**1. Introduction**

Electronics and power generation, food industry, pharmaceuticals, aerospace, fuel cells and etc. are examples of the wide application of hydrogen in recent years [[1-3](#_ENREF_1)]. The primary sources of hydrogen production are steam reforming of natural gases and oil mixtures [[4](#_ENREF_4), [5](#_ENREF_5)]. For production and process design, accurate predictions of hydrogen and hydrogen containing mixtures properties are highly important which can be done by means of equations of state (**EOS**s) [[6-9](#_ENREF_6)]. Except low temperature and high density conditions, hydrogen shows classical behavior [[10](#_ENREF_10)].

Literatures review shows that substantial reports devoted to the application of Equations of State, especially Cubic Equations of State (**CEOS**), for prediction or correlation of hydrogen and hydrogen containing mixtures properties. The simple form and robustness of Cubic Equations of state made them acceptably predictive and thus popular however they have limitation on the range they cover. The most application of Cubic Equations of State is in the correlation of the vapor pressures of pure substances and prediction of properties along the vapor–liquid coexistence curve [[11](#_ENREF_11), [12](#_ENREF_12)].

One of the most applied equations used in petroleum and natural gas industries is the Benedict-Webb-Rubin equation (**BWR**) which has been developed on the basis of Virial equation of state[[13](#_ENREF_13)] by addition of some empirical terms. Thus, in following paragraphs, the development of a new equation of state based on Virial Equation of State will be illustrated following a brief introduction of some Cubic Equation of States studied in this paper. The method of calculations and measures of goodness of the fit are introduced. Also, for the optimization of measures, we employed a new optimization method i.e. Black Hole (**BH**) method which is completely new in such problems [[14](#_ENREF_14)]– as far as we know. The feasibility and applicability of new model together with selected models will be discussed in details. Then, the extension of model to hydrogen containing mixtures will be presented.

**2. Theoretical**

**2.1. Cubic Equations of State**

the Generic Cubic Equation of State (**GEOS**) is defined by **Eq. 1**[[15](#_ENREF_15)];

1. 

Here,  and  are pure numbers – same for all substances - for each Equation of State. Based on the substance of under study, parameters  and  will have different values. There’re two methods for determination of the unknown constants corresponding to each substance, (**i**) Data fitting using available PVT data and (**ii**) estimation from the critical temperature and pressure values[[15](#_ENREF_15)]. The concept behind method (**ii**) is that the critical isotherm shows a horizontal inflection in critical point, from which one can conclude;

1. 

Applying these two conditions (**Eq. 2**) in critical point, one would be able to calculate the unknown constrains of **Eq. 1** as presented in **Eq. 3** and **4**[[15](#_ENREF_15)];

1. 
2. 

Here, and  are pure numbers and independent of the substance which are determined for each equation of state based on the values assigned to  and. The function is an empirical expression and specific to each equation of state.

Using **Eq. 1**, the widely available equations of state can be implemented in a computer script/program for the property calculations. **Table 1.** summarizes the equations of state used [[11](#_ENREF_11), [12](#_ENREF_12)] in current study to be compared to new proposed model.

**Table 1.** The details of cubic equations of state used (**Eq. 1**).

**2.2. Modified Virial Equation of State (mV-EOS)**

The Virial equation of state has following two forms [[15](#_ENREF_15)];

1. 
2. 

In fact, the idea of expressing equations of state of gases and liquids by means of series was presented by Kamerlingh Onnes for the first time, and the Virial equation of state, up to three terms, is a truncated and reduced form of that series which is sufficient in most engineering applications.

For development of new modified model (**mV-EOS**), the **Eq. 5** has been used. here for  and these two equations exist [[15](#_ENREF_15)];

1. 
2. 

Here  and are second and third Virial coefficients as defined in **Eq. 9** and **10**;

1. 
2. 

By inserting **Eq. 9** and **10** in **Eq. 5,** Equation **5** can be reformed in following form;

1. 

Which can be rewritten in reduced form as **Eq.** 12;

1. 

As this expression is in reduced form, one then can investigate the applicability of the model for other gases and liquids or their mixture.

For,,,  and , following Equations exist[[16](#_ENREF_16)];

1. 
2. 
3. 
4. 
5. 

In these equations,  and is the normal boiling point temperature. Equations **13-16** are all only function of reduced temperature () and **Eq. 17** is a function of and. Thus, the proposed model has following main equation as **Eq. 18**;

1. 

Here  is error of truncating corresponding to the real values which must be minimized. According to **Eq. 13-16**, we expect the functional coefficients of new proposed model () to be of the form of a polynomial of **maximum** order of 10th with respect to. The exemption is the fifth functional coefficient which defined in the form **Eq. 19** inspired by **Eq. 17**;

1. 

In calculations section, our task is to find the optimum order/degree of polynomials of the proposed model’s functional coefficients which minimize. Finding these degrees, the model (**mV-EOS**) establishment is finalized.

**3. Calculations**

To measure how close is the predicted values to real and experimental values of a property of interest, there’s always a required to need to define a proper parameter. Common statistical parameter are Accumulative Absolute Relative Deviation (**AARD**) and Individual Absolute Relative Deviation (**IARD**), however, in this research, four more reliable statistical parameters were utilized to measure the agreement between predictions and experimental data together with an overview of how much the fitting is successful by the model. These parameters are described in following paragraphs, followed by the method of minimization employed in this study.

**3.1. Statistical Parameters**

Four parameters have been defined i.e. **SSE**, **R2**, **R2-adj** and **RMSE** for a comprehensive and in-depth comparison between the proposed model and real behavior of the experimental data which are described as follows [[17](#_ENREF_17), [18](#_ENREF_18)].

Sum of Squares due to Error of the fit (**SSE**) as defined by **Eq. 20** used to measure the total deviation of the predicted values () from the model to the experimental values (). Here  are weight values that in this study are assumed as unity.

1. 

**R-square (or R-sq., R2)** is the square of the correlation between the solubility values and the predicted solubility values. This parameter (**Eq. 21**) measures how successful the model is in explaining the variation of the data. In other words, it is the square of the correlation between the experimental values and the predicted values.

1. 

Where, **SSR** means the sum of squares of the regression and **SST** the total sum of squares as described in **Eq. 22-23**. Here, **SST** = **SSR** + **SSE** and  is the average of all data.

1. 
2. 

**Adj R-sq.** is defined to handle the models have many constants. In fact, when the number of models coefficients increase, R-square will increase but the model may not improve in a practical sense. This parameter (**Eq. 24**) is the degrees of freedom adjusted R-square. In this Equation **n** is number of data and **m** is number of coefficient in the model.

1. 

**RMSE** is the model standard error and the standard error of the regression. It is an estimation of the standard deviation of the random component in the data and can be defined as **Eq. 25**.

1. 

It’s worthwhile to mention four rules of thumb as;

1. A **SSE** value closer to zero indicates a fit that has a smaller random error component and is more useful for prediction,
2. An **R-sq.** value closer to **1** indicates that a greater proportion of variance is accounted for by the model
3. An **Adj R-sq.** value closer to **1** indicates a better fit however it can take on any value less than or equal to **1**, and
4. A **RMSE** value closer to **0** indicates a fit that is more useful for prediction.

Individual Absolute Relative Deviation (**IARD**) and Accumulative Absolute Relative Deviation (**AARD**) can be defined by **Eq. 26** and **27**;

1. 
2. 

**3.2. Optimization Method**

Here, for the first time – as far as we know – we utilized a new heuristic optimization approach i.e. Black Hole Optimization Method (**BH**) in such problem of study[[14](#_ENREF_14)]. As the method is new, we provide a short but precise description of the **BH** Method.

This method, Black Hole (**BH**), is a population-based method (**PBM**) such as Genetic Algorithm (**GA**) and Particle Swarm Optimization (**PSO**) Method. There’re features which are common among these population-based methods. In a **PBM** methods, some solution of the problem under study are generated randomly, which are then evaluated using fitness functions. The best evaluated solution will be used to guide all other solutions candidates to the best values. The mechanism of directing the solution to the optimal solution differs in each optimization method.

As an example[[19](#_ENREF_19)], mutation and crossover are used in **GA** while in **PSO** the best found locations are used to move the candidate solutions around. In **BH** method, which were used in this study, all the candidates (stars) will be moved towards the best candidate in each iteration (the black hole) and candidates entering within the range of the black hole are replaced by newly generated candidates. An interested reader would refer to [[14](#_ENREF_14)] for more detailed instruction on **BH** method. The main steps in the **BH** method are summarized in **Table 2**. It’s worthwhile to mention that BH method is like PSO in nature.

**Table 2**. The main steps in the BH method

Four statistical parameters defined in proceeding section used as objective functions.

**4. Result and Discussion**

**4.1. Application to Hydrogen**

In order to examine the application and accuracy of proposed model in prediction and correlation for pure Hydrogen’s properties (especially compressibility here), the thermodynamic properties of Hydrogen compressibility factor were collected form available literatures[[16](#_ENREF_16), [20](#_ENREF_20)]. It’s required to determine the proposed model functional coefficients using available compressibility factor data. To do this, the method of calculations mentioned in **section 3** were followed and the obtained coefficients of the model are listed in **Table 3**. Also, these coefficients can be expressed as function of  which is reported in **Table 3** but with much higher errors. The statistical parameters value corresponding to correlation results are summarized in **Table 4**. The result of model for PVT data (density) prediction can be seen in **Figure 1**.

**Figure 1**. The result of model for PVT data prediction.

**Table 3**. Optimum model coefficients obtained for pure hydrogen using procedure described in **section 3**.

**Table 4**. Obtained correlation results for application of model for determination of thermodynamic properties of hydrogen.

According to obtained results, it’s clear that the model with coefficients listed in **Table 3** is able to (**i**) correlate and predict the compressibility factor data of pure hydrogen and (**ii**) can be readily employed and assessed to calculate the thermodynamic properties. For example, properties which have related to compressibility factor (such as fugacity coefficient) are more favorable as the model’s coefficients were optimized the compressibility factor data here.

Now, the applicability of model for hydrogen containing mixtures will be discussed.

**4.2. Extension to mixtures**

To be able to assess the applicability of the proposed model for hydrogen containing mixtures, the compressibility factor data of five hydrogen containing mixtures which are common in natural gas and petroleum industries were measured experimentally. These five systems compositions are listed in **Table 5** together with pseudo critical properties. To measure these data experimentally method of Pycnometer was used. The Pycnometer data were shown in **Figure 1** through **5**.

**Table 5**. The composition of five hydrogen containing mixtures.

**Figure 2**. Experimental compressibility factor (Z) data for **GU1**.

**Figure 3**. Experimental compressibility factor (Z) data for **GU2**.

**Figure 4**. Experimental compressibility factor (Z) data for **NIST1**.

**Figure 5**. Experimental compressibility factor (Z) data for **NIST2**.

**Figure 6**. Experimental compressibility factor (Z) data for R**G2**.

Using optimum obtained coefficients of model as listed in **Table 3** and pseudo critical properties, the correlation results of model are as summarized in **Table 6**. The optimum obtained coefficient of model in the case of using the measured experimental data for hydrogen containing mixtures are listed in **Table 7**. The correlation results of proposed model and Cubic EOSs are summarized in **Table 8**. Again, these coefficients can be expressed as function of  which is reported in **Table 8** but with higher errors. Also, **Figure 7** shows the accuracy of proposed model together with Cubic EOSs studied for **GU2** at Tr=0.7982 as an example.

**Table 6**. The correlation results of model obtained for hydrogen containing mixtures using coefficients listed in **Table 3**.

**Table 7**. Optimum model coefficients obtained for hydrogen containing mixtures using procedure described in **section 3**.

**Table 8**. Obtained correlation results for application of model for determination of thermodynamic properties of hydrogen containing mixtures.

**Figure 7.** The accuracy of proposed model together with Cubic EOSs studied for **GU2** at Tr=0.7982.

According to obtained results, it’s clear that the model with those coefficients listed in **Table 3** – or even **Table 7** - is able to (**i**) correlate and predict the compressibility factor data of hydrogen containing mixtures and (**ii**) can be utilized readily for calculation of the thermodynamic properties which are related to the compressibility data (for other properties, an assessment is welcomed). The accuracy of this simple model is desirable according to comparisons to some Cubic EOSs.

**5. Conclusion**

A thermodynamic model was developed from Virial Equation of State, here, to predict and correlate hydrogen and hydrogen containing mixtures. The proposed model’s functional coefficients were determined and calculated using four well-defined statistical parameters. The minimization of errors and optimization of models’ performance were done using the Black Hole Optimization Method. According to obtained results and measured experimental data, it can be concluded that the model would be used for thermodynamic property calculations of hydrogen and hydrogen containing mixtures with desirable accuracy.

**6. Further Development Opportunity**

* The wide application and desired accuracy of BWR correlation, which were developed on the basis of Virial EOS, feed the idea of new models and correlations as followed here.
* It would be worthwhile to examine the model in the way it can cover a wider range of materials.
* An attempt to compare the model to solely empirical correlations reported in literatures would be interesting.
* For faster calculations is optimization part of determination of model’s functional coefficients, one may use some faster optimization algorithms. Here, we used the Black Hole Optimization method as this was new in such problems.

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