Evaluation of the GERG-2008 Equation of State for the Simulation of Oxyfuel Systems

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1.Introduction

The design of power plant systems requires a considerable amount of modelling and simulation. Thermodynamic property models or equations of state that are used to describe the volumetric, energetic and transport behaviour of fluids involved such as flue gases, steam and cooling water are always applied. Most of the former projects in the power plant industry could be realized with only a few relatively simple equations of state because the fluids involved displayed almost ideal behaviour (except water for which quite complex equations were developed decades ago).

The situation is completely different for Oxyfuel power plants. The additional processes and units that are needed to operate an Oxyfuel power plant (air separation units, flue gas cleaning systems, purification units, compressors and others) are always dealing with complex fluid mixtures with strong real-gas behaviour and very different parameters (e.g. supercritical CO2). Calculation of these processes using the simple "ideal" equations will produce relatively large errors, if it is even possible at all.

Therefore more sophisticated equations of state that are capable of representing the complex behaviour of the fluids need to be used. Ideally, a single equation of state would be used for all relevant processes. This would have the advantage of consistent results and numbers, especially at the interfaces of the different parts of the power plant. Additionally, this could lead to a smaller number of software packages that are used in the overall concept and design of new power plant projects.

2. GERG-2008 Formulation

One of the mentioned equations of state is the GERG-2008 [Kunz 2011] formulation that was originally developed to calculate the thermodynamic properties of natural gas mixtures. The advantage of this formulation is the (theoretical) ability to provide consistent thermodynamic property data for the most relevant processes in an Oxyfuel power plant. Whether this is true for all conceivable cases and all relevant ranges of pressures, temperatures and mixtures will be discussed on this poster.

The GERG-2008 formulation is an equation of state to calculate thermodynamic properties of mixtures with natural gas components (see figure 1).

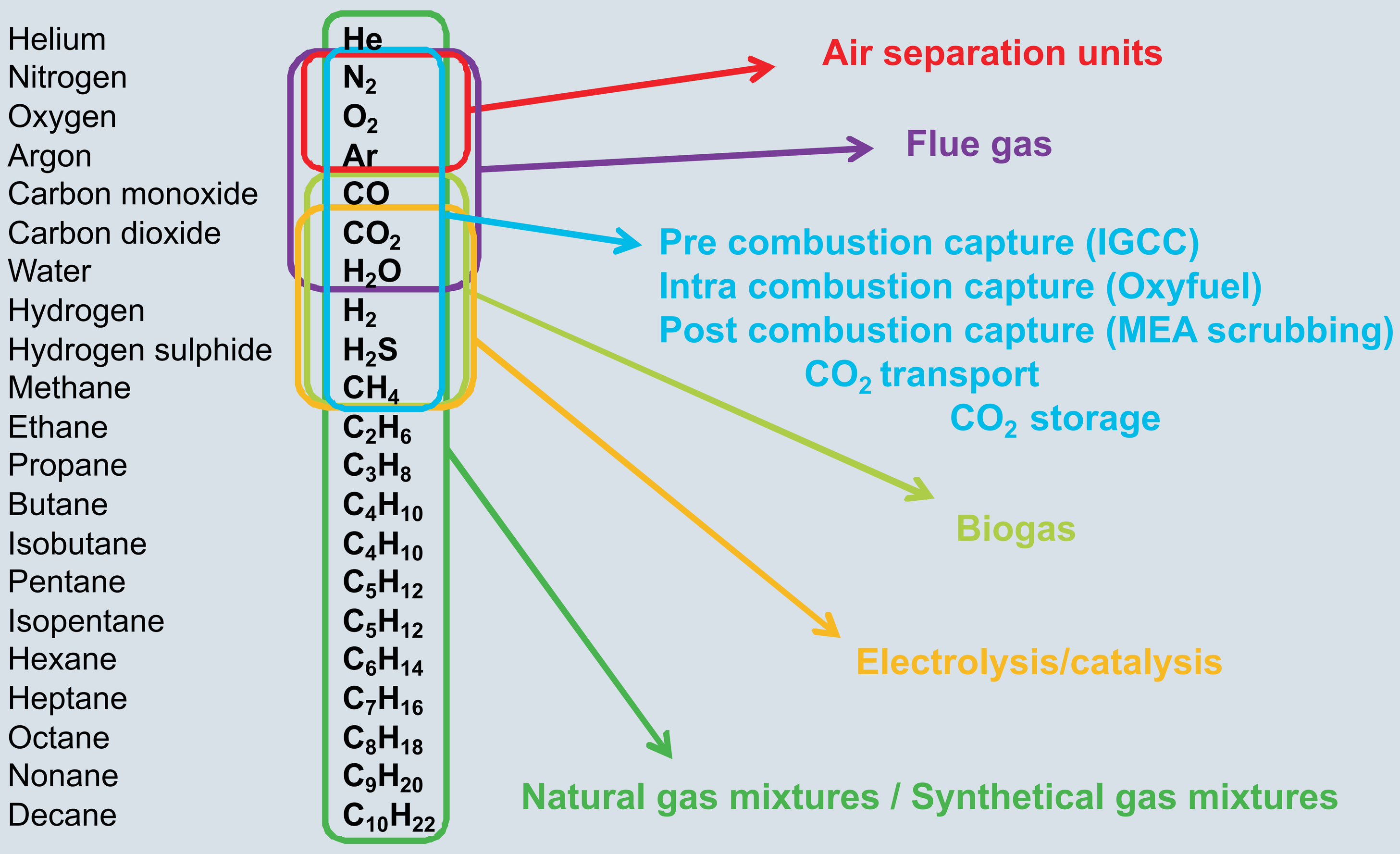


Figure 1: Mixture components and processes/applications

3. Capabilities for Process Simulations Using GERG-2008

The GERG-2008 equation could theoretically be used to derive thermodynamic properties for modelling and simulation of many different processes. In the special case of Oxyfuel power plants these applications include:

- cryogenic air separation units
- flue gas systems (boiler, flue gas treatment units)
- water/steam cycles
- CO2 processing units

Usage is restricted by the constituents of the flue gas that have to be considered in the calculations. For example sulphur dioxide, a typical flue gas component, is not covered by the equations. Another restriction is the absence of equations describing the transport properties.

The extended range of validity is -153.15 °C to 426.85 °C at pressures below 700 bar if a higher uncertainty of results is acceptable. Extrapolation behaviour is reported to be good and some examples will be presented later. The equation is applicable to gaseous, liquid, supercritical and vapor-liquid equilibrium states for any mixture with the above-mentioned components, leading to the ability to use it in the simulation of very different processes.

The GERG-2008 formulation is an extension of the former GERG-2004 [Kunz 2007] equation (which is an international reference equation for natural gases) and is currently under preparation for adoption as an international standard (ISO 20765-2 und ISO 20765-3).

Calculable properties include (see figure 2):

Compressibility factor	z	
Specific volume, Density	v, ?	
Enthalpy, Entropy, internal Energy	h, s, u	
Heat Capacity isob./isoc.	c_p, c_v	
Speed of sound, isentropic exponent	w, ?	
Joule-Thompson coefficient	µ	
Partial derivatives of several properties	(e.g.: $(\partial p/\partial T)_\rho$)	
Fugacities	f_i	
Molar masses	M	
…		

As functions of:

Pressure and temperature	f(p,T)
Pressure and enthalpy	f(p,h)
Pressure and entropy	f(p,s)
Volume and temperature	f(v,T)
Volume and internal energy	f(v,u)

VLE/flash calculations
Dew and boiling points
Phase envelopes

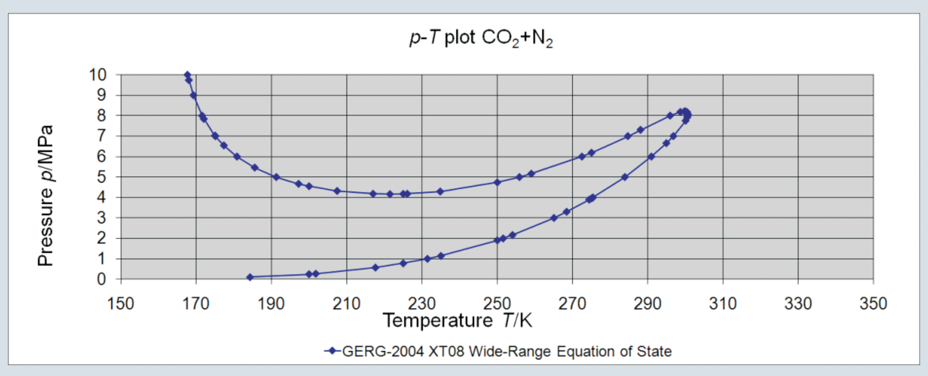


Figure 2: Calculable Properties

Current availabilty of the GERG EOS (as known to the authors) is shown in figure 3:

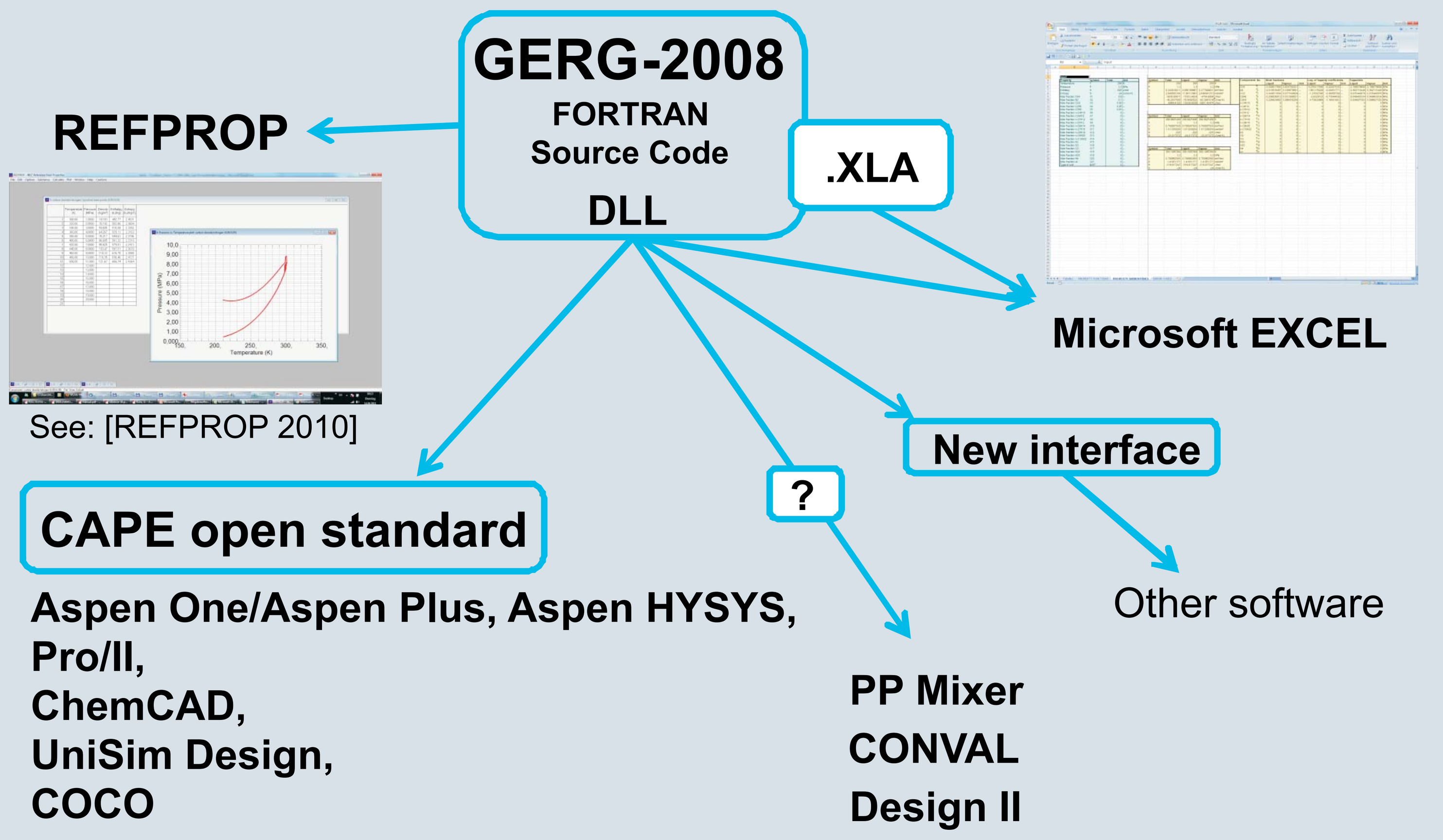


Figure 3: Software packages using GERG-2004/2008

4. Comparison to Measurement Data and Other Equations of State

A large quantity of measurement data was used for fitting the parameters and coefficients of the GERG-2008 equation. Any lack of measurement data will therefore directly influence the uncertainty of the calculated values, which is especially true for mixtures. Because the equation uses binary interaction equations of different kinds some mixtures are represented more accurately than others, depending on the amount of reliable measurement data for the binary mixture. Especially for mixtures consisting mainly of minor natural gas components like carbon dioxide, oxygen, water and others, there were fewer measurement data and less complex equations were used for fitting (For example mixtures containing Co2, see figure 4).

Therefore it should be tested whether a given mixture is represented with acceptable uncertainty by the GERG-2008 equation. For the Oxyfuel application five different fluids or mixtures of fluids were examined: water and steam (steam cycle conditions), air (standard air) under conditions of air separation units, flue gas, pure CO_2 impure CO_2 (see figures 4-9).

Mixture	Data points VLE	Data points heat capacity	Data points pTp and w	Total
CO2 + CH4	156	-	1431	**1587**
CO2 + N2	115	203	888	**1206**
CO2 + Ar	10	-	446	**456**
CO2 + H2O	-	-	446	**446**
CO2 + H2	68	-	316	**384**
CO2 + O2	-	-	-	**0**
CO2 + CO	-	-	-	**0**

Figure 4: Binary data used to fit GERG-2008
GERG-2008 is primary a natural Gas EOS
→Li reported up to 18% deviations for liquid CO2 mixtures [Li 2011]

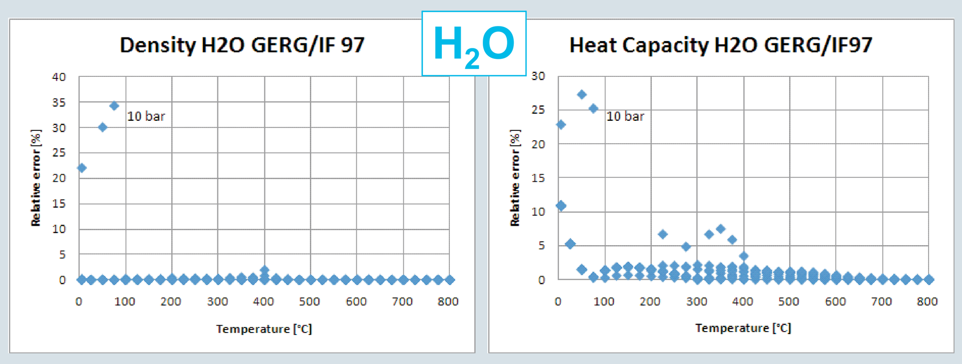


Figure 5: Comparison of GERG and IF97 [Wagner 2000]
Temperatures: 5…800 °C
Pressures: 1…300 bar

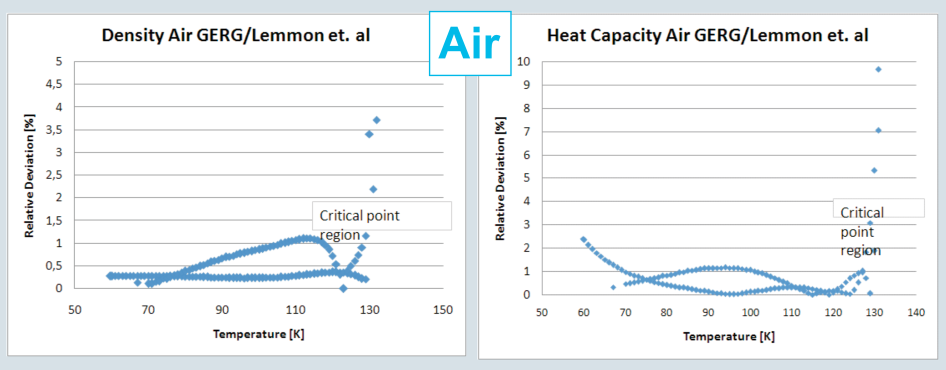


Figure 6: Comparison of GERG and Lemmon et. al [Lemmon 2000]
Temperatures: 60…133 K
Pressures: 0,002…10,5 MPa

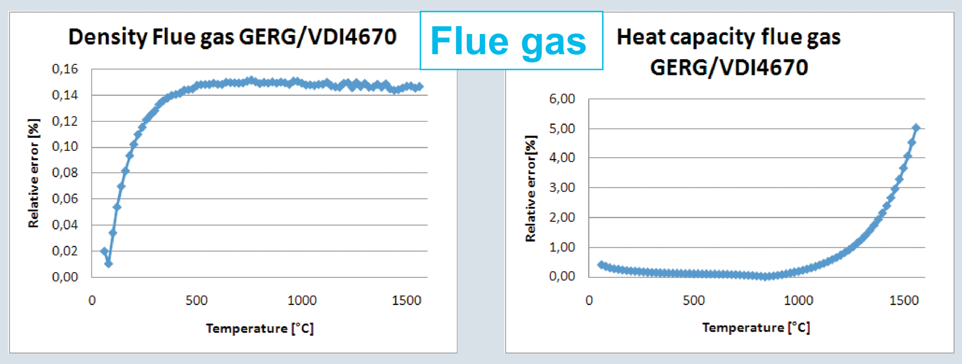


Figure 7: Comparison of GERG and VDI 4670
Flue gas composition (lignite):
N_2:0,629 O_2:0,029 CO_2:0,196 H_2O:0,143 SO_2:0,002
1 bar, 0…1600°C

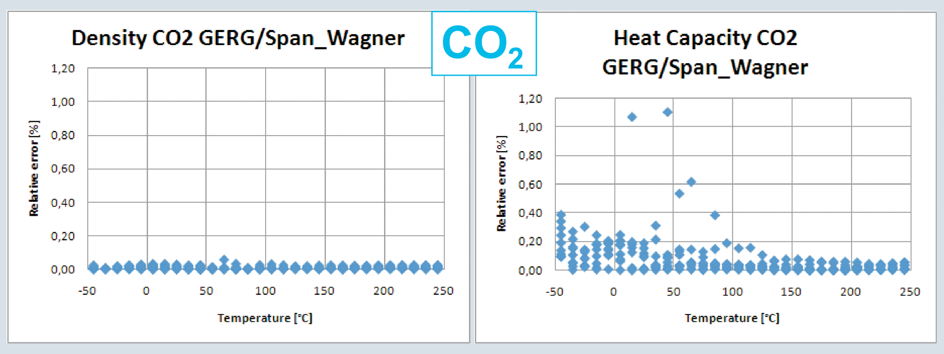


Figure 8: Comparison of GERG and Span/Wagner Equation for CO_2 [Span 1996]
Temperatures: -50…250°C °C
Pressures: 1…300 bar

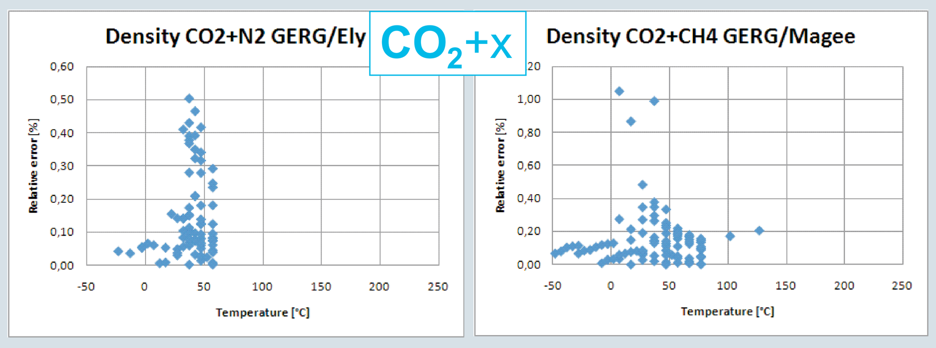
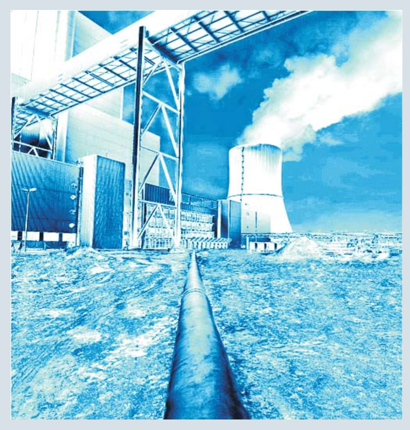


Figure 9: Comparison of GERG and meas. data [Ely 1989, Magee 1988]
CO_2+ 1,8 % N_2 CO_2+ 2 % CH_4
Temperatures: -50…250°C °C
Pressures: 1…300 bar

5. Conclusions

- GERG2008 is excellent for providing properties of natural gas mixtures
- Larger errors for liquid air (or other liquid mixtures) are to be expected
- For gaseous mixtures there are smaller errors
- There are some problems with water (deviations and software bugs in the excel implementation)
- There are larger errors for CO_2 mixtures in critical point region
- Even if small amounts of other gases are present, CO_2 mixture properties will be predicted less reliable
- Good for a first guess of properties occuring in Oxyfuel systems
- Good for simulations - if results are compared to measurement data in parallel and time is no restriction
- Transport properties are not regarded at all



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