Geologic and Geochemical Controls on Oil Quality

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Abstract

Oil quality is a key variable in establishing the economic viability of a hydrocarbon accumulation, especially in deep water. Lower quality crude oils, with low API gravity values, higher sulfur and metal contents, and elevated TAN (total acid number) values, tend to be more viscous and yield at the refinery a smaller percentage of high value products, while requiring additional upgrading. These oils also tend to be more difficult to produce. An examination of oils and their generation, migration, and alteration histories reveals that there are a number of key geologic and geochemical factors which impact oil quality. Among the key factors is the nature of the source rock, with carbonate and siliceous source rocks yielding higher sulfur crude oils than argillaceous source rocks. A second factor is thermal maturity of the source rock or thermal stress applied to an oil. Lower thermal maturity levels yield lower quality crude oils at time of generation, while greater thermal stress applied to the reservoir can increase API gravities through thermal cracking. One of the most important factors, and very often the most important factor, in establishing oil quality is the extent of bacterial alteration. The extent of biodegradation is controlled by the thermal and filling histories of the reservoir, the nature of the oil-water contact, and the availability of micronutrients (possibly as a result of mineral diagenesis). Biodegraded oils are generally heavy and may also display high TAN values and sulfur contents. Mixing of oils also plays a role in establishing final oil quality. Mixing can result in the overall improvement of oil quality through the introduction of unaltered and often lighter crude oils into a degraded oil pool. Dysmigration or remigration of oil can also impact quality through phase segregation, where a residual and daughter product is formed.

KEYWORDS: API gravity, biodegradation, phase segregation, remigration, source rock, sulfur, TAN, thermal cracking, and thermal maturity.

Resumen

La calidad del aceite es una variable clave en el establecimiento de la viabilidad económica de una acumulación de hidrocarburos, especialmente en aguas profundas. Crudos de menor calidad con bajos valores de densidad API, alto contenido de azufre y metales y valores elevados de TAN (número ácido total), tienden a ser más viscosos y dan en refinería un menor porcentaje de productos de alto valor, mientras que requieren mejoramiento adicional. Estos aceites también tienden a ser más difíciles de extraer del subsuelo. Un examen de los aceites y sus historias de generación, migración y alteración revela que hay varios factores geológicos y geoquímicos clave que impactan en la calidad del aceite. Entre estos factores clave está la naturaleza de la roca generadora con rocas generadoras carbonatadas y silíceas dando crudos de mayor contenido de azufre que las rocas generadoras arcillosas. Un segundo factor es la madurez térmica de la roca generadora o el esfuerzo térmico aplicado a un crudo. Niveles menores de madurez térmica dan crudos de menor calidad al tiempo de la generación, mientras que un mayor esfuerzo térmico al yacimiento puede incrementar la densidad API a través del craqueo térmico. Uno de los factores más importantes, y muy a menudo el más importante, en establecer la calidad del crudo es la magnitud de la alteración bacteriana. La magnitud de la biodegradación está controlada por las historias térmica y de llenado de un yacimiento, la naturaleza del contacto aceite-agua y la disponibilidad de micronutrientes (posiblemente como resultado de la diagénesis mineral). Los aceites biodegradados son generalmente pesados y pueden también mostrar altos valores de TAN y contenido de azufre. La mezcla de aceites también juega un papel en el establecimiento de la calidad final del crudo. La mezcla puede resultar en la mejora general de la calidad del aceite a través de la introducción de crudos inalterados y con frecuencia ligeros a un yacimiento de crudo biodegradado. La dismigración o remigración de crudo pueden también tener un impacto en la calidad a través de segregación de fases donde se forma un producto hijo o residual.

Palabras clave: Densidad API, biodegradación, segregación de fases, remigración, roca generadora, azufre, TAN, craqueo térmico, y madurez térmica.
INTRODUCTION

Hydrocarbon charge is one of the key risk elements considered during the exploration process. Among the components examined when assessing hydrocarbon charge risk are hydrocarbon availability (volume), phase (oil vs gas), and oil quality. Historically there has been strong interest in the pre-drill assessment of hydrocarbon volumes and phase but there has recently been a growing interest in the assessment of oil quality. This is partially a result of the increase in deepwater exploration, the more limited refining margins when poorer quality crudes are processed, and the ever changing character of the available resource. Over time there has been an increasing percentage of poorer quality crudes (high acid, high sulfur, and low API gravity) becoming available (Szklo et al., 2006). All of these factors suggest that a more complete pre-and post-drill assessment is needed to fully examine the economic value of an exploration opportunity.

As a result of production and development costs the oil quality component becomes increasingly importance in the offshore, and in particular deepwater. Fafet et al. (2008) suggested that in deepwater the quality of the oil is as important as the volume of oil. In part, this increased importance of hydrocarbon quality is a result of the dependence of flow rate on oil quality (viscosity). Wehunt et al. (2003) suggested that offshore development requires 5 to 10 times greater production rates and reserves than most onshore operations. Wehunt et al. (2003) also suggest that for deepwater wells production rates of 10,000 bbl/day or greater may be required. Achieving such flow rates is difficult when oil quality is low. In addition, logistical and economic considerations limit the transfer of enhanced oil recovery techniques employed onshore to recover heavier oils in the offshore and deepwater (Mehta et al., 2004) thus reducing ultimate recovery. These considerations may include, but are not limited to heat management, artificial lift and chemical injection. In fact, there are some heavy oil accumulations which have been by-passed as a result of production limitations resulting from poor oil quality.

COMPONENTS OF OIL QUALITY AND VALUE PROPOSITION

Oil quality is a reflection of a number of physical and chemical properties including API gravity, distillate yield, average molecular weight, viscosity, asphaltenes, metal, salt, and sulfur contents, as well as total acid number (TAN). Although a number of measures of quality are available the most commonly cited is API gravity. API gravity is a measure of specific gravity at a constant temperature of 60°F. In general, lower API gravity oils are considered poorer quality oils. Low API gravity fluids tend to be enriched in resins and asphaltenes and depleted in hydrocarbons. API gravity is often used as the general quality indicator. The utility of API gravity as a general indicator of oil quality can be seen in its relationships to other indicators such as sulfur content (Figure 1) and viscosity (Figure 2).

Figure 1.- Sulfur content as a function of API gravity for a suite of 693 oils from the Gulf of Mexico. Data made available by GeoMark Research, Inc.

Figure 2.- Viscosity as a function of API gravity for a suite of 256 oils from around the world. Data made available by GeoMark Research, Inc.
Oil quality and composition directly affect product value as well as development and facility costs, impacting the number of wells, the nature of the tubular goods, and the requirements for emulsion processing (Wenger et al., 2002). The value of crude oil tends to increase with increasing API gravity (Figure 3). Different prices at the wellhead are driven by the products that can be produced and their value at the marketplace. As a consequence of increasing demand for higher value refined products such as gasoline and low sulfur diesel the price differential between light and heavy crude oils has increased over time along with the rise in the price of crude oil (Figure 4). Although poorer quality crude oils remain less expensive they are harder (i.e., more costly) to refine and also tend to produce lower value products (Figure 5). In part, the increase in the cost of refining these poorer quality crudes is a result of the need for hydrogenation to maximize value. Typically poorer quality crudes tend to be blended prior to refining.

Heavy oil also introduces additional exploration and production challenges in the offshore. For example, as a result of the smaller density contrasts between heavy oil and water the use of direct hydrocarbon indicators and AVO is limited. On the production side of the equation, flow rate is controlled by reservoir and fluid properties as well as the energy level of the reservoir. As noted above, there is a general relationship between API gravity and viscosity (Figure 2). Lower API gravity crudes tend to display higher viscosity values and hence lower flow rates, thus negatively impacting their value particularly in deepwater. Although a general relationship exists, variations in viscosity at constant API gravity are observed and could be a reflection of gas content. The strongest compositional influence on subsurface fluid behavior is the gas-oil ratio (Di Primio et al., 1998).

Sulfur is another important quality component because it is carried forward through the normal refining
process (i.e., high sulfur crude oils yield a high sulfur diesel without any additional processing). With increasing environmental restrictions, the sulfur contents of refined products need to be reduced using additional processing methods including hydrotreating. The costs of the required additional processing are compensated for by reducing the wellhead value of sulfur-rich crude oils.

TAN is the industry standard for measuring acid content in crudes, with values greater than 0.5 mg KOH/g considered high. Organic acids may be derived from the source rock, biodegradation of oils, and/or biosynthesis by the microbes responsible for biodegradation (Watson et al., 2002). Elevated organic acid contents can also impact both production and refining. High TAN values are associated with a number of serious issues at the refinery (Turnbull et al., 1998). Naphthenic acid corrosion and catalyst poisoning can negatively impact a number of refining processes (including crude distillation, coking and waste water processing). Most refineries are limited to TAN values between 0.3 and 0.5 mg KOH/g. High TAN crudes are, therefore, often blended with low TAN oils for refining. It has recently been suggested that TAN may not be the best measure of corrosion risk (Barth et al., 2004) because most problems are associated with a specific group of naphthenic acids. It appears, therefore, that the distribution of acid species is more important than absolute acid abundance. In addition to the corrosion issues, high TAN oils result in lower cetane number diesels at the refinery. (Cetane number measures the ignition quality of a diesel fuel). These lower cetane values also limit the quantities of high TAN crude oils that a refinery can run.

In addition to the downstream issues production problems associated with organic acids seem to be becoming increasingly important. Organic acids can react with high pH brines to form calcium naphthenate, sodium emulsion soaps, or high calcium oils. The high calcium oils have lower wellhead values as a result of increased metal ion content. The sodium soaps form viscous emulsions that can plug the separator and water treatment equipment. The calcium naphthenates form hard scales that restrict production and can also decrease water discharge quality while sodium carboxylates stabilize emulsions. Recent work has suggested that there is a key sensitivity to tetrameric naphthenic acids or “ARN” acids and not simply total acid content. For example, the presence of “ARN” species is the key to the deposition of calcium naphthenates (Baugh et al., 2005; Shepherd et al., 2006).

Salt in crude oil are typically contained in small droplets dispersed in the crude from both natural and anthropogenic sources (Fortuny et al., 2008). The presence of salt in crude oil leads to several problems including corrosion of lines, fouling, and deactivation of catalysts. Controls on Oil Quality

Oil quality is controlled by several major factors including source rock character and lithology, thermal maturity of the source and stress of the reservoir, biodegradation, and filling history. Evans et al. (1971) suggest that post-accumulation processes are probably of greater importance than source rock attributes, with biodegradation probably being the dominant factor in most geographic settings (Katz et al., 2007). These major factors are discussed in detail below. Other alteration processes that may also impact oil quality include gas deasphalting, phase segregation, gravity segregation, and water washing.

Gas deasphalting increases API gravity through the precipitation (removal) of asphaltenes via the introduction of light hydrocarbons into an oil-bearing reservoir and may be one of the mechanisms for the formation of tar mats (Peters and Fowler, 2002).

Phase segregation occurs when a single-phase fluid is physically separated into a two phase system as pressure drops below the bubble point. This separation may take place through uplift, leakage, or the addition of dry gas. After the fluids are re-equilibrated to the new conditions the two phases follow different migration paths. Migration of the lighter phase away from the original pool (Silverman, 1965) results in a lighter daughter product and a heavier residual. This process preferentially removes lower molecular weight saturated hydrocarbons leaving a residual oil richer in aromatic and cyclic compounds. Compositional effects of phase segregation can vary, with the degree of fractionation being dependent on the relative volatility of the individual compounds. The nature of the daughter and residual oil are the products of a complex relationship among a number of parameters including pressure, temperature, and oil composition (including the relative amount of oil and gas; van Graas et al., 2000). In general, condensates and light oils formed through phase segregation appear more paraffinic than the residual oil (van Graas et al., 2000).

In reservoirs with high permeability and a large vertical oil column gravity segregation may occur. The bulk characteristics of a gravity segregated oil column may appear similar to a biodegraded oil column (i.e., heaviest and most viscous oils are found near the base of the oil column). Khavari-Khorasani et al. (1998) suggest a graded oil column is not a result of the diffusion of hydrocarbon components but rather continuous density overturn through bulk flow when the charge history displays a maturity range sufficient to cause a density contrast and when the reservoir volume is large relative to the charge available.

Water washing, the interaction of an oil column with a water leg, results in a decrease in API gravity.
This decrease in API gravity is a result of a decrease in gasoline-range hydrocarbons and aromatics leading to a relative enrichment in heavy components such as asphaltenes (Milner et al., 1977; and Kuo, 1994). The removal of these light hydrocarbons is largely proportional to their solubility in water, leading for example to a depletion of benzene and toluene (George et al., 2002). Laboratory simulations, supported by field observations, indicate that oils within limestone reservoirs are more effectively water washed than those in sandstone reservoirs. This is thought to be a result of differences in the relative permeability to water within their respective pore networks (Kuo, 1994).

Source Rock

Hunt (1961) showed that argillaceous source rocks tend to yield an original oil that is medium gravity and low in sulfur. Carbonate-derived oils tend to contain relatively lower amounts of gasoline-range hydrocarbons and proportionately lower amounts of hydrocarbons when compared to shaley source rock systems (Di Primio and Horsfield, 1996). These differences are thought to be at least, in part, a result of the lack of iron within carbonate (and siliceous) systems. Clays provide the iron that reacts rapidly to remove available H\textsubscript{2}S, effectively reducing the available sulfur. When iron (clay) is not available the sulfur is incorporated into the organic matter through a series of early diagenetic reactions (Peters and Moldowan, 1991). This enrichment in organic sulfur can result in the formation of a type II-S kerogen. In addition to the higher sulfur content in the generated oils, these high-sulfur kerogens generate at a lower level of thermal maturity as a result of their weaker carbon-sulfur bonds (Baskin and Peters, 1992). Espitalié et al. (1980) also suggested that the low surface activity of carbonate minerals limits the retention of heavy hydrocarbons reducing the probability of further cracking within the source resulting in heavier oils being available for pooling.

Tissot and Roucache (1980) and Jones (1984) also reported that carbonate-derived oils tended to be richer in cyclic hydrocarbons as a result of the lack of terrestrial plant waxes in their source. Higher land plant input into carbonate and siliceous source rock systems is limited. Hedberg (1968) observed that, in general, high wax crudes had a significant terrestrial component in their source. Gransch and Posthuma (1974) also proposed other source rock properties, including depositional setting, may explain low sulfur content. For example, source rocks formed in fresh to brackish water settings would have limited sulfur availability. Similarly within an oxic marine environment early sulfate reduction is limited.

An example of the influence of source rock character can be seen in the Gulf of Mexico, where the Upper Cretaceous, argillaceous, Eagleford Formation and the Oxfordian, calcareous Smackover Formation are among the region's source rocks (Comet et al., 1993; and Hood et al., 2002). The Eagleford Formation was deposited in an open marine system under dysoxic conditions. It contains organic-rich intervals with types II, II/III, and III kerogens (Wagner et al., 1994; and Hood et al., 2002). In contrast, the Smackover Formation was deposited within a restricted setting under anoxic conditions. The organic-rich micrites and marls contain type II and II-S kerogens (Wenger et al., 1990; and Hood et al., 2002). These two source rocks produced markedly different oils (Figure 6). Unaltered Eagleford-derived oils display API gravity values between 34 and 45º and contain less than 0.5% sulfur. Unaltered Smackover-derived oils display API gravity values between 20 and 30º and contain between 1 and 3% sulfur. Although the API gravity decreased and sulfur content increased with biodegradation, these initial differences in oil quality carry forward throughout the biodegradation process (Figure 6).

![Figure 6.- A comparison of the biodegradation trends for Eagleford Formation (•) and Smackover Formation (■) derived oils. The Eagleford Fm. represents an argillaceous source rock system in the Gulf of Mexico with the Smackover Fm. represents a calcareous system (from Katz and Robison, 2006. AAPG © 2006 reprinted by permission of the AAPG whose permission is required for further use).](image-url)

Even within individual source rock systems multiple organic facies may be present and influence oil character. This can be observed in oils derived from the Cobán
Formation in Guatemala. The organic-rich carbonate intervals of the Cobán Formation were deposited during transgressive drowning events of a massive carbonate-evaporite platform (Fourçade et al., 1999). The suite of nondegraded oils display API gravity values between 7.0 and 31.0° and contain between 0.2 and 4.8% sulfur. The ultra-heavy and sulfur-rich crude oils are associated with the more highly restricted basinal facies of the source rock.

Thermal Maturity and Thermal Stress

During hydrocarbon generation, expelled and trapped hydrocarbons show a progressive evolution at both the bulk and molecular level (Figure 7; Landes, 1967; Monthioux et al., 1985; England et al., 1987; England and Mackenzie, 1989; Pepper and Dodd, 1995; Baskin and Peters, 1992; and Di Primio et al., 1998). Among the changes that are observed with increasing thermal maturity are a decrease in sulfur content (Gransch and Posthumus, 1974), an increase in saturated hydrocarbons, and an increase in API gravity. With the extent of hydrocarbon generation being a function of time and temperature it becomes evident that in the deepwater, lower temperatures at the mudline relative to those on the shelf and at the surface onshore can reduce the rate and extent of generation significantly under the same amount of overburden and with the same geothermal gradient (i.e., the exposure temperature through time is lower). As a result less mature and poorer quality oils could be anticipated in deepwater systems even from the same source at comparable burial depths.

Oil cracking occurs when thermal stress is applied to an accumulation. It is a dynamic process, with numerous simultaneous reactions (Hill et al., 2003). Oil cracking involves the redistribution of hydrogen from the precursor oil to more stable gas and pyrobitumen. High molecular weight hydrocarbons, resins, and asphaltenes are transformed into low molecular weight compounds, resulting in higher API gravity oils (Figure 8). Increasing thermal alteration results in an increase in saturates, a slight decrease in low-ring number aromatics, a marked decrease in high-ring number aromatics and resins, as well as a decrease in asphaltenes (Milner et al., 1977). Essentially there is a progressive shift toward lower molecular weight compounds and the concentration of thermally stable compounds, including diamondoids and polyaromatic hydrocarbons. The presence of thermally stable high molecular weight polyaromatic hydrocarbons, diamondoids, and pyrobitumen provides evidence for thermal alteration. Aromatic oils yield more pyrobitumen than paraffinic oils (Hill et al., 2003). Nonhydrocarbon gas yields also increases with the degree of oil cracking. Pyrobitumens and diamondoids may result in production problems (e.g., flow assurance).

Figure 8.- Changes in API gravity as a result of thermal stress on a suite of Smackover-derived oils from Louisiana and Arkansas.

Although there has been considerable debate on the thermal stability of oil it appears, based on the available literature, that oil cracking begins between 150 and 200°C (Hill et al., 2003) or a vitrinite reflectance equivalent of about 1.1% (Wei et al., 2007b). Faster heating
rates require higher temperatures for cracking (Wang et al., 2006). There is also evidence to support catalytic cracking of oil by clay minerals (including montmorillonite and illite; Wei et al., 2007b) and/or transition metals (Wang et al., 2006).

Cracking rates appear dependent on the saturation to aromatic ratio (Pepper and Dodd, 1995), as well as the molecular distribution of the original oil (Huang and Otten, 2001). Higher saturation to aromatic ratios are associated with higher cracking temperatures, over a narrower range compared with aromatic oils. Short chain n-alkanes display greater thermal stability than long chain n-alkanes, with branched and cyclic alkanes being less stable than n-alkanes. There is considerable overlap in the cracking range of the different fractions and the abundance of each fraction is controlled by their relative rates of formation and destruction (Hill et al., 2003; and Wang et al., 2006). Cracking rates were also found to be enhanced up to 600-700 bars, above which they appear to be suppressed (Hill et al., 1996).

Thermochemical sulfate reduction (TSR) is another high temperature crude oil alteration process where abiotic oxidation of pooled hydrocarbons occurs through the reduction of sulfate, typically derived from gypsum or anhydrite. H₂S is the most abundant product and can result in concentrations of the gas significantly greater than that which can be produced through simple oil cracking alone. TSR results in an increase in thiophenic and sulfidic hydrocarbons (Zhang et al., 2008). These aromatic sulfur compounds form as a byproduct of H₂S generation. TSR lowers the saturate/aromatic ratio while diamondoid concentrations increase (Dahl et al., 1999).

TSR is thought to begin at reservoir temperatures exceeding 125ºC, although Machel (2001) suggests that the onset temperature for TSR may be as low as 100ºC. The onset temperatures for TSR are lower than those associated with thermal cracking. As with cracking, initiation appears to be dependent on oil composition (Peters and Fowler, 2002). Branched and normal alkanes in the gasoline range fraction are most susceptible to TSR, followed by cyclic alkanes and monoaromatic species. Bildstein et al. (2001) suggested that the rate controlling step for TSR is diffusion. Consequently, TSR is favored near the oil-water contact or within the transition zone.

Biodegradation

It has been suggested that the majority of the global petroleum resource base has been biodegraded to one degree or another (Head et al., 2003). The effects of biodegradation are empirically well established although the actual processes remain obscure (Larter and Di Primio, 2005). Biodegraded crude oils are generally depleted in saturated hydrocarbons, enriched in aromatic hydrocarbons and in nonhydrocarbons (resins and asphaltenes). Furthermore, the saturated hydrocarbon fraction becomes dominated by naphthenes at the expense of normal and branched alkanes (Figure 9). There are, however, examples where aromatic hydrocarbons are preferentially removed relative to saturated hydrocarbons. Although the reason for this is unclear it may be a result of nutrient deficiency (Taylor et al., 2001) or bacterial preference. The impact of the biodegradation induced changes in composition is a reduction in API gravity, while increasing TAN and sulfur content.

Figure 9.- A comparison of the bulk composition of unaltered and a heavily biodegraded oils from the Campos basin, offshore Brazil.

The explanation for the observed changes results from petroleum biodegrading organisms having a specific order of preference for compounds that they remove from oils. Anaerobic n-alkane degraders exhibit pronounced substrate specificity with respect to chain length (Skaare et al., 2007). In general, the simpler the molecular structure and lower the molecular weight the more likely it is to be biodegraded. Although lower molecular weight compounds are preferentially removed high molecular weight, long-chain waxes may also be consumed during biodegradation (Figure 10). Within the naphthene fraction there is preferential preservation of higher molecular weight compounds as well (Volkman et al., 1984), with susceptibility to biodegradation decreasing with increasing ring number (Wei et al., 2007a). Volkman et al. (1984) suggested the following biodegradation order for aromatic hydrocarbons – benzene > toluene > naphthalene > phenanthrene > polycyclic aromatic hydrocarbons. The observed molecular weight range impacted
Biodegradation suggests that a consortium of bacteria is probably responsible for the biodegradation process rather than a single bacterium.

In addition to the removal of compounds there are additions and molecular transformations associated with biodegradation. For example, Watson et al. (2002) observed that after extensive biodegradation there was the addition of higher molecular weight (>C20) branched and cyclic carboxylic acids, including the “ARN” acids. Barth et al. (2004) reported that the elevated acid levels are due to microbial production of organic acids rather than their concentration resulting from the removal of other components. This conclusion was drawn as a result of changes in organic acid molecular weight distributions while examining a biodegradation series. Carboxylic acids formed, in part, during biodegradation may be the major contributor to an oil’s TAN value (Wolcott et al., 1989; and Meredith et al., 2000). The 25-norhopanes also form through molecular transformation rather than increase through their concentration during biodegradation (Huang et al., 2004).

It is important to note, however, that there are examples of high TAN oils that do not exhibit signs of biodegradation and there does not appear to be a direct correlation between organic acid concentration and degree of biodegradation (Watson et al., 2002). Meredith et al. (2000) suggested that the absence of the correlation may be organic facies related. They suggested that environments leading to high sulfur oils can often also produce high TAN crudes.

Different petroleum systems may host different microbial communities, exhibiting different degradative capability (Peters and Moldowan, 1991; and Elias et al., 2007) and different orders of hydrocarbon removal (Jones et al., 2008). It has been suggested that both anaerobic and aerobic biodegradation occur within petroleum reservoirs. It had been largely assumed that the bulk of biodegradation involved aerobic bacteria (Milner et al., 1977) and could occur on a human timescale. Aerobic biodegradation requires significant volumes of meteoric water movement (Horstad et al., 1992), often which cannot be explained. Consequently, there has been an increasing acceptance that although significantly slower, acting on a geologic timescale, anaerobic bacterial processes may be responsible for biodegradation (Aitken et al., 2004). For example, Jones et al. (2008) suggest that the strictly anaerobic process of methanogenesis is an active part of biodegradation. The role of anaerobic bacteria is also supported by the presence of their metabolites, including reduced naphthoic acids, in formation waters associated with biodegraded crude oils (Skaare et al., 2007). These metabolites are not thought to survive long after their formation and are, therefore, believed to indicate active biodegradation. This is similar to Mackenzie et al. (1981) suggestion that high TAN values imply that biodegradation is recent or ongoing.

Biodegradation requires that water, nutrients, and hydrocarbons are available, with microbial activity occurring largely at the oil-water contact (Head et al., 2003). Nutrient (or electron acceptor) availability appears to be a major limiting factor (Huang et al., 2004). Key nutrients are probably supplied by mineral dissolution and diffusion leading to graded oil columns (Larter et al., 2003 and Huang et al., 2004). The availability of nutrients is partially controlled by aquifer volume and reservoir topography, which controls the ratio between the oil-water contact and water leg volume and, therefore, the accessi-
bility to nutrients. These conditions are not static. The oil-water contact is not stationary through time but migrates downward as the reservoir is filled (Khavari-Khorsani et al., 1998) changing the ratios through time. The timescale of oilfield degradation and filling appear similar (Larter, 2003). Wenger et al. (2002) suggested that irreducible (bound) water may also provide the necessary water for bacterial activity extending biodegradation into the oil leg. Biodegradation is limited to reservoirs with temperatures less than 65 to 80ºC. Wilhelms et al. (2001) further suggested that biodegradation can be precluded in reservoirs that are currently cooler as a result of prior uplift, if the reservoir was previously exposed to more elevated temperatures (>80ºC) and was essentially sterilized. Water washing rather than microbial activity may be important in the alteration of petroleum in these uplifted situations (Huang et al., 2004). Other shallow reservoirs, independent of temperature history, may contain unaltered oils as a result of insufficient residence time (Yu et al., 2002) or the absence of a water leg (Larter et al., 2003). The extent and associated risk of biodegradation is a function of temperature history and residence time (Yu et al., 2002). Head et al. (2003) suggest that between 1 and 2 m.y. may be required to lightly degrade a 100 meter oil column, with the removal of n-alkanes requiring between 5 and 15 m.y.

In deepwater settings the lower temperatures present at the mud-line compared with shallow water and onshore exploratory environments may deepen and broaden the “biodegradation-window” (Figure 11).

Wenger et al. (2002) suggested that highly saline formation waters may inhibit bacterial degradation as may high H₂S levels (> 5%; Peters and Fowler, 2002). Metabolites associated with biodegradation may naturally inhibit further biodegradation if not swept from the system (Watson et al., 2002).

Volkman et al. (1984) and Peters and Moldowan (1993) presented scales for ranking the degree of biodegradation based on the relative abundance of the different hydrocarbon classes. However, individual compounds are degraded simultaneously at different rates at various biodegradation levels (Elias et al., 2007). As a result alteration patterns do not appear ubiquitous when large datasets are examined (Bennett and Larter, 2008). Different alteration levels can be observed over a very limited depth range within an individual field (Bennett and Larter, 2008). Elias et al. (2007) suggested that there is probably a need to calibrate alteration scales individually, while Bennett and Larter (2008) noted these scales are complicated by the mixing of oils within the reservoir. It has also been suggested that the published biodegradation scales appear to be insufficient because of their focus on the more severe levels of biodegradation, while the greatest impact on oil quality occurs at much lower levels (Wenger et al., 2002; and Elias et al., 2007). Elias et al. (2007) reported that the loss of as much as 85% of some compounds may occur in an apparently “nonbiodegraded” oil using conventional biodegradation index scales.

Biodegradation consumes a significant proportion of the original oil introduced into a reservoir. A comparison of bulk and molecular differences in oil chemistry from places such as Central Sumatra and offshore Brazil suggest that this reduction may exceed 40% (Katz and Robison, 2006). As a consequence of these reductions, Larter and Di Primio (2005) note that biodegradation plays an important part in establishing the magnitude of the oil leg and dry gas cap.

High wax crudes, like those of SE Asia, when attacked at slight to moderate levels, while displaying a reduction in API gravity, often display lower pour points and lesser wax contents and improved production characteristics (Colling and Robison, 1991; and Wenger et al., 2002).

Filling and Mixing Histories

The charge history and the rate of mixing of fresh oil into the system are likely the dominant controls on the apparent level of degradation within the reservoir (Yu et al., 2002; and Huang et al., 2004). Barnard and Bastow (1991) and Koopmans et al. (2002) concluded that large variations in oil properties including viscosity can be explained through a simple mixing model. Filling
Multiple hydrocarbon charging events are often suggested by internal inconsistencies within an oil’s chemistry (Requejo et al., 1994). Examples of such inconsistencies exist when:

- Higher molecular weight n-alkanes are absent, a significant naphthenic envelope is present as are a full-range of gasoline and mid-range hydrocarbons (Horstad and Larter, 1997).
- A full suite of both n-alkanes and 25-norhopanes.
- There are elevated abundances of both diamondoids and biomarkers (Dahl et al., 1999); or
- Thermal maturity estimates based on the different hydrocarbon fractions differ.

These geochemical inconsistencies may indicate an initial oil charging event, followed by biodegradation, followed in turn by the injection of and mixing with non-biodegraded hydrocarbons; an initial charging of thermally unaltered or less mature oil, which may or may not be biodegraded, followed by the injection of and mixing with a thermally more mature or thermally stressed (cracked) oil; or an initial charging event, which may or may not be biodegraded, followed by the injection and mixing with a daughter product of phase segregation. Each oil injection episode may represent derivation for a common source or different sources depending on the generation and migration histories. Under certain circumstances such oils can give the impression of variable degrees of biodegradation. Wilhelms and Larter (2004) observed that for most oil accumulations there is a significant mismatch between biomarker and light hydrocarbon maturity indices, the latter being representative of the bulk of the oil. These differences lead them to conclude that all oils are mixtures.

Often the filling history of a reservoir or field is associated with tertiary migration, remigration or dysmigration. Remigration is typically controlled by fault trends and patterns as well as the position of spillpoints (Horstad and Larter, 1997), although basin tilting may play a role (Feiyu et al., 2000). The importance of faults as conduits for hydrocarbon movement is often supported by seismic amplitude anomalies (i.e., “bright spots” associated with the fault zones; Anderson, 1993).

Whelan et al. (1994) described one process of fault-related fluid remigration termed “dynamic fluid injection”, where the introduction of “new” hydrocarbons is episodic as a result of pressure build-up followed by the rapid release of oil and gas from a geopressed interval. Such a process can occur over a very short time period, on the order of years.

SUMMARY AND CONCLUSIONS

Hydrocarbon quality has increasingly become an important component of risk assessment during exploration and may under some circumstance be as important as the volume of hydrocarbons available. This increasing emphasis results from the shift of exploration to deepwater settings, reduced refinery margins, and the overall change in the nature of the remaining global resource-base. Poorer quality crudes may be more difficult to explore for, often have increased development costs and production problems, yield lower wellhead prices, are more difficult to refine, and produce lesser amounts of high value products.

Oil quality reflects a number of physical and chemical characteristics of a crude oil, including API gravity, viscosity, bulk and molecular composition, metal and sul-
fur content, and TAN value. The observed changes may reflect removal and hence concentration of components, the formation of new compounds through both bacterial processes as well as through a number of chemical processes.

Oil quality is controlled by a number of factors including source rock character and lithology, thermal maturity and stress, biodegradation, and filling history. In addition gas deasphalting, phase and gravity segregation as well as water washing may impact oil quality. Post-accumulation factors are probably key in establishing oil quality.

Calcareous and siliceous source rocks lacking significant clay contents generally produce poorer quality crude (i.e., higher sulfur and lower API gravity) than their argillaceous counterparts. This appears to be a result of the greater availability of organic sulfur in these clay-poor source rocks and the earlier generation of crude oil from them.

Increasing thermal maturity and stress increases both API gravity and oil quality. More mature products tend to have lower sulfur contents and higher API gravity. Cracking also lightens the crude oil, while forming a pyrobitumen. Although there is considerable debate on the thermal stability of crude oil, it appears that cracking begins at temperatures between 150 and 200°C and is dependent of the composition of the original oil.

Thermochemical sulfate reduction is another high temperature alteration process. This process oxidizes pooled hydrocarbons increasing their thiophenic and sulfidic hydrocarbon content. TSIR is initiated at lower temperatures than thermal stability of crude oil and is dependent on the composition of the original oil.

Biodegradation is probably the most important factor impacting crude oil quality. It reduces hydrocarbon content and increases non-hydrocarbons, while increasing organic acid content. More than 40% of the original oil in-place may have been removed through biodegradation. Both aerobic and anaerobic processes may be involved. Biodegradation is probably the result of a consortium of bacteria. The extent or degree of biodegradation may be limited by filling history, the thermal history of the reservoir, the nature of the oil-water content, extent of the water leg, and the salinity of the formation waters.

The charge history and the introduction and mixing of fresh oil in a reservoir may mitigate the quality issues caused by biodegradation. There are a number of ways to identify mixed oils, typically relying on internal inconsistencies in there geochemical characteristics. The mixing of oils may differ among fault blocks within a single field, occur very rapidly and may be very common.

References


Recibido: 25 de diciembre de 2009.

Aceptado: 08 de febrero de 2010.