

PRACTICAL ASPECTS OF CHARACTERIZING PETROLEUM FLUIDS

by

Tor Austad¹

John Hvidsten²

Haakon Norvik²

Curtis H. Whitson¹

¹ Rogaland Regional College

² Rogaland Research Institute

presented at the conference on

North Sea Condensate Reservoirs and Their Development

May 24-25, 1983

London

This paper describes the essential aspects of chemical and pressure-volume-temperature (PVT) analysis of gas condensates. It also discusses the use of cubic equations of state (EOS) for modelling gas-condensate phase behavior. Particular emphasis is placed on characterization of petroleum fractions defining the heptanes-plus (C₇₊) group. Although we have chosen to concentrate our discussion on gas condensates, in keeping with the conference theme, most parts of the paper are equally applicable to black oils.

A gas condensate is, by definition, a naturally occurring petroleum mixture found at reservoir temperature greater than the mixture's critical temperature and less than its cricondenterm (see Fig. 1). The most distinguishing feature of a gas condensate is retrograde condensation, defined in the present context as an increasing accumulation of liquid (condensate) during isothermal pressure reduction. Other typical characteristics of gas condensates include producing gas-oil ratios greater than 3000 scf/STB (535 Sm³/Sm³), stock-tank oil gravity greater than 45 degrees API (0.8 g/cc), and reservoir temperatures often greater than 200 °F (95 °C).

The first part of the paper concerns chemical analysis of separator samples. Description of experimental techniques is supplemented with North Sea gas-condensate data measured at Rogaland Research Institute (RRI). These data typify the fluid character of richer North Sea fluids.

The chemical characterization of heptanes-plus is discussed in detail. Numerous experimental procedures are reviewed and data from North Sea condensate samples are presented. Also, a complete distillation analysis up to C₂₀ is presented for a mixture of North Sea heptanes-plus fractions representing black-oil and gas-condensate systems. Properties of carbon-number groups should give useful estimates for normal boiling points, specific gravities, and molecular weights when experimental distillation data are not available.

Next we review the most common PVT analyses offered by commercial and in-house laboratories. The constant-volume

depletion procedure is considered in more detail since it closely simulates the physical process a gas condensate undergoes during depletion.

Finally, we describe the use of cubic equations of state (Peng-Robinson's equation in particular) for modelling phase behavior. Heptanes-plus characterization is reviewed and its importance to EOS predictions is emphasized. A procedure for matching experimental PVT data is given, and it is tested on a North Sea gas condensate previously published in the literature.

A convenient literature guide is given following the References section. These sources give access to a wide range of information on gas-condensate fluids.

CHEMICAL ANALYSIS

Analytical information yielding compositional data for petroleum reservoir fluids is useful during exploration, production and gas-cycling phases of a gas-condensate reservoir. Analytical data, in combination with PVT analysis, can be used to accurately describe phase behavior and physical properties. Fig. 2 illustrates schematically several processes which are highly dependent on proper fluid characterization - near-wellbore effects, vertical flow, surface separation, platform or wellsite processing, transportation, refining, and miscible/immiscible gas displacement.

The obvious first step in properly characterizing a reservoir fluid is to determine its composition. Petroleum in general, and gas condensates specifically, are very complex mixtures of hydrocarbons and light non-hydrocarbons. On a routine basis it is only possible to define the molar quantities of a few relatively light components, including hydrogen sulphide (H_2S), carbon dioxide (CO_2), nitrogen (N_2) - the most common non-hydrocarbons - methane (C_1), ethane (C_2), propane (C_3), iso-butane (iC_4), normal butane (nC_4), iso-pentane (iC_5), normal pentane (nC_5), grouped hexanes and similar-sized compounds (C_6), and the heptanes-plus fraction (C_7+) combining all remaining heavier constituents.

The heptanes-plus fraction may consist of hundreds or thousands of paraffinic, naphthenic and aromatic compounds. The C₇+ fraction is commonly described by experimental molecular weight, density (i.e, specific gravity, relative to water) and sulfur content. Other properties used to characterized the lumped C₇+ fraction include viscosity, refractive index and Watson characterization factor.

Fluid samples used for chemical analysis during exploration and production phases are normally sampled from a test separator. The well is produced through separator equipment at monitored pressure and temperature (e.g., 1500 psia and 100 °F; 10000 kPa and 40 °C). After producing gas-oil ratio (GOR) stabilizes, equilibrium is assumed and samples are collected. Gas and oil samples are taken in stainless steel cylinders to prevent leakage and contamination. Usually 200 to 300 cc samples of both oil and gas are available (measured at separator conditions).

Rogaland Research Institute (RRI) has developed a routine procedure for analyzing separator oil and gas samples. Having determined respective compositions on weight and molar bases, the wellstream composition is calculated using separator GOR, temperature and pressure. The following is a discussion of RRI's procedure.

Laboratory Equipment

The laboratory is equipped with standard equipment such as a low-temperature distillation apparatus, gas chromatograph (GC), density meter (atmospheric pressure), freezing-point depression molecular weight apparatus, and X-ray fluorescence used for determining sulfur content.

Additional equipment used for detailed analysis of the heptanes-plus fraction include a high-temperature distillation column, high-pressure liquid chromatograph, GC equipped with a capillary column, and a mass spectrometer facility based on GC. Necessary data processing equipment includes micro- and mini-computers.

Prior to GC analysis, the gas-sample cylinder is heated about 10 °C above sampling temperature. Instrumentation includes an HP-5880, level four GC with two detectors. The GC run is made using a thermal conductivity detector (TCD) to determine the content of non-hydrocarbons and paraffin constituents from methane to butane. The second GC run is made using a flame ionization detector (FID). This run first determines pentanes and hexanes content, then uses backflush to quantify heptanes-plus. Fig. 3 illustrates the procedure for analyzing separator-gas samples.

The chromatograph detects mass of certain substances and responds by drawing a peak on the chromatogram (see Fig. 4). The area under the curve for a given peak indicates the relative mass of that substance (weight fraction). From previous calibration it is known when a specific compound will be detected by the chromatograph. Assigning the area to the specific compound, it is then possible to define the composition of the gas. Identical injected quantities (moles) of gas is ensured for each run by temperature control and a back-pressure gauge.

Results from each run are stored on tape and then recombined automatically to yield weight and molar compositions. Molecular weight of hexanes and heptanes-plus used to convert to molar basis are 86.0 and 100.0, respectively; these values represent the molecular weights of normal hexane and heptane. Table 1 gives an example report of separator-gas analysis from a North Sea gas-condensate sample.

Separator-Oil Analysis

The pressured-oil sample is distilled roughly into three batches. First, the lighter components including non-hydrocarbons and methane to butanes are separated by boiling the separator oil to about 23 °C. Pentanes and hexanes are then separated by boiling up to 94 °C. The remaining mixture is considered heptanes-plus. Fig. 3 illustrates the distillation procedure.

The first distillation batch is collected in preevacuated receivers. By recording temperature, pressure and volume it is possible to calculate the mass of gas collected. The pentanes-to-hexanes batch is weighed directly, as is the remaining heptanes-plus fraction.

GC analysis is used to determine weight fractions of components found in the first two distillation batches (see Fig. 3); each batch is analyzed separately and results are stored on tape. The C₇+ fraction is characterized by measuring its specific gravity, molecular weight and sulfur content. When combined with the GC results for the two lighter batches, the total separator oil composition is determined. Compounds with seven carbon atoms which are carried over in the pentanes-to-hexanes batch are detected by the GC. The measured C₇+ molecular weight and specific gravity is corrected for these constituents by assuming they have properties of normal heptane. Table 2 gives an example of separator-oil analysis for a North Sea gas-condensate sample. Fig. 5 shows chromatograms for runs 1 and 2 (distillation batches 1 and 2) of a North Sea gas condensate.

Recombination and Consistency Check

It is usually of interest to recombine the separator gas and oil compositions to yield a composite wellstream composition. This is done by a simple material balance if separator GOR, pressure and temperature are known. An example of recombination is given in Table 3 for the separator samples given above.

To check the consistency of separator-fluid compositions it may be helpful to use a method proposed by Hoffman, Crump and Hocott for correlating equilibrium constants (K-values). By definition, K-value is the ratio of normalized mole fraction in the vapor (gas) phase to the normalized mole fraction in the liquid (oil or condensate) phase. Hoffman, Crump and Hocott noted that if the product K_p is plotted versus a temperature function, F , on semi-log paper, then the resulting curve is linear. This relation is particularly accurate at pressures and temperatures encountered at separator conditions.

The temperature function F is different for each component. It is defined as the product of b and the quantity $(1/T_b - 1/T)$, where T_b is the normal boiling point of the component and b is a composite function of critical pressure and temperature and normal boiling point. Standing gives modified values for b and T_b for light compounds which should be used instead of the true values. Table 3 shows an example calculation of K_p vs F for the same gas condensate fluid analysed earlier. A plot of the function is given in Fig. 6. Note that the C_{7+} F -value is not well-defined, so it can not be included in the consistency check directly.

Inconsistent compositions due to leakage, improper analysis or lack of equilibrium during sampling may be spotted on a $\log K_p$ vs F plot which is nonlinear. Such an example is given in Fig. 6.

Another helpful consistency check is to estimate the Watson characterization factor using measured C_{7+} molecular weight and specific gravity. The correlation given by Whitson is,

$$K_w = 4.5579 \cdot M^{0.15178} \cdot \gamma^{-0.84573} \dots\dots\dots (1)$$

We have found that the K_w value for a given oil or gas-condensate field varies only slightly (e.g., 12.00 ± 0.02) for the C_{7+} fraction. This is illustrated in Table 4 for several North Sea gas-condensate and black-oil reservoirs. Fig. 7a shows the very slight variation in K_w value for a North Sea gas-condensate reservoir. Fig. 7b shows an analogous plot for a North Sea black-oil reservoir.

If a laboratory can establish the characterization factor K_w for a given field (or even a given well), then each time new measurements of C_{7+} molecular weight and specific gravity are made, the resulting K_w value can be checked to see if it is close to the field average. If the value deviates more than ± 0.01 to 0.02 then the molecular weight measurement (which is much more difficult to perform) should be questioned; a new measurement of both specific gravity and molecular weight should probably be made.

In the last column of Table 4 we have calculated C7+ molecular weight using Eq. 1 with measured specific gravity and the field-average characterization factor. It is seen that the range in K_w of ± 0.02 suggests a maximum error in molecular weight of approximately 2 to 3 (usually less than 1.5%).

SPECIAL ANALYSIS OF HEPTANES-PLUS FRACTION

Characterizing all compounds with more than six carbon numbers as a single component is acceptable for many engineering applications. It may be necessary, however, to better define the constituents making up heptanes-plus. One example would be for the pricing of oil or condensate; i.e., it is necessary to determine the relative quantities of fuel oils, gasolines, etc. which can be refined from the produced fluid. Another example would be if an equation of state is used for predicting phase behavior at conditions other than those measured experimentally. The predictive capability of all equations of state is severely limited if only heptanes-plus properties can be defined; in general it is necessary to split C7+ into at least three to five pseudocomponents.

There are many ways to extend the analysis of heptanes-plus fractions. Perhaps the oldest and most common is true boiling point (TBP) distillation. Because this technique is both time consuming and expensive, it may be replaced by simulated distillation using gas chromatography. Although simulated distillation may only require a small fraction of the time and expenses required by TBP analysis, it does not provide the engineer with the same data base for each fraction. Instead of measuring boiling point, volume distilled, specific gravity and perhaps molecular weight, viscosity and refractive index of each fraction, the only real data simulated distillation gives is weight fraction and a calculated estimate of boiling point.

The research laboratory at RRI has developed a special analysis procedure for characterizing heptanes-plus fractions. Starting with the previously mentioned procedure for analysing separator oil, the C₇+ mixture is subjected to one or more of the following analyses:

- carbon-number distillation from C₇ to C₂₀ with a remaining C₂₁+ residue; normal paraffin boiling points are used to define single carbon-number groups (ASTM D 2892-78).
- TBP distillation using predefined volume-percent cuts to separate the petroleum fractions - e.g., 3% per cut.
- simulated distillation using GC with high-precision slice widths of 6 seconds (240 detector readings per slice).
- aromatic analysis of carbon-number fractions up to C₂₀ using high-pressure liquid chromatography.
- paraffin-naphthene-aromatic analysis of carbon-number fractions up to C₁₀ using mass spectrometry based on GC.
- molecular weight and specific gravity measurements of all petroleum fractions determined by carbon-number or TBP distillation.

Depending on the particular need, some or all of the above procedures may be justified. Usually, however, only simulated distillation can be run on a routine basis. This might be practical for analysis of production fluids where calibration of the GC has been determined based on more reliable TBP or carbon-number distillation results. The other analyses would need to be justified for a specific use requiring particularly detailed description of the C₇+ fraction. Some results from experimental work on North Sea heptanes-plus mixtures are presented in the following discussion.

Results of a carbon-number distillation based on the ASTM D 2892-78 method is presented in Table 5 and Fig. 8. There are several aspects of interpreting distillation data worth noting. First let us start off by asking "what is the normal boiling point of a given fraction?" First, by normal it is inferred that the boiling point corresponds to atmospheric (normal) pressure - i.e., the vapor pressure equals atmospheric pressure at its normal boiling point temperature.

Suppose the distillation cut we are considering starts boiling at 68 °C and stops boiling at 98 °C (boiling points of normal paraffins C₆ and C₇). If 8 volume percent of the initial C₇+ mixture boils off in this interval, then one point on the distillation curve would be 0% and 68 °C and another would be 8% and 98 °C. Suppose that 6 volume percent boils between 98 °C and 126 °C. The next point on the distillation curve would be 14% (8% + 6%) and 126 °C. Having three points on the distillation curve, a smooth line can be drawn. The normal boiling point for the first (C₇) cut would be read from the curve at the mid-volume point - i.e., at 4%. The normal boiling point for the second cut (C₈) would be read from the curve at its mid-volume point - i.e., at 11% (8% + 14% divided by two). The engineer who does not have a background in petroleum distillation might consider working through the example data given in Table 5.

If distillation is performed to high carbon-number groups such as C₂₀, then the resulting residue (C₂₁+) will be a semi-solid at room temperature. To avoid large losses the column should be rinsed with a volatile solvent after distillation is completed. The extracted residue can be retrieved by evaporating the solvent. We have found that total distillation losses can be minimized using this procedure.

Properties of the residue are not readily obtained by direct measurement due to its semi-solid character at room conditions. It may be necessary to back-calculate residue properties using measured C₇+ properties and mass/mole

balances. Unfortunately, small errors in C₇₊ molecular weight may result in unphysical values of residue molecular weight. Engineering judgement should be used, though direct estimation of residue molecular weight is desirable.

The example distillation presented in Table 5 and Fig. 8 represents a mixture of numerous C₇₊ fractions separated using the procedure outlined in the previous section. Both black-oil and gas-condensate samples were mixed, though the properties of the mixture suggest a more gas-condensate character. Carbon-number boiling points, specific gravities and molecular weights up to C₂₀ can probably be used as estimates for most North Sea fluids if measured data are not available.

Simulated Distillation

A chromatogram for simulated distillation by GC is shown in Fig. 9. It is for the same C₇₊ mixture analyzed in the previous section. Normal hexane is used as the internal standard. For paraffinic oils it is easy to locate normal paraffin peaks on the chromatogram. Instead of using peak integration mode, area slice mode is chosen. This mode is useful because simulated distillation analysis depends on the distribution of area under the chromatographic curve, rather than on the amount of specific peaks. The area slice mode provides this basic area distribution data.

A nine-foot by 1/8-inch stainless steel column packed with 10% SP-2100 on 80/100 supelcoport was used to conduct the present analysis. A blank test showed that normal C₂₀ eluted prior to any significant bleeding of the column material. This observation suggests that base-line shift will not be observed up to C₂₀.

A flame ionization detector was applied and normal hexane was used as an internal standard (2.5 weight percent of the injected sample). Although the FID should give similar response on a weight basis for various hydrocarbons, we found it gave values systematically low. By increasing the response factor of the internal standard by 15.5%, we found that simulated results match true distillation data very

well. Also, reproducibility was good. Fig. 10 shows a comparison of distillation curves on a weight basis.

It should be noted that the correction to response factor is probably dependent on the particular fluid. If a fluid has not been studied previously, then a TBP or carbon-number distillation should probably be run to calibrate the internal-standard response factor.

PNA Analysis Using Mass Spectrometry

Using GC-based mass spectrometry, RRI has been able to determine the paraffin-naphthene-aromatic (PNA) content of carbon-number distillation fractions C₇ to C₁₀. The basic technique is to identify compounds showing responses with mass-to-charge values, m/z , approximately equal to molecular weights of the compounds in a given family for a given carbon number. These values are approximately $14 \cdot n + a$, where n is the number of carbon atoms and a equals +2 for paraffins, 0 for naphthenes, and -6 for aromatics (for the C₁₀ fraction, values of -6 and -8 are used for aromatics). Having located all compounds with the specified m/z ratio, relative amounts are found by integrating the various peaks in the total-ion-count, TIC, chromatogram.

An example spectrogram is given in Fig. 11 for the naphthene family. Only those peaks found in the proper time interval are integrated; others are ions which result from the breakdown of large compounds.

Presently the identification and integration of TIC peaks is done manually for each carbon number group. A program is now being developed to automate the calculations; it is based on a procedure somewhat different than presently performed manually. Such a program should make PNA analysis from mass spectrometry more routine.

Alternative methods for estimating PNA content have been proposed. These methods rely on measured physical properties including refractive index, viscosity and density.

The conventional experimental procedures performed on gas condensates include

- constant-volume depletion (CVD)
- constant-composition (-mass) expansion (CCE)
- separator flash

The first two experiments are conducted in a high-pressure cell with some means of visually observing phase behavior during pressure changes. Mercury is usually used as an injection medium for changing the pressure. Reservoir temperature is maintained by a circulating-air system enclosing the cell.

Separator flash experiments are designed with the intention of (1) checking the recombined fluid composition and (2) analyzing the effect of separator pressure and temperature on oil gravity and total surface gas-oil ratio. Using the Hoffman-Crump-Hocott method it may be possible to determine a low-pressure K-value correlation from compositional data reported from separator flash tests.

Constant-composition expansion is merely an isothermal pressure-volume experiment. Starting at or above initial reservoir pressure with a known number of moles of reservoir fluid, pressure is reduced and volume is measured. At undersaturated conditions (above the dew point), volume measurements can be converted into compressibility factors ($Z=pV/NRT$). Below the dew point (at saturated conditions) retrograde condensation can be observed. The volume of liquid condensate is reported as a percent of dew-point volume. CCE data are not sufficient to calculate compressibility factors of saturated vapor in equilibrium with liquid condensate; number of moles in the vapor phase is not known, only its volume.

Description of the constant-volume depletion procedure is taken from Whitson and Torp:

"A CVD experiment is conducted at reservoir temperature and begins at saturation pressure. Cell volume, or the volume contained by the saturated fluid, is used as a reference volume."

"Mercury is withdrawn from the bottom of the cell, thereby lowering the pressure as fluid expands. During this process, a second phase evolves - either retrograde liquid (for gas condensates) or solution gas (for volatile oils)."

"Mercury withdrawal is ceased when a predetermined pressure is reached. Some laboratories measure liquid volumes at several pressures before any vapor has been removed; these values, reported relative to cell volume, represent CCE. They closely approximate volumes that would have been measured if the process had been CVD..."

"Mercury is reinjected into the cell at constant pressure while simultaneously withdrawing an equivalent volume of vapor. When initial cell volume is reached, mercury injection is ceased. Withdrawn vapor is analyzed using gas chromatography to determine compositions. Moles of vapor produced are calculated using the real gas law and are reported as a cumulative percent of initial moles. Compressibility factor also is calculated noting produced vapor surface volume and equivalent cell volume (at pressure and temperature). From measured vapor gravity and composition, heptanes-plus molecular mass is back-calculated. Liquid volume is measured visually and reported as a percent of cell volume, which is actually a type of hydrocarbon liquid saturation."

"The experimental procedure is repeated several times until a low pressure is reached. The remaining liquid is removed, distilled, and analyzed using gas chromatography. Measured liquid composition should check with material-balance derived composition. (Some major laboratories smooth and adjust measured vapor compositions until the material balance checks. This procedure is discouraged. It is good practice to ask if a laboratory reports measured or smoothed

data, and to what extent material-balance-derived data are used in final CVD reports.)"

Whitson and Torp also show that reported CVD data are sufficient to calculate other physical properties, including liquid density, composition, and heptanes-plus molecular weight, vapor density (using two independent methods), K-values at depletion pressures, and black-oil PVT properties used by numerical reservoir simulators.

Engineers working with gas-condensate phase behavior should certainly become familiar with the CVD procedure and data which are reported in conventional reports. There are numerous concepts such as two-phase Z-factors and wellstream surface volumes which are not well-documented or understood in the industry.

CUBIC EQUATIONS-OF-STATE APPLICATION

What is a cubic equation of state? It is an equation relating pressure, temperature, composition and volume. Slightly oversimplified, we write a general form of the cubic equation as

$$V^3 + a \cdot V^2 + b \cdot V + c = 0 \dots\dots\dots (2)$$

Constants a, b and c are defined by pressure, temperature, composition and moles of the fluid. Since the equation is cubic in volume, there may be one, two or three volumes which satisfy the specific conditions. Which one do you choose if there are, say, three volumes? In practice we merely define the largest volume as a vapor and the smallest volume as a liquid; if a third volume exists between these two then it is merely ignored. If only one volume satisfies the equation defined by specified conditions, then there is obviously no problem in choosing the correct volume.

Why do we choose a cubic form? The answer lies in the behavior of real fluids. Consider water for a moment. At room conditions water behaves as a liquid and has a density

of approximately 1 g/cc. When we begin to heat water its density decreases slightly (mass remains constant while volume increases). However, once we reach 100 °C the water becomes a vapor (steam) and its density changes abruptly, becoming several orders of magnitude lower than at 99 °C. At 100 °C we can actually say that water has two densities - the saturated vapor density (steam) and saturated liquid density (heated water). To correctly predict this abrupt change in density (i.e., volume, assuming a constant mass), the cubic equation merely chooses the larger volume solution to describe steam, and the smaller volume solution to describe heated water.

Cubic equations are usually expressed in terms of the compressibility factor, Z, which is defined by the real gas law: $Z = pV/NRT$. The general form of any cubic equation then becomes,

$$Z^3 + e \cdot Z^2 + f \cdot Z + g = 0 \dots\dots\dots (3)$$

where constants e, f and g are defined by pressure, temperature, and composition. If we consider only pure compounds for the moment, then we can express e, f and g for one of the more popular cubic equations of state - the Peng-Robinson (PR) equation,

$$\begin{aligned} e &= B - 1 \\ f &= A - 3B^2 - 2B \dots\dots\dots (4) \\ g &= B^3 + B^2 - AB \end{aligned}$$

where

$$\begin{aligned} A &= 0.45724 \cdot (p/T^2) \cdot (T_c^2/p_c) \\ B &= 0.07780 \cdot (p/T) \cdot (T_c/p_c) \dots\dots\dots (5) \end{aligned}$$

To calculate volume of a pure compound, first specify pressure, p, temperature, T, and critical constants p_c and

T_C . Calculate A and B using Eqs. 5; actually Peng and Robinson introduce a correction factor for the A-term, dependent on reduced temperature (T/T_C) and acentric factor (along the same line as suggested by Soave). Having calculated A and B, constants e, f and g are found. The cubic equation (Eq. 3) is solved for Z. Analogous to our previous discussion of multiple-volume roots, the largest Z-factor is assumed to represent vapor and the smallest Z-factor is assumed to represent liquid; no choice is posed if only one Z-factor root exists. Given Z, volume is found from $ZNRT/p$. Density is merely NM/V or pM/ZRT , where M is molecular weight.

The procedure for finding volume and density is essentially the same for mixtures. Given composition, the terms A and B are calculated using appropriate mixing rules. If the mixture lies in the single-phase region, this simplified procedure can be applied directly to the mixture composition. If the mixture splits into two phases, then the procedure is performed for each phase; this requires, however, that the composition of each phase be known. Vapor-liquid equilibria (VLE) calculations necessary for determining phase compositions are complicated and will not be discussed here.

Three points deserve mention at this point in the discussion. First, the PR EOS is an example of a two-constant equation. The two constants are A and B, as defined by Eq. 5. Second, the numerical constants - 0.45724 and 0.07780 (approximate) - result from forcing two rigid thermodynamic criteria proposed by van der Waals. Third, the critical properties (as well as acentric factor and molecular weight) required for each component in a mixture are not well-defined properties for petroleum fractions. In fact they are very difficult to estimate, and one may find that different correlations give considerably different estimates.

Another general observation about two-constant equations is that constant A usually dictates VLE and vapor density predictions, whereas B usually dictates liquid density prediction. Consequently, T_C has more influence on VLE and

vapor density predictions than p_c . Also, a second correction factor - the so-called binary interaction parameter - is often used to correct VLE deficiencies for mixtures of compounds with unlike properties. Binary coefficients are also applied to constant A.

This short explanation of cubic equations of state has been given to help the reader understand methods presently used for tuning or matching an EOS to measured PVT data. Adjustments made to an EOS during the tuning process are usually localized to the components describing the C7+ fraction. This is logical when one realizes that the greatest uncertainty lies in proper definition of critical properties for components which are actually mixtures of tens or hundreds of pure compounds. In addition to adjustment of heavy-fraction critical properties, the interaction parameter between methane (or carbon dioxide) and heavy fractions may be adjusted to match saturation pressure.

MATCHING AN EQUATION OF STATE TO MEASURED PVT DATA

None of the cubic equations of state presently available have been able to accurately predict VLE and volumetric properties of petroleum reservoir fluids without some kind of adjustment. This is really not difficult to understand when you consider our inability to define constituents found in petroleum fractions, as well as inherent limitations of cubic equations. In fact, a new field of research has evolved to develop more accurate methods of correcting EOS predictions. A few of these efforts are summarized below.

One method for improving EOS predictions is to improve the equation itself. This can be done in a number of ways. What we might consider as the purest modification is exemplified by the work of Peng and Robinson. Their conclusions give a summary of their goals and the limitations of the proposed equation:

"By modifying the attraction pressure term of the semi-empirical van der Waals equation a new equation of

state has been obtained. This equation can be used to accurately predict vapor pressures of pure substances and equilibrium ratios of mixtures."

"While the new equation offers the same simplicity as the SRK (Soave-Redlich-Kwong) equation and although both equations predict vapor densities and enthalpy values with reasonable accuracy, more accurate liquid densities can be obtained with the new equation. In regions where engineering calculations are frequently required the new equation gives better agreement between predictions and experimental PVT data."

"Since two-constant equations have their inherent limitations, and the equation obtained in this study is no exception, the justification for the new equation is the compromise of simplicity and accuracy." (our emphasis)

Similar efforts by numerous other researchers and engineers has led to an enormous availability of cubic equations of state (mostly two-constant equations). The Peng-Robinson equation is certainly one of the more well-accepted and widely used equations.

Another approach which has gained considerable acceptance in the petroleum industry was proposed by Joffe, Schroeder and Zudkevich. They suggested that a second correction term be used for the Redlich-Kwong EOS constant B. According to their method, the correction terms for A and B are found simultaneously by matching vapor pressures and saturated liquid densities of pure components. Unfortunately the resulting corrections can not be readily expressed in functional form. The net result of the method is to improve liquid-density predictions. In general, the improvement in liquid density using this method is superior, though certainly more complicated, than results given by Peng and Robinson.

The last approach we will consider does not directly change the form of the equation by using pure component data. Instead, a set of measured PVT data are chosen to represent the true phase behavior of the reservoir fluid. Selected parameters used by the EOS are chosen as regression

variables and can be altered to match the measured PVT data. Commonly the critical properties of C₇₊ fractions are considered regression variables. Binary interaction parameters between methane (or carbon dioxide) and C₇₊ fractions allow a simple means of matching saturation pressure.

An alternative to adjustment of critical properties and acentric factor is, as suggested by Coats, to adjust the two numerical constants (e.g., 0.45724 and 0.07780 for the PR EOS) in the defining equations for A and B. It should be noted that for isothermal processes (e.g., CVD), only two of the three properties (T_c , p_c , and ω) are independent. Thus only two of them need (should be) adjusted simultaneously. The disadvantages of Coats approach are 1) its unclear physical implications, and 2) the resulting EOS constants can not be used in other simulators based on the PR EOS.

One problem with the matching procedure is that no assurance can be made that a global minimum of the error function can be found. This is illustrated by an example match of a North Sea gas condensate previously presented in the literature (called NS-1 by Whitson and Torp, and Condensate B by Coats).

Coats introduced three pseudocomponents to describe the C₇₊ fraction; Whitson and Torp originally give carbon-number groups up to C₂₀, plus a C₂₁₊ residue, as well as a proposed five-pseudocomponent regrouping. The original Whitson-Torp match of CVD data was excellent except for liquid dropout, which was overestimated by several volume-percent. An automatic regression routine was not used, and manual adjustments were made based on previous experience with matching condensate fluid behavior.

Coats improved the liquid dropout match at the expense of a poorer C₇₊ description (molecular weight and mole fraction). The adjustment of EOS constants for methane is probably responsible for better gas densities (Z-factors). Unfortunately they infer a substance with properties similar to argon; this alteration is not entirely satisfactory.

We started the present analysis using Coats final three-pseudocomponent C₇₊ characterization but retain methane as a pure component. Equivalent critical properties were calculated as suggested by Whitson.

The error function used in this study was the average of absolute deviation of dew-point pressure and root-mean-square of all other CVD data. The regression routine is a simplex algorithm for minimization (Nelder and Mead).

Regression variables included critical temperature, critical pressure and acentric factor for all three C₇₊ pseudocomponents. Also, interaction coefficient between methane and the heaviest C₇₊ fraction (F13). All ten parameters were not adjusted simultaneously. Instead, repeated minimization was made with groups of three parameters. Table 6 shows the sequence of parameter adjustment. For early runs the methane-F13 interaction coefficients was adjusted to give an exact match of dew-point pressure. For the two final runs these coefficients were included in the optimization routine as a fourth regression variable. Table 7 gives the complete fluid characterization used by the Peng-Robinson EOS for the "best" match. The choice of three-parameter groups for each regression was made arbitrarily.

Total error reduction during the entire regression sequence (manual and automatic) was more than 2.4 %, resulting in a final error slightly greater than 2.0%. The initial error was undefined because of convergence problems.

This procedure does not guarantee a global minimum will be found. In fact this example shows an interesting feature. If only critical pressure and temperature of the heaviest C₇₊ fraction are used as regression variables then the resulting error function is found to have a valley of local minima as shown in Fig. 12. The valley is actually bounded; the 10-% contour encircles the valley only slightly outside the p_c - T_c bounds in Fig. 12. Two test runs show approaches to local minima along the valley (A1 to A5 and B1 to B6). Although local minima have numerical values nearly identical (ca. 2 %), the resulting liquid dropout curve has a

distinctly different character at the upper and lower ends of the valley (see Fig. 12). Global minima have been located for other examples we have studied.

Fig. 13 shows results of predicted CVD data using the PR EOS. Note that C₇₊ molecular weights are poorly predicted, similar to Coats results. Vapor compressibility factor is not predicted as well as by Coats. In general, however, the present match is as good or better than matches previously obtained by Whitson and Torp and Coats.

Proper characterization of petroleum reservoir fluids, and particularly gas condensates, can be divided into three categories.

1. Chemical analysis, based on chromatography, distillation and mass spectrometry, provides the necessary data to determine composition and properties of pure compounds and petroleum fractions making up reservoir fluids.

2. PVT analysis provides phase behavior data of the reservoir fluid as a whole. These data, including volumetric and vapor-liquid equilibria, can be used directly in engineering calculations or as the basis for matching an equation of state.

3. Prediction of reservoir fluid behavior at conditions other than those measured experimentally is made possible by thermodynamic property correlations. One of the more powerful correlations is the cubic equation of state (EOS). Simulation of complex physical processes such as development of miscibility can be achieved by an EOS due to its consistent behavior in near-critical regions.

Our purpose has been to review these three areas of fluid characterization. Most of our observations are based on experience we have gained by working with gas-condensate fluids from the North Sea. Hopefully some of the measured data we present will be useful for those working with North Sea gas condensates.

In closing, we would like to thank American Petrofina Exploration Company of Norway and Phillips Petroleum Company Norway for support which has allowed us to perform much of the analysis presented in this paper.

REFERENCES

1. Annual Book of ASTM Standards: "Standard Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)," ASTM D 2892 (1979), Part 24, 802-839.
2. Coats, K.H.: "Simulation of Gas-Condensate Reservoir Performance," Paper SPE 10512 presented at the Sixth SPE Symposium on Reservoir Simulation, New Orleans, Jan. 31 - Feb. 3, 1982.
3. Coats, K.H. and Smart, G.T.: "Application of a Regression-Based EOS PVT Program to Laboratory Data," Paper SPE 11197 presented at the 57th Annual Fall Technical Conference and Exhibition, New Orleans, Sept. 27-29, 1982.
4. Hoffman, A.E., Crump, J.S., and Hocott, C.R.: "Equilibrium Constants for a Gas-Condensate System," Trans. AIME (1953) 198, 1-10.
5. Joffe, J., Schroeder, G.M., and Zudkevich, D.: "Vapor-Liquid Equilibria with the Redlich-Kwong Equation of State," AICHE J. (May, 1970), 16, 3, 496-498.
6. Katz, D.L. and Firoozabadi, A.: "Predicting Phase Behavior of Condensate/Crude-Oil Systems using Methane Interaction Coefficients," J.Pet.Tech. (Nov., 1978), 1649-1655; Trans. AIME, 228.
7. Nelder, J.A. and Mead, R.: "A Simplex Method for Function Minimization," Comp.J. (1965), 7, 308-313.
8. Norvik, H.: PVT Program, User's Manual and Documentation, Report Number T4-83, Rogaland Research Institute, Stavanger, Norway.
9. Peng, D.-Y. and Robinson, D.B.: "A New Two-Constant Equation of State," Ind. and Eng. Chem. Fund. (1976), 15, 1, 59-64.
10. Soave, G.: "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," Chem. Eng. Sci. (1972) 27, 6, 1197-1203
11. Standing, M.B.: "A Set of Equations for Computing Equilibrium Ratios of a Crude Oil/Natural Gas System at Pressures Below 1000 psia," J.Pet.Tech. (Sept. 1979) 1193-1195.
12. Whitson, C.H.: "Characterizing Hydrocarbon Plus Fractions," EUR 183, presented at the EUROPEC Conference, London, Oct. 21-24, 1980.
13. Whitson, C.H. and Torp, S.B.: "Evaluating Constant Volume Depletion Data," J.Pet.Tech. (March, 1983) 610-620.
14. Whitson, C.H.: "Effect of Physical Properties Estimation on Equation-of-State Predictions," Paper SPE 11200 presented at the 57th Annual Fall Technical Conference and Exhibition, New Orleans, Sept. 26-29, 1982.

1. Eaton, B.A. and Jacoby, R.H.: "A New Depletion Performance Correlation for Gas-Condensate Reservoir Fluids," J.Pet.Tech. (July, 1965) 852-856
Trans. AIME, 234
2. Eilerts, C.K., et al.: Phase Relations of Gas-Condensate Fluids, Monograph 10, USBM, Washington D.C. (1957).
3. Jacoby, R.H., Koeller, R.C., and Berry, V.J., Jr.: "Effect of Composition and Temperature on Phase Behavior and Depletion Performance of Rich Gas-Condensate Systems," J.Pet.Tech. (July, 1959) 58-63; Trans. AIME, 216, 406-411.
4. Katz, D.L. and Kurata, F.: "Retrograde Condensation," Ind.Eng.Chem. (1940), 32, 817-827.
5. Katz, D.L., et al.: Handbook of Natural Gas Engineering, McGraw Hill Book Co., Inc., New York City (1959).
6. Reid, R.C., Prausnitz, J.M., and Sherwood, T.K.: Properties of Gases and Liquids, 3rd Edition, McGraw Hill Co., Inc., New York City (1977).
7. Standing, M.B.: Volumetric and Phase Behavior of Oil Field Hydrocarbon Systems, Society of Petroleum Engineers, Dallas, 1977.
8. Yarborough, L.: "Application of a Generalized Equation of State to Petroleum Reservoir Fluids," Equations of State in Engineering and Research, Advances in Chemistry Series No. 182, ACS, Washington, D.C. (1979), 385-439.

TABLE 1 - Example Analysis of a Separator-Gas Sample.

ANALYSIS OF NATURAL GAS

| | | | |
|----------------|----------|------------------|----------|
| Sample arrived | 83.04.07 | Sample analysed: | 83.04.14 |
| Field: | NSCC/1B | Sampling date: | 83.03.13 |
| Well No: | 8 | Sampling time: | 20:37:33 |
| | | | hrs |

Sampling conditions:

| | | | | |
|-------------------|--------|------------|---|--------------|
| Sep. temperature: | 146.0 | °F | Specific gravity: (Operator enter value) | 0.6814 |
| Sep. pressure: | 664.7 | PSIG | Oil flow: | 525.0 |
| Choke size: | | /64 inches | Gas flow: | 13475 |
| Flowing density: | 2.140 | LBS/CUFT | H ₂ S (Dräger): | 10 |
| Mass flow: | 705580 | LBS/DAY | CO ₂ (Dräger): | 2.3 volume-% |

PR: 15:30 April 14, 1983

| Component | Weight-% | Mole-% | Molecular Weight |
|----------------|----------|--------|------------------|
| nitrogen | 0.82 | 0.59 | 28.02 |
| carbon dioxide | 4.57 | 2.09 | 44.01 |
| methane | 66.90 | 83.84 | 16.04 |
| ethane | 11.40 | 7.63 | 30.07 |
| propane | 6.61 | 3.01 | 44.09 |
| iso-butane | 1.41 | 0.49 | 58.12 |
| normal butane | 2.73 | 0.95 | 58.12 |
| iso-pentane | 1.28 | 0.36 | 72.15 |
| normal pentane | 1.44 | 0.40 | 72.15 |
| hexanes | 2.24 | 0.52 | 86.17* |
| heptanes-plus | 0.60 | 0.12 | 100.20* |
| total | 100.00 | 100.00 | 20.11** |

* Assumed
 ** Specific Gravity = 0.6942 (air=1).

$$y_i = w_i \cdot \frac{\bar{M}}{M_i}$$

where

$$y_i = \text{mole-}\%$$

$$w_i = \text{weight-}\%$$

$$M_i = \text{molecular weight}$$

$$\bar{M} = \text{average molecular weight}$$

$$= 100 / (\sum w_i / M_i)$$

$$= (\sum y_i \cdot M_i) / 100$$

Analysed by

TABLE 2 - Example Analysis of a Separator-Oil Sample.

ANALYSIS OF PRESSURED OIL

| | | | |
|----------------|----------|------------------|----------|
| Sample arrived | 83.04.07 | Sample analysed: | 83.04.22 |
| Field: | NSCC/1B | Sampling date: | 83.03.13 |
| Well No: | 8 | Sampling time: | 20:38:01 |
| | | | hrs |

Sampling conditions:

| | | | | |
|-------------------|--------|------------|---|--------|
| Sep. temperature: | 157.6 | °F | Specific gravity: (Operator enter value) | 0.6954 |
| Sep. pressure: | 707.2 | PSI | Oil flow: | 525.0 |
| Choke size: | | /64 inches | Gas flow: | 13475 |
| Flowing density: | 226.6 | LB/BBL | Water flow: | |
| Mass flow: | 232440 | LBS/DAY | | |

PR: 13:31 April 22, 1983

| Component | Weight-% | Mole-% | Molecular Weight |
|----------------|----------|--------|------------------|
| nitrogen | 0.01 | 0.04 | 28.02 |
| carbon dioxide | 0.27 | 0.63 | 44.01 |
| methane | 2.12 | 13.37 | 16.04 |
| ethane | 1.36 | 4.56 | 30.07 |
| propane | 1.99 | 4.57 | 44.09 |
| iso-butane | 0.86 | 1.49 | 58.12 |
| normal butane | 2.39 | 4.16 | 58.12 |
| iso-pentane | 1.82 | 2.55 | 72.15 |
| normal pentane | 2.40 | 3.36 | 72.15 |
| hexanes | 8.78 | 10.30 | 86.17* |
| heptanes-plus | 78.00 | 54.97 | 143.4** |
| total | 100.00 | 100.00 | 101.07 |

* Assumed
 ** Heptanes-plus Specific Gravity = 0.7802 (water=1)

$$y_i = w_i \cdot \frac{\bar{M}}{M_i}$$

where

$$y_i = \text{mole-}\%$$

$$w_i = \text{weight-}\%$$

$$M_i = \text{molecular weight}$$

$$\bar{M} = \text{average molecular weight}$$

$$= 100 / (\sum w_i / M_i)$$

$$= (\sum y_i \cdot M_i) / 100$$

Analysis of C7+:

| | | | | |
|-------------------------------|--------|--------------|----------------------|-----|
| Real specific gravity 60/60F: | 0.7747 | BS&W: < 0.06 | wt%, Salt: < 0.00011 | wt% |
| Average mol. wt.: | 143.4 | Analysed by: | | |
| Sulfur content: | 0.03 | | | wt% |

Analysis of non-pressurized oil sample:

TABLE 3 - Results of Recombination and Consistency Check for Separator-Gas and Oil Samples.

Sample Description : Field NSGC/1B, Well 8 (83.03.13)
 Separator Pressure (psia) : 700.6
 Separator Temperature (°F) : 151.8
 Separator Gas-Oil Ratio (scf/STB) ... : 25670

| Component | Compositions (mole-%) | | | Hoffman-Crump-Hocott Analysis | | | | |
|----------------|-----------------------|--------|--------|-------------------------------|-------------|--------|-------------|------------------------|
| | x | y | z | F | K (=y/x) | Kp | b (~·OR) | T _b (°R) |
| nitrogen | 0.04 | 0.59 | 0.57 | 3.544 | 14.75 | 10330. | 470.0 | 109.0 |
| carbon dioxide | 0.63 | 2.09 | 2.04 | 2.295 | 3.317 | 2324. | 652.0 | 194.0 |
| methane | 13.37 | 83.84 | 81.48 | 2.701 | 6.272 | 4394. | 300.0 | 94.0 |
| ethane | 4.56 | 7.63 | 7.53 | 1.907 | 1.673 | 1172. | 1145.0 | 303.0 |
| propane | 4.57 | 3.01 | 3.06 | 1.384 | 0.659 | 461.5 | 1799.0 | 416.0 |
| iso-butane | 1.49 | 0.49 | 0.52 | 0.995 | 0.329 | 230.4 | 2037.0 | 471.0 |
| normal butane | 4.16 | 0.95 | 1.06 | 0.866 | 0.228 | 160.0 | 2153.0 | 491.0 |
| iso-pentane | 2.55 | 0.36 | 0.43 | 0.498 | 0.141 | 98.91 | 2368.0 | 542.0 |
| normal pentane | 3.36 | 0.40 | 0.50 | 0.399 | 0.119 | 83.41 | 2480.0 | 557.0 |
| hexanes | 10.30 | 0.52 | 0.85 | 0.013 | 0.050 | 35.37 | 2780.0 | 616.0 |
| heptanes-plus | 54.97 | 0.12 | 1.96 | - | 0.00218 | 1.53 | * | * |
| | 100.00 | 100.00 | 100.00 | | | | | |

C7+ Sp. Gravity : 0.7802 - 0.7789
 C7+ Mol. Weight : 143.4 100.2 142.0
 C7+ Watson K_w : 11.95 - 11.95
 Tot. Mol. Weight : 101.1 20.11 22.84

Summary of Results From Same Well During First Flow Test (81.05.21)

Separator Pressure (psia) : 1099.9
 Separator Temperature (°F) : 193.7
 Separator Gas-Oil Ratio (scf/STB) ... : 9929

C7+ Sp. Gravity : 0.7911 - 0.7898
 C7+ Mol. Weight : 162.7 100.2 161.1
 C7+ Watson K_w : 12.04 - 12.04
 Tot. Mol. Weight : 102.6 19.40 26.1

* b and T_b are not readily defined for C7+ fractions. T_b can be approximated by the relation, T_b = (K_w·γ)³, where γ is the C7+ specific gravity of the wellstream fluid. The value of b can be back-calculated, where F(C7+) is read from the log Kp vs F straight line, extrapolated to the measured Kp value.

TABLE 4a - continued

| Well No. | Date Tested | Measured | | K _w | Calculated Molecular Weight (K _w =12.02) |
|------------|-------------|------------------|------------------|----------------|---|
| | | Molecular Weight | Specific Gravity | | |
| NSGC/1A-13 | 81.06.28 | 170.2 | 0.7970 | 12.04 | 168.1 |
| | 81.08.30 | 172.7 | 0.7976 | 12.06 | 168.8 |
| | 82.02.04 | 163.4 | 0.7935 | 12.01 | 164.0 |
| | 82.06.17 | 164.3 | 0.7920 | 12.04 | 162.3 |
| NSGC/1A-10 | 82.09.02 | 161.1 | 0.7908 | 2.02 | 161.0 |
| | 81.07.14 | 159.0 | 0.7881 | 12.03 | 157.9 |
| | 81.08.30 | 152.6 | 0.7861 | 11.98 | 155.7 |
| | 81.11.11 | 150.3 | 0.7904 | 11.98 | 160.5 |
| NSGC/1A-15 | 81.12.04 | 153.7 | 0.7849 | 12.01 | 154.4 |
| | 82.06.16 | 151.9 | 0.7821 | 12.03 | 151.3 |
| | 82.09.03 | 149.8 | 0.7813 | 12.01 | 150.5 |
| | 82.12.03 | 148.4 | 0.7801 | 12.01 | 149.2 |
| NSGC/1A-1 | 81.06.30 | 163.0 | 0.7896 | 12.06 | 159.6 |
| | 82.03.04 | 155.0 | 0.7846 | 12.03 | 154.0 |
| | 82.05.10 | 150.9 | 0.7822 | 12.01 | 151.4 |
| | 82.06.17 | 154.2 | 0.7835 | 12.03 | 152.8 |
| NSGC/1A-4 | 82.09.02 | 153.6 | 0.7823 | 12.04 | 151.5 |
| | 81.08.31 | 172.5 | 0.7999 | 12.03 | 171.6 |
| | 81.11.10 | 167.8 | 0.7948 | 12.04 | 165.5 |
| | 82.02.01 | 164.2 | 0.7939 | 12.02 | 164.5 |
| NSGC/1A-4 | 82.05.02 | 158.8 | 0.7919 | 11.98 | 162.2 |
| | 83.02.21 | 171.6 | 0.7992 | 12.03 | 170.7 |
| | 81.08.29 | 165.3 | 0.7918 | 12.06 | 162.1 |
| | 81.11.06 | 164.4 | 0.7929 | 12.03 | 163.4 |
| NSGC/1A-20 | 82.05.04 | 158.3 | 0.7873 | 12.03 | 157.0 |
| | 82.11.02 | 157.6 | 0.7869 | 12.03 | 156.6 |

TABLE 4a - Heptanes-Plus Characterization Based on Molecular Weight and Specific Gravity Measurements: Field NSGC/1A.

| Well No. | Date Tested | Measured | | K _w | Calculated Molecular Weight (K _w =12.02) |
|------------|-------------|------------------|------------------|----------------|---|
| | | Molecular Weight | Specific Gravity | | |
| NSGC/1A-16 | 81.02.14 | 154.3 | 0.7872 | 11.99 | 156.9 |
| | 81.07.24 | 161.8 | 0.7907 | 12.03 | 160.8 |
| | 81.10.01 | 150.3 | 0.7810 | 12.02 | 150.2 |
| | 82.01.09 | 150.9 | 0.7830 | 12.00 | 152.3 |
| | 82.02.04 | 155.9 | 0.7875 | 12.00 | 157.2 |
| | 82.05.08 | 148.5 | 0.7815 | 11.99 | 150.7 |
| | 82.06.19 | 151.2 | 0.7809 | 12.03 | 150.0 |
| | 82.07.07 | 155.2 | 0.7843 | 12.04 | 153.7 |
| | 83.01.09 | 150.1 | 0.7798 | 12.04 | 148.9 |
| | NSGC/1A-3 | 81.02.13 | 164.9 | 0.7947 | 12.01 |
| 81.04.03 | | 166.7 | 0.7950 | 12.03 | 165.8 |
| 81.06.28 | | 164.1 | 0.7928 | 12.03 | 163.2 |
| 81.08.28 | | 165.9 | 0.7942 | 12.03 | 164.8 |
| 81.10.06 | | 163.8 | 0.7936 | 12.02 | 164.2 |
| 81.12.04 | | 162.4 | 0.7917 | 12.02 | 162.0 |
| 82.01.09 | | 161.5 | 0.7935 | 11.99 | 164.0 |
| 82.04.01 | | 160.0 | 0.7905 | 12.01 | 160.6 |
| 82.06.15 | | 161.2 | 0.7902 | 12.03 | 160.3 |
| NSGC/1A-19 | | 81.02.16 | 159.6 | 0.7909 | 12.00 |
| | 81.04.09 | 160.9 | 0.7907 | 12.02 | 160.8 |
| | 81.07.22 | 162.9 | 0.7913 | 12.04 | 161.5 |
| | 81.08.31 | 155.5 | 0.7879 | 11.99 | 157.7 |
| | 81.09.30 | 159.9 | 0.7878 | 12.05 | 157.6 |
| | 81.12.05 | 154.4 | 0.7858 | 12.01 | 155.4 |
| | 82.01.10 | 154.8 | 0.7848 | 12.03 | 154.3 |
| | 82.04.08 | 152.9 | 0.7826 | 12.01 | 151.9 |
| | 82.07.07 | 150.1 | 0.7813 | 12.02 | 150.5 |
| | 82.10.06 | 150.6 | 0.7813 | 12.02 | 150.5 |
| NSGC/1A-20 | 83.01.07 | 149.0 | 0.7792 | 12.03 | 148.2 |
| | 81.04.09 | 165.3 | 0.7958 | 12.00 | 166.7 |
| | 82.05.01 | 170.9 | 0.7986 | 12.03 | 170.0 |
| | 82.08.08 | 164.5 | 0.7936 | 12.02 | 164.2 |
| NSGC/1A-20 | 82.11.04 | 163.0 | 0.7935 | 12.01 | 164.0 |
| | 83.02.21 | 169.9 | 0.7990 | 12.01 | 170.5 |

TABLE 4b - continued

| Well No. | Date Tested | Measured | | K _w | Calculated Molecular Weight (K _w =12.02) | |
|------------|-------------|------------------|------------------|----------------|---|-------|
| | | Molecular Weight | Specific Gravity | | | |
| NSGC/1B-16 | 81.03.11 | 172.3 | 0.7989 | 12.04 | 170.4 | |
| | 81.05.12 | 166.8 | 0.7967 | 12.01 | 167.8 | |
| | 82.02.14 | 151.0 | 0.7834 | 12.00 | 152.7 | |
| | 82.07.13 | 149.2 | 0.7793 | 12.03 | 148.3 | |
| | 82.09.14 | 148.9 | 0.7793 | 12.03 | 148.3 | |
| | 82.11.04 | 146.4 | 0.7774 | 12.02 | 146.4 | |
| | 83.02.04 | 143.7 | 0.7765 | 12.00 | 145.4 | |
| | NSGC/1B-20 | 81.03.11 | 174.9 | 0.8001 | 12.05 | 171.8 |
| | | 81.05.11 | 172.2 | 0.7991 | 12.04 | 170.6 |
| | | 81.10.07 | 166.7 | 0.7953 | 12.03 | 166.1 |
| 82.02.04 | | 161.2 | 0.7925 | 12.00 | 162.9 | |
| 82.05.21 | | 159.5 | 0.7903 | 12.01 | 160.4 | |
| 82.07.16 | | 159.7 | 0.7904 | 12.01 | 160.5 | |
| 82.12.09 | | 155.6 | 0.7875 | 12.00 | 157.2 | |
| NSGC/1B-9 | | 81.03.11 | 177.7 | 0.8031 | 12.04 | 175.4 |
| | | 81.05.10 | 168.4 | 0.7955 | 12.04 | 166.4 |
| | | 82.04.10 | 151.5 | 0.7827 | 12.01 | 152.0 |
| | 82.05.16 | 151.5 | 0.7824 | 12.02 | 151.6 | |
| | 82.06.17 | 152.9 | 0.7826 | 12.03 | 151.9 | |
| | 83.02.13 | 153.0 | 0.7855 | 12.00 | 155.0 | |
| | NSGC/1B-6 | 81.03.31 | 181.4 | 0.8040 | 12.07 | 176.5 |
| | | 81.10.08 | 166.6 | 0.7960 | 12.02 | 166.9 |
| | | 81.11.29 | 163.2 | 0.7930 | 12.02 | 163.5 |
| | | 82.05.16 | 157.0 | 0.7873 | 12.02 | 157.0 |
| 82.07.13 | | 154.7 | 0.7845 | 12.03 | 153.9 | |
| 82.09.13 | | 153.5 | 0.7839 | 12.02 | 153.3 | |
| 82.11.03 | | 150.1 | 0.7835 | 11.99 | 152.8 | |
| 83.02.03 | | 148.2 | 0.7813 | 11.99 | 150.5 | |
| NSGC/1B-3 | | 81.04.01 | 181.6 | 0.8058 | 12.05 | 178.7 |
| | | 81.06.14 | 174.0 | 0.8000 | 12.04 | 171.7 |
| | 82.01.23 | 164.3 | 0.7963 | 11.99 | 167.3 | |
| | 82.05.15 | 159.8 | 0.7898 | 12.02 | 159.8 | |
| | 82.08.12 | 165.3 | 0.7935 | 12.03 | 164.0 | |
| | 82.10.10 | 160.5 | 0.7900 | 12.03 | 160.0 | |
| | 82.12.09 | 158.3 | 0.7896 | 12.01 | 159.6 | |
| | 83.01.09 | 169.3 | 0.7975 | 12.03 | 168.7 | |
| | NSGC/1B-18 | 81.04.01 | 174.2 | 0.7995 | 12.05 | 171.1 |
| | | 81.06.10 | 170.0 | 0.7976 | 12.03 | 168.8 |
| 82.01.23 | | 155.9 | 0.7873 | 12.01 | 157.0 | |
| 82.05.19 | | 154.0 | 0.7851 | 12.01 | 154.6 | |
| 82.08.09 | | 151.3 | 0.7821 | 12.02 | 151.3 | |
| 82.10.07 | | 149.0 | 0.7804 | 12.01 | 149.5 | |
| 83.01.06 | | 148.5 | 0.7785 | 12.03 | 147.5 | |
| NSGC/1B-8 | | 81.06.14 | 162.4 | 0.7904 | 12.04 | 160.5 |
| | | 81.10.08 | 158.3 | 0.7877 | 12.03 | 157.5 |
| | | 82.01.23 | 150.8 | 0.7833 | 12.00 | 152.6 |
| | 82.02.14 | 147.8 | 0.7804 | 12.00 | 149.5 | |
| | 82.04.11 | 149.4 | 0.7804 | 12.02 | 149.5 | |
| | 82.06.19 | 146.9 | 0.7780 | 12.02 | 147.0 | |
| | 82.09.14 | 145.1 | 0.7765 | 12.02 | 145.4 | |
| | 82.11.04 | 145.0 | 0.7755 | 12.03 | 144.4 | |
| | NSGC/1B-5 | 81.08.30 | 164.0 | 0.7936 | 12.02 | 164.2 |
| | | 81.11.28 | 152.2 | 0.7838 | 12.01 | 153.2 |
| 82.04.09 | | 150.4 | 0.7817 | 12.01 | 150.9 | |
| 82.05.21 | | 158.0 | 0.7898 | 12.00 | 159.8 | |
| 82.06.18 | | 154.7 | 0.7864 | 12.00 | 156.0 | |
| 82.08.07 | | 154.0 | 0.7858 | 12.00 | 155.4 | |
| 82.10.05 | | 156.0 | 0.7881 | 12.00 | 157.9 | |
| 83.01.01 | | 155.5 | 0.7878 | 12.00 | 157.6 | |

TABLE 4c - Heptanes-Plus Characterization Based on Molecular Weight and Specific Gravity Measurements: Field NSGC/2.

| Well No. | Date Tested | Measured | | K _w | Calculated Molecular Weight (K _w =11.99) |
|----------|-------------|------------------|------------------|----------------|---|
| | | Molecular Weight | Specific Gravity | | |
| NSGC/2-5 | 81.04.22 | 143.6 | 0.7774 | 11.99 | 143.9 |
| | 81.09.24 | 142.2 | 0.7763 | 11.98 | 142.8 |
| | 82.06.22 | 139.4 | 0.7720 | 12.00 | 138.5 |
| | 83.02.18 | 134.1 | 0.7683 | 11.98 | 134.8 |
| NSGC/2-9 | 81.03.14 | 150.6 | 0.7840 | 11.99 | 150.9 |
| | 82.01.09 | 139.1 | 0.7719 | 12.00 | 138.4 |
| | 82.02.10 | 137.0 | 0.7730 | 11.96 | 135.5 |
| | 82.07.18 | 138.7 | 0.7718 | 12.00 | 138.3 |
| | 82.12.23 | 134.1 | 0.7678 | 11.99 | 134.3 |
| NSGC/2-8 | 81.03.13 | 148.3 | 0.7817 | 11.99 | 148.4 |
| | 81.09.24 | 141.6 | 0.7760 | 11.98 | 142.5 |
| | 82.12.23 | 134.4 | 0.7685 | 11.98 | 135.0 |
| NSGC/2-1 | 81.03.13 | 151.6 | 0.7848 | 11.99 | 151.7 |
| | 81.09.26 | 142.7 | 0.7756 | 12.00 | 142.1 |
| | 82.03.21 | 138.8 | 0.7721 | 11.99 | 135.0 |
| NSGC/2-4 | 81.04.21 | 144.9 | 0.7783 | 11.99 | 144.9 |
| | 82.01.10 | 140.4 | 0.7740 | 11.99 | 140.5 |
| | 82.02.12 | 139.4 | 0.7740 | 11.98 | 140.5 |
| | 82.05.16 | 139.6 | 0.7733 | 11.99 | 139.8 |
| | 82.07.18 | 138.7 | 0.7718 | 11.99 | 138.3 |
| | 82.12.23 | 134.1 | 0.7678 | 11.99 | 134.3 |
| NSGC/2-3 | 81.04.22 | 145.1 | 0.7771 | 12.01 | 143.6 |
| | 82.01.08 | 137.4 | 0.7722 | 11.97 | 138.7 |
| | 82.02.11 | 137.3 | 0.7714 | 11.98 | 137.9 |
| | 83.02.17 | 133.5 | 0.7670 | 11.99 | 133.5 |

TABLE 4d - Heptanes-Plus Characterization Based on Molecular Weight and Specific Gravity Measurements: Field NSBO/3B.

| Well No. | Date Tested | Measured | | K _w | Calculated Molecular Weight (K _w =11.90) |
|------------|-------------|------------------|------------------|----------------|---|
| | | Molecular Weight | Specific Gravity | | |
| NSBO/3B-1 | 81.10.25 | 217.7 | 0.8446 | 11.90 | 217.4 |
| | 81.12.17 | 229.8 | 0.8535 | 11.89 | 230.5 |
| | 82.04.19 | 228.9 | 0.8532 | 11.89 | 230.0 |
| | 81.02.13 | 245.5 | 0.8621 | 11.90 | 243.7 |
| NSBO/3B-14 | 81.09.13 | 247.8 | 0.8646 | 11.90 | 247.7 |
| | 81.10.08 | 245.7 | 0.8637 | 11.90 | 246.2 |
| | 82.03.24 | 245.9 | 0.8636 | 11.90 | 246.1 |
| | 82.10.04 | 244.3 | 0.8637 | 11.89 | 246.2 |
| | 82.12.02 | 246.7 | 0.8634 | 11.91 | 245.8 |
| | 81.02.13 | 251.0 | 0.8669 | 11.90 | 251.4 |
| NSBO/3B-19 | 82.02.09 | 251.6 | 0.8672 | 11.90 | 251.9 |
| | 82.06.16 | 255.7 | 0.8670 | 11.93 | 251.5 |
| | 83.02.08 | 250.9 | 0.8658 | 11.91 | 249.6 |
| | 81.06.14 | 228.0 | 0.8530 | 11.89 | 229.7 |
| NSBO/3B-11 | 81.12.08 | 222.2 | 0.8502 | 11.87 | 225.6 |
| | 82.04.19 | 223.7 | 0.8506 | 11.88 | 226.1 |
| | 81.06.08 | 257.9 | 0.8711 | 11.90 | 258.2 |
| NSBO/3B-10 | 82.08.07 | 256.6 | 0.8704 | 11.90 | 257.1 |
| | 83.02.05 | 252.8 | 0.8702 | 11.87 | 256.8 |
| | 81.06.11 | 242.7 | 0.8607 | 11.91 | 241.5 |
| NSBO/3B-18 | 82.03.16 | 241.3 | 0.8605 | 11.90 | 241.2 |
| | 82.06.12 | 240.5 | 0.8610 | 11.89 | 242.0 |
| | 83.03.09 | 244.0 | 0.8618 | 11.91 | 243.2 |
| | 81.10.08 | 223.9 | 0.8490 | 11.90 | 223.8 |
| NSBO/3B-6 | 82.02.12 | 219.6 | 0.8482 | 11.88 | 222.6 |
| | 82.06.14 | 223.7 | 0.8486 | 11.90 | 223.2 |
| | 82.08.08 | 219.6 | 0.8468 | 11.89 | 220.6 |
| | 82.10.04 | 219.7 | 0.8474 | 11.89 | 221.4 |
| | 82.10.04 | 219.0 | 0.8470 | 11.88 | 220.9 |
| | 82.03.18 | 241.6 | 0.8596 | 11.91 | 239.8 |
| NSBO/3B-9 | 82.08.08 | 242.2 | 0.8610 | 11.90 | 242.0 |
| | 82.04.22 | 244.1 | 0.8628 | 11.89 | 244.8 |
| NSBO/3B-7 | 82.10.24 | 245.8 | 0.8654 | 11.89 | 249.0 |
| | 82.12.07 | 242.6 | 0.8613 | 11.90 | 242.5 |

TABLE 6 - Minimization Procedure for Matching CVD Data with the Peng-Robinson Equation of State.

| Run No. | Adjusted Parameter (C7+ Fraction) | Initial Value | Final Value | Data Matched | Error Reduction |
|---------|-----------------------------------|---------------|-------------|--------------|-----------------|
| 1 | δ (C1-F3) | 0.2 | 0.3368 | Pd | undefined |
| 2 | Tc (F1) | 976.1 | 1018.0 | CVD | undefined |
| | Tc (F2) | 1168.0 | 1261.0 | | |
| | Tc (F3) | 1408.0 | 1395.0 | | |
| 3 | δ (C1-F3) | 0.3368 | 0.3380 | Pd | 0.6 |
| 4 | Pc (F1) | 419.8 | 429.0 | CVD | 0.6 |
| | Pc (F2) | 268.9 | 260.2 | | |
| | Pc (F3) | 148.5 | 151.7 | | |
| 5 | δ (C1-F3) | 0.3380 | 0.3385 | Pd | -0.4 |
| 6 | ω (F1) | 0.5844 | 0.6040 | CVD | 0.1 |
| | ω (F2) | 0.6801 | 0.6800 | | |
| | ω (F3) | 0.8042 | 0.8030 | | |
| 7 | δ (C1-F3) | 0.3385 | 0.3388 | Pd | -0.3 |
| 8 | Tc (F3) | 1395.0 | 1320.0 | CVD and Pd | 1.8 |
| | Pc (F2) | 260.2 | 303.1 | | |
| | ω (F1) | 0.6040 | 0.4887 | | |
| | δ (C1-F3) | 0.3388 | 0.3840 | | |
| 9 | Tc (F1) | 1018.0 | 1010.0 | CVD and Pd | 0.2 |
| | Pc (F2) | 303.1 | 302.3 | | |
| | ω (F3) | 0.8027 | 0.8040 | | |
| | δ (C1-F3) | 0.3840 | 0.3840 | | |

Notes:

- δ (C1-F3) = binary interaction parameter between methane and the heaviest C7+ fraction, F3.
- Pd = dew-point pressure
- Undefined error reductions result from convergence problems with Run 1.
- Critical temperature, Tc, and critical pressure, Pc, have units OR and psia, respectively; acentric factor, ω , is dimensionless.
- The error function after Run 2 was 4.8 %. The final error function after Run 9 was 2.2 %. The error function is the average of the absolute deviation in saturation pressure and the root mean square of errors for CVD data.

TABLE 7 - Final "best-fit" Properties used in the Peng-Robinson EOS to Predict Constant-Volume Depletion Data from Field NSGC/1B.

| Component | Z (%) | M (g/mol) | T _g (OR) | P _c (psia) | ω | Y (water=1) |
|--------------------|-------|-----------|---------------------|-----------------------|----------|-------------|
| 1 - carbon dioxide | 2.37 | 44.010 | 547.57 | 1071.0 | 0.2250 | |
| 2 - nitrogen | 0.31 | 28.013 | 227.27 | 493.0 | 0.0400 | |
| 3 - methane | 73.19 | 16.043 | 343.04 | 667.8 | 0.0104 | |
| 4 - ethane | 7.80 | 30.070 | 549.76 | 707.8 | 0.0986 | |
| 5 - propane | 3.55 | 44.097 | 665.68 | 616.3 | 0.1524 | |
| 6 - iso-butane | 0.71 | 58.124 | 734.65 | 529.1 | 0.1848 | |
| 7 - normal butane | 1.45 | 58.124 | 765.32 | 550.7 | 0.2010 | |
| 8 - iso-pentane | 0.64 | 72.151 | 828.77 | 490.4 | 0.2223 | |
| 9 - normal pentane | 0.68 | 72.151 | 845.37 | 488.6 | 0.2539 | |
| 10 - hexanes | 1.09 | 84.000 | 931.97 | 483.0 | 0.2500 | |
| 11 - fraction 1 | 4.04 | 125.3 | 1010.37b | 429.0b | 0.4887b | |
| 12 - fraction 2 | 3.44 | 213.2 | 1261.27b | 302.3b | 0.6804b | |
| 13 - fraction 3 | 0.73 | 370.1 | 1319.87b | 151.7b | 0.8040b | |

Binary Interaction Coefficients^a

| | | | | | | | | | | | | |
|---|-------|------|------|------|------|------|------|------|------|------|------|-------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| 1 | -.200 | .100 | .130 | .135 | .130 | .130 | .125 | .125 | .125 | .110 | .110 | .110 |
| 2 | | .036 | .050 | .080 | .095 | .090 | .095 | .100 | .100 | .100 | .100 | .100 |
| 3 | | | | | | | | | | .039 | .049 | .384b |

a. Equal to zero except where specified otherwise.

b. Adjusted during regression.

Table 5 - Carbon-Number Distillation (ASTM D 2892-78) Results for a Mixture of Numerous Heptanes-Plus Fractions Sampled from North Sea Gas-Condensate and Black-Oil Reservoirs.

Initial Weighed Amount of C₇+ Material : 2073.1 g
 Reflux Ratio : 5 to 1
 Reflux Cycle : 18 seconds

Distillation at Atmospheric (Normal) Pressure : 94 to 175 °C
 Distillation at 100 mm Hg : 175 to 244 °C
 Distillation at 10 mm Hg : 244 to 345 °C

| Carbon No. | Normal Boiling-Point Range (°C) | Normal Boiling Point (°C) | Weight (g) | Density (g/cc) | Molecular Weight (g/mol) | Volume (cc) | Moles (mol) | Cumulative | | Moles (%) |
|---------------|---------------------------------|---------------------------|------------|----------------|--------------------------|-------------|-------------|------------|------------|-----------|
| | | | | | | | | Volume (%) | Weight (%) | |
| 7 | 69 - 98a | 90 | 90.2b | 0.7276 | 96 | 124.1 | 0.940 | 4.83 | 4.35 | 8.05 |
| 8 | 98 - 126 | 113 | 214.6 | 0.7452 | 110 | 288.0 | 1.951 | 16.03 | 14.70 | 16.70 |
| 9 | 126 - 151 | 139 | 225.3 | 0.7651 | 122 | 294.5 | 1.847 | 27.49 | 25.57 | 15.81 |
| 10 | 151 - 175 | 163 | 199.3 | 0.7704 | 137 | 258.7 | 1.455 | 37.56 | 35.18 | 12.46 |
| 11 | 175 - 194 | 184 | 128.8 | 0.7823 | 151 | 164.6 | 0.853 | 43.96 | 41.40 | 7.30 |
| 12 | 194 - 216 | 205 | 136.8 | 0.7902 | 161 | 173.1 | 0.850 | 50.70 | 48.00 | 7.28 |
| 13 | 216 - 235 | 226 | 123.8 | 0.8040 | 181 | 154.0 | 0.684 | 56.69 | 53.97 | 5.86 |
| 14 | 235 - 256 | 246 | 120.5 | 0.8214 | 193 | 146.7 | 0.624 | 62.40 | 59.78 | 5.34 |
| 15 | 256 - 273 | 265 | 101.6 | 0.8229 | 212 | 123.5 | 0.479 | 67.20 | 64.68 | 4.10 |
| 16 | 273 - 288 | 281 | 74.1 | 0.8271 | 230 | 89.6 | 0.322 | 70.69 | 68.26 | 2.76 |
| 17 | 288 - 304 | 296 | 76.8 | 0.8283 | 245 | 92.7 | 0.313 | 74.29 | 71.96 | 2.68 |
| 18 | 304 - 318 | 311 | 58.2 | 0.8370 | 259 | 69.5 | 0.225 | 77.00 | 74.77 | 1.93 |
| 19 | 318 - 332 | 325 | 50.2 | 0.8458 | 266 | 59.4 | 0.189 | 79.31 | 77.19 | 1.62 |
| 20 | 332 - 345 | 339 | 45.3 | 0.8528 | 280 | 53.1 | 0.162 | 81.37 | 79.37 | 1.39 |
| 21+ | 345 - | | 427.6 | 0.8933c | 545c | 478.7 | 0.785 | 100.00 | 100.00 | 6.72 |
| Total/Average | | | 2073.1 | 0.8066 | 177 | 2570.2 | 11.679 | | | 100.00 |

- Most likely some of the C₇ cut was lost during distillation of C₅ to C₆ fractions and the period of storage during which samples were analyzed (ca. 2 years).
- Distillation loss was 5.0 grams (0.3 %); this weight was added to the C₇ cut.
- Not measured, but back-calculated from measured C₇+ properties.

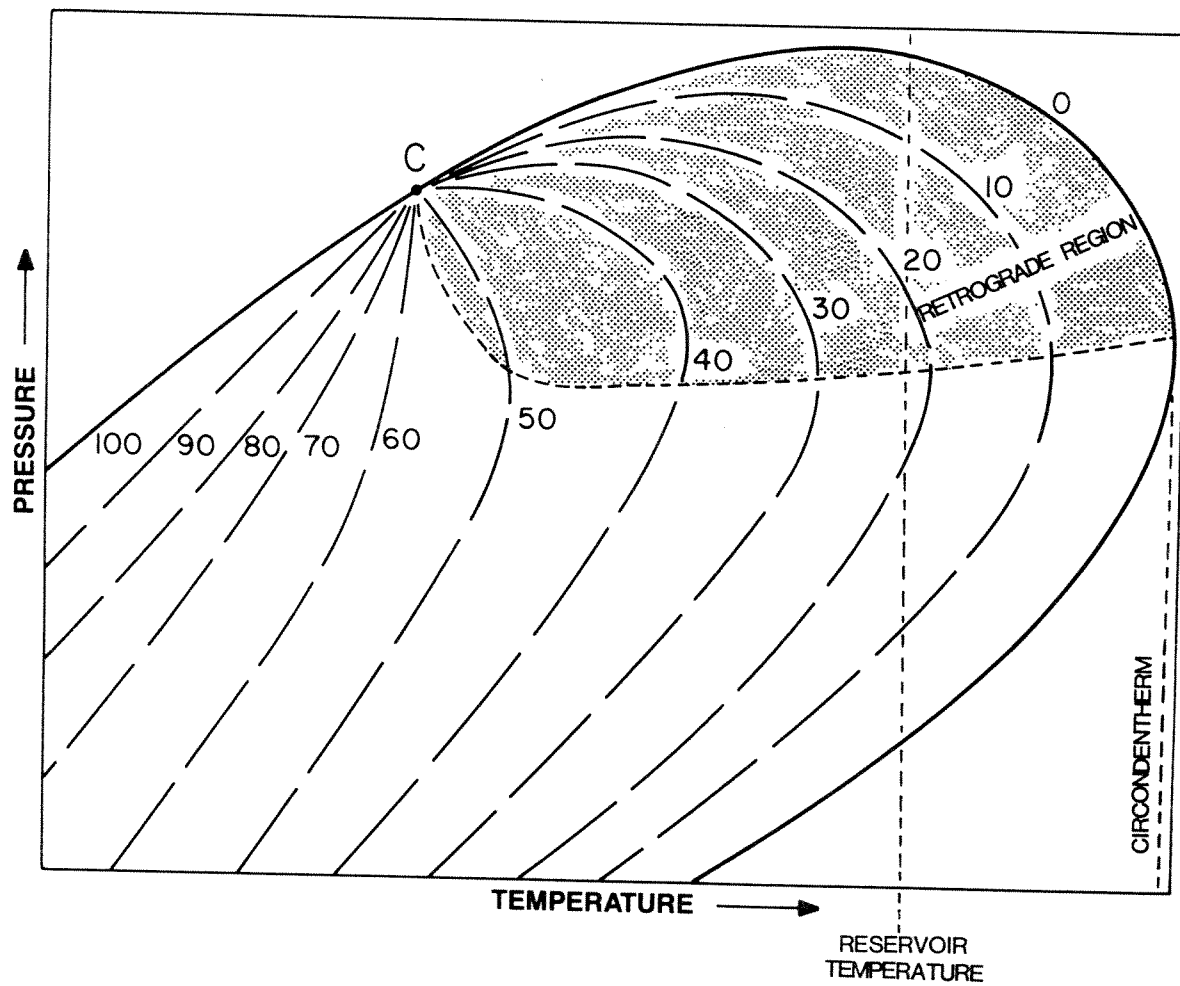


Fig. 1 - Hypothetical pressure-temperature phase diagram showing the isothermal retrograde region for a gas condensate.

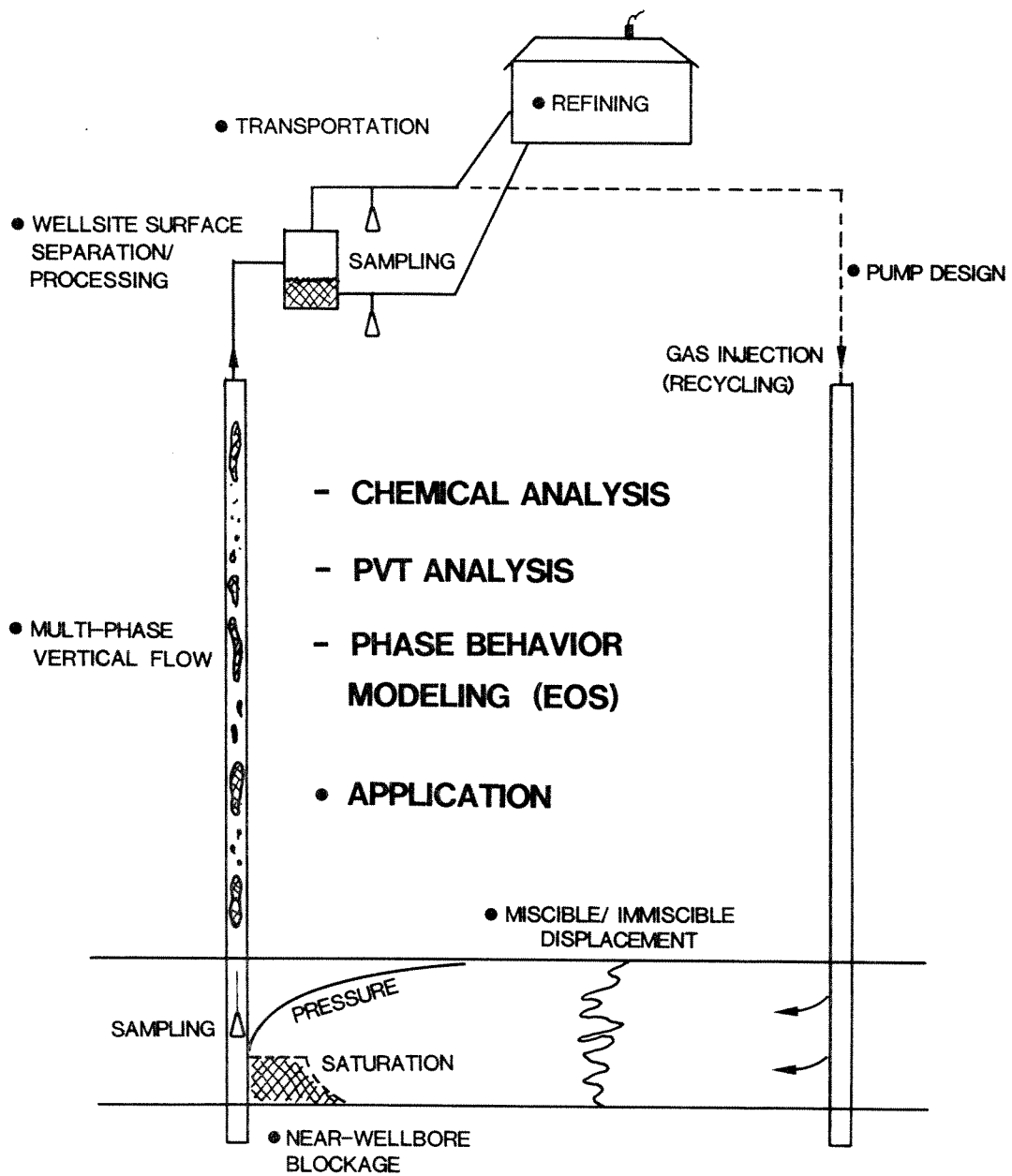


Fig. 2 - Schematic illustrating processes which are highly dependent on proper fluid characterization of gas condensate fluids.

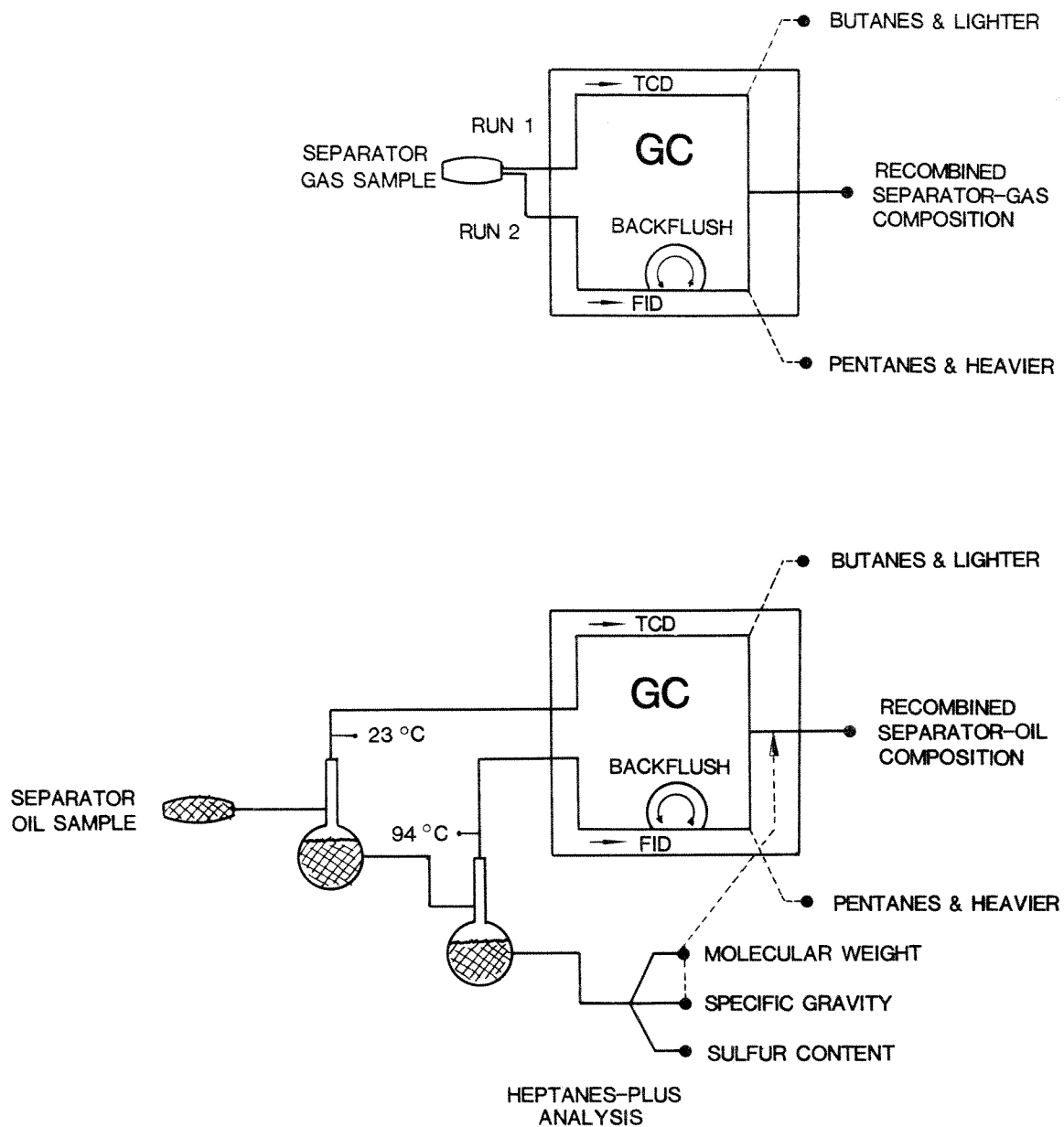


Fig. 3 - Schematic of separator-gas and separator-oil analyses using programmed gas chromatography, low-temperature distillation, and heptanes-plus characterization.

SEPARATOR-GAS ANALYSIS

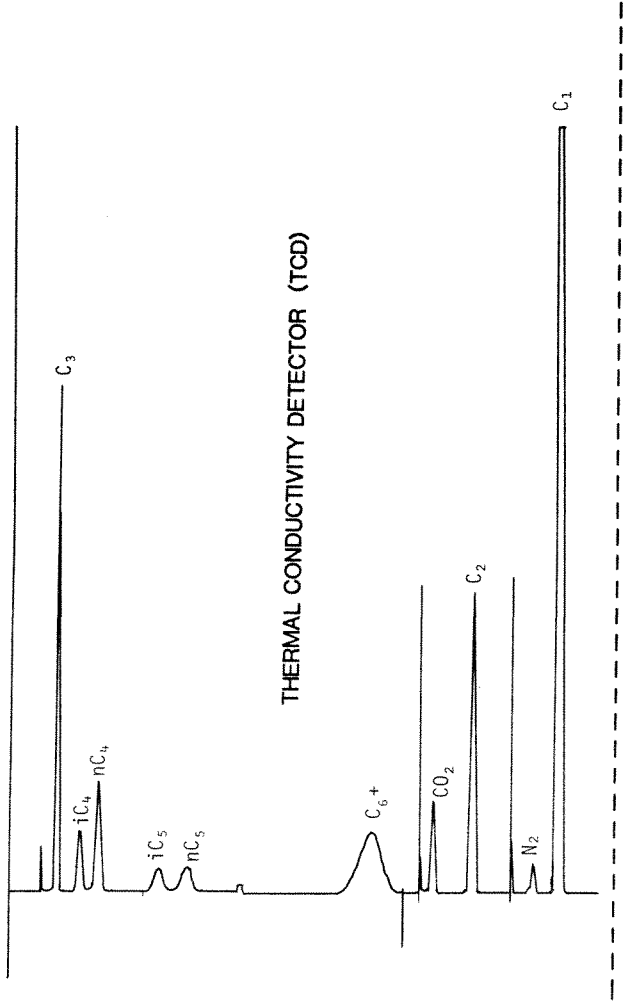


Fig. 4 - Two gas chromatograph runs (TCD and FID) used to analyze separator gas from Well 8, Field NSGC/1B, tested 83.03.13.

SEPARATOR-OIL ANALYSIS

(DISTILLATION BATCHES 1 & 2)

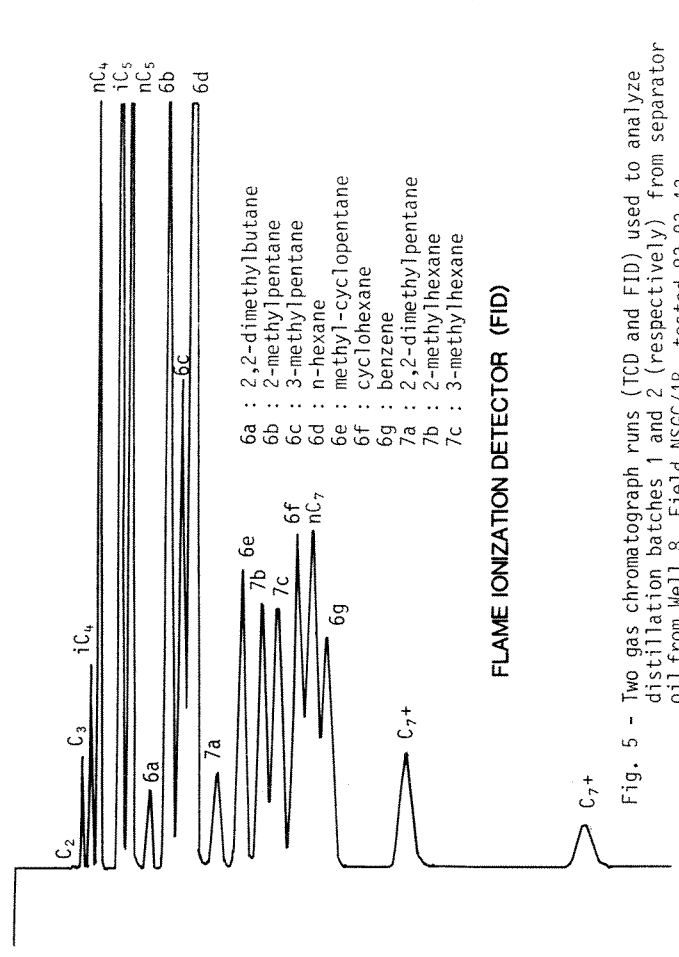
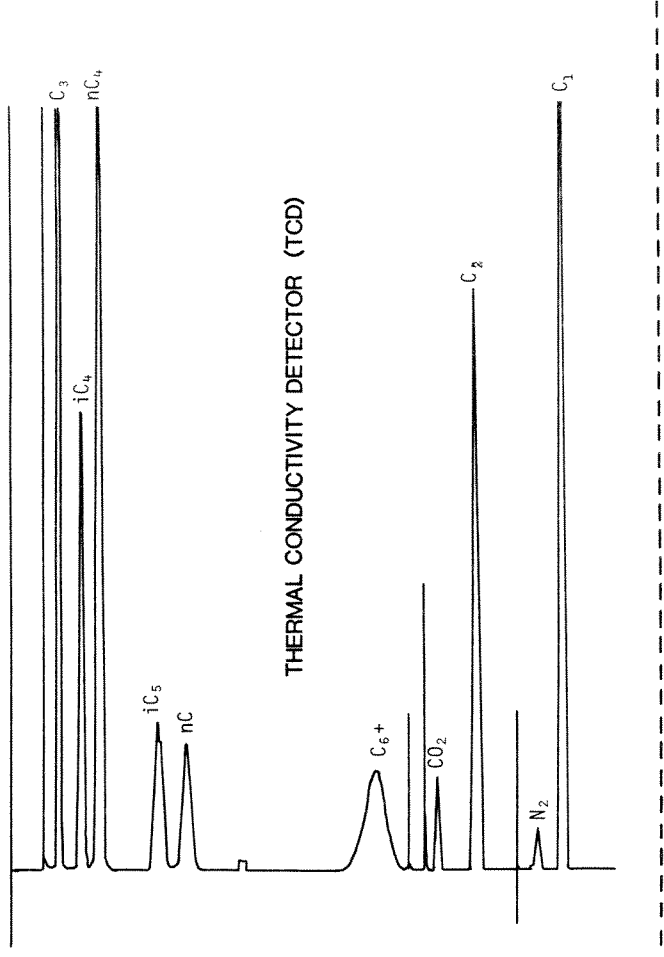


Fig. 5 - Two gas chromatograph runs (TCD and FID) used to analyze distillation batches 1 and 2 (respectively) from separator oil from Well 8, Field NSGC/1B, tested 83.03.13.

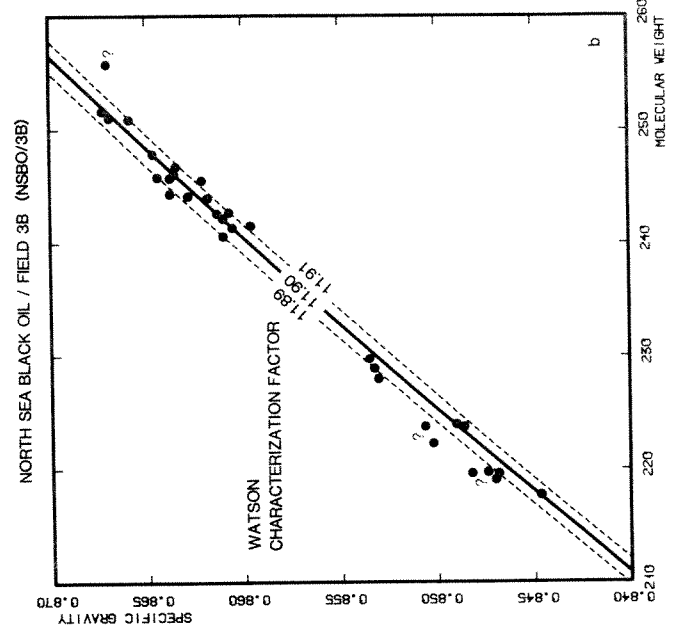
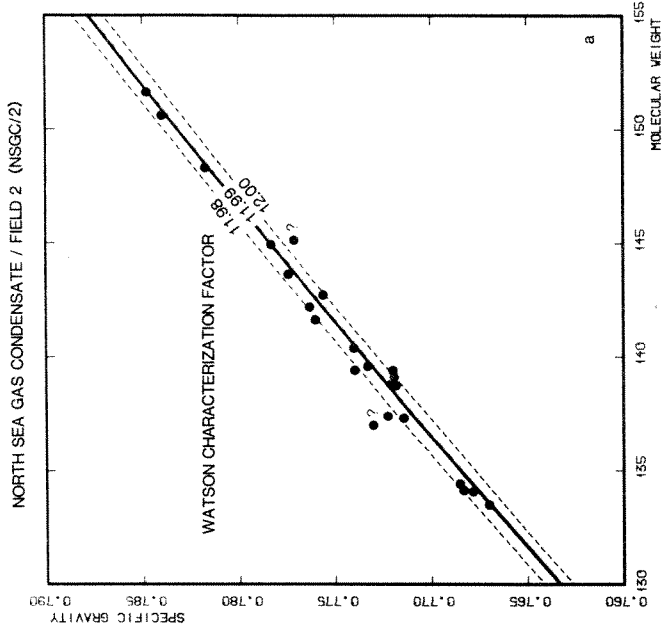


Fig. 7 - Heptanes-plus characterization based on measured molecular weight and specific gravity using the Watson characterization factor.

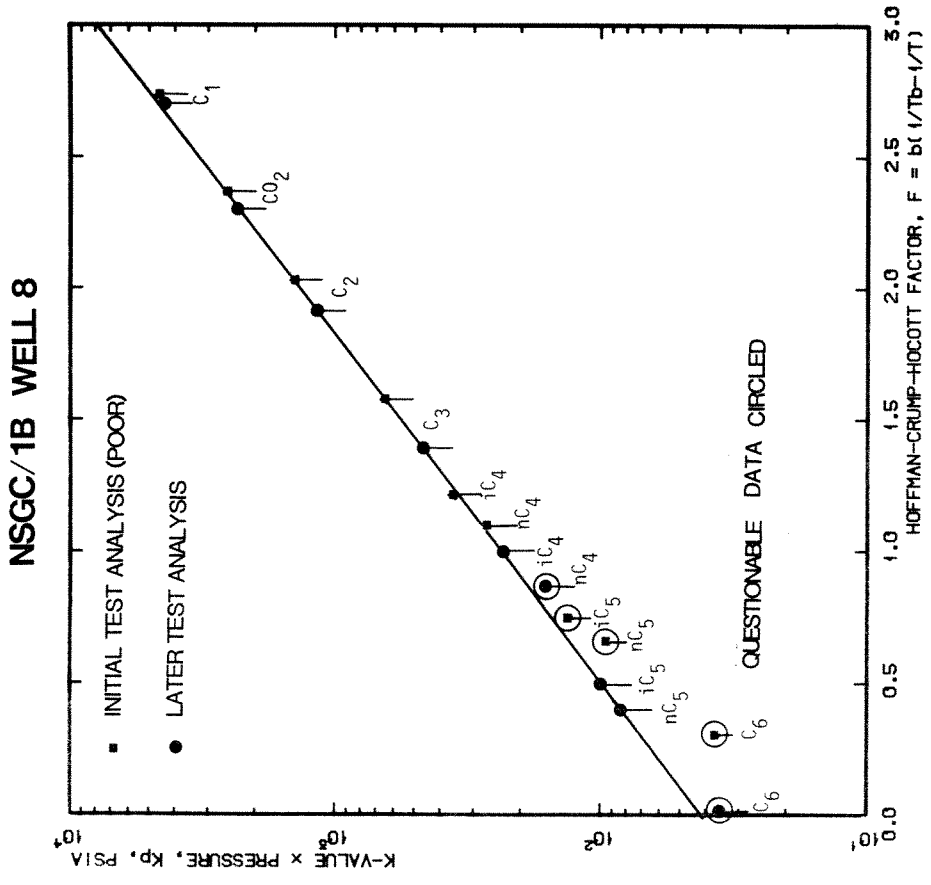


Fig. 6 - Illustration of how the Hoffman-Crump-Hocott method can be used to isolate possible errors in separator-fluid analysis due to sample-container leakage, inaccurate analysis or lack of equilibrium during sampling.

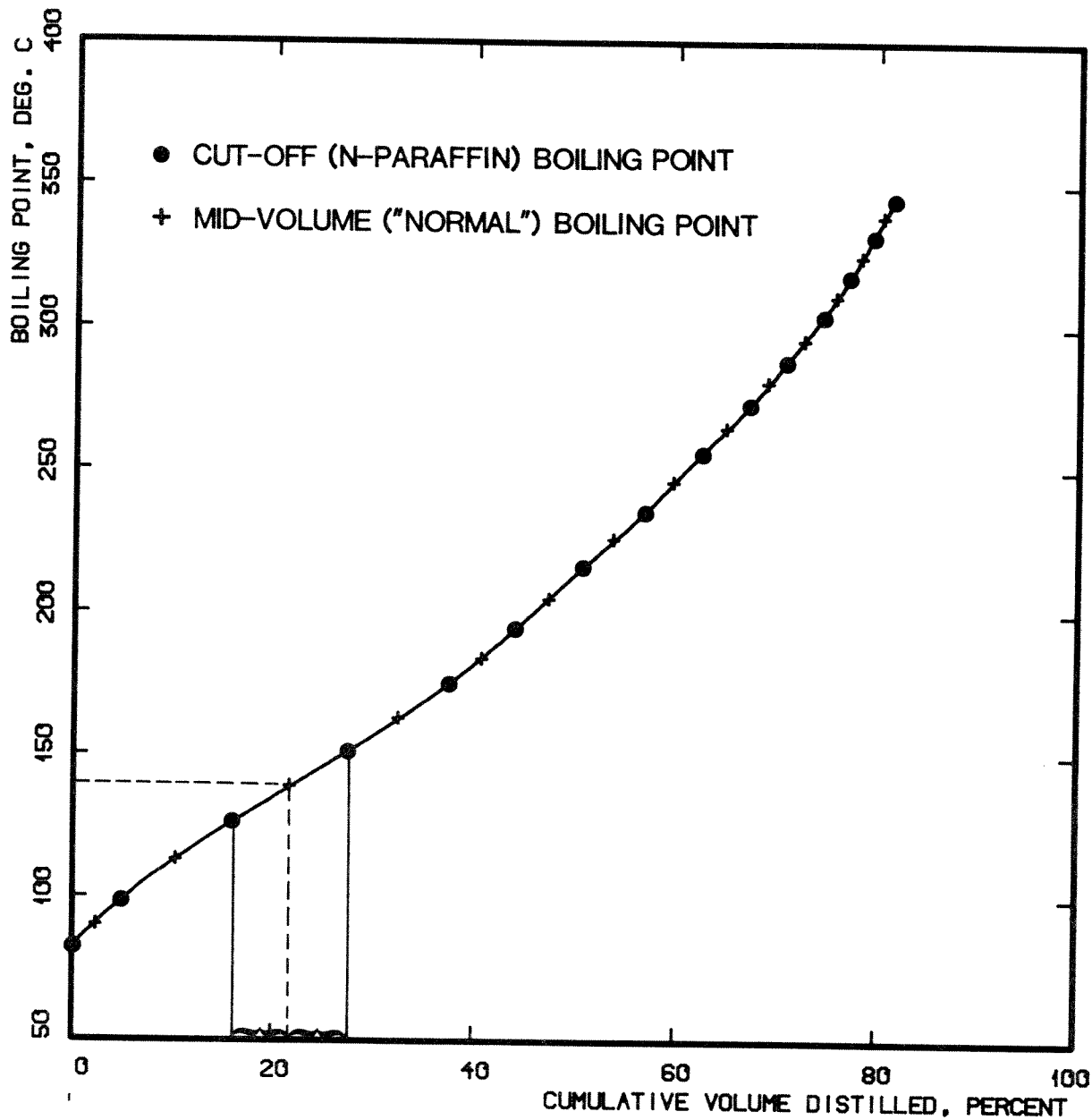
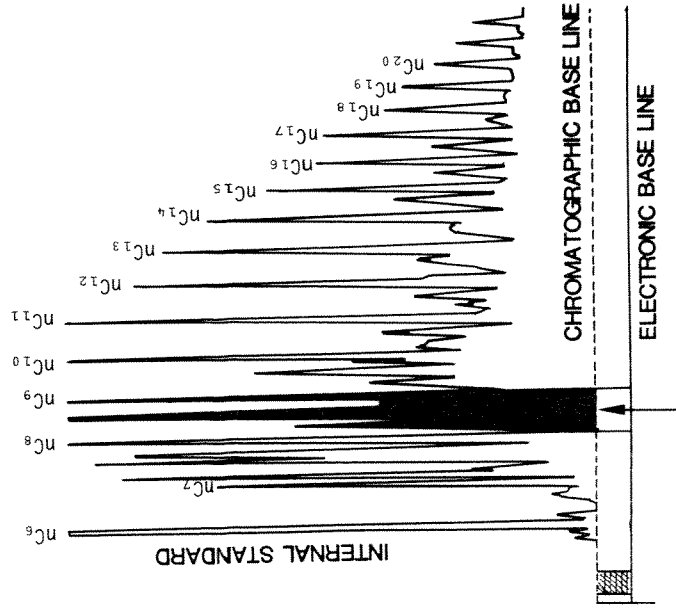


Fig. 8 - Carbon-number distillation (ASTM D 2892-78) boiling point curve for a blend of heptanes-plus fractions from gas-condensate and black-oil reservoirs in the North Sea.

GC SIMULATED DISTILLATION CHROMATOGRAM



CARBON NUMBER 9

Fig. 9 - Simulated distillation gas chromatogram for a blend of heptanes-plus fractions from gas-condensate and black-oil reservoirs in the North Sea.

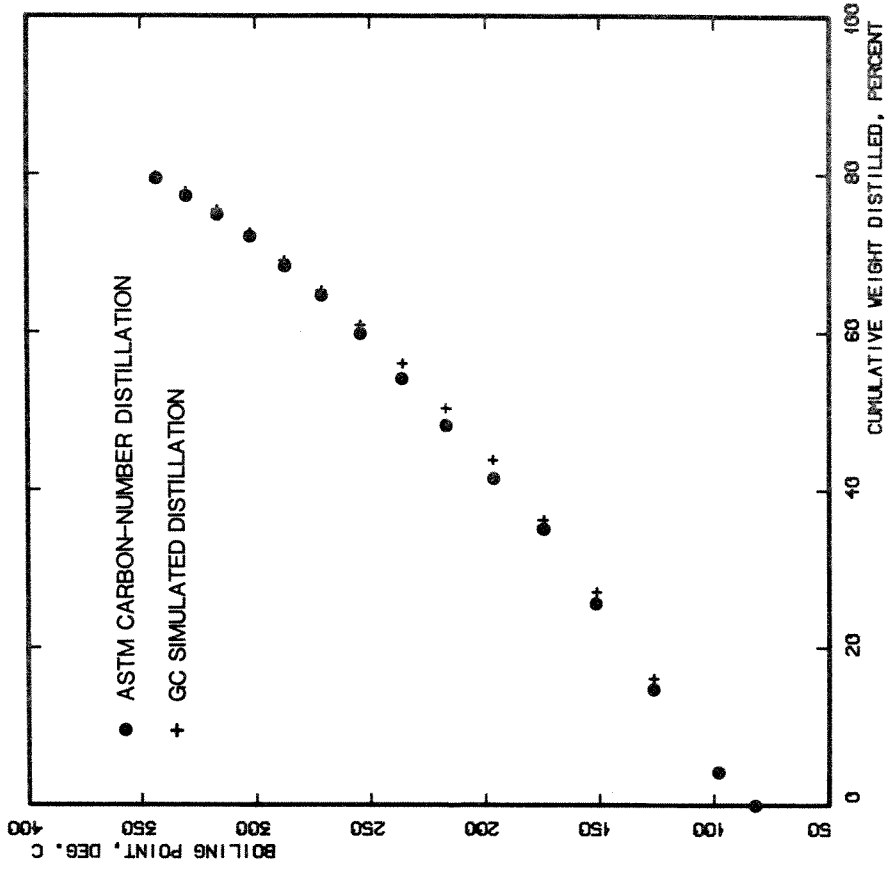


Fig. 10 - Comparison of ASTM carbon-number and GC-simulated boiling point curves (on weight-percent basis) for a blend of heptanes-plus fractions from gas-condensate and black-oil reservoirs in the North Sea.

NAPHTHENES MASS SPECTROGRAM

(TOTAL ION COUNT - TIC)

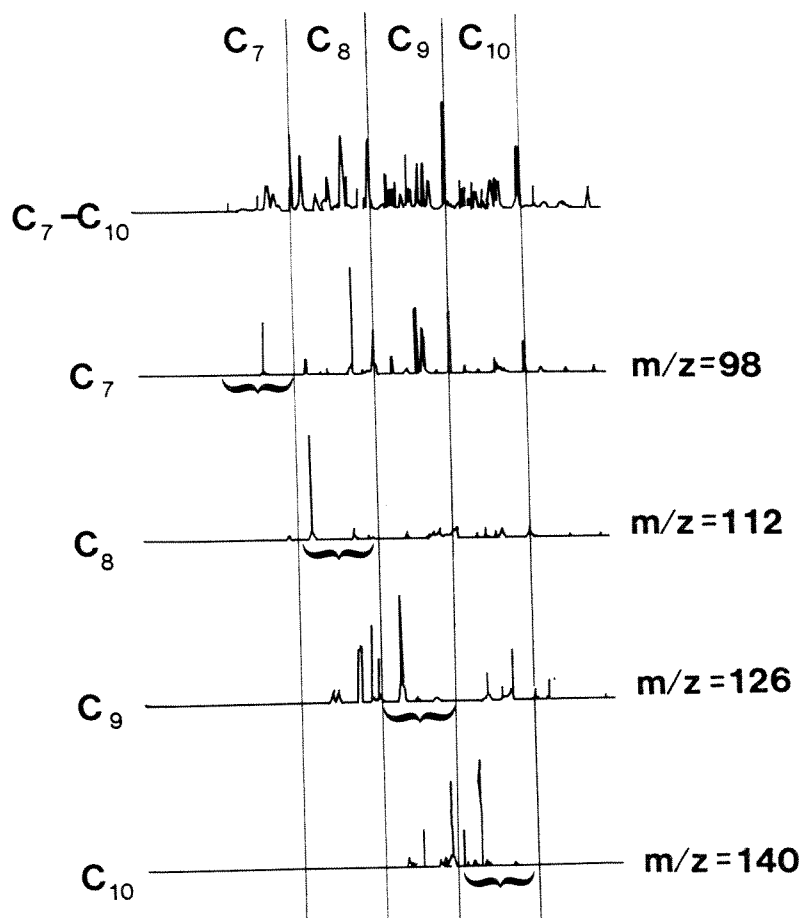


Fig. 11 - Example of GC-based mass spectrography used to isolate and quantify the content of a particular hydrocarbon family (naphthenes) in carbon-number distillation fractions up to C₁₀; analogous spectrograms can be made for paraffin and aromatic hydrocarbon families.

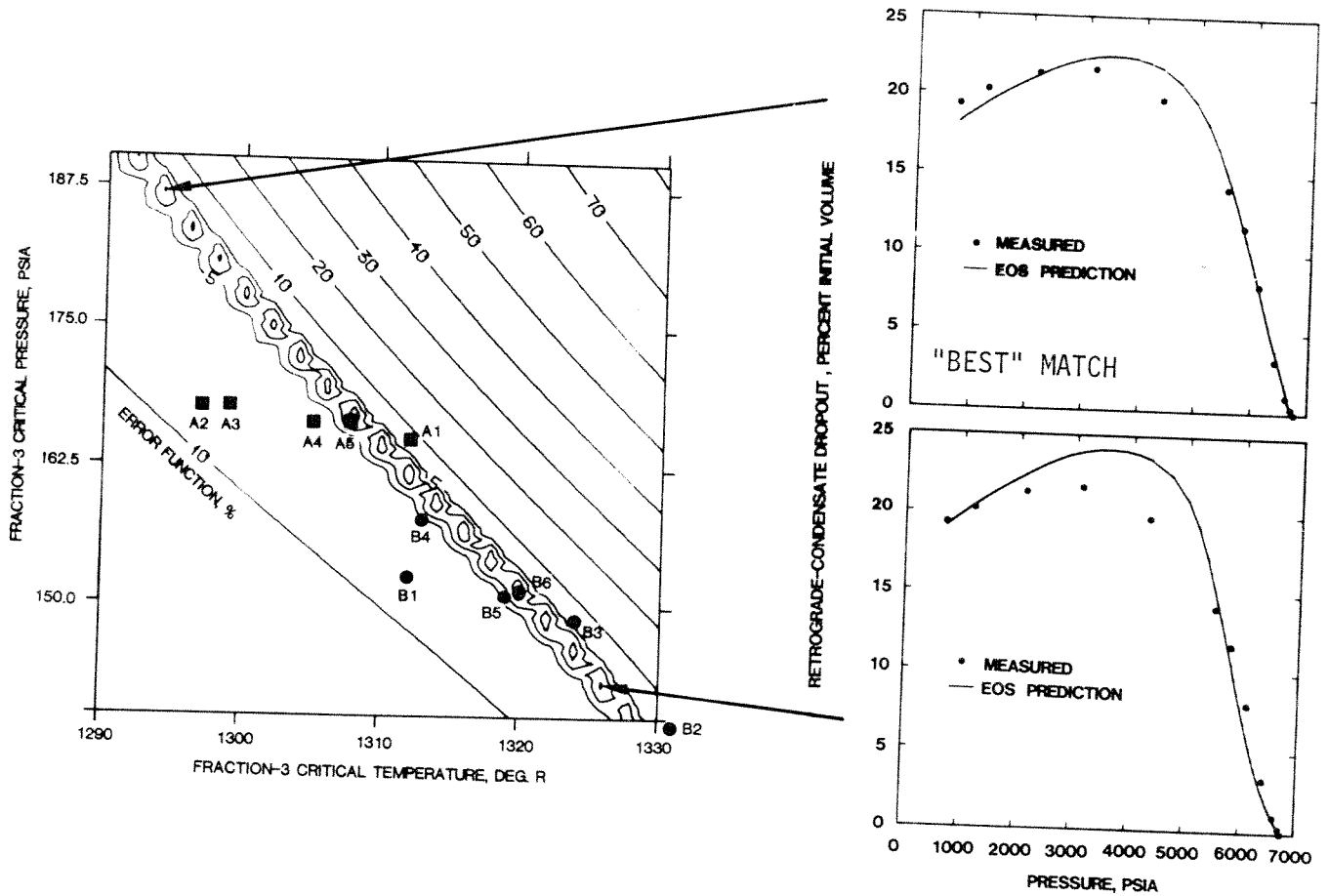


Fig. 12 - Results of Peng-Robinson EOS match for constant-volume depletion data from Field NSGC/1B illustrating two retrograde-condensation dropout curves for EOS predictions with the same overall error function (approximately 2 percent).

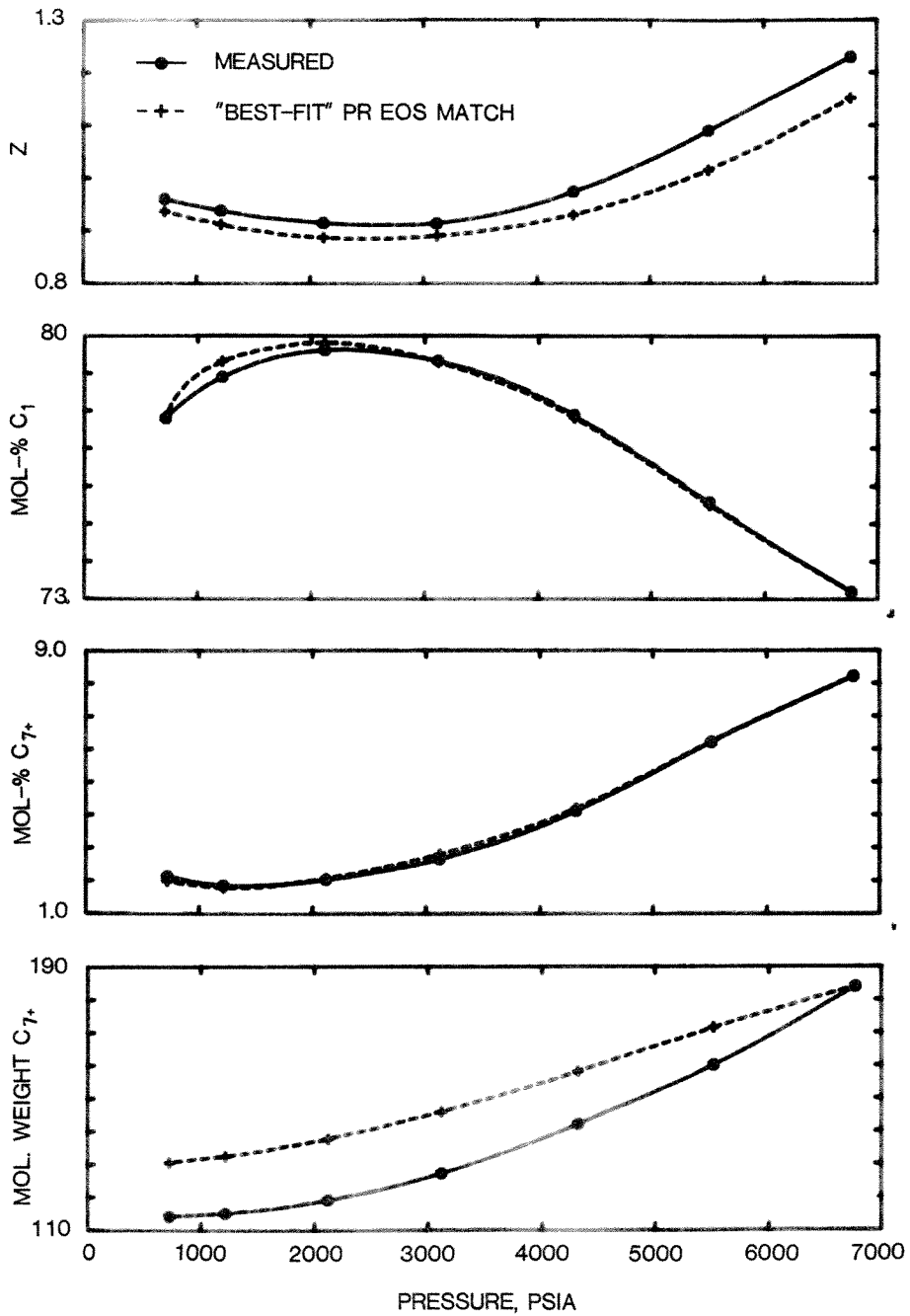


Fig. 13 - Results of predicted CVD data using the Peng-Robinson EOS and the proposed minimization routine ("best" match corresponds to liquid dropout curve in Fig. 12, upper inset).