Simulation of thermochemical sulfate reduction of gaseous hydrocarbons in Wushenqi area, Ordos Basin, China

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Abstract. Prediction of the H₂S distribution is critical to lower the risks during petroleum exploration and development in the exploration area. Natural gas of two wells produced from the Ordovician Majiagou Formation Ma5-6 section from Wushenqi area show great difference in H₂S content. To investigate whether the different thermal maturity of the two wells contributes to the different H₂S content, the thermal mature history and transformation ratio of gas hydrocarbons and sulfate into H₂S and CO₂ through TSR (thermochemical sulfate reduction) were simulated by using Petromod 2016. Simulation result shows that difference of thermal maturity of the two wells is about 0.6%. Propane and butane have all been consumed to generate H₂S. The transformation ratio of ethane is higher for the well with higher thermal maturity. The high H₂S content in the well with high thermal maturity and no H₂S in the well with lower thermal maturity was not caused by the different thermal maturity. Some other geological factors should be considered.

1. Introduction

In recent years, the exploration for natural gas at the eastern palaeouplift in Ordos Basin has made some breakthrough. One of the discoveries is the H₂S rich natural gas production from layers under gypsolyle at lower Paleozoic [1]. As H₂S is toxic, corrosive and economically-damaging, identifying its origins and fate is critical to lower the risks during petroleum exploration and development in the exploration area [2]. There are three origins for H₂S in oil and gas reservoirs, including bacterial sulfate reduction, the decomposition of sulfur-compounds and thermochemical sulfate reduction. Abundant H₂S in carbonate petroleum reservoirs is usually a result of the thermochemical sulfate reduction (TSR) [3-6].

Thermochemical sulphate reduction (TSR) is the abiotic stepwise reduction of sulfate by hydrocarbons at elevated temperatures, whereby SO₄²⁻ is reduced to sulfide coupled with the oxidation of hydrocarbons to CO₂ [7-8]. Laboratory experiments and geological observations have proven that TSR could influence the chemical composition and carbon isotope of gases [5, 9-11]. Large amount of H₂S was generated during the catalytic stage of TSR. Geological observations suggested various thresholds for TSR, ranging from a minimum of 80°C to a much higher 180°C. The great discrepancy of the onset temperature for TSR can be attributed to the controlling factors of TSR that usually vary.
from place to place [12-13]. Quantum mechanics density functional theory calculation proved that contact ion pairs and bisulfate ion, which are more readily to oxidize hydrocarbons compared with free $SO_4^{2-}$, were suggested to be the most feasible oxidants for TSR in the initiation stage [14]. The concentration of contact ion pairs [MgSO$_4$]$_{CIP}$ and bisulfate ion HSO$_4^-$ could influence the reaction rate of TSR [8]. In addition, higher sulfur content of original oils, lower PH and higher salinity of formation waters can accelerate the reduction of sulfate [15-18].

As little solid bitumen was found in the $H_2S$-rich natural gas reservoir in Wushenqi area, it is speculated that TSR of hydrocarbon gases was responsible for the $H_2S$ generation. The activation energy and frequency factor for the TSR hydrocarbon gases had been calculated by using the chemical composition of gaseous hydrocarbons from the Norphlet Formation in the Mobile Bay area [8]. By combining the experimental results and theoretical calculation, the kinetic parameters for the TSR of methane were calculated by [19]. To investigate whether the differences in burial and hydrocarbon generation history between wells were responsible for the variation of $H_2S$ content in production wells, reported kinetic parameters for TSR of gaseous hydrocarbons were used in the hydrocarbon generation and cracking simulation through modeling by using the software PetroMod2016.

2. Geological background
The Ordos Basin located in northern-central China is the second largest sedimentary basin in China with large oil and gas resource potential. It comprises six major structural units including the Yimeng uplift in the north, the Weibei uplift in the south, the Tianhuan depression and western edge thrust belt in the west, the linxi fold belt in the east and the central Yishan slope (Fig. 1). The lower Paleozoic strata are mainly composed of carbonate rocks and gypsum. During the Ordovician, Carboniferous and Permian time periods, the basin went through a transition from marine to continental facies, therefore, the lower part of Upper Paleozoic strata was deposited as transitional facies and the upper part of Upper Paleozoic strata was made up of terrestrial clastic rocks and coal measures. Several giant gas fields have been discovered in this basin, including the Jingbian gas field sourced from Ordovician deposits and the Sulige, Wushenqi, Yulin, Daniudi and Mizi gas fields in Upper Paleozoic [20-21].
By analyzing the tectonic background and type of the basin and using the apatite fission track method, thermal gradients in early and late Paleozoic and Mesozoic were restored [22]. In the early Paleozoic, the basin belonging to passive margin was a wide continental shelf facing the Qinling Paleo-ocean, the temperature gradient was 25-30 °C/km. From late Paleozoic to early Mesozoic, the basin transformed from a littoral-neritic sea to a cratonic setting with a low thermal gradient of 22-24 °C/km. As a result of the strong middle Yanshan tectonic event, the thermal gradient increased to 33-45°C/km in late Mesozoic. Subsequently, the basin was uplifted and went through intense erosion from the late Early Cretaceous-Early Miocene and the thermal gradient dropped to 22-32 °C/km with an average value of 28 °C/km [23-24]. Inner part of the basin was uplifted in a faster rate in Mesozoic and the erosion thickness was approximately 2000m in the eastern basin [22-23, 25].

3. Method
Basin simulation technique has been used to quantitatively simulate the generation, migration and accumulation of hydrocarbons in petroliferous basin [24, 26-27]. In this work, PetroMod 2016 (1D) developed by Schlumberger was used to simulate the burial and geothermal history, hydrocarbon generation and TSR of gaseous hydrocarbons of two wells named Jintan 1 and Tong 52. To build the model, parameters of strata (age, thickness and lithology), boundary conditions (paleo-heat flow, paleo-water depth and deposition water interface temperature), tectonic events (unconformity, erosion time and erosion thickness), geochemical parameters of source rocks and kinetic parameters of hydrocarbon generation were needed. Measured vitrinite reflectance was used to adjust the model.

4. Results and Discussion
4.1 Burial history

Figure 2. The burial history of wells JT1 and T52.

The model result demonstrates that the burial history of JT1# and T52# from Cambrian or Ordovician and ended at Quaternary is related with the tectonic subsidence history of the study area (Fig. 2). From Cambrian to Ordovician, marine sediments including shale and carbonates were successively deposited. By the end of Ordovician, the basin was uplifted and Middle-Upper Ordovician strata was heavily eroded for 150-180 Ma due to the tectonic event of Caledonian movement [28]. Then, the basin went through constant subsidence from the Middle Cretaceous to Late Triassic [29]. During this period, the basin transformed from a littoral-neritic sea to a cratonic setting. Accordingly, the sediment changed from interbedding of shale, carbonate and coal into shale and sandstone. Influenced by the tectonic event of Indosinian movement, the basin experienced a small uplift at late Triassic and went through the second erosion event, resulting in the erosion of upper Yanchang Formation [30]. From Jurassic to Cretaceous, interbedding of shale and sandstones was the main sediment, coal was found in Jurassic Yanan Formation. At the end of Early Cretaceous, the burial depth of the two wells is the
highest. Due to the tectonic event of Yanshan movement, the basin was uplifted and went through erosion at late Jurassic and the end of Early Cretaceous. For the four times of erosion, the most severe one happened at Early Cretaceous. The erosion thickness becomes smaller from eastern to western part of the basin. The erosion thickness reached 2000m in the eastern basin. The largest burial depth of JT1 is about 5000m and is 600m deep than T52 (Fig. 2).

4.2 Thermal mature history

The thermal mature history shows that the section 5-6 of Majiagou Formation in which the TSR of gaseous hydrocarbon happened entered into oil generation stage at Jurassic and reached gas generation period at Cretaceous, indicating that the Yanshan tectonic event is significant for the thermal mature of the source rock and TSR reaction of gaseous hydrocarbon. At the Early Cretaceous, the thermal maturity of Ordovician carbonate rocks reached the highest value of about 2.5% for JT1 and 1.9% for T52. During that period, the thermal gradient for well T52 is a little higher than that of well JT1. However, the final thermal maturity of T52 is higher than that of JT1, which is related with the larger burial depth of JT1. Although the difference of largest burial depth between JT1 and T52 (600m) is small, the Ro difference is about 0.6% (Fig. 3). The large thermal gradient 81-95 mW/m2 during the Early Cretaceous could be the main cause. The conditions of late hydrocarbon gas generation at Cretaceous and no large tectonic movement afterwards were favorable for the gas preservation [22-23].

4.3 TSR of gaseous hydrocarbons

Compared with the non-H₂S gas produced from T52, gas produced from JT1 is dryer and rich in H₂S (13.31%). Differences in the gas content might be influenced by many factors including thermal maturity, reactants and so on. As the two wells differ in thermal maturity, this study was conducted to investigate whether the thermal maturation process could contribute to the differences in the content of H₂S.

The kinetic parameters for the TSR of gaseous hydrocarbons, including the frequency factor and activation energy, had been calculated based on the chemical composition evolution with TSR reaction degree and experiments [8, 19]. The kinetic parameters were used to simulate the H₂S generation. The TSR of liquid hydrocarbons and kerogen was also simulated for comparison [4]. Simulation result shows that TSR of almost all organic matters (OM) from kerogen to ethane took place in the two wells during Triassic-Cretaceous (Fig. 4). The TSR of hydrocarbons with lower molecular weight happened at higher temperature and thermal maturity. As the kinetic parameters of kerogen has a large range of 213.53-314.01 KJ/mol, the TSR of kerogen happened at the oil generation stage and the transformation ratio is 80-85% for the two wells. It could be noted that the transformation ratio of propane and butane is similar at the same geological time as the kinetic parameters of the two reactants are similar. At Early Cretaceous, both propane and butane were exhausted. Except for the differences in the time when the TSR of OM started, the transformation ratio of ethane for T52 is lower than that of JT1. This is mainly related with the low thermal maturity of T52. TSR of methane didn’t occur in this simulation. The simulation of the TSR of OM was based on the hypothesis that no
reduced sulfur was available at the reservoir. Previous work documented that the presence of reduced sulfur could lower the activation energy of TSR of various hydrocarbons including methane [19, 31]. The presence of considerable amount of reduced sulfur generated during the TSR of other hydrocarbons with larger molecule weight might bring about the TSR of methane [19].

Based on the assumption that there were enough bisulfate ions (HSO$_4^-$) and/or magnesium sulfate contact ion-pairs [MgSO$_4$]$_{CIP}$ and no reduced sulfur in the gas reservoir, abundant H$_2$S could be generated for the two wells. This implies that the difference in thermal mature history between the two wells is not the cause for the different H$_2$S content. The low concentration of HSO$_4^-$ and [MgSO$_4$]$_{CIP}$ or the consumption of H$_2$S by metal ions forming minerals might play an important role in the differences in H$_2$S content.

5. Conclusion
The influence of thermal maturation on the H$_2$S content of two wells located around Wushenqi area was investigated through simulating the thermal mature history and transformation ratio of hydrocarbon gases of the two wells based on the burial strata data and tectonic events.

Simulation results show that thermal maturity of well JT1 located at the western part of Wushenqi area is higher than that of T52 at the eastern part of Wushenqi area. For the two wells, propane and butane have all been transformed by TSR reaction into CO$_2$ coupled with the generation of H$_2$S. The transformation ratio of ethane for JT1 is higher than that of T52, which is related with the higher thermal maturity of JT1. Thermal mature difference between the two wells is not the main factor for the high H$_2$S content in JT1 and no H$_2$S in T52. Some other geological factors should be considered.

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