EXPERT REPORT
U.S. v. BP Exploration & Production, Inc., et al.

EQUATION-OF-STATE FLUID CHARACTERIZATION AND ANALYSIS
OF THE
MACONDO RESERVOIR FLUIDS

Prepared on Behalf of the United States

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GLOSSARY

Acentric Factor. A component property determined by the temperature dependence of the component's vapor pressure.

Binary Interaction Parameter. An equation-of-state parameter that accounts for interactions between a given pair of components.

Black-Oil Table. A simple fluid phase behavior model in which the relative amounts, compositions, and properties of the equilibrium phases are tabulated functions of just a few (usually one or two) independent state variables, such as pressure and temperature. Any additional state variables that should normally be independent (such as composition) are assumed to depend in a predictable way on the tabulated variables. The applicability of the model is limited to processes for which that assumption remains valid.

Boiling Point. At standard, atmospheric pressure, the temperature at which a given component boils (when it can coexist in both a gas phase and a liquid phase, in equilibrium with each other).

Bubble Point. Any set of conditions at which a fluid transitions from a single-phase state to a two-phase state, with the second, incipient phase being less dense than the primary phase.

Chueh-Prausnitz Correlation. A correlation for the binary interaction parameter between two components based on their critical volumes.

Component. A single molecular species (e.g., nitrogen, methane, benzene, or n-decane), or a collection of similar species that is approximated (for EOS purposes) by a single, hypothetical species (e.g., C7, C15, C21-C25, or C30+). The former type of component is sometimes distinguished by the term *pure component*, while the latter type is sometimes distinguished by the term *pseudocomponent*. An equation of state makes no distinction between the two types of components, but they must generally be *characterized* differently (see *Fluid Characterization*).

Composition. The relative amounts (in terms of *mass* or *moles*) of all *components* that constitute a fluid.

Constant Composition Expansion. A lab experiment in which the fluid composition within a PVT cell is held constant while the pressure is varied. It is used to measure the saturation pressure and to measure the volume fractions (or saturations) of the equilibrium phases for all pressures below the saturation pressure.

Corresponding States. The principle that the behaviors of different components can be related by the ratios of the critical properties.

Critical Point. For a given fluid (possibly just a single component), the temperature and pressure at which two equilibrium phases become indistinguishable.

Critical Pressure. The pressure at a *critical point*. For a single component, this is the component's maximum vapor pressure.

Critical Temperature. The temperature at a *critical point*. For a single component, this is the maximum temperature at which a vapor pressure exists.

Critical Z-Factor. The z-factor of a component at the component's critical point. This component property is a key parameter in some viscosity models.

Dew Point. Any set of conditions at which a fluid transitions from a single-phase state to a two-phase state, with the second, incipient phase being more dense than the primary phase.

Differential Liberation Expansion. An experiment in which the fluid in a PVT cell is expanded a number of times to lower pressures, with the removal of all equilibrium gas after each expansion. The amount of liquid remaining in the cell is measured at each pressure, along with the amount, composition, and properties of the removed gas.

Equation of State. A mathematical equation (or set of equations) that models the relationships between a fluid's pressure, volume, temperature, and composition (which constitute the *state* of the fluid). An EOS also models a fluid's *phase behavior*, predicting when and how the fluid will partition into *equilibrium phases* (typically gas and liquid), giving the relative amounts, compositions, and properties of those phases. To apply an EOS to a fluid (or collection of related fluids), an EOS *fluid characterization* is required.

Equilibrate. To reach a state of *equilibrium*.

Equilibrium. A stable *state* of a system. When in equilibrium, a system will undergo no changes in state as long as there are no external influences on the system. In particular, there will be no phase changes and no transfer of mass or energy between phases.

Flash. The process in which a fluid separates into two phases as it *equilibrates*.

Fluid Characterization. A set of components, along with their physical and thermodynamic properties, serving as input to an equation of state to model the phase behavior of the characterized fluid(s). The necessary component properties include molecular weight, critical temperature, critical pressure, acentric factor, and volume shift factor. These properties are well known for many pure components, but they must be estimated somehow (from correlations and/or *regression*, e.g.) for *pseudocomponents*. A fluid characterization might also include a matrix of binary interaction parameters (BIPs), with one entry for each unique pair of components. Additionally, the composition of any fluid of interest will need to be expressed in terms of the characterization's components.

Formation Volume Factor. This is defined as the volume of reservoir fluid (at some specified temperature and pressure) that is required to produce a unit volume of stock tank oil through some specified process. Because the initial conditions and the process must both be specified before the term has any meaning, the formation volume factor is not an intrinsic property of a reservoir fluid. It can take on almost any value, depending on the specifications. For separation processes, it is the inverse of the separator shrinkage factor.

Gas Chromatography. A compositional analysis technique in which a fluid sample is injected into a fractionating column (along with a carrier gas) and the amount of effluent is measured as a function of time. The heavier the component (the higher its boiling point), the longer it takes to elute. The relative masses of each identifiable component and each single carbon number group (not counting any heavy end that never elutes) can thus be determined. The relative amount of the heavy end can be calculated from an additional analysis of the sample with a known amount of an internal standard added.

Gas-Oil Ratio. This is defined as the volume of gas at standard conditions (60 F and 1 atm) that is (or can be) removed from a specified fluid through some specified process per volume of liquid that will remain at the end of the process. Because the process must be specified before the term has any meaning, the gas-oil ratio is not an intrinsic property of a reservoir fluid. It can take on almost any value, depending on the specifications.

Interfacial Tension. A contracting force (per unit length) exerted between two fluid phases in contact with each other. This can have an influence on multiphase flow.

Library Component. Any pure, identifiable molecular species whose properties have been well established experimentally. Those properties can be looked up from the built-in component libraries of most commercial phase behavior software, such as PhazeComp.

Lohrenz-Bray-Clark Viscosity Model. An industry standard model that predicts the viscosity of a fluid mixture, given the temperature, pressure, density, and composition of the mixture and the critical properties of the mixture's components.

Mass. The amount of a substance that is proportional to its weight. The mass of a substance equals its moles multiplied by its molecular weight.

Molar volume. The volume per mole of a substance, where a mole is defined as a certain fixed number of molecules.

Moles. The amount of a substance that is proportional to the number of its molecules. The moles of a substance equal its mass divided by its molecular weight.

Near-Critical Fluid. A fluid whose conditions of temperature, pressure, and composition are very near those of a *critical point*.

Orrick-Erbar Correlation. A method of estimating liquid viscosities for pure components.

Parachor. A component property for use in the *Weinaug-Katz interfacial tension model*.

Peng-Robinson EOS. One of the most commonly used equations of state in the petroleum industry.

Peneloux Volume Shift Parameter. An industry standard extension to an EOS (adding an extra EOS parameter for each component) that greatly improves the accuracy of the densities predicted by the EOS.

Phase. A distinctive physical form (e.g., gas, liquid, or solid) assumed by all or part of a fluid. The composition and physical properties of a phase will all be at least continuous, if not uniform. Note that it might not be possible to label a phase (as a gas or a liquid, for example) with any certainty unless it is in the presence of another phase with which it can be compared.

Phase Behavior. How the *equilibrium state* of a fluid system responds to external influences on any of the *state variables*. Generally, how the number, amounts, compositions, and properties of the equilibrium phases change with changes to the pressure, volume, temperature, or overall composition of the system.

Phase Envelope. A plot that shows the boundaries (in terms of state variables like pressure and temperature) between regions of phase behavior exhibiting different numbers of equilibrium phases.

PhazeComp. A state-of-the-art equation-of-state program for compositional phase behavior modeling and fluid characterization. See Appendix F for more details.

Pseudocomponent. A component that represents more than one molecular species, even if they would not be expected to behave identically.

Pseudoization. The procedure of combining groups of components into new pseudocomponents. Done correctly, the procedure determines the EOS parameters of the new pseudocomponents from those of the original components in a way that conserves mass, conserves moles, and preserves the exact pressure-volume relationship (and its temperature derivative) for a specified fluid at a specified temperature.

Pseudo-Steady State. A state of a physical system in which the properties of interest are not changing appreciably over time.

PT Diagram. A diagram showing the *phase envelope* for the state variables of pressure and temperature.

PVT. Relating to pressure, volume, and temperature.

PVT Cell. A laboratory vessel in which the pressure-volume relationship of a fluid sample can be measured at a specified temperature.

Regression. A mathematical procedure to estimate a model's unknown parameters by comparing the model's predictions to observed data and adjusting (or tuning) the parameters to minimize the differences.

Saturation Pressure. The pressure at which a fluid transitions from a single-phase state to a two-phase state. The saturation pressure can either be a bubble point, a dew point, or a critical point.

Separator. A laboratory or production vessel in which a petroleum fluid is allowed to separate into equilibrium liquid and gas phases at a specified temperature and pressure.

Shrinkage Factor. This is defined for separator tests as the volume of stock tank oil produced per volume of oil that went into the separators. It is somewhat of a misnomer, because the more the oil shrinks, the lower its shrinkage factor. The shrinkage factor is the inverse of the formation volume factor.

Single Carbon Number. A group of molecular species that have a boiling point range or a GC elution time between those of consecutive normal alkanes, the carbon number being that of the heavier alkane. For example, C15 is the single-carbon-number group that falls between n-$C_{14}H_{30}$ (exclusive) and n-$C_{15}H_{32}$ (inclusive).

Slip Velocity. The difference in velocities between gases and liquids in the vertical flow of two-phase mixtures through a pipe because of the slip between the two phases.

Soave Redlich-Kwong EOS. One of the most commonly used equations of state in the petroleum industry.

State. The set of conditions that define a physical system. For a fluid system, this means the amount, temperature, pressure, volume, and composition of each identifiable phase.

State Variables. The variables (temperature, pressure, volume, and composition) that define the state of a physical system.

Stock Tank Oil. Oil as it exists at atmospheric pressure and an ambient temperature (typically 60 F). Oil is usually accounted for, transported, and sold on the basis of its stock tank volume. Oil that is produced from a reservoir is converted to stock tank oil through some sort of separation process that removes the hydrocarbons that will not stay in the liquid phase at stock tank conditions. The amount of the hydrocarbons that can be stabilized in the stock tank oil will depend on the separation process.

Tuning. See *Regression*.

Twu Adjustable Parameter. A parameter that PhazeComp adds to the Twu correlations to allow more flexibility in tuning the correlation between molecular weights and boiling points.

Twu Correlations. A set of industry standard correlations relating the molecular weight, specific gravity, boiling point, critical temperature, critical pressure, and critical volume of a hydrocarbon component.

Vapor Pressure. At a given temperature, the pressure at which a given component boils (when it can coexist in both a gas phase and a liquid phase, in equilibrium with each other). The vapor pressure at the component's *boiling point* temperature is, by definition, exactly one standard atmosphere. The vapor pressure at the component's *critical temperature* is, by definition, its *critical pressure*.

Volatility. The tendency of a component to transfer from a liquid phase to a vapor phase.

Volume Shift Parameter. See *Peneloux volume shift parameter*.

Weinaug-Katz Interfacial Tension Model. Any industry standard model for predicting the interfacial tension between two fluid phases, given their compositions, molar densities, and component *parachors*.

Z-Factor. Also called compressibility factor. A multiplier that accounts for the deviation of a fluid's pressure-volume-temperature relationship from that of an ideal gas.

ABBREVIATIONS

AF	Acentric factor
Atm	Atmospheres of pressure
BIP	Binary interaction parameter
BP	Bubble point
CCE	Constant composition expansion
DLE	Differential liberation expansion
DP	Dew point
EOS	Equation of state (noun) or equation-of-state (adjective)
F	Fahrenheit
FVF	Formation volume factor
GC	Gas chromatograph (or -graphy or -graphic)
GOR	Gas-oil ratio
LBC	Lohrenz-Bray-Clark, a viscosity model named after its creators
MW	Molecular weight
PC	Critical pressure
Psia	Pounds per square inch of pressure, absolute
Psig	Pounds per square inch of pressure, gauge (i.e., in excess of 1 atm)
PT	Pressure-Temperature
PVT	Pressure-Volume-Temperature
R	Rankine (degrees Rankine = degrees Fahrenheit + 459.67)
SCN	Single carbon number (noun) or single-carbon-number (adjective)
SF	Shrinkage factor
SG	Specific gravity
SRK	Soave-Redlich-Kwong, an EOS named after its creators
TB	Boiling point temperature
TC	Critical temperature
VC	Critical volume
VS	Volume shift factor
ZC	Critical z-factor

1. BACKGROUND AND QUALIFICATIONS

I have been working in the field of petroleum engineering for almost 30 years, ever since receiving my Ph.D. in chemical engineering from Stanford University in 1983. During that entire period, I have specialized in the area of equation-of-state (EOS) modeling of petroleum fluid phase behavior.

I started my career at ARCO Oil and Gas Company's research center in Plano, TX. There, I wrote EOS solution algorithms, EOS fluid characterization software, and portions of three compositional reservoir simulators. I used my characterization software to analyze phase behavior data and build EOS fluid models for several reservoir development projects, the most important being the Prudhoe Bay Miscible Gas Project, the largest such project ever undertaken (at the time, at least). I developed ARCO's phase behavior modeling software, EOSPHASE, a state-of-the-art program at the time for equation-of-state phase behavior modeling and reservoir fluid characterization.

I started Zick Technologies in 1993, doing similar work on behalf of various oil and gas clients. I also wrote my own software program for phase behavior modeling and EOS fluid characterization, using the ideas I had developed from my time with ARCO. That program is called PhazeComp, which I have offered commercially since 2002. PhazeComp is a state-of-the-art program that puts no limits on the construction of EOS fluid characterizations. PhazeComp is designed specifically for phase behavior experts and, as such, is used by some of the most experienced and prominent fluid characterization specialists in the petroleum industry. PhazeComp licensees include ConocoPhillips, Statoil, Maersk, Saudi Aramco, the Norwegian University of Science and Technology, the University of Calgary, and PERA A/S.

From time to time, I have also taught industry courses on subjects such as "Advanced PVT and EOS Fluid Characterization." A more detailed description of my qualifications is found in Appendix A.

2. EXECUTIVE SUMMARY

The United States Department of Justice (DOJ) retained me to assess the available Macondo fluid *PVT*[1] (pressure, volume, temperature) laboratory data and to develop a specific type of phase behavior model—an *equation-of-state fluid characterization*—for the Macondo reservoir fluids. I created this fluid phase behavior model to predict the Macondo reservoir fluids' physical, thermodynamic, and transport properties as functions of temperature, pressure, and fluid composition. These model predictions can be used to support many types of engineering calculations employed to assess the extent of the Deepwater Horizon oil spill. My role was not to make such calculations, but other experts, also retained by the DOJ, have used my fluid model to help estimate, for example, the total flow of oil from the Macondo well into the Gulf of Mexico.

My fluid phase behavior model can also be used to evaluate the conversion, through different processes, of reservoir barrels of oil, by which the flow from the reservoir into the well is measured, to stock tank barrels, by which the extent of the oil spill is measured.

In simple terms, an EOS is an equation (or a set of equations) designed to model the relationships between pressure, temperature, volume, and *composition* for a wide variety of fluids, given the appropriate input parameters (described below) for any specific set of fluids. An EOS also models a fluid's *phase behavior*, predicting when and how the fluid will partition into *equilibrium* phases (typically gas and liquid) and giving the relative amounts, compositions, and properties of those phases. This makes an EOS especially useful for engineering calculations of multiphase fluid flow, an important factor in the evaluation of the Macondo disaster.

To apply an EOS to a specific set of fluids, you need an EOS *characterization* of those fluids. The EOS fluid characterization (or EOS fluid model) consists of a suite of components to constitute the fluids of interest, along with those components' physical properties, which are used as EOS parameters. This report describes the EOS fluid characterization I built (as input for the industry standard *Peng-Robinson EOS*[2]) to describe the phase behavior of the Macondo reservoir fluids.[3]

There is no such thing as a universal EOS fluid characterization that can be applied equally well to any set of fluids under any set of conditions. Instead, for optimum accuracy, it is best to build and tune a characterization specifically for the given fluids and conditions of interest. To that end, based on all available Macondo PVT and compositional data, I used PhazeComp to build an 11-component EOS fluid

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[1] Terms that are italicized in the body of the Report are defined in the Glossary on page v. An index of Abbreviations follows on page x.

[2] Robinson, D. B., and Peng, D. Y. "The Characterization of the Heptanes and Heavier Fractions." Research Report 28, Gas Producers Association, Tulsa, OK (1978).

[3] Within this report, following common industry shorthand, I will often refer to the EOS fluid characterization that I built for the Macondo reservoir fluids, together with the Peng-Robinson EOS for which it was built, as the Macondo EOS or simply my EOS, even though the EOS itself is an industry standard that I did not modify in any way. Similarly, I might refer to an EOS fluid characterization built by BP as simply BP's EOS.

characterization for the Macondo reservoir fluids. I took into account all of the experimental data that had been obtained by three different laboratories (commissioned by BP during the oil spill response) on 15 separate fluid samples. I focused mainly on the 4 samples for which the most complete experiments were performed, which I refer to as the "primary samples" in this report. I tuned the characterization to produce an optimized match to approximately 1000 individual data measurements. I built the Macondo EOS using the same procedures I employ when doing similar work for industry clients, and the result was an EOS fluid model of comparable quality to those I typically provide to such clients.

An EOS fluid characterization should be judged by two criteria: (1) how well it predicts the experimental data to which it was tuned, and (2) how physically realistic its component properties are. While no EOS fluid model is perfect, it is my professional opinion, based on my 30 years of experience in petroleum fluid engineering, that the Macondo EOS I developed for this project predicts the experimental data to which it was tuned as well as possible and represents, with a high degree of certainty, the physical properties of the released hydrocarbons. This report provides the details of my EOS and compares its most relevant predictions with the corresponding experimental measurements. It also explains why I developed my EOS to replace the fluid model provided to the government by BP during the oil spill response.

My Macondo EOS was provided to other DOJ experts for use in their flow calculations. For some simulations that were unable to utilize an EOS directly, I simplified my model to a set of lookup tables of fluid properties as functions of temperature and pressure. These tables, commonly called *black-oil tables* within the industry, provide an adequate replacement for the original EOS fluid model as long as they are used under the conditions assumed during the creation of the tables. In industry practice, black-oil tables are often used to stand in for an original EOS fluid model whenever the use of the EOS itself might not be practical.

My report also analyzes the appropriate conversion of the flow from the Macondo well to units of stock tank barrels. Since industry standard production operations normally use optimized multistage separations in favor of inefficient, single-stage separations, it is my professional opinion that any estimate of the stock tank barrels of oil discharged from the Macondo well should be based on the assumption of a multistage separation process to define the stock tank oil. I calculated that a multistage separation process (as specified by BP) would result in about 11% more stock tank oil than would a single-stage separation process. If an estimate is based on the assumption of a single-stage separation instead, it should be increased by 11% to better reflect the production operations that BP would have likely utilized.

3. EQUATION-OF-STATE FUNDAMENTALS

As noted above, engineering calculations involving fluids require a model of the fluid's properties and *phase behavior* under different conditions of pressure, volume, temperature, and/or overall *composition*. The relevant fluid properties might include molecular weight, density, and viscosity. The fluid's *phase behavior* describes when and how the fluid will partition into different phases (gas, liquid, and/or solid) and what the compositions of those phases might be, which in turn will determine the properties of those phases. Very simple models will often suffice, but sometimes the fluids are known to behave in very complex, ever-changing ways that require a complex model. An *equation of state*, together with an *equation-of-state fluid characterization*, can provide such a model. Through the laws of thermodynamics, such an EOS can also predict the *equilibrium* phase behavior of a modeled fluid system for any given set of independent state variables, such as temperature, pressure, and overall *composition*. There are many different equations of state that have seen use within the petroleum industry, but the two most common are the 1978 version of the *Peng-Robinson EOS* and the *Soave-Redlich-Kwong EOS*.[4] Both are industry standard equations of state and the choice between them is typically based on personal experience and preference. I chose the 1978 Peng-Robinson EOS for the Macondo modeling.

Tailoring an EOS to a given fluid system requires development of a fluid *characterization* to be used as an input parameter. An EOS fluid characterization consists of four elements: (a) the set of components that constitute the fluids of interest, (b) the estimated physical and thermodynamic properties of each component, (c) a matrix of *binary interaction parameters* (BIPs) to account for possible interactions between every unique pair of components, and (d) *compositions* of the fluids of interest, expressed as relative amounts of the characterization's components.

The process of building an EOS fluid characterization consists of choosing or defining an appropriate suite of components, estimating the initial properties for each component and the BIPs for all component pairs, casting the fluid *compositions* of interest in terms of the defined suite of components, and *tuning* the EOS parameters to optimize the prediction of available phase behavior data. In most cases, the *tuning* of the EOS fluid characterization is followed by the estimation (and possible tuning) of parameters for auxiliary models that are often used together with the EOS fluid model to predict additional, non-EOS fluid properties, such as viscosity and *interfacial tension*, which can be important for multiphase fluid flow calculations.

In the next section, I provide a brief explanation of the multistep process I undertook to develop the Macondo EOS fluid characterization.

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[4] Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.* **27** (1972), No. 6, 1197.

4. BUILDING THE MACONDO EOS FLUID MODEL

As previously discussed, an EOS fluid *characterization* consists of a set of components and an optimized set of properties for those components. The process of building the fluid characterization is fairly involved, however. Even if one used the same set of components for every reservoir fluid, there is too much variation, from reservoir to reservoir, to use the same set of properties. Specific to any given reservoir, those properties must be first estimated, and then tuned, in a multistep process. The details of how I built the Macondo EOS fluid model are given in Appendix D, but this section outlines the multistep process that I used.

Whenever I build an EOS fluid characterization, including the Macondo EOS, I make sure all of the component properties are correlated with each other, and with the laboratory-measured data, in ways that keep them physically realistic for the fluids of interest. For the Macondo fluid model, I set about doing this by first correlating measured specific gravities with measured molecular weights (refer to Section D.1 of Appendix D). This correlation formed the basis for subsequent property estimations.

Next, I defined a set of *single-carbon-number* (SCN) components (C6, C7, etc.) to represent the various Macondo fluid samples (Section D.2). This was the most convenient representation because, when the labs (commissioned by BP[5]) analyzed the samples by *gas chromatography* (GC), the compositions were reported as mass fractions according to carbon number.

I then set the properties of all identifiable, pure components to their *library* values, and for all non-library components, I used my commercial PhazeComp[6] software to correlate the component properties with each other and with the available molecular weight and density measurements that the labs had reported for the various Macondo samples (Section D.3). At the same time, I estimated other initial EOS parameters, including binary interaction parameters (BIPs), from various correlations, published recommendations, and prior experience.

At this point, I had a preliminary SCN characterization of the Macondo reservoir fluids, but the number of components in this characterization was too large for practical purposes (such as computational efficiency), so a new, smaller set of components was defined by combining groups of the original SCN components together into

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[5] BP employed three PVT laboratories—Pencor, Schlumberger, and Intertek—to analyze Macondo reservoir fluid samples and perform PVT experiments on them. I focused mainly on the data from four samples for which the most extensive lab experiments were performed: Pencor Samples 19 and 53, Intertek Sample 1812, and Schlumberger Sample 1.18. The laboratory reports for these samples can be found at Pencor Volatile Oil Reservoir Fluid, Report No. 36126-19-5010068508, June 30, 2010 (BP-HZN-2179MDL00063084), Pencor Volatile Oil Reservoir Fluid, Report No. 36126-53-5010068379, June 10, 2010 (BP-HZN-2179MDL01872218), Schlumberger Fluid Analysis on Macondo Samples, June 9, 2010 (BP-HZN-MDL217900062844-62893), Intertek Multistage Separator Test Final Report WTC-10-001812, June 10, 2010 (BP-HZN-MDL217904440978-998), respectively. My EOS characterization also takes into account data from compositional analyses, atmospheric flash separations, and viscosity measurements of the remaining samples as appropriate. Appendix C identifies all of the fluid samples and PVT experiments I considered.

[6] PhazeComp is described in more detail in Appendix F.

pseudocomponents (e.g., C4-C5, C10-C12, C20+). The *pseudoization* procedure (Section D.4) also produced averaged properties (including BIPs) for each new pseudocomponent.

The above procedures resulted in a functional EOS fluid characterization, but it was not yet optimized to the experimental PVT data collected by BP's contractor laboratories. The next step, then, was to select a few of the most uncertain, and most influential, parameters for tuning (Section D.5). These included some of the BIPs, some of the properties of the heaviest pseudocomponent, and some of the various correlation parameters, with additional parameters tried as well. I again used PhazeComp for the tuning procedures. PhazeComp is designed to simulate the PVT experiments of interest, compare the EOS predictions with the measured data, and automatically make adjustments to the chosen tuning parameters until the predictions match the data as well as possible. Even so, it was necessary to perform this process repeatedly, in a trial-and-error manner, with many different sets of possible tuning parameters, and with varying emphasis on different subsets of the data, until I identified a final set of tuned parameters that predicted the measured data more accurately than all other sets. This final set of parameters formed my optimized Macondo EOS fluid characterization (Section D.5).

The Macondo fluid characterization was not complete, however, until I assigned the parameters for the auxiliary, non-EOS models that are required for viscosity and interfacial tension predictions. I estimated the critical z-factors for the Lohrenz-Bray-Clark viscosity model[7] (Section D.6) and then tuned those z-factors to optimize the model's predictions of the available Macondo viscosity experiments (Section D.7). I also estimated the component *parachors* for the Weinaug-Katz interfacial tension model.[8] No interfacial tension data were available to which they could be further tuned, however.

The end result was my finalized Macondo EOS fluid characterization, as specified in the next section.

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[7] Lohrenz, J., Bray, B. G., and Clark, C. R., "Calculating Viscosities of Reservoir Fluids from their Compositions," *JPT* (Oct. 1964), 1171; *Trans.*, AIME **231**.

[8] Weinaug, C. F., and Katz, D. L., "Surface Tensions of Methane-Propane Mixtures," *Ind. & Eng. Chem.* **35** (1943), 239.

5. FINALIZED MACONDO EOS FLUID CHARACTERIZATION

This section provides the specifications for my Macondo EOS fluid characterization and demonstrates how well it predicts the phase behavior of the Macondo reservoir fluids.

My finalized Macondo EOS fluid characterization (for the 1978 *Peng-Robinson EOS*) is given in **Table 1**. The first part of the table lists the components, their essential EOS properties (molecular weight, critical temperature, critical pressure, acentric factor, and volume shift parameter), their critical z-factors for use in the *Lohrenz-Bray-Clark* viscosity model, and the parachors for use in the *Weinaug-Katz* interfacial tension model. The second part of the table shows the matrix of binary interaction parameters.

Table 1
Final EOS Fluid Characterization

Component	MW	Tc (R)	Pc (psia)	AF	VS	ZcVis	Pchor
N2	28.014	227.16	492.84	0.03700	-0.16758	0.29178	59.10
CO2	44.010	547.42	1069.51	0.22500	0.00191	0.27433	80.00
C1	16.043	343.01	667.03	0.01100	-0.14996	0.28620	71.00
C2	30.070	549.58	706.62	0.09900	-0.06280	0.27924	111.00
C3	44.097	665.69	616.12	0.15200	-0.06381	0.27630	151.00
C4-C5	63.370	767.52	521.40	0.21328	-0.05005	0.27048	204.92
C6-C7	89.779	941.96	449.50	0.27691	0.00117	0.26458	250.47
C8-C9	113.271	1041.93	397.68	0.33414	0.02830	0.25395	308.85
C10-C12	151.237	1171.61	337.32	0.42755	0.05886	0.25340	357.37
C13-C19	215.517	1330.41	270.20	0.57931	0.08930	0.26000	552.24
C20+	441.107	1606.72	182.26	1.09027	0.00389	0.28268	1093.66

BIPS	N2	CO2	C1	C2	C3	C4-C5	C6-C7	C8-C9	C10-C12	C13-C19	C20+
N2	0	0.00000	0.02500	0.01000	0.09000	0.09943	0.11000	0.11000	0.11000	0.11000	0.09453
CO2	0.00000	0	0.10500	0.13000	0.12500	0.11587	0.11500	0.11500	0.11500	0.11500	0.09962
C1	0.02500	0.10500	0	0.00097	0.00319	0.00689	0.01123	0.01478	0.01981	0.02690	0.06074
C2	0.01000	0.13000	0.00097	0	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.02106
C3	0.09000	0.12500	0.00319	0.00000	0	0.00000	0.00000	0.00000	0.00000	0.00000	0.02106
C4-C5	0.09943	0.11587	0.00689	0.00000	0.00000	0	0.00000	0.00000	0.00000	0.00000	0.02106
C6-C7	0.11000	0.11500	0.01123	0.00000	0.00000	0.00000	0	0.00000	0.00000	0.00000	0.02106
C8-C9	0.11000	0.11500	0.01478	0.00000	0.00000	0.00000	0.00000	0	0.00000	0.00000	0.02106
C10-C12	0.11000	0.11500	0.01981	0.00000	0.00000	0.00000	0.00000	0.00000	0	0.00000	0.02106
C13-C19	0.11000	0.11500	0.02690	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0	0.02106
C20+	0.09453	0.09962	0.06074	0.02106	0.02106	0.02106	0.02106	0.02106	0.02106	0.02106	0

Table 2 shows the representative fluid compositions for the four primary samples, in terms of the *mole fractions* of the components of the final EOS fluid model. It also shows the overall molecular weight for each sample. The samples are listed in order from lightest to heaviest, in terms of either MW or C1 mole fraction. The fluid labeled "Average" is the average of the lightest (Sample 19) and the heaviest (Sample 1.18) reservoir fluid samples analyzed by BP's contractor labs.

Table 2
Reservoir Fluid Molar Compositions for Final EOS Fluid Model

Component	**Sample 19**	**Sample 53**	**Sample 1812**	**Sample 1.18**	**Average**
N2	0.003408	0.004447	0.004954	0.003346	0.003377
CO2	0.009079	0.009197	0.009217	0.009875	0.009477
C1	0.658568	0.655102	0.647775	0.641219	0.649894
C2	0.064481	0.064224	0.063902	0.070778	0.067630
C3	0.046253	0.045750	0.045875	0.050140	0.048197
C4-C5	0.051099	0.051006	0.050682	0.053516	0.052307
C6-C7	0.033827	0.034398	0.037816	0.033463	0.033645
C8-C9	0.035822	0.036590	0.041786	0.035710	0.035766
C10-C12	0.028560	0.028990	0.028295	0.030287	0.029424
C13-C19	0.035887	0.037184	0.035595	0.037221	0.036554
C20+	0.033015	0.033114	0.034103	0.034445	0.033730
MW	**51.99**	**52.46**	**53.21**	**53.39**	**52.69**

The composition of Schlumberger Sample 1.18 was modified during the tuning process to correct for apparent errors in the laboratory's compositional analyses (as described in Section D.5 of Appendix D), but the compositions of the other samples were derived directly from the measured mass fractions of the reported analyses (and then converted to mole fractions with the EOS characterization's MWs).

An EOS fluid characterization is validated by how well it predicts the experimental data to which it was tuned. I present a detailed validation of my Macondo EOS in Appendix E. Here, however, it is worth discussing the EOS predictions of the experimentally measured saturations pressures, which are generally quite important for the EOS to predict accurately.

Figure 1 shows the so-called *PT diagram*, or pressure-temperature *phase envelope*, for the average Macondo reservoir fluid from **Table 1**. The experimental saturation pressure data from the three PVT labs working for BP and the EOS predictions are both plotted. In general, this type of diagram shows the saturation pressure as a function of temperature. Inside the envelope, the fluid will separate into two equilibrium phases. Outside of the envelope (above, below, and to the right in the figure), the fluid will remain in a single-phase state. At a given temperature, the saturation pressure can be either a *bubble point*, a *dew point*, or a *critical point*. When the two-phase region is entered from a bubble point, the first appearance of the second, incipient phase will be a bubble of a less dense phase (more vapor-like). Conversely, when the two-phase region is entered from a dew point, the first appearance of the second, incipient phase will be a droplet of a denser phase (more liquid-like). When the two-phase region is entered from a critical point, however, the first appearance of the second, incipient phase will be indistinguishable from the primary phase. The two phases will have the same compositions and the same properties, and their relative amounts will be indeterminate. Not until the conditions have moved a considerable distance within the phase envelope will it be possible to recognize the two phases and their relative amounts. By that time, there will usually be a considerable amount of both phases (much more than just a bubble or a droplet of each). If there is a critical point anywhere along the phase envelope, it will always be between a region of bubble points and a region of dew points (that is the only way bubble points can transition into dew points, or vice versa). This is illustrated by Figure 1's EOS-predicted bubble-point and dew-point curves, which are separated by EOS-predicted critical points.

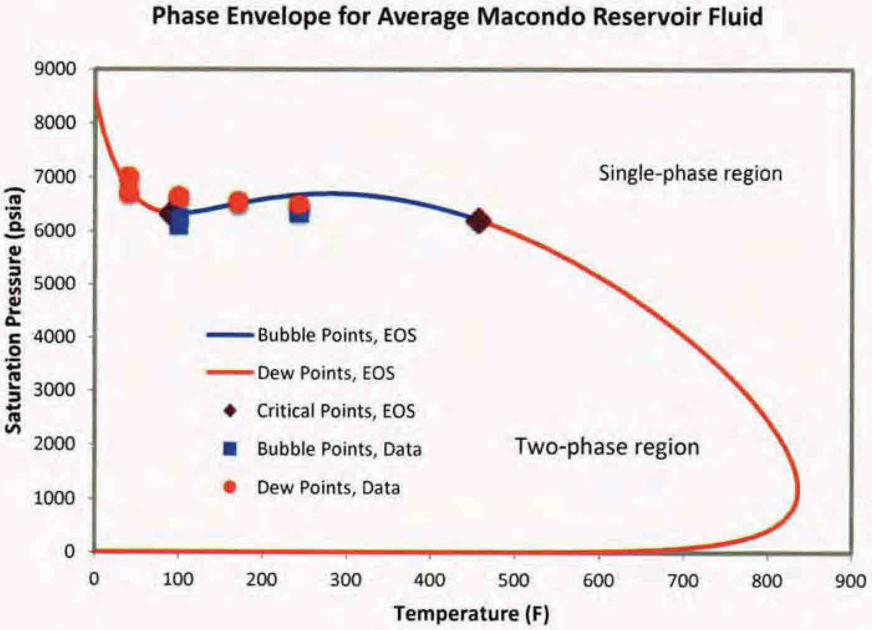

Figure 1. Pressure-temperature phase envelope for the average Macondo reservoir fluid, comparing EOS predictions with experimental saturation pressure data.

One thing that is clear from the available data is that all of the samples were very near-critical in their observed behavior, over a considerable range of temperatures (at least from 100 F to 243 F). That behavior could have made some of the laboratory measurements somewhat difficult to interpret. This potential difficulty is illustrated by the types of saturation pressures reported by the labs. The Schlumberger and Intertek samples were reported as bubble points, while both Pencor samples were reported as dew points, but instead of having the bubble points and dew points separated by a critical temperature as would be expected, they seem to overlap each other in temperature (as shown by the red and blue experimental data points in Figure 1). That should not happen (as illustrated by the EOS-predicted bubble-point and dew-point curves, which do not overlap but instead meet at critical points). The compositions of the four experimental samples were slightly different, and that might be enough to explain an overlap of a few degrees, but not to the extent exhibited by the experimental bubble points and dew points. I have no reason to suspect any of the labs of determining the experimental saturation pressures incorrectly, so I cannot really explain the anomalous behavior, but neither could the labs or BP. Experimental inconsistencies are, unfortunately, all too common among compositional and PVT data, especially when the data come from multiple labs. Unless it can be determined that some of the inconsistent data are obviously in error (which was not the case here), the best one can do is to tune the EOS to the average data. With my

EOS, I was able to match the observed bubble points with predicted bubble points, and the low-temperature experimental dew points with predicted dew points, but I could only manage to predict bubble points (the blue curve) for the high-temperature experimental dew points (the red data points). That was the compromise I had to make for the inconsistent observations at the higher temperatures for these near-critical Macondo samples.

For the Macondo EOS to predict the observed near-critical behavior, it was necessary for it to predict a critical point at a temperature not too far removed from the experimental temperatures. My tuned EOS ended up predicting a critical point at a temperature of 90.5 F, which was about as close to the experimental temperatures as I could tune it to be without using unrealistic EOS parameters.[9] One interesting feature of this EOS-predicted critical point is that it is a liquid-liquid critical point, rather than the typical liquid-vapor type (my EOS predicts one of those, too, but at 456.5 F, well above any temperature of interest). On either side of a liquid-liquid critical point (which is completely consistent with the experimental data), the primary phase will always be liquid-like, while the incipient phase will always be a second liquid phase, denser on the low-temperature, dew-point side and less dense on the high-temperature, bubble-point side.[10] It is not easy tuning an EOS to predict a liquid-liquid critical point where the data suggest there should be one, but that was the key to getting the Macondo EOS to predict the observed near-critical behavior.

Even though my Macondo EOS does not predict the correct type of saturation pressure for every sample, I do not consider that to be a significant modeling deficiency. It predicts the correct behavior on average. Also, the more near-critical the phase behavior, the less important it is to predict the actual type of the saturation pressure, as long as the near-critical behavior is predicted reasonably well. My EOS does predict a nearby critical point, as the data would require, and it does predict the actual saturation pressures quite accurately, as shown in Figure 1. Additional predictions of the near-critical phase behavior will be demonstrated in Appendix E.

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[9] The Pencor data suggest that the critical temperature should be slightly greater than 243 F, the Intertek data suggest that it should be somewhat less than that, and the Schlumberger data suggest that it should even be less than 100 F.

[10] It does not appear that BP considered the possibility of a liquid-liquid critical point, which may explain why BP did not seem to believe Pencor's reports of dew-point behavior (see the deposition of Yun Wang for BP, October 24, 2012).

6. BLACK-OIL TABLES

My EOS fluid characterization can be used as the Macondo fluid model within any engineering software that supports the Peng-Robinson EOS and the Lohrenz-Bray-Clark viscosity model. That includes reservoir simulators, pipe-flow simulators, and surface process simulators.

Some engineering software is not able to use an EOS directly, however. For such cases, it was necessary to simplify my EOS to a set of lookup tables of fluid properties as functions of temperature and pressure. This type of simplification removes the independent variables of composition, making it applicable only to physical processes for which any compositional variations can be anticipated during the creation of the tables. However, as long as the assumed compositional path is realistic for the problem at hand, the resulting set of tables (commonly called *black-oil tables* within the industry) provides an adequate replacement for the original EOS fluid model.

I was asked to provide a set of black-oil lookup tables for use in the computation of fluid flow from the Macondo reservoir, through the damaged wellbore, to the spill site at the bottom of the Gulf of Mexico. For the black-oil tables to be an adequate replacement for the complete EOS fluid model, I had to anticipate the compositional path from the reservoir to the spill site, in order to build that into the tables.

BP's engineers apparently determined during the response that the bottom-hole flowing pressure of the well had never dropped below the saturation pressure of the reservoir fluid,[11] so the fluid entering the wellbore would have been the original, single-phase reservoir fluid. Within the well, all the way to the point where the fluid spilled into the Gulf, it would be safe to assume *pseudo-steady-state* flow, where the flow of material out of any arbitrary section of the flow path would be the same as the flow of material into that section (in other words, there would be no increase or decrease, over time, of any fluid component within that section). Under that scenario, the overall flowing composition must remain constant at every point along the flow path.

I therefore generated a set of black-oil tables under the assumption that the overall flowing composition was constant (at the original, average reservoir composition), but that the temperature and pressure could vary widely. For any given combination of temperature and pressure (at regular intervals), the tables provide:

- The number of equilibrium phases.
- The molar and volumetric proportions of each phase.
- The molecular weights of each phase.
- The compressibility factor of each phase and of the overall fluid.
- The molar volume of each phase and of the overall fluid.
- The density of each phase and of the overall fluid.
- The viscosity of each phase.
- The molar composition of each phase.

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[11] Tony Liao, BP, Pressure Losses for Mike Levitan (Flow Inside Casing) with BHPs.xls (BP-HZN-2179MDL04920968-969).

These quantities make it possible to completely specify the phase behavior and fluid properties at any point along the flow path, given the temperature, pressure, and any *slip velocity* between the phases (all of which would have to be determined as part of the fluid flow computations).

Appendix G contains an excerpt from my final black-oil lookup tables. Because of their size and format, however, I am providing the complete tables only in electronic form.

7. WHY I CREATED MY MACONDO EOS FLUID MODEL

In the summer of 2010, BP provided the government an EOS characterization of the Macondo reservoir fluids,[12] but it provided no proof of its model's accuracy, or even of its consistency with the PVT data that had been obtained by its contractor laboratories. As part of my work for the DOJ, I analyzed BP's EOS to determine whether it would adequately describe the Macondo fluids, or whether a new EOS fluid model would need to be created. Although the general accuracy of BP's EOS did not seem unreasonable, I found it to have certain shortcomings. In particular, the laboratory PVT experiments showed the Macondo fluid samples to be very *near-critical* (simply put, they exhibited phase behavior that was difficult to distinguish between oil-like and gas-like), but BP's EOS did not reflect that very well and did not predict the liquid-liquid critical point that was suggested by the data. In addition, some of the component properties that defined BP's fluid characterization were physically not very realistic.

In my opinion, these inaccuracies and omissions raised questions about the BP fluid model's predictions for the two-phase, near-critical conditions just below the saturation pressures, and for fluid compositions that were not considered during BP's EOS-tuning process.

I felt confident that I could construct a new EOS fluid model that would better represent the Macondo reservoir fluids. As a result, I created a new, more accurate EOS fluid characterization and distributed it to other experts working for the United States for use in their fluid flow modeling.

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[12] Preliminary EOS for Olga_062410.fdb

8. FLUID SEPARATION PROCESSES

The previous sections of this report address the creation and validation of my Macondo EOS, which was provided to other DOJ experts in their work to estimate the Macondo flow rates. This section turns to another subject: the significance of the process through which oil is produced. The process is very important because it directly affects the volume of stock tank oil recovered at surface conditions.[13] Not surprisingly, oil companies have developed strategies to maximize stock tank oil production, as I discuss below.

Oil companies can use a number of different strategies to separate a stable stock tank oil from a reservoir fluid by removing dissolved gas. The simplest approach—though not one used frequently in industry practice—is a single-stage separation that takes the reservoir fluid from its conditions of reservoir temperature and pressure directly to stock tank conditions (usually defined as 60 F and 1 atm). Far more common in the industry, however, are multistage separation processes. In a multistage separation, the fluid produced from the well is passed through several separators in sequence, usually at declining temperatures and pressures, in order to bring the fluid to stock tank conditions more gradually and to reduce the shrinkage that occurs when a reservoir fluid is brought directly to stock tank conditions. In other words, by using a multistage separation process, oil companies are able to maximize the amount of gas that stays dissolved in the stock tank oil, thus maximizing the volume of stock tank oil produced from a reservoir. This makes economic sense because stock tank oil (which is sold by the barrel) is far more valuable, commercially, than any separated gas.

I can illustrate the importance of the separation process by comparing a single-stage and a four-stage process for my EOS model's average reservoir fluid. The single-stage process takes the fluid from the reservoir temperature of 243 F and the calculated saturation pressure of 6679.85 psia directly to stock tank conditions (60 F and 1 atm). The four-stage process is specified in **Table 9** of Appendix E. BP directed the three PVT laboratories (Pencor, Intertek and Schlumberger) to use the four-stage separation process for an experimental determination of the Macondo samples' FVFs, SFs, and GORs.[14] The straightforward EOS calculations of FVF, SF, and GOR for the two separation processes yield the results shown in **Table 3.** The resulting volume of stock tank oil is directly

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[13] There is often a lot of confusion about the definition of *stock tank oil* and a reservoir fluid's *formation volume factor* (FVF), *shrinkage factor* (SF, the inverse of FVF), and *gas-oil ratio* (GOR). These concepts are poorly defined. None is an intrinsic property of a reservoir fluid. Reservoir oil can be converted to stock tank oil through any number of processes, including differential liberation expansions, single-stage separations, or multistage separations, to name a few. The FVF, SF, and GOR help quantify the conversion from reservoir oil volumes to stock tank oil volumes, but their values depend on the conversion process chosen. Thus, in the absence of information about the initial conditions, the final conditions, and the conversion process used, these terms do not have clear meaning.

[14] Pencor Volatile Oil Reservoir Fluid, Report No. 36126-19-5010068508, June 30, 2010 (BP-HZN-2179MDL00063084), Pencor Volatile Oil Reservoir Fluid, Report No. 36126-53-5010068379, June 10, 2010 (BP-HZN-2179MDL01872218), Schlumberger Fluid Analysis on Macondo Samples, June 9, 2010 (BP-HZN-MDL217900062844-62893), Intertek Multistage Separator Test Final Report WTC-10-001812, June 10, 2010 (BP-HZN-MDL217904440978-998. Because BP requested that each PVT lab perform a multistage separator test at those conditions for each sample, it seems likely that BP had projected their production separators for the Macondo well to operate at those conditions.

proportional to SF. Also shown are the percentage differences between the two processes for each result. The bottom line is that the 4-stage process specified by BP will result in 11.1% more stock tank oil than will the single-stage process, simply because it stabilizes more of the hydrocarbons in the liquid phase and loses fewer of them to the gas phase.

Table 3
Comparison of a Single-Stage and a 4-Stage Separation

Process	FVF	SF	GOR (scf/bbl)
1-stage	2.473	0.4043	2826
4-stage	2.227	0.4490	2418
Difference (%)	-9.9	11.1	-14.4

In my estimation, and based on industry standard reservoir engineering practices, a multistage separation process is a more realistic assumption for the purpose of converting the Macondo reservoir fluids to stock tank barrels, and that such a process would yield approximately 11% more stock tank oil than would a single-stage separation process.

9. CONCLUSIONS

Based on my 30 years of hydrocarbon phase behavior modeling for the petroleum industry, it is my opinion that the EOS fluid model I developed for the Macondo reservoir fluids is as accurate as an EOS can be, especially for near-critical fluids such as these. Additionally, it is my opinion that stock tank oil volumes should not be derived from an assumed, single-stage separation process (as though the oil that spilled into the Gulf of Mexico went immediately from reservoir temperatures and pressures to ambient surface conditions), but rather, from a multistage separation process that would more accurately reflect the way stock tank oil is normally produced. I calculate that a multistage separation of the Macondo reservoir fluid (using specifications provided by BP) would yield about 11% more barrels of stock tank oil than would a single-stage process.

INFORMATION REQUIRED BY THE FEDERAL RULES OF CIVIL PROCEDURE

1. This report contains my opinions, conclusions, and reasons therefore.
2. A general statement of my qualifications is contained in the Background section, page iv. A more detailed statement of my qualifications is included in Appendix A.
3. I have not authored any publications in the last ten years.
4. My compensation for the preparation of this report and any testimony as an expert witness at trial or deposition is as follows: $200 per hour.
5. I have not previously testified as an expert witness.
6. The facts and data I considered in forming my opinions are listed in Appendix H.

The opinions expressed in this report are my own and are based on the data and facts available to me at the time of writing. Should additional relevant or pertinent information become available, I reserve the right to supplement the discussion and findings in this report.

Appendix A. CURRICULUM VITAE

Aaron A. Zick, Ph.D.

EXPERIENCE

President, Zick Technologies (Since 10/93).
Petroleum engineering consulting and software development, specializing in the area of reservoir fluid phase behavior modeling. Key achievements:

- Wrote PhazeComp, a new, state-of-the-art program from Zick Technologies for equation-of-state phase behavior modeling, reservoir fluid characterization, and the robust, efficient calculation of minimum miscibility conditions.
- Collaborated with Curtis H. Whitson and his companies, PERA A/S and Petrostreamz A/S, on numerous engineering and software projects.
- Wrote Streamz, unique Petrostreamz A/S software for translating, manipulating, and managing vast quantities of fluid stream information.
- Designed and helped write Pipe-It, unique Petrostreamz A/S software for managing and manipulating petroleum resources, processes, and projects.
- Developed numerous equation-of-state and black-oil fluid characterizations for various major oil companies and as a sub-contractor for PERA A/S.
- Recommended phase behavior experimentation and modeling guidelines for several major oil companies.
- Taught numerous industry courses on phase behavior, equations of state, reservoir fluid characterization, and miscible gas injection processes.
- Designed and helped implement a new set of equation-of-state routines for the in-house reservoir simulator of a major oil company.
- Advised the architects of a major commercial reservoir simulator on ways to significantly improve their equation-of-state routines.

Director of Research, Reservoir Simulation Research Corporation (6/91–10/93).
Responsible for the research and development of more efficient, accurate, and reliable techniques for modeling reservoir fluid phase behavior within MORE® (a fully-compositional, equation-of-state reservoir simulator). Also responsible for improving three-dimensional visualization of reservoir simulator output, and for occasional consulting work. Key achievements:

- Designed and implemented new equation-of-state solution algorithms for MORE®, improving both efficiency and robustness while using less memory.
- Developed a powerful and flexible interface between MORE® and TECPLOT™ (three-dimensional surface contouring software from AMTEC Engineering).

Senior Principal Research Engineer, ARCO Oil and Gas Company (9/83–5/91).
Developed expertise in reservoir fluid phase behavior, phase behavior modeling, compositional reservoir simulation, and relative permeability modeling. Designed and analyzed PVT experiments. Created equation-of-state reservoir fluid characterizations.

Developed ARCO's phase behavior modeling software and relative permeability modeling software. Helped develop several of ARCO's compositional and limited compositional reservoir simulators. Key achievements:

- Discovered the true, condensing/vaporizing mechanism of oil displacement by enriched hydrocarbon gases.
- Represented ARCO on the Prudhoe Bay co-owners' Enhanced Oil Recovery Task Force for the Prudhoe Bay Miscible Gas Project.
- Designed and analyzed most of the PVT and slim-tube experiments for the Prudhoe Bay Miscible Gas Project.
- Created the equation-of-state reservoir fluid characterization adopted by the operating companies for the Prudhoe Bay Miscible Gas Project.
- Developed the miscibility pressure correlations used by the facility operators for the Prudhoe Bay Miscible Gas Project.
- Developed EOSPHASE, a then state-of-the-art program for equation-of-state phase behavior modeling, reservoir fluid characterization, and the robust, efficient calculation of minimum miscibility conditions.
- Developed SLIMTUBE, a special-purpose, equation-of-state simulator for slim-tube displacements.
- Developed new, compositionally-consistent, three-phase relative permeability models for ARCO's compositional simulators and wrote data-fitting software for those models.
- Developed the phase behavior and relative permeability routines for a new, limited compositional reservoir simulator and assisted on other aspects of it.
- Continually added improvements to various in-house reservoir simulators.
- Regularly taught in-house courses on the phase behavior of miscible gas displacement processes.

IMPORTANT AND MOST RECENT PUBLICATIONS

A. A. Zick, "A Combined Condensing/Vaporizing Mechanism in the Displacement of Oil by Enriched Gases," presented at the 61st Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, New Orleans, LA (October, 1986).

D. E. Tang and A. A. Zick, "A New Limited Compositional Reservoir Simulator," presented at the 12th SPE Symposium on Reservoir Simulation, New Orleans, LA (March, 1993).

Editorial Review Committee, *Phase Behavior* by C.H. Whitson and M.R. Brulé, Monograph Volume 20, Society of Petroleum Engineers, Richardson, TX (2000).

AWARDS

1990: ARCO President's Award for "Advancing and Applying Compositional Technology."

1990: ARCO Vice President's Award for "Limited-Compositional Reservoir Simulator Development."

1986: ARCO Special Achievement Award for "Development of the State-of-the-Art EOSPHASE Phase Behavior Program."

1978: National Science Foundation Graduate Fellowship.

EDUCATION

Ph.D.	(1983)	Chemical Engineering, Stanford University.
M.S.	(1979)	Chemical Engineering, Stanford University.
B.S.	(1978)	Chemical Engineering, University of Wisconsin.

Appendix B. EQUATION-OF-STATE DETAILS

For an EOS fluid model to be complete, one needs to define a suite of components, a minimum set of properties for each component, and an optional matrix of binary interaction parameters. To perform equilibrium calculations, one must also specify the necessary independent variables (such as overall composition, temperature, and pressure), but those are usually considered as input to the EOS, rather than part of the EOS itself.

The properties that are absolutely required for each component of a cubic EOS (such as the Peng-Robinson or the Soave-Redlich-Kwong) are the component's *critical temperature* and *critical pressure*. One should also specify each component's *acentric factor*, which helps determine the temperature dependence of the component's *vapor pressure* (the pressure for a given sub-critical temperature at which the component can coexist as both a liquid and a vapor). For density calculations, one must also specify each component's molecular weight, and for *accurate* density calculations, one should also specify a Peneloux volume shift parameter[15] (an extension to the original EOS formulation). The volume shift parameter is allowed to be a function of temperature, although it is usually treated as a constant. All of the other parameters should be constants. For calculations involving only one component at a time, the EOS is completely specified by this list of five component properties, but for phase behavior calculations involving mixtures of components, the accuracy can be greatly improved by adding a matrix of *binary interaction parameters* (BIPs). One can specify a BIP for each pair of unique components. Thus, for fluids with n components, the EOS can include up to $n(n-1)/2$ unique BIPs, each of which can be a function of temperature (although they are usually treated as constants). Considering the other five parameters for each component, a typical 10-component EOS, for example, could require up to 95 input parameters.

The greatest challenge in using an EOS is in determining an appropriate set of component properties and BIPs. For pure, well-defined components like methane or carbon dioxide, the critical properties, acentric factor, and molecular weight can be found in any good reference source (e.g., Poling *et al.*[16]). Universally applicable volume shift parameters are not available (especially since they might depend on the temperatures of interest), but EOS software will often be able to suggest values for its library components.

The real complexity in building an EOS fluid model, however, comes in assigning the properties and BIPs of components that are not well defined. Every reservoir fluid contains a countless number of molecular species, with molecular weights that can range into the thousands. The individual species include all possible isomers of alkanes (hydrocarbons with no double bonds) that can be further characterized as paraffins (which contain no ring structures) or napthenes (which contain ring structures). They also include aromatic compounds, which contain at least one benzene ring, with or without additional hydrocarbon branches. Each individual molecular compound has its own

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[15] Peneloux, A., Rauzy, E., and Freze, R., "A Consistent Correction for Redlich-Kwong-Soave Volumes," *Fluid Phase Equilibria* **8** (1982), 7.

[16] Poling, B. E., Prausnitz, J. M., and O'Connell, J. P., *The Properties of Gases and Liquids*, Fifth Edition, McGraw-Hill, New York (2001), A.1.

unique set of physical and thermodynamic properties, but there are far too many such compounds to consider individually. Instead, they must be grouped into collections of compounds that will be treated as though they were individual components. These are often called *pseudocomponents*, but an EOS cannot distinguish between them and pure, single-species components, so here they will both be called simply *components* (unless there needs to be a distinction). Typically, such a *component* might be defined as all species having boiling points between two specified temperatures, or all species that elute from a gas chromatograph within a specified time span. For example, C15 is usually taken as all of the many compounds (within a given fluid) that fall between the unbranched alkanes n-tetradecane and n-pentadecane (either in boiling point or elution time, depending on the analysis method), while C30+ might refer to all compounds with boiling points or elution times greater than those of n-nonacosane ($n\text{-}C_{29}H_{60}$). Any analysis of a fluid's composition, of course, must then be cast in terms of the defined components. The number of those components can be kept manageable, but whenever a component is comprised of more than one individual species, its properties cannot be determined uniquely, but will instead depend on how those species are distributed within the component. Because of the infinite number of possible distributions of species within each component, no two reservoir fluids, even if they are characterized by the same set of components, will have the same set of properties for those components.

Even if it were somehow possible to isolate each component of a given reservoir fluid and either measure or estimate its EOS parameters with any degree of confidence, no EOS is exact. An EOS can only approximate the behavior of real fluid systems. Its accuracy can be highly dependent on the temperatures, pressures, and compositions of interest. To improve the accuracy for a given application, an EOS always needs to be *tuned*. This involves simulating various relevant phase behavior experiments and adjusting the estimated EOS parameters in an attempt to optimize the prediction of the available experimental data.

The calculation of some fluid properties, such as viscosity and thermal conductivity, requires additional, separate models in conjunction with the phase behavior EOS. These models also generally require parameter estimation and tuning for optimal accuracy. Even though these additional models are technically independent of the EOS, they are often considered to be a necessary element of an EOS fluid characterization, depending on the requirements of a particular engineering application.

Appendix C. PVT SAMPLES AND EXPERIMENTS

I considered the following experiments, listed by PVT laboratory and laboratory-assigned sample nickname, during the various steps of building the Macondo EOS:

Sample Number	Laboratory Tests Performed
Intertek	
Sample 1812	▪ Compositional analyses ▪ Atmospheric flash ▪ Constant composition expansion at 243 F ▪ Multistage separator test
Pencor	
Sample 10	▪ Compositional analyses ▪ Atmospheric flash
Sample 19	▪ Compositional analyses ▪ Atmospheric flash ▪ Constant composition expansion at 100 F ▪ Constant composition expansion at 170 F ▪ Constant composition expansion at 242 F ▪ Differential liberation at 242 F ▪ Multistage separator test ▪ Viscosity experiment at 242 F
Sample 20	▪ Compositional analyses ▪ Atmospheric flash
Sample 21	▪ Viscosity experiment at 40 F ▪ Viscosity experiment at 100 F ▪ Viscosity experiment at 170 F ▪ Viscosity experiment at 242 F
Sample 27	▪ Compositional analyses ▪ Atmospheric flash
Sample 36	▪ Compositional analyses ▪ Atmospheric flash
Sample 37	▪ Compositional analyses ▪ Atmospheric flash
Sample 44	▪ Compositional analyses ▪ Atmospheric flash
Sample 53	▪ Compositional analyses ▪ Atmospheric flash ▪ Constant composition expansion at 100 F ▪ Constant composition expansion at 170 F ▪ Constant composition expansion at 243 F ▪ Differential liberation at 243 F ▪ Multistage separator test ▪ Viscosity experiment at 40 F ▪ Viscosity experiment at 100 F

	▪ Viscosity experiment at 170 F ▪ Viscosity experiment at 243 F
Sample 54	▪ Compositional analyses ▪ Atmospheric flash
Schlumberger	
Sample 1.06	▪ Compositional analyses ▪ Atmospheric flash
Sample 1.07	▪ Compositional analyses ▪ Atmospheric flash
Sample 1.13	▪ Compositional analyses ▪ Atmospheric flash
Sample 1.14	▪ Compositional analyses ▪ Atmospheric flash
Sample 1.18	▪ Compositional analyses ▪ Atmospheric flash ▪ Constant composition expansion at 100 F ▪ Constant composition expansion at 243 F ▪ Multistage separator test

Appendix D. DETAILS OF BUILDING THE MACONDO EOS FLUID MODEL

As discussed in Section 4 of this report, I built the Macondo EOS fluid model following a multi-step process. These steps included:

1. Correlating specific gravities with molecular weights.
2. Defining a preliminary *single-carbon number* characterization.
3. Correlating molecular weights with boiling points.
4. *Pseudoizing* the SCN characterization to the desired component suite.
5. Tuning the EOS parameters to match all available PVT data.
6. Estimating viscosities for individual components.
7. Tuning the viscosity parameters to match viscosity data

I provide greater detail on each these seven steps below.

D.1. Correlating Specific Gravities with Molecular Weights

Every petroleum reservoir has a unique correlation between the specific gravities (SGs) and the molecular weights (MWs) of its constituent components. For any component that exists as a liquid at the standard conditions of 60 degrees Fahrenheit (60°F, or simply 60 F) and atmospheric pressure (1 atm), its SG is defined as its density divided by the density of water at those conditions. For a given MW, components that are comprised of mainly paraffinic compounds will have relatively low SGs, components that have high aromatic content will have relatively high SGs, and components that are more naphthenic will have intermediate SGs. It is possible to distill a sample into individual cuts whose MWs and SGs can actually be measured, but that was not done by BP or any of its contractors for any Macondo sample. As a result, the only way to estimate the MWs and SGs of the individual fluid components was through a combination of correlations, starting with a correlation of SG with MW.

MW divided by SG is proportional to molar volume. Molar volume, in turn, tends to be proportional to MW for components that are comprised of similar distributions of paraffins, naphthenes, and aromatics, as components from the same reservoir usually are. Therefore, a plot of MW/SG versus MW will normally be quite linear for related components or mixtures of those components.

There were no measurements of MW or SG for any individual component of the Macondo fluid, but there were several such measurements for various fluid mixtures, namely most of the flashed liquid, separator liquid, and stock tank liquid samples whose compositions were analyzed. Figure 2 shows the plot of MW/SG versus MW for those samples (including values for known normal alkanes and aromatic compounds—the limiting extremes—for comparison purposes). The correlation was indeed quite linear, so it was applied to all non-library components (those that were not recognized as pure components) that would be defined as part of the Macondo EOS characterization.

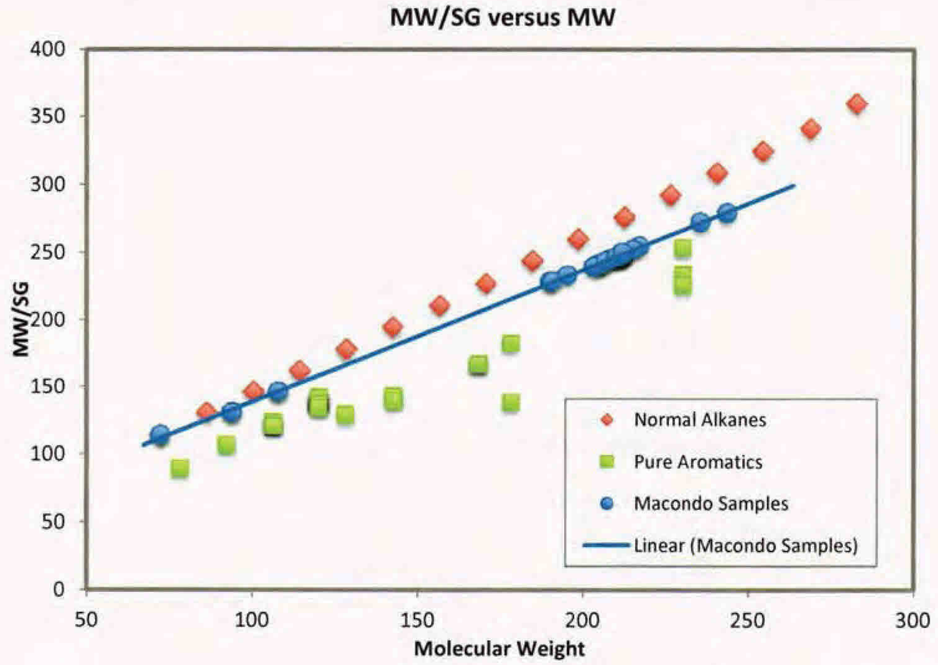

Figure 2. Correlation of measured specific gravities with measured molecular weights.

D.2. Defining a Preliminary *Single-Carbon Number* Characterization

I defined a preliminary EOS characterization that treated each single-carbon-number (SCN) group as a component (C6, C7, C8, etc.), up to the final C30+ component. This characterization made it easy to input the compositions measured in the laboratories, since the analyses by gas chromatography (GC) were measured and reported as SCN mass fractions.[17]

The component properties of the SCN characterization were estimated by the previously determined correlation of SG with MW, a correlation between MW and boiling point temperature (TB) that would be determined in the next step, and industry standard correlations for the component critical properties as functions of SG, MW, and TB. I then used the resulting SCN characterization to calculate the bulk MWs and densities of the various liquid samples for which those quantities had been measured. Next, I tuned the correlation between MW and TB to optimize the predictions of those bulk MW and density measurements. The resulting SCN characterization formed the starting point for the final EOS fluid characterization, which I then tuned to match the available PVT data.

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[17] A lab will also report molar compositions, but these should not be used. They are based on the measured mass fractions and a standard set of *estimated* MWs, which are usually not the most appropriate for the fluids of interest.

D.3. Correlating Molecular Weights with Boiling Points

Every petroleum reservoir has a unique correlation between the MWs and the average boiling point temperatures (TBs) of its constituent components. The average boiling point can be estimated by how the component is defined. If the component happens to be one of the individual cuts from a distillation analysis, then the average boiling point of that cut would serve as the component's boiling point. If the fluid was analyzed by GC, however, then the GC analysis will report the composition by carbon number. Carbon number n will include all compounds that elute after the normal alkane of carbon number n-1 up to the normal alkane of carbon number n. Since the elution time is fairly well correlated with boiling points, one should then expect the average boiling point of that carbon number group to fall somewhere between the boiling points of the two normal alkanes. If the group is highly paraffinic, its average boiling point should be at the high end of the range, whereas if it is highly aromatic, its average boiling point should be at the lower end of the range.

For any given SCN component, PhazeComp uses a proprietary algorithm to estimate the appropriate boiling point, based on how aromatic the previously established correlation between SG and MW appears to be. Once TB has been estimated, PhazeComp will then estimate MW and SG (two unknowns, so far) by solving a combination of two equations: the SG/MW correlation and the industry standard Twu correlation,[18] which establishes a relationship between MW, SG, and TB based on the documented values of more than 800 pure components.

So far, the procedure for establishing MW, SG, and TB for each SCN has been described, but a different procedure is required for the final *plus* fraction from a GC analysis (such as C30+ or C36+, typically). There is no upper limit on TB, MW, or SG for a *plus* fraction like that, so we need a different technique for estimating the average values. In the case of the Macondo fluids, the simplest procedure was to treat the C30+ MW as an adjustable parameter and to tune it to help best match all of the available bulk liquid MW and density data.

For each liquid sample analyzed by GC, the lab reports the overall MW and density of the sample, and the mass fractions of each component (SCNs up to the final plus component). The lab has no way of measuring the individual component MWs, SGs, or TBs, however. The lab always provides a set of estimated MWs and SGs, but the same standard estimates are given for every fluid, so they should rarely be used. A better procedure is to make the plus fraction MW an adjustable parameter, determine the TB and SG of the plus fraction from that MW with the SG/MW and tunable Twu correlations, direct the phase behavior program to calculate the bulk MWs and densities

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[18] Twu, C. H., "An Internally Consistent Correlation for Predicting the Critical Properties and Molecular Weights of Petroleum and Coal-Tar Liquids," *Fluid Phase Equilibria* (1984), No. 16, 137. The Twu correlation is usually quite effective, but it sometimes ends up slightly under-predicting the MWs for highly paraffinic petroleum fractions. To help compensate for that, PhazeComp has added a proprietary, adjustable parameter to the Twu correlation that allows the MW prediction for a given TB to be shifted toward that of a pure paraffin with the same TB. This additional parameter can be tuned to help match any available MW measurements (typically taken from bulk liquid samples). In the case of the Macondo fluids, it did help to tune the MWs toward the more paraffinic values.

for all liquid samples (given their component mass fractions as input), and tune the plus fraction MW and the Twu adjustable parameter to optimize the match with the experimental bulk MWs and densities.

Bulk liquid MW and density measurements were available for 21 Macondo liquid samples. Comparisons of the tuned predictions with the experimental data are shown in Figure 3 (MWs) and Figure 4 (densities). The predictions are well within the accuracy limits of the measurements.

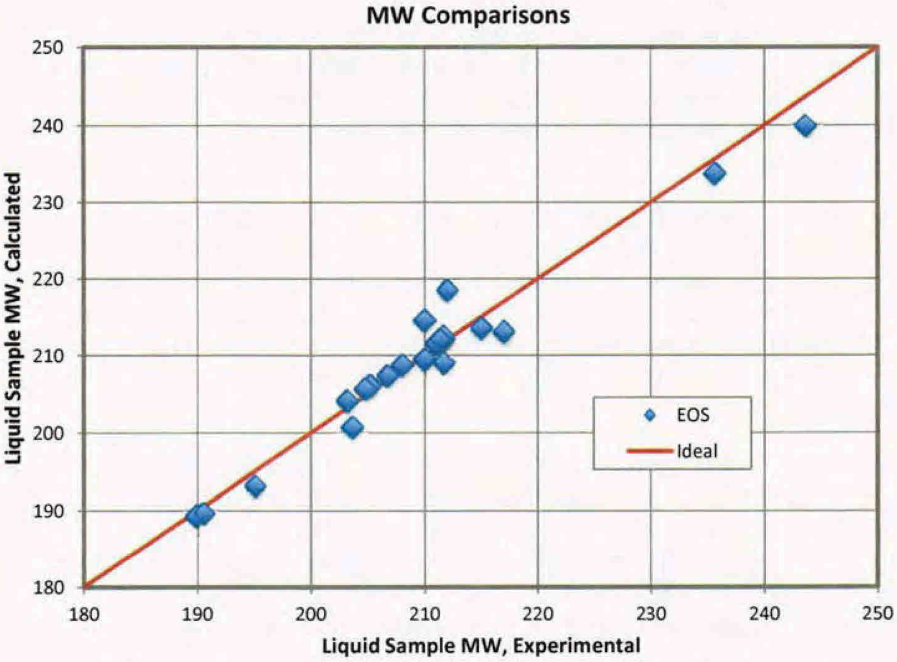

Figure 3. Comparison of calculated bulk molecular weights with the experimental values for 21 Macondo liquid samples. Perfect predictions would fall along the "Ideal" line.

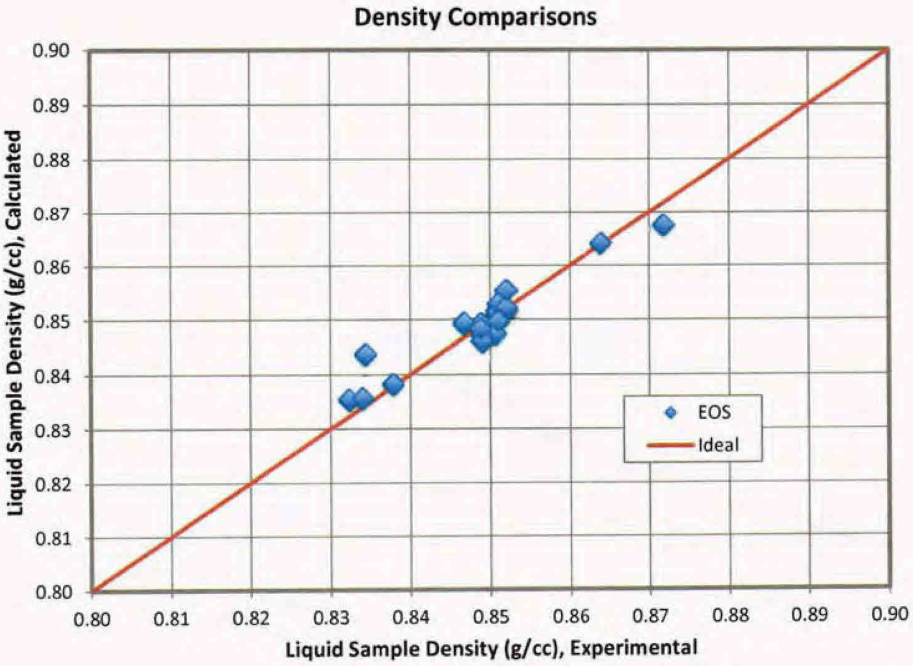

Figure 4. Comparison of calculated bulk densities with the experimental values for 21 Macondo liquid samples. Perfect predictions would fall along the "Ideal" line.

After the tuning of the Twu parameter and the C30+ MW, the resulting relationship between MW and TB for the SCN components is shown in Figure 5 and the relationship between SG and MW is shown in Figure 6 (honoring the correlation shown previously in Figure 2). The relationships for known normal alkanes and aromatic compounds (the limiting extremes) are also shown in these figures for comparison purposes.

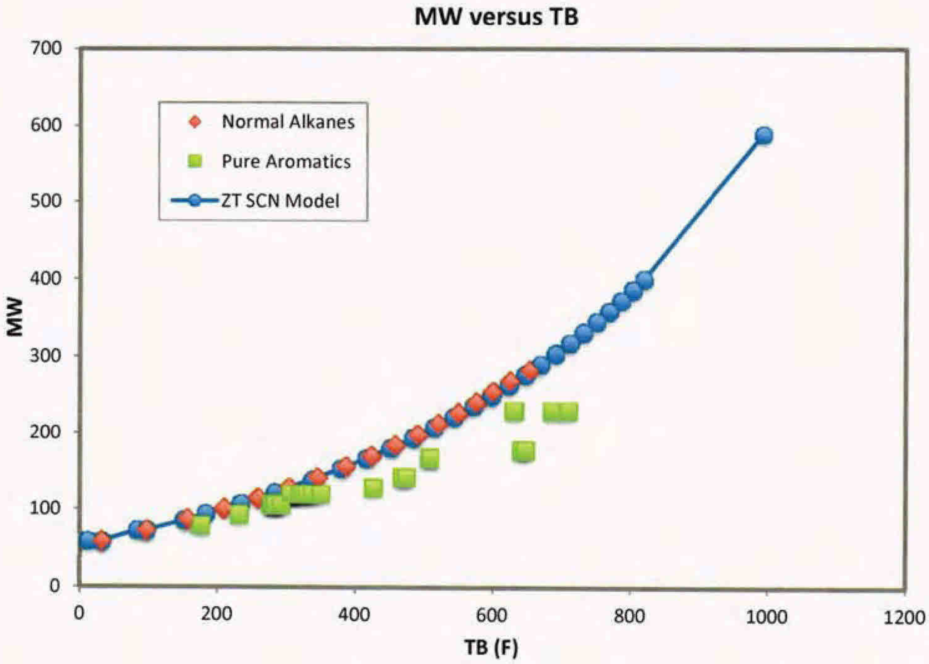

Figure 5. Component molecular weights by boiling point for the Zick Technologies SCN fluid characterization.

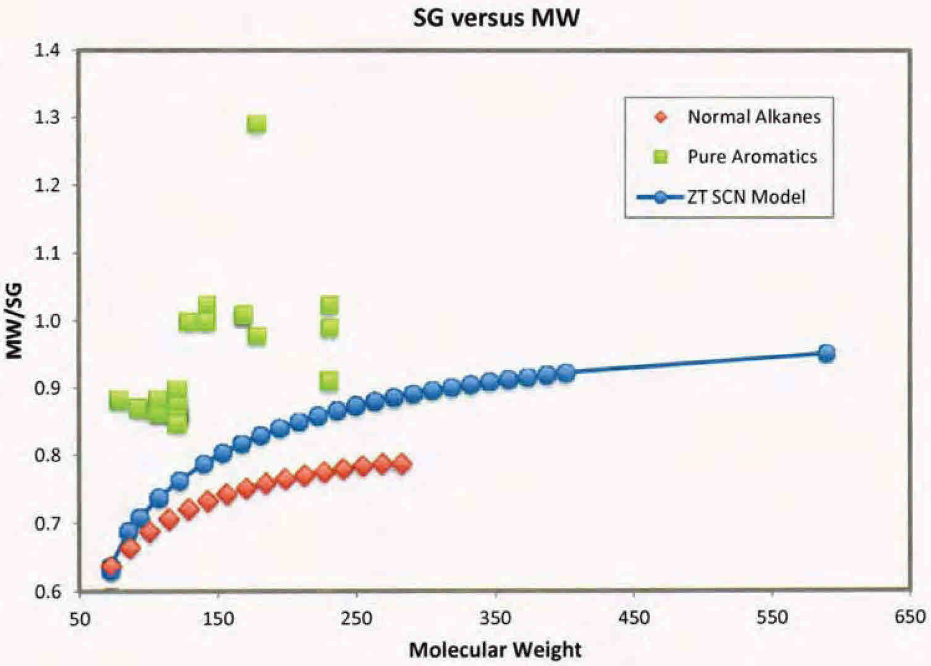

Figure 6. Component specific gravities by molecular weight for the Zick Technologies SCN fluid characterization.

D.4. *Pseudoizing* the SCN characterization to the desired component suite

At this point, a preliminary, 35-component fluid characterization had been initialized with the components, MWs, SGs, and TBs shown in **Table 4**. The first 10 components (N2 through N-C5) were pure, library components. The next 24 (C6 through C29) were SCN components and the last one would represent the C30+ fraction of each fluid. The properties had been correlated with each other, with the Twu correlation, and by carbon number (except the C30+ MW, which was an optimized parameter) to give the best possible match to the bulk MWs and densities of 21 Macondo liquid samples.

Table 4
Preliminary Single-Carbon-Number Fluid Characterization

Component	MW	SG	TB (F)
N2	28.014	0.28339	-320.625
CO2	44.010	0.76193	-126.879
H2S	34.082	0.83007	-78.613
C1	16.043	0.14609	-258.868
C2	30.070	0.32976	-127.690
C3	44.097	0.50977	-43.989
I-C4	58.123	0.57043	11.015
N-C4	58.123	0.59055	31.071

I-C5	72.150	0.62952	82.423
N-C5	72.150	0.63585	97.136
C6	85.041	0.68697	150.933
C7	93.175	0.70696	182.640
C8	107.155	0.73617	233.599
C9	121.852	0.76147	283.115
C10	139.703	0.78665	338.474
C11	153.401	0.80284	377.835
C12	167.116	0.81690	414.830
C13	180.844	0.82924	449.673
C14	194.583	0.84014	482.549
C15	208.330	0.84985	513.619
C16	222.083	0.85855	543.028
C17	235.842	0.86638	570.904
C18	249.604	0.87347	597.365
C19	263.369	0.87992	622.516
C20	277.136	0.88582	646.454
C21	290.904	0.89122	669.265
C22	304.673	0.89620	691.029
C23	318.442	0.90079	711.820
C24	332.211	0.90505	731.702
C25	345.981	0.90900	750.739
C26	359.750	0.91268	768.985
C27	373.518	0.91611	786.491
C28	387.286	0.91932	803.305
C29	401.054	0.92234	819.471
C30+	589.127	0.95031	992.158

Initial values of the additional EOS parameters, TC (critical temperature) and PC (critical pressure), were estimated from the MW, SG, and TB of each component by additional Twu correlations.[18] Each component's acentric factor (AF) and volume shift parameter (VS) were automatically updated by PhazeComp to ensure that the previously specified values of TB and SG, respectively, were always honored by the EOS predictions (TB and SG are predicted by the EOS; they are not EOS parameters themselves).

Based on my previous experience, I initialized the BIP matrix with typical values (the exact values are not crucial, since any or all entries may be modified by the EOS tuning process).

A 35-component EOS is sometimes not very practical for reservoir simulation and other engineering calculations, however. Such calculations can be performed much faster if the EOS is limited to 10 or 12 components (just enough to preserve most of the accuracy of a more detailed characterization). At this point, then, the characterization was reduced to an 11-component by a procedure known as *pseudoization*. In this procedure, the mixing rules of the EOS are applied to a specified fluid composition (in this case, Schlumberger Sample 1.18) to find the effective EOS properties (including BIPs) of components that are grouped together as specified by the pseudoization strategy. The MWs, SGs, and TBs of the initial pseudoized characterization are shown in **Table 5**.

Table 5
Initial Properties of the Pseudoized Fluid Characterization

Component	MW	SG	TB (F)
N2	28.014	0.28339	-320.625
CO2	44.010	0.76193	-126.879
C1	16.043	0.14609	-258.868
C2	30.070	0.32976	-127.690
C3	44.097	0.50977	-43.989
C4-C5	63.364	0.60501	50.067
C6-C7	89.770	0.69899	169.504
C8-C9	113.266	0.74735	254.532
C10-C12	151.237	0.80048	371.647
C13-C19	215.517	0.85449	528.453
C20+	441.107	0.92984	855.323

D.5. Tuning the EOS parameters to match PVT data

At this point, the PVT and compositional data from 22 laboratory experiments on the four primary Macondo samples (992 data points in all), along with the necessary instructions for simulating those experiments, were included in the PhazeComp input files. The input files were also given instructions to tune various EOS parameters (or correlation parameters that would affect the EOS parameters indirectly). Each execution of PhazeComp would build the initial SCN fluid characterization, pseudoize it, simulate the PVT experiments, compare the EOS predictions with the experimental data, modify the specified tuning parameters according to its built-in optimization algorithms in an attempt to match the measurements with the predictions (a process known as *regression*), and repeat the process until an optimum set of tuning parameters was found for that particular run. This was done repeatedly with different chosen sets of tuning parameters, their initial values, and/or their constraints. Eventually, by trial and error, a final set of optimized tuning parameters was selected as the best overall, resulting in the final EOS.

The ultimate set of EOS modifications consisted of:

- Increasing the PC of the initial SCN characterization's C30+ component from its initial, correlated value by 20%. This increased the *volatility* of the C30+ component, making the predictions of the overall fluid phase behavior more *near-critical*.
- Applying the Chueh-Prausnitz correlation[19] (with a tuned parameter) to assign all BIPs (of the initial SCN characterization) that paired C1 with any other hydrocarbon component. This improved the saturation pressure predictions.

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[19] Chueh, P. L., and Prausnitz, J. M., "Vapor-Liquid Equilibria at High Pressures. Calculation of Partial Molar Volumes in Nonpolar Liquid Mixtures." AIChE Journal (1967) **13**, 1099–1107.

- Adding a tuned constant to all BIPs (of the initial SCN characterization) that paired C30+ with any other component. This also increased the *volatility* of the C30+ component, making the predictions of the overall fluid phase behavior more *near-critical*.
- Adjusting the SCN composition of Schlumberger Sample 1.18. This corrected some inconsistencies between Sample 1.18's PVT predictions and those of the other samples.

These sorts of adjustments and tuning are standard, accepted procedures, typical of those required to tune an EOS fluid model to predict measured PVT data. Note that all of the modifications were made to the preliminary SCN characterization, before it was pseudoized to the final characterization. Other strategies were explored, but this one was found to produce the best results.

The first three modifications listed above were fairly straightforward, but the final one requires further explanation. EOS predictions are affected not only by the EOS parameters, but also by the input compositions. One would like to think that those compositions can be measured in the laboratory with great accuracy, but that is not always the case. When building an EOS characterization of several fluid samples, there will sometimes be one or more samples that are apparent outliers, where the EOS predictions for those samples cannot be brought in line with those of all the other samples. In such cases, the reported compositions of those outlying samples are most likely in error. That seemed to be the case with Schlumberger Sample 1.18. I did not believe it was appropriate to ignore all of those PVT data, but the EOS predictions of them were quite poor (especially for the saturation pressures), compared to the predictions for the other samples. The only recourse was to look for a justifiable way of adjusting the sample's composition.

It is first necessary to describe how the composition of a bottom-hole sample, like Sample 1.18, is measured in the lab, and how errors can be occur in those measurements.

To measure the composition of a bottom-hole sample like Sample 1.18, it must first be removed from the pressurized sample vessel and brought to ambient laboratory conditions. This causes the sample to separate (or flash) into two phases. The compositions of the flashed gas and the flashed oil must be analyzed separately. The original sample is then physically recombined at the same gas-oil ratio (hopefully) that was measured for the flash separation, and its composition is calculated by the *mathematical* recombination of the two phase compositions. Several errors can be introduced by this procedure.

During the physical recombination, a metered amount of the flashed gas is added back to a weighed amount of the flashed liquid. The weight of the liquid should be quite accurate, but if the metering of the gas is not, then the gas-oil ratio of the physical recombination will not agree with that of the mathematical recombination, and the reported composition (from the mathematical recombination) will not be the same as that of the physically recombined fluid that was actually put through all of the subsequent PVT experiments. If that is the case, it is unlikely that the EOS will be able to predict any of the experimental results very accurately. In particular, the errors in the predicted separator gas-oil ratios (which are fairly insensitive to the EOS parameters) will be about the same as the error between the physical and mathematical recombination ratios. In the case of Sample 1.18, however, the EOS-predicted gas-oil ratios were not too bad, so a recombination inconsistency did not seem likely.

The GC analysis of the flashed liquid is prone to procedural errors, instrumentation errors, and calibration errors. The potential errors can affect any component, but they are most likely to affect the heaviest portion of the liquid (the C36+, in Schlumberger's case), which never actually elutes from the GC column. Its mass fraction can only be back-calculated from two separate analyses, one of which must be run with a known amount of an internal standard added to the original liquid sample. Any errors in either analysis, or in the measured amount of the internal standard, will accumulate in the reported C36+ mass fraction. This type of error should be suspected if the calculated MW of the sample (using the reported mass fractions and the component MWs estimated by the procedures described in Section D.3) differs significantly from the measured MW.

This seemed to be the case for Sample 1.18's flashed liquid. Its measured MW was only 212, but its calculated MW was about 218.6. That made Sample 1.18 the most prominent outlier shown in Figure 3's comparisons between predicted and experimental MWs. The most justifiable fix for this type of problem is simply to adjust the amount of the heaviest fraction of the flashed liquid (renormalizing the rest) so the calculated MW will match the measured value. I performed the necessary adjustment for the Sample 1.18 flashed liquid as shown in **Table 6**.

Table 6
Compositional Adjustment of the Sample 1.18 Flashed Liquid

Component	Original Mass Fraction	Adjusted Mass Fraction
N2	0.000000	0.000000
CO2	0.000000	0.000000
H2S	0.000000	0.000000
C1	0.000000	0.000000
C2	0.000000	0.000000
C3	0.000900	0.000945
I-C4	0.000600	0.000630
N-C4	0.002000	0.002099
I-C5	0.002300	0.002414
N-C5	0.003701	0.003883
C6	0.013003	0.013644
C7	0.034007	0.035683
C8	0.055711	0.058458
C9	0.049910	0.052371
C10	0.050510	0.053000
C11	0.041508	0.043555
C12	0.038008	0.039882
C13	0.038008	0.039882
C14	0.035407	0.037153

C15	0.036907	0.038727
C16	0.032507	0.034109
C17	0.029306	0.030751
C18	0.029406	0.030856
C19	0.026805	0.028127
C20	0.023905	0.025083
C21	0.022705	0.023824
C22	0.020704	0.021725
C23	0.019204	0.020151
C24	0.018004	0.018891
C25	0.016703	0.017527
C26	0.016203	0.017002
C27	0.015303	0.016058
C28	0.014703	0.015428
C29	0.014503	0.015218
C30+	0.297560	0.262926

The GC analysis of the flashed gas is prone to a different sort of error. The gas is predominantly methane (C1), and the area of its tall and narrow GC peak, relative to the combined areas of all the other, much smaller peaks, can be difficult to measure and integrate accurately. Even a small error in the reported C1 fraction of the flashed gas can prevent the EOS from making accurate predictions for the recombined fluid, especially for saturation pressures.

I suspected that such errors had been made in Schlumberger's GC analysis of Sample 1.18's flashed gas. With no adjustment to the flashed gas composition, the saturation pressure calculations for Sample 1.18 were at least 10% too high, even when the saturation pressures were being predicted quite accurately for the other samples. The previously described adjustment to the flashed liquid composition was insufficient to cure the problem, and any adjustment to the recombination ratio would have thrown off the separator gas-oil ratio predictions. The most justifiable solution was to adjust the C1 fraction of the flashed gas by a variable amount and then to recombine the flashed gas with the adjusted flashed liquid at the reported recombination ratio. The C1 adjustment was then tuned during the regression process, which brought the predictions for Sample 1.18 into line with those for the other samples. **Table 7** shows the final, optimized adjustment to the flashed gas composition, while **Table 8** shows the final adjustment to the recombined composition, which includes the adjustments to both the flashed liquid and the flashed gas. The adjustments might seem quite minor (differences of only about 2.5 mole percent C1 and less than 0.2 mole percent C30+), but they are enough to lower the saturation pressure calculations by about 10% (without throwing off the separator gas-oil ratio calculations).

Table 7
Compositional Adjustment of the Sample 1.18 Flashed Gas

Component	**Original Mole Fraction**	**Adjusted Mole Fraction**
N2	0.003604	0.003974

CO2	0.010635	0.011727
H2S	0.000000	0.000000
C1	0.783689	0.761471
C2	0.076222	0.084051
C3	0.053225	0.058692
I-C4	0.010697	0.011796
N-C4	0.023684	0.026116
I-C5	0.008554	0.009433
N-C5	0.009858	0.010870
C6	0.009254	0.010204
C7	0.007190	0.007929
C8	0.002783	0.003069
C9	0.000508	0.000561
C10	0.000082	0.000091
C11	0.000015	0.000016
C12+	0.000000	0.000000

Table 8
Compositional Adjustment of the Recombined Sample 1.18

Component	Original Mole Fraction	Adjusted Mole Fraction
N2	0.003063	0.003346
CO2	0.009040	0.009875
H2S	0.000000	0.000000
C1	0.666149	0.641219
C2	0.064790	0.070778
C3	0.045911	0.050140
I-C4	0.009431	0.010296
N-C4	0.021260	0.023201
I-C5	0.008316	0.009063
N-C5	0.010061	0.010955
C6	0.012879	0.013964
C7	0.018077	0.019498
C8	0.019410	0.020849
C9	0.013860	0.014861
C10	0.011923	0.012778
C11	0.008883	0.009520
C12	0.007456	0.007990
C13	0.006890	0.007383
C14	0.005965	0.006392
C15	0.005808	0.006224
C16	0.004798	0.005142
C17	0.004074	0.004365
C18	0.003862	0.004139
C19	0.003337	0.003576

C20	0.002828	0.003030
C21	0.002559	0.002742
C22	0.002228	0.002387
C23	0.001977	0.002119
C24	0.001777	0.001904
C25	0.001583	0.001696
C26	0.001477	0.001582
C27	0.001343	0.001439
C28	0.001245	0.001334
C29	0.001185	0.001270
C30+	0.016558	0.014942

After adjusting the Sample 1.18 composition and tuning the other EOS parameters, the result was an optimized, 11-component EOS fluid characterization. This was presented in the main part of this report (Section 5), along with the viscosity parameters that were optimized as described in the following sections.

D.6. Estimating viscosities for individual components

After the EOS parameters are finalized, the task remains to assign a critical z-factor (ZC) to each component. These parameters do not affect any of the EOS's PVT calculations, but they are required for the viscosity model.

Viscosity models are more empirical, and less accurate, than the EOS phase behavior model. They are very sensitive to the component ZCs, and can easily predict non-physical component viscosities even when the ZCs appear reasonable.

My solution for this problem is to initialize each component ZC so that the component will have a liquid viscosity (at atmospheric pressure and the temperature of interest) that is estimated by the Orrick-Erbar correlation. Then, if any further adjustments are made to the ZCs, I make sure the resulting component viscosities remain reasonably close to the Orrick-Erbar estimates, and that they still increase monotonically with MW. I was able to satisfy those criteria for the component viscosities predicted by my final viscosity model, as shown in Figure 7.

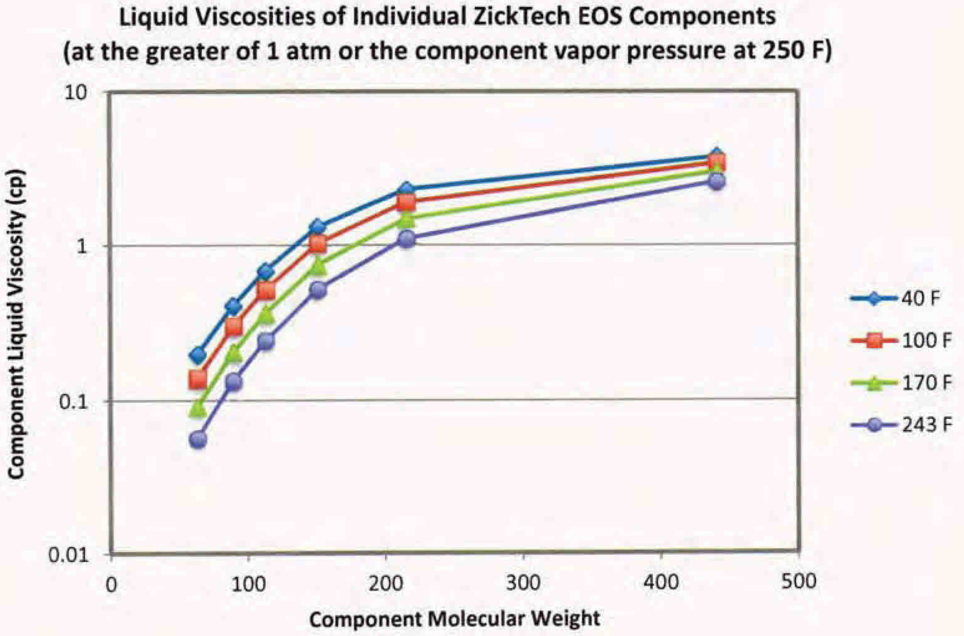

Figure 7. LBC-predicted component viscosities by molecular weight for the Zick Technologies EOS fluid characterization.

D.7. Tuning the viscosity parameters to match viscosity data

It is usually not sufficient to estimate the component ZCs solely from the Orrick-Erbar correlation, however. Those estimates are only approximations, and while they provide good starting points for the component ZCs, they will not necessarily predict the most accurate viscosities possible for the fluid *mixtures* of interest. That requires simulating all of the available viscosity experiments and tuning one or more of the component ZCs until the optimal prediction of the viscosity data is found. In the case of the Macondo fluids, that required tuning the ZC parameter for the heaviest two components of the pseudoized characterization (C13-C19 and C20+). I made sure, however, that the predicted component viscosities remained physically realistic (as shown in Figure 7). An example of the accuracy of the resulting viscosity predictions for Pencor Sample 53 is shown in Figure 16, Appendix E.

Appendix E. VALIDATION OF MY MACONDO EOS FLUID MODEL

An EOS fluid model is validated by how well it predicts the experimental data to which it was tuned. In this appendix, I compare my EOS predictions with the key data from the laboratory experiments on the Macondo fluid samples, demonstrating the accuracy of my EOS.

E.1. Constant Composition Expansions

The labs each performed a type of experiment called a *constant composition expansion* (CCE) on each of the Macondo samples. In this type of experiment, the fluid composition within a *PVT cell* is held constant while the pressure and volume are varied. A CCE is used to measure the saturation pressure, as well as the volume fractions (or saturations) of the equilibrium phases for all pressures below the saturation pressure. This is a very useful type of experiment for tuning an EOS fluid model, because those volume fractions help indicate how near-critical a fluid is, and they are relatively difficult to match, especially with a poorly tuned EOS.

Figure 8 shows the liquid saturations (predicted and measured) from the CCEs performed at reservoir temperature. Figure 9 shows them at 100 F. At each temperature, the rapid change of liquid saturation for relatively small changes of pressure (just below the saturation pressure) is indicative of the near-critical behavior of the fluids.

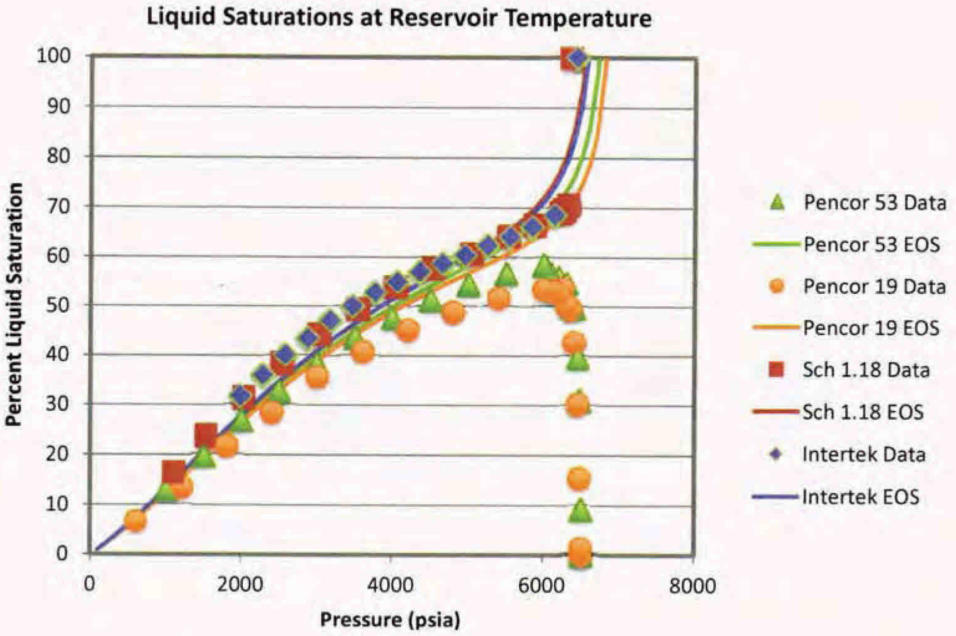

Figure 8. Liquid saturations from the constant composition expansion experiments performed at reservoir temperature, comparing the EOS predictions with the experimental data for the four samples.

In general, the EOS-predicted saturations were quite accurate except near the saturation pressures for the Pencor samples. I was unable to find an EOS tuning that would reproduce the reported dew points (at least, not without predicting dew points for the Schlumberger and Intertek samples as well).[20] I do not have any reason to disbelieve any of the lab data, but there were simply too many inconsistencies to be able to match the entire saturation curve for every sample. Nevertheless, my EOS predicted the important behavior of each sample relatively well. For a fluid that is very nearly critical, the exact saturations just below the saturation pressure are not as important as they might seem. In fact, they will be nearly indeterminate and the properties of the two phases will be nearly identical. The important things to match for such a fluid are the saturations well below the saturation pressure and the near-critical nature of the fluid, even if the near-critical saturations are not predicted perfectly. I believe my EOS meets those criteria.

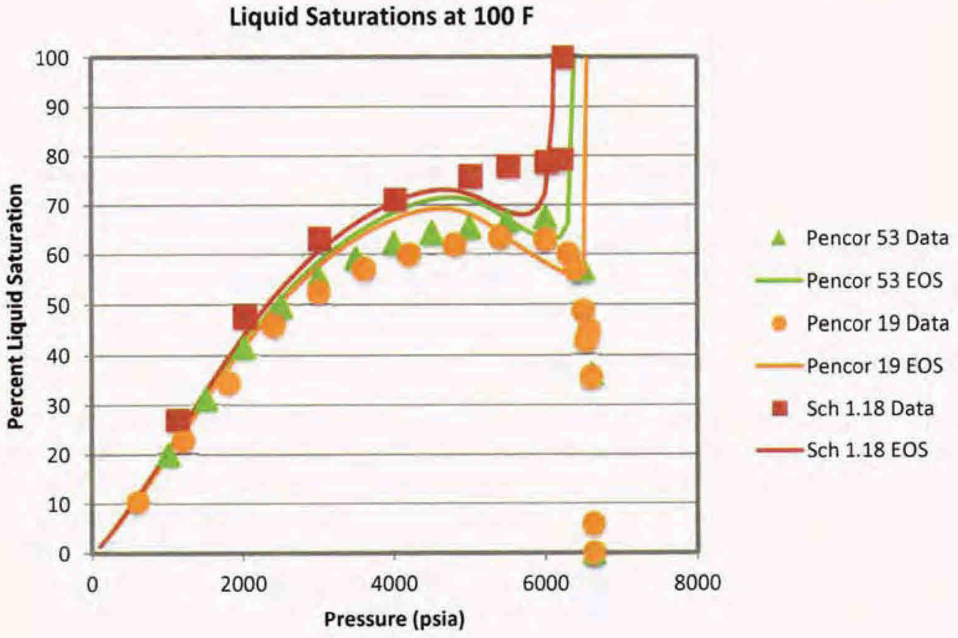

Figure 9. Liquid saturations from the constant composition expansion experiments performed at 100 F, comparing the EOS predictions with the experimental data for the three samples.

Another important measurement from the CCE experiments is the overall density of the fluid as a function of pressure. The EOS predictions are compared with the lab data in Figure 10. The comparisons are nearly perfect. Similar results were found for the other samples.

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[20] At the saturation pressure, 100% liquid indicates a bubble point while 0% liquid indicates a dew point. A critical point would have an indeterminate liquid saturation.

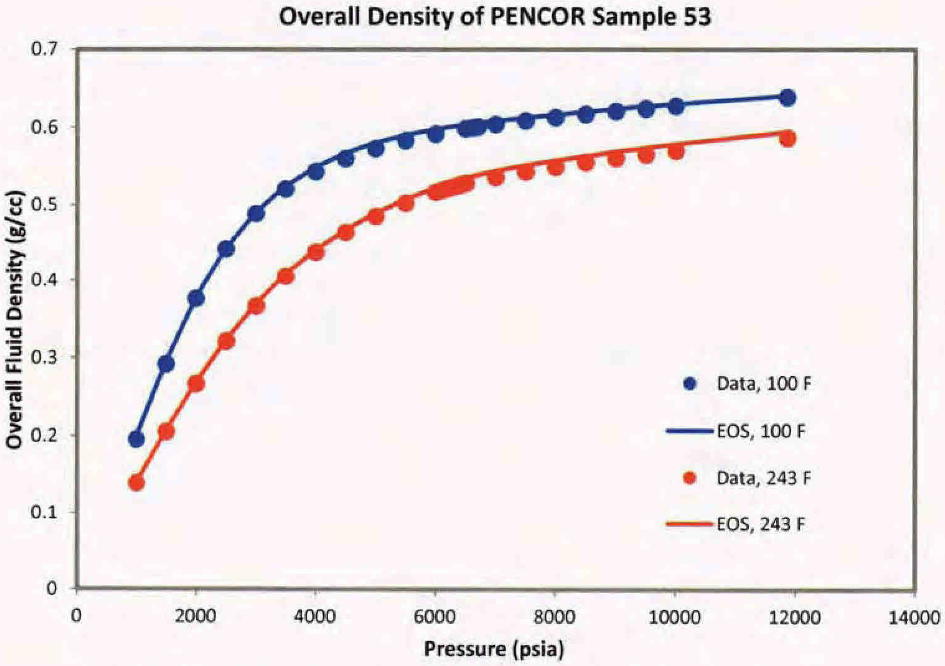

Figure 10. Overall density of Pencor sample 53 during constant composition expansions at 100 and 243 F, comparing the EOS predictions with the measured data.

E.2. Differential Liberation Expansions

Pencor also performed *differential liberation expansion* (DLE) experiments on its samples. In this type of experiment, the fluid in a PVT cell is expanded a number of times to lower pressures, with the removal of all equilibrium gas after each expansion. The amount of liquid remaining in the cell is measured at each pressure, along with the amount, composition, and properties of the removed gas. These experiments are designed to estimate the behavior of the oil during natural depletion of the reservoir. Since the Macondo reservoir was never depleted below its saturation pressure, these experiments are not as relevant as the CCEs for evaluating the oil spill, but they nevertheless provide a lot of valuable information for tuning an EOS fluid characterization.

The relative amount of liquid remaining in the PVT cell after each depletion of equilibrium gas is shown in Figure 11 for Sample 53. The cumulative gas-oil ratio (the total standard volume of gas removed, divided by the volume of liquid remaining in the cell after each depletion) is shown in Figure 12. The densities of both equilibrium phases at each depletion pressure are shown in Figure 13. In all cases, the EOS predictions are compared with the experimental data, and in all cases the agreement is excellent. This is particularly impressive for such a near-critical fluid. Similar results were found for Sample 19.

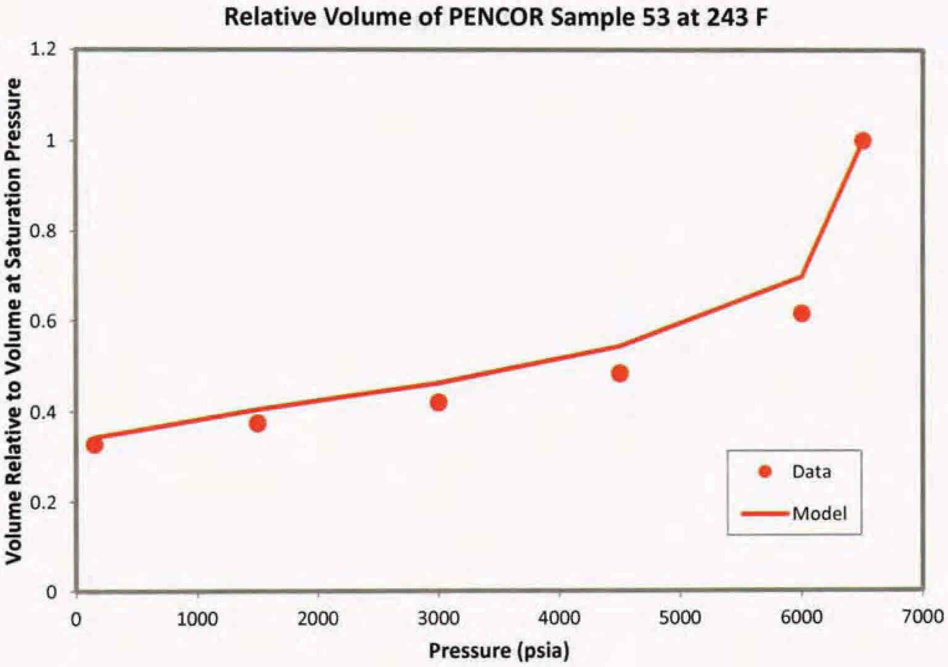

Figure 11. Relative volume of Pencor sample 53 during a differential liberation expansion, comparing EOS predictions with experimental data.

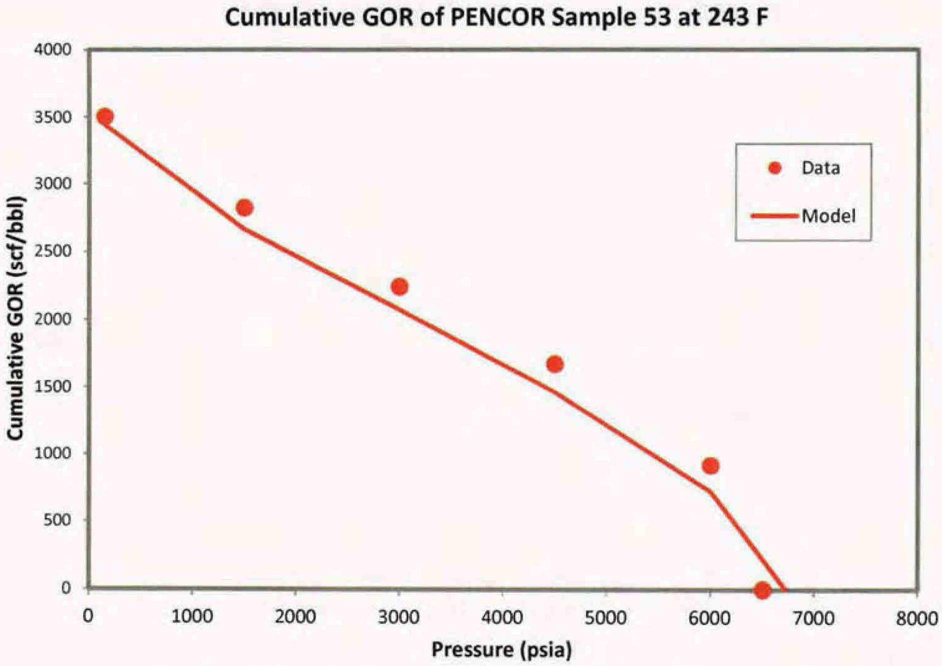

Figure 12. Cumulative gas-oil ratio of Pencor sample 53 during a differential liberation expansion, comparing EOS predictions with experimental data.

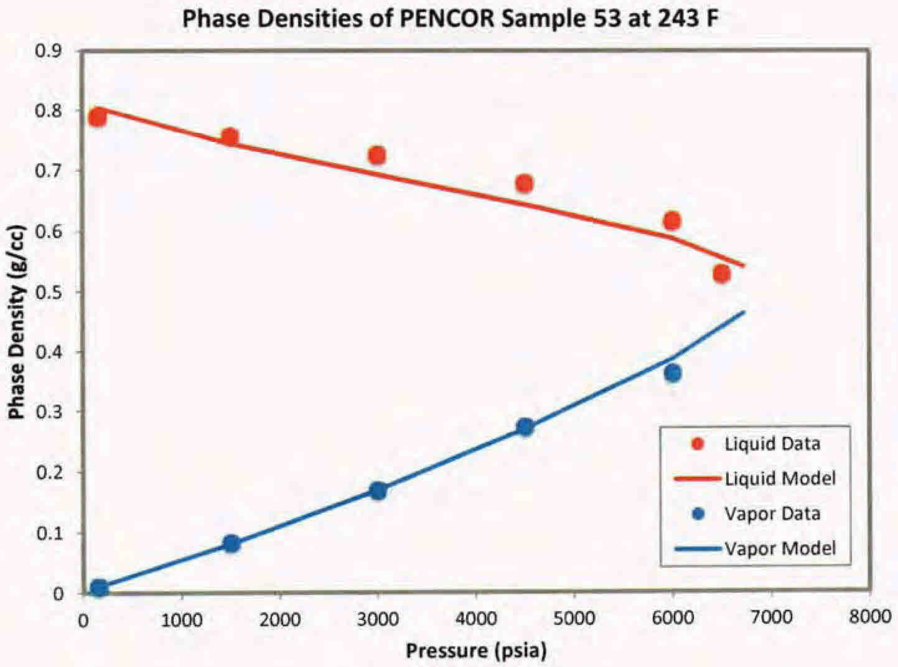

Figure 13. Equilibrium phase densities of Pencor sample 53 during a differential liberation expansion, comparing EOS predictions with experimental data.

E.3. Separator Tests

A separator test measures the amounts of gas and liquid that a fluid sample separates into as it is taken from reservoir conditions (of temperature and pressure) to stock tank conditions (usually 60 F and 1 atm) in a specified way. The results of a separator test include the *gas-oil ratio* (the total volume of the produced gas divided by the volume of the remaining stock tank liquid), the *shrinkage factor* (the volume of the remaining stock tank liquid divided by the volume of the initial reservoir liquid), and the *formation volume factor* (the inverse of the shrinkage factor). A separator test can have one or more stages. At each stage, the fluid equilibrates at a specified temperature and pressure. The equilibrium gas phase is removed and measured. The volume of the equilibrium liquid phase is measured, and then the liquid is re-equilibrated at the conditions of the next stage (if any).

Single-stage and multistage separator tests were performed by the PVT labs on each Macondo sample. The single-stage tests simply flashed the samples from the saturation pressure (at reservoir temperature) directly to stock tank conditions (60 F and 1 atm). The multistage tests passed the samples through the four separation stages shown in **Table 9** (actually, there were slight variations in the conditions from sample to sample, but only the nominal values are presented here).

Table 9
Multistage Separator Conditions

Separator	Temperature (F)	Pressure (psia)
1	130	1250
2	120	450
3	120	150
4	60	15

Comparisons between the EOS-predicted shrinkage factors and the experimental values are shown in Figure 14. There is excellent agreement between the predictions and the data. Comparisons between the EOS-predicted gas-oil ratios and the experimental values are shown in Figure 15. Again, there is excellent agreement between the predictions and the data, except for one outlier.[21]

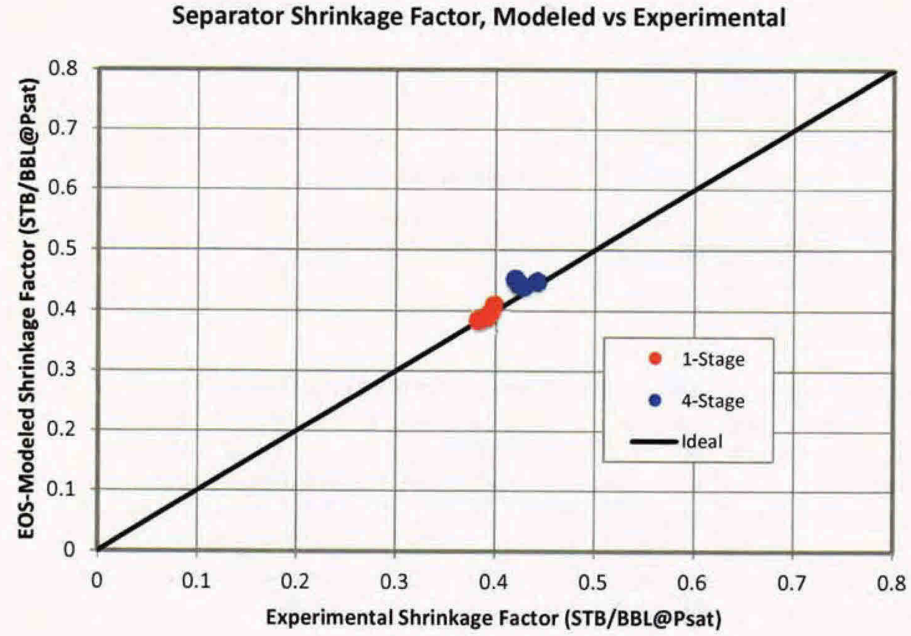

Figure 14. Comparisons between EOS-modeled and experimental values of separator shrinkage factor. Perfect predictions would fall along the "Ideal" line.

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[21] Something must have gone wrong during Intertek's 4-stage separation of Sample 1812, because their reported GOR is completely out of line with the GORs of the other three samples. In fact, it is almost as high as the GOR from Intertek's single-stage separation of Sample 1812, and that simply cannot be a valid result.

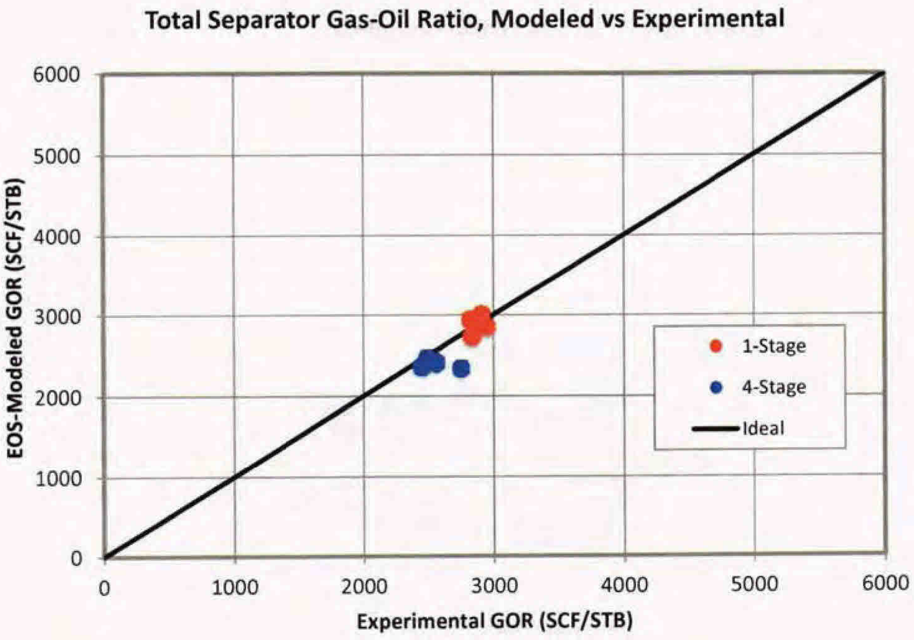

Figure 15. Comparisons between EOS-modeled and experimental values of total separator gas-oil ratio. Perfect predictions would fall along the "Ideal" line.

E.4. Viscosity Experiments

Pencor also performed viscosity experiments on two of their samples. At each pressure, the fluid sample is equilibrated and a small object (usually a metal ball) is dropped through a column of the equilibrium liquid phase. The viscosity is determined by the time it takes for the object to fall a certain distance. The predictions of the tuned Lohrenz-Bray-Clark viscosity model are compared with the experimental data in Figure 16 for Sample 53. The predictions for Sample 21 were very similar. The agreement, though not perfect, is about as good as it ever gets for viscosity predictions.

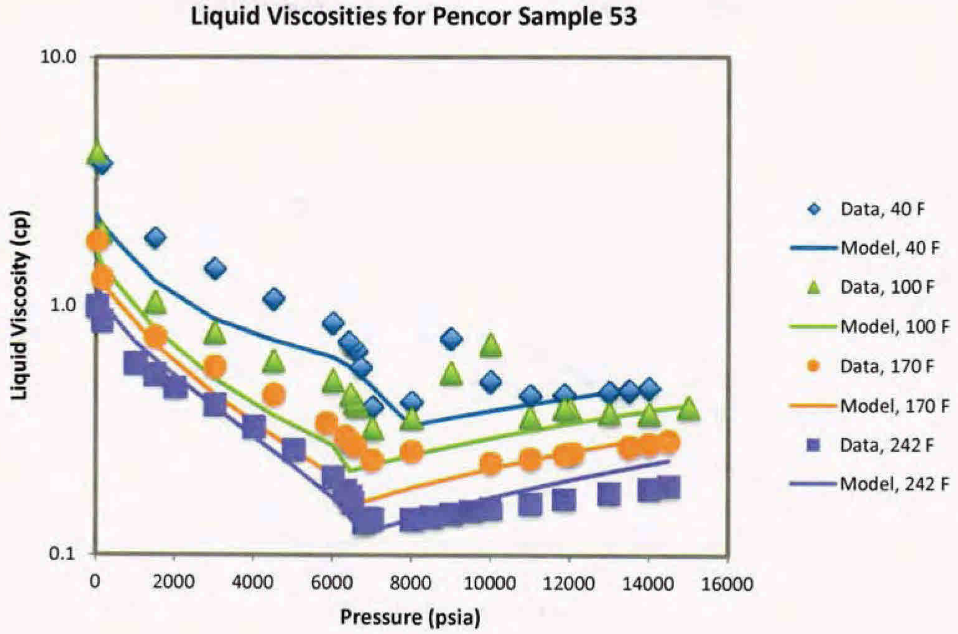

Figure 16. Liquid viscosities for Pencor sample 53 at four different temperatures, comparing LBC model predictions with experimental data.

E.5. Overall Evaluation

My overall conclusion is that the EOS fluid characterization I developed for the Macondo reservoir fluids is about as accurate as you will ever find, especially for near-critical fluids such as these. Even the viscosity, which is always very difficult to model accurately, is predicted reasonably well.

Appendix F. PHAZECOMP

PhazeComp is the state-of-the-art, equation-of-state PVT program I wrote for compositional phase behavior modeling and fluid characterization. It embodies the culmination of my 20-plus years of experience in writing EOS and PVT software. PhazeComp has been available commercially since 2002; it has been licensed by many of the most expert phase behavior specialists in the industry, including those at PERA, ConocoPhillips, Statoil, Maersk, Saudi Aramco, Petrostreamz, the Norwegian University of Science and Technology (NTNU), and the University of Calgary.

PhazeComp acts as a virtual PVT (pressure-volume-temperature) laboratory and as a vehicle for tuning EOS fluid characterizations. PhazeComp performs all of the industry standard calculations of a petroleum engineering PVT program, including the simulation of all standard PVT experiments, the prediction of gravity-induced compositional gradients, and the generation of black-oil PVT tables. In addition to that industry standard functionality, PhazeComp offers unparalleled features for tuning EOS fluid characterizations. PhazeComp's unique benefits include allowing multiple fluid characterizations to be used; enabling the automatic calculation of acentric factors and volume shift factors from component boiling points and specific gravities, respectively (or vice versa); and allowing any number of named *variables* to be defined by the user and adjusted (within user-specified bounds) by regression. PhazeComp performs all EOS calculations to the limits of machine precision, an accuracy level unmatched by any other PVT program but essential for fluids that are near critical points.

Appendix G. BLACK-OIL LOOKUP TABLES BASED ON MY EOS

Table 10 shows a small excerpt from the black-oil tables that were built from my Macondo EOS. Due to their size and format, however, the complete black-oil tables are provided separately in electronic form in the folder entitled "Appendix G – Black-Oil Lookup Tables Based on My EOS."

Table 10
Excerpt from the Macondo Black-Oil Tables

Temp (F)	Pres (psia)	Liq Vol Frac	Gas Vol Frac	Liq Den (kg/m3)	Gas Den (kg/m3)
200	2000	0.30535	0.69465	710.29	114.63
200	2200	0.33567	0.66433	703.32	127.62
200	2400	0.36486	0.63515	696.63	140.86
200	2600	0.39282	0.60718	690.21	154.31
200	2800	0.41948	0.58052	684.02	167.96
200	3000	0.44482	0.55518	678.04	181.80
200	3200	0.46883	0.53117	672.27	195.82
200	3400	0.49152	0.50848	666.69	210.02
200	3600	0.51292	0.48708	661.28	224.41
200	3800	0.53307	0.46693	656.04	238.98
200	4000	0.55204	0.44796	650.94	253.76
200	4200	0.56990	0.43010	645.97	268.76
200	4400	0.58674	0.41326	641.09	283.98
200	4600	0.60270	0.39730	636.28	299.44
200	4800	0.61797	0.38203	631.47	315.15
200	5000	0.63281	0.36719	626.60	331.12
200	5200	0.64762	0.35238	621.59	347.38
200	5400	0.66300	0.33700	616.31	363.95
200	5600	0.67985	0.32015	610.60	380.89
200	5800	0.69968	0.30032	604.26	398.33
200	6000	0.72526	0.27474	596.96	416.48
200	6200	0.76246	0.23754	588.19	435.76
200	6400	0.82760	0.17240	576.94	457.13
200	6600	1	0	560.31	483.49
200	6800	1	0	562.93	562.93
200	7000	1	0	565.46	565.46
200	7200	1	0	567.92	567.92
200	7400	1	0	570.30	570.30
200	7600	1	0	572.61	572.61
200	7800	1	0	574.86	574.86
200	8000	1	0	577.04	577.04

Appendix H. FACTS AND DATA CONSIDERED IN FORMING MY OPINION

LNL097-0001 - LNL097-0091
BP-HZN-2179MDL00062844 -893
BP-HZN-2179MDL01587889
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ADR032-061971 - 62078
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DW 0005079 - DW 0005167
Transcript of 30(b)(6) Deposition of Pencor - Jason LeBlanc (20120910)
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STC-MDL-0003254 -3291
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Robinson, D. B., and Peng, D. Y, "The Characterization of the Heptanes and Heavier Fractions," Research Report 28, Gas Producers Association, Tulsa, OK (1978).
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Transcript of 30(b)(6) Deposition of Schlumberger - Albert DeCoste (20121205)
Relied-Upon Modeling Runs