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Authors		
Author(s) Name	Organisation	E-mail address
Geir Skaugen	SINTEF Energy Research	Geir.Skaugen@sintef.no
Han Deng	SINTEF Energy Research	Han.Deng@sintef.no

Abstract

Table of Contents

1 Introduction

In the simulation of heat recovery from humid exhaust gas, an accurate thermodynamic model is critical. The aim of this task is to implement thermodynamic and transport property models for humid exhaust gases. By accurately predict the composition of both the gaseous and liquid phase as the water is condensed, this can be used as basis for calculation of thermodynamic including reactions and prediction of for instance acid formation in cases with flue gases containing Sulphur components. This will significantly increase the ability to accurately consider e.g. heat recovery from gaseous sources with condensable components.

The work in 2018 includes:

- Implementing a thermodynamic model for humid gas, which employing THERMOPACK
- Testing various thermodynamic libraries and comparing with reference library hxlib that was described in the HighEFF Deliverable D2_1.2017.01 as one of the many "in-house tools"
    - Generating psychrometric charts
    - Comparing dew point temperature
    - Comparing thermodynamic properties
    - TP-flash calculation and phase identification

1.1 Mixtures of ideal gas

In the Dalton model of gas mixtures, the properties of each component of the mixture are considered as each component exists separately and independently at the temperature and volume of the mixture [1]. Based on the assumption that the gas mixture and the separated components behave as the ideal gas model and obey the ideal gas law, the gas mixture of N components can be expressed as,

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

$$n = n_1 + n_2 + \cdots + n_N \tag{2}$$

And for the components

$$P_i V = n_i RT \quad i = 1, 2, \dots, N$$

Thus, the partial pressures of the individual components and the total pressure P have the relationship,

$$P = \sum P_i$$
$$P_i = Z_i P$$

where Z_i is the mole fraction of each component.

1.2 A gas-vapor mixture

Based on the assumption that the gaseous phase can be treated as a mixture of ideal gases, the total pressure of the humid gas P can be expressed as,

$$P = P_g + P_v \tag{3}$$

where the subscript 'g' stands for dry gas, and 'v' for water vapor. Humid air is one of the most familiar gas-vapor mixture, which is a mixture of air and water vapor. In the following, air refers to the standard air, and gas refers to general gas of which compositions should be specified.

The *absolute humidity* is the total mass of water vapor present in a given volume or mass of gas, regardless of temperature. It is normally expressed as the ratio of the mass of the water vapor to the volume of the gas-water vapor mixture.

The *relative humidity ϕ* of a gas-vapor mixture is defined as the ratio of the mole fraction of the vapor in the mixture to the mole fraction of vapor in a saturated mixture at the same temperature and total pressure [1].

$$\phi = \frac{Z_v}{Z_{v,sat}} \tag{4}$$

where Z_v is the mole fraction of vapor in mixture. Considering the ideal gas model, the relative humidity of gas-water vapor mixture can be derived as,

$$\phi = \frac{P_v}{P_{v,sat}} \tag{5}$$

$P_{v,sat}$ is the saturation pressure of water vapor at the same temperature. The relative humidity is normally expressed as a percentage. The gas becomes saturated at 100% relative humidity.

The *humidity ratio ω* of gas-water vapor mixture is defined as the ratio of the mass of water vapor to the mass of dry gas [1], which is also known as *specific humidity*,

$$\omega = \frac{m_v}{m_g} = \frac{Z_v M_v}{\sum_{i=1}^{N-1} Z_{g,i} M_{g,i}} \quad \text{with} \quad Z_v + \sum_{i=1}^{N-1} Z_{g,i} = 1 \tag{6}$$

where $Z_{g,i}$ and $M_{g,i}$ are the mole fraction and molar mass of component *i* of gas, and M_v is the molecular weight of water vapor. The mole fraction of each component in the dry gas keeps constant, namely,

$$Z_{g,i} = Z'_{g,i}(1 - Z_v) \quad \text{with} \quad \sum_{i=1}^{N-1} Z'_{g,i} = 1, \quad i = 1 \dots N - 1$$

where index *N* is reserved for water vapor, and $Z'_{g,i}$ is the mole fraction of each component in dry gas.

It can be further derived based on the assumption of ideal gases and mixtures,

$$\omega = \frac{M_v P_v}{M_g P_g} = \frac{M_v P_v}{M_g(1 - P_v)} \quad \text{with} \quad M_g = \frac{\sum_{i=1}^{N-1} Z_{g,i} M_{g,i}}{(1 - Z_v)} \tag{7}$$

Based on the above equations, the relative humidity and humidity ratio have the relationship for general mixture as,

$$\omega = \frac{M_v Z_v}{M_g(1 - Z_v)} = \frac{M_v Z_{v,sat} \phi}{M_g(1 - Z_{v,sat} \phi)} \tag{8}$$

With ideal gas assumption, it can be derived with Eq. (5) and Eq. (7), as,

$$\omega = \frac{M_v P_{v,sat} \phi}{M_g(P - P_{v,sat} \phi)} \tag{9}$$

The dew point, dry bulb, and wet bulb temperatures are important to determine the state of humid gas. The *dew point temperature* (DPT) of a gas-water vapor mixture is the temperature at which the vapor begins to condense or solidify when it is cooled at constant pressure. Also, it corresponds to a saturated gas of 100% relative humidity.

Figure 1 shows a psychrometer, which uses the flow of air past dry-bulb and wet-bulb thermometers. The *dry bulb temperature* (DBT) is simply the measured gas temperature. The *wet-bulb temperature* (WBT) is the temperature read by a wet-bulb thermometer which is covered in wet cloth wick over which air is passed. WBT is influenced by heat and mass transfer rates and not simply on thermodynamic equilibrium properties, which won't be explained in detail here. The *thermodynamic wet-bulb temperature* (TWBT) can be defined as the adiabatic saturation temperature, at which a volume of air would have if cooled

adiabatically to saturation by evaporation of water into it, all latent heat being supplied by the volume of air. The TWBT is a thermodynamic property of a mixture of gas and water vapour. The value indicated by a simple wet-bulb thermometer often provides an adequate approximation of the TWBT.
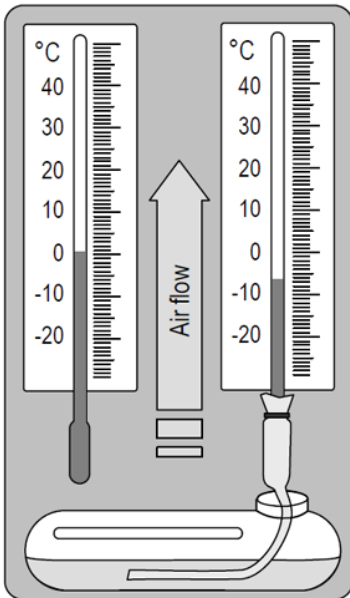

Figure 1 Dry-bulb thermometer (left) and wet-bulb (right) thermometer [2]

Based on the Dalton model, the enthalpy of the gas-water vapor mixture can be written as the sum of the enthalpy of the dry gas and the water vapor,

$$h = h_g + \omega h_v \tag{10}$$

in the unit of kJ/kg of dry gas. It is worth noting that the enthalpy is calculated based on certain reference. The enthalpy of dry air h_g at given temperature is referred to the enthalpy of dry air at 0°C. The reference for enthalpy of water vapor is taken at saturated water at 0°C.

The specific heat of the gas-water vapor mixture can be expressed as,

$$c_p = c_{p,g} + \omega c_{p,v} \tag{11}$$

The second term is very small compared to the first term, thus the humid specific heat of gas-water vapor mixture can be approximated to the specific heat of the dry gas, with the unit kJ/(kg of dry gas · K).

1.3 Psychrometric chart

Figure 2 is a psychrometric chart for humid air at barometric pressure of 1 bar at sea level. The psychrometric chart represents the thermodynamic properties of air-water vapor mixtures. The humidity ratio is plotted as a function of the dry bulb temperature, with relative humidity, enthalpy per unit mass of dry air and specific volume per unit mass of dry air as parameters. The thermodynamic state of humid air is fixed for a given total pressure, and two other independent properties. For example, a red point is located in the chart with known dry bulb temperature and humidity ratio. Then the relative humidity can be obtained from the constant relative humidity lines. The wet bulb temperature is then the temperature corresponding to the point where the constant enthalpy line (blue arrow) and the saturation line (100% relative humidity) intersect. Following the constant humidity ratio (orange arrow), the dew point temperature can be found at the point where it intersects with the saturation line. It can be seen that, the wet bulb temperature is always between the dew point temperature and dry bulb temperature within the bounded region, except the points on the saturation line where the three temperature are identical.
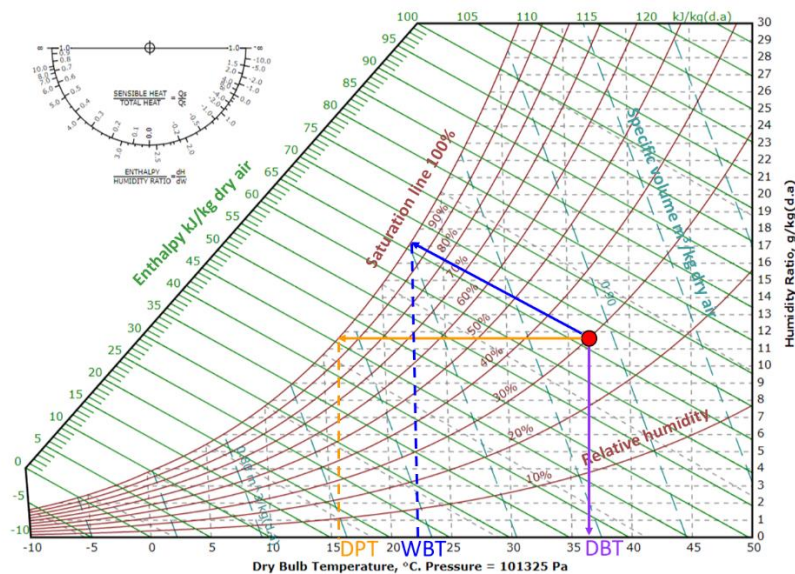
Figure 2 Psychrometric chart of humid air [3]

1.4 Psychrometric chart for general humid gas

In this section, the different methods are used to generate psychrometric chart for general humid gas. A dry gas of 79% N_2 and 21% O_2 with water vapor is used as an example.

1.4.1 With ideal gas assumption

Relative humidity lines are generated based on Eq. (9), the relationship between relative humidity and humidity ratio with ideal gas assumptions. Given the relative humidity ϕ and gas temperature (referred to DBT), the humidity ratio can be calculated. Similarly, if the enthalpy and temperature are set, the humidity ratio can be calculated from Eq.(10).

Figure 3 shows psychrometric chart generated with "hxlib" and"hglib". In the library "hxlib", the dry gas is calculated as ideal gas and water vapor as real gas. In "hglib", the dry gas and water vapor are calculated with specific equation of state (EOS) and Peng-Robinson EOS is used here as an example. Still, the relationship for ideal gas mixtures Eq. (9) is assumed to be satisfied.

In Figure 3, the relative humidity lines are different from the two calculation methods which results from the difference in water vapor saturation pressure at a given temperature, as shown in Figure 4. The correlation used in hxlib is almost identical to the data obtained from REFPROP. The difference in enthalpy lines also comes from the difference in the calculation of water vapor enthalpy. With the increase of humidity ratio/water mole fraction, this difference becomes greater.
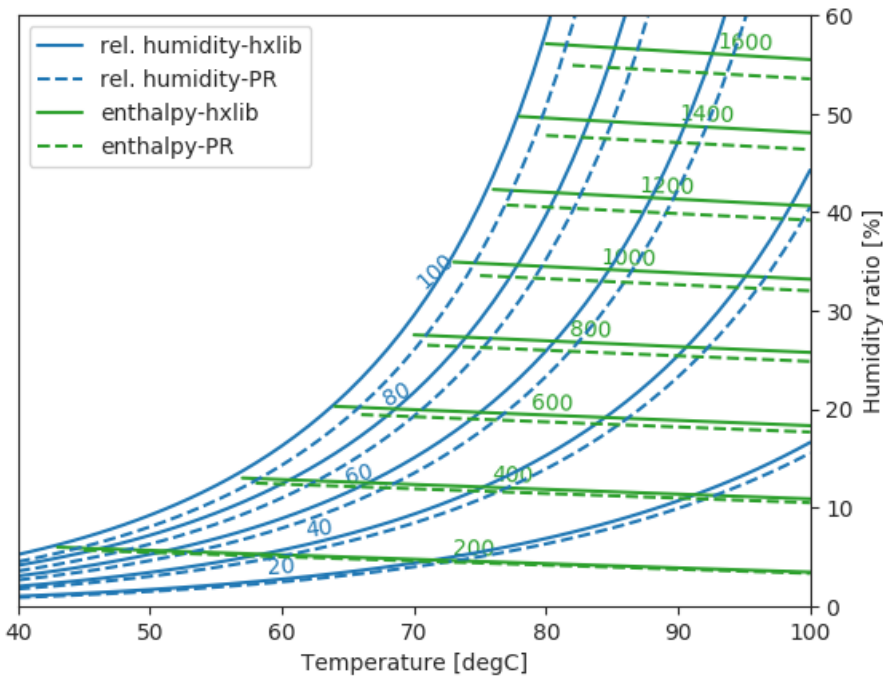
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Figure 3 Psychrometric chart of a specific gas at 1 bar, and comparison of results from hxlib and hglib
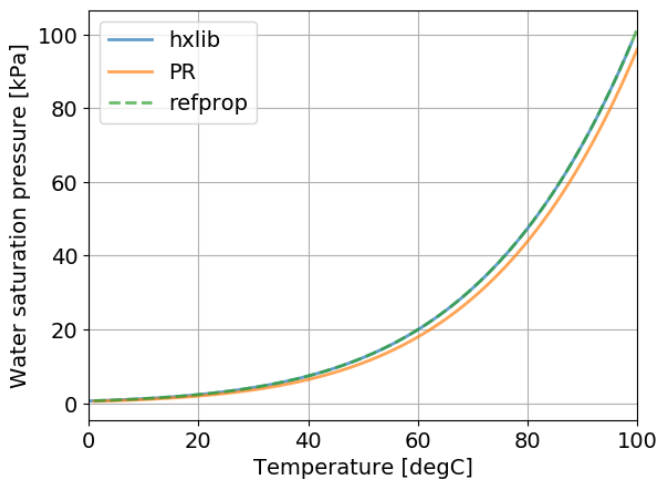

Figure 4 Water vapor saturation pressure at given temperatures calculate

Figure 5 shows the psychrometric charts calculated at different pressures, 1, 2 and 5 bar with Peng-Robinson EOS for gas and vapor. With the increase of total pressure, the humidity ratio at the same temperature and relative humidity decreases, based on Eq. (9).
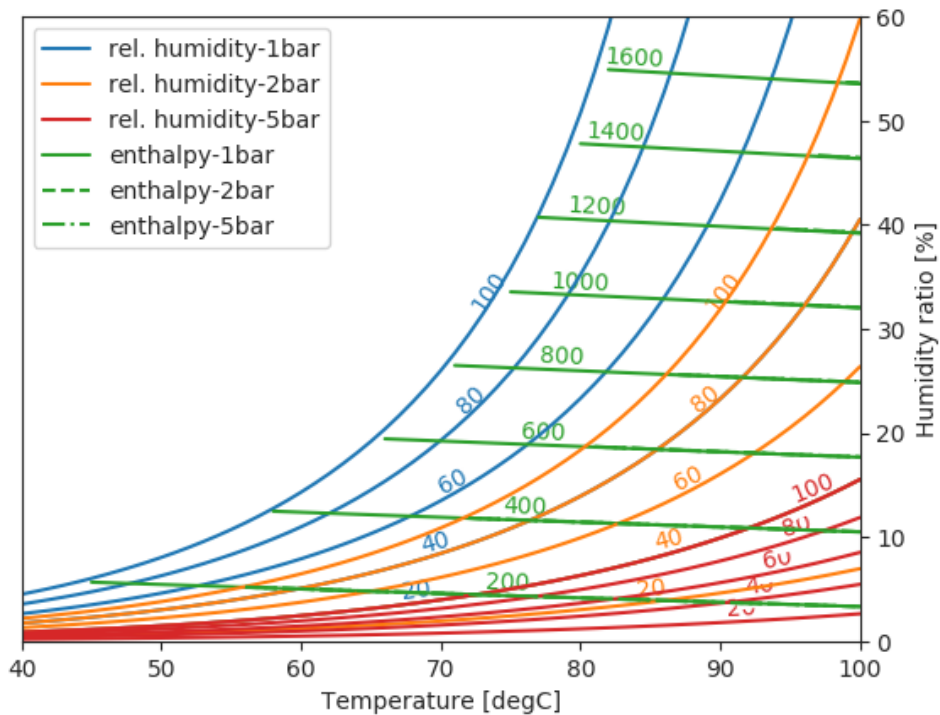
Figure 5 Psychrometric chart of a specific gas at different pressures

1.4.2 With general gas assumption

In this section, the relationship for general gas mixture Eq. (8) is used to generate the relative humidity lines. In the above section, the humidity ratio is calculated from relative humidity and temperature. Now the calculation should be the other way around. By specifying the vapor mole fraction Z_v in mixture, the humidity ratio could be obtained from Eq. (6). With the humid gas composition, the dew point of the mixture can be calculated with given EOS. Meanwhile, the vapor mole fraction is actually the vapor mole fraction in a saturated mixture corresponding to the dew point temperature, namely $Z_{v,sat} = Z_v$. Then, the line of 100% relative humidity is obtained. For the other relative humidity lines, the vapor mole fraction can be calculated based on the definition of relative humidity Eq. (4), and then the humidity ratio can be obtained from Eq. (6). The relative humidity lines based on Eq. (8) with general gas mixture are compared to the reference case by hxlib in Figure 6. As an example, the thermodynamic library EOSCG is used. It can be seen that the relative humidity lines are almost identical to those generated with hxlib.

The enthalpy lines are neglected here, since an iteration is required to obtain the mole fraction of the water vapor in the mixture at a given enthalpy. Instead, the comparison of enthalpy calculated from different methods is presented in Section 2.1.

Figure 7 shows the dew point temperature calculated by different EOS at 1 bar. The results by the model EOSCG and GERG-2008 are almost the same as that given by hxlib over the whole range of the mole fraction of water vapor. The dew point temperature calculated with Peng-Robinson is slightly higher than the rest of EOS at the same mole fraction of water vapor.
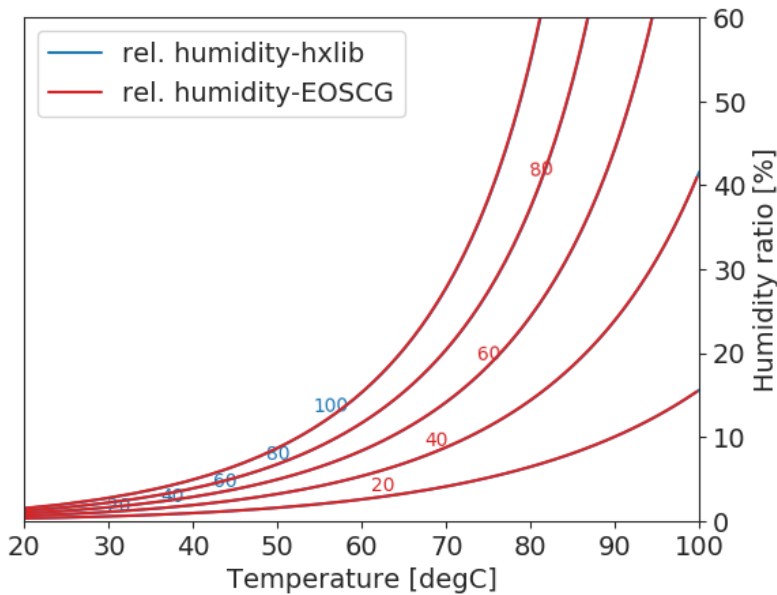
Figure 6 Comparison of relative humidity lines for general gas mixture with hxlib
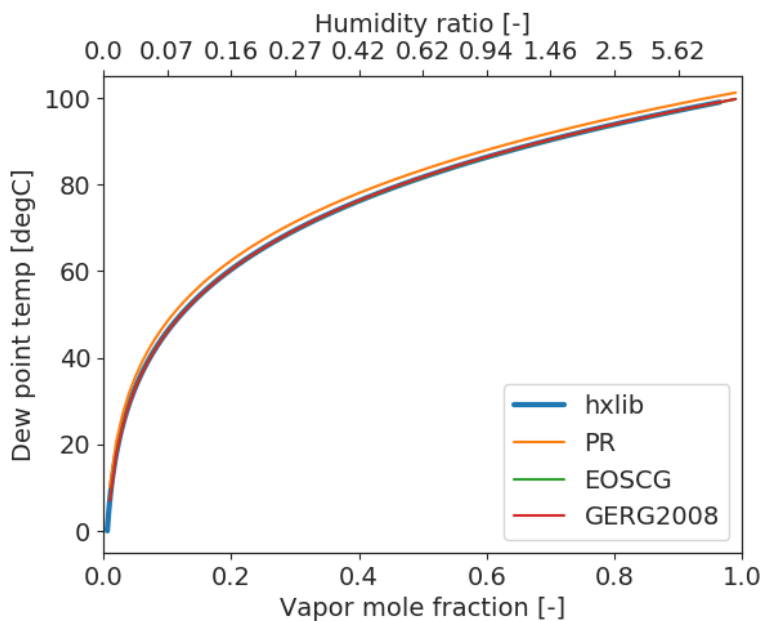

Figure 7 Dew point temperature vs. vapor mole fraction at 1 bar

2 Real thermodynamic calculations

2.1 Thermodynamic properties of humid gas

The thermodynamic properties of humid gas are calculated with different methods, as following:

1. hxlib – ideal gas for dry gas and real gas for water vapor
2. hglib_EOS – EOS for dry gas and water vapor separately

3. hglib_mix_EOS – EOS for humid gas as one mixture

The properties have been converted to the same mass basis per kilo dry gas. In the calculation of specific heat, results fall into two groups. The group from the method 2 with EOS: PR, PC-SAFT, GERG-2008, EOSCG-GERG gives higher specific heat than the reference method 1.

All these methods result in almost same specific enthalpy and specific volume (overlapped lines in figure).
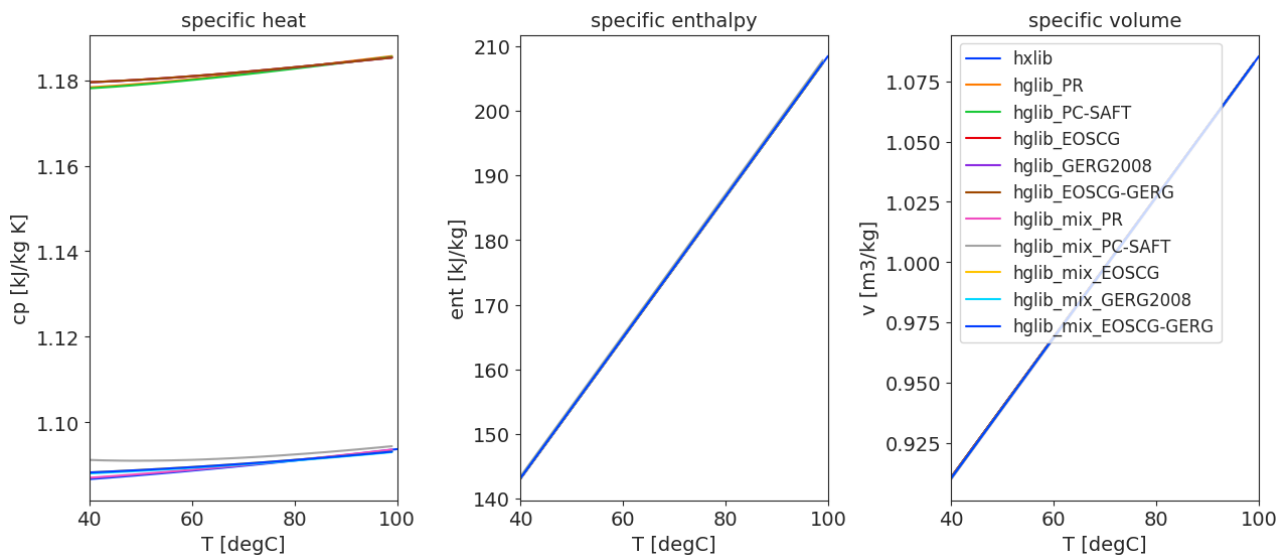

Figure 8 Comparison of thermodynamic properties

2.2   Real thermodynamics for identification of phases

In the simulation for cooling of humid gas, it is important to identify when the liquid phase water presents. As a start point, Peng-Robinson is used for testing the humid gas with relatively lower water vapor of mole fraction 0.06, as shown in Figure 9. When starting at high temperature 100 °C, the humid gas is in single-gas phase. With temperature decreasing to about 38 °C, the liquid phase presents, which is almost pure water from the calculation results. It is worth noting that the calculated liquid composition is varied based on the EOS used. The vapor mole fraction in gas mixture starts to decrease due to condensation of the water vapor. When the temperature is below 0 °C, it is expected that the liquid water and solid ice both exist. With temperature decreasing and reaching at about −40 °C, the calculated vapor mole fraction in gas phase is less than 1E-4. It can be assumed that the water vapor in gas mixture has been depleted and the remaining gas is dry gas.
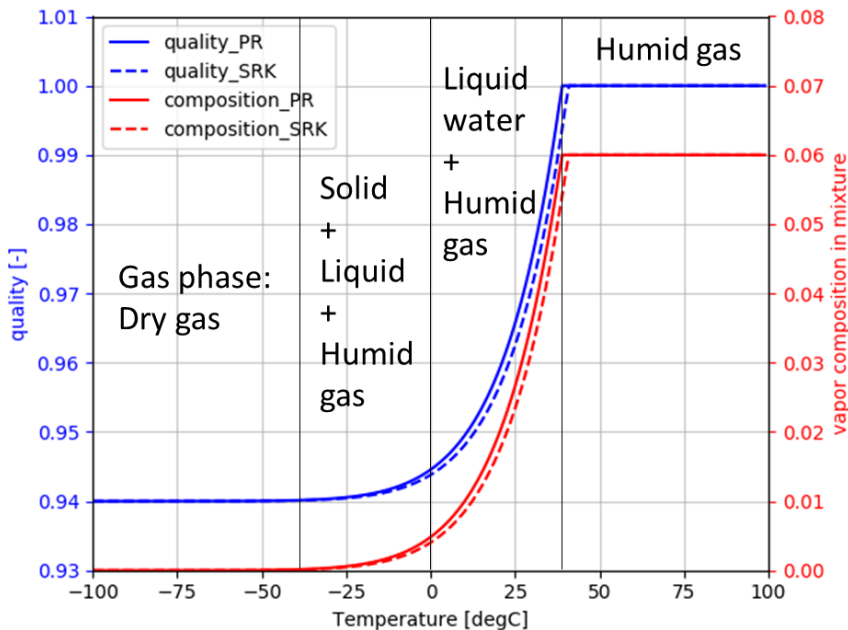
Figure 9 Identification of phases of humid gas mixture, calculated by PR and SRK at 1 bar

3 Conclusion and future work in 2019

In 2018, a library for general humid gas "hglib" has been built based on the similar structure to "hxlib". The library hglib has connected to the interface of THERMOPACK, so that various libraries can be used for calculation of the thermodynamics of humid gas as real gas. The EOS such as PR, EOCGC, GERG2008 have been tested with the reference result by hxlib at low pressure. The models EOCGC, GERG2008 perform well in the calculation for dew point temperature and other thermodynamic properties.

In 2019, the work on general humid gas will be continued. The main tasks are as follows,

- Test TP-flash with TREND libraries for general humid gas
- Implement methods for humid gas transport properties
- Investigate effect on heat transfer and heat exchanger design, including:
    - Simple cases: humid air flowing over a surface
    - Full HX case study
- Implementation in FlexHX:
    - Enthalpy calculation
    - Robust solving of heat balance
    - Effect of moisture/ice layer on material properties

References

[1]   C. Borgnakke, R. E. Sonntag, and G. J. Van Wylen, *Fundamentals of thermodynamics*. Wiley, 2009.

[2]   "Dry-bulb and wet-bulb thermometer." [Online]. Available: https://i.stack.imgur.com/TdpcQ.png.

[3]   "Free Online Interactive Psychrometric Chart." [Online]. Available: http://www.flycarpet.net/en/psyonline. [Accessed: 04-Dec-2018].