Errors Due to Use of the AGA8 Equation of State Outside of Its Range of Validity

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1   INTRODUCTION

In any measurement system (apart from the most trivial) the model(s) used to convert the basic outputs of transducers to the final quantity of interest form an integral part of the system and will have an impact on the overall uncertainty of measurement achievable. For example, a resistance-temperature device such as a platinum resistance thermometer makes use of an equation relating the resistance of platinum wire to temperature. Similarly, an ultrasonic flow meter makes use of a model describing the time of flight of the ultrasonic signal across the flowing fluid. In both these cases (and many others), the direct influence of the models are reduced, through calibration of the complete measurement system. However, in the case of gas metering systems, for example those used to account for production in the North Sea, this is not necessarily the case.

For custody-transfer standard flow measurement of dry, processed gaseous hydrocarbons in the UK sector of the North Sea, OGA's 'Guidance Notes for Petroleum Measurement' specify that the flow rate measurements may be in either volumetric or mass units [1]. They also stipulate that where volume is the agreed measurement unit, it should be referred to the standard reference conditions of 15 °C temperature and 1.01325 bar absolute pressure (bar (a)). This requires determination of the gas density at the flow meter, which may be achieved by

- continuous direct measurement by an on-line densitometer or
- calculation, using a recognised equation of state together with measurements of gas composition, temperature and pressure.

If the calculation method is used, the performance of the model (the equation of state) will have a direct impact on the uncertainty of the parameter of interest, the quantity of flowing gas.

Numerous equations of state have been developed, including cubic models such as the Peng-Robinson [2] and Redlich-Kwong-Soave [3] models or corresponding-states models such as that of Lee and Kesler [4] and used for the calculation of gas density from composition.

More recently, the AGA 8 [5] method has been fairly universally adopted for the calculation of natural gas density and, for example, forms an integral part of the measurement infrastructure in the North Sea, being programmed in to flow computers and written in to many gas sales agreements. However, gas compositions may or may not lie within the pipeline quality gas specifications required to obtain the lowest uncertainty with the AGA 8 method, possibly due to the compositional changes from ageing fields or for complex fields exhibiting non-

standard gas compositions. This leads to the requirement to review the use of the AGA 8 method and investigate possible alternatives.

2 BACKGROUND

The AGA 8 method is based on a residual Helmholtz free energy equation of state which enables the calculation of thermodynamic properties of natural gases consisting of up to 21 components. The structure of the equation of state is based on a total of 58 polynomial terms and polynomial terms in combination with exponential functions which require 860 different parameters. The current version of the method, AGA 8-1992 [5], is the method recommended in ISO 12213:2005 [6] when a detailed composition is available.

Although the range of validity of the AGA 8 method is limited to the gas phase, it is most often applied to the supercritical state, but, despite this, it generally performs sufficiently well.   If all the components are within the specified composition ranges for pipeline quality gas [5], calculated densities will have an uncertainty of the order of 0.1 % (at k=2) for temperatures between -10 and 65 °C at pressures up to 120 bar (a). Table 1 summarises the limits required to obtain the 0.1 % uncertainty in calculated density.

Table 1 – AGA 8 Applicability Limits (Pipeline Quality Gas)

Parameter	Min	Max	Parameter	Min	Max
pressure / MPa	0	12	butanes / mol%	0.0	1.5
temperature / K	263	338	pentanes / mol%	0.0	0.5
superior cal value / MJ m^{-3}	30	45	hexanes / mol%	0.0	0.1
relative density / -	0.55	0.80	heptanes / mol%	0.0	0.05
methane / mol%	70.0	100.0	octanes+ / mol%	0.0	0.05
nitrogen / mol%	0.0	20.0	hydrogen / mol%	0.0	10.0
carbon dioxide / mol%	0.0	20.0	carbon monoxide / mol%	0.0	3.0
ethane / mol%	0.0	10.0	helium / mol%	0.0	0.5
propane / mol%	0.0	3.5	water / mol%	0.0	0.015

However, for mixtures with components in the extended composition range and / or at temperatures and pressures outside the above limits (see Table 2), the uncertainty increases to between 0.2 and 0.5 % (at k=2) and is effectively indeterminate for compositions outside the extended range of applicability (see Annexes E and F in ISO 12213:2005 Part 2 [6]).

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Table 2 – AGA 8 Wider-Range Applicability Limits
(Extensions highlighted in red)

Parameter	Min	Max	Parameter	Min	Max
pressure / MPa	0	65	butanes / mol%	0.0	1.5
temperature / K	225	350	pentanes / mol%	0.0	0.5
superior cal value / MJ m^{-3}	20	48	hexanes / mol%	0.0	0.1
relative density / -	0.55	0.90	heptanes / mol%	0.0	0.05
methane / mol%	50.0	100.0	octanes+ / mol%	0.0	0.05
nitrogen / mol%	0.0	50.0	hydrogen / mol%	0.0	10.0
carbon dioxide / mol%	0.0	30.0	carbon monoxide / mol%	0.0	3.0
ethane / mol%	0.0	20.0	helium / mol%	0.0	0.5
propane / mol%	0.0	5.0	water / mol%	0.0	0.015

To overcome these limitations, Ruhr-Universität Bochum developed a new wide-range equation of state for natural gases and other mixtures, covering the same 21 components as the AGA 8 method. The method, explicit in the Helmholtz free energy, was adopted by GERG in 2004 [7] and a revised version was adopted in 2008 [8]. The mixture model uses accurate equations of state in the form of fundamental equations for each mixture component along with formulations developed for binary mixtures that take into account the residual mixture behaviour. Although the quoted uncertainty in density for the gas phase is similar to that for the AGA 8 method [5,6], the GERG-2008 method achieves this over a wider range of temperatures, pressures and compositions. The GERG-2008 method has now been adopted as an ISO standard, ISO 20765-2 [9].

The Peng-Robinson model [2] is a cubic equation of state of general applicability and has been widely used to model the phase behaviour of hydrocarbon systems. One common requirement for all phase equilibria models is for binary interaction parameter (BIP) information. BIPs represent the deviations from ideality for interactions between a given binary pair. Since the general approach to mixtures is the treatment of a mixture as a combination of binary pairs, the BIPs are extremely important for the representation of correct behaviour. For the Peng-Robinson model, for example, the results obtained, in particular for the location of the vapour – liquid phase boundary, are sensitive to the availability and exact values of the BIPs. Furthermore, particularly in regions close to the phase boundary, the uncertainties in key properties such as the density and compressibility of a mixture can become quite large.

In addition to having access to the GERG-2008 method (through the Bochum University implementation), TUV NEL has its own package, PPDS, for the calculation of thermophysical properties of fluids and fluid mixtures. All of the methods used in PPDS are taken from open literature and the user can select which method(s) to apply for each calculation. For the case studies presented in this paper the Peng-Robinson method was used with the PPDS default BIP values and the PPDS implementation of the AGA 8 method was used.

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A key limitation of both the AGA 8 and GERG-2008 methods is the fixed 21-component data set. This means that components present in a real gas mixture which are not within this list must be assigned to existing components. Guidance is provide on appropriate assignments [5,6]; for example, benzene is assigned to *n*-pentane, toluene to *n*-heptane. However, there still remains the problem of dealing with components for which no specific assignments are given; for case study two, for example, two of the compositions included pseudo-components. These are effectively unidentified petroleum fractions obtained from laboratory analysis and defined by boiling point and molecular weight.

To overcome this limitation, TUV NEL has implemented a Petroleum Fractions package within its PPDS package. A petroleum fraction is a pseudo-component composed of a mixture of components, usually hydrocarbons. It is usually defined by some of its physical properties, particularly boiling point and density. The Petroleum Fractions package is a subroutine of prediction and estimation methods which calculates the thermodynamic and transport properties from this input. For example, liquid density is calculated using the Hankinson and Thomson method [10]. In the PPDS implementation, pseudo-components can be mixed with pure components from the PPDS System Pure databank to create representative mixtures.

3   CASE STUDIES

Two case studies are presented which illustrate potential problems when using the AGA 8 method outside its range of validity. Case study one is an example of where some of the components have compositions outside even the extended composition ranges allowed by the AGA 8 method whilst case study two examines the effect of mixtures with components not in the 21-component AGA 8 list.

3.1   Components Concentrations Outside Allowed Ranges

This case study represents a system in which export gas is produced by two stages of separation of the hydrocarbon fluid recovered from the well and subsequent compression of the flashed gas to a pressure to enable export to be completed. In normal operation gas from the second stage separation goes for final compression and export. Special cases occur where the gas from the second stage (low pressure) separator does not go through to export, resulting in a lighter gas being exported.

Calculations were carried out for six cases, three for normal operation and three for the situation when the low pressure separator was off. For all six cases the density and compressibility at base conditions (T = 15°C, P = 1.01325 bar(a)) and average line conditions (T = 37.22°C, P = 117.46 bar(a)) were calculated by the various methods and the results compared.

For normal operation, the three compositions used were average data representing an extended period of operation plus data for two compositions corresponding to samples with the minimum and maximum methane contents respectively.

Similarly, for operation with the low pressure separator off, the same three input compositions were used.

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Table 3 shows the input compositions (full 21 component AGA 8 requirement) and Table 4 the calculated values of the outputs (molecular weights, densities and compressibilities) from the AGA 8 method.

Tables 5 and 6 show the differences between the results calculated by the AGA 8 method and the Peng-Robinson method and between the AGA 8 method and the GERG-2008 method respectively.

3.1.1 Discussion

At base conditions all three calculation methods produce very similar values, with a maximum difference of -0.05 % in density for one composition. However, at line conditions significant differences are observed, with a maximum of 2.30 % for one composition between the AGA 8 and Peng-Robinson methods and 4.14 % between the AGA 8 and GERG-2008 methods for the same composition.

These differences are consistent with the observation that for all the compositions studied, several of the components had mole fractions significantly outside even the extended AGA 8 ranges, with the errors having an almost linear dependence on the methane and propane concentrations, as shown in Figures 1 and 2 respectively.

Table 3 – Case Study 1: Input Compositions (mol %)

Component	Normal operation			LP off		
	Average	CH_4 min + C_3H_8 max	CH_4 max + C_3H_8 min	Average	CH_4 min + C_3H_8 max	CH_4 max + C_3H_8 min
Methane	48.76	41.00	51.57	55.41	49.02	60.72
Nitrogen	1.11	0.84	1.18	1.27	1.05	1.41
Carbon Dioxide	2.76	2.51	2.91	3.02	2.75	3.21
Ethane	15.93	16.27	16.06	15.78	15.76	15.68
Propane	20.04	24.24	18.71	16.51	19.67	14.11
Water	0.00	0.00	0.00	0.00	0.00	0.00
Hydrogen Sulphide	0.00	0.00	0.00	0.00	0.00	0.00
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00
Carbon Monoxide	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	0.00	0.00	0.00	0.00	0.00	0.00
i Butane	3.52	4.66	3.03	2.55	3.53	1.79
n Butane	5.77	7.80	4.81	3.98	5.81	2.53
i Pentane	0.96	1.25	0.82	0.65	0.97	0.29
n Pentane	0.83	1.05	0.69	0.56	0.85	0.22
Hexane	0.27	0.33	0.23	0.23	0.41	0.04
Heptane	0.04	0.05	0.02	0.06	0.15	0.00
Octane	0.04	0.00	0.00	0.01	0.03	0.00
Nonane	0.00	0.00	0.00	0.00	0.00	0.00
Decane	0.00	0.00	0.00	0.00	0.00	0.00
Helium	0.00	0.00	0.00	0.00	0.00	0.00
Argon	0.00	0.00	0.00	0.00	0.00	0.00

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Table 4 – Case Study 1: AGA 8 Results

	Normal operation			Normal operation		
	Average	CH$_4$ min + C$_3$H$_8$ max	CH$_4$ max + C$_3$H$_8$ min	Average	CH$_4$ min + C$_3$H$_8$ max	CH$_4$ max + C$_3$H$_8$ min
Molecular weight / amu	29.978	32.734	28.812	27.530	30.062	25.399
Density$_{base}$ / kgm^{-3}	1.278	1.398	1.227	1.172	1.281	1.080
Compressibility$_{base}$ / -	0.9923	0.9905	0.9929	0.9936	0.9922	0.9948
Density$_{line}$ / kgm^{-3}	314.52	378.09	284.13	250.29	316.56	200.64
Compressibility$_{line}$ / -	0.4338	0.3941	0.4616	0.5006	0.4323	0.5762

Table 5 - Case Study 1: Differences Between AGA 8 and PPDS Calculations

	Normal operation			LP off		
	Average	CH$_4$ min + C$_3$H$_8$ max	CH$_4$ max + C$_3$H$_8$ min	Average	CH$_4$ min + C$_3$H$_8$ max	CH$_4$ max + C$_3$H$_8$ min
δMW / %	0.00	0.00	0.00	0.00	0.00	0.00
$\delta\rho_{base}$ / %	-0.03	-0.02	-0.04	-0.05	-0.03	-0.05
δZ_{base} / %	0.03	0.02	0.04	0.04	0.03	0.05
$\delta\rho_{line}$ / %	1.68	2.30	0.84	0.08	1.84	-0.81
δZ_{line} / %	-1.66	-2.25	-0.83	-0.08	-1.81	0.81

Table 6 - Case Study 1: Differences Between AGA 8 and GERG-2008 Calculations

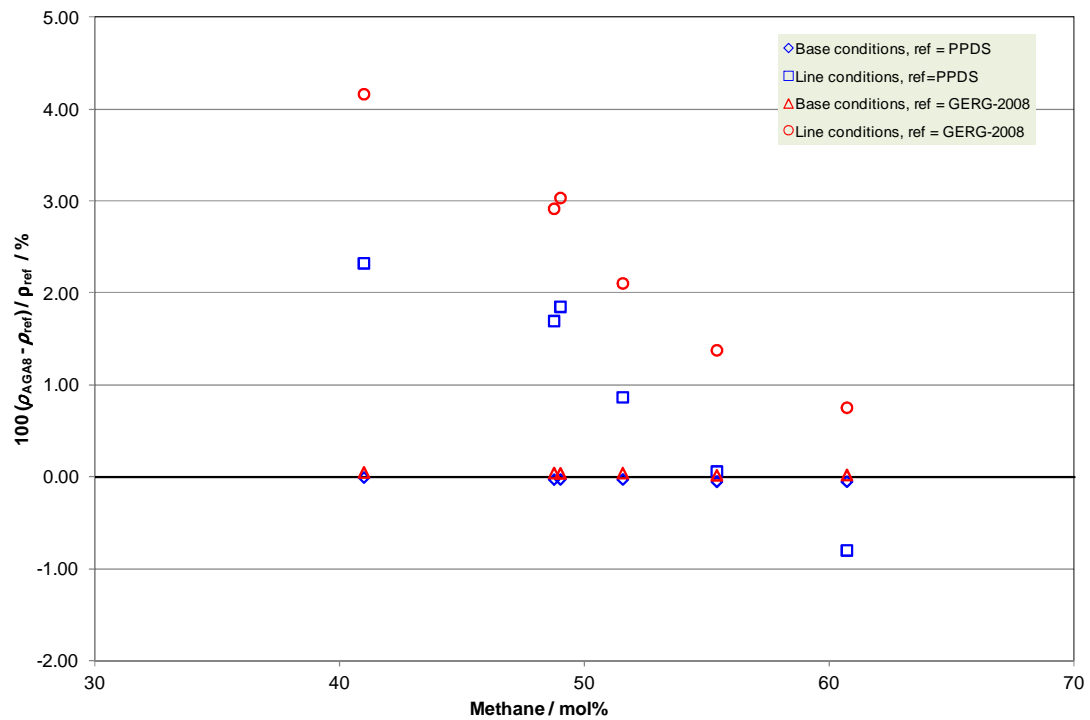|	Normal operation			LP off		
	Average	CH$_4$ min + C$_3$H$_8$ max	CH$_4$ max + C$_3$H$_8$ min	Average	CH$_4$ min + C$_3$H$_8$ max	CH$_4$ max + C$_3$H$_8$ min
δMW / %	0.01	0.00	0.00	0.00	0.00	0.00
$\delta\rho_{base}$ / %	0.04	0.04	0.03	0.03	0.04	0.02
δZ_{base} / %	-0.03	-0.03	-0.03	-0.02	-0.03	-0.02
$\delta\rho_{line}$ / %	2.91	4.14	2.08	1.40	3.02	0.75
δZ_{line} / %	-2.82	-3.98	-2.03	-1.38	-2.93	-0.74

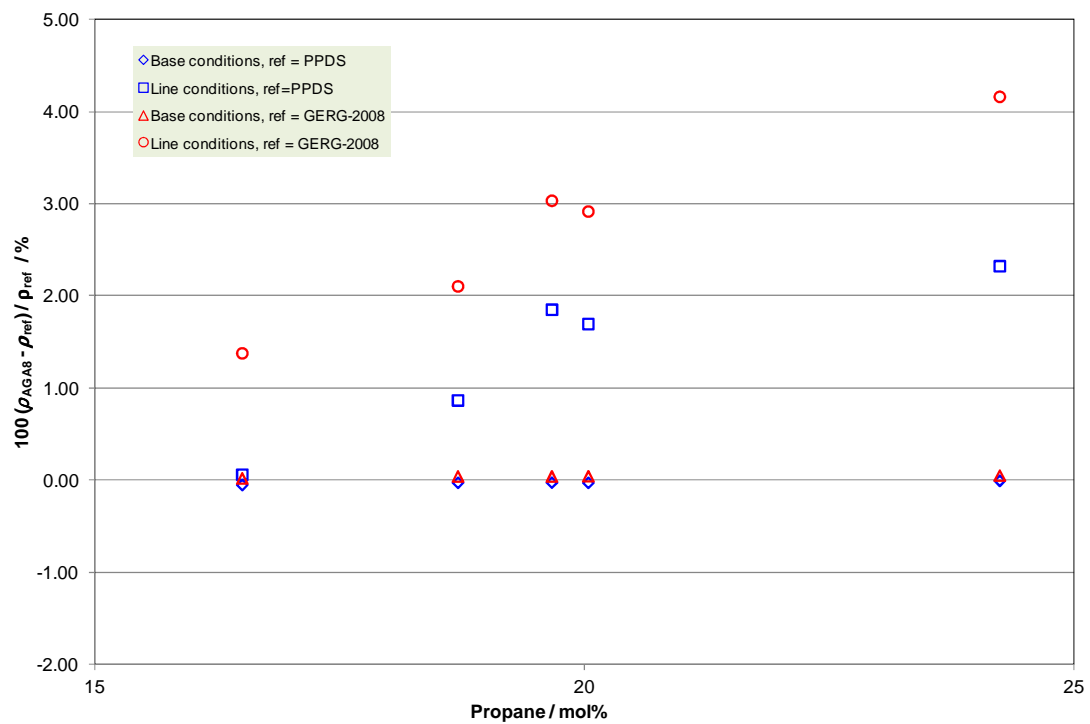Fig. 1 – Case Study 1: AGA8 Differences as a Function of Methane Concentration at Line Conditions

Fig. 2 – Case Study 1: AGA8 Differences as a Function of Propane Concentration at Line Conditions

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3.2   Components not in AGA 8 List.

This case study examined the impact of changes in gas composition on the calculated properties (in particular the density and compressibility) of gas mixtures entering a gas processing plant from a number of different fields. For this case study it was assumed that the feed gas custody transfer metering package was based on the use of an in-line ultrasonic flow meter, to provide volumetric flow rate data, and a gas chromatograph, to enable density to be calculated from composition. However, depending on which fields are producing, there may be components in the feed gas stream that are not in the 21 component set covered by the AGA 8 method [5,6]. If a number of partners were involved in such a project, it would be important that whatever method was used to determine the gas density, it was accepted by all partners and also by the regulator.

For the five mixtures examined in this case study, phase envelopes were calculated using TUV NEL's PPDS implementation of the Peng-Robinson method and compared with those obtained using the Bochum University implementation of the GERG-2008 method. In addition, for each case the density and compressibility of the gas was calculated at its normal operating temperature and pressure using all three methods, with the AGA 8 values being taken as the reference.

For the first two mixtures, pseudo-components were added to the feed gas compositions by creating PPDS pseudo-components based on representative boiling point, molecular weight and density data.

To examine the impact of components such as hydrogen sulphide and the 'BTEX' components (benzene, toluene, ethyl-benzene and xylene), calculations were done for three variations for each of the five mixtures:

1. H_2S etc + BTEX all set to representative maximum values,
2. H_2S etc + BTEX all set to 0.5 x representative maximum values, and
3. H_2S etc + BTEX all set to 0.

Table 7 shows the input compositions for these three variations for Mixture 1. The compositions for Mixture 2 were broadly similar, the main difference being that the methane content was about two percent lower, with the balance being made up of slightly higher ethane and propane contents. Mixture 3 was mainly methane (96.24 mol% excluding BTEX components) whilst Mixtures 4 and 5 had methane contents of ~66 and ~78 mol% respectively, with most of the remainder of these mixtures being ethane and propane.

Calculations were carried out for the three variations for all five mixtures. For all of the compositions all the components are available within the System Pure databank in TUV NEL's PPDS package or had been created as pseudo-components and hence calculations using the Peng-Robinson model could be undertaken using the input compositions.

When using the AGA 8 and GERG-2008 models it was necessary to assign 'missing' components. Specifically, this relates to the BTEX components, undecane and the pseudo-components. For the BTEX components, the assignments were done in accordance with Table 1 in ISO 12213:2005 [2], as shown in Table 8.

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Table 7 – Case Study 2: Input Compositions for Mixture 1
(mol %)

Component	H₂S etc and BTEX set to max values	H₂S etc and BTEX set to 0.5 x max values	H₂S etc and BTEX set to 0
Nitrogen	0.272	0.275	0.279
Methane	87.540	88.660	89.810
Ethane	5.272	5.339	5.409
Propane	2.621	2.655	2.689
i-Butane	0.411	0.416	0.421
n-Butane	0.657	0.666	0.674
i-Pentane	0.217	0.220	0.223
n-Pentane	0.209	0.212	0.215
Hexane	0.067	0.068	0.069
Heptane	0.033	0.033	0.034
Octane	0.013	0.013	0.013
Nonane	0.003	0.003	0.003
Decane	0.001	0.001	0.001
Undecane	0.000	0.000	0.000
PseudoComp1	0.019	0.019	0.019
PseudoComp2	0.081	0.082	0.083
PseudoComp3	0.031	0.031	0.031
PseudoComp4	0.022	0.022	0.022
PseudoComp5	0.004	0.004	0.004
Hydrogen sulphide	1.478	0.748	0.000
Carbon dioxide	0.735	0.372	0.000
Water	0.035	0.018	0.000
Benzene	0.178	0.090	0.000
Toluene	0.075	0.038	0.000
Ethyl benzene	0.013	0.007	0.000
o-Xylene	0.013	0.007	0.000

Table 8 – Case Study 2: Assignment of Minor Components
(as per ISO 12213:2005)

Minor or Trace Component	Assigned to
Benzene	n-pentane
Ethyl-benzene	n-hexane
Xylene	n-hexane
Toluene	n-heptane
Undecane	n-decane

Mixtures 1 and 2 included the pseudo-components. Since neither the AGA 8 nor GERG-2008 methods have defined methods for dealing with such components, three allocation methods were used:

1. to provide a worst case, all the pseudo-components were summed with n-decane,
2. to show the effect of ignoring pseudo-components, their compositions were set to zero, and
3. to provide the most realistic case, the pseudo-components were assigned by boiling point, as shown in Table 9.

Table 9 – Case Study 2: Assignment of Pseudo-components

Pseudo-component	Assigned to
PseudoComp1	*n*- hexane
PseudoComp2	*n*-hexane
PseudoComp3	*n*- heptane
PseudoComp4	*n*-heptane
PseudoComp5	*n*-octane

3.2.1 Effect of assignment of pseudo-components – mixtures 1 and 2.

For both cases the effects of assigning the pseudo-components are significant. For Mixture 1 the density difference between the AGA 8 and GERG-2008 methods changes from -0.52 % to +0.10 % whilst the density difference between the AGA 8 and the Peng-Robinson methods changes from -0.59 % to -0.16 %. The corresponding changes for Mixture 2 are slightly smaller, from -0.09 % to +0.07 % and -0.38 % to -0.09 % respectively, probably due to the slightly lower amounts of the pseudo-components in the Mixture 2 composition.

The effect of totally ignoring the pseudo-components is even more significant. Even taking the most realistic assignment, i.e. by boiling point, shifts of about 1.0 % and 0.7 % are seen for Mixtures 1 and 2 respectively for all three methods. Clearly, if such components are present, they must be accounted for, ideally in the most realistic manner possible. Although the AGA 8 and GERG-2008 methods do not explicitly include assignments for such components, since the shifts in density observed for all three models were consistent, assignment by boiling point would appear to be the best approach. However, this recommendation must be treated with some caution, since the amounts of the pseudo-components in these mixtures were relatively small.

The extreme effect of assigning the pseudo-components to *n*-decane for the GERG-2008 method on the phase envelopes can be seen by comparing Figures 3 and 4. For each sub-set within a case, the solid and dashed curves for each colour compare the phase envelopes calculated by the GERG-2008 and Peng-Robinson methods respectively.

For the base case (the green curves), the phase envelopes calculated by the two methods are fairly similar. As expected, adding the pseudo-components increases the size of the two phase region, moving the cricondbar to higher pressure and the cricondtherm to higher temperature. However, the shifts are very much more significant when the pseudo-components are assigned to *n*-decane rather than being assigned by boiling point, e.g. comparing the solid red curves in Figures 3 and 4 shows that the cricondbar has increased from about 115 bar(a) to over 140 bar(a). Similar effects were seen for Mixture 2.
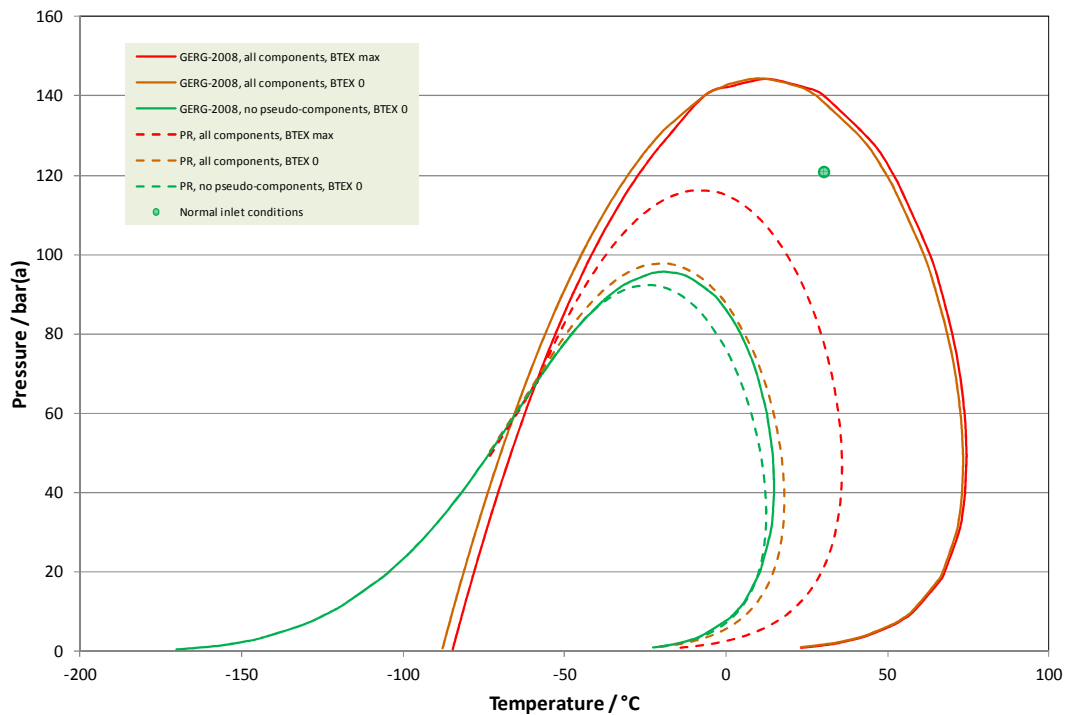
Fig. 3 – Case Study 2: Phase Envelopes for Mixture 1:
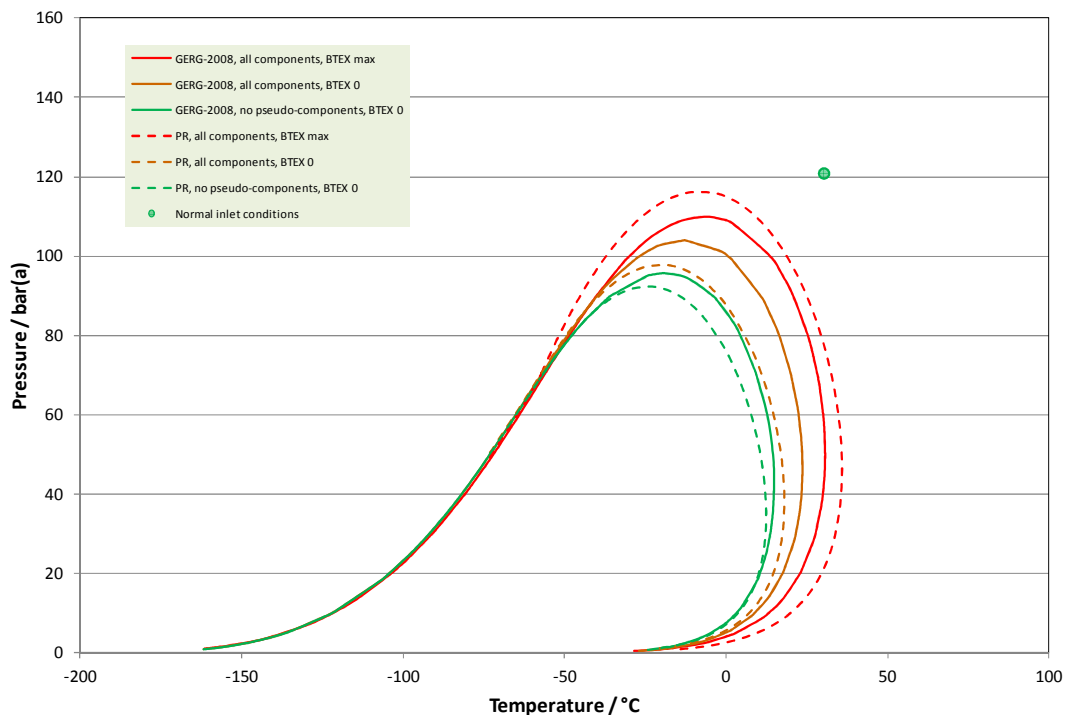Pseudo-components Assigned to C_{10}

Fig. 4 – Case Study 2: Phase Envelopes for Mixture 1:
Pseudo-components Assigned by Boiling Point

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3.2.2 Effects of other minor components – mixtures 3 to 5.

Although there are none of the pseudo-components present in the compositions for Mixtures 3 to 5, the effects of the other minor components can be clearly seen on the calculated densities and phase envelopes.

Since Mixture 3 is mainly methane (96.24 mol% excluding BTEX components), all the other components are essentially minor components, so significantly altering any of them will have a large effect. For all three methods, the differences in density between setting the H_2S etc and BTEX component compositions to their maximum values or to zero causes changes in density of between 5.8 % and 6.2 %. This also results in significant shifts in the calculated phase envelopes, as shown in Figure 5, resulting in much larger two-phase regions and shifts in the cricondbar and cricondtherm.

An apparent anomaly in the performance of the GERG-2008 and Peng-Robinson methods with regard to the effects of the minor components on the phase envelope and calculated densities is worth examining, as it illustrates some of the difficulties inherent in undertaking such calculations.

For Mixture 3, when all the minor components are set to their maximum concentrations, the densities calculated by the GERG-2008 and Peng-Robinson methods are in close agreement (89.210 and 89.205 kgm^{-3} respectively, i.e. less than 0.1 %) even though the calculated phase envelopes are quite different. On the other hand, when all the minor components are set to zero, although the calculated phase envelopes are similar, the calculated densities differ by 0.36 % (84.301 and 83.998 kgm^{-3} for the GERG-2008 and Peng-Robinson methods respectively).

These differences are believed to arise from the method of calculating the density. With both methods, the equation of state is solved at the specified conditions to determine the phase split and the phase compositions, based on the input compositions. In the GERG 2008 method the equation of state is also used to directly calculate the density. PPDS can also operate in this mode ('Consistent') but due to the known limitations of simple cubic equations of state, there is also an option to operate in 'Accurate' mode, in which the properties required are calculated by equations chosen to provide better representations of the those properties. Throughout this work PPDS was used in 'Accurate' mode, meaning that densities were calculated by applying a Lee-Kesler correction from the density calculated by the equation of state at the phase boundary to the required conditions.

For Mixture 3, the differences in the calculated phase boundaries between the GERG-2008 and Peng-Robinson methods when all the minor components are set to their maximum values reflects the differences in the BIPs used by the two methods for these minor components. The significant shift in the position of the phase boundary between the two extreme sub-cases (all minor components set to zero or set to maximum values) as calculated by the Peng-Robinson method makes a big difference in the magnitude of the correction applied by the PPDS calculation for the density. This is the likely origin of the apparent anomaly with regard to the performance of the two methods and clearly illustrates the importance of understanding the calculation methods in sufficient detail to explain such discrepancies. With PPDS, the user has full control over the calculation modes and all the key parameters (including BIPs) and the package also provides quality codes that provide information on corrections applied.
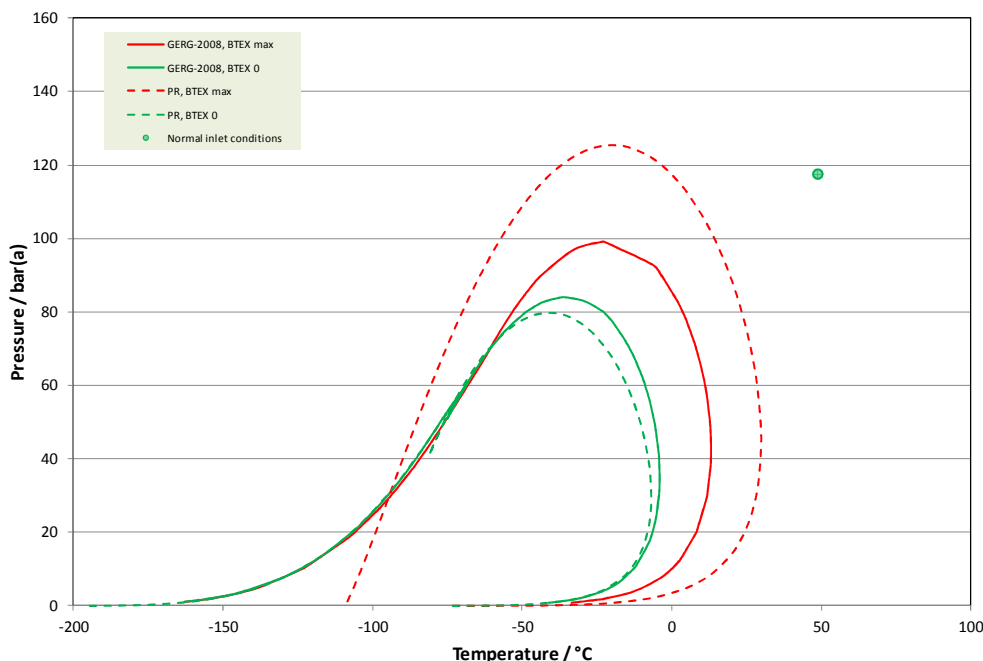
Figure 5 – Case Study 2: Phase Envelopes for Mixture 3

For Mixtures 4 and 5 the methane content is much lower that for the other three cases. For Mixture 4 it is actually below the normal limit for the AGA 8 method (70 mol%) and although it is within the extended range (down to 50 mol%), the propane content (almost 14 mol%) is significantly above even the extended limit (5.0 mol%). For Mixture 5, although the propane content is just above the extended limit (5.2 mol%), the butanes content (3.0 mol%) is double the limit (1.5 mol%). Not surprisingly, this leads to significant differences in the densities calculated by the three methods but, as with the first three cases, the trends are not immediately obvious.

For both cases, ignoring the minor components causes the calculated densities to change by between 3.3 % and 4.7 % from the values when all the components are set to their maximum values. The most extreme effects are seen with Mixture 4, where the density difference between the AGA 8 and GERG 2008 methods changes from -0.79 % to -0.63 % while the density difference between the AGA 8 and Peng-Robinson methods changes from +0.59 % to -0.12 %, again indicating the sensitivity of the properties to BIPs and calculation modes. For Mixture 5 the corresponding shifts are from -0.20 % to -0.12 % for the AGA 8 / GERG-2008 differences and from +0.44 % to -0.10 % for the AGA 8 / Peng-Robinson differences.

In contrast to Mixture 3 however, the shifts in the phase boundaries for Mixtures 4 and 5 are much less significant when the BTEX components are ignored, as shown in Figures 6 and 7.
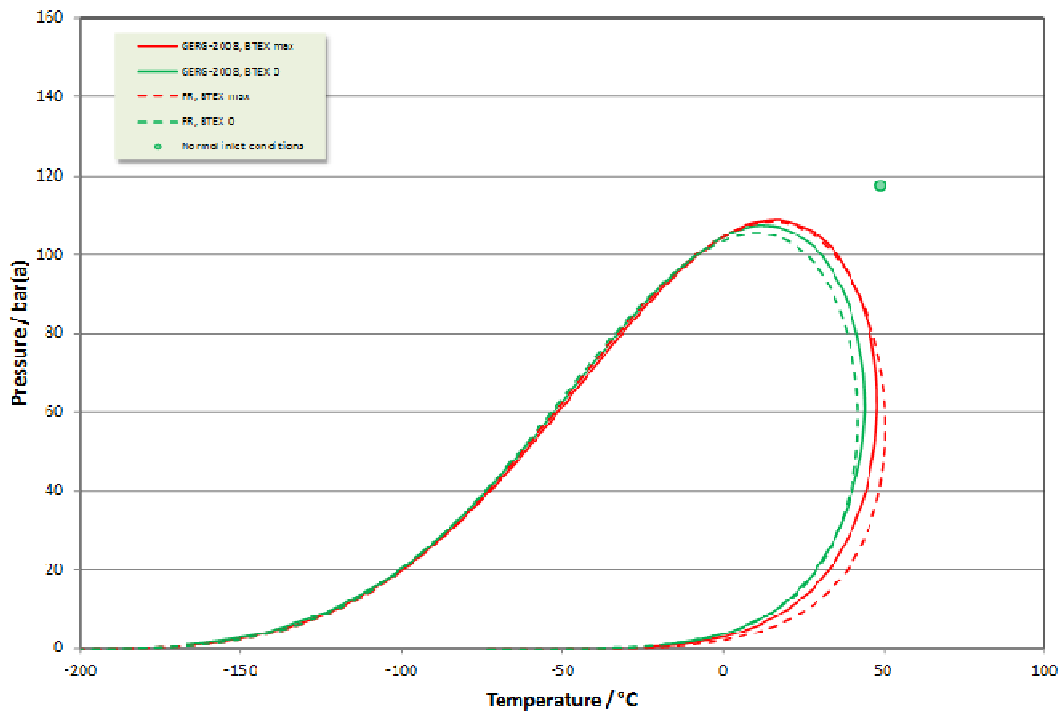
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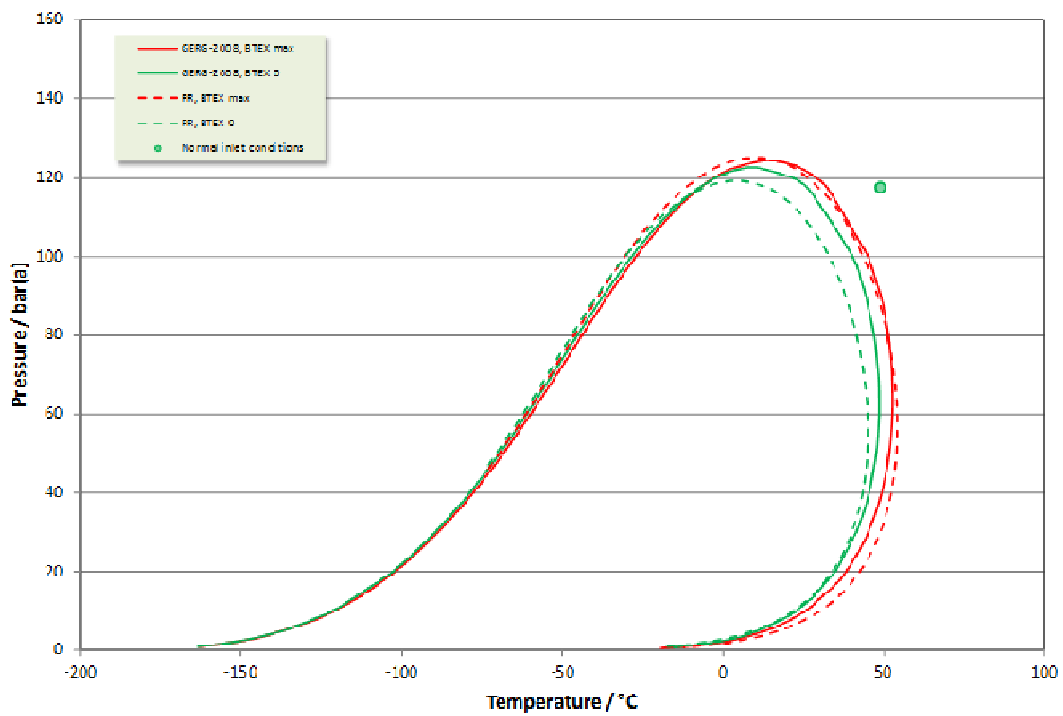Figure 6 – Case Study 2: Phase Envelopes for Mixture 4

Figure 7 – Case Study 2: Phase Envelopes for Mixture 5

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Figure 7 – Case Study 2: Phase Envelopes for Mixture 5

4   CONCLUSIONS

If all the components are within the specified composition ranges for pipeline quality gas, densities calculated using the AGA 8 method are claimed to have an uncertainty of 0.1 % (at $k=2$) for temperatures between -10 and 65°C at pressures up to 120 bar(a).   However, for mixtures with components in the extended composition range and / or at temperatures and pressures outside the standard limits, the uncertainty increases to between 0.2 and 0.5 % (at $k=2$) and is effectively indeterminate for compositions outside the extended range of applicability.   Comparison with values calculated using the GERG-2008 method generally confirms these claims. However, even for compositions that are within the extended AGA 8 range, the differences can exceed 1 % and the effect of ignoring pseudo-components or components not in the 21-component data set can cause differences of over 5 %.

Given the known limitations of the AGA 8 method and the lack of clarity of the likely uncertainties in calculated densities and compressibilities when used in its extended range, the use of an alternative method would be preferable.

Although the GERG-2008 method still has the same 21-component data set as the AGA-8 method, it is claimed to retain its uncertainty (0.1 %) over a much wider range of compositions. However, it is of course important that all minor and trace components are accounted for to ensure uncertainties are minimised and measurements are as accurate as possible. This is successfully achieved by assigning them by boiling point to the corresponding component in the data set. To increase accuracy, this should also be done for pseudo-components known to be present. However, this recommendation must be treated with some caution, as it has only been tested for mixtures with relatively small amounts of pseudo-components so far.

A further problem is that of ensuring that all the components in the gas stream are measured. This is because the majority of on-line gas chromatographs only discriminate hydrocarbons up to heptanes (C_7), although some newer models are now able to discriminate up to undecane (C_{11}), with all higher hydrocarbons being lumped in with the highest carbon number discriminated. Although the total amounts of higher hydrocarbons may be small, as with pseudo-components, even this can cause percentage errors in calculated properties. Furthermore, additional sensors are also necessary to allow for components such as hydrogen sulphide and carbon dioxide.

One solution to this is sampling and off-line analysis, which can provide much more detailed compositional information. However, this method is obviously not capable of providing real-time information for input to a flow computer.   In addition, obtaining representative samples and ensuring that they do not change composition (due to flashing of high volatile components) presents significant challenges and potential safety risks.

Furthermore, it is not possible to simply assume that ignoring one component in a mixture will always have the same effect on the calculated properties as the error will depend on the temperature and pressure of the mixture and how far those conditions are from the phase boundary, with positive or negative errors being possible. This significantly complicates the application of corrections to on-line calculations of gas properties based on off-line analysis of samples, particularly for systems where conditions change on a frequent basis.

However, these issues must be addressed when dealing with gas fields whose compositions are outside the pipeline quality gas specification required by the AGA 8 method, as the potential financial exposure can run to hundreds of millions of dollars per annum for a region such as the North Sea.

5   REFERENCES

[1]   Guidance Notes for Petroleum Measurement, Issue 9.2.   Oil and Gas Authority, Aberdeen, October 2015.

[2]   Peng, D.J. and Robinson, D.B.   A New Two-Constant Equation-of-state. Ind. Eng. Chem. Fundam. **15**, 59-64, 1976.

[3]   Soave G.   Equilibrium Constants for Modified Redlich-Kwong Equation-of-state. Chem. Eng. Sci. **27**, 1196-1203, 1972.

[4]   Lee, B.I. and Kesler, M.G.   A Generalized Thermodynamic Correlation based on Three-parameter Corresponding States. AIChE J. **21**, 510-527, 1971.

[5]   Starling, K.E. and Savidge, J.L. Compressibility Factors of Natural Gas and Other Related Hydrocarbon Gases. Transmission Measurement Committee Report No.8, American Gas Association (1515 Wilson Boulevard, Arlington, Virginia 22209, USA), 2nd Edition, November, 1992.

[6]   BS EN ISO 12213-2:2005 Natural gas - Calculation of compression factor – Part2: Calculation using molar-composition analysis. BSI, London.

[7]   Zunz, O., Klimeck, R., Wagner, W., and Jaescke, M.   The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures. GERG Technical Monograph 15 and Fortschr.-Ber. VDI, Reihe 6, Nr. 557, VDI Verlag, Düsseldorf, 2007.

[8]   Kunz, O. and Wagner, W. The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004. J. Chem. Eng. Data, **57** (11), 3032–3091, 2012.

[9]   ISO 20765-2:2015   Natural gas -- Calculation of thermodynamic properties -- Part 2: Single-phase properties (gas, liquid, and dense fluid) for extended ranges of application.

[10]   Hankinson, R. W. and Thomson, G. H.   A New Correlation for Saturated Densities of Liquids and Their Mixtures. AIChE Journal **25** (4): 653–663, 1979.