ICRN-14

EXPIRED

IAPWS Certified Research Need – ICRN

Thermophysical Properties of Humid Air and Combustion-Gas Mixtures

The IAPWS Working Groups "Thermophysical Properties of Water and Steam" and “Industrial Requirements and Solutions” have examined the published work and common industrial practice in the area of the thermodynamic and transport properties of humid air, combustion gases, and combustion gas related mixtures, which are required for accurate system design of power plants and has found that both the available information and the common technical practice are deficient in a number of respects.

The available information is not sufficiently accurate and comprehensive to permit:

(a) the evaluation of the performance of power plants now under construction and soon to be constructed

(b) the optimization of the economic performance of power plant systems and the proper economic sizing of components, and

(c) the development of power generation technologies aiming at sustainable power generation without or with reduced atmospheric CO_2 emission.

Although encouraging this work, IAPWS is not able under its statutes to provide financial support. The IAPWS contact can provide any further development information and will liaise between research groups.

Issued by the

International Association for the Properties of Water and Steam

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Thermophysical Properties of Humid Air and Combustion-Gas Mixtures

Background

The gas turbine industry is currently exploring different roots for the development of economically feasible and environmentally friendly ways to use fossil energy. These approaches include

- improving efficiency and power output of new and existing gas-turbine power-plants by compressor intercooling, typically realised as inlet over-fogging or spray intercooling,
- development of highly efficient and competitive wet gas-turbine cycles, be it with steam injection or with humidification of the compressed air,
- development of gas turbine processes with CO_2 separation allowing for use of fossil energy sources without atmospheric CO_2 emissions,
- development of compressed-air energy-storage plants.

Analysing the corresponding processes in more detail, it becomes obvious that the thermophysical property models used in gas-turbine engineering today, which form the basis for all process calculations, become questionable in these new processes.

To date, gas turbines are developed using thermophysical property models based on the assumption that the working fluid in compressor and turbine (humid air and combustion gas, respectively) behaves like an ideal gas or like a mixture of ideal gases. At working pressures up to about 3 MPa to date and possibly even higher in future systems, this assumption is principally questionable. However, for the design of conventional gas turbines the ideal gas approach leads only to minor uncertainties, since high pressures are obtained always in combination with high temperatures.

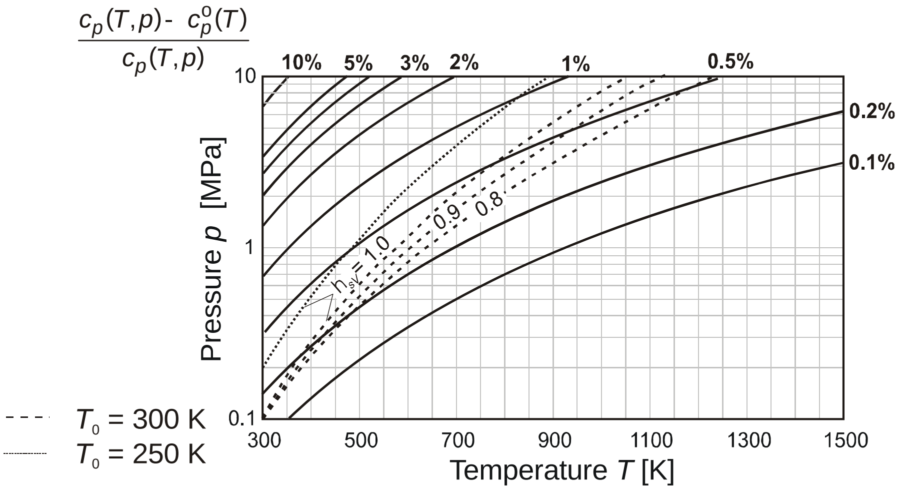

Figure 1. Deviations between ideal and real gas heat capacities of dry air. The blue lines correspond to typical adiabatic compression curves.

Figure 1 illustrates this fact using the heat capacity of dry air, for which the actual deviation from the ideal gas behaviour can be accurately determined, as an example. At ambient temperature and a pressure of about 3 MPa, the deviation between ideal gas (c_p^0) and real gas heat capacity (c_p) amounts to unacceptable 5%. However, in an adiabatic compression process, as it is common in gas turbines to date, the corresponding pressure is typically reached at temperatures above 800 K, where the error of the ideal gas assumption amounts only to about 0.5% – ideal gas models are acceptable unless very high accuracy is required.

For gas turbines with **inlet over-fogging** or (spray) **intercooling** of the compressor this conclusion does not hold since the operating pressure of the gas turbine is reached at much lower temperature. Problems resulting from increasingly uncertain thermophysical data become worse since the injection of water results in a highly humidified stream of compressed air. While real gas effects can be accurately calculated for dry air (see Fig. 1), corresponding models for humid air are not yet available.

For **humid air turbines (HAT)**, including the part flow humidified **EvGT process**, humid air properties have to be calculated at high pressures and low temperatures as well. Compared to the processes discussed above the resulting problems become worse, since water-air phase-equilibria have to be calculated at high temperatures. The common idealised assumption, that the partial pressure of water in the saturated gas phase is equal to the vapour pressure of water does not hold under these conditions. Figure 2 shows deviations between partial pressures at saturation calculated with the common idealised assumption and partial pressures calculated considering a first order correction based only on the well known properties of pure water. Having in mind that the observed differences have a direct impact on both the mass and the energy balance of the process, these deviations are not acceptable for typical calculations in gas-turbine engineering. However, whether the shown first order correction represents the true behaviour of saturated air is not clear – accurate real fluid models for humid air are not yet available. Similar problems occur in process calculations for **compressed air energy storage** plants.

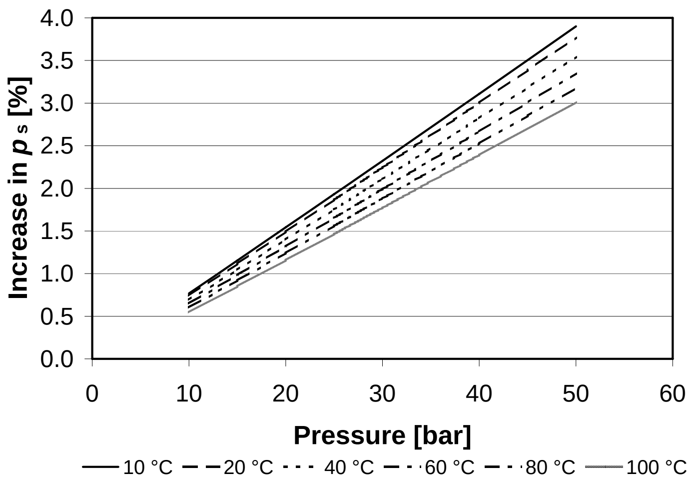

Figure 2. Deviations between water partial pressures in saturated humid air calculated with the common idealised model and partial pressures calculated considering a first order correction.

For gas-turbine processes with **massive steam injection** as well as for **HAT** processes, combustion gas mixtures with up to 50% water content are calculated using ideal gas models to date. Even though high combustion-gas pressures occur in combination with high temperatures in these processes, this approach is questionable due to the thermophysical characteristics of water. At $T = 1000$ K and $p = 3$ MPa for example, the real gas effect for thermophysical properties of water is about 4 times stronger than for dry air. However, real-fluid models for combustion gases with high water content are not yet available.

Combustion gas related thermophysical-property problems become worse for simulations of **zero-emission gas-turbine processes** based on **oxyfuel concepts**, be it with external air-separation unit or with integrated membrane-reactor. In these processes the typical combustion gas is replaced by a CO_2 / H_2O mixture containing only small amounts of other components. Since the processes are designed as semiclosed processes, the CO_2 / H_2O

mixture has to be considered not only at high temperatures downstream of the combustor (or membrane reactor) but also at low temperatures, e.g. in the compressor. Phase equilibria have to be calculated in order to describe the separation process required to prepare the CO_2 for sequestration. Again, no real-fluid models for CO_2 / H_2O mixtures are available, which could describe thermophysical properties required for process simulations with acceptable accuracy.

Figure 3 summarises the described situation with regard to thermophysical-property related problems in gas-turbine engineering. The expression “Serious Problems” refers to problems relevant enough to make results of process simulations a priori questionable. The expression “Problems” refers to problems resulting in a questionable accuracy of process calculations. CO_2 / H_2O mixtures are considered as “Flue Gas” in this figure.

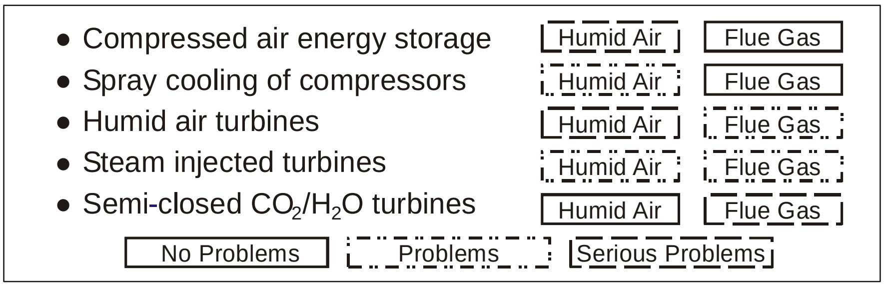

Figure 3. Summary of the thermophysical-property related problems described above.

The Range of Thermophysical Properties Required

For process calculations thermodynamic and transport properties, in particular the viscosity, are required for humid air with water contents reaching up to the level of saturation at a temperature of approximately 500 K. Pressures up to 3 MPa are relevant to typical gas turbine applications, but for compressed air energy storage pressures as high as 20 MPa may be encountered. In principle, temperatures in the range from ambient conditions to 2000 K have to be considered. However, at high temperatures deviations from ideal gas behaviour become negligible. Thus, the investigation of real gas effects can focus on temperatures up to about 700 K. At higher temperatures a thorough analysis of the impact of dissociation on thermophysical properties is more important than an analysis of real gas effects.

Properties for combustion gases are required in the same temperature and pressure range. Thermophysical property models for process simulations need to cover the composition range from dry air over typical gas-turbine flue gases containing (on a molar basis) about 4% CO_2 and 8% water, humidified gas-turbine flue gases containing about 4% CO_2 but up to 40% water, to the working fluids of future semi-closed gas-turbine processes consisting mainly of CO_2 and water with compositions ranging from almost pure CO_2 to almost pure water. These requirements can only be met by real fluid models able to describe arbitrary mixtures of the main air components with CO_2 and water, whereby special attention has to be directed to the residual effects implied by the mixture CO_2 / water. For certain applications it is necessary to consider the impact of components with small concentrations, like SO_2 and SO_3, as well. Again, the investigation of real gas effects can focus on temperatures up to about 700 K. At higher temperatures an analysis of the impact of dissociation is considered more important than an analysis of real gas effects.

Previous Work and Current Studies

In principle, a broad range of property models common in chemical engineering can be applied to the mixtures described above. Acceptable results for phase equilibrium calculations in humidified gas turbines were obtained, e.g., with the model by Hyland and Wexler. However, the accuracy of these models is in general not acceptable for detailed simulations of energy processes, where not only phase equilibrium data but also accurate data for caloric properties at homogeneous states are required.

To date, a sufficiently accurate model is available only for dry air (E. W. Lemmon et al., J. Phys. Chem. Ref. Data, 29, 2000, 331 – 385). For the system CO_2 / water an accurate model was published in 1993 (Gallagher et al., J. Phys. Chem. Ref. Data, 22, 1993, 431-513). However, this model covers only CO_2 concentrations up to 30% and cannot be applied to the tasks discussed above. Recent work inspired directly by industrial demands was restricted to an improved description of ideal gas properties (B. J. McBride et al., NASA Technical Memorandum 4513, 1993; VDI Technical Guideline 4670, 2001; D. Bücker et al., J. Eng. Gas Turbines and Power, 125, 2003, 374-383).

As part of an European research project related to the development of advanced compressed-air energy-storage technology, an experimentally focussed consortium has formed that investigates thermophysical properties of humid air. From this project, an improved data base for the development of real gas models for humid air will result within about two years. However, the range of states covered in this project is not fully sufficient for the description of humidified gas-turbine processes. Experimental work needs to be extended to humid air at higher temperatures and with higher water content and to combustion gas like mixtures including the whole range of CO_2 / water mixtures. Engineering models that accurately describe thermophysical properties of the corresponding systems need to be developed; theoretical work to guide and improve these models would also be useful.

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