J. of Supercritical Fluids 101 (2015) 140–149

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Carbon dioxide compressibility factor determination using a robust intelligent method

Erfan Mohagheghian [a], Alireza Bahadori [b,*], Lesley A. James [a]

[a] Faculty of Engineering and Applied Science, Memorial University of Newfoundland, St. John's, NL, Canada
[b] Southern Cross University, School of Environment, Science and Engineering, Lismore, NSW, Australia

ARTICLE INFO

Article history:
Received 26 December 2014
Received in revised form 22 March 2015
Accepted 23 March 2015
Available online 31 March 2015

Keywords:
Carbon dioxide
Compressibility factor
Supercritical fluids
Least square support vector machine

ABSTRACT

Owing to the demanding applications and wide uses of supercritical carbon dioxide in oil, gas and chemical industries, fast and precise estimation of carbon dioxide compressibility factor is of a vital significance in order to be imported into the relevant industrial simulators. In this study, a data bank covering wide range of temperature and pressure was gathered from open literature. Afterwards, a rigorous novel approach, namely least square support vector machine (LSSVM) optimized with coupled simulated annealing (CSA) was proposed to develop a reliable and robust model for the prediction of compressibility factor of carbon dioxide. Reduced temperature and pressure are the inputs of the model. 80% of the dataset was used for training the model and the remaining 20% was used to evaluate its accuracy and reliability. Statistical and graphical error analyses have been conducted to investigate the performance of the model and the obtained results from the proposed model have been compared with those of six equations of state, REFPROP package and two correlations. It was demonstrated that the proposed CSA–LSSVM model is more efficient and reliable than all of the studied empirical correlations, equations of state and the software package, hence it can be utilized confidently for the prediction of carbon dioxide compressibility factor.

1. Introduction

Supercritical carbon dioxide, as the most commonly used supercritical fluid, has been used in polymer processing as a solvent, anti-solvent or plasticizer which reduces the system viscosity and allows lower temperatures of the process. The low temperature sterilization technology by means of supercritical CO_2 can be incorporated in removing hazardous contaminants in food and pharmaceutical industries. It can be utilized as a cleaning agent in micro-electronics, for continuous hydrogenation, as a solvent in oxidation processes and also can be combined with biocatalysts to enhance their activity and stability [1].

Moreover, it has been used for more than thirty years in enhanced oil recovery which can be combined with carbon sequestration in mature oil fields [2,3] and also has found some applications as a refrigerant [2] and a working fluid in gas turbines providing high efficiency [4].

The compressibility factor (*Z*-factor) of CO_2 is vital in most chemical engineering calculations and design of processing units due to its effect on mathematical models and also in oil and gas industry for CO_2 compression, design of pipeline, material balance calculations and surface facilities design [5].

Compressibility factor as a thermodynamic property is obtained via experimental laboratory procedures. Experimental measurements are usually expensive, time consuming and cumbersome [6], and while there is lack of experimentally measured data, engineers would have to determine them through equations of state (EOS's) or experimentally derived correlations [7].

The challenge with equations of state is that they are all implicit in terms of *Z*-factor. The compressibility factor has to be determined as the EOS root which yields the minimum free Gibbs energy. The mathematical approach to determine *Z*-factor is lengthy and requires proper root selection which adds to numerous engineering calculations [8]. An extremely large number of carbon dioxide *Z*-factors is required in the simulation of CO_2 injection as an enhanced oil recovery method in oil reservoirs or for the purpose of CO_2 sequestration and the large number of root selections adds to the simulations run time. Correlations are usually faster and much easier to use [6]; however, they sometimes involve multiple steps and complicated calculations and are limited to the data for which the correlation was formulated [9]. A small error in *Z*-factor will be propagated in the prediction of other properties such as gas

* Corresponding author. Tel.: +61 0422789572; fax: +61 266269857.
E-mail address: alireza.bahadori@scu.edu.au (A. Bahadori).

http://dx.doi.org/10.1016/j.supflu.2015.03.014
0896-8446/

isothermal compressibility, gas formation volume factor for carbon storage calculations and thermal conductivity of supercritical carbon dioxide [10].

According to the above, the need is felt to find a fast and reliable method which can predict the compressibility factor of supercritical carbon dioxide quickly and accurately. Recently, support vector machine (SVM) as a supervised learning algorithm has been a tool for classification and regression analysis. It has found applications in PVT properties estimation, determination of porosity and permeability from log data, text categorization, protein classification in medical science, etc. In a modified version of support vector machine, namely least square support vector machine (LSSVM), the inequality constraint is replaced by an equality, which eliminates the necessity of solving a difficult quadratic programming problem. The LSSVM has shown high capability in solving nonlinear and complex problems and it has been applied for the prediction of several chemical properties of oil and gas [11–17]. To the best of the authors' knowledge, this method has not yet been applied for the prediction of the *Z*-factor of CO_2.

In this study, a collection of 178 data points for the compressibility factor of supercritical carbon dioxide as a function of temperature and pressure up to 1273.15 K and 50 MPa has been gathered from the literature [18]. Afterwards, least square support vector machine (LSSVM) has been applied to predict the *Z*-factor of CO_2 and coupled simulated annealing (CSA) has been utilized as an optimization technique to determine the LSSVM hyper-parameters. Next, statistical and graphical error analyses have been conducted to measure the accuracy and reliability of the model, and finally, the results have been compared with six equations of state, namely Peng–Robinson EOS, Redlich–Kwong EOS, Soave–Redlich–Kwong EOS, Schmidt–Wenzel EOS, Patel–Teja EOS, and Lawal–Lake–Silberberg EOS, a software package named REFPROP developed by NIST as well as two correlations, namely Bahadori–Vuthaluru correlation and the Virial coefficients correlation.

2. Compressibility factor

Gas compressibility or deviation factor (*Z*-factor) is defined as the ratio of the actual volume to the ideal volume and is an indication of the gas deviation from ideal behaviour. Some thermodynamic properties such as density, isothermal compressibility and viscosity can be calculated by means of *Z*-factor.

According to the law of corresponding states proposed initially by van der Waals, all gases behave the same at the same reduced pressure P_r and reduced temperature T_r [6]. In the mathematical form:

$$Z = f(T_r, P_r) \tag{1}$$

where

$$T_r = \frac{T}{T_c} \tag{2}$$

$$P_r = \frac{P}{P_c} \tag{3}$$

where T_c and P_c are the temperature and pressure at the critical point, respectively. The compressibility factor of a pure gas or gas mixture can be estimated by means of either equations of state or empirical correlations.

2.1. Equations of state

Several equations of state have been developed to calculate PVT properties of gas systems. The van der Waals type equations of state which are normally used in petroleum industry can be expressed in the following general format:

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + uv - w^2} \tag{4}$$

The above general equation can be rewritten in terms of compressibility factor as a cubic equation for calculation of volumetric behaviour:

$$Z^3 - (1 + B - U)Z^2 + \left(A - BU - U - W^2\right)Z - \left(AB - BW^2 - W^2\right) = 0 \tag{5}$$

where dimensionless parameters *A*, *B*, *U* and *W* are functions of only pressure and temperature for a pure substance and are defined as follows:

$$A = \frac{aP}{(RT)^2} \tag{6}$$

$$B = \frac{bP}{RT} \tag{7}$$

$$U = \frac{uP}{RT} \tag{8}$$

$$W = \frac{wP}{RT} \tag{9}$$

where the parameters *a* and *b* are expressed by

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \alpha(T_r, \omega) \tag{10}$$

$$b = \Omega_b \frac{RT_c}{P_c} \tag{11}$$

where α is the temperature dependency term, ω is the acentric factor, Ω_a and Ω_b are the generalized coefficients of the parameters in the original van der Waals equation which can be constant or functions of acentric factor and critical compressibility factor in the modified equations of state [19]. Six of widely used equations of states consisting of Redlich–Kwong (RK) [20], Soave–Redlich–Kwong (SRK) [21], Peng–Robinson (PR) [22], Schmidt–Wenzel (SW) [23], Patel–Teja (PT) [24] and Lawal–Lake–Silberberg (LLS) [25] equations of state are reviewed in Section A in the Supplementary information.

In 1996, Span and Wanger derived an EOS specifically for CO_2 by applying modern strategies for the optimization of the mathematical form of the EOS and for the simultaneous nonlinear fit to the experimental data. This EOS covers the wide temperature and pressure range of 216 K (triple point of CO_2) to 1100 K and 0 to 800 MPa, respectively, is an empirical representation of the fundamental equation explicit in Helmholtz free energy as a function of density and temperature and is claimed to be accurate [26]. The drawback of this EOS for calculation of *Z*-factor making it improper for engineering purposes is first that it is implicit in density. As the result, to calculate density and then *Z*-factor, the function should be inverted and since there is no analytic form for that, an iterative method such as Newton's method should be employed and an initial guess for density should be made for the pressure to converge in an iterative procedure. Apart from that, the derivative of the Helmholtz energy must be calculated and there are many coefficients and exponents in the equation (more than 180). These features make the computational procedures lengthy and unreasonable to be employed as an engineering tool. The fundamental equations and the equations for density calculation can be viewed in Section A in the Supplementary information as well.