Analyzing Hydrocarbons in the Borehole

A rapid evaluation of hydrocarbon fluid composition is now available with a new fluid-sampling tool. The quality of samples taken for later analysis can be determined before filling the sampling cylinder. The tool is sufficiently sensitive to determine compositional gradients within a formation.

Understanding crude oil composition early in the development process helps optimize resource exploitation. Such information is now available from a wireline tool, giving results in real time that allow optimization of fluid sampling based on the measured in-situ composition.

An early determination of gas composition and gas/oil ratio (GOR) may be necessary to decide whether to complete a well, or even whether to develop a field at all. For example, the economics of developing fields that contain a rich hydrocarbon gas and those that contain a
high percentage of carbon dioxide \([\text{CO}_2]\) in the gas are markedly different. \(\text{CO}_2\) is highly corrosive, so its presence can change requirements for flowlines and surface equipment. In addition, commingling prospects with incompatible compositions may need to be avoided. Flow assurance also is impacted by problems with asphaltene, wax, hydrate and organic scale buildup in flowlines. The fluid composition can restrict allowable drawdown pressures and flow rates to prevent fluid dropout.

This article update presents recent developments in fluid analysis available with the MDT Modular Formation Dynamics Tester. A new module, the CFA Composition Fluid Analyzer, provides a measurement of fluid composition from samples drawn directly from the formation. It discriminates the fractions of methane, light hydrocarbons, heavy hydrocarbons, carbon dioxide and water present in a sample. The tool makes this determination based on light absorption and fluorescence of the fluids; results are transmitted to surface in real time. Case studies from the Middle East and the North Sea demonstrate the effectiveness of this new module.

### Analyzing Oil and Gas

The terms gas and oil describe the state of a hydrocarbon as vapor or liquid, but do not specify the chemical composition. A detailed measurement of the constituents of a hydrocarbon, as determined in a surface laboratory, can be used to predict the constituents of the gas and oil phases—as well as other physical properties like density and viscosity—at various temperatures and pressures. These detailed laboratory measurements can take a long time to obtain. The new CFA tool, in conjunction with other modules on an MDT assembly, provides a quick determination of some of the components and indicates the degree of drilling-mud contamination before samples are taken for further analysis.

Hydrocarbon fluids comprise a multitude of constituents ranging from single-carbon methane to very long-chain carbon compounds, as well as cyclic, aromatic and other complex molecules such as asphaltenes and waxes. These constituents determine the phase behavior of a given reservoir fluid, which is often indicated using a pressure-volume-temperature (PVT) phase diagram (above right). A hydrocarbon fluid is in single phase if the pressure and temperature are outside the phase envelope. At conditions within this envelope, two phases coexist. However, the phase composition changes within this two-phase region. Near the bubblepoint curve, the gas phase is predominantly methane, but further into the two-phase region, more light and intermediate components enter the gas phase.

Similarly, the first liquid components to drop out after passing the dewpoint are the heavier components; lighter components go into the liquid phase at conditions further from the dew-point curve. This phenomenon is important when sampling gas-condensate fluids: once a fluid enters the two-phase region, heavy components are lost into the liquid phase. This behavior is used in the CFA design to determine when a fluid crosses the dewpoint.

The pressure and temperature condition at which the bubblepoint and dewpoint curves meet is called the critical point. At that point, the density and composition of the liquid and gas phases are identical. The maximum temperature at which two phases can coexist is termed the cricondentherm.

Reservoir temperature is usually almost constant—unless cold or hot fluids are injected into the reservoir—so most depleting reservoirs follow a downward vertical path on a pressure-temperature phase diagram. If reservoir temperature is between the critical temperature and the cricondentherm, light can drop out of the gas phase within the reservoir. These are termed gas-condensate, or retrograde-condensate, reservoirs. Gas in a reservoir with a temperature greater than the cricondentherm is termed a wet gas if liquid drops out because of pressure and temperature decreases in the production system, or a dry gas if no liquid falls out in either the reservoir or production system.

Economic decisions early in an exploration project often hinge upon characterizing the type of hydrocarbon in a reservoir. This determination is particularly true offshore, where an expensive platform infrastructure or subsea tiebacks may need to be designed to handle reservoir fluids. Early hydrocarbon typing is also needed in remote areas where satellite fields may not be quantified.
economic to produce unless a tieback configuration or additional facilities are built to market the gas. Sound production practices also require knowledge of fluid-phase behavior. If reservoir pressure drops below the dewpoint, liquid condensate drops out in the formation. At low saturation, liquid in the pore spaces is not mobile and decreases the gas relative permeability. Two negative economic impacts result: productivity declines and valuable condensate liquids are left behind in the reservoir. Pressure support through gas or water injection often is required to keep reservoir pressure above the dewpoint. Similar practices can be followed to keep an oil reservoir above the bubblepoint to avoid gas breakout.

**Fluid Sampling**

For many years, the industry has evaluated fluids by collecting samples from a formation, bringing them to surface, and analyzing them in a laboratory that may be far from the wellsite. This process can be time-consuming and is subject to errors in collection, handling or sample degradation during transport.

The PVT Express onsite well-fluid analysis service is a recent advance in fluid-property determination. This system can deliver detailed fluid-analysis data a few hours after samples reach the surface. A unique minicell for PVT property determination allows onsite measurement of dewpoint pressure on gas-condensate samples. The compact, modular, mobile laboratory can be transported to any geographic location. Delays associated with sample shipment are eliminated. Fluid quality and fluid properties can be determined while the opportunity to obtain additional samples is still available. Decisions relating to additional wireline formation testing or drillstem testing operations can be made more quickly with the PVT Express service.

Taking the next step, Schlumberger makes some fluid properties evaluations downhole. The LFA Live Fluid Analyzer for the MDT tool provides a means to analyze in-situ fluids to determine when contamination from drilling mud has decreased sufficiently to obtain a fluid sample with acceptable quality. This minimizes the time required to collect fluid samples, decreasing both rig costs and the risk of the tool becoming stuck because it was on the formation for too long.

The LFA module includes a channel specifically tuned to record the presence of methane, providing a means to obtain GOR. Downhole GOR measurements help identify whether different formations are compartmentalized. A sampling program can be directed to reveal compositional variation within a given compartment, helping to optimize completion programs. Agreement between downhole, wellsite and laboratory crude-oil property measurements engenders confidence in the derived fluid properties.

The LFA channels also measure the oil’s color, which usually changes as drilling mud is flushed out of the formation. A sophisticated algorithm indicates the cleanup time required to
obtain a representative formation-fluid sample in the MDT sample modules. This evaluation pre qualifies fluid samples for more extensive analysis at the surface, provides basic fluid property data such as GOR and helps define fluid variability at different depths. These measurements are critical for adjusting a sampling and analysis plan while the MDT tool is in the borehole, which helps an operator realize maximum benefit of a logging run.

Gas-condensate reservoirs present special challenges for fluid-sample collection. A sampling tool must apply a pressure differential to pull fluid out of the formation into its sampling chambers. If this drawdown is too large, the pressure can drop below the dewpoint and the segregated liquid phase may be trapped in the reservoir. As a result, the sample collected will not be representative. Even if the phase transition occurs outside the formation, that is, the fluid becomes multiphase within the tool’s probe and pumpout modules or in the flowlines leading to the sampling chamber, differences in fluid density and viscosity and phase segregation within the tool can lead to an unrepresentative sample composition. This problem of a reservoir fluid breaking into two phases is even more severe when the samples are obtained at surface during a drillstem test, which uses a larger pressure drawdown than a sampling tool on wireline.

The new CFA module—a joint development of Schlumberger-Doll Research Center, Ridgefield, Connecticut, USA; Schlumberger Kabushiki Kaisha Technology Center, Fuchinobe, Kanagawa, Japan; and Schlumberger Sugar Land Product Center, Sugar Land, Texas, USA—was designed specifically to detect dew formation as a second hydrocarbon phase using a fluorescence detector. This is the first downhole tool with dew-detection capabilities. With this capability, the module can differentiate between single- and multiple-phase flow and can show when pressure in the tool drops below the dewpoint pressure. Used in combination with an LFA module, a CFA tool indicates the proper time and conditions for obtaining a fluid sample, even in the difficult environment of gas-condensate reservoirs.

In addition to the fluorescence detector, the CFA tool incorporates absorption spectrometers that measure the opacity, or optical density, of a fluid at several wavelengths. These measurements distinguish several components of hydrocarbon fluids, not only enhancing dew detection, but also providing a compositional analysis. This compositional analysis capability will be discussed first, with fluorescence detection described later in the article.

Evaluating Gas Composition

Hydrocarbon molecules interact with light in the visible and near-infrared wavelength band that is sampled by the CFA spectrometers. Interaction with electronic energy bands gives oils their color, with complex molecules absorbing more light than simple ones. Oils with a significant quantity of resins and asphaltene are darker than oils containing primarily paraffins. Gas condensates tend to be relatively clear, with little electronic absorption.

A different type of interaction occurs in the near-infrared region, where light absorption excites molecular vibration. The type of molecular bond between carbon [C] and hydrogen [H] atoms determines the frequency of absorbed light. The dominant vibrational absorption interactions occur in three types of molecular configurations:

- a carbon atom surrounded by four hydrogen atoms, that is, CH₄
- a carbon atom with three hydrogen atoms, –CH₃
- a carbon atom with two hydrogen atoms, –CH₂–

Methane is the unique example of the first mode. Ethane is an example of the second case, because it contains two carbon atoms that are each connected to three hydrogen atoms. However, longer-chain hydrocarbons are predominantly –CH₂– but also have the –CH₃ group at each end of a chain. The –CH₂– group dominates light absorption by such long-chain compounds, but there also is some –CH₃ absorption. For example, 77% of the carbon-hydrogen bonds of n-dodecane, a common paraffin with 12 carbon atoms in a linear chain, are in –CH₂– groups.

There is a complication in the analysis of hydrocarbon spectra: the absorption spectra overlap. Spectral interpretation requires proper accounting for this overlap. These complexities are overcome in the CFA analysis by employing a technique called principal component regression. This mathematical procedure extracts maximal information content in any dataset, in this case the vibrational spectra.

The CFA interpretation algorithm incorporates five detectors to determine four components:

- methane, which is termed C1 in the CFA analysis
- other hydrocarbon gases, termed C2-C5
- hydrocarbon liquids, termed C6+
- carbon dioxide, CO₂

Distinct spectral signatures can distinguish both methane and carbon dioxide. The other hydrocarbon gases are dominated by –CH₃ and –CH₂– groups dominate hydrocarbon liquids. Thus, the principal component regression results are interpretable in terms of spectral characteristics.

In the same part of the infrared spectrum, water has a broad and strong absorption peak. The presence of water can swamp the other signals, particularly the CO₂ signal. The CFA module has a detector tuned to the water vibrational mode, indicating when the responses from the other detectors are influenced by water.

The CFA tool is recommended for fluids with a GOR exceeding 1000 scf/bbl [180 m³/m³], because fluids with a lower GOR have a color signal that is strong enough to interfere with the vibrational-mode absorption peaks. This recommended range includes gases, gas condensates, volatile oils and some black oils.

The following sections show how these compositional measurements were used to detect injected gas in a monitoring well and to discover a compositional gradient within the oil leg of a reservoir with a gas cap.

8. Nonhydrocarbon compounds found in oil, such as those containing nitrogen, oxygen and sulfur, also contribute to color. Dark oils can contain large amounts of these components.
9. The dashes indicate a connection to other carbon atoms: CH₃ connects to one carbon atom, and –CH₂– connects to a carbon atom on each side of the indicated carbon atom.
11. In this terminology, the number following the letter C indicates the number of carbon atoms in the compound. Thus, C1 is methane, with molecular formula CH₄.
12. A standard correlation of oil type to GOR is that black oil GOR is less than 2000 scf/bbl [360 m³/m³], volatile oils range from that value to 3300 scf/bbl [594 m³/m³], then gas condensates extend to 50,000 scf/bbl [9006 m³/m³], and gases have GOR greater than 50,000 scf/bbl.
Detecting Injection Gas

The CFA module was used in a gas-injection pilot project that had been in operation for several years in an onshore carbonate reservoir in the United Arab Emirates (UAE). As part of an ongoing evaluation program, the operator, Abu Dhabi Company for Onshore Oil Operations (ADCO) drilled a new monitoring well to determine the progress of the injected gas. An MDT sampling string containing the CFA tool was equipped with a dual-packer module, a pumpout module, an LFA module and 18 single-phase multisample chambers. Single-phase samples of sufficient quality for later, detailed laboratory analyses were obtained from six different stations.

The CFA tool provided fluid compositional information prior to sample collection at the first four stations. The drilling fluid was a water-base mud, so some water was detected during the analysis. The characteristics of the pumpout module—described in “Detecting a Multiphase Condition,” page 60—caused the water to appear as slugs passing the CFA window. The tool monitored the cleanup of the drilling fluid prior to sampling.

The upper zone sample was virtually all oil (left). The second sample station clearly showed a high concentration of gas coming from the formation. The two lowest zones produced some gas. This indicated that, at the monitor well, the top zone was unswept, and the second zone had been swept the most by the injected gas. The results demonstrated that these two upper zones were not in communication.

The CFA results were obtained after about two hours of pumping to clean out drilling mud. After an additional two to three hours at each station, changes in the LFA color channels indicated that the fluid had cleaned up enough to take a sample in a single-phase sampling cylinder. These samples were analyzed in a laboratory, and the results match reasonably well with the real-time CFA data. These results helped ADCO understand the flow characteristics and gas-injection efficiency of their field.

Discovering a Compositional Gradient

Statoil, the operator of a Norwegian Sea appraisal well, wanted to establish the gas/oil contact (GOC) and oil/water contact (OWC) and obtain fluid samples for laboratory analysis. A drillstem test in a discovery well had not provided conclusive fluid-phase property data. This was the only appraisal well drilled before developing facilities to process a complex, near-critical reservoir-fluid system. Statoil felt it was
water-base mud filtrate. The formation resistivity high gas density, low oil density and invasion by that no separation was seen, probably because of and fluid properties in this reservoir were such normally a sign of a gas zone, but the formation logs did not indicate a crossover. Crossover is a thin, possibly impermeable zone exists at about XY30. The invaded-zone resistivity (Track 3) implies a water zone up to XY10, with a transition zone up to about XX95 and perhaps a third zone above XX75. The pressure measurements (Track 2) confirm three gradients, with a gas/oil contact at XX75 and an oil/water contact at XY10. Both optical density from the CFA color channel and gas/oil ratio (GOR) (Track 5) show a gradient in composition, which is also seen in the CFA compositional analysis (Track 4). The numbers to the left of the CFA compositions indicate the sampling order in the wellbore. The thin bars below each CFA result are later laboratory results, which were scaled to exclude the water fraction measured by the CFA tool, allowing direct comparison of the hydrocarbon components. Laboratory GOR measurements (Track 5) also confirm the compositional gradient, although the magnitude is somewhat different from the CFA result.

A wireline triple combo log indicated 100 m [328 ft] of relatively featureless reservoir, except for a possibly impermeable streak at about XY30 (above). The density and neutron porosity logs did not indicate a crossover. Crossover is normally a sign of a gas zone, but the formation and fluid properties in this reservoir were such that no separation was seen, probably because of high gas density, low oil density and invasion by water-base mud filtrate. The formation resistivity was uniform, but the resistivity due to the water-base mud in the invaded region indicated a probable change in the flushed-zone water saturation, with a likely OWC at XY10.

Statoil next obtained pressure gradients in the formation using an MDT tool to find the different fluid sections. The MDT logging system comprised a probe module, a pumpout module, a CFA module, an LFA module and multiple sample-chamber modules. The probe module had a high-grade quartz pressure gauge.

Within the 100-m span identified by the wireline logs, the operator obtained 25 pressure measurements. These data identified three different pressure gradients corresponding to gas, oil and water, all in hydraulic communication. However, the pressure gradient alone was inadequate to resolve a compositional gradient in the hydrocarbon zone. Statoil had investigated compositional grading at other locations around the world and wanted to study this oil leg in greater detail.14

Once the pressures were obtained, the operator repositioned the tool string to analyze the formation fluids using the CFA module and to collect samples in high-pressure sample bottles from an area in the lower part of the oil leg. The CFA module obtained a quick reading of sample composition before filling each sampling cylinder. The results, transmitted to surface in real time, indicated that the fluid composition stabilized within 1000 to 2000 seconds, or 17 to 33 minutes. The CFA compositional measurements typically were taken after an hour of cleanup time. However, slugs of water-base mud continued to pass through the apparatus, and it typically took more than two additional hours for the mud contamination to become acceptably low to obtain each sample for surface analysis.

Next, the probe was positioned in the gas cap. The GOR was high, with large concentrations of C1 and C2–C5 components. The optical density at the color channel was almost zero in the gas cap, consistent with the presence of a very light hydrocarbon system.

After obtaining a fluid sample in the gas cap, the tool was repositioned to obtain a second sample 14 m [46 ft] above the first oil sample. The operator suspected there might be a compositional gradient in the oil zone. The CFA results from the two oil stations indicated a significantly higher GOR at the upper position. The color optical density also was less at the upper station, indicating a greater content of gas components at the higher position.

With this information, the operator was able to change the logging plan immediately. The probe module was placed as close to the oil/water contact as possible, then as close to the gas/oil contact as possible. The CFA readings over the full extent of the oil column confirmed the existence of a fluid compositional gradient and more than a 60% increase in GOR over about

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For Statoil, the important point was that the existence of a compositional gradient within the oil leg was noticed and confirmed in real time. Knowing that there was a compositional gradient in the formation and knowing the expected range of GOR helped the company develop a wellbore drawdown strategy to optimize production.

Because the operator planned to develop the field using horizontal wells, placement of the wells in relation to the gas/oil and water/oil contacts was crucial. An MDT permeability test performed during this testing sequence provided additional information for well placement. The in-situ properties determination provided by the combination of the CFA and LFA modules assured that quality samples were obtained in the sampling cylinders. Since the produced fluids from this field will be tied in to other fields, a quality fluid compositional analysis and determination of compatibility with the other fluids were important for flow assurance.

Subtle changes in composition can be easily obscured if the fluid passing through the detectors has separated into two phases. This can occur if the drawdown pressure is too great. The use of fluorescence is key to detecting when a fluid passes through its dewpoint.

**An Aromatic Afterglow**

Aromatic hydrocarbons fluoresce. The distinguishing characteristic of fluorescence is that there is a brief time delay between light absorption and its reemission, and that the reemission occurs at a lower energy—that is, a longer wavelength—than the absorbed light (left).^{15}

The CFA module incorporates a fluorescence detection unit (FDU) along the flowline, about 7 cm [3 in.] from the absorption spectrometer. Since they are close together, the two types of detector sample essentially the same fluid. This allows the two measurements to be used simultaneously to evaluate fluids.

The FDU shines blue light onto a window in the flow tube. One detector tuned at the source wavelength is placed at the reflection angle. This provides a measure of direct reflection of light, reducing the possibility of false-positive fluorescence detection. Two other detectors in the FDU record the intensity and spectrum of the fluorescence.

The FDU is particularly sensitive to fluorescence from fluid on the surface of the flow-tube window. Dew formation often causes a liquid coating on the flow-tube surfaces. When the fluid is in a single phase, the detector measures the properties of the fluid flowing near the window. Once the pressure drops below the dewpoint, liquid drops out of solution and condenses. The condensed liquid phase wets the detector window, so the fluorescence detector is most sensitive to the properties of the liquid phase. Since the heavy ends are enriched in the liquid phase, the FDU is sensitive to the presence of a liquid phase dropping out from a gas condensate. This makes it an excellent tool for detecting when a fluid drops below its dewpoint.

**Detecting a Multiphase Condition**

The first use of an FDU in the field showed that the drawdown pressure being used at that sampling station was too large, generating a two-phase condition. The operator moved to another location a few centimeters away and resampled, this time obtaining a good sample. This section describes how the fluids separated in the pumpout module and how the FDU detected this two-phase condition caused by excessive drawdown at the first location.
During an MDT logging run, a probe seals against the formation, then the pump pulls fluid from the formation into the tool. Ideally, the drawdown will be sufficient to remove the fluid from the formation, but not so much as to drop the fluid below its dewpoint pressure. However, both the formation permeability and the differential between dewpoint pressure and formation pressure are unknown or poorly known before most MDT jobs in exploration wells begin. In fact, determining the dewpoint is one of the main reasons for obtaining fluid samples. Without knowing permeability and dewpoint pressure, establishing a proper drawdown pressure to keep a gas in single phase is difficult. The FDU on the CFA tool provides a check of this condition in situ.

When water may be present in the flowline, the CFA unit should be placed downstream of the pumpout module to avoid continuous swamping of the longer wavelength absorption spectrometers by the strong water-absorption peak. The water is still present in the flowlines in this configuration, but the residence time in the pump is sufficient for phase segregation to occur. Thus, the water, oil and gas phases will flow through the spectrometers separately (right). On the downstroke, the lower part of the pump fills from the formation, and the upper part discharges to the flowline. The discharge point is at the bottom of the upper pump chamber, so the first fluid pumped out is water, followed by oil, then gas. On the upstroke, the chambers reverse function. Now, the lower chamber discharges to the flowline, but this time does so from the upper part of the chamber. The first fluid expelled is gas, followed by oil, then water.

The CFA tool clearly distinguishes flowing phases using the water and hydrocarbon vibrational-energy absorption peaks and the main FDU fluorescence channel. The hydrocarbon vibrational channels provide an indicator of the amount of gas passing through the flowline when the ratio of C1 to C6+ is high. The FDU is sensitive to the presence of a liquid hydrocarbon phase. Thus, a plot of these three quantities—water absorption, C1/C6+ ratio and the main fluorescence channel—shows the three phases passing through the flowline.

This procedure indicated three-phase flow during sampling of a gas cap in a North Sea well. In this case, the operator suspected that the gas cap might contain a retrograde condensate. The gas was near a saturated condition, and the pumpout unit drew the pressure down to about 25 bar [370 psi] below formation pressure. Because a large drawdown was used to pump the fluids out of the formation, two hydrocarbon phases were observed; a sample taken from this depth would be invalid because of a high likelihood of formation-fluid damage at this point. After moving the MDT string a few centimeters to obtain an unaffected fluid sample, the operator found this new sample contained more liquid than the first. Detecting the inappropriate sampling condition and moving to a new location was possible because of the real-time CFA results.

Real-Time Advantages

Capabilities provided by the FDU are being incorporated into real-time CFA services, increasing the sensitivity for detecting phase transitions and providing additional information about in-situ fluid compositions.

The ability to distinguish methane and light hydrocarbons from heavier hydrocarbons greatly increases the amount of information available in real time from gas-condensate reservoirs. This determination allows an operator to quickly make important economic decisions about a reservoir. The operator can then follow up with more extensive measurements in a surface laboratory, using samples whose quality has been assured—before collection—using these innovative downhole sampling tools. —MAA

\(^{15}\) One way for a molecule to decay from an excited state is by emitting a photon. If some of the excitation energy has dissipated, for example through collision, the reemitted light is at a lower energy than the absorbed light.