Acta Oceanol. Sin., 2018, Vol. 37, No. 1, P. 50–59
DOI: 10.1007/s13131-018-1158-8
http://www.hyxb.org.cn
E-mail: hyxbe@263.net

Chemical kinetics evaluation and its application of natural gas generation derived from the Yacheng Formation in the deep-water area of the Qiongdongnan Basin, China

SU Long[1*], ZHANG Dongwei[1, 2], YANG Haizhang[3], CHEN Ying[3], CHEN Guojun[1], ZHENG Jianjing[1], XU Yongchang[1]

[1] Key Laboratory of Petroleum Resources, Gansu Province/Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Sciences, Lanzhou 730000, China

[2] University of Chinese Academy of Sciences, Beijing 100049, China

[3] Research Center of China National Offshore Oil Corporation, Beijing 100027, China

Received 20 January 2017; accepted 31 May 2017

Abstract

The natural gas generation process is simulated by heating source rocks of the Yacheng Formation, including the onshore-offshore mudstone and coal with kerogens of Type II_2-III in the Qiongdongnan Basin. The aim is to quantify the natural gas generation from the Yacheng Formation and to evaluate the geological prediction and kinetic parameters using an optimization procedure based on the basin modeling of the shallow-water area. For this, the hydrocarbons produced have been grouped into four classes (C_1, C_2, C_3 and $C_{4\text{-}6}$). The results show that the onset temperature of methane generation is predicted to occur at 110°C during the thermal history of sediments since 5.3 Ma by using data extrapolation. The hydrocarbon potential for ethane, propane and heavy gaseous hydrocarbons ($C_{4\text{-}6}$) is found to be almost exhausted at geological temperature of 200°C when the transformation ratio (TR) is over 0.8, but for which methane is determined to be about 0.5 in the shallow-water area. In contrast, the end temperature of the methane generation in the deep-water area was over 300°C with a TR over 0.8. It plays an important role in the natural gas exploration of the deep-water basin and other basins in the broad ocean areas of China. Therefore, the natural gas exploration for the deep-water area in the Qiongdongnan Basin shall first aim at the structural traps in the Ledong, Lingshui and Beijiao sags, and in the forward direction of the structure around the sags, and then gradually develop toward the non-structural trap in the deep-water area basin of the broad ocean areas of China.

Key words: deep-water area, geological prediction, natural gas, Yacheng Formation, evaluation, Qiongdongnan Basin

Citation: Su Long, Zhang Dongwei, Yang Haizhang, Chen Ying, Chen Guojun, Zheng Jianjing, Xu Yongchang. 2018. Chemical kinetics evaluation and its application of natural gas generation derived from the Yacheng Formation in the deep-water area of the Qiongdongnan Basin, China. Acta Oceanologica Sinica, 37(1): 50–59, doi: 10.1007/s13131-018-1158-8

1 Introduction

The Qiongdongnan Basin (QDNB), to the southeast of Hainan Island, is an important Cenozoic sedimentary basin with rich oil and gas resources in the northern continental shelf of the South China Sea. The gas resources of the QDNB are estimated to be more than 1.0×10^{11} m^3 (Gong et al., 1997). A number of depressions and uplifts have developed within the basin. Its sedimentary sequences, from bottom to top, are listed as follows: Eocene, Yacheng Formation (early Oligocene), Lingshui Formation (late Oligocene), Sanya Formation (early Miocene), Meishan Formation (middle Miocene), Huangliu Formation (late Miocene), Yinggehai Formation (Pliocene), and Ledong Formation (Quaternary), respectively. This area experienced multi-episodic extensional rifting (Hu et al., 2013), and therefore multi-episodic heating events in the Cenozoic period (He et al., 2001; Yuan et al., 2009; Zhang et al., 2012, 2014). The initial, early, and late rifting phases corresponded to the Paleocene, Eocene, and Oligocene heating events, respectively.

The current geothermal fields in the QDNB have been discussed in a series of studies (He et al., 2001; Shi et al., 2003; Yuan et al., 2009; Zhang et al., 2010, 2014, 2016; Wu et al., 2013). The recent advances in research are associated with the “hot basin”, i.e., high heat flow, high-maturity and high geothermal gradient, associated with the basin developed in the southern area of the China's mainland, attributed to the QDNB characterized with a large subsidence since 5.3 Ma (Su et al., 2012b). The western area of the QDNB is a deep depression containing Cenozoic strata with more than 10 km thickness in particular. The maximum of the burial depth with prominent local sag in the central depression belt is about 12 km, such as in the Ledong sag, according to

Foundation item: The Western Light Talent Culture Project of the Chinese Academy of Sciences under contract No. Y404RC1; the National Petroleum Major Projects of China under contract No. 2016ZX05026-007-005; the Key Laboratory of Petroleum Resources Research Fund of the Chinese Academy of Sciences under contract No. KFJJ2013-04; the Science and Technology Program of Gansu Province under contract No. 1501RJYA006; the Key Laboratory Project of Gansu Province of China under contract No. 1309RTSA041.
*Corresponding author, E-mail: longsu@lzb.ac.cn

the drilling data and seismic data (Zhu et al., 2007, 2008; Zhang et al., 2010, 2016; Zhao et al., 2015). Therefore, the hydrocarbon source rocks of Yacheng Formation were buried deeply at a high subsidence rate and matured rapidly, and have also reached high-maturity or over-mature stages (Huang et al., 2003, 2012). The hydrocarbon source rocks of Yacheng Formation, including coal, carbonaceous mudstone and dark mudstone, in the QDNB with kerogens of Type II_2-III are the most important gas-potential source rocks (Zhu et al., 2008; Zhang et al., 2012). The timing and extent of natural gas generation depends on the burial history of a source rock interval and the type of organic matter preserved therein. The reaction kinetics of the natural gas generation from Yacheng Formation or associated kerogen mainly results from the thermal breakdown of macromolecular organic matter to oil and gas (Whiticar, 1990; Dieckmann et al., 2004). The application of the basin modelling procedures, permits the prediction of organic matter transformation to oil and gas, under variable geological conditions. Simplified kinetic models are commonly applied, with a distribution of activation energies and a single average frequency factor (Ungerer and Pelet, 1987; Krooss et al., 1993, 1995). When conducted under controlled time-temperature conditions, at different heating rates (Schaefer et al., 1990, Schenk and Horsfield, 1998; Dieckmann et al., 2004; Schenk and Dieckmann, 2004; Li et al., 2008), the measured natural gas generation rate versus temperature curves provide reliable input data for the calculation of kinetic parameters. This, in turn, allows extrapolation from laboratory to geological heating rates, which are ten orders of magnitude lower (Dieckmann et al., 2004; Schenk and Dieckmann, 2004; Li et al., 2008).

The experience gained from kinetic modeling of the natural gas generation has little application in the investigation of the natural gas generation process in the deep-water area. The aim of this study is to predict the natural gas generation from source rocks of Yacheng Formation in the deep-water area with lower exploration, by using accepted protocols, evaluation kinetic parameters, and geological extrapolations. The research will focus on the formation of methane, ethane, propane, and heavy gaseous hydrocarbons (C_{4-6}) in the gas fractions, by the use of non-isothermal open system pyrolysis and the kinetics methods. A major aspect of the study is to combine the laboratory-derived kinetic data, with a realistic temperature history of the basin modeling, obtained from the Ya13-1 gas field of the Yanan sag, and Wells YC26-1-1 and YC21-1-4 (Hu et al., 2005) of the shallow-water area in the QDNB were selected, of which the basic geological conditions for the migration and accumulation model are similar to those of the deep-water area (Zhu et al., 2007; Zhang et al., 2010, 2014).

2 Materials and methods

2.1 *Sampling*

Owing to the lower exploration for oil and gas in the deep-water area of the QDNB (Gong et al., 1997; Zhu et al., 2007; Zhang et al., 2012, 2014, 2016), the core samples of Yacheng Formation are collected from the shallow-water area of the QDNB (Fig. 1). The total organic carbon (TOC) and the pyrolysis data of the rocks were determined by a Rock-Eval VI instrument. The organic geochemical characteristics of the samples are listed in Table 1. The data clearly show that the type of organic matter of the source rocks from the Yacheng Formation is Type II_2-III.

2.2 *Method*

In order to investigate the prediction and the natural gas generation from Yacheng Formation in the QDNB with a high geothermal gradient (4.0°C every 100 m), the method of anhydrous pyrolysis was contacted under open-system conditions and this method provided the closest approach to primary cracking reactions of kerogen to gas rather than oil to gas. In each experiment, the organic material of the whole rock was pyrolysed by an apparatus of an open-system non-isothermal pyrolysis (Krooss et al., 1993, 1995; Schaefer et al., 1990; Dieckmann et al., 2004). Similar experiments were conducted, the whole rocks were pyrolysed at heating rates of 2°C/min and 20°C/min, using a furnace set up from 250°C (initial temperature) to up to 1 100°C (final temperature). The processing of the experiment is shown in Su et al. (2012a). For compositions analysis of the hydrocarbon gas, the gas sample and carrier gas were carried from a glass flask into a gas chromatography (Agilent 6890) unit, and the gaseous hydrocarbons were separated and quantified by a gas chromatographic analysis. The rates of generation for methane, ethane, propane and heavy gaseous hydrocarbons (C_{4-6}) were calculated by using the respective peak areas and the known concentration of the components in the calibration standard. Additionally, the experimental data, as shown in Table 2, was performed according to the scheme, the distribution of activation energy and a pre-exponential factor were obtained by special kinetics software 2005.

3 Results and discussion

3.1 *Distributed model*

According to the distributed kinetic model, the natural gas generation yield versus the temperature was analyzed. The activation energies of dark mudstone and coal, which ranges from 188 to 400 kJ/mol and 188 to 400 kJ/mol, respectively, and the pre-exponential factor was also calculated. The activation energies and the corresponding pre-exponential factors from the dark mudstone for methane, ethane, propane, and heavy gaseous hydrocarbons obtained from this evaluation, ranging from 188 to 400 kJ/mol at 5.66×10^{11} s^{-1}, from 192 to 380 kJ/mol at 1.28×10^{12} s^{-1}, from 196 to 360 kJ/mol at 3.64×10^{15} s^{-1}, from 202 to 350 kJ/mol at 7.34×10^{15} s^{-1} (Fig. 2), respectively. In contrast, the activation energies and the corresponding pre-exponential factors from coal for methane, ethane, propane, and heavy gaseous hydrocarbons obtained from this evaluation, ranging from 188 to 400 kJ/mol at 1.86×10^{13} s^{-1}, from 188 to 400 kJ/mol at 8.79×10^{14} s^{-1}, from 208 to 400 kJ/mol at 5.29×10^{15} s^{-1}, from 205 to 400 kJ/mol at 3.26×10^{15} s^{-1}, respectively. The activation energy distributions of those hydrocarbon gases showed an asymmetrical appearance. These pre-exponential factors are similar to the values of about 10^{12}–10^{13} s^{-1} (Pepper and Corvi, 1995), and slightly higher than the values of 10^{13}–10^{15} s^{-1} (Forbes et al., 1991; Braun and Burnham, 1992; Behar et al., 1997).

In all of the evaluations performed, the proportion of dominant frequency of activation energy for the hydrocarbon gases increased gradually, as well as its main activation energy. The corresponding pre-exponential factor (increasing exponentially) was increased with increasing carbon number of hydrocarbon in the dark mudstone and coal (Fig. 2). Although the proportion of the dominant frequency, and its main activation energy for heavy gaseous hydrocarbons is less than C_1-C_2-C_3 hydrocarbon, its corresponding pre-exponential factor increased exponentially. Both the decrease of the activation energy and the increase of its corresponding pre-exponential factor of heavy gaseous hydrocarbons will have a greater contribution toward the constant of the reaction rate according to a first-order rate law (Braun and Burnham, 1987; Krooss et al., 1995; Dieckmann et al., 2004).

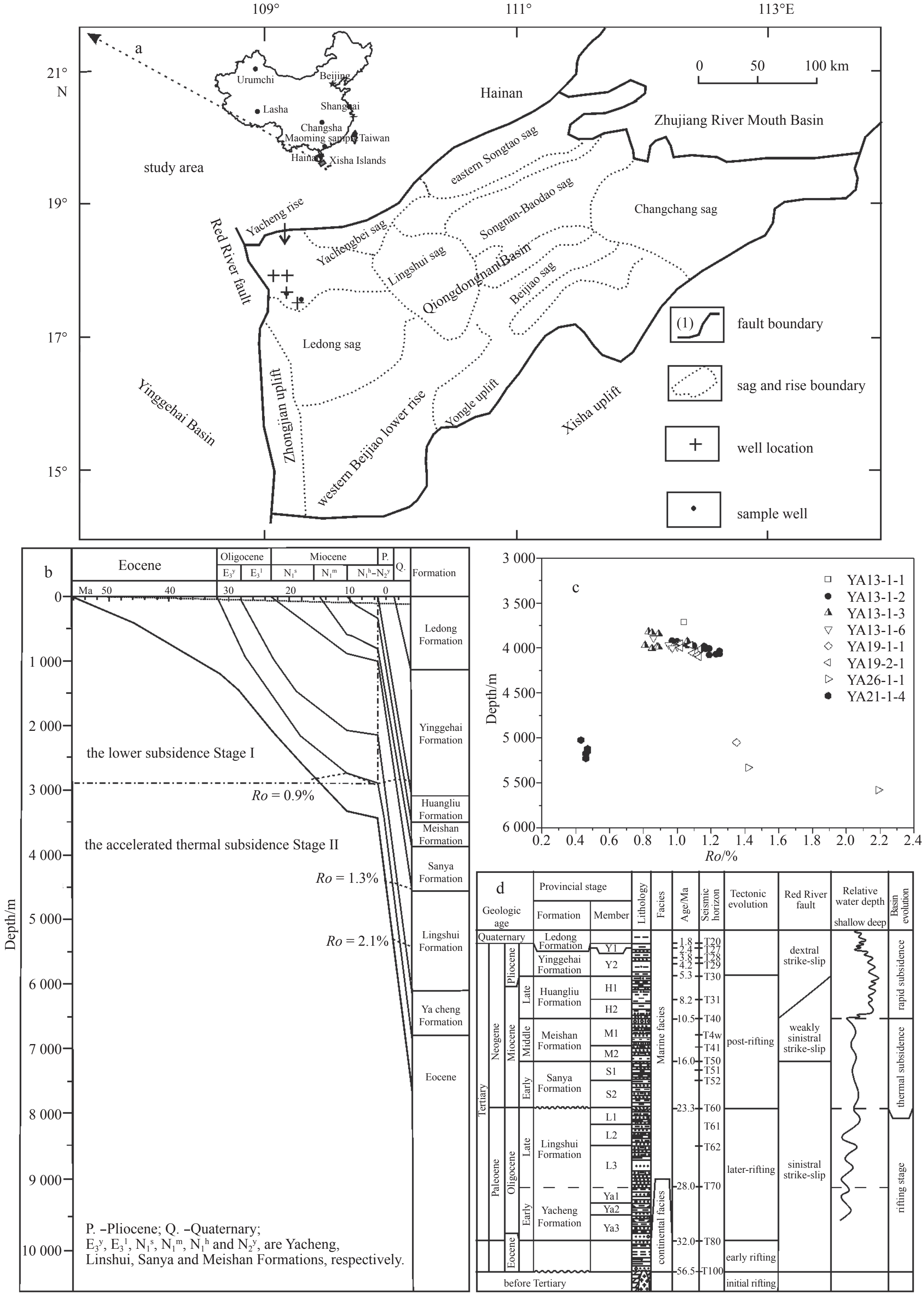

Fig. 1. Map showing: a. the tectonic units and locations of the sampling wells in the QDNB (revised after Zhang et al. (2010), Su et al. (2012a, b); b. the burial history curves for Yacheng Formation of the Qiongdongnan Basin based on Ya13-1 gas field and parameter Well YC13-1-4 (revised after Huang et al. (2003) and Hu et al. (2005b)) the burial depth and vitrinite reflectance collected from the drilling data of Well 8 in the shallow-water area; c. the tectonic evolution in the Qiongdongnan Basin (revised after Yuan et al. (2008)) and d. the sedimentary sequences, the tectonic evolution, and the mature stage of the source rocks for Yacheng Formation in the Qiongdongnan Basin in the South China Sea (revised after Gong et al., 1997). *Ro* is the vitrinite reflectivity.

Table 1. Selected samples of Yacheng Formation properties

Location	Lithology	Depth/m	T_{max}/°C	*TOC*/%	*IH*/mg·g^{-1}	*IO*/mg·g^{-1}	*Ro*/%
YC13-1-3	mudstone	4 016–4 018	455	1.24	66	248	0.89
YC13-1-6	coal	3 978–3 980	439	72.13	128	7	0.85

Note: *IH* and *IO* are abbeeviated from hydrogen index and oxygen index. *Ro* is vitrinite reflectivity of the sample in the paper.

Table 2. The experimental data are phase yields of C_1 and C_2^+ gas fractions generation derived from dark mudstone and coal of Yacheng Formation in the Qiongdongnan Basin[1)]

Heating rate	*T*/°C	C_1/mL·g^{-1}		C_2/mL·g^{-1}		C_3/mL·g^{-1}		$C_{4\text{-}6}$/mL·g^{-1}	
		DM	coal	DM	coal	DM	coal	DM	coal
2°C·min^{-1}	250	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	300	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	350	0.05	0.02	0.01	0.01	0.01	0.01	0.02	0.11
	400	1.20	0.27	0.35	0.08	0.24	0.05	0.82	1.17
	450	9.47	12.97	3.73	4.27	0.93	0.75	5.98	23.76
	500	23.33	64.74	5.66	27.99	1.27	11.55	8.77	82.40
	550	32.00	99.48	3.02	42.83	0.75	12.08	5.05	88.88
	600	25.56	89.74	1.77	12.72	0.37	2.27	3.17	22.84
	650	19.40	51.86	1.20	1.83	0.21	0.16	2.34	3.26
	700	14.97	32.68	0.49	0.61	0.06	0.02	0.99	1.42
	750	12.41	13.48	0.18	1.55	0.01	0.02	0.38	2.07
	800	8.88	7.32	0.10	1.11	0.01	0.01	0.22	1.33
	850	4.57	5.42	0.05	1.56	0.01	0.02	0.11	2.24
	900	2.30	2.76	0.04	1.30	0.01	0.01	0.06	1.68
	950	1.27	1.81	0.04	0.56	0.01	0.01	0.05	0.82
	1 000	0.91	0.84	0.03	0.36	0.01	0.01	0.07	0.63
	1 050	0.61	0.34	0.03	0.24	0.01	0.01	0.07	0.46
	1 100	0.48	0.11	0.01	0.15	0.01	0.01	0.06	0.42
20°C·min^{-1}	250	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
	300	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.07
	350	0.01	0.48	0.01	0.07	0.02	0.06	0.02	1.28
	400	0.02	9.62	0.02	2.18	0.03	0.91	0.04	13.54
	450	0.80	43.74	0.21	14.69	0.21	8.07	0.64	49.00
	500	7.12	76.71	2.73	22.50	1.14	6.68	5.79	54.85
	550	15.47	51.07	4.08	4.53	1.18	0.87	7.48	9.20
	600	16.44	43.82	1.60	1.45	0.29	0.17	2.47	3.73
	650	13.74	20.38	0.42	0.26	0.09	0.04	0.77	1.09
	700	9.40	10.88	0.18	1.04	0.04	0.02	0.31	1.85
	750	6.75	11.81	0.16	1.33	0.02	0.02	0.22	2.18
	800	5.55	5.30	0.14	0.13	0.02	0.01	0.29	0.01
	850	3.61	2.02	0.12	0.06	0.02	0.01	0.29	0.01
	900	2.44	1.63	0.10	0.24	0.02	0.01	0.26	0.01
	950	1.95	1.05	0.08	0.24	0.01	0.01	0.28	0.01
	1 000	1.68	0.35	0.06	0.21	0.01	0.01	0.32	0.01
	1 050	1.54	0.12	0.04	0.12	0.01	0.01	0.29	0.01
	1 100	1.48	0.04	0.02	0.06	0.01	0.01	0.30	0.01

Note: [1)] The data derived from open-system non-isothermal pyrolysis of samples at two heating rates of 2.0°C/min and 20°C/min after normalization to initial organic carbon (Schenk and Horsfield, 1998). C_1 indicates methane, C_2 ethane, C_3 propane, $C_{4\text{-}6}$ heavy gaseous hydrocarbons, and DM dark mudstone.

3.2 *Geological predictions*

Earlier studies showed that the gas generation under laboratory conditions resulted mainly from the thermal cracking reactions of kerogen, and therefore the gas generation over geological time could be reliably extrapolated from the pyrolysis of the appropriate samples (Braun and Burnham, 1987; Schenk and Dieckmann, 2004; Dieckmann et al., 2004). The pyrolysis experiment was aimed at finding the most efficient approach of determining the kinetic parameters for the natural gas generation, and the laboratory observations could be extrapolated and confirmed. On the basis of the laboratory-derived kinetic parameters, the gas generation curves can be calculated for any geological heating condition (Dieckmann et al., 2004). However, it was impossible to evaluate reasonable kinetic parameters for the formation of single compounds by an arbitrary burial and thermal history model, as well as the optional slow or fast heating rates and a fictitious geological heating rate, due to the supposed related major variations in predictions of oil and gas generation. Therefore, the burial history and the realistic geological heating rate calculated by the mathematical method have discussed in the following section.

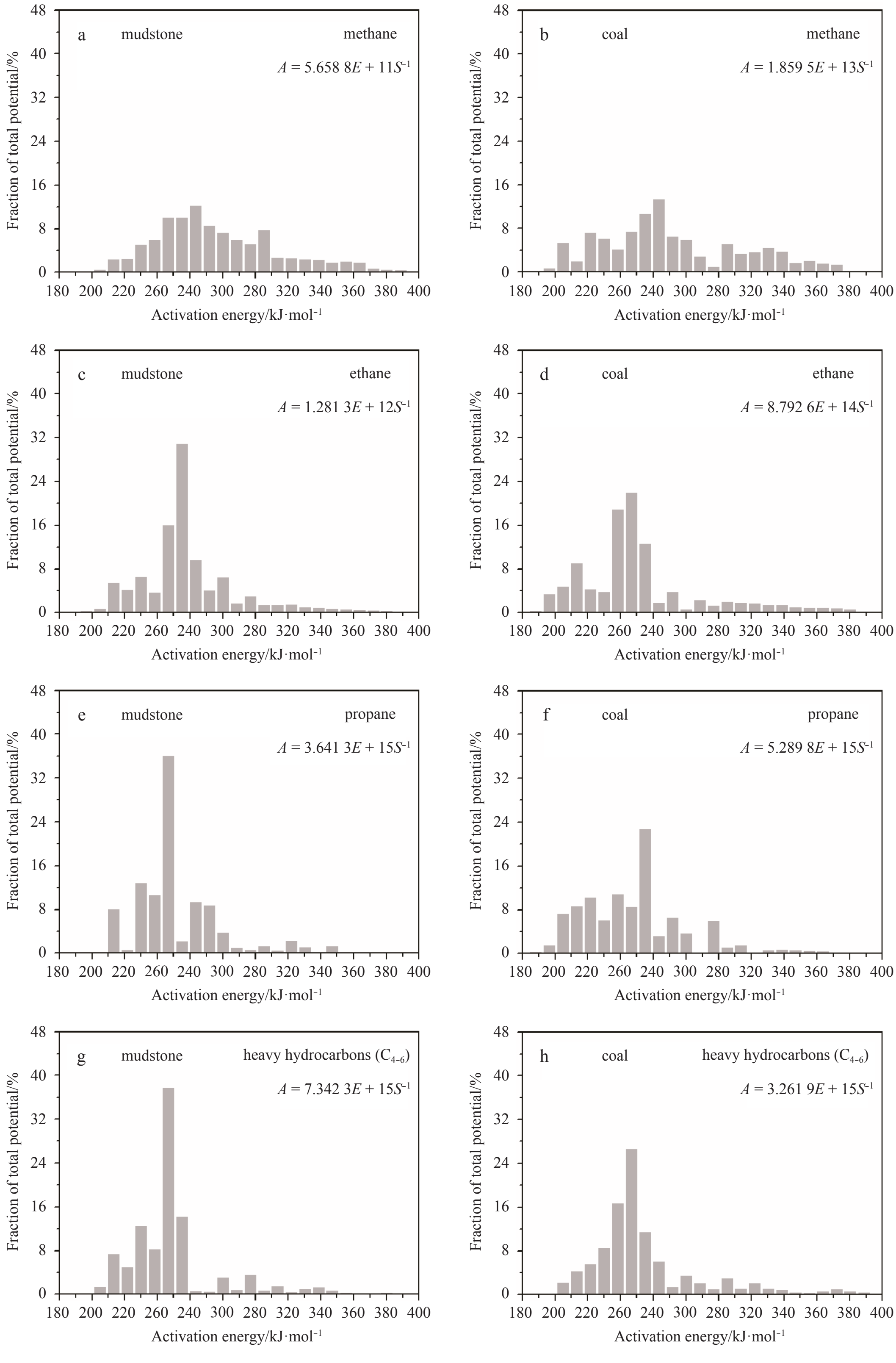

Fig. 2. Kinetic parameters of hydrocarbon gas generation from dark mudstone and coal: methane (a, b), ethane (c, d), propane (e, f) and heavy gaseous hydrocarbons (g, h). *A*, *E* and *S* are the corresponding pre-exponential factor of activation energy, and index expression in mathematics, respectively.

3.2.1 *Calculated geological heating rates*

The prediction of the natural gas generation in the deep-water area can utilize the basin modeling, which results from Huang et al. (2003) and Hu et al. (2005) based on the modeling Ya13-1 gas field and the parameter of well YC13-1-4 (Fig. 1b). The lower subsidence stage I, during the early Oligocene (32 Ma) to late

Miocene (5.3 Ma) age, brought the source rocks of Yacheng Formation to a burial depth of about 2 800 m in the sags of the shallow-water area of the QDNB. The Cenozoic tectonic evolution of the QDNB experienced three-episodic stages, namely, the syn-rifted stage, the post-rifted stage (Gong et al., 1997; Xie et al., 2008; Zhang et al., 2012) and the accelerated thermal subsidence Stage II. This corresponded to the Eocenee-Oligocene, the mid to late Miocene, and Pliocenee-Holocene heating events in Cenozoic periods (He et al., 2001; Yuan et al., 2009; Zhang et al., 2010, 2014, 2016), respectively. Since 5.3 Ma, the QDNB has been characterized by the rapid subsidence, the high sedimentation rate, the high heat flow and the high geothermal gradient, resulting in the thick sediments of the western QDNB. The total subsidence rate in the central depression belt is over 200 m/Ma, and in the prominent local anomalies is up to 550 m/Ma (Gong et al., 1997). Therefore, high average geothermal gradients of 4.0°C/(100 m) have been developed in the Yanan sag area. The geological heating rate by R_h (°C/Ma) can be expressed as

$$R_h = Z_i G / t, \tag{1}$$

where Z_i is the burial depth (m) of hydrocarbon source rocks during time t (Ma), and G is the geothermal gradient using units 1°C/(100 m) of measurement.

3.2.2 *Geological predictions in the shallow-water area*

The results of the geological heating rates calculated by Eq. (1) are based on the basic geological burial history (Fig. 1b), and indicate that the paleo-temperature for the source rocks of Yacheng Formation in the sags is about 120°C. These are related to a burial depth of about 3 000 m, and reached the peak oil generation window (*Ro*=0.9%) from the early Oligocene to late Miocene age. The peak gas generation window is 150°C (*Ro*=1.3%, burial depth of about 3 500 m) for the sags of the continental shelf of in the QDNB since late Miocene age. Rapid subsidence and deposition brought source rocks of Yacheng Formation to its present calculated depth of 4 000–7 000 m (Huang et al., 2003, 2012) for over 160–280°C. The best burial depth, temperature and vitrinite reflectivity of YC26-1-1 by contrast to the eight wells (shown in Fig. 1c) are about 5 577.6 m, 230°C and 2.19%, respectively. This indicates that the source rocks of Yacheng Formation have reached the stage of dry gas generation since the late Miocene age (Fig. 1d).

3.2.3 *Prediction of temperature for methane generation*

On the basis of the geological burial process of source rocks of Yacheng Formation in the shallow-water area, the extrapolation is illustrated in Fig. 3. It compares the transformation ratio for the different hydrocarbon gas fractions at different heating rates which correspond to the calculated burial depth. Methane is a dominative gas, especially during the initial gas generation. Its onset geological temperature, illustrated as Point A in Fig. 3, with the geological conditions from source rocks of Yacheng Formation, is extrapolated to occur at about 100°C (Figs 3a and b), which is similar to those predicted from the coal of western Siberia with open system conditions (Schaefer et al., 1999). It must be emphasized that all of these predictions reported from studies pertain to the primary cracking of macromolecular organic matter to methane. The kinetic parameters are given by Behar et al. (1997), and the onset temperature for the methane generation, which is similar to that predicted by Dieckmann et al. (2004), is around 110°C. In contrast, the kinetics derived by Braun and Burnham (1992) predicted higher temperatures for the methane generation of lacustrine organic matter, with the methane generation starting at about 140°C and 150°C, respectively. These temperatures are nearly 150°C, which is considered as the initial generation temperature of methane inalgal rich organic matter (Berner et al., 1995). It is obvious that the onset temperature of gas generation predicted for ethane, propane and heavy gaseous hydrocarbons (C_{4-6}) generation is 110–120°C (Figs 3c–h), which is much higher than 0–10°C, which is the methane generation predicted in the study.

The peak geological temperature during the main methane generation period (shown as Point B in Fig. 3) is about 140–160°C, which is higher than that of the ethane, propane and heavy gaseous hydrocarbons (C_{4-6}) generation. Meanwhile, the geological temperature of the end of the main methane generation period (shown as Point C in Fig. 3) is 220°C, which is higher than those of 60–80°C for ethane, propane and heavy gaseous hydrocarbons (C_{4-6}) generation. This is due to the broader range for the activation energy distributions of methane.

Furthermore, the transformation ratio (normalized to 1) for ethane, propane and heavy gaseous hydrocarbons (C_{4-6}) generation under geological conditions, is to the cumulative plateau of the curve at over 0.8 at 200°C, while that of the methane generation is about 0.5. It is obvious that the hydrocarbon potential for ethane, propane and heavy gaseous hydrocarbons (C_{4-6}) generation from the study samples are almost exhausted at a geological temperature of over 220°C by extrapolations, on the basis of the geological burial depth of 5 500 m for the source rocks of Yacheng Formation in the shallow-water area.

Even the primary methane generation directly originating from the kerogen of the dark mudstone and coal cannot assume to be exhausted at a high level of maturity. It is the reason that we are required to perform the prediction of the natural gas generation and geological extrapolations for the samples required to be performed. However, the temperature of 220°C marks the limit of the applied concept, rather than the real end of the methane generation in the study and in the geological condition. It is well known that methane, together with coke, is the final products of the organic matter thermal degradation in a source rock. Therefore, Dieckmann et al. (2004) assumed that the methane generation takes place up to those levels of thermal maturity and at higher molecular mass, and the hydrocarbon gases are completely thermally degraded. So the methane generation after reaching the plateau region should be reconsidered. But an obvious problem is how much of the potential super-mature methane precursors are still in a source rock of a continental slope area with extremely high levels of maturity, and at a burial depth of more than 5 500 m, which resulted during the late Miocene period.

It may be underestimated of the super-mature methane generation here, as the applied concept does not consider the decrease of gas generation curves after reaching the plateau region. This is one of the reasons for the prediction of the natural gas generation from the source rocks of Yacheng Formation in the deep-water area. On the other hand, the pyrolysis experiments were conducted on an immature sample, for the gas-prone source rock of Yacheng Formation, and obtained an upper limit of maturity for the gas generation or "the deadline of gas generation". It is equal to 4.38% of the vitrinite reflectivity (*Ro*) for the whole rock of Type II kerogens, where the gas generation rates change infrequently with the increase of maturation, the value increment of the *Ro* is 0.83 % of the maximum related to the *Ro* of

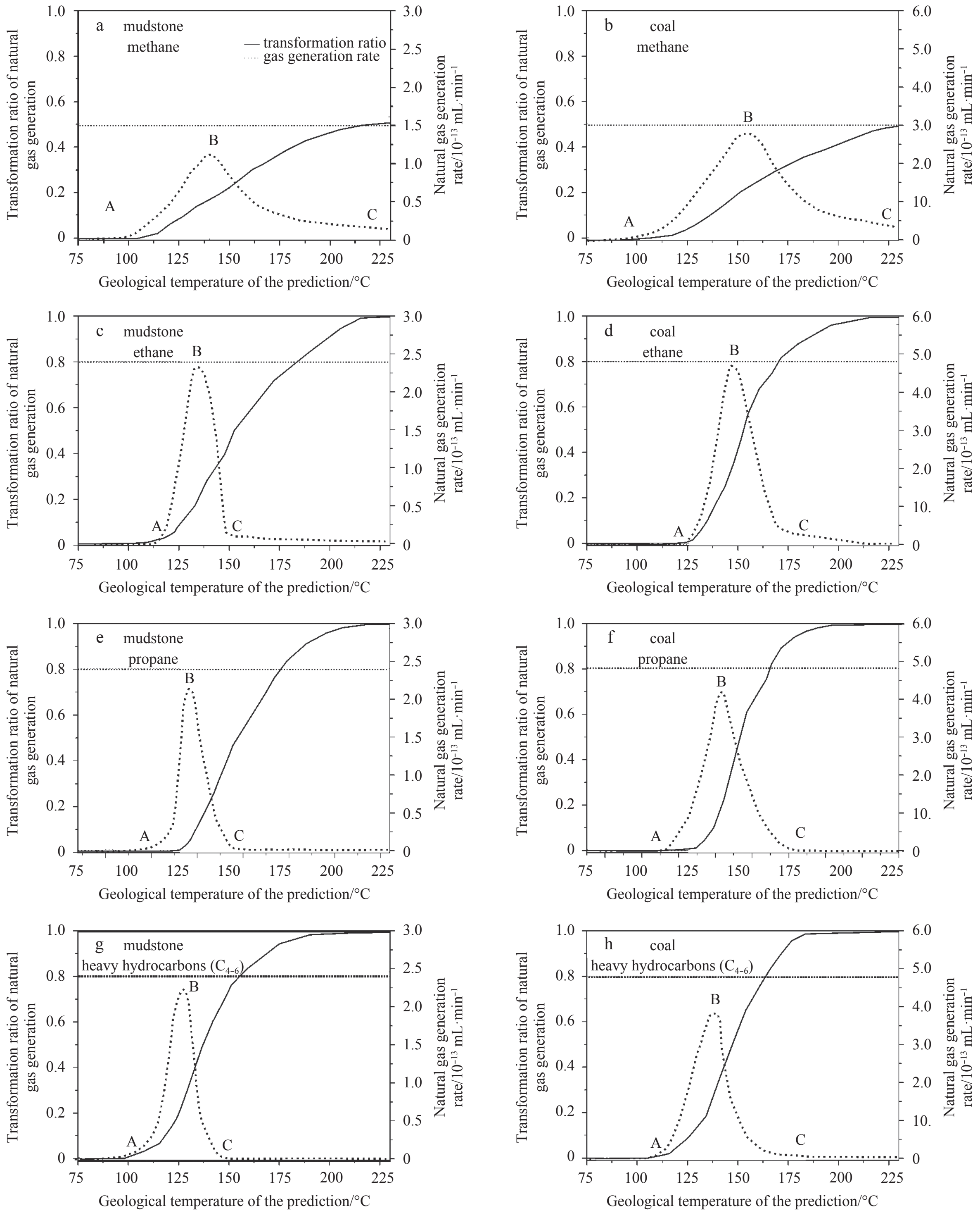

Fig. 3. The geological temperature of hydrocarbon gas generation predicted from dark mudstone and coal: methane (a, b), ethane (c, d), propane (e, f) and heavy gaseous hydrocarbons (C_{4-6}) (g, h). Points A, B and C are the geological temperature of the onset, the peak and the end during the main gas generation period, respectively.

4.38%, and the source rock rarely occurs in the end process of the generation of hydrocarbon gas while the *Ro* is over 4.38 % (Su et al., 2012a).

Rapid subsidence and deposition have brought source rocks of Yacheng Formation from the deep-water area to its present depth of over 10 km since 5.3 Ma (Zhang et al., 2010, 2014, 2016; Zhu et al., 2008) according to the drilling and seismic data. Likewise, the geological temperature of this maximum burial depth of 10 km being 400°C is calculated by Eq. (1) using the selected geothermal gradients of 4.0°C/(100 m). Thereby, the mean geological heating rate is 14.8°C/Ma (8.6×10^{-13} mL/min), calculated by a mathematical method which is based on the data.

3.2.4 *Geological predictions in the deep-water area*

The predicted temperature of the methane generation in the deep-water area of the QDNB is shown in Fig. 4, and is based on the same laboratory-derived kinetic parameters of the dark mudstone and coal. At an initial stage, the predicted methane generation exhibited rate is rather high, from 110°C to around 300°C (Point C in Fig. 4). Additionally, the geological temperature of the peak gas generation rate (values of about 6.5×10^{-15}) is about 190°C for dark mudstone and 220°C for coal. However, this decreases after reaching 300°C for the geological temperature, and over 0.8 for the predicted transformation ratio.

Methane dominates the gas generation from both the dark mudstone and coal, especially in the dry gas generation stage. This is because ethane, propane and heavy gaseous hydrocarbons ($C_{4\text{-}6}$) generation are almost exhausted at the geological temperatures over 200°C with a transformation ratios of about 0.8. Kerogen is an exclusive source for methane in the samples at a high maturity level. The generation of methane simulated under the geological conditions exclusively corresponds to the primary cracking of kerogens into gas, when heating experiments were performed in the open system pyrolysis devices.

3.2.5 *Potential of Yacheng Formation in the deep-water area*

The average values of TOC of the dark mudstones and coal of Yacheng Formation in the shallow-water area are 8.55% and 95.90 %, respectively (Huang et al., 2012), and the average values of Rock-Eval pyrolysis data (S_1+S_2) are 16 and 94 mg/g, respectively (Su et al., 2012b). These results show a high hydrocarbon generation potential. The types of organic matter in the source rocks of Yacheng Formation are mainly II_2-III, with a high pyrolysis peak temperature (>430°C) and low hydrogen indexes. The source rocks of Yacheng Formation, including coal, carbonaceous mudstone and mudstone, are the major source rocks in the QDNB. This is due to the high hydrocarbon generation potential. During the sedimentary period of Yacheng Formation, the source rocks in the northern depression zone were mainly developed as delta, tidal flat and lagoon environments, where there was abundant terrigenous organic matter. Presently, the total thickness of the mudstone, which is based on the data of the drill Well in the deep-water area, is 419 m in Well LS331 (Huang et al., 2012). The range and average TOC values of the dark mudstones in Well LS331 are 0.33%–1.17% and 0.79%, respectively. The range of the values for TOC of the dark mudstones Well LS211 is 1.24%–1.46%. The range and the average values of TOC of the dark mudstones in Well LS421 are 0.52%–3.73% and 1.36%, respectively. The experimental results show that the higher temperature in the deep-water area of the QDNB can accelerate the methane generation in the deep-water sags, and that it can also speed up the cracking of the widespread residual hydrocarbons (ethane, propane and heavy gaseous hydrocarbons) to methane. Therefore, the source rocks of Yacheng Formation have the high gas generation potential in the deep-water area of the QDNB.

3.2.6 *Target of the deep-water area for natural gas exploration*

Over the entire maturity interval of the gas generation, the proportion of methane in the gas can reach at 80%, and at 2.5% of *Ro* in the onset of the secondary cracking for the compounds of ethane, propane and heavy gaseous hydrocarbons ($C_{4\text{-}6}$) at extreme laboratory temperatures (Sweeney and Burnham, 1990; Huang et al., 2003; Dieckmann et al., 2004). The gas composition derived from the source rocks of Yacheng Formation becomes drier with increasing maturity in the Yacheng depression of the QDNB (Huang et al., 2003; Wu et al., 2013), and is predicted to become slightly drier with increasing maturity, at over 2.5% of *Ro* in the deep-water area, based on the similarities for the same geological conditions. Furthermore, the reservoirs of the natural gas generated from the source rocks of Yacheng Formation may be Eocene and Oligocene transitional sandstones; Neogene-Quaternary marine continental slope sandstones; and reef carbonates in the central canyon of the deep-water area of the QDNB (Wu et al., 2009; Li et al., 2011). Seal rocks are widely developed, and the Oligocene mudstone and Neocene marine mudstone are the seal for this region. There are structural traps, with the main styles of draping being anticline and fault traps, and non-structural traps of the levee-overbank sediments in the central canyon and in the deep water fan. These can accumulate oil and gas if there is cooperation with the fault or “gas chimney”.

In particular, it is indicated that small-scale patches, pinnacle reefs or atolls, were well developed in the Ledong sag, Lingshui sag and Beijiao sag by using a high-resolution sequence stratigraphic analysis and the combined geological and geophysical data (Wu et al., 2009), whereas the analysis shows that the impedance values of reefs in the Beijiao, Ledong and Lingshui sags for 800–900 g/(cm²·s), are somewhat lower that of the LH11-1 reef reservoir for 800–1 000 g/(cm²·s). These natural gases were not expected to obviously effect nar source kitchens via short distance lateral migration (Zhang et al., 2007; Zhu et al., 2008), as well as the Ya13-1 gas field, or focused and episodic migration along with any other alteration effect (Huang et al., 2003). There

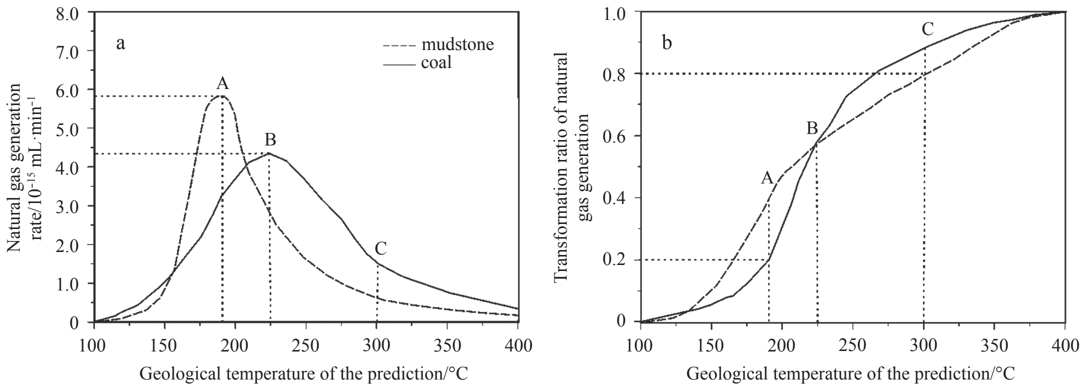

Fig. 4. Geological predictions of gas generation rate (a) and transformation ratio (b) as a function of temperature of the methane generation calculated from the kinetic parameters derived from the pyrolysis of dark mudstone and coal at 2.0 and 20°C/min under the same geological conditions. Points A, B and C are the peak maximum and the end of the geological temperature for dark mudstone and coal, respectively.

are clear indications for a significant delay of thermal evolution and hydrocarbon generation in the strongly over-pressured source systems (Huang et al., 2003; Xie et al., 2008), while the source rocks of Yacheng Formation, in normal pressure systems, underwent rapid thermal maturation. All of these factors improved the hydrocarbon expulsion efficiency and represented important targets for the deep water natural gas exploration. The natural gas exploration for the deep water area in the Qiongdongnan Basin should first aim at the structural traps in the Ledong, Lingshui and Beijiao sags, and in the forward direction of the structure around the sags, and then gradually develop toward the non-structural trap in the deep-water area basin of the broad ocean areas of China.·

4 Conclusions

The source rocks of Yacheng Formation, including coal, carbonaceous mudstone and mudstone, are the major source rocks in the QDNB. The types of organic matter are mainly II_2-III, with the high pyrolysis peak temperature (> 430°C) and low hydrogen indexes. The data related to the drill well in the deep-water area of the QDNB indicate that the source rocks of Yacheng Formation have the high hydrocarbon generation potential. Kinetic parameters are derived from the dark mudstone and coal by open-system experiments using an optimization procedure, which determines a unique pre-frequency factor and a distribution of chemical classes for gas fractions, according to a discrete series of activation energies. The activation energies and corresponding pre-exponential factors from the dark mudstone and coal for methane, ethane, propane, and heavy gaseous hydrocarbons obtained from this evaluation, ranging from 188 to 400 kJ/mol at 5.66×10^{11} –7.34×10^{15} s^{-1}. By the extrapolations under the geological conditions obtained from the Ya13-1 gas field and the selected well in the QDNB, the onset and end of natural gas generation for methane predicted are 110°C and 300°C, respectively. The result of the study can be used in the evaluation of the resource potential for oil and gas in the hydrocarbon source rock in the deep-water area of the QDNB, as well as other basins with lower exploration in the northern area of the South China Sea. At the same time, it can reduce the risks occurring during exploration.

Acknowledgements

The authors thank two anonymous reviewers for their careful review and constructive comments which lead to a great improvement to this manuscript.

References

Behar F, Vandenbroucke M, Tang Y, et al. 1997. Thermal cracking of kerogen in open and closed systems: determination of kinetic parameters and stoichiometric coefficients for oil and gas generation. Organic Geochemistry, 26(5–6): 321–339

Berner U, Faber E, Scheeder G, et al. 1995. Primary cracking of algal and landplant kerogens: kinetic models of isotope variations in methane, ethane and propane. Chemical Geology, 126(3–4): 233–245

Braun R L, Burnham A K. 1987. Analysis of chemical reaction kinetics using a distribution of activation energies and simpler models. Energy & Fuels, 1(2): 153–161

Braun R L, Burnham A K. 1992. PMOD: a flexible model of oil and gas generation, cracking, and expulsion. Organic Geochemistry, 19(1–3): 161–172

Dieckmann V, Fowler M, Horsfield B. 2004. Predicting the composition of natural gas generated by the Duvernay Formation (Western Canada Sedimentary Basin) using a compositional kinetic approach. Organic Geochemistry, 35(7): 845–862

Forbes P L, Ungerer P M, Kuhfuss A B, et al. 1991. Compositional modeling of petroleum generation and expulsion: trial application to a local mass balance in the Smorbukk sor field, Haltenbanken area, Norway. AAPG Bulletin, 75(5): 873–893

Gong Zaisheng, Li Sitian, Xie Xinong, et al. 1997. Continental Margin Basin Analysis and Hydrocarbon Accumulation of the Northern South China Sea (in Chinese). Beijing: Science Press, 1–126

He Lijuan, Wang Kelin, Xiong Liangping, et al. 2001. Heat flow and thermal history of the South China Sea. Physics of the Earth and Planetary Interiors, 126(3–4): 211–220

Hu Bo, Wang Liangshu, Yan Wenbo, et al. 2013. The tectonic evolution of the Qiongdongnan Basin in the northern margin of the South China Sea. Journal of Asian Earth Sciences, 77: 163–182

Hu Zhongliang, Xiao Xianming, Huang Baojia, et al. 2005. Acquirement of fluid inclusion paleo-pressure and it relation to reservoiring-Taking YA 21–1 structure in Qiongdongnan basin as an example. Natural Gas Industry (in Chinese), 25(6): 28–31

Huang Baojia, Li Xushen, Wang Zhenfeng, et al. 2012. Source rock geochemistry and gas potential in the deep water area, Qiongdongnan Basin. China Offshore Oil and Gas (in Chinese), 24(4): 1–7

Huang Baojia, Xiao Xianming, Li Xuxuan. 2003. Geochemistry and origins of natural gases in the Yinggehai and Qiongdongnan basins, offshore South China Sea. Organic Geochemistry, 34(7): 1009–1025

Krooss B M, Leythaeuser D, Lillack H. 1993. Nitrogen-rich natural gases. Qualitative and quantitative aspects of natural gas accumulation in reservoirs. Erdöl und Kohle, Erdgas, Petrochemie vereinigt mit Brennstoff-Chemie, 46(7–8): 271–276

Krooss B M, Littke R, Müller B, et al. 1995. Generation of nitrogen and methane from sedimentary organic matter: implications on the dynamics of natural gas accumulations. Chemical Geology, 126(3–4): 291–318

Li Dong, Wang Yingmin, Wang Yongfeng, et al. 2011. The sedimentary and foreground of prospect for Levee-Overbank in Central Canyon, Qiongdongnan Basin. Acta Sedimentologica Sinica (in Chinese), 29(4): 689–694

Li Xianqing, Xiao Xianming, Mi Jingkui, et al. 2008. Kinetic parameters of methane generated from source rocks in the Kuqa depression of Tarim basin and their application. Acta Geologica Sinica, 82(1): 154–163

Pepper A S, Corvi P J. 1995. Simple kinetic models of petroleum formation. Part I: oil and gas generation from kerogen. Marine and Petroleum Geology, 12(3): 291–319

Schaefer R G, Galushkin Y I, Kolloffa A, et al. 1999. Reaction kinetics of gas generation in selected source rocks of the West Siberian Basin: implications for the mass balance of early-thermogenic methane. Chemical Geology, 156(1–4): 41–65

Schaefer R G, Schenk H J, Hardelauf H, et al. 1990. Determination of gross kinetic parameters for petroleum formation from Jurassic source rocks of different maturity levels by means of laboratory experiments. Organic Geochemistry, 16(1–3): 115–120

Schenk H J, Dieckmann V. 2004. Prediction of petroleum formation: the influence of laboratory heating rates on kinetic parameters and geological extrapolations. Marine and Petroleum Geology, 21(1): 79–95

Schenk H J, Horsfield B. 1998. Using natural maturation series to evaluate the utility of parallel reaction kinetics models: an investigation of Toarcian shales and carboniferous coals, Germany. Organic Geochemistry, 29(1–3): 137–154

Shi Xiaobin, Qiu Xuelin, Xia Kanyuan, et al. 2003. Characteristics of surface heat flow in the South China Sea. Journal of Asian Earth Sciences, 22(3): 265–277

Su Long, Zheng Jianjing, Chen Guojun, et al. 2012a. The upper limit of maturity of natural gas generation and its implication for the Yacheng formation in the Qiongdongnan Basin, China. Journal of Asian Earth Sciences, 54–55: 203–213

Su Long, Zheng Jianjing, Wang Qi, et al. 2012b. Formation mechanism and research progress on overpressure in the Qiongdongnan Basin. Natural Gas Geoscience (in Chinese), 23(4): 662–672

Sweeney J J, Burnham A K. 1990. Evaluation of a simple model of vitrinite reflectance based on chemical kinetics. AAPG Bulletin, 74(10): 1559–1570

Ungerer P, Pelet R. 1987. Extrapolation of the kinetics of oil and gas formation from laboratory experiments to sedimentary basins. Nature, 327(6117): 52–54

Whiticar M J. 1990. A geochemial perspective of natural gas and atmospheric methane. Organic Geochemistry, 16(1–3): 531–547

Wu Jingfu, Yang Shuchun, Zhang Gongcheng, et al. 2013. Geothermal history and thermal evolution of the source rocks in the deep-water area of the northern South China Sea. Chinese Journal of Geophysics (in Chinese), 56(1): 170–180

Wu Shiguo, Yuan Shengqiang, Zhang Gongcheng, et al. 2009. Seismic characteristics of a reef carbonate reservoir and implications for hydrocarbon exploration in deepwater of the Qiongdongnan Basin, Northern South China Sea. Marine and Petroleum Geology, 26(6): 817–823

Xie Yuhong, Wang Zhenfeng, Tong Chuanxin. 2008. Petroleum geology of Yacheng 13–1, the largest gas field in China's offshore region. Marine and Petroleum Geology, 25(4–5): 433–444

Yuan Yusong, Zhu Weilin, Mi Lijun, et al. 2009. "Uniform geothermal gradient" and heat flow in the Qiongdongnan and Pearl River Mouth Basins of the South China Sea. Marine and Petroleum Geology, 26(7): 1152–1162

Zhang Gongcheng, He Yuping, Shen Huailei, et al. 2012. Distribution of Yachen formation coal measure in Yabei sag in Qiongdongnan Basin. Natural Gas Geoscience, 23(4): 654–661

Zhang Gongcheng, Mi Lijun, Wu Shiguo, et al. 2007. Deepwater area-the new prospecting targets of northern continental margin of South China Sea. Acta Petrolei Sinica, 28(2): 15–21

Zhang Gongcheng, Zhu Weilin, Mi Lijun, et al. 2010. The theory of hydrocarbon generation controlled by source rock and heat from circle distribution of outside-oil fields and inside-gas fields in South China Sea. Acta Sedimentologica Sinica (in Chinese), 28(5): 987–1005

Zhang Gongcheng, Zhang Yina, Shen Huailei, et al. 2014. An analysis of natural gas exploration potential in the Qiongdongnan Basin by use of the theory of "joint control of source rocks and geothermal heat". Natural Gas Industry: B, 1(1): 41–50

Zhang Gongcheng, Zhang Houhe, Zhao Zhao, et al. 2016. "Joint control of source rocks and geothermal heat"-Oil enrichment pattern of China's offshore basins. China Petroleum Exploration (in Chinese), 21(4): 38–53

Zhao Zhongxian, Sun Zhen, Wang Zhenfeng, et al. 2015. The high resolution sedimentary filling in Qiongdongnan Basin, Northern South China Sea. Marine Geology, 361: 11–24

Zhu Weilin, Zhang Gongcheng, Gao Le. 2008. Geological characteristics and exploration objectives of hydrocarbons in the northern continental margin basin of South China Sea. Acta Petrolei Sinica (in Chinese), 29(1): 1–9

Zhu Weilin, Zhang Gongcheng, Yang Shaokun, et al. 2007. Natural Gas Geology of the Continental Margin Basin, North of South Sea, China (in Chinese). Beijing: China Petroleum Industry Press, 1–391