

Theoretical study of light hydrocarbon analysis technique in the evaluation of oil and gas water

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Abstract: - Light hydrocarbon analysis technique, the distribution and volume fraction of the light hydrocarbon components are determined from the macro level, and the properties of the reservoir are determined by the molecular level until the functional groups. This paper mainly describes the basic theory of the light hydrocarbon logging technology and the accurate identification of chromatographic peaks and the principle of the evaluation of oil, gas and water. The molecular sieve effect of rock and its correlation with the porosity and permeability are discussed. The molecular sieve effect is the basis of accurate evaluation of oil and gas reservoir. The advantage of light hydrocarbon logging technology is mainly reflected in the information that can be obtained from two aspects of drilling fluid and cuttings, which has the characteristics of strong anti pollution ability, simple sampling and analysis parameters, and the defects can not be distinguished.

Keywords: - light hydrocarbon logging, basic theory, molecular sieve, the advantages of molecular sieve, Oil reservoir evaluation, parameters, spectrum, evaluation method

I. INTRODUCTION

The light hydrocarbon logging technology is the latest mud logging technology. It is a simple and fast analytical technique combined with the pretreatment of the sample, and the light hydrocarbon analysis can get the concentration and relative percent content of each unit of C₉. The detector finally get light hydrocarbon chromatogram will in the process of drilling back to ground cutting or drilling fluid bottling sealing sample through the changes in the pressure and temperature of the gas desorption and evaporation, bottle easy volatile components gradually and headspace gas a gas - liquid equilibrium state, the gas-liquid equilibrium samples injected instrument, after different temperature changes will all compounds separated makes each component is fixed phase retention time different, which according to the certain order by fixed phase out. According to the physical and chemical properties of these compounds, the oil and gas layer and water flooded layer can be quickly and accurately evaluated.

II. CURRENT STATUS AND PROGRESS OF LIGHT HYDROCARBON ANALYSIS TECHNOLOGY

Light hydrocarbon analysis technology in foreign countries in 1970, has been widely used by Western oil companies, and successfully used in single well oil and gas, hydrocarbon source rock evaluation. 1983, Jiangnan Petroleum Institute analysis and testing research center and the South China Sea oil company research institute cooperation, the first time in the domestic establishment of light hydrocarbon analysis method; 1985 the former oil industry will light hydrocarbon analysis into the new technology of oil and gas exploration.

The study of light hydrocarbon analysis of 2258 different types of crude oil in the world (major North America) by Mango was studied by [1-2] in 1987. During the year 2000, Nanyang Oilfield, Liu Huan is 1998 and Li Yuhuan etc. successively put forward application of rock pyrolysis analysis to establish the porosity and remaining oil saturation chart for evaluating water flooded layer method. Li Yuhuan in 2000 also tried to use the physical simulation of water flooding oil to study the change of the water flooding process in the Central Plains and the application of fluorescence image analysis technique in the evaluation of water flooded layer [3]. 2002 in Dagang Oilfield Zhao Xiaoli, tried to use the chemical analysis to establish the porosity and total pyrolysis hydrocarbon content of chart for evaluating water flooded layer method, and test [4] in the Zaoyuan region. A comprehensive evaluation method of water flooded layer is analyzed by means of geochemical analysis and P-K (small nuclear magnetic resonance analyzer), Chen Shaochun, Jilin oilfield, Zhongyuan Oilfield, Zhongyuan oil field in 2003. Jiang Qigui, Zhang Zhirong, et al., and the application of light hydrocarbon fingerprint analysis in the Wuxi Institute of petroleum exploration and development. , Xia Liang., and Li Yuhuan, the exploration and development of light hydrocarbon analysis technology in the exploration and Development Research Institute of Henan Oilfield Company in 2005. JiaShiliang [5] of Yangtze University and Li Shengli of the China Petroleum Exploration Bureau in 2007 to further explore the research and application of light hydrocarbon analysis

technology in oil and gas exploration. Liu Liping of the Daqing oil field geological logging company in 2005 further explored the fluorescence microscopic image points[6].

The light hydrocarbon analysis technique used in oil and water layer identification and evaluation of water flooded layer is the domestic emerging technology in recent years, there is no mature method of application.

III. THE THEORY BASIS OF LIGHTER HYDROCARBON SAMPLING METHOD

Logging light hydrocarbon analysis technique 1 analysis from C to C, 9 were alkanes, isomerization alkane, cyclanes and aromatics four class component chromatographic peak of 103, contains abundant geological information. Light hydrocarbon analysis using the top gas sampling, oil and gas sample seal in the container, the light component of oil and gas to evaporate into the air with the top of the container, the formation of the multicomponent mixed gas, because of its physical properties of components and relative contents of different, in the mixed gas with certain pressure and temperature of saturated vapor pressure. At the top of the gas sampling method using the basic principle is the partial pressure of Dalton's law and Raoult's law. Sealed in a container of oil and gas with gas and liquid, it would inevitable gas-liquid balance and gas in a gas-liquid balance accordingly in line with the partial pressure of Dalton's law, the liquid phase should comply with Raoult's law. According to Dalton's law of partial pressures, p_1, p_2, \dots, p_n for light hydrocarbon partial pressure of each composition, X_1, X_2, \dots, X_n for each component in the mole fraction in the mixed gases, p as the total pressure, are:

$$\begin{aligned} p_1 &= X_1 p \\ p_2 &= X_2 p \\ &\dots \\ p_n &= X_n p \quad (n = 1, 2, \dots, n) \quad (1) \end{aligned}$$

The physical meaning of the formula (1) is that the partial pressure of each component of the mixture is equal to the product of the mole fraction of the mixture and the total pressure of the mixture. Any liquid at a specified temperature has a certain saturated vapor pressure, which is determined by the nature and temperature of the liquid, regardless of the volume of the container. Due to the C₁ - C₉ light hydrocarbon is composed of normal paraffin paraffin, isoparaffin, naphthenic hydrocarbon, aromatic more than 100 kinds of compounds mixture can also be regarded as a mixed solution of liquid. The components are mutually as solvent and co solutes, p_0z said a single group of saturated vapor pressure, P_z said with the temperature when the vapor pressure of the solvent in the solution, x_z said the group in solution of mole fraction and available mathematical expressed as:

$$p_z = p_0z X_z \quad (2)$$

This expression is called Raoult's law, and Raoult's law is an important rule in the experiment. The law pointed out that under certain temperature gas-liquid phase balance, gas above the solution phase with arbitrary group branch pressure equal to the component at the same temperature of saturated vapor pressure is multiplied by the group divided into mole fraction in the liquid phase. Thus when the temperature is fixed, the saturated vapor pressure value of the fixed, of the composition in the gas phase and partial pressure of the components in the mole fraction in the liquid phase is proportional to; when the mole fraction of fixed, of the composition in the gas phase and partial pressure of saturated vapor pressure is directly proportional to temperature. This law can also be expressed as: the vapor pressure of a substance in solution is related to the mole fraction in the unit volume solution, but not to the type of matter. According to Dalton's law of partial pressure and Raoult's law, the saturated vapor pressure of hydrocarbon in the light hydrocarbon is independent of the volume of the container and the monomer hydrocarbon. Therefore, it is not necessary to consider the difference between the volume and light hydrocarbon.

IV. EFFECT OF LIGHT HYDROCARBON SAMPLING CONDITIONS ON THE ANALYSIS RESULTS

According to the above theoretical analysis, the results of the analysis of the light hydrocarbons are to be obtained and the results are reproducible and geological, which require the sample to be sealed in a stable closed system. Now the sampling method of debris not by washing, drilling fluids and cuttings a bottling and saturated brine seal (with saturated brine, the main purpose is sterilization and reduce the light hydrocarbon in water solubility). The analysis is heated to a certain temperature, and then a light hydrocarbon chromatographic analysis of the top gas is carried out under the unified instrument analysis. The sampling method is less affected by the factors, which can ensure the repeatability and the representative of the light hydrocarbon analysis result, and satisfy the requirement of the rapid analysis and evaluation.

The premise of ensuring the authenticity of the light hydrocarbon analysis is the representation of the sample. As long as the debris is not distorted, light hydrocarbon analysis and do not need to pick the sample, the

representative of the general will not appear problems. But if the difference is too big, it will affect the light hydrocarbon analysis results, and there is no geological reality.

As is known to all, there are 3 kinds of phase state, liquid phase, gas phase and solid phase and liquid phase in the system. The solid phase is mainly composed of the debris of the drilling fluid and salt water. The liquid phase is only a little part of the liquid phase, the main component of the liquid phase is water vapor. Solid relatively light hydrocarbon analysis results of the impact problem remains to be discussed below, now only analysis in both the liquid and gas effect of phase composition of light hydrocarbon analysis results.

Liquid phase was mainly composed of water, oil and gas in the liquid phase rarely, the mole fraction of smaller, sample containers empty part in sealing is air, sealed, air and water occupy the empty part of the vast majority of volume. According to Raoult's law, the gas above the solution phase with arbitrary group branch pressure equal to the component at the same temperature of saturated vapor pressure is multiplied by the group divided into mole fraction in the liquid phase, self-evident, light hydrocarbon in the gas phase pressure is very small. Since the partial pressure of light hydrocarbon in the gas phase is a minimum, the quality of each sample is not very different, and it has no effect on the interpretation of the hydrocarbon bearing formation. If the quality difference between the sample and the sample is too large, it will directly affect the results of the light hydrocarbon analysis. In the same time, the quality of the sample is proportional to the light hydrocarbon content. So, to ensure the authenticity of the light hydrocarbon analysis, we must do the same as the sample size of each sample.

V. MOLECULAR SIEVE EFFECT OF ROCK IS THE BASIS OF EVALUATION

5.1 Molecular sieve effect of rock

Oil and gas in the rock storage state and light hydrocarbon desorption equilibrium is a very complex physical processes, but the light hydrocarbon logging technology basic theory research and have to deal with, so only put aside all the intermediate process, directly with the results and elimination method to infer the physical phenomena. This is the only way to take the research approach, despite the uncertainties.

Debris contained in the oil and gas from the bottom of the well to the ground loss is inevitable, in the process of drilling in the rock hydrocarbon loss can be divided into three stages: broken bits, drilling fluid scouring, part of the hydrocarbon invasion drilling fluid; oil gas debris with returning to the drilling fluid, the pressure is reduced, gas diffusion, part of hydrocarbon invasion drilling fluid; oil gas debris to reach the ground in the open system, gaseous hydrocarbons in the cuttings eventually almost entirely lost into the air, liquid hydrocarbon part residue in cuttings.

So, the gas hydrocarbon in cuttings is much more or less in cutting fluid, but only from the angle of pressure drop. But the experimental analysis shows that the gaseous hydrocarbon in cuttings is much higher than that of the drilling fluid. The total mass of natural gas in drilling fluid sample analysis is several times lower than that of natural gas. This phenomenon can not be explained by the theory of non connected porosity, adsorption and dissolution. Especially natural gas, in drilling with PDC bit under, debris was single sand granular, natural gas how saves a considerable amount of in cuttings without completely lost; there must be a deeper reason.

It has been found that the adsorption of hydrocarbon is not easy desorption phenomenon. It is only one of the one-sided view that the adsorption of the micro hole is not the only one. In the eighties of the 20th century to establish the acidolysis hydrocarbon analysis method is dissolved with hydrochloric acid damage the crystal structure of the rock cavity or cage, the adsorption hydrocarbon released, the acid solution of the actual role may is the elimination of rock of the molecular sieve effect. Because of the role of rock, the light hydrocarbons in the rocks are not lost, which is the theoretical basis for the evaluation of the hydrocarbon bearing formation in the light hydrocarbon content of cuttings.

5.2 The molecular sieve effect of rock and the condition of hole infiltration

In the case of oil gas source, the condition of hole infiltration is the premise to determine the size of molecular sieve effect, therefore, the size of the molecular sieve effect can also be inferred from the reservoir porosity and permeability conditions. Under the same light hydrocarbon sampling and analysis conditions, the total mass of the light hydrocarbon is related to the molecular sieve effect of the rock, and the reservoir porosity and permeability. So the light hydrocarbon logging technique is very accurate to evaluate oil and gas reservoir and to estimate the reservoir capacity. So the molecular sieve effect of the rock is the basis of the accurate evaluation of oil and gas reservoir.

According to the above principle, we can make further inferences: in the condition of reservoir hole infiltration, the reservoir sandstone is better, the higher the surface area is, the higher the reservoir pressure is, the higher the molecular sieve effect is. The reservoir pressure is proportional to the molecular sieve effect. Under high pressure, it may cause the multilayer adsorption of light hydrocarbon molecules.

Oil and gas can not enter the inner of the rock crystal, which is basically in the surface of the rock crystal. Otherwise, the oil and gas will penetrate the oil and gas reservoir, it is impossible to have the current oil and gas reservoirs. The practice of light hydrocarbon logging proved that the above inference is correct.

It is needed to explain that the light hydrocarbons in the top of the gas may be mainly derived from the desorption of hydrocarbons from the molecular sieve, and other hydrocarbons derived from the pores and the surface of the rock. The methods of hydrocarbon removal from molecular sieves are 3: one is to destroy the crystal structure; the two is to heat up the hydrocarbon desorption temperature; the three is the pressure reducing and desorption. Under the present conditions of light hydrocarbon sampling analysis, there is no damage to the crystal structure, the sample heating temperature can not reach the conditions of the total desorption of hydrocarbons, only the main pressure and desorption process is the main hydrocarbon desorption process. Therefore, there is no desorption of hydrocarbons in the molecular sieve, as long as the amount of adsorption and desorption is proportional to the ratio of the amount of hydrocarbon.

VI. EVALUATION OF OIL, GAS, AND WATER PRINCIPLE OF LIGHT HYDROCARBON ANALYSIS PARAMETERS

It is well known that the content and distribution of light hydrocarbon in crude oil not only depend on the origin type of crude oil, but also depend on the degree of thermal evolution and the intensity of secondary evolution. In the same block, the same layer of crude oil can be considered to be the same as the thermal evolution and the extent of the secondary evolution[1]. The difference of light hydrocarbon parameters and reservoir properties of different samples.

The light hydrocarbons in crude oil by normal paraffin paraffin, isoparaffin, naphthenic hydrocarbon, aromatic is composed of four parts, and is an important component of the crude oil. In particular, the C 6 ~ C 9 range of the monomer hydrocarbons, the relative percent content of crude oil can reach the highest value. Using the basic physical and chemical properties of the light hydrocarbon component, the change law of the light hydrocarbon parameters in different environments or different reservoir properties is studied.

The absolute content of light hydrocarbon, light hydrocarbon components volume fraction. It is affected by the oil sands oil abundance and crude oil properties, temperature and light hydrocarbon loss degree of influence. The relative percent content of light hydrocarbons, which is only affected by the composition of crude oil. The physical significance of the relative percentage contents of the light hydrocarbon parameters is characterized by the percent content of the monomer or the homologues in the crude oil, and the changes in the properties of the crude oil, and the physical significance of the absolute content of the light hydrocarbon parameters[2].

Light hydrocarbon of six single ring aromatic hydrocarbons due to the presence of conjugated bonds, stable chemical properties and with weak polarity, according to the principle of similar compatibility, aromatics with the highest solubility in water. In the oil layer, the relative percent content of aromatic hydrocarbon is basically stable at a certain value.

Cycloalkanes often accounted for most of the petroleum hydrocarbon, light hydrocarbon, naphthenic hydrocarbon content is generally higher than that of n-alkanes, C 9 before can detection and characterization of 34, consisting mainly of cyclopentane, cyclohexane and with different substituents positive and negative of cyclopentane and cyclohexane. The chemical properties of naphthenic hydrocarbon stability, low solubility, less affected by the secondary evolution. So we cycloalkanes stable chemical properties, in evaluating storage reservoir properties, cycloalkanes as denominator, to highlight the different storage reservoir properties caused by the change of other parameters of light hydrocarbon.

The positive carbon number of the light hydrocarbon is 9 can be characterized with 9 normal alkanes and more than 50 isomers. Alkane solubility in water below aromatics, higher than that of cycloalkanes, with the same carbon number of alkanes and compared with the normal alkanes, heterogeneous than normal alkane solubility to a little higher, the chemical stability to some low. Alkanes in the poor chemical stability with quaternary carbon atoms of the alkane, the carbon atoms connected with three methyl groups, multi branched, low boiling point, the polar centers do not overlap, in term of oil-water coexistence state. This parameter and naphthenic hydrocarbons ratio will significantly reduce.

VII. EVALUATION OF LIGHT HYDROCARBON PARAMETERS IN RESERVOIR

The distribution and content of light hydrocarbon components were determined by light hydrocarbon analysis technique, and the properties of the reservoir were determined from the molecular level until the functional groups. However, in many of the light hydrocarbon parameters, how to choose the most representative, sensitivity, specificity of the reservoir evaluation parameters and parameters of the correct or not, is the key to determine the application of light hydrocarbon analysis[3].

The reservoir properties are generally divided into gas reservoir, reservoir, oil and water layer, water layer and dry layer. The parameters of reservoir evaluation should be considered in three aspects: one is the content of light hydrocarbon and the distribution of light hydrocarbon, two is the chemical stability; the three is the solubility of light hydrocarbon in water.

7.1 Selection of light hydrocarbon parameters in reservoir

In the same analysis and sampling conditions, the light hydrocarbon content in the same area is far greater than that of the oil and water and other properties of the reservoir.

In the same area, the secondary evolution of oil layer in the same area is smaller than that of oil and water, so the number of light hydrocarbon is more than 85.

The light hydrocarbons in the reservoir did not have the dissolution of water, and the content of aromatics was high[4]. Poor chemical stability, the relative ratio of the light hydrocarbon component with quaternary carbon is higher and can be detected, which is the important index of the oil layer.

Figure 2, figure 3, figure three is the same area oil layer, oil-water layer, the water layer of the 1 light hydrocarbon chromatogram, the total variation trend is a significant difference. Also different storage set layer properties of alkanes, aromatics and naphthenes ratio changes are more obvious, relative ratio is distinguishing oil of main parameters.

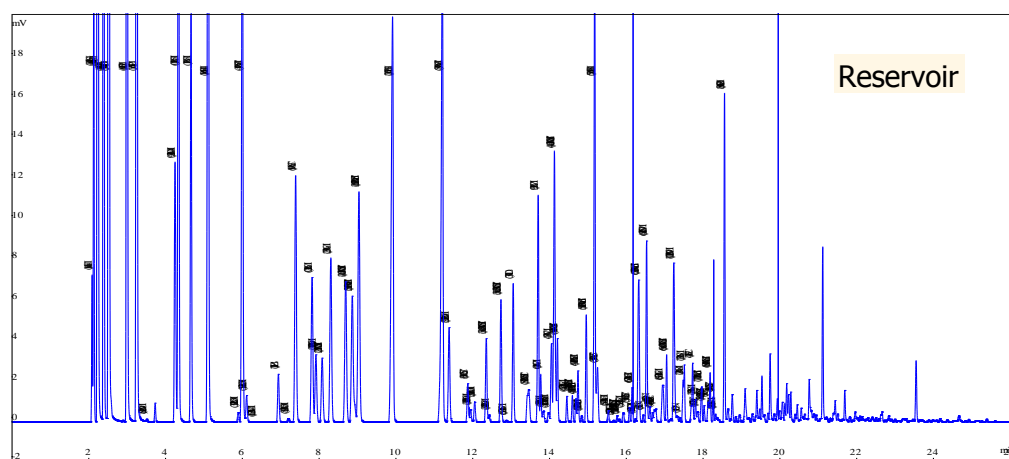


Figure 1 oil layer light hydrocarbon chromatogram

7.2 Selection of light hydrocarbon parameters for oil and water and oil layer

Because of the long-term coexistence of oil and water in the same layer, in the role of water, the secondary evolution is high, leading to the reduction or disappearance of light hydrocarbons which are soluble in water and chemical properties. So the oil-water layers in the light hydrocarbon content than the reservoir low; light hydrocarbon a number of peaks generally between 55 ~ 85; poor chemical stability of quaternary carbon light hydrocarbon group points decrease in water under the action of the trend is very obvious; discriminant oil-water layer of main relative parameters for aromatic, with JiTangan group isoparaffin and is easy to dissolve in water multi branched alkanes and cycloalkanes ratio.

Fig. 2 the difference of the total variation trend of the oil and water with the light hydrocarbon chromatogram of the oil layer is clear at a glance.

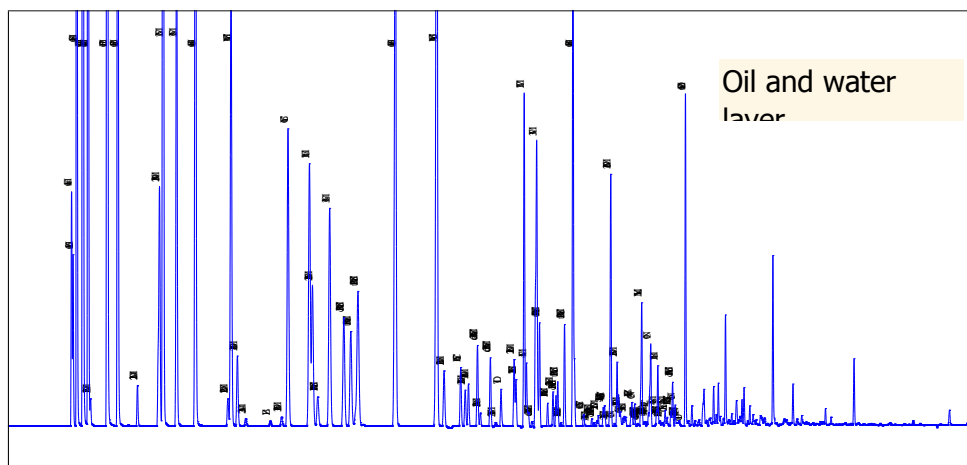


Fig. 2 oil / water and light hydrocarbon chromatogram

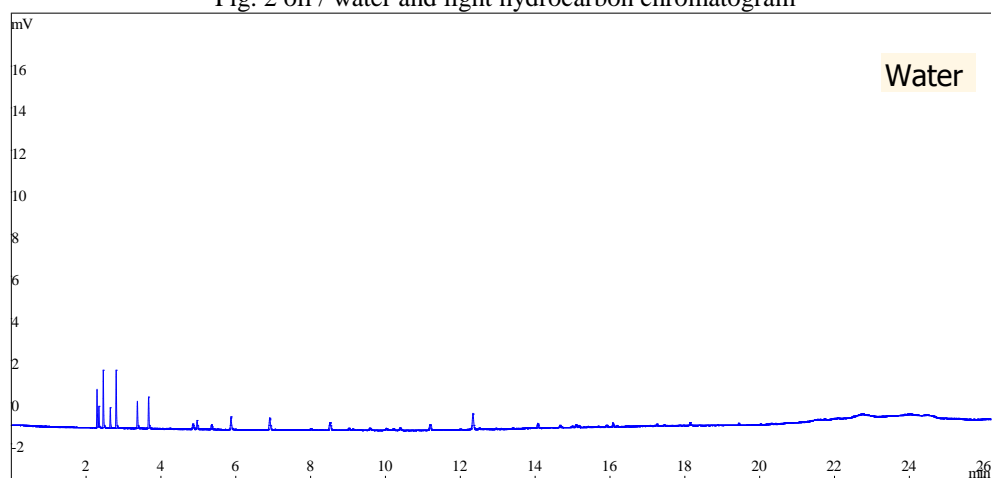


Fig. 3 light hydrocarbon chromatogram

7.3 Selection of light hydrocarbon parameters in the discrimination layer

The real water layer is very difficult to detect the light hydrocarbon component, and the reservoir near the reservoir may be the channel of oil gas migration. It may be the oil saturation is low, the relative permeability is zero. Due to under the action of water and oil from the secondary evolution strongly, led to the reduction or disappearance of the soluble to water chemistry instability of light hydrocarbon, so light hydrocarbon content ratio of oil to water with low level; light hydrocarbon a number of peaks are generally lower than 55; aromatic hydrocarbons, with quaternary carbon functional groups of different alkanes and is easy to dissolve in water MULTI BRANCHED isoparaffin and stability of cycloalkanes relative ratio below the oil-water layers. The C 6 ~ C 8 between is heterogeneous alkanes, aromatics and branched naphthenes with most of the losses, which is the layer of light hydrocarbon chromatogram characteristics, as can be seen from Figure 3 layer light hydrocarbon chromatogram.

7.4 Selection of light hydrocarbon parameters in gas reservoir and dry layer

Relative content of dry gas and moisture layer due to containing C 4 hydrocarbon less, light hydrocarbon distribution range is narrow, so it can use light hydrocarbon composition of discrimination; containing coagulation intermittent oil reservoir discrimination based on the severity of the light hydrocarbon ratio parameter, C 5 and C 5 after the ratio of gas reservoir than high, peak number less than oil. The light hydrocarbon parameters of the dry layer are similar to that of the reservoir, but the light hydrocarbon content is lower than that of the reservoir, and the number of the peaks is less than that of the reservoir.

7.5 General method for selecting parameters of light hydrocarbon ratio

In the use of light hydrocarbon parameters to evaluate the reservoir, the ratio parameters are generally adopted. In the choice of parameter ratios, be sure to select the carbon number range similar or the same, close boiling hydrocarbon fractions compared to the, can avoid the influence of temperature, light hydrocarbon loss. At the same time, we should make a contrast with the parameters that have different physical and chemical properties, which can reflect the change of parameters.

The above parameters and map features can be applied to the reservoir evaluation of general oil properties, which is not suitable for the reservoir evaluation of high density, high viscosity, strong oxidative degradation and biodegradation. The light hydrocarbon parameters for reservoir and water flooded layers are only one aspect of the application of light hydrocarbon analysis techniques. Light hydrocarbon in biological degradation degree of the oil source correlation and oil, synthetic contribution ratio, and other aspects are important parameters in this does not repeat.

VIII. CONCLUDING REMARKS

The basic theory and the application of light hydrocarbon logging technique to evaluate the oil and gas properties of the reservoir are not profound, but it is a little abstract. The key is to have a solid basic knowledge, flexible use of its principle, in the work to find and solve the problem, the accumulation of light hydrocarbon logging experience, in order to play the advantages of light hydrocarbon logging technology, improve the accuracy of interpretation of oil and gas.

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