Mathematical Model for Determination of Liquefied Natural Gas Density by Its Parameters and Composition

E A Shalovnikov\textsuperscript{1}, M Yu Prakhova\textsuperscript{1}, Ye A Khoroshavina\textsuperscript{1}

\textsuperscript{1}Faculty of industrial processes automation, Ufa state petroleum technological university, 16-21, Mira st., Ufa, Russia, 450064

E-mail: fareastcon.2019@gmail.com

Abstract. Liquefied natural gas (LNG) production and export are becoming one of the most strategically important segments in the Russian gas industry, and therefore the maintenance of LNG production and transporting infrastructure is deemed a critical problem. The commercial accounting of LNG is carried out in the tankers of LNG marine vessels using the static method. The shifting to the indirect dynamic method used in commercial accounting for other liquid hydrocarbons is hindered by the lack of a change measurement chain for flow and density transmitters. The regulatory documents recommend defining the density through calculations using the modified Klosek-McKinley method applied to the LNG composition, which leads to certain difficulties. This article offers a mathematical model for the calculation of density using the compositional analysis and the state parameters of LNG. The adequacy of the model was tested on five LNG mixtures with different compositions (from 72\% up to 90\% methane), temperatures (from 110 K up to 130 K), and pressure (from 0.08 MPa up to 0.4 MPa). In all cases, the calculation error did not exceed 0.15\%. Using this model will help to shift to the dynamic method of LNG commercial accounting. It can also be used for forecasting density values based on changing LNG parameters, which can be useful during overseas transporting and reservoir filling in order to increase the safety of these processes.

1. Introduction

Nowadays, liquefied natural gas (LNG) is playing an increasingly important role in the global hydrocarbon market. New exporters and importers appear, gas liquefaction technologies are being improved, various new solutions and developments are introduced in LNG transport and storage activities, more production and regasification facilities are being built, liquefied gas tankers fleet is undergoing modernization. It is worth noticing that the LNG industry abroad has been successfully functioning since the mid-1960-es [1]. Due to this, studying and analyzing the experience of other countries and developing scientific bases of calculation for processes taking place during LNG transportation are all relevant problems in Russia [2, 3].

One of the key stages of LNG production and export is its commercial accounting. Like other liquid hydrocarbons, it can be performed by using one of three methods: direct static method (using the tank volume of the gas carrier vessels), direct dynamic method (using mass meters), or indirect dynamic method (using volume flow and density).

The static method of LNG accounting is the most widely spread in the world. The accounting is carried out at the moment of gas shipment or loading into the gas carrier tankers, that is using the filling level in a vessel’s reservoirs and correction charts [4]. Gas mixture composition is ascertained by
analyzing LNG samples, and settlement payments for LNG are performed based on the calorific value of the LNG. All these operations and methods are defined by the international protocol of the GIIGNL (International Group of LNG Importers) [5].

Despite the extensive use of this method in LNG accounting around the world, it has a number of limitations. The precision of gas volume metering, for instance, depends on the pipeline and reservoir protection, the condition of vessel’s metal, and the oscillating motion of the ship. It can also be influenced by the precision of LNG sampling, which depends on the operator. Besides, the static method is not used at some operators’ LNG terminals, because it is impossible to perform reconciliation check with the tanker. The NMI (Netherlands Measurement Institute) data shows that the real error of liquefied gas amount measurements during loading and unloading operations falls in the range between ± 0.5 and ± 0.78% [6], while it should be between ± 0.15 and ± 0.20%. Therefore, the participants of the general session of GIIGNL decided that it was necessary to develop dynamic methods of LNG measurement and accounting, similar to those used for oil, oil products, and natural gas during pipeline transportation, with continuous commercial accounting by flow transmitters and quality index measurement instruments, notably density meters.

2. Setting the research objective

Mass flow rate can be calculated by multiplying the density of the substance $\rho$ by the volume flow rate $Q$, (m$^3$/s):

$$Q_M = \rho \cdot Q.$$

In this case, accounting precision will be defined by two components: the flow transmitter error and the density meter error. Various flow transmitters are analyzed in order to understand, whether they can be used for the commercial accounting of LNG, in many works, for example [7 – 10]. Measuring the density of LNG is a rather difficult task, and this component of commercial accounting largely defines the general error value. The main document concerning commercial accounting of LNG [11] states that the density can be received by two methods: either measured directly or calculated. It reserves though, that despite the clear advantages of the first method, such as its independence of LNG composition and parameters, its technical implementation is currently significantly complicated, and thus the second method - the calculation - is used. Among the several known LNG density calculation methods listed, it is the modified Klosek-McKinley method that they recommend using. Despite the simplicity of the formula (the density is a quotient of molecular weight of the mixture and its molecular volume in l/mole), the calculation itself is quite labor-intensive due to the necessity of finding out a number of adjustment factors in order to adjust the density value to standard conditions. That is why we aim at developing a mathematic model for calculating the density using liquefied natural gas parameters and composition, which would simplify the calculations.

3. Main part

We used several LNG specification mixtures [5] with different amounts of CH$_4$, C$_2$H$_6$, C$_3$H$_8$, i-C$_4$H$_{10}$, n-C$_4$H$_{10}$, i-C$_5$H$_{12}$, n-C$_5$H$_{12}$, N$_2$ as feed data. The percentage of the main component of LNG – methane – fell between 72.27 and 90.07%. Table 1 shows the composition of mixture A. All of the following data are given for this mixture since the calculations for all other mixtures were carried out using the same methods. There were four or five trials for each of the mixtures with different temperatures (from 110 K to 130 K depending on the mixture) and pressures (from approximately 0.08 MPa to 0.4 MPa, each mixture had its own pressure range). The density of liquefied natural gas was measured at the output using oscillating transducer density meter to the precision of 0.1% (table 2) [12, 13].
Table 1. Component composition of mixture A (LNG).

| Component | Mixture A composition, % |
|-----------|--------------------------|
| CH₄       | 85.34                    |
| C₂H₆      | 7.9                      |
| C₃H₈      | 4.73                     |
| i-C₄H₁₀   | 0.85                     |
| n-C₄H₁₀   | 0.99                     |
| i-C₅H₁₂   | 0.10                     |
| n-C₅H₁₂   | 0.09                     |
| N₂        | 0.00                     |

Table 2. Measured density of mixture A at different temperature and pressure values.

| Trial number | x₁ = T (K) | x₂ = P (MPa) | y = ρₑxp (kg/m³) |
|--------------|------------|--------------|------------------|
| 1            | 110        | 0.0787       | 484.09           |
| 2            | 115        | 0.1172       | 477.32           |
| 3            | 120        | 0.1686       | 470.57           |
| 4            | 125        | 0.2351       | 463.69           |
| 5            | 130        | 0.3210       | 456.64           |

Due to the lack of sufficient information about the modeled object, the mathematical formulation equations can be expressed as mathematical statistics of trial data, and the model is represented as a black box [14]. Concerning the density of liquefied natural gas during loading in and unloading from gas carrier vessels, the following model was used (figure 1):

\[ T \text { is the temperature of LNG (K); } P \text { is the gas pressure (MPa); } r_i \text { is the composition of the mixture, with the amount of each hydrocarbon in } \% (\text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, \text{i-C}_4\text{H}_{10}, \text{n-C}_4\text{H}_{10}, \text{i-C}_5\text{H}_{12}, \text{n-C}_5\text{H}_{12}, \text{N}_2); \rho \text { is the density of LNG (kg/m}^3\text{)).} \]

Study subject - the LNG loading/unloading system for gas carrier vessels

Figure 1. Black box model for LNG density calculation.

In order to select the type of functionality \( \rho = f(T, P) \), the following approach is used: in three-dimensional space, points with the values of \( T, P, \) and \( \rho \) are located according to table 2 for specification mixture A using the MathCad software package.

Figure 2 shows the graph for LNG mixture A. Its analysis shows that it is possible to use linear dependence between \( \rho, T, P \) parameters for this mixture. Thus, the model will look this way:

\[ y = a + b_1x_1 + b_2x_2, \quad (1) \]

where \( y = \rho; x_1 = T; x_2 = P; a, b_1, b_2 \) are the regression equation factors.

To get the mathematical model, it is necessary to define the regression equation factors \( a, b_1 u b_2 \). In order to do that, the least square method is used [15]:

\[ F(a, b_1, b_2) = \sum_{i=1}^{n}(y_i - (a + b_1x_{1i} + b_2x_{2i}))^2 \rightarrow \min. \quad (2) \]

Therefore, the finding of regression factors is reduced to the problem of defining the functional minimum. Partial function derivatives have to be equal to zero for initial values (factors) in order to use the minimum of the function.
\[ \frac{\partial F}{\partial a} = -2 \sum_{i=1}^{n}(y_i - (a + b_1 x_{1i} + b_2 x_{2i}))(1) = 0, \]
\[ \frac{\partial F}{\partial b_1} = -2 \sum_{i=1}^{n}(y_i - (a + b_1 x_{1i} + b_2 x_{2i}))(x_{1i}) = 0, \]
\[ \frac{\partial F}{\partial b_2} = -2 \sum_{i=1}^{n}(y_i - (a + b_1 x_{1i} + b_2 x_{2i}))(x_{2i}) = 0. \]

After transformation, we get a system of linear equations with three unknown variables \((a, b_1, b_2)\):
\[ \begin{align*}
    a &+ n + b_1 \sum_{i=1}^{n} x_{1i} + b_2 \sum_{i=1}^{n} x_{2i} = \sum_{i=1}^{n} y_i,
    a \sum_{i=1}^{n} x_{1i} + b_1 \sum_{i=1}^{n} x_{1i}^2 + b_2 \sum_{i=1}^{n} x_{1i} x_{2i} = \sum_{i=1}^{n} y_i x_{1i},
    a \sum_{i=1}^{n} x_{2i} + b_1 \sum_{i=1}^{n} x_{1i} x_{2i} + b_2 \sum_{i=1}^{n} x_{2i}^2 = \sum_{i=1}^{n} y_i x_{2i}.
\end{align*} \tag{4} \]

Let us introduce the following notations:
\[ S_1 = \sum_{i=1}^{n} x_{1i} ; \quad S_2 = \sum_{i=1}^{n} x_{2i} ; \quad S_3 = \sum_{i=1}^{n} x_{1i}^2 ; \quad S_4 = \sum_{i=1}^{n} x_{1i} x_{2i} ; \quad S_5 = \sum_{i=1}^{n} x_{1i} x_{2i} ; \quad S_6 = \sum_{i=1}^{n} y_i ; \quad S_7 = \sum_{i=1}^{n} y_i x_{1i} ; \quad S_8 = \sum_{i=1}^{n} y_i x_{2i}. \]

In view of the notations set, the system (4) will look the following way:
\[ \begin{align*}
    a &+ n + b_1 S_1 + b_2 S_2 = S_6,
    a S_1 + b_1 S_3 + b_2 S_4 = S_7,
    a S_2 + b_1 S_4 + b_2 S_5 = S_8. \tag{6} \end{align*} \]

The unknown factors \(a, b_1, b_2\) are calculated using Cramer’s rule, after which the equation adequacy is tested.

Thus, the regression model for LNG mixture A looks the following way:
\[ y_a = 626.88 - 1.29 x_1 - 6.39 x_2. \tag{7} \]

In order to test the adequacy of the mathematical model, its response variances from the average system response value are used [16]. Variances are compared using Fisher’s predictive criterion (F-test) [17]:
\[ F_P = \frac{S_{gen}^2}{S_{ad}^2}, \tag{8} \]
where \(S_{gen}^2 = \frac{\sum_i(y_i - \bar{y})^2}{n - k_1 - 1} = \frac{0.0024325}{2} = 0.0012163\) is the variance of the output parameter or the general variance;
\(S_{ad}^2 = \frac{\sum_i(y_i - \bar{y})^2}{k_1} = \frac{469.6739}{2} = 234.8357\) is the adequacy variance or the residual variance;
\(k_1\) is the number regression equation factors, except the free term \(a\).

The predicted value of \(F_P\) criterion
\[ F_P = \frac{0.0012163}{234.8357} = 5.179 \cdot 10^{-6}. \tag{9} \]

The critical value of Fisher’s quantile at the significance level of \(q=0.05\) is calculated according to table [17]: \(F_{crit}(2;2;0.05) = 19.00\).

Since \(5.179 \cdot 10^{-6} < 19.00\), we can, with the probability of 95%, state that the regression equation is adequate and can predict experimental results.

The standard error of the regression \(S_{gen}\) (standard error of estimate) is regarded as the measure of observation data deviation from the modeled values. Standard regression error is calculated using the following formula:
\[ S_{gen} = \sqrt{\frac{\sum_i(y_i - \bar{y})^2}{n - k_1 - 1}} = \sqrt{\frac{0.0024325}{2}} = \sqrt{0.0012163} = 0.034875. \tag{10} \]

The determination factor, also known as determination measure function, characterized the quality of the created regression model graph. This quality is expressed by the degree of correlation between the initial data and the regression model (calculated data). The determination measure function is always within the [0;1] interval. For the model in question, it equals 0.94, which denotes good convergence of the regression line and the initial data.

Linear correlation factor is used to assess the association of \(x_1, x_2\) and \(y\) variables, and it characterized the degree of linear association between the two samples.
If the correlation factor is greater than 0.9, it means that the association is very strong, i.e. there is a linear dependence.

Student’s criterion is used to test the significance of the correlation factor:

\[
t_{\text{calc}} > t_{cr} ,
\]

\[
t_{\text{calc}} = \frac{r_{xy} \sqrt{k}}{\sqrt{1-r_{xy}^2}} = \frac{0.9697\sqrt{2}}{\sqrt{1-0.9697^2}} = 5.6 ,
\]

\[
t_{cr} = f(k, q) = f(2; 0.05) = 4.3 [17].
\]

If Student’s criterion is fulfilled, it means that there is some dependence between the variables of \(x_1, x_2\) and \(y\) and the calculated correlation factor is significant.

The significance of linear regression equation factors is also tested using Student’s criterion \(t\). In order to achieve this, actual (calculated) values \(t_{\text{calc}}\) of factor criterion for \(a, b_1, b_2\) are calculated and compared with the critical value. For this model, the calculated factor values amounted \(t_a = 412.983; t_{b_1} = 89.578; t_{b_2} = 5.392\), i.e. criterion (12) is fulfilled for all of them, which proves the significance of regression equation factors.

The values of confidential intervals upper and lower 95% limits for regression equation factors \(a, b_1, b_2\) can be found in table 3.

**Table 3.** The values of confidential intervals upper and lower 95% limits for regression equation factors.

| Index       | \(a\)          | \(b_1\)        | \(b_2\)        |
|-------------|----------------|----------------|----------------|
| Lower 95 %  | \(a - S_a \cdot t_a\) | \(b_1 - S_{b_1} \cdot t_{b_1}\) | \(b_2 - S_{b_2} \cdot t_{b_2}\) |
| Upper 95 %  | \(a + S_a \cdot t_a\) | \(b_1 + S_{b_1} \cdot t_{b_1}\) | \(b_2 + S_{b_2} \cdot t_{b_2}\) |
| Factor value| 626.88 \(\pm\) 6.53 | \(-1.29 \pm 0.06\) | \(-6.39 \pm 5.10\) |

If the regression factors values exceed their confidential intervals, it proves the significance of these factors.

The quality of the developed regression model can be assessed with mean approximation error that can be calculated using this formula:

\[
\bar{A} = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{(y_i - y_i^p)}{y_i} \right| \cdot 100 \% \approx 0.41 .
\]

The permissible error value range does not exceed 8-10%, and thus the model is of high quality.

**4. Practical relevance**

In order to test the model, the respective values of temperature \(T\), pressure \(P\), and density were used for each of the mixtures. The results of the comparison of the experimental density \(\rho_{\text{exp}}\) and calculated density \(\rho_{\text{calc}}\) for mixture A are given in table 4.

**Table 4.** Data to test the regression model for LNG mixture A.

| Trial number | \(T\), K | \(P\), MPa | \(\rho_{\text{exp}}\), kg/m³ | \(\rho_{\text{calc}}\), kg/m³ | Absolute error, kg/m³ | Relative error, % |
|--------------|----------|------------|------------------------------|----------------------------|------------------------|-------------------|
| 1            | 110      | 0.0787     | 484.09                       | 484.48                     | 0.39                   | 0.08              |
| 2            | 115      | 0.1172     | 477.32                       | 477.78                     | 0.46                   | 0.1               |
| 3            | 120      | 0.1686     | 472.57                       | 472.00                     | 0.57                   | 0.12              |
| 4            | 125      | 0.2351     | 463.69                       | 464.13                     | 0.44                   | 0.1               |
| 5            | 130      | 0.3210     | 456.64                       | 457.13                     | 0.49                   | 0.1               |
Apparently, the correlation of the calculation results of $\rho_{\text{calc}}$ received using the suggested mathematical model and the experimental results of $\rho_{\text{exp}}$ is quite good, and the error does not exceed 0.15%.

5. Conclusions
The use of the suggested model allows for the simplification of the commercial accounting of LNG without losing its precision.

The research conducted and the practical results obtained from them help solve the pressing problem of rationalization of the shifting to the direct dynamic method for liquefied natural gas weight measurement during its loading to and unloading from gas carrier vessels at the shore-based terminal.

Yet another area of application for the suggested model is forecasting density values with changing LNG state parameters. This problem is quite relevant for reservoir filling operations and LNG overseas transportation due to the possibility of rollover effect. This term denotes the process of LNG stratification into horizontal layers of varied density, which can lead to a rapid increase of pressure in the tank that could damage it. The developed model allows monitoring LNG density in real time and using the current parameters of LNG being loaded into the reservoir or stored in the tank of the gas carrier vessel.

References
[1] Belyayeva М А The outlook of using liquefied natural gas as engine fuel URL: http://snbtul.bmstu.ru/doc/843714.html
[2] LNG transportation URL: http://lngas.ru/transportation-lng
[3] Transporting liquefied natural gas by sea transport (gas carrier vessels) URL: http://korabley.net/news/perevozka_szhizhennogo_prirodnogo_gaza_morskim_transportom_gazovozy/2010-10-01-653
[4] Danilenko N V, Rathwell G E, Safonov A V and Safonova M A 2013 Liquefied natural gas. Metrological support for measurement SFERA Oil and gas 3(36) URL:http://www.imsholding.ru/upload/FileUpload/files/SFERA._Neft_i_Gaz_3_2013.pdf
[5] Physical and chemical properties of natural gas: LNG URL: http://lngas.ru/natural-gas-lng/fiziko-ximicheskie-svojstva-spg.html
[6] Netherlands metrological institute NMI URL: http://www.nmi.nl/metrology
[7] Hogendoorn J, Boer A and Danen H 2014 Commercial accounting for liquefied natural gas Oil and Gas of Siberia 4(17) URL: http://sib-ngs.ru/journals/article/148
[8] Hogendoorn J, Boer A and Danen H 2014 Commercial accounting for LNG using KROHNE products SFERA Oil and gas 6(44) URL: http://www.s-ng.ru/pdf/main_1630.pdf
[9] Zamaletdinova E Yu and Zamaletdinov R R Direct dynamic measurement method for liquefied natural gas URL: https://cyberleninka.ru/article/v/pryamoy-metod-dinamicheskih-izmereniy-szhizhennogo-prirodnogo-gaza
[10] Hogendoorn J and Boer A 1999 Experience with Ultrasonic Flowmeters in Fiscal Applications for Oil (products) 17th North Sea Flow Measurement Workshop
[11] GIIGNL reference book on commercial accounting for LNG URL: https://giignl.org/publications
[12] Haynes W M 1982 Measurements of Orthobaric-Liquid Densities of Multicomponent Mixtures of LNG components Between 110 and 130 K Thermodynamics 14 pp 603-612
[13] Liquefied Natural Gas Densities: Summary of Research Program at the National Bureau of Standards URL: https://www.gpo.gov/fdsys/pkg/GOVPUB-C13-16ca58fc90bc2aad4934e273d548b908/pdf/GOVPUB-C13-16ca58fc90bc2aad4934e273d548b908.pdf
[14] Dougherty K 1999 Introduction to econometrics: Translation from English (Moscow.: INFRA-M) 402 p
[15] Kruga G K 1983 Statistic methods in engineering research (Moscow: Higher School) 216 p
[16] Parameter identification for models’ linear regression URL:
http://www.math.spbu.ru/user/gran/papers/VSPU2014_2708.pdf

[17] Using Fisher’s criterion to test regression model signification URL: http://www.chem-astu.ru/science/reference/fischer.html