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Gas-Generating Potential of the Over-Mature Coal-Related Source Rocks

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Original the hydrocarbon-generating simulation experiment temperature is 550~600ºC for technology condition limit, and the corresponding vitrinite reflectance is about 2.0%~2.5%. When the experiment temperature is higher than 600ºC (that is Ro>2.0% or 2.5%), whether the coal-related source rocks can generated gas or not, and how much they can produce, which have a big disagreement, but the great majority of scholars tends toward they can produce gas , however, none of these have proven true by experiment.

In rock pyrolysis, the coal, carbonaceous mudstone and lake facies mudstone pyrolysis peak (S_2 peak) were not up to the base line position, that is the organic matter have not fully pyrolysed. They are different in that the coal and carbonaceous mudstone hydrocarbon-generating track is far from the base line (that is the remaining hydrocarbon-generating potential is large) while the lake facies mudstone is close to the base line (that is the remaining hydrocarbon-generating potential is relatively small) when the temperature is 600ºC. the difference is related with the two kinds of organic matter kerogen structure, the coal kerogen structure is relatively complicated and the breakage of bond or hydrocarbon-generating need the larger energy .The above phenomenon shows that original if we evaluate the source rocks by S_1+S_2 and HI, then the hydrocarbon-generating capacity is undervalued because the S2 value are analyzed lower.

As for the gas-generating potential at the over-mature stage, we used the Rock-Eval rock pyrologger and TG-MS high-temperature pyrogenating simulated experiment device to carry out a series of experiment and research. In terms of the knowledge of the mechanism of gas generation, in particular the knowledge of gas-generating potential at the over-mature stage of source rock, we have made some breakthroughs and successfully revealed the gas-generating potential at the over-mature stage of source rock. In a whole, the source rock can still generate a great deal of natural gas at the over-mature stage. The volume of gas generation of coal-related source rock accounts for 20%-30% of the total gas generation, or even more, but the gas generated from lake facies and sea facies source rock at this stage is comparatively less, accounting for approximately 10% of the total gas generation. This will largely increase the scale

of natural gas in China or even in the world, which will further build up the confidence of exploration.

By using the coal and carboniferous carbonaceous mudstone of Jurassic in Junggar Basin and crop coal sample of the Permian system in Ordos Basin, we carried out the gas-generating simulation experiment and the temperature is from 300ºC to 800ºC. According to the result, all the rocks have generated a lot of gas when the temperature is lower than 600ºC (that is Ro<2.0%~2.5%). This may be the main reason why the maximum experiment temperature was setted at 10ºC for the rock pyrologger. However, when increasing the experiment temperature from 600ºC to 800ºC, which means to raise Ro from 2.0%~2.5% to 5.0%, we found that both the coal and the carbonaceous mudstone in Junggar Basin and the Permian coal in Ordos Basin can generate a great amount of natural gas between 600 ~ 800ºC. This is something we never found before or didn't notice before. Specifically, the gas generated from Jurassic coal in Junggar Basin at this stage accounts for 33.98% of the total volume. The gas generated from the carboniferous carbonaceous mudstone in Junggar Basin at the over-mature stage accounts for 34.39% of the total gas volume. The coal at Tongbao Coal Mine of the Permia system in Ordos Basin and the two coal at Haerwusu coal mines at the over-mature stage account for 25.38%, 28.44% and 24.57% respectively of the total gas generation. The gas generated from the samples of several regions coal-related source rock at the over-mature stage accounts for 20% ~ 35% of the total generated gas volume. This is, so far, the most important discovery of gas generation of coal-related source rock at the over-mature stage. The percentage of gas generated at the over-mature stage in the total volume is so high, which is also an amazing discovery.

In order to make a comparison, we have carried out the pyrolysis gas-generating simulation experiment of the mud stone at lake facies and sea and land facies at the over-mature stage. The gas generating rate of the tertiary lake facies mudstone of the Qikou Sag has no significant difference from that of the coal-related source rock between 600 ~ 900ºC. The gas generated at Well Gang94, Gangshen74-1, Bai10-3 and Well Gang2033 accounts for 23.48%, 23.68%, 36.25% and 30.30% of the total volume respectively when the temperature is higher than 600ºC. The percentage is similar to that of coal facies, with the tendency of deteriorating in different kerogens and increasing the gas generating rate when the temperature is higher than 600ºC. Nevertheless, the gas generating rate of the Permian lake facies mudstone in the in Junggar Basin and that of carboniferous transitional facies is obviously decreased when compared with the coal-related source rock when the temperature is between 600 ~ 800ºC, accounting for 8.4% and 10.1% of the total generated gas volume respectively. The major root cause for such phenomenon is the skeleton structure. The worse the kerogen type is, the more substance containing gas generated at late stage it will be, the more component of late pyrolysis will be.

In an attempt to verify the above phenomenon, we have cooperated with Northeast Petroleum University to carry out the source rock thermogravimetric-mass-spectrometric thermal simulated experiment and have got very similar result. Coal and carboniferous mud stone can generate enormous natural gas when the temperature is between 600 ~ 800ºC, accounting for 20% of the total generated gas volume, which can best verify the opinion that the source rock can

generate enormous natural gas at the over-mature stage. At the meantime, in order to check the conversion degree of gas-generating through coal, we further increased the experiment temperature to 1000ºC, that is, to increase Ro to 6% or so. The generated gas volume stops increasing when the temperature is between 800 ~ 1000ºC, indicating that the conversion rate has fully reflected the capacity of coal to generate gas when the temperature is lower than 800ºC. From the perspective of application of petroleum geography, there is almost no sediment basin that has evolved into such a condition. From the angle of chemistry, coal has begun to graphitization under the condition of such mature. Therefore, the whole-day gas generation should have a lower limit, rather than without any prohibition.

According to the result of thermogravimetric-mass-spectrometric experiment on the shale of sea facies for Xiamaling formation at Qingbaikou in the Proterozoic era in north of JIbei and the cretaceous mud stone at Songliao Basin, when the simulated temperature increases to 600 ~ 800ºC, the mud stone of Lake Facies ad Sea facies will generate a lot natural gas, however, the gas-generating volume much smaller than the coal-related source rock. The residue sea facies source rock gas-generating accounts for 8% of the total generated gas volume. As for the two samples of source rock of Lake Facies, the organic matter of II_2 residue gas-generating when the temperature is between 600 ~ 800ºC accounts for 7% of the total generated gas volume or so. The organic matters of II_1 organic matter accounts for 5% of the total generated gas volume. In terms of the Lake Facies mud stone, there is a tendency in which the type of organic matter is worsening and the residue gas volume is reducing at high temperature, which is similar to that experiment result on the above-mentioned pyrogenating gas generation rate. When the temperature is between 800 ~ 1000ºC, the gas-generating potential disappears, which is consistent with the experiment result of coal-related source rock.

The coal contains a great deal of alkylphenol compound, which is also the major component of lignin and fibrin. These substances have complicated structure, with higher degree of cyclized. Therefore, the activation energy is higher too. It can only be pyrolyzed extensively under high temperature to produce methane. In addition, as for the coal-related source rock, the kerogen is rich in fragment aromatic core structure, with higher bond energy. It is not easy to pyrolyze under the condition of low temperature. When it is in high temperature, demethylating reaction will occur to the aromatic core structure. The straight chain alkyl on the aromatic core can have pyrolyzed (a), forming alkyl on it. It will further demethylate to produce methane. The broken straight chain alkyl can be connected to another aromatic core quickly and repeat the above reaction, accordingly increasing the generated volume of gaseous hydrocarbon. The kerogen structure of mudstone of Lake Facies and sea facies is different from that of coal-related source rock, in which most substances have lower activation energy and more substances have broken the bond to produce hydrocarbon before the temperature is up to 600ºC. Therefore, the residue gas volume at the over-mature stage is reduced. When the temperature reaches up to 700ºC or above, most organic hydrocarbon-generating process will finish, and the residue gas volume generated may be neglected. As a result, the experiment temperature reaching up to 700ºC would be considered appropriate.

In conclusion, the gas generation from coal is basically on the whole-day basis. The gas can be generated from the raw materials to the graphitization process, but the gas-generating volume, gas-generating substance and gas composition at different stage are different. Due to the characteristics of kerogen of coal-related source rocks, it contains a great deal of alkylphenol compound and substances of aromatization structure, which requires high temperature for pyrolysis. Therefore, a large amount of natural gas can be generated at the over-mature stage.