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Numerical analysis of accidental hydrogen releases from high pressure storage at low temperatures

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ABSTRACT

Evaluations of the performance of simplified engineering and CFD models are important to improve risk assessment tools e.g. to predict accurately releases from various types of hydrogen storages. These tools have to predict releases from a wide range of storage pressures (up to 80 MPa) and temperatures (down to 20 K), e.g. cryogenic compressed gas storage covers pressures up to 35 MPa and temperatures between 33 K and 338 K. Accurate calculations of high pressure releases require real gas EOS. This paper compares a number of EOS to predict hydrogen properties typical in different storage types. The vessel dynamics are modeled using a simplified engineering and a CFD model to evaluate the performance of various EOS to predict vessel pressures, temperatures mass flow rates and jet flame lengths. It is shown that the chosen EOS and the chosen specific heat capacity correlation are important to model accurately hydrogen releases at low temperatures.

Introduction

In risk assessment a large number of scenarios have to be analyzed to give a comprehensive evaluation of the associated consequences and risks. This is needed to establish a robust risk informed decision support for risk management purposes. At ambient conditions and moderate storage pressures the use of CFD calculations and engineering equations based on the ideal gas equation-of-states (EOS) give sufficiently accurate results to make proper decisions.

Present technological developments, though, enable to store hydrogen at a temperature of about 20 K in the liquid state under a low pressure <1 MPa or at ambient temperatures in the gaseous state at very high pressures up to 80–100 MPa. Additional, the operational regime of cryo-compressed hydrogen (CcH2) stores hydrogen at temperatures from 338 K down to 33 K and covers pressures of up to 35 MPa [1,2]. Modeling the consequences of hydrogen accidents, hydrogen may be considered as an ideal gas over a wider temperature and pressure range, but which is unfortunately not valid for such wide ranges of temperatures and pressures as described above. Thus the assumption of ideal gas behavior and application of the ideal gas equations of state (EOS) is not adequate and the more complicated adoption of real gas EOS is required. Therefore, for the analysis of accident scenarios at very high pressure and cryogenic temperatures real gas behavior needs to be taken into account to reduce the level of

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uncertainty in the evaluations. This is illustrated in Fig. 1 for five isotherms at 100 K, 150 K, 200 K, 300 K and 500 K using the state-of-the-art reference data recommended by NIST [3] and the EOS for ideal gas. It is shown that the ideal gas EOS over predicts the densities of stored hydrogen and its application results in increasingly deviations from about 15 MPa at 500 K, but starting at lower pressure for lower temperatures.

Traditionally, CFD and simplified engineering models (SEM) use less complex real gas EOS that have been developed over time, e.g. the cubic EOS type (equations by e.g. Abel-Nobel[1]; van-der-Waal; Redlich–Kwong; Redlich–Kwong–Soave; Peng–Robinson; Beatty–Bridgeman). These cubic EOS correct for the finite volumes of the molecules and the intermolecular forces to describe for the non-ideal behavior of gases. The different capability of these EOS predicting hydrogen's temperature- pressure behavior at constant density of 23.2 kg/m^3, which is the ambient temperature density of hydrogen stored at a pressure of 35 MPa, is illustrated in Fig. 2. Recently, Nasrifar [4] published a comprehensive review comparing eleven cubic EOS expressions (e.g. Redlich–Kwong type and Peng–Robinson type EOS) in their performance to predict various supercritical properties of hydrogen. For a pressure (0.1–100 MPa) and temperature (50 K–1500 K) range, Nasrifar [4] recommend the Peng–Robinson–Mathias–Copeman to be used for most hydrogen applications. He found for temperatures above 200 K that most reviewed EOS predicted the different hydrogen properties with good accuracy. In more detail, the review recommended the following EOS to predict the following three hydrogen properties:

1. **Compressibility factor** (accuracy better than 1% in the temperature range 50–1500 K): The EOS by Nasrifar–Bolland, Redlich–Kwong–Soave, or Peng–Robinson–Mathias–Copeman
2. **Heat capacity** (accuracy better than 1% in the temperature range 160–1500 K): The EOS by Patel–Teja, Redlich–Kwong–Soave, or Peng–Robinson; and
3. **Speed of sound** (accuracy better than 3% in the temperature range 50–1500 K): The EOS by Peng–Robinson–Twu–Coon–Cunningham, Peng–Robinson–Stryjek–Vera, or Peng–Robinson–Gasem–Gao–Pan–Robinson.

The need to use real gas EOS is recognized by the scientific community and different approaches describing high pressure gas releases from storage tanks at ambient conditions e.g. [5–8] and within vehicles e.g. [9] are described. Li et al. [10] compare the harm distances of cryo-compressed hydrogen storages with storage of CNG and LNG. Petitpas and Aceves [11] describe a model for sudden expansion of hydrogen stored at 62 K and 34.5 MPa. Friedrich et al. [12] describe release experiments of horizontal cryogenic hydrogen jets in the temperature range 35–65 K at pressures below 3 MPa, while Travis et al. [13] give an example of a simulation of cryo-compressed vessel filling with para-hydrogen using the GASFLOW CFD code in about the same pressure and temperature range as Friedrich et al. Thus presently, only limited information on release experiments and simulations in the low temperature

[1] The Abel-Nobel EOS only assumes corrections to the finite volume of the molecules.

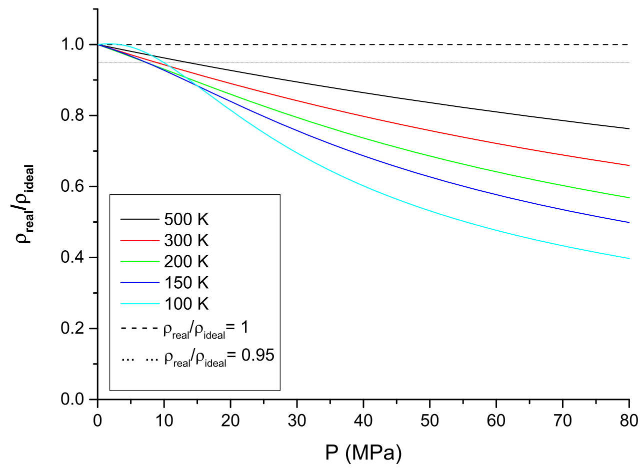

Fig. 1 – The ratio of real gas density to ideal gas density vs. vessel pressure is shown to indicate the real gas deviations for a number of isotherms compared to ideal gas behavior for hydrogen.

range are found in the literature. As no research results have been recognized by the authors for the region between 65 K and 300 K, this paper is intended to approach this important temperature and pressure range for the promising cryo-compressed hydrogen storages. This paper will focus on the accuracy to model time dependent vessel pressures and temperatures and mass release rates using different real gas EOS and different expressions of the heat capacity. The theoretical analysis is done using a simplified engineering model (SEM) and a commercial CFD code (CFX) to identify the potential uncertainty in the predictions of hydrogen releases at storage temperatures of 200 K. The models are used to simulate the accidental release mass flow rate and the vessel dynamics for a 27 L and a 200 L pressurized storage vessel. The simulations are using different EOS commonly used in the

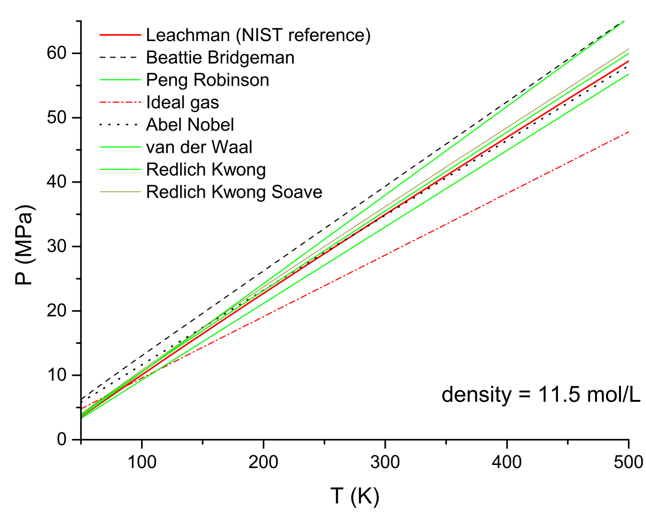

Fig. 2 – Isochoric temperature –pressure plots for 11.5 mol/L (density at 35 MPa at ambient temperature) showing the accuracy of some cubic EOS compared to the NIST data and the ideal EOS.