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Application of the Modified Benedict–Webb–Rubin Equation of State (EoS) for Predicting Hydrogen Gas Mass Production

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ABSTRACT
This study aims to predict hydrogen gas production using equations of state (EoS). It highlights the behaviour of real gases, which deviates from that of ideal gases under extreme conditions. The EoS considered are the ideal gas (PVT), Peng–Robinson (PR), and Modified Benedict–Webb–Rubin (MBWR) models. These models are used to compare predicted hydrogen gas production based on volume, pressure, and temperature parameters. The results indicate that at low temperatures and pressures, predictions from the ideal gas (PVT) and PR models are agree with experimental data. However, significant deviations occur at higher temperatures and pressures. Predictions using the MBWR equation show deviations up to 20% at 25 to 150 °C for pressure up to 20 MPa. The PVT and PR models exhibited deviations of up to 90%, Overall, the simulation demonstrates that the MBWR equation provides a higher accuracy compared to the other two models.

Keywords: Ideal Gas, Modified Benedict-Webb-Rubin, Peng-Robinson, Very High Temperature Reactor

ABSTRAK
Penelitian ini bertujuan untuk memprediksi produksi gas hidrogen menggunakan berbagai persamaan keadaan (*equations of state* (EoS)). Penelitian ini memperlihatkan perilaku gas nyata yang menyimpang dari perilaku gas ideal pada kondisi ekstrem. Persamaan keadaan yang digunakan meliputi model gas ideal (PVT), Peng–Robinson (PR), dan *Modified* Benedict–Webb–Rubin (MBWR). Ketiga model tersebut digunakan untuk membandingkan prediksi produksi gas hidrogen berdasarkan parameter volume, tekanan, dan temperatur. Hasil penelitian menunjukkan bahwa pada temperatur dan tekanan rendah, prediksi yang dihasilkan oleh model gas ideal (PVT) dan PR bersesuaian dengan data eksperimen. Namun, penyimpangan yang signifikan mulai terjadi pada temperatur dan tekanan yang lebih tinggi. Prediksi menggunakan persamaan MBWR menunjukkan deviasi hingga 20% pada rentang temperatur 25–150 °C dan tekanan hingga 20 MPa. Deviasi untuk pemodelan PVT dan PR mencapai 90%. Secara keseluruhan, hasil simulasi menunjukkan bahwa persamaan MBWR memberikan tingkat akurasi yang lebih tinggi dibandingkan dengan dua model lainnya.

Kata kunci: Gas Ideal, *Modified* Benedict-Webb-Rubin, Peng-Robinson, Reaktor Temperatur Sangat Tinggi

1. Introduction

Nuclear energy is a major energy source capable of producing large amounts of power with high energy density, making it crucial for meeting future energy demands. The Very High Temperature Reactor (VHTR) is one of the Generation IV nuclear reactors concepts, employing helium as a coolant and graphite as a moderator, and operating at temperatures in the range of 700–950 °C. Its key advantages include enhanced safety and reliability, reduced CO_2 emissions, and the ability to supply high-temperature heat for industrial

applications such as hydrogen production [1]. The thermal efficiency of the Very High Temperature Reactor (VHTR) operating with the Brayton cycle was calculated to be 50.37% [2]. The VHTR can function either as a power plant using a direct cycle gas turbine or as a hydrogen production system (or other process heat applications), incorporating an intermediate heat exchanger (IHX) between the reactor's primary coolant system and the process application. The IHX is typically designed as a helium gas-to-gas heat exchanger, often followed by a secondary heat exchanger to prevent mixing between the process fluid and the reactor coolant in the event of a leak. In process heat configurations, the IHX and primary gas circulator are generally housed in a separate power conversion vessel adjacent to the reactor system. The development of a VHTR technology involves advancements in high-temperature-resistant materials to withstand extreme operating conditions, as well as improvements in fuel safety [3]. With ongoing progress in material science and safety system design, the VHTR represents a promising option for future nuclear energy systems. In addition, as part of the Generation IV framework, VHTR offer the capability to produce hydrogen an environmentally friendly energy carrier particularly when operating at very high temperatures, typically between 750 °C and 1000 °C [4].

High temperatures enable chemical reactions that enhance hydrogen production rates while reducing the need for additional energy input. By integrating clean hydrogen production processes, the VHTR can significantly lower greenhouse gas emissions compared to conventional fossil fuel-based technologies. For example, thermochemical methods such as the Sulphur iodine cycle allow hydrogen production without CO_2 emissions. In addition, the VHTR can utilize Thorium as a fuel, which is more abundant than uranium and presents a lower risk of nuclear proliferation [5]. Research on estimating the Levelized Cost of Hydrogen (LCOH) for a Gen-VI: Lead-cooled Fast Reactor (LFR) has been conducted. The results indicate that the estimated LCOH is comparable to the cost of hydrogen production from renewable energy sources and other nuclear technologies. However, it remains higher than the cost of hydrogen produced from fossil fuel-based processes [6]. Currently, more than 85% of global hydrogen production relies on Steam reforming of natural gas, operating at temperatures of 800–1000 °C and driven by energy from fossil fuel combustion. Ongoing research aims to reduce the operating temperature to around 300 °C, enabling the use of medium-temperature nuclear reactors as alternative heat sources. The conventional steam reforming process involves two main reactions: an endothermic reforming reaction followed by an exothermic water–gas shift reaction, making it the most established hydrogen production technology. As an alternative, processes such as dimethyl ether (DME) steam reforming at approximately 300 °C are also being developed [7], [8]. The VHTR represents an attractive option in the evolving energy landscape, as hydrogen production using Generation IV nuclear reactors offers a sustainable pathway to meet future energy demands while reducing the environmental impact of conventional energy systems.

The Ideal gas law is a fundamental concept in thermodynamics that describes the behaviour of gases under simplified conditions. An ideal gas is defined as one that strictly follows this law, where the product of pressure (P) and volume (V) is proportional to the number of moles (n) and the absolute temperature (T) of the gas [5]. At the molecular level, an ideal gas is assumed to consist of small, rigid spheres in continuous random motion. Within the temperature and pressure ranges where the ideal gas approximation holds, the average distance between molecules is much larger than their size. The molecular diameter is typically on the order of $2–3 \times 10^{-10}$ m, and under standard conditions, the average intermolecular distance is approximately 50 times greater than the molecular diameter [5]. An important refinement of the Van der Waals equation was introduced by Ding-Yu Peng and Donald B. Robinson in 1976 through the development of the Peng-Robinson (PR) equation. This model was designed to improve the prediction of liquid densities, which had been poorly estimated by earlier equations. The PR equation provides better accuracy for reservoir fluid density compared to many other models, although it remains less accurate in describing volumetric behaviour near the critical point. It is one of the most widely used equations of state due to its balance between accuracy and simplicity, and it generally yields smaller vapor pressure errors than the Soave–Redlich–Kwong equation (SRK). While both PR and SRK produce similar enthalpy values, the PR formulation is often preferred for its practical applicability. For heavy compounds, the PR equation incorporates a volume translation (or correction) to improve liquid density predictions, effectively introducing an additional parameter beyond the critical temperature, critical pressure, and acentric factor used in the SRK equation [9]. This modification significantly enhances liquid density estimation, particularly for complex fluids. Research conducted a model and simulation of hydrogen production with minimum CO_2 production using the PR equation and ASPEN One Suites Ver 11 software. The results obtained from the modelling and simulation showed that gasification temperature, oxygen to coal ratio, and pressure are key factors that can be manipulated to increase hydrogen production to significantly reduce CO_2 emissions [10]. By utilizing a nuclear reactor, it is hoped that it can be improved and the carbon footprint process of hydrogen production can be further reduced. The Benedict–Webb–Rubin (BWR) equation of state, developed by Benedict et al. (1931), was introduced to overcome the limitations of earlier equations

by incorporating additional parameters that account for molecular interactions and the finite volume occupied by gas molecules [11]. The equation was subsequently extended into the Modified Benedict–Webb–Rubin (MBWR) equation of state, which was specifically developed to provide a more accurate thermodynamic representation of para-hydrogen [12].

The objective of this study is to predict the amount of hydrogen gas produced as a function of pressure (P) and temperature (T) in a VHTR system. The EoS considered are the ideal gas, PR, and Modified Benedict–Webb–Rubin (MBWR) models. This study aims to provide a deeper understanding of hydrogen behaviour under non-ideal conditions. This work offers insights into hydrogen behaviour in nuclear energy systems and supports the design of efficient hydrogen production processes, particularly within nuclear reactor applications. Furthermore, it seeks to advance technological understanding related to hydrogen utilization, including its potential role in hydrogen-based vehicles and its production from nuclear energy sources.

2. Methodology

The VHTR cogeneration concept for electricity generation and hydrogen production involves transferring heat from the primary system at approximately 1000 °C through an IHX, which can deliver heat at around 950 °C for hydrogen production processes. The high temperatures required for these reactions can be supplied by a helium-cooled nuclear reactor, such as a VHTR [13], [14]. The Hybrid Sulphur Process (HyS) is a variant of the sulphur-based thermochemical cycle that uses the high-temperature decomposition of sulfuric acid like the sulphur-iodine (S-I) cycle to produce sulphur dioxide and oxygen. However, instead of another thermochemical reaction for hydrogen production, the Hybrid Sulphur Process uses a sulphur dioxide depolarization electrolyser which reduces the need for electrical energy. In this process only hydrogen, oxygen, and sulphur species are involved, making it a hybrid cycle between thermochemical and electrochemical reactions [15]. A circuit must be designed to conduct heat from the VHTR and recover and distribute it to other parts of the system operating at medium and low temperatures. This is crucial to ensure optimal functioning of all plant components and to ensure the energy produced is not wasted. The circuit design must comply with all applicable safety and operational regulations for nuclear and chemical plant facilities, including considerations of pressure, temperature, and material construction. Safety is a top priority, especially when starting up nuclear reactors and potentially hazardous chemical processes [16]. The physical distance between the VHTR and the Hydrogen production plant must be maintained for safety reasons and to ensure the system operates smoothly. This distance also influences the circuit design, including the length of piping and the number of heat exchangers required, helping to reduce the risk of potential accidents and ensure system integrity [17]. By utilizing a nuclear reactor as the thermal energy source, the consumption of methane as a reactant can be minimized. The very high-temperature heat generated in the VHTR reactor system is transferred via a heat exchanger to a mixture of steam and methane gas, enabling hydrogen production. Equation (1) represents the ideal gas equation used to estimate the amount of hydrogen produced, where P is pressure, V is gas volume, n is the number of moles, R is the ideal gas constant (8.314 J·mol^{-1}·K^{-1}), and T is the gas temperature.

$$PV = nRT \tag{1}$$

Equation (2) is the PR equation, where V_m is the molar volume of the gas (V_m 1 mol = 22.4 L), and ω is a parameter representing molecular shape and intermolecular interactions, with a value of 0.0115 [18]. Tc is Critical temperature (T_c = 33.3 K), and P_c is Critical pressure, (P_c = 1.297 MPa). The critical temperature and critical pressure define the critical point, at which the liquid and vapor phases of a substance become indistinguishable and coexist as a single supercritical fluid. Beyond this point, there is no distinct boundary between the liquid and gaseous phases. a and b are a constant contains of critical temperature and pressure.

$$P = \frac{RT}{V_m - b} - \frac{a\alpha(T)}{V_m^2 + 2bV_m - b^2} \tag{2}$$

$$a = \frac{0.45724 R^2 T_c^2}{P_c};\ \ T_c = 33.3 \text{ K}$$

$$b = \frac{0.07780 R T_c}{P_c};\ \ P_c = 1.297 \text{ MPa}$$

$$\alpha(T)=\left[1+\left(0.37464+1.54226\omega-0.26992\omega^2\right)\left(1-\frac{T}{T_c}\right)\right]^2$$

The MBWR equation, developed by Younglove in 1982, is an extension of the Benedict–Webb–Rubin equation designed to accurately describe the behaviour of real gases over a wide range of temperatures and pressures [12]. It was specifically formulated to provide a more precise thermodynamic representation of cryogenic fluids, such as parahydrogen. With its 32 modified terms, the MBWR equation is capable of accurately calculating fluid properties in the single-phase region and has been widely used to correlate thermodynamic property data. Equation (3) presents the MBWR formulation applied in this study, where ρ denotes the molar density, T the temperature, R the universal gas constant, γ a model parameter, and exp ($\gamma\rho$) represents the exponential term accounting for variations in pressure, temperature, and volume. The constants used in the calculations are listed in Table 1 [12].

$$\begin{aligned}P=\rho RT+\rho^2&\left(G(1)T+G(2)T^{1/2}+G(3)+\frac{G(4)}{T}+\frac{G(5)}{T^2}\right)+\rho^3\left(G(6)T+G(7)+\frac{G(8)}{T}+\frac{G(9)}{T^2}\right)\\&+\rho^4\left(G(10)T+G(11)+\frac{G(12)}{T}\right)+\rho^5G(13)+\rho^6\left(\frac{G(14)}{T}+\frac{G(15)}{T^2}\right)+\rho^7\left(\frac{G(16)}{T}\right)\\&+\rho^8\left(\frac{G(17)}{T}+\frac{G(18)}{T^2}\right)+\rho^9\left(\frac{G(19)}{T^2}\right)+\rho^3\left(\frac{G(20)}{T^2}+\frac{G(21)}{T^3}\right)\exp\left(\gamma\rho^2\right)\\&+\rho^5\left(\frac{G(22)}{T^2}+\frac{G(23)}{T^4}\right)\exp\left(\gamma\rho^2\right)+\rho^7\left(\frac{G(24)}{T^2}+\frac{G(25)}{T^3}\right)\exp\left(\gamma\rho^2\right)\\&+\rho^9\left(\frac{G(26)}{T^2}+\frac{G(27)}{T^4}\right)\exp\left(\gamma\rho^2\right)+\rho^{11}\left(\frac{G(28)}{T^2}+\frac{G(29)}{T^3}\right)\exp\left(\gamma\rho^2\right)\\&+\rho^{13}\left(\frac{G(30)}{T^2}+\frac{G(31)}{T^3}+\frac{G(32)}{T^4}\right)\exp\left(\gamma\rho^2\right)\end{aligned}\tag{3}$$

Table 1. The constant value of MBWR [12].

coefficient	Coefficient
G(1) = 0.00004675528393416	G(17) = $4.051941401315\times10^{-10}$
G(2) = 0.004289274251454	G(18) = 0.0000001157595123961
G(3) = –0.05164085596504	G(19) = $-1.269162728389\times10^{-09}$
G(4) = 0.2961790279801	G(20) = –4.983023605519
G(5) = –3.027194968412	G(21) = –16.06676092098
G(6) = 0.000001908100320379	G(22) = –0.0192679918531
G(7) = –0.0001339776859288	G(23) = 0.9319894638928
G(8) = 0.03056473115421	G(24) = –0.00003222596554434
G(9) = 5.161197159532	G(25) = 0.0001206839307669
G(10) = 0.0000000199981550224	G(26) = –0.0000000384158819747
G(11) = 0.00002896367059356	G(27) = –0.000004036157453608
G(12) = –0.002257803939041	G(28) = $-1.250868123513\times10^{-11}$
G(13) = –0.0000002287392761826	G(29) = $1.976107321888\times10^{-10}$
G(14) = 0.000002446261478645	G(30) = $-2.411883474011\times10^{-14}$
G(15) = –0.0001718181601119	G(31) = $-4.127551498251\times10^{-14}$
G(16) = –5.465142603459E-08	G(32) = $8.91797288361\times10^{-13}$

The above equations are applied in this study to estimate the amount of hydrogen gas produced in a nuclear reactor. The calculated results are then compared with experimental data reported by previous researchers [19].

3. Result and Discussion

3.1. Prediction of Hydrogen Density by Ideal Gas EoS

Figure 1(a) illustrates the hydrogen gas density predictions obtained using the ideal gas equation over a temperature range of 100–1000 °C. Figure 1(b) compares the model predictions with experimental data at temperatures ranging from 25 to 150 °C [19]. The ideal gas (PVT) model exhibits significant deviations from the experimental data for pressure up to 20 MPa reaching up to 90% in the low-density region. Furthermore, the ideal gas equation of state (EoS) demonstrates substantial prediction errors across the entire pressure range. For hydrogen production applications associated with Very High Temperature Reactor (VHTR) systems operating under elevated temperature and pressure conditions, the use of more advanced and accurate equations of state is strongly recommended. Improved thermodynamic models are essential for enhancing prediction reliability and ensuring accurate estimation of hydrogen gas properties under real operating conditions.

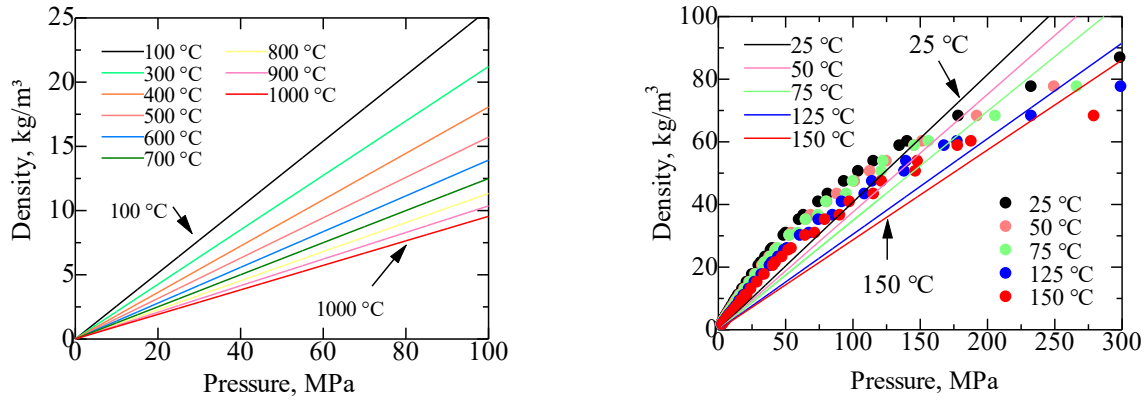

Figure 1. (a) Prediction of hydrogen gas density using the ideal gas for 100 to 1000 °C, and (b) comparison between the simulation (line) and the experimental data (symbol) at 25 °C to 150 °C.

3.2. Prediction of Hydrogen Density by Peng-Robinson (PR) EoS

Figure 2(a) presents the hydrogen density predictions obtained using the Peng–Robinson (PR) equation of state. Figure 2(b) compares the model predictions with experimental data [19] over a temperature range of 25–150 °C. The PR equation of state exhibits considerable deviations from the experimental data, for pressure up to 20 MPa reaching up to 90% across the investigated pressure range. Conversely, at elevated temperatures (e.g., 1000 °C), the density curves become less steep and tend to converge compared with those at lower temperatures. This behaviour indicates that intermolecular interactions become less significant as temperature increases, causing the gas to exhibit behaviour closer to that of an ideal gas. Consequently, the thermodynamic properties of hydrogen become less sensitive to pressure variations at higher temperatures.

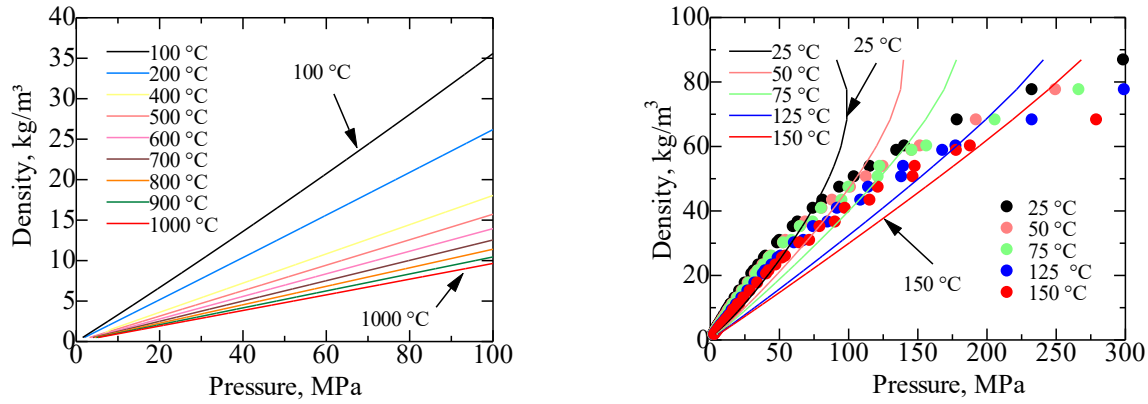

Figure 2. (a) Prediction of hydrogen gas density using the PR equation for 100 to 1000 °C, and (b) deviation between the calculated results (line) using models and the experimental results (symbol) at 25 °C to 150 °C.

3.3. Prediction of Hydrogen Density by Modified Benedict–Webb–Rubin (MBWR) EoS

Figure 3(a) presents the hydrogen gas density predictions obtained using the Modified Benedict–Webb–Rubin (MBWR) equation of state. Figure 4(c) illustrates the deviation between the model predictions and experimental data at temperatures ranging from 25 °C to 150 °C [19]. The results indicate that the MBWR equation provides reasonably accurate predictions at lower temperatures; however, the deviation tends to increase with increasing pressure. Despite this trend, the MBWR equation demonstrates superior predictive performance compared with the other two equations of state investigated in this study. The smaller deviations obtained using the MBWR model suggest that the predicted hydrogen density are more representative of actual thermodynamic behaviour and therefore provide more realistic conditions for reactor simulations. Although the MBWR equation of state still exhibits noticeable deviations of up to 20% at pressures below 20 MPa, the deviations remain relatively consistent across the investigated temperature range. These findings indicate that the MBWR model offers improved reliability for predicting hydrogen properties under conditions relevant to reactor operation.

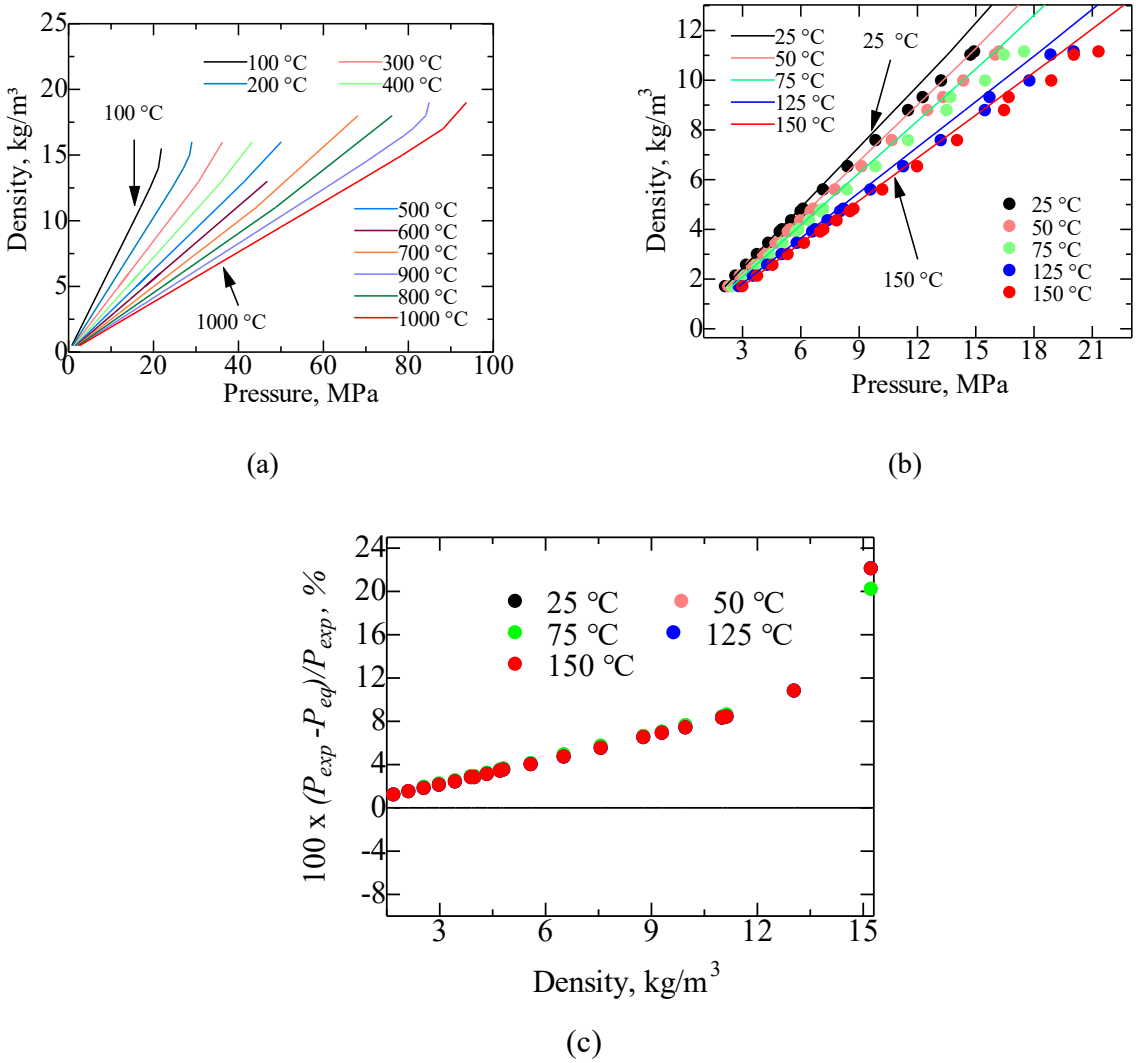

Figure 3. (a) Prediction of hydrogen gas density using the MBWR equation at for 100 to 1000 °C, (b) prediction (line) vs experimental data (symbol), the line colours correspond to the colours of the symbols, and (c) deviation between the calculated results at 25 °C to 150 °C and the simulation.

Table 2 presents the sample summary of hydrogen density values at 25 °C predicted using three different models. At 25 °C and 0.1 MPa, assuming a gas volume of 1 m³, the PVT and the PR EoS predict a hydrogen mass of approximately 0.04 kg, while the MBWR EoS predicts a mass of 0.09 kg. This corresponds to a discrepancy of approximately 125% relative to the PVT-based result, which decreases to 101% at 7 MPa. The deviation of the MBWR model is more pronounced at lower pressures compared with the other EoS. These comparison results highlight the importance of validating EoS against experimental databases to ensure reliable predictions of hydrogen mass production, particularly under high-temperature and high-pressure

conditions relevant to VHTR operation. Although the MBWR EoS generally provides better representation of real-gas behaviour than the ideal gas (PVT) and PR equations, its predictive accuracy still requires further improvement before direct implementation in engineering applications.

Table 2. Sample summary of hydrogen density relate to EoS.

Temperature, °C	Pressure, MPa, for n=1	density of H_2, kg/m^3 (PVT EoS)	density of H_2, kg/m^3 (PR EoS)	density of H_2, kg/m^3 (MBWR EoS)
25	0.1	0.04	0.04	0.09
	7	2.85	2.98	5.74
50	0.1	0.04	0.04	0.08
	7	2.63	2.69	5.27

4. Conclusion

Predictions of hydrogen gas production have been successfully carried out using the ideal gas equation of state (EoS), the Peng–Robinson (PR) equation, and the Modified Benedict–Webb–Rubin (MBWR) equation. The simulation results show that at low temperatures and pressures, predictions from the ideal gas and Peng-Robinson (PR) equations are in good agreement with experimental values. However, significant deviations occur at higher temperatures and pressures up to 85%. Predictions based on the MBWR equation exhibit deviations up to 20% at 25 °C to 150 °C for pressure up to 20 MPa. Overall, these simulations indicate that the MBWR equation provides a higher accuracy than the other two equations.

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