X ₂	X ₃	X ₄							
9.36	16.17	16.13	58.28	308.15	308.54	304.00**	0.128	1.347**	C ₄ -C ₃₀₊	
11.15	20.27	15.33	53.24	304.15	303.90	305.90***	0.083	0.575***	C ₁ -C ₃₀₊	
17.24	25.41	14.92	42.43	312.15	312.91	311.80***	0.244	0.112***	C ₂ -C ₃₀₊	
15.08	22.87	15.69	46.35	313.20	312.13	313.40*	0.341	0.064*	C ₁ -C ₄₆₊	
12.75	23.12	17.62	46.51	304.15	304.32	304.00**	0.055	0.049**	C ₁ -C ₃₀₊	
AAD%								0.0170	0.112***	
									0.064*	
									1.347**	
									0.344***	
									0.049**	

*Predicted data with correlation Eq. (4), this work; **Model prediction based on (Hansen et al., 1988); *** Model prediction based on (Lira-Galeana et al., 1996); * Model prediction based on (Pan et al., 1997); ** Model prediction based on (Escobar-Remolina, 2006)

Table 3: Data pertaining to the model variables and the experimental WAT compared with the calculated value with their thermodynamic models (literature) and correlation based on Eq. (5)

H/C no. C ₁₀ -C ₁₅	H/C no. C ₁₆ -C ₂₀	H/C no. C ₂₁ -C ₃₀₊	WAT _{exp} (K)	WAT _{Pri} (K)		Models AD%		carbon ranges		
				Eq. (5)*	Lit.	Eq. (5)*	Lit.			
X ₁	X ₂	X ₃								
38.96	45.92	14.91	273.80	273.80	272.70**	0.0006	0.402**	C ₁₀ -C ₂₃		
43.60	46.03	10.37	271.20	271.20	271.10**	0.0005	0.037**	C ₁₀ -C ₂₄		
0.41	12.65	79.63	341.35	341.35	300.48***	0.0001	11.973***	C ₁₅ -C ₃₄		
3.20	20.18	54.32	302.85	302.85	306.63***	0.0000	1.247***	C ₁₁ -C ₄₀		
0.46	23.36	68.55	322.75	322.75	296.73***	0.0002	8.061***	C ₁₅ -C ₃₃		
AAD%								0.00028	0.22**	
									7.09***	

*Predicted data with correlation Eq. (5), this work; **Model prediction based on Queimada et al. (2001); *** Model prediction based on (Alghanduri et al., 2010)

3.4. Validation of correlations with experimental data and thermodynamic wax models

The absolute deviation (AD) and average absolute deviation (AAD) are used to compare the correlations with other literature works. The ADD is calculated by the following equations.

$$AAD\% = 100 \frac{\sum_{i=1}^{N_t} \sqrt{\frac{(y_i^{exp} - y_i^{pred})^2}{y_i^{exp 2}}}}{N_t} \quad (6)$$

The same hydrocarbon compositions range which used to develop correlation also have been used in the thermodynamic model works of Hansen et al. (1988), Lira-Galeana et al. (1996), Pan et al. (1997), Escobar-Remolina (2006), Alghanduri et al. (2010), and Queimada et al. (2001) to calculate WAT. These calculated WAT based on the thermodynamic models are used as comparison to validate these correlations (Tables 2 and 3). As these correlations in Eq. (4) and Eq. (5) consider different hydrocarbon composition range which it is the first approach in its kind to develop a correlation to estimate the WAT of the crude oils. Though WAT can be measured via DSC or CPM, the availability of the facilities on site is a hindering factor. Thermodynamic models can also be used for WAT prediction but they are subjected to various assumptions.

The analyses for the Eq. (4) are shown in Table 2 and Fig. 3. As can be seen from Table 2, the AAD% as 0.0170 for correlation (Eq. 4) is considered lesser than the other thermodynamics models used. The R^2 values for the correlation and thermodynamic wax models are 0.973 and 0.768 indicating that the correlation shows the better result to calculate the WAT. The reasons for the lesser AAD% and R^2 for Eq. (4) might be to simplicity of the correlation in calculating the WAT in comparison to thermodynamic model meaning correlation uses only hydrocarbon compositions but thermodynamic model needs more data and lots of assumptions causing them to have more errors.

The analyses for the Eq. (5) are presented in Table 3 and Fig. 4 and show that the R^2 values for the developed correlation and thermodynamic wax models are 0.999 and 0.614. Also, the AAD% as 0.00028 for correlation (Eq. 5) is considered lesser than the thermodynamics wax models used. Therefore results indicating that the developed correlation exhibit better prediction compared to the thermodynamic wax models for the Eq. (5).

The R^2 and AAD% values show that these two correlation equations i.e. Eq. (4) and Eq. (5) are accurate in estimating the WAT of the crude oils and might be concluded that thermodynamic wax models are weaker than correlations in estimating the WAT of the crude oils. The reasons why correlations are better than thermodynamic wax models in the estimation of the WAT are the assumptions and approaches used by thermodynamic wax models to calculate WAT leading them to have errors in calculating the WAT. The correlation equations are not as complicated as the

thermodynamic wax models as they are only based on the hydrocarbon compositions of the crude oils. Another reason why thermodynamic wax models cannot be accurate is due to the use of the wax precipitation experimental data to tune the model. Therefore, the correlation between the two grouping methods is capable of estimating the WAT of crude oils. This new method and approach for determining the WAT are subject to availability of the hydrocarbon composition range as indicated in Tables 2 and 3. In addition, these correlations are not predictive as thermodynamic models in calculating of the phase equilibriums at any temperatures and pressures and solely based on the hydrocarbon compositions of the crude oils.

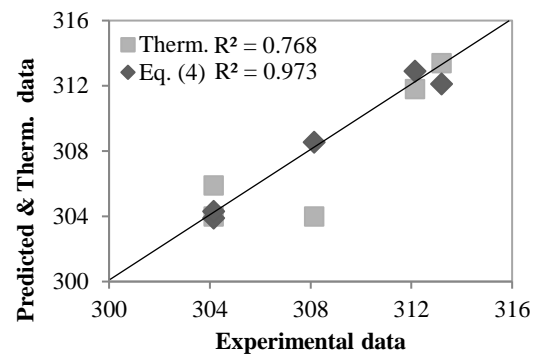


Fig. 3: Experimental data versus predicted data for Eq. (4) and thermodynamic models

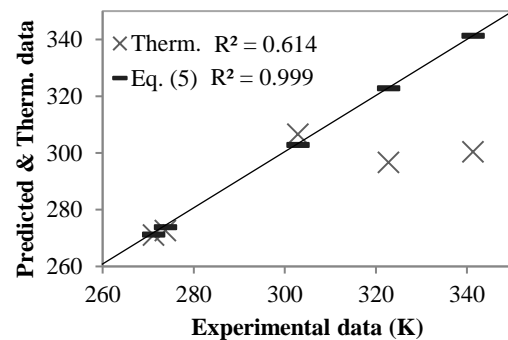


Fig. 4: Experimental data versus predicted data for Eq. (5) and thermodynamic models

4. Conclusion

Two correlations were developed to predict the wax appearance temperature based on the hydrocarbon compositions of crude oil. The accuracy and reliability of these correlations were verified experimentally and thermodynamically by different thermodynamic models. The R^2 and AAD% for these correlations (Eq. 4 and 5) are 0.973, 0.999, 0.0170 and 0.00028 respectively. It can be concluded that the developed correlation exhibit better prediction compared to the thermodynamic models in predicting the WAT of the crude oils. However, this correlation does not have the capability of thermodynamic wax models in prediction of the phase equilibriums at any temperatures and pressures.

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Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

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