Hydrocarbon Generation in the Lacustrine Mudstones of the Wenchang Formation in the Baiyun Sag of the Pearl River Mouth Basin, Northern South China Sea

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ABSTRACT: The lacustrine mudstones of the Eocene Wenchang Formation are the primary source rocks of natural gas in the Baiyun Sag of the Pearl River Mouth Basin, China. The hydrocarbon generation kinetic parameters and the characteristics of lacustrine mudstones sampled from the Eocene Wenchang Formation at well LF13-2-1 were investigated on the basis of a thermocompression simulation experiment in a closed system. In addition, combined with the burial history and paleothermal history, the gas generation process of the Eocene Wenchang Formation source rocks in the Baiyun Sag was investigated through the hydrocarbon generation equations established from parameters of hydrocarbon generation kinetics. The gas generation process of the Eocene Wenchang Formation lacustrine mudstones has three thermal evolutionary stages: the middle mature stage (39–30 Ma), the late mature stage (30–23.5 Ma), and the main gas generation stage (23.5–0.0 Ma). The main hydrocarbon generation stage in the central area of the Baiyun Sag occurred from 24 Ma to 22 Ma, while the main hydrocarbon generation stage in the eastern and northern areas occurred at ∼15 Ma.

1. INTRODUCTION

The Pearl River Mouth Basin (PRMB) is located in the northeast of the South China Sea (SCS). The Baiyun Sag (BYS) is the largest sag of the Zhu II Depression in the PRMB. The BYS underwent an interactive process of plate tectonic movement between the Pacific plate, the Eurasia plate, and the Indian plate, and it was influenced by the spreading of the SCS.¹ Thermal subsidence caused by a greatly thinned lithosphere and active magmatism made the BYS a subsidence and deposition center. The maximum residual Paleogene thickness is ∼8000 m.² Recently, as a result of a series of commercial discoveries starting with wells LW 3-1-1 and PY30-1,³–⁵ the discovered petroleum reserves in the BYS have more gas (∼2000 × 10⁶ m³) than oil (3500 × 10⁶ m³).⁶ The BYS has become a new focus for deepwater exploration with a huge hydrocarbon potential.⁷

As indicated by recent studies, the BYS has a vertical migration pathway from deep source rock to a shallow reservoir.⁸ Therefore, it is critical to analyze the mechanisms of hydrocarbon generation of source rocks in the BYS. In this study, based on a thermocompression simulation experiment,⁹ the chemical kinetic equations of the hydrocarbon generation of the Wenchang Formation source rocks were established, and the hydrocarbon generation process was simulated using the BasinMod software.

2. GEOLOGICAL SETTING

The PRMB consists of two depression zones, separated by three uplift zones: the North Uplift Zone, the North Depression Zone (consisting of the Zhu I and Zhu III Depressions), the Central Uplift Zone, the South Depression Zone (consisting of the Zhu II and Chaoshan Depressions), and the Southern Uplift Zone.¹⁰ The BYS is the largest sag in the Zhu II Depression, with an area of ∼15 000 km² in a water depth of 200–2800 m beyond the slope-break zone of the SCS¹¹ (see Figure 1).

The northern SCS has experienced a transition, from a Mesozoic active continental margin to a Cenozoic passive margin. The BYS experienced three tectonic stages: (1) Paleogene rifting in three phases, which formed lacustrine and terrestrial-marine transitional strata; (2) a phase of Neogene thermal subsidence; and (3) a phase of Phiocene-Quaternary neotectonic movement.¹² From top to bottom, the BYS develops the Paleogene Formations of Shenhua, Wenchang, Enping, and Zhuhai, the Neogene Formations of Zhuijiang, Hanjiang, Yuehai, and Wanshan, and the Quaternary Formation (see Figure 2). From the Palaeocene to the Early Oligocene, fluvial facies, lacustrine facies, and swamp facies have developed in the study area, and the sediments of the delta and open sea have been developing from the Late Oligocene to the present. Because of the expansion of Baiyun Lake, high-quality lacustrine source rocks were widely developed during the period from the Eocene to the early Oligocene. The deep lacustrine source rocks of the Eocene Wenchang Formation, in particular, are the major resource rocks with huge hydrocarbon potential, since the deep lacustrine facies were developed in the primary rifting stage.¹³
The bottom section of the Eocene Wenchang Formation drilled in the well PY27-2-1 is composed of brown mudstones interbedded with grayish-white gravel-containing sandstones, which indicates a river channel facies. The top section is composed of sandstones interbedded with dark gray mudstones and contains coal-bearing source rocks in certain areas, which indicates a swamp facies. The transitional coal-bearing source rocks are the major source of gas, as represented by the Enping Formations in the PRMB. Meanwhile, the lacustrine source rocks of the Eocene Wenchang Formations were found in the LW4-1 tectonic zone. Compared with the seismic reflection characteristics of the Zhu I Depression, the sequence boundaries can be identified in the Eocene Wenchang Formation (see Figure 3). The BYS trends NE-SW and is composed of multiple half-grabens and grabens from a series of secondary faults. Syn-rifting lacustrine sediments, i.e., the Eocene Wenchang Formation, are extensively developed in the BYS, which are the deep source rocks with typical features:

![Figure 1. Regional location of the Baiyun Sag.](image)

![Figure 2. Simplified lithostratigraphy and sea-level changes of the Pearl River Mouth Basin.](image)

![Figure 3. Sequence boundary identification of the Eocene Wenchang formation in the Baiyun Sag.](image)
moist climate, very thick strata, high deposition rate, and strong parallel seismic reflection facies.\textsuperscript{1}

The seismic characteristics of the Eocene Wenchang Formation in the center of the BYS are continuous medium-high amplitude, parallel and low-frequency,\textsuperscript{21} which are similar to the reflection features of deep lacustrine mudstones in the Zhu I Depression. Low amplitude, continuous and parallel seismic reflection features are widely found in the top section of the Eocene Wenchang Formation, indicating shallow lacustrine facies (see Figure 4a).\textsuperscript{22}

The deep lacustrine strata are deposited in the center of the BYS, which has the tendency of becoming thinner toward both sides of the northern slope and southern uplift (Figure 4b). Based on seismic reflections, the estimation of the maximum thickness of the Wenchang Formations is ∼6000 m. During the sedimentary period of the lowstand system tract, the lake basin was limited by the northern fault zone and had a small area with deep lacustrine facies in the center of the BYS. In the corresponding period, shore-shallow lacustrine facies developed near the peripheral area of the BYS (Figure 4c). During the sedimentary period of the transgression and highstand system tracts, the ancient lake basin expanded gradually, and deep lacustrine sedimentation expanded to the western fault zone. In addition, a relatively deep lacustrine facies developed east of the BYS (Figure 4d).

3. SAMPLES AND METHODS

3.1. Hydrocarbon Generation Kinetics Principle. The kerogen pyrolysis produces both liquid hydrocarbons (C\textsubscript{6−14} and C\textsubscript{15+}) and gaseous hydrocarbons (C\textsubscript{1} and C\textsubscript{2−3}). The kinetics of kerogen pyrolysis have been successfully modeled with either a first-order reaction or a system of parallel first-order reactions.\textsuperscript{23} The parallel reaction model is a more extensive application, because kerogen is regarded as multi-compositional and the product composition is changed tremendously during pyrolysis.\textsuperscript{24,25} Based on the kinetic principles of the primary cracking reaction proposed by Espitalie and Ungerer,\textsuperscript{26} a multicomponent kinetic model for gas generation can be built for the thermal degradation of kerogen by viewing it as a series of parallel first-order reactions with different activation energies (E\textsubscript{i}) and frequency factors (A\textsubscript{i})

\[ X(t) = \sum X_i(t) \] \hspace{1cm} (1)

The gas generation of the ith reaction (at time point t) is

\[ X_i(t) = X_{i0}[1 - \exp(-k_i(t))] \] \hspace{1cm} (2)

where

\[ k_i = A_i \exp\left(-\frac{E_i}{RT}\right) \] \hspace{1cm} (3)

where X is the total amount of gas generation at time point t (mL/g TOC), X\textsubscript{i0} the original amount of potential gas generation of the ith reaction at time point t (mL/g TOC), k\textsubscript{i} the Arrhenius reaction rate factor of the formation of the ith gas, t the time (h), E\textsubscript{i} the activation energy (J/mol), A\textsubscript{i} the frequency factors (s\textsuperscript{-1}), R the universal gas constant (R = 8.31441 J/(mol K)), and T the absolute temperature (K).

The experimental data and theoretical calculations of the natural gas generation potential were fitted and optimized using BasinMod 1D software. Furthermore, the chemical kinetic parameters, including the activation energy (E\textsubscript{i}), the frequency factor (A\textsubscript{i}), and the original potential of kerogen (X\textsubscript{i0}), of a number n of parallel first-order reactions were determined for each kerogen component.\textsuperscript{27,28}

3.2. Source Rocks of the Wenchang Formation. The composition and structure of kerogen depends on the origin of the organic matter from which it has evolved, as well as its degree of evolution. Based on the carbon, hydrogen, and oxygen content, kerogens are usually classified into three main types (from the work of Tissot and Welte\textsuperscript{26}). There have been two additional subclassifications: Type-II\textsubscript{1} and Type-II\textsubscript{2}. Type-II\textsubscript{1} is a kerogen of mixed origin that contains lipids with a hydrogen:carbon ratio (H/C) ranging from 1.0 to 1.4, an oxygen:carbon ratio (O/C) ranging from 0.10 to 0.15, a...
hydrogen index ($I_H$) ranging from 450 mg/g TOC to 650 mg/g TOC, and an oxygen index ($I_O$) ranging from 25 mg/g to 50 mg/g. Type-II$_2$ is commonly rich in aromatic hydrocarbons with a hydrogen:carbon ratio (H/C) ranging from 0.8 to 1.0, an oxygen:carbon ratio (O/C) ranging from 0.15 to 0.20, a hydrogen index ($I_H$) ranging from 100 mg/g TOC to 450 mg/g TOC, and an oxygen index ($I_O$) of >50 mg/g. 

The geochemical analysis of the crude oil, collected from the core samples of the Zhujiang Formation north of the BYS, suggested it was from the deep Wenchang Formation. In addition, the high concentration of 4-methylsterane in the oil indicates that the Wenchang Formation in the Zhu II Depression has developed the deep lacustrine source rocks, similar to the source rocks in the Zhu I Depression. The Wenchang Formation of the Huizhou Sag in the Zhu I Depression primarily developed grayish-black deep lacustrine to shore-shallow lacustrine mudstones, interbedded with gray sandstone and coal bed in some areas. The organic matter in the deep lacustrine source rocks is higher than that in the shore-shallow lacustrine source rocks (see Figure 5 and Table 1). 

The kerogen of the deep lacustrine mudstones are mainly Type-I and Type-II$_1$, whereas the kerogen of the shore-shallow lacustrine mudstones are Type-II$_2$ and Type-III (Figure 6). In the Huizhou Sag, the Wenchang source rocks discovered in well LF13-2-1 are controlled primarily by a third-order/fourth-order sequence and characterized by a relatively high abundance of organic matter (Figure 7). 

The tectonic evolution, sedimentary environment, and source rocks of the Zhu II Depression are well-correlated with the Zhu I Depression. The Wenchang source rocks in the BYS are primarily composed of deep lacustrine mudstones, which are similar to the source rocks in the Zhu I Depression (see Figure 5), and the kerogen H/C ratios range from 1.0 to 1.5 and are mostly 1.2. The microscopic examination shows that the kerogen is primarily Type-II$_1$, and the chromatographic characteristics of the pyrolysis gas show that the kerogen is Type-I and Type-II$_1$. The Wenchang source rocks in the BYS have a relatively high hydrogen index ($I_H$), in the range of 446–566 mg/g TOC. The TOC content of the Wenchang source rocks ranges from 0.75% to 24.84%, with a mean value of 3.21%. The highest TOC value of 24.84% was found in the deep lacustrine grayish-brown mudstones drilled from the well PY27-2-1 (Table 2). The sources rocks of the Wenchang Formation have high hydrocarbon generation potentials, ranging from 8.18 mg/g to 13.64 mg/g. The majority of the lacustrine source rocks of the Wenchang Formation are at the late mature stage to main gas generation stage.

### 3.3. Thermocompression Simulation Experiment.

There are three types of pyrolysis systems: an open system, an anhydrous closed system, and a closed system. Natural gas is more likely to be generated under closed and semiclosed geological conditions than under open geological conditions. Thus, the experiment was performed under confined system conditions using a closed gold-tube autoclave system at the Provincial Petroleum Laboratory of the Research Institute of Petroleum Exploration & Development of the PetroChina North China (Huabei) Oilfield Company. The experimental instruments primarily consisted of the following three parts:

1. the reaction kettle, which functions under a designed pressure of 19.6 MPa and is manufactured by Dalian Automatic Control Equipment Factory (Liaoning, China) (Model GCF-0.25L); 
2. the temperature controller with a digital regulator (Model XMT-131); and 
3. the experimental setup.

<table>
<thead>
<tr>
<th>facies</th>
<th>total organic carbon content, TOC (%)</th>
<th>hydrocarbon generation potential, $S_1 + S_2$ (mg/g)</th>
<th>highest pyrolysis peak temperature, $T_{max}$ (°C)</th>
<th>hydrogen index, $I_H$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>deep lacustrine</td>
<td>3.06 (7.75–1.93)/17</td>
<td>12.33 (28.82–0.64)/17</td>
<td>438.41 (442–434)/17</td>
<td>410.35 (606–268)/17</td>
</tr>
<tr>
<td>Shore-Shallow lacustrine</td>
<td>1.33 (3.31–0.61)/26</td>
<td>1.75 (4.02–0.6)/26</td>
<td>447.23 (461–441)/26</td>
<td>114.88 (162–71)/26</td>
</tr>
</tbody>
</table>

“Data taken from ref 33. Average given as the range of values (maximum to minimum)/number of samples.
The adopted method in this experiment involves heating the original samples separately at several separate temperature levels; that is, at each temperature value, the original samples react in an enclosed system and the presumed outcomes would not be isolated from this system. Eight temperature values at 200, 250, 275, 300, 325, 350, 400, and 500 °C are chosen to explore the stages of thermal evolution of the source rock. For each simulated temperature, 80 g of the sample with the grain size of 5–10 mm was added to the reaction kettle with deionized water that amounts to a concentration of 10–20 wt %. The reactor was first tested for leakage by repeating the tests by filling and vacuum pumping the nitrogen at a pressure of 4–6 MPa 3–5 times. The evacuated reactor was then heated to a series of temperatures in a closed system. When the simulated temperature is no more than 300 °C, the heating time can be 24, 48, or 72 h. In contrast, when the simulated temperature is no less than 325 °C, the heating time must be limited to <24 h. The evacuated reactor was maintained for 24 h at a set temperature in a closed system. The gas and liquid produced were collected for analysis once a reaction was completed.

4. RESULTS AND DISCUSSION

4.1. Results. The thermocompression simulation experiment conducted on the brown mudstone of the Wenchang Formation from well LF13-2-1 has eight points within the temperature range from 200 °C to 500 °C. The parameters, such as the gas generation rate, oil generation rate, and the hydrocarbon generation rate, were obtained from each temperature point (see Table 4).

The original sample contains a certain amount of oil, which made the initial oil generation ∼100 kg/t TOC (see Figure 8). As the maturity increased, the organic matter evolved from the

Table 2. Source Rock Characteristics of the Wenchang Formation in the PRMB

<table>
<thead>
<tr>
<th>well</th>
<th>depth (m)</th>
<th>thickness (m)</th>
<th>hydrocarbon content, HC (%)</th>
<th>facies</th>
<th>TOC (%)</th>
<th>H (mg/g TOC)</th>
<th>I$_{fi}$ (mg/g TOC)</th>
<th>T$_{max}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PY27-2-1</td>
<td>4624–4791</td>
<td>37.99</td>
<td>22.75</td>
<td>deep lacustrine</td>
<td>7.93 (0.75–24.84)/12</td>
<td>117 (85–150)/5</td>
<td>463 (451–524)/12</td>
<td></td>
</tr>
<tr>
<td>XJ24-1-1</td>
<td>3601–3776</td>
<td>26.78</td>
<td>15.30</td>
<td>fluvial</td>
<td>0.72 (0.08–1.44)/17</td>
<td>142 (91–220)/17</td>
<td>443 (436–450)/17</td>
<td></td>
</tr>
<tr>
<td>HFZ11-1-1</td>
<td>4228–4456</td>
<td>93.71</td>
<td>41.10</td>
<td>shallow lacustrine</td>
<td>0.96 (0.06–1.8)/23</td>
<td>116 (69–200)/23</td>
<td>455 (418–470)/23</td>
<td></td>
</tr>
<tr>
<td>LF13-2-1</td>
<td>3140–3280</td>
<td>115.5</td>
<td>82.50</td>
<td>deep lacustrine</td>
<td>3.19/(2.02–7.75)/17</td>
<td>411 (269–705)/17</td>
<td>440 (437–444)/17</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Description of Source Rock Samples Used in the Study

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>well</td>
<td>LF13-2-1</td>
</tr>
<tr>
<td>depth (m)</td>
<td>3126.5–3167.5 m</td>
</tr>
<tr>
<td>color</td>
<td>brown</td>
</tr>
<tr>
<td>facies</td>
<td>deep lacustrine</td>
</tr>
<tr>
<td>total organic content, TOC (%)</td>
<td>2.02</td>
</tr>
<tr>
<td>H (mg/g TOC)</td>
<td>502</td>
</tr>
<tr>
<td>I$_{fi}$ (mg/g TOC)</td>
<td>440</td>
</tr>
<tr>
<td>T$_{max}$ (°C)</td>
<td>0.56</td>
</tr>
<tr>
<td>reflectance of vitrinite, Ro (%)</td>
<td>440</td>
</tr>
</tbody>
</table>
are in agreement with the patterns of Tissot and Welte.\textsuperscript{28} The characteristics of the sample generation rate of 347.48 kg/t TOC were achieved (see Figure 8). The generation rate of 379.79 kg/t TOC and a maximum gas value of Ro reached 3.13% in the experiment, the maximum oil generated as the value of Ro increased beyond 2%. When the value of Ro reaches 1.92%. A large amount of dry gas was levels, which slightly increases the oil generation rates when the Type-I, with some highly stable bonds cracking at high maturity (Ro values of 1.25%) first degraded to generate hydrocarbons at high temperatures and maturity, and the components bond energy are breakdown of macromolecular matter. Components with low transformation in sedimentary basins is a result of the thermal catalysis hydrocarbon-generation stage (the Ro value ranges from 0.7% to 1.2%) to the oil-cracking gas stage (the Ro value ranges from 1.2% to 2.0%). The amount of oil generation from kerogens is less than the amount of secondary cracking of oil, and the rate of oil generation decreased as the value of Ro increased beyond 0.94%. During the main hydrocarbon-generation stage, the range of the Ro values was between 0.7% and 1.15%, and the rate of the hydrocarbon generation increased dramatically, reaching a peak of 179.56 kg/t TOC when the Ro value reached 0.94%. During the main gas-generation stage (Ro values of 1.15%–1.25%), a large amount of gas was generated rapidly. The sample has experienced a high maturity (Ro values of 1.25%–2.0%), and the generation rate of hydrocarbons increased steadily. The organic matter degradation in sedimentary basins is a result of the thermal breakdown of macromolecular matter. Components with low bond energy are first degraded to generate hydrocarbons at relatively low temperatures and maturity, and the components with higher bond energy are cracked at relatively higher maturity levels. The kerogen of the source rock sample is composed of 71.43% Type-II\textsubscript{1}, 19.05% Type-II\textsubscript{2}, and 9.52% Type-I, with some highly stable bonds cracking at high maturity levels, which slightly increases the oil generation rates when the value of Ro reaches 1.92%. A large amount of dry gas was generated as the value of Ro increased beyond 2%. When the value of Ro reached 3.13% in the experiment, the maximum oil generation rate of 379.79 kg/t TOC and a maximum gas generation rate of 347.48 kg/t TOC were achieved (see Figure 8). The characteristics of the sample’s hydrocarbon generation are in agreement with the patterns of Tissot and Welte.\textsuperscript{28}

### 4.2. Hydrocarbon Generation Kinetic Parameter Correction

The hydrocarbon generation process of the brown mudstone of the Wenchang Formation from well LF13-2-1 was simulated by using the BasinMod 1D software to obtain the optimal fit between the numerical simulation and the thermocompression experimental data.\textsuperscript{60,61} The kinetic parameters of the source rocks of the Wenchang Formation, such as the activation energy, hydrocarbon generation potential, and crude-oil cracking parameters, were obtained (Table 5). The numerical simulation is consistent overall with the thermocompression experimental results (see Figure 9), except for the hydrocarbon conversion rate at 84% (Ro = 1.92%), when the numerical simulation is higher than experimental results.

Components with low bond energy would be first degraded to generate hydrocarbons at low temperatures and maturity. In contrast, the components with high bond energy would only degrade to generate hydrocarbons when the temperature and maturity are high.\textsuperscript{62,63} The range of activation energies is 46–63 kcal/mol, and the relatively broad distribution of the hydrocarbon generation potential is skewed negatively (see Figure 10). A relatively broad distribution of activation energies are directly related to the heterogeneity of kerogens.\textsuperscript{61} The activation energies of hydrocarbon generation of kerogen were primarily concentrated between 54 kcal/mol and 59 kcal/mol when hydrocarbon generation potentials were more than 8%. Most hydrocarbon generation potentials of crude oil cracking are higher than 10% and distributed discretely. The highest hydrocarbon generation potential of crude oil cracking is 35%, when the activation energy reaches 53 kcal/mol (Figure 10).

### Table 4. Production of Gas and Liquid during the Pyrolysis Process of the Samples

<table>
<thead>
<tr>
<th>Simulation temperature (°C)</th>
<th>Sample amount (g)</th>
<th>TOC (%)</th>
<th>Gas yield (kg/t TOC)</th>
<th>Condensate oil (kg/t TOC)</th>
<th>Light oil (kg/t TOC)</th>
<th>Remaining oil (kg/t TOC)</th>
<th>Oil yield (kg/t TOC)</th>
<th>Hydrocarbon yield (kg/t TOC)</th>
<th>Ro (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original sample</td>
<td>80</td>
<td>2.02</td>
<td>0</td>
<td>0</td>
<td>105.04</td>
<td>105.04</td>
<td>105.04</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>80</td>
<td>2.02</td>
<td>0.20</td>
<td>19.99</td>
<td>20.98</td>
<td>62.35</td>
<td>103.31</td>
<td>0.64</td>
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<tr>
<td>250</td>
<td>80</td>
<td>2.02</td>
<td>2.28</td>
<td>34.59</td>
<td>29.58</td>
<td>30.66</td>
<td>94.83</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>275</td>
<td>80</td>
<td>2.02</td>
<td>19.13</td>
<td>65.90</td>
<td>39.98</td>
<td>37.76</td>
<td>143.64</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>80</td>
<td>2.02</td>
<td>35.21</td>
<td>100.93</td>
<td>57.36</td>
<td>21.26</td>
<td>179.56</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>80</td>
<td>2.02</td>
<td>96.16</td>
<td>132.67</td>
<td>16.27</td>
<td>6.03</td>
<td>154.98</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>80</td>
<td>2.02</td>
<td>216.88</td>
<td>26.42</td>
<td>24.94</td>
<td>4.15</td>
<td>55.51</td>
<td>1.27</td>
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<tr>
<td>400</td>
<td>60</td>
<td>2.02</td>
<td>234.28</td>
<td>34.32</td>
<td>45.38</td>
<td>4.64</td>
<td>84.34</td>
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<tr>
<td>500</td>
<td>50</td>
<td>2.02</td>
<td>347.48</td>
<td>10.59</td>
<td>17.82</td>
<td>3.90</td>
<td>32.32</td>
<td>3.13</td>
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</tbody>
</table>

**Figure 8.** Relationship between the hydrocarbon generation rates and the Ro values of the samples.

**Table 5. Kinetic Parameters of Catalytic Degradation of the Samples**

<table>
<thead>
<tr>
<th></th>
<th>Hydrocarbon Generation of Kerogen</th>
<th>Crude Oil-Cracking Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_i$ (%)</td>
<td>$E_i$ (kcal/mol)</td>
</tr>
<tr>
<td>1</td>
<td>46</td>
<td>$3.18 \times 10^{11}$</td>
</tr>
<tr>
<td>2</td>
<td>48</td>
<td>$3.18 \times 10^{11}$</td>
</tr>
<tr>
<td>3</td>
<td>49</td>
<td>$3.18 \times 10^{11}$</td>
</tr>
<tr>
<td>5</td>
<td>51</td>
<td>$3.18 \times 10^{11}$</td>
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<td>$3.18 \times 10^{11}$</td>
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<td>$3.18 \times 10^{11}$</td>
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<td>8</td>
<td>54</td>
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<td>9</td>
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<td>7</td>
<td>61</td>
<td>$3.18 \times 10^{11}$</td>
</tr>
<tr>
<td>6</td>
<td>62</td>
<td>$3.18 \times 10^{11}$</td>
</tr>
<tr>
<td>5</td>
<td>63</td>
<td>$3.18 \times 10^{11}$</td>
</tr>
<tr>
<td>4</td>
<td>64</td>
<td>$3.18 \times 10^{11}$</td>
</tr>
</tbody>
</table>

$X_i$ is the original amount of potential gas generation, where $i = 1, 2, \ldots; N_i$; $E_i$ is the activation energy; and $A_i$ is the frequency factor.
The components with high activation energy have larger initial hydrocarbon generation potentials, compared to the components with low activation energy, because the low-activation-energy components may vanish with increasing maturity.

The organic matter in lacustrine kerogens is generally described as very homogeneous, compared with other types of organic matter. Lacustrine source rocks, such as the Green River Formation, are usually associated with oil accumulation. The Green River shale is a typical lacustrine source rock, and its kerogen type is Type-I. The colors are generally light brown, dark brown, dark gray to black, and they are enriched in lipids. The characteristics of biomarkers of shale in the Green River Formation, including isoprenoid, steranes, and terpanes, showed that the organic matter is mainly from aquatic organisms, including bacteria and algae, and the shale formed in a high reduction environment. The main organic matter composition is lacustrine planktonic algae and includes a small amount of vitrinite, intortodetrinite, alginite, and bituminite.

Existing research has discussed the kinetic model of the lacustrine Green River shale (see Figure 11 and Table 6) in the Uinta Basin. The variability of chemical bonds of the lacustrine Green River shale is described with a single dominating activation energy of 57 kcal/mol, with a frequency factor of $1.8451 \times 10^{13}$ 1/m. This bond energy is characterized as being thermally stable, compared to other types of organic matter. The very limited distribution range of activation energy supports the homogeneous kerogens of the Green River shale.

Compared to the lacustrine Green River, the kinetic evaluation of the Wenchang Formation results in a relatively broad activation energy distribution and a lower frequency factor of $3.18 \times 10^{11}$ 1/m (minute). The type of kerogen in the Wenchang Formation sample is primarily Type-II, and contains 3.52% sapropelinite, 17.03% exinite, 65.16% exinite–vitrinite hybrid (a mixture of a relatively high content of sapropelinite and exinite in vitrinite), 13.18% vitrinite, and 0.37% inertinite. The lacustrine organic matter of the Wenchang Formation contains aquatic organisms, such as planktonic algae. Deep lacustrine source rocks formed in a reduction environment, and shore-shallow lacustrine source rocks formed in a weak oxidation environment. The broad activation energy distribution supports the high level of heterogeneity of the Wenchang Formation source rock, which is clearly different from the Green River shale.

**4.3. Gas Generation Analysis.** In this paper, the rifting and post-rift subsidence process of the BYS was simulated via forward and inverse modeling. Numerous measured vitrinite reflectance values are used to examine the simulation results under an extensional basin model. When the “simulated” Ro values have fitted the “measured” Ro values reasonably well, the geologic model provided the process of thermal evolution. Based on the thermal evolution simulation of four wells, the hydrocarbon generation process of the Wenchang Formation source rock in the BYS was established by the obtained kinetic parameters.

**4.3.1. Thermal History.** Thermal history is important to the timing, amount, and composition of hydrocarbon generation. The present-day heat flow is calculated from thermal conductivities of the rocks and the subsurface geothermal gradients, which are determined by measured temperatures. Paleoheat flow is affected by the tectonic evolution of the BYS, which dominated by lithospheric stretching during the Paleocene to early Oligocene rifting period and subsequent regional subsidence from Miocene to Quaternary. The heat flow measurements reported by Shi et al. were used to establish the geological model in this study. Four simulation wells (marked in Figure 1) were established to analyze the burial and thermal evolution in the study area. The Wenchang Formation is divided into two sections to describe the burial and thermal evolution (Figure 12), which are the

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**Table 6. Rock-Eval TOC Characteristics of the Sample from the Green River Shale**

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
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</tr>
<tr>
<td>$I^H$</td>
<td>900</td>
</tr>
<tr>
<td>$T_{\text{max}}$</td>
<td>438</td>
</tr>
<tr>
<td>$I_0$</td>
<td>2</td>
</tr>
<tr>
<td>type</td>
<td>Type-I</td>
</tr>
</tbody>
</table>

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**Figure 9.** Comparison of hydrocarbon conversion between the actual measurements of the thermocompression experiment data and the numerical simulation results from well LH13-2-1.

**Figure 10.** Activation energy distributions of the hydrocarbon generation of kerogen and crude oil cracking from well LF13-2-1.

**Figure 11.** Bulk kinetic parameters from the programmed pyrolysis from the Green River shale.

**Figure 12.**
further evolved into the main gas-generation stage, with the period from 32.5 Ma to 26 Ma. The Wenchang Formation into the late mature stage, with the Ro = 1.0% during the period from 39 Ma to 32.5 Ma, and then evolved into the overmature stage. The bottom of the Wenchang Formation (WC-bot) was in the middle mature stage, with Ro = 0.7%–1.0% from 32 Ma to 27.8 Ma, the late mature stage with Ro = 1.0%–1.3% during the depositional period of the Zhuhai Formation (30–23.5 Ma), the main gas-generation stage with Ro = 1.3%–2.0% from 25.2 Ma to 20.5 Ma, and the dry gas-generation stage, with Ro > 2.0% from 15 Ma to the present (see Figure 14).

Based on the degrees of evolution of different sections, the thermal evolution of the Wenchang Formation can be divided into three stages: the middle mature stage, from 39 Ma to 30 Ma; the late mature stage during the sedimentation period of the Zhuhai Formation (30–23.5 Ma); and the main gas-generation stage, from 23.5 Ma to the present.

4.3.2. Stage of Gas Generation. Overall, most of the organic matter in the source rocks of the Wenchang Formation evolved into the stage of secondary crude oil cracking gas and overmature oil-type kerogen cracking gas. At present, the source rocks of the Wenchang Formation generated a small amount of oil in the eastern area (well 3) and the northern area (well 2). The source rocks of the Wenchang Formation are mainly in the stage of gas generation (Figure 15).

The gas generation rates at the top of the Wenchang Formation were simulated in four simulation wells (see Figure 4). The central area (well 1) has a main gas-generation stage, which began from 23 Ma to 20 Ma. The hydrocarbon generation peak occurred at ~22 Ma, with a current gas generation of 430 mg/g TOC (Figure 15a). The main gas generation in the northern area (well 2) began 23.5 Ma until 10.5 Ma, and the hydrocarbon generation peak occurred at ~15 Ma, with a current gas generation of 370 mg/g TOC (Figure 15b). The main gas generation in the eastern area (well 3) began at ~16.5 Ma to 10.5 Ma, and the hydrocarbon generation peak occurred at ~15 Ma, with a current gas generation of 280 mg/g TOC (Figure 15c). In the central and western area, the main gas generation (well 4) began at ~24 Ma to 14 Ma, and the hydrocarbon generation peak occurred at ~23 Ma, with a current gas generation of 430 mg/g TOC (Figure 15d). The simulation results of the BYS show that the hydrocarbon generation peak (~24–22 Ma) in the central area appeared earlier than that (~15 Ma) in the eastern and northern areas.

Because the BYS is located in the continental transitional crust of the northern SCS, Cenozoic structural movements have strongly deformed the sag, which is characterized by the greatly thinned lithosphere and active magmatism. The BYS developed thicker sedimentary sequences in the central area than on both sides of the northern slope and southern uplift and also developed thick lacustrine source rocks in the Eocene Wenchang Formation during the rifting stage. Starting at 23.8 Ma, the BYS evolved from rifting to post-rifting thermal subsidence and became the center of subsidence and deposition in the PRMB. The rising mantle under the BYS caused a partial melting of the upper mantle, which accommodated extensional strain and caused nonfaulted vertical subsidence. In the center of the BYS, the tectonic subsidence and sedimentation rate is larger than other areas. Therefore, the thermal subsidence in BYS is the reason for the earlier peak in hydrocarbon generation in the central area. Furthermore, the total gas generation (~430 mg/g TOC) in the central area was apparently higher than that of the eastern (310 mg/g TOC) and northern (370 mg/g TOC) areas.

Figure 12. Temperature modeling and burial history in well 3. [Formation names: WC-bot = the bottom of the Wenchang Formation; WC1 = the lowstand system tract of the Wenchang Formation; WC2 = the lake transgression and the highstand system tracts of the Wenchang Formation; EP1 = the lower part of the Enping Formation; EP2 = the upper part of the Enping Formation; ZH = the Zhuhai Formation; ZJ1 = the lower part of the Zhuhai Formation; ZJ2 = the upper part of the Zhuhai Formation; HJ1 = the lower part of the Hanjiang Formation; HJ2 = the upper part of the Hanjiang Formation; and Yh-Q = the Yuehai Formation to Quaternary.] The locations of the modeled wells are shown in Figure 1.

Figure 13. Simulated Ro modeling matches with the measured Ro data in well 3.

The Wenchang Formation source rocks are currently in an overmature stage. The bottom of the Wenchang Formation (WC-bot) was in the middle mature stage, with Ro = 0.7%–1% during the period from 39 Ma to 32.5 Ma, and then evolved into the late mature stage, with the Ro = 1.0%–1.3% during the period from 32.5 Ma to 26 Ma. The Wenchang Formation further evolved into the main gas-generation stage, with the value of Ro being >1.3% during the period from 26 Ma to the present. The top of the Wenchang Formation also has experienced multiple thermal stages, which are the middle mature stage, with Ro = 0.7%–1.0% from 32 Ma to 27.8 Ma, the late mature stage with Ro = 1.0%–1.3% during the depositional period of the Zhuhai Formation (30–23.5 Ma), the main gas-generation stage with Ro = 1.3%–2.0% from 25.2 Ma to 20.5 Ma, and the dry gas-generation stage, with Ro > 2.0% from 15 Ma to the present (see Figure 14).
Figure 14. Thermal and maturity history of the Wenchang Formation at well 1. (The locations of the modeled well are shown in Figure 1. [Formation names: WC-bot = the bottom of the Wenchang Formation; WC1 = the lowstand system tract of the Wenchang Formation; WC2 = the lake transgression and the highstand system tracts of the Wenchang Formation; EP1 = the lower part of the Enping Formation; EP2 = the upper part of the Enping Formation; ZH = the Zhuhai Formation; ZJ1 = the lower part of the Zhujiang Formation; ZJ2 = the upper part of the Zhujiang Formation; HJ1 = the lower part of the Hanjiang Formation; HJ2 = the upper part of the Hanjiang Formation; and Yh-Q = the Yuehai Formation to Quaternary.] The locations of the modeled wells are shown in Figure 1.

Figure 15. Cumulative amount and rate of gas generation of modeled wells. The locations of modeled wells are shown in Figure 1. System Epoch: E, eocene; O, oligocene; M, miocene; P, pliocene.
5. CONCLUSIONS

In this study, the thermocompression experimental data and the simulation results were well fitted during the hydrocarbon generation process, and the hydrocarbon generation characteristics of the Wenchang lacustrine mudstones were investigated based on a hydrocarbon generation kinetic equation.

(1) The thermocompression simulation experiment showed that the brown mudstones from well LH13-2-1 had a hydrocarbon generation rate of 377.97 kg/t TOC and a gas generation rate of 347.48 kg/t TOC.

(2) The activation energy of the brown mudstones from well LH13-2-1 primarily ranges from 46 kcal/mol to 63 kcal/mol, and their hydrocarbon generation potentials had a negatively skewed distribution. The activation energies of the hydrocarbon generation of kerogen were concentrated within the range from 54 kcal/mol to 59 kcal/mol, while the hydrocarbon generation potentials were >8%. The hydrocarbon generation potential of crude oil cracking were mostly >10% and were distributed discretely with a peak at 35% when the activation energy was 53 kcal/mol.

(3) The thermal evolution of the Wenchang Formation can be generally divided into three stages: the middle mature stage, during the period from 39 Ma to 30 Ma; the late mature stage, during the sedimentation period from 30 Ma to 23.5 Ma; and the main gas-generation stage, from 23.5 Ma to the present.

(4) The central area of the BYS has a gas generation peak from 23 Ma to 22 Ma, which was earlier than that (~15 Ma) of the northern area and the western area.

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Notes
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