ON THE USE OF HIGHLY ACCURATE THERMODYNAMIC PROPERTY MODELS IN PROCESS SIMULATION

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ABSTRACT

Liquefaction, transport and evaporation are the most essential processes in the LNG (Liquefied Natural Gas) process chain. For the efficiency of this process chain particularly the very energy intensive liquefaction process needs to be optimised. Commercially available process-simulation tools in combination with very detailed in-house models for key components are used to determine the layout of this process. The simulation involves complex mass and energy balances, and requires primarily accurate data for phase equilibrium, density, enthalpy and entropy of the involved fluids. To predict amount and composition of the gas fed into the pipeline grid after re evaporation of the LNG, phase equilibria during transport an evaporation need to be described and the density of the LNG needs to be known with high accuracy. An analysis of CCS (Carbon Capture and Storage) processes shows that similar requirements result from energy processes at high pressure (particularly relevant for integrated capture in IGCC plants and for oxyfuel gas-turbines), from compression of the resulting CO_2-rich mixtures and from issues related to their pipeline or ship transport. Security and operability issues require consideration of complex phase equilibria, which involve vapor, liquid and solid phases, and of additional properties like speed of sound and Joule-Thomson effect.

In the above mentioned applications, thermodynamic properties are commonly calculated from typical engineering equations of state, in most cases from cubic equations of state provided by the commercial simulation packages. It is shown that the application of such simple models results in significant deviations for thermodynamic properties, which are highly relevant for process simulations particularly at low temperature and at supercritical states. A Cape Open interface [1] was programmed to enable the use of state of the art fundamental equations of state for mixtures in process simulation tools. While the most advanced of these equations, the GERG-2008 model by Kunz and Wagner [2,3], describes natural gas mixtures very well [4], some modifications are required to achieve an accurate description of CCS relevant systems as well [5].

1. INTRODUCTION

Evaporation, transport and liquefaction are important processes in the LNG process chain. High expectations on the economic efficiency, the product quality and environmental safety result in increasing demands on design and operation of these systems. Fundamental contributions to the optimisation of systems can be expected from detailed and sufficiently accurate simulations of the processes. For these simulations an accurate representation of thermophysical properties is essential.

Results of process simulations are influenced by the property model used. New, highly accurate equations of state represent an unused potential for process modelling. The GERG-2008 by Kunz and Wagner [2] is an equation of state that describes mixtures of arbitrary composition consisting of up to 21 specified components. It covers the gas and liquid phase as well as the overcritical region and the vapour-liquid equilibrium with the highest accuracy possible. It was adopted by the GERG (Groupe Européen de Recherche Gazières) as new reference equation of state for natural gases. In order to embed the new reference equation into various simulation tools, the software available for the GERG-2008 equation of state has been adapted to the CAPE-OPEN standard [1]. This standard defines rules and interfaces that allow CAPE (Computer-Aided Process Engineering) applications or components to interoperate. Because the standard is supported by various commercial simulation tools the programmed GERG-2008 property package is not limited to a single simulation software alone. Using the property package allows consistent and stable calculations of thermodynamic properties.

In order to examine the influence of different property models on process simulation, cubic equations by Peng and Robinson [6] and by Redlich, Kwong and Soave [7] are taken into account. Furthermore, the modified Benedict-Webb-Rubin type equation of state by Lee and Kesler [8] in connection with the mixture model by Plöcker [9] is reviewed. For all these property models, the binary parameters of Knapp et al. [10] are used. It is shown that the uncertainties of these simple equations of state result in uncertainties for simulations of processes in the liquefied natural gas processes chain.

While conventional power cycles can be calculated with ideal gas models - except for the properties of water and steam - using these ideal gas models leads to invalid results for typical applications in the Carbon Capture and Storage (CCS) chain. For example, the density of CO_2 at pipeline pressure deviates from the density calculated from the ideal gas model by about 150%. Demands for accurate thermophysical property models of mixtures were formulated both by companies involved in the development of CCS technologies and by international standardization organizations, e.g. by IAPWS [11]. As one of the projects funded by the E.ON International Research Initiative, the project Equation of State for Combustion Gases and Combustion Gas Like Mixtures (EOS-CG) focuses on a thermodynamic property model that is sufficiently accurate in the relevant range of mixtures, temperatures, and pressures (from humid air to compressed liquefied carbon dioxide). It has been shown that among the available property models the GERG-2008 equation of state yields the best description of CCS relevant mixtures as well. However, some improvements are required for binary systems, which are highly relevant for CCS applications while they are less important for the natural gas applications the equation was originally developed for.

2. Comparing Results for Thermodynamic Properties

As LNG is transported and stored in the saturated liquid phase, an accurate representation of thermodynamic properties in this region is significant. The density is an essential thermal property for billing of LNG and for modelling of partial vaporisation processes during a ship transport. Caloric properties must be considered e.g. for the simulation of heat exchangers. As the enthalpy needs a defined reference point that has an influence on the comparison of property models for calculating caloric properties, the isobaric heat capacity is studied. The isobaric heat capacity c_p describes the derivative of the enthalpy h with respect to temperature T at constant pressure p.

Low temperatures in the liquid phase of natural gases result in experimental difficulties and ultimately in a lack of experimental data for properties of LNG. However, the GERG-2008 equation [3] and the

equations of Peng-Robinson [6], Redlich-Kwong-Soave [7] and Lee-Kesler-Plöcker [8,9] allow for calculations of thermodynamic properties of LNG.

Table 1: Typical composition of LNG being shipped from Libya [mol-%]

CH_4	N_2	C_2H_6	C_3H_8	$n-C_4H_{10}$
83.2	0.9	11.8	3.5	0.6

Figure 1 and Figure 2 show deviations of calculated and measured densities and isobaric heat capacities from results of the GERG-2008 equation. Calculations were conducted along the saturated liquid line for a temperature range from 110 to 195 K and for the LNG composition given in Table 1. The plotted experimental data represent different compositions, which were of course considered when deviations to the GERG-2008 equation were calculated. The LNG densities were measured at the National Bureau of Standards in the USA (today: National Institute of Standards and Technology, NIST) by Haynes and Hiza [12,13] with an uncertainty of $\Delta\rho/\rho \leq 0.1$ %. The experimental data for the isobaric heat capacities of a LNG mixture were measured at the Koninklijke/Shell-Laboratory in Amsterdam, Netherlands by van Kasteren und Zeldenrust [14]. The uncertainty is estimated by the authors with $\Delta c_p/c_p \leq 1$ %.
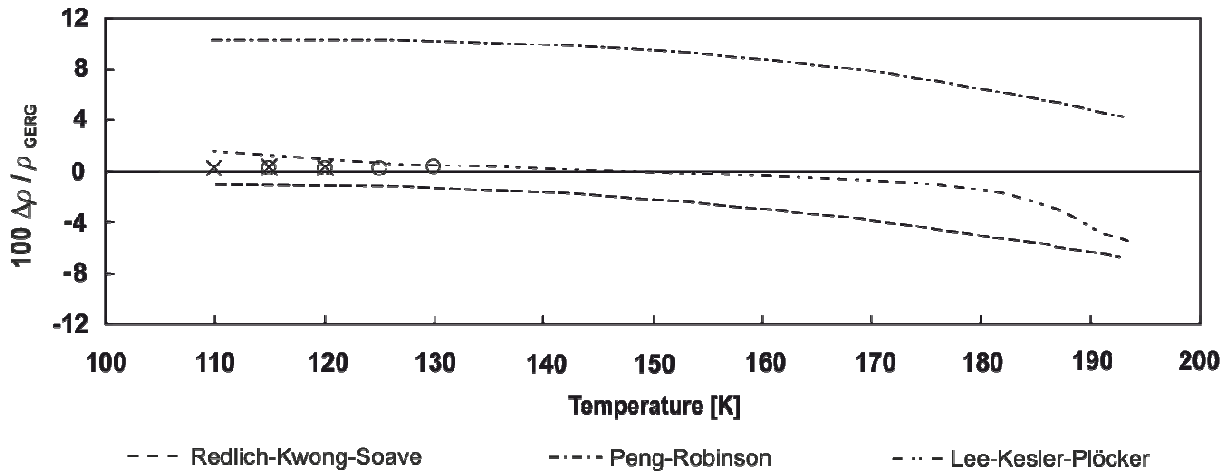

Figure 1: Percentage deviations of saturated liquid densities of LNG measured by [12,13] and calculated with different property models from results obtained with the GERG-2008.
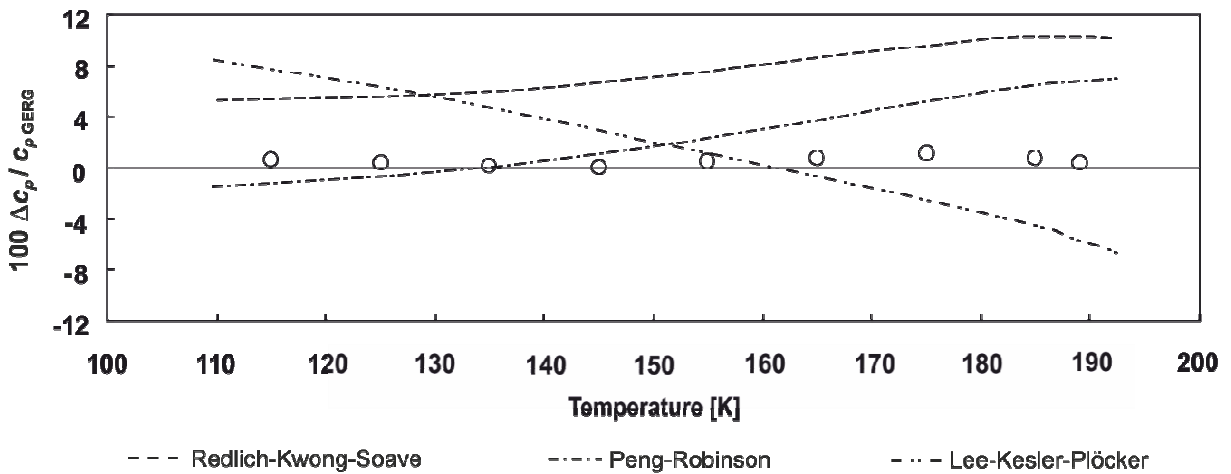

Figure 2: Percentage deviations of liquid isobaric heat capacities of LNG measured by [14] and calculated with different property models from results obtained with the GERG-2008.

Saturated liquid densities calculated with the equation of Peng-Robinson deviate by more than 10 % from results of the GERG-2008. Maximum deviations of the Redlich-Kwong-Soave model are above -7 % for higher pressures. The Lee-Kesler-Plöcker model results in deviations of -5 % at a pressure of 4 MPa. For LNG mixtures, the GERG-2008 equation accurately represents the experimental data for densities within ±(0.06 – 0.4)%. The deviations observed for the analysed property models exceed this uncertainty by far.

Measured isobaric heat capacities at saturated liquid conditions are described by the reference equation within ±1 % which is in agreement with the experimental uncertainty of the available data. Figure 2 shows the poor quality of cubic equations for caloric properties in the liquid phase. The maximum deviation exceeds the uncertainty of the GERG-2008 equation by a factor of 5. Significant differences can also be found for the Lee-Kesler-Plöcker model as deviations increase to 8%.

While typical natural gas systems are described very well, some systematic deviations were found particularly for the system CO_2 / water, which is probably the most important binary system for the calculation of thermodynamic properties in CCS processes. As an example, Figure 3 shows deviations between measured densities and densities calculated from the GERG-2008 model. Some improvements are reported for a preliminary modified model resulting from the EOS-CG project.
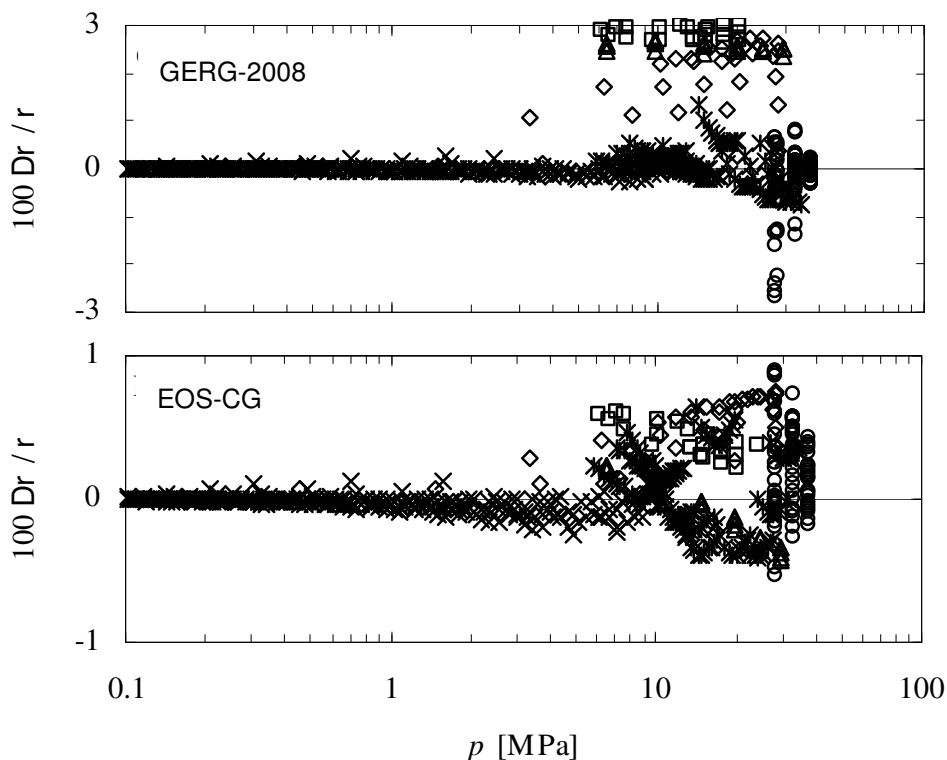

Figure 3: Comparison of experimental and calculated density values for the system CO_2 / Water. The zero line represents values calculated from the GERG-2008 [3] model and from a preliminary modified model. For details on the selected data sets see [5].

3. Comparisons for Process Simulations

Within the LNG value chain, the liquefaction of natural gas is the process generating the highest investment and operating costs. Thus, its accurate simulation is of great importance. The only liquefaction plant in Europe is called "Snøhvit" and is operated in Hammerfest / Norway. By means of some data measured during actual operation and provided by Statoil the whole LNG sub cooling

process has been modelled with the simulation software Aspen HYSYS (V7.1) of AspenTech. The influence of different property models on the accuracy of the simulation can be shown by comparing calculated results with measured data. Figure 3 illustrates the simplified Snøhvit sub cooling process on the graphical user interface of Aspen HYSYS.
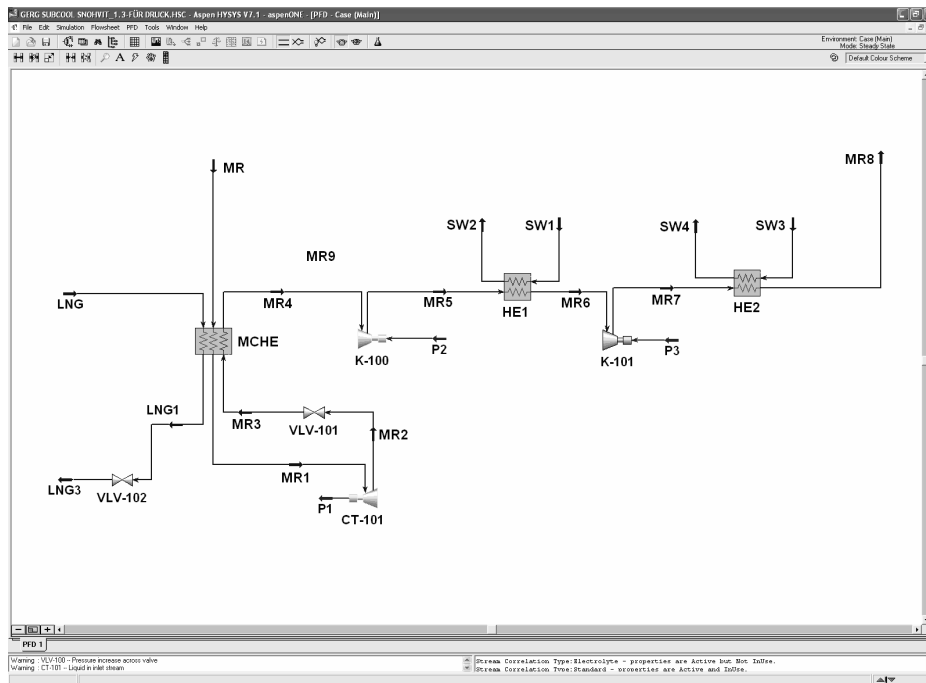

Figure 4: Simplified Snøhvit LNG sub cooling process shown on the graphical user interface of Aspen HYSYS

The most important component in the sub cooling process is the main cryogenic heat exchanger (MCHE) where a hydrocarbon mixture provides refrigeration for cooling LNG to approximately 120 K. Based on measured mass flow, temperature and pressure at the inlet and outlet of the heat exchanger an energy balance can be set up. It is assumed that heat losses are negligible compared to the transmitted heat flows. Theoretically this postulates that the sum of provided heat flow of the hot streams equals the sum of absorbed heat flow of the cold streams. For each property model examined the percentage deviation of the provided heat flow from the absorbed heat flow is given in Table 2.

Table 2: Percentage deviation of the provided heat flow from the absorbed heat flow for a modelled main cryogenic heat exchanger on basis of different property models.

Dev. [%]	GERG-2008 implemented via Cape Open	Peng-Robinson	Redlich-Kwong-Soave	Lee-Kesler-Plöcker
$100 \cdot \left(\dot{Q}_{hot} - \dot{Q}_{cold} \right) / \dot{Q}_{cold}$	-0.12	2.48	2.73	7.01

The simulation based on the GERG-2008 implemented into Aspen HYSIS via the Cape Open interface describes the heat balance with a deviation as small as -0.12%. Results shown in Table 2 confirm that the GERG-2008 simulates the LNG sub cooling heat exchanger with the highest accuracy of all property models examined. As experimental liquid phase isobaric enthalpy differences are represented by the GERG-2008 to within $\pm(0.5 - 1)\%$, deviations of simulated and measured heat flows are within the uncertainties of the reference equation. The use of cubic equations results in deviations of more than 2.4%, which are basically caused by their inaccuracy regarding the description of the vapour-liquid equilibrium of hydrocarbon mixtures. Large uncertainties for representing caloric properties at saturated liquid conditions of hydrocarbon mixtures with the equation of Lee-Kesler-

Plöcker were illustrated in Figure 2. They explain why simulated results for heat flows deviate by up to 7% from measured data.

For CCS applications, no comparisons of simulated processes with established equipment could be carried out yet. However, comparisons between simulations based on different thermodynamic property models show results rather similar to those observed for natural gas and liquefied natural gas. While deviations are rather small in the gas phase, significant differences in the results can be observed at supercritical states, for the calculation of phase equilibria and in the liquid phase. The GERG-2008 model [3] is superior to typical engineering equations of state. However, large deviations are observed for calculations involving water rich liquid phases. Work on modifications improving the GERG-2008 model with regard to these systems is on its way [5,15].

4. CONCULSION AND OUTLOOK

It has been shown that the application of accurate fundamental equations of state for mixtures in process simulations leads to a significantly increased accuracy of results. For the liquefied natural gas process chain application of the GERG-2008 model [3] yields superior results. With the Cape Open interface developed by Dauber and Span [1] the software available for the GERG-2008 can easily be adapted to common process simulation tools.

For the simulation of processes typical for Carbon Capture and Storage the GERG-2008 model is superior to common engineering equations as well, but some modifications are required. Ongoing work addresses the description of the system CO_2 / water, of water rich liquid phases and an improved calculation of phase equilibria. Complex phase equilibria involving liquid / liquid and liquid / solid equilibria will be addressed as well. In principle it has already been shown that fundamental equations of state models for the fluid phase of mixtures allow for an accurate description of such systems.

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