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The Limit of Gas Generation Potential of Highly to Over Mature Humic Coals: Theoretical Consideration

Jianping Chen¹, Yongge Sun², Chunping Deng¹

¹RIPED, Petrochina, Beijing, China

²Zhejiang University, Hangzhou, Zhejiang, China

The kerogen thermal-degraded theory suggested by Tissot and Welte (1984) defines that petroleum generation from sedimentary organic matter mainly taken place in what called “oil window” and “gas window”, normally equivalent to the vitrinite reflectance of $R_o=0.7-1.5\%$. However, several previously studies claimed that there is still gas generation potential of coals even if it is in the highly to over mature stage ($R_o > 1.5\%$). Therefore, what is the upper maturity limit in terms of gas generation potential of coals, or called “deadline of gas generation”? Before reaching the deadline, how big the gas generation is? Is this a commercial significance? This is an important issue in respect to petroleum exploration in coal-bearing basins with highly to over thermal experience

1. Upper maturity limit of thermal degraded gas from coals

The H/C atom ratio in kerogen can be a good indicator for hydrocarbon generation potential of source rock, but the ratio shows a decreasing trend during thermal evolution and also is used as an important maturity parameter (Tissot and Welte, 1984; Baskin, 1997). Statistic results suggested that initial H/C atom ratio is in the range of 1.35 to 1.50 (average 1.45) for type I kerogen, and with a hydrogen content of <10%, initial H/C atom ratio of 1.20 to 1.35 (average 1.25) for type II kerogen and a hydrogen content of <8%, and initial H/C atom ratio of <1.20 for type III kerogen, respectively. While the initial H/C atom ratio of most humic coals (type III organic matter) is lower than 1.0, as showed in Figure 1(a).

The hydrogen content and H/C atom ratio of kerogen will decrease accompanying hydrocarbon generation process during maturation. The H/C atom ratio of type I and II kerogens will reach up to 0.6–0.7 at the end of oil window ($R_o=1.3\%$), and about 0.6 for type III and humic coals. Then the sedimentary organic matter evolved into condensates and wet gas generation stage to be defined as “gas window”. The loss of H/C atom ratio of type I and type II kerogens is about 0.9–0.6 through oil window. Whereas the loss of H/C atom ratio of coals is about 0.2–0.3 and significantly lower than that of type I and type II kerogens.

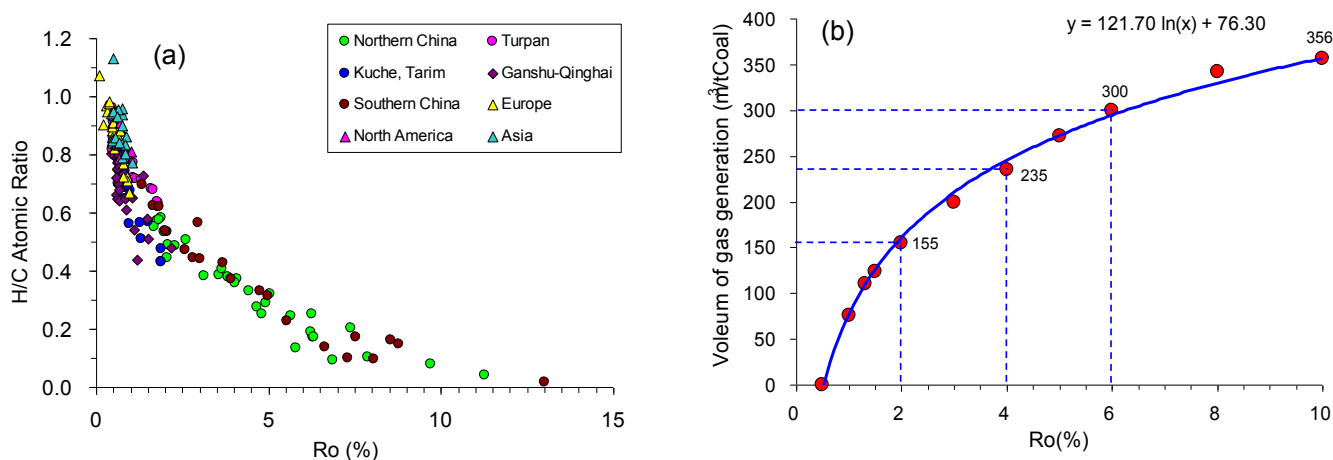


Fig. 1: Variations in H/C atomic ratios of coals (a) and their gas generation potential (b) with increasing maturity.

The decreasing rate of H/C atom ratio of coals in natural thermal evolution, corresponding to the “gas window” (condensates, wet gas and dry gas) is still very slow even if coals reach high rank stages (e.g. anthracite and ultra anthracite). As showed in Figure 1, the H/C atom ratio of coals is about 0.42 at the vitrinite reflectance of 3.0%, about 0.37 at the vitrinite reflectance of 4.0%. The H/C atom ratio of coals decreases to lower than 0.1 at the vitrinite reflectance of 10.0% (graphite stage).

It is well known that graphite is the end product of sedimentary organic matter during geological evolution and no gas generation potential due to its high aromaticity with ordered array and layer structure. The hydrocarbon generation stage from humic coals shows a wide maturity range up to vitrinite reflectance up to 10%. Thereafter, the vitrinite reflectance of 10% is defined as “deadline of gas generation from humic coals”.

2. The limit of gas generation potential from humic coals

The sedimentary organic matter is mainly composed of elements C, H, O, N and S, and among these elements, carbon and hydrogen are the main constituents with a H/C atom ratio of <2.0. It is well known that kerogen thermal degradation is a loss of hydrogen in organic matter. Therefore, hydrocarbon generation potential strongly depends on the hydrogen content in sedimentary organic matter, here is kerogen. Using mass balance calculation, the limit of gas generation potential from humic coals can be determined by the turnover of hydrogen in kerogen.

If the initial H/C atom ratio of humic coals is theoretically defined as 0.1, and the decreasing trend of H/C atom ratio derived from natural evolution of humic coals as reference, the gas generation potential can be calculated corresponding to different mature stage. As listed in Table 1 and printed in Figure 1(b), the gas generation potential of humic coals reaches up to 111m³/t coal at the end of oil window, about 31% of total hydrocarbon generation potential. The

accumulated gas generation potential will reach up to $155\text{m}^3/\text{t}$ coal at the end of wet gas stage, about 43% of total hydrocarbon generation. There is still $200\text{m}^3/\text{t}$ coal potential left at the dry gas stage and latter. The limit of gas generation potential from theoretical calculation suggests that there is no distinct peak in respect to hydrocarbon generation process from humic coals and there should be great potential of gas generation of humic coals than expected during highly to over mature stage, although normally it is difficult to reach this mature stage in most petroliferous basins.

Because theoretical calculation for the limit of gas generation potential from humic coals uses mass balance of carbon and hydrogen and this is purely theoretical coals, the real limit should be lower than the presented data here, and depends on the coal compositions. For example, the sum of carbon and hydrogen content in low rank coals is about 80% of total organic matter and the left for oxygen, nitrogen and sulfur etc (Spiro et al, 1982). According to the average carbon and hydrogen contents in actually low rank coals, a rough estimation of the limit for the gas generation from humic coals is about 80% of theoretical results. This is still a theoretical data because a pure coal without minerals is used. In terms of mineral matrix in coals, the limit for the gas generation from humic coals is at least about 80% of theoretical data from pure coal.

3. Mechanisms on controlling gas generation from highly to over mature humic coals

It is well known that there is a significant difference between coals and the disseminated organic matter in sediments (type I, II and III) in terms of their chemical characters, especially of macromolecular structures, resulting in gas generation potential of highly to over mature coals.

3.1 Mechanisms associated with gas generation from coal thermal degradation

The difference of macromolecular structure between coal and disseminated organic matter revealed that there is a relatively high concentration of aliphatic chains in macromolecular net from disseminated organic matter with enrichment of aliphatic hydrogen and less aromatic hydrogen. In type I immature organic matter, the relative concentrations of hydrogen in different structural units are 80% from aliphatic straight and/or branched chain unit, 13% from aliphatic cyclic unit and only 7% from aromatic unit, respectively. Whereas this proportion in immature type II organic matter is 60%, 22%, and 18%, respectively, and 50%, 17%, and 33%, respectively in immature type III organic matter.

Using NMR measurements, Qin (1990) demonstrated that the 91 percent of total hydrogen in Fushen oil shale from North China are from aliphatic unit and the 7.4 percent of total hydrogen are from aromatic unit, and the average aliphatic chain length is about 10.5 carbon numbers. This result is very similar with what Behar (1987) observed from type I kerogens. In one Tertiary brown coal from Huang County, East China, the relative concentrations of aliphatic and aromatic hydrogen are 72% and 21% respectively, and the average aliphatic chain length is about 3.8 carbon numbers, showing a lower aliphatic hydrogen content and short aliphatic chain length compared to that of Fushun oil shale. However, the relative concentration of aromatic hydrogen in the coal structural models (Xie, 2002) ranges from 21% to 36%, higher than that of

brown coal from Huang county. More deep measurements showed that total hydrogen content from $-\text{CH}_3$ and $-\text{CH}_2$ in aliphatic chain is 63%, and only 4% contributed from $-\text{CH}_3$ and 2% from aromatic hydrogen in Fushun oil shale. Whereas in brown coal from Huang County, the total hydrogen content from $-\text{CH}_3$ and $-\text{CH}_2$ in aliphatic chain is 39%, and only 9% contributed from $-\text{CH}_3$ and 9% from aromatic hydrogen. There is a much less concentration of hydrogen from $-\text{CH}_2$ and $-\text{CH}$ in highly to over mature coals. The results clearly suggested that the type I and II disseminated organic matter are dominated by long chain aliphatic units and less short chain aliphatic units. Therefore, the concentration of aliphatic hydrogen is significantly higher than that of coals. The abundant aromatic carbon in coals results in its increase of aromatic hydrogen compared to the disseminated organic matter, even to type III organic matter.

Theoretically, thermal stability of macromolecular organic matter strongly depends on the bond energy distributed in the net. Generally bond energy can be divided as polynuclear aromatic > aromatic > cycloalkanes > alkenes > alkanes (Xie, 2002). The longer of the side chain in aromatics and more aromatic cycle numbers in polynuclear aromatic units, the less the thermal stability of side chain is.

According to the kerogen thermal degradation theory, compared to the short chain aliphatic units, long chain aliphatic units in kerogen net are more easy to be degraded, followed by expulsion and formation of hydrocarbons. This result suggests that the better the organic matter type is, the more aliphatic fractions there are within oil window. Thereafter, compared to coal organic matter, organic matter with an enrichment of hydrogen has a quick decrease of hydrogen content in kerogen during thermal maturation. In contrast, there should be a slow decrease of hydrogen content in coal organic matter and still has gas generation potential even in highly to over mature level due to its enrichment of short chain aliphatic hydrogen and aromatic hydrogen, usually with higher bond energy to be broken.

3.2 Stages in respect to gas generation from coals

The on-line pyrolysis-gas chromatography-isotope ratio-mass spectrum analyses of different maturity coals showed that it can be divided into four stages (A, B, C, D, in the Fig. 2) in terms of gas generation process:

The stage A corresponds to traditional oil window (0.5–1.3% R_o). In this stage, long chain aliphatic units, naphthene units and part of aromatic units in coal organic matter were degraded and generated natural gas with a predominant of methane and minor heavy hydrocarbon gas and liquid oil. The stable carbon isotopic compositions of methane in this stage were characterized by a depletion of ^{13}C compared to the whole gas generation process, indicating a source from low energy bonds broken (e.g. long side chain attached to the aromatics).

The stage B is a main stage in terms of gas generation and corresponds to equivalent vitrinite reflectance about 1.3–1.8% R_o . In this stage, natural gas are mainly derived from short chain aliphatic units both attached to aromatics and bridged between aromatics and/or from secondary cracking of generated products retained in coals. Because of the difference of bond energy between $^{13}\text{C}-^{13}\text{C}$ and $^{12}\text{C}-^{12}\text{C}$, the stable carbon isotopic compositions of methane show a linear increasing trend to ^{13}C enrichment with increasing thermal maturity.

The stage C is associated with highly to over mature level (2.0–6.0% R_o). The stable carbon isotopic compositions of methane demonstrated a significant decrease, suggesting a source from aromatic attached methyl and/or alkylphenol methyl. The alkylphenols are derived from lignin and cellulose which are the main constituents of vitrinite in coals (Dieckmann et al, 2006; Mahlstedt et al., 2008), resulting in a large quantities of gas generation during highly mature stage. Because the aromatic attached methyl and/or alkylphenol methyl inherit the light carbon isotopic character from bioprecursors, the stable carbon isotopic compositions of methane from these fractions have a relative enrichment of ^{12}C .

The stage D can be correlated with over mature stage ($R_o > 6.0\%$). In this stage, aromatic cycles will be opened due to very high maturity followed by a polycondensation accompanied by minor methane generation. The maximum of methane products from this stage is 40mg/g TOC and similar to the theoretical calculated utmost value using hydrogen content. The stable carbon isotopic compositions of methane are typically characterized by an enrichment of ^{13}C .

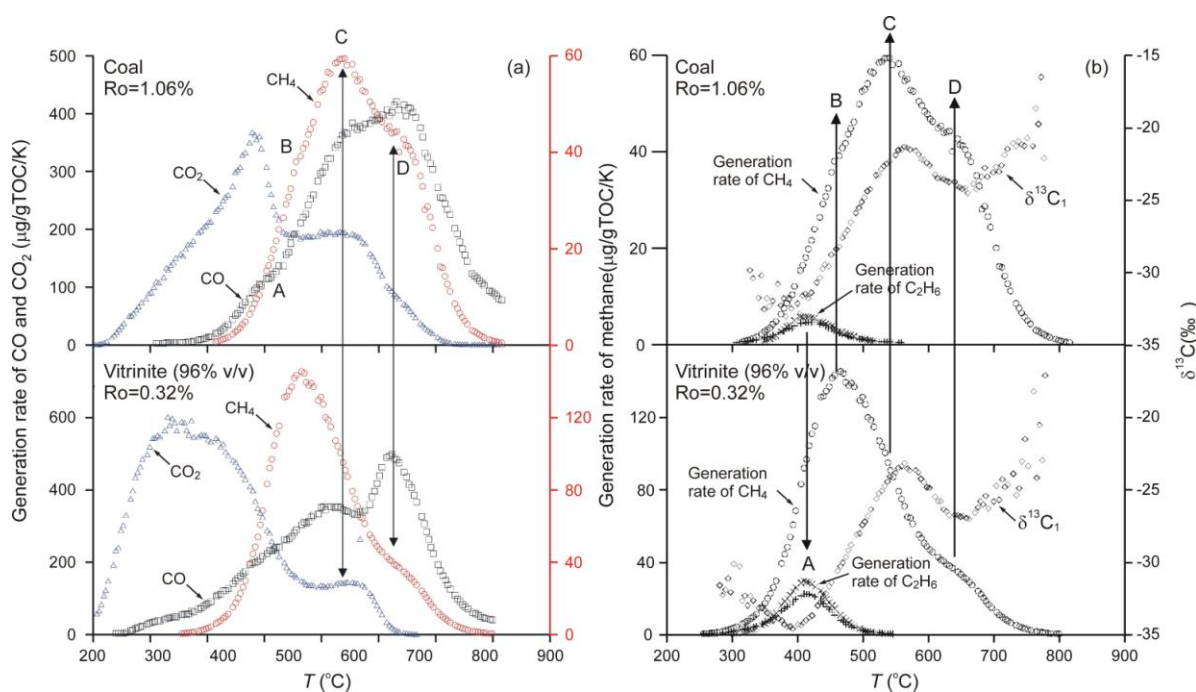


Fig. 2. The on-line PYGC-isotope ratio-mass spectrum analyses of different maturity coals

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