NORWEGIAN SOCIETY OF CHARTERED ENGINEERS

NORTH SEA FLOW METERING
WORKSHOP

13 - 15 October 1987

Stavanger Forum, Stavanger

NATURAL GAS DENSITY PREDICTION IN THE HIGH PRESSURE REGION

AN EVALUATION OF DIFFERENT EQUATIONS OF STATE

4.5

Lecturer: Department Engineer Nils-Erik Hannisdal,
Statoil - Norway

NATURAL GAS DENSITY PREDICTION IN THE HIGH PRESSURE REGION

AN EVALUATION OF DIFFERENT EQUATIONS OF STATE.

Introduction

Offshore gas pipelines are usually characterized by high flow-rates. In the North Sea one single metering device in a fiscal metering station may measure more than 3 billion standard cubic meters per year. Natural gas is usually accounted for by mass flowrate using orifice meters. The calculation formula obtained by ISO 5167 can be simplified to:

$$Qm = k\sqrt{2\Delta p \rho} \qquad (1)$$

where
Qm = mass flow rate
k = coefficient dependent of different factors, mainly tube and orifice diameters
Δp = differential pressure
ρ = density

This means that an error of 1 % in density gives an error of 0.5 % in flow rate (since density is a square root function of flow). The density error is then worth up to 2 million dollars pr. year for each metering run in one metering station.

If volumetric meters are chosen (vortex, ultrasonic, turbine meters), the density will be even more important if the gas is accounted for in mass:

$$Qm = Qv \rho \qquad (2)$$

where
Qv = volumetric flow rate

The error in mass flow rate will now equal the error in density.

Density can today be measured by an on-line density meter within an accuracy of +/- 0.2 - 0.3 %, assuming ideal conditions. Since installation and calibration effects often will decrease this accuracy, on-line density calculation is often used to check the on-line measurement. In some countries such back-up calculation is required by the authorities.

For different reasons (e.g. cost, stable gas composition, or bad experience with density meters), some like to exclude density measurement in preference to on-line density (or compressibility) calculation - usually combined with an on-line gas chromatograph or sampler.

The density may be calculated by using the non-ideal gas law:

$$\varrho = \frac{P \ MW}{z \ R \ T} \qquad\qquad (\ 3\ )$$

where
P = pressure
MW = mole weight
R = universal gas constant
T = temperature
z = compressibility factor

Pressure and temperature are usually measured anyway, and mole-weight is known from composition. The compressibility factor (or z-factor) is then found from an equation of state (z-factor equation). Apart from different fixed parameters for each gas component; temperature pressure and composition (x) are usually the only necessary inputs:

$$z = f\ (\ T,\ P,\ x\ ) \qquad\qquad (\ 4\ )$$

The supercompressibility factor (Fpv) - often used in the U.S. in the AGA 3 method - is related to the z-factor by:

$$Fpv = \sqrt{\frac{z_b}{z}} \qquad\qquad (\ 5\ )$$

where
Fpv = supercompressibility factor
z_b = compressibility at base or standard condition (14.73 psia, 60 F)

Apart from being a fundamental parameter in natural gas metering, the compressibility factor is also a key parameter for calculating other thermodynamic properties for natural gas mixtures like enthalphy, entrophy, isentropic exponent, velocity of sound, viscosity, etc. Research on state equations should for that reason have interest to a broad range of engineers for process and metering calculations.

Experimental data.

An investigation into the accuracy of equations of state requires first of all - experimental data for comparisons.

Statoil and Rogaland Research Institute (Norway) organized last year a joint project to establish a database - DENSBASE (14). The database was later updated (15) within Statoil and contains now more than 2000 experimental compressibility and density data distributed amoung 83 different compositions of natural gases and similar laboratory made gases. The database have the necessary possibilities for graphics and search commands.

Why collect all these experimental data when comparisons with state equations have been done before? Several articles about such comparisons have been published, and the paper presented by GERG Inforformation Commitee (1) is probably the most extensive and well known.

However, this and other papers concentrate their work in the pressure range up to 100 bara (1450 psia). In North Sea pipelines - the pressure is often above 100 bara and it may even exceed 200 bara (2900 psia). Experimental data and comparisons between

3

experimental and calculated results are very limited within this pressure range.

Equations of state.

Six different equations of state were compared with experimental data:

- VENNIX-KOBAYASHI (2); a method originally developed for methane, but later adjusted to lean natural gas mixtures.

- OU/GRI (AGA Report No 8) (3); A recently developed method which cover a wide range of natural gas components. This method has now replaced the NX 19 method (4). Comparisons between OU/GRI and NX 19 has been done earlier by Starling & Kumar (3,5). NX 19 was for that reason only tested with a few points in the work presented in this paper.

- STANDING & KATZ (6) is a simple method widely used in flow-computers.

- BENEDICT-WEBB-RUBIN (BWR) (7,8) and

- SOAVE-REDLICH-KWONG (SRK) (9) are well known state equations widely used in the process as well as the metering industy. One should be aware that there are several versions of these equations.

- PENELOUX (10) is a modification of the SRK method.

(The Peng-Robinson(11) method was also compared with a few points versus the Peneloux method but did not give promising results.)

Coefficients or other parameters have not been adjusted to improve the results. The aim of the evaluation was to investigate the accuracy of different available methods. The program SONFLOW (16) has computed the z-factors for Vennix- Kobayashi, BWR and OU/GRI; Katz (17) is the computerprogram for the Standing-Katz method and Statpack (18) is used for SRK and Peneloux.

Results and discussions.

The first problem one meets when comparing experimental and calculated values is: Which is right ? In other words; Are the accuracies of the experimental data satisfactory and within the claims of the experimentalists ?

The ideal situation would be to let two laboratories measure the same gas with different equipment, and then compare the results. This is often done for pure components, where comparisons are easy. For natural gas mixtures, this would require close cooperation between laboratories since exchange of gas samples would be necessary. Unfortunately, this is not often the case, especially not in the pressure area above 100 bars (1450 psia).

It was decided to make a first comparison between the experimental data and an equation of state experienced to give a good accuracy in the pressure area below 100 bara. The OU/GRI method was selected

because the accuracy of this equation is well documented in the litterature (5).

For the uncertainty analysis the average absolute percent deviation was used:

$$A.A.D.(\%) \quad = \quad \frac{1}{n} \sum_{i=1}^{n} \left| \frac{\exp_i - Z_{calc_i}}{Z_{exp_i}} \right| \cdot 100 \quad (6)$$

We carefully picked datapoints mainly in the range from 100 to 250 bara (1450-3625 psia) with a few controlpoints below 100 bara. Since the deviation is larger in the high pressure area than in the low pressure area, one should be aware that to include a lot of good low-pressure data would give a "better" - but more misleading - overall accuracy.

The temperature range was from 0 to 100 C (32 - 212 F). The results are given in Table 1 and the conditions are given in Table 2.

Total Oil Marine (U.K), Elf Aquitaine (Norway), The Norwegian Petroleum Directorate and Statoil (Norway) are now running a joint research project with the Dantest Laboratory (Denmark) to investigate natural gas density meters. After 3 years of different comparisons between density meters and experimental densities obtained by a laboratory z-meter, we are now confident that the results are within 0.1% accuracy. The Dantest results (12,13) are for that reason shown separate. The last serie of experiments with comparisons are given in Fig. 1 and Table 3, since these results give a representative view of the overall comparison.

Conclusions.

1) The comparisons of 6 equations of state versus experimental data gave the following ranking (average absolute deviation is given in parenthesis):

     * OU/GRI and Vennix-Kobayashi (0.3 %)
     * Benedict-Webb-Rubin   (0.4 %)
     * Standing & Katz   (1.1 %)
     * Peneloux   (2.2 %)
     * Soave-Redlich-Kwong   (2.8 %)

2) Both OU/GRI and V-K gave an average absolute deviation of 0.3 %. However, at pressures of about 200 bara there is no reason to expect better accuracy than 0.5 %.

3) V-K seems to be the best available method for lean gases (C1 > 85 mole %) up to 150 bara, but are not suitable for gases with a high C3 + - fraction.

4) The simple Standing & Katz method which is widely used in flowcomputers, seems to be capable of calculating z-factors/ densities to an accuracy of 1.5 % in the total PVT-range of interest to practical gas metering. Compared with most references the Katz densities are too high (Katz z-factors too

low). This is also experienced by comparisons against density meters at the Kårstø terminal.

5) SRK and Peneloux are not suitable methods for calculating high pressure z-factors/ densities of interest for gas metering purposes (note that other modifications of the Redlich-Kwong than SRK may give other results).

6) There is an obvious need for accurate measurement of z-factors in the pressure range 100 to 200 bara (1450 - 3625 psia).

7) The experimental data for gases close to the dew point are uncertain. At low temperatures there is a big scatter between experimental z-factors and also between the different state equations.

References.

1. Melvin, A. et al. "Accurate Measurement and Prediction of the Compressibility Factor for Natural Gas Mixtures for Use in Transition", presented by the GERG Information Commitee on the Thermodynamic Properties of Natural Gases at the 15th World Gas Conference, Lausanne 1982.

2. Vennix, A.J. and Kobayashi, R. "An equation of state for methane in the gas and liquid phases", AIChe J., Vol. 15, No. 6, Nov. 1969, pp. 926-931.

3. Starling, K.E. & Kumar K.H. "Computer Program for Natural Gas Supercompressibility Factor, Custody Transfer Calculations and Process Calculations Using the OU/GRI Correlation", presented at 64th Annual GPA Convention, March 18-20, 1985, Houston, Texas.

4. "Manual for the Determination of Supercompressibility Factors for Natural Gas", American Gas Association Publication, New York, 1963.

5. Starling, K.E., et al. "The Thermodynamic Properties of Natural Gas - Physical Properties", presented at the Congress of Gas Quality, April 22-25, 1986, Groningen.

6. Dranchuk, P.M., et al. "Computer Calculations of Natural Gas Compressibility Factors using the Standing and Katz Correlation", Institute of Petroleum Technical Series, No. IP 74-008, 1974.

7. Benedict, M., et al. "An empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures", Journal of Chemical Physics, Vol. 8, No. 4, 1940, pp. 334-345.

8. Benedict, M., et al. "An empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures - Constants for Twelve Hydrocarbons", Chem. Eng. Progress, Vol.47, No. 8, 1951, pp. 419-422.

9. Soave, G. "Equilibrium constants from a modified Redlich-Kwong equation of state", Chem. Eng. Sci. Vol. 27, 1972, pp. 1197- 1203.

10. Peneloux, A. and Freze, R. "A consistent correlation for Redlich-Kwong-Soave volumes", Fluid Phase Equilibria No. 8, 1982, pp. 7-23.

11. Peng, D.Y. and Robinson, D.B. " A New two-constant Equation of State", Ind. Eng. Chem., Fundam., Vol. 15, No. 1, 1976, p. 59.

12. Rosenkilde, L. and Tambo, M. "Calibration and examination of gas density meters", Dantest Report, June 1983.,

13. Wilcox, P., et al. "An investigation into the velocity of sound correction applied to gas density measurement", presented at North Sea Flow Metering Workshop, Nov. 5-7, 1985.

14. Svartås,T.M. and Nordvik,H. "DENSBAS, Natural gas density data base", Report from Rogaland Reasearch Institute, Dec. 1985.

15. Staurland,S., Hannisdal,N.E. and Halvorsen,N. "DENSBASE, En database for eksperimentelt bestemte tettheter og Z-faktorer for naturgass", Statoil User Manual, Sept. 1986.

16. Weberg,T. and Thomassen,D. "SONFLOW 86, a computer program for isentropic gas flow and thermophysical data computation for natural gas mixtures", User Manual from Institute for energy technology (IFE), Nov. 1986.

17. "KATZ" - internal computerprogram programmed by A.P. Fosse.

18. "STATPACK - manual for the program package", User Manual from CALSEP, Okt. 1986.

	BWR	V-K	OU/GRI	S-Katz	SRK	Peneloux
Dantest	0.18	0.09	0.12	0.97	1.49	1.15
All points	0.38	0.30	0.29	1.09	2.79	2.18

Table A1: Average absolute percent deviation between experimental
and calculated z-factors.

	MW	Methane	P-bara (psia)	T C (F)
Dantest	17.1-18.8	93.8-82.7	10-150(145-2175)	30-35 (86-95)
All points	16.0-18.8	100 -82.7	10-300(145-4351)	0-67 (32-152)

Table A2: Range for mole weight, methane content (mole percent),
pressure and temperature for the test points.

REF 83	T = 30 C						
P (BARA)	EXP. Z	BWR	DEV	V-K	DEV	GRI/OU	DEV
10.0220	.9775	.9766	.0920	.9766	.0920	.9769	.0613
20.0320	.9543	.9532	.1152	.9534	.0943	.9538	.0523
30.0410	.9315	.9304	.1180	.9299	.1717	.9309	.0644
40.0500	.9088	.9069	.2090	.9077	.1210	.9082	.0660
50.0600	.8867	.8843	.2706	.8855	.1353	.8860	.0789
70.0800	.8445	.8415	.3552	.8434	.1302	.8435	.1184
90.0900	.8067	.8038	.3594	.8061	.0743	.8057	.1239
110.1100	.7768	.7740	.3604	.7762	.0772	.7752	.2059
130.1200	.7560	.7542	.2380	.7557	.0396	.7544	.2116
150.1400	.7457	.7449	.1072	.7458	.0134-	.7440	.2279
BIAS (%)			.2225		.0922		.1211
AVER. ABS DEV (%)			.2225		.0949		.1211

REF 83	T = 30 C						
P (BARA)	EXP. Z	ST-KATZ	DEV	SRK	DEV	PENELOUX	DEV
10.0220	.9775	.9757	.1841	.9771	.0409	.9767	.0818
20.0320	.9543	.9513	.3143	.9545	.0209-	.9537	.0628
30.0410	.9315	.9271	.4723	.9323	.0858-	.9311	.0429
40.0500	.9088	.9032	.6161	.9108	.2200-	.9092	.0440-
50.0600	.8867	.8797	.7894	.8900	.3721-	.8880	.1466-
70.0800	.8445	.8350	1.1249	.8517	.8525-	.8490	.5328-
90.0900	.8067	.7959	1.3387	.8196	1.5991-	.8161	1.1652-
110.1100	.7768	.7654	1.4675	.7958	2.4459-	.7914	1.8795-
130.1200	.7560	.7457	1.3624	.7815	3.3730-	.7763	2.6851-
150.1400	.7457	.7372	1.1398	.7766	4.1437-	.7706	3.3391-
BIAS (%)			.8810		1.3072-		.9604-
AVER. ABS DEV (%)			.8810		1.3154		.9980

Table A3: Comparisons between experimental z-factors from the Dantest project (12,13) and calculated z-factors from different state equations. (The experimental values are not previously released. The exact temperature vary from 29.95 to 29.99 C)

Composition (mole %):
N2: 0.62 C3: 1.04
CO2: 0.79 iC4: 0.04
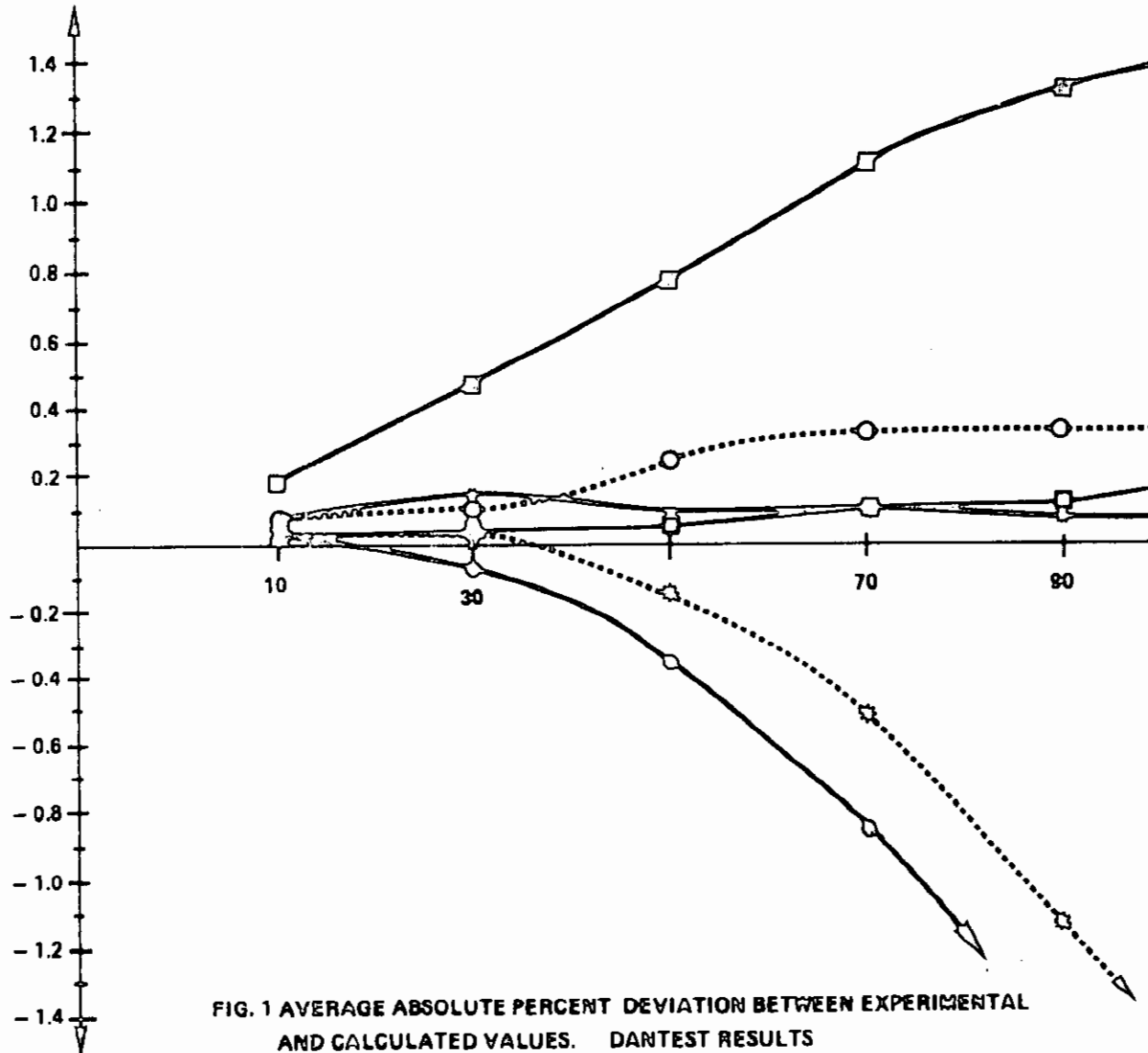C1: 82.71 nC4: 0.08
C2: 14.70 C5: 0.00
C6: 0.01

FIG. 1 AVERAGE ABSOLUTE PERCENT DEVIATION BETWEEN EXPERIMENTAL
AND CALCULATED VALUES.   DANTEST RESULTS