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Aikuan Wang

China University of Mining and Technology School of Resources and Geosciences

qinghui wang (✉ wangqinghui0615@163.com)

zhong guo kuang ye da xue zi yuan yu di qiu ke xue xue yuan: China University of Mining and Technology School of Resources and Geosciences <https://orcid.org/0000-0001-7931-5256>

Pei Shao

China University of Mining and Technology School of Resources and Geosciences

Tian Fu

China University of Mining and Technology School of Resources and Geosciences

Moran Cao

China University of Mining and Technology School of Resources and Geosciences

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Simulation of biogenic coalbed gas from anthracite in south of Qinshui Basin, China

Aikuan Wang^{1,2} Qinghui Wang^{1,2*}, Pei Shao³, Tian Fu^{1,2} Moran Cao^{1,2}

¹ Key Laboratory of Coalbed Methane Resources & Reservoir Formation Process, Ministry of Education, China
University of Mining & Technology, Xuzhou 221008, China

² School of Resources and Geosciences, China University of Mining & Technology, Xuzhou 221116, China

³ Department of Surveying and Planning, Shangqiu Normal University, Shangqiu 476000, China

ABSTRACT:

High rank coal, such as anthracite, has been considered difficult to generate biogas because of the high coalification degree. Selecting anthracite from Sihe coal mine, Qinshui basin, China, as substrate, this study carried out a simulation experiment of biogas generation for 80 days, the purpose of which was to verify whether anthracite could be bio-degraded to produce biogas under laboratory conditions. The results showed that the selected anthracite can be utilized by methanogenic bacteria to produce biogas and the approximate production field was 1.79mL/g, which was less than that of lower rank coal of other published studies. The generation process can be divided into a rapid growth stage (0-30d) and a slow descent stage (30-80d). CO₂ and CH₄ are the main components of biogas, although some heavy-hydrocarbons were also tested. The CO₂ concentrations were low (<30%) and the $\delta^{13}\text{C}_{\text{-CH}_4}$ values were positive (-39.9‰ to -45.8‰), which suggested that the main biogas generation pathway was acetic fermentation. But at the same time, the concentrations of CH₄ and CO₂ were mutually increasing and decreasing with the passage of experiment time, and $\delta^{13}\text{C}_{\text{-CH}_4}$ tends to be lighten in the later stage(40-80d), suggesting that parts of biogenic CH₄ was generated by way of CO₂-reduction.

Keywords: biogas generation; anthracite; simulation experiment; producing process; biogas composition, isotope composition

1. Introduction

In recent years, as a new kind of unconventional natural gas, biogenic coalbed gas has been found in many coal-bearing basins all over the world (Warwick et al., 2008; Strapoć et al., 2011; Yun et al., 2012 ; Yoon et al., 2016). Microorganisms can degrade coal organic matter and convert it into coalbed gas through their own metabolic activities when coal reservoirs have a suitable external environment (Green et al., 2008; Jones et al., 2010; Penner et al., 2010; Beckmann et al., 2011; Haider et al., 2013; Wang et al, 2019). In the actual production of coalbed gas, many companies (Luca Technologies, Ciris Energy and Next Fuel) in the United States have achieved significant economic benefits by strengthening microbial activity and other ways to increase the production of biogenic coalbed gas (Daniel et al., 2015). Apex Australia injected methanogenic

bacteria into coal seams in the Sydney Basin to stimulate biogas generation (Faiz et al., 2013).

The generation of biogenic coalbed gas is a multi-step process involving the common metabolism of bacteria and methanogens (methanogens). Organic compounds in coal are considered the substrates. At the initial stage of bio-transformation, complex organic compounds in coal are decomposed into simpler molecules by hydrolyzed bacteria, such as polyaromatic hydrocarbons (PAHs), monoaromatic carboxylic acids, ketones, long-chain alkanes and long-chain fatty acids. These molecules are then converted to simple compounds such as acetate, CO₂ and H₂, methanol and formic acid. There are two pathways to produce CH₄ gas, namely CO₂-reduction and acetic acid fermentation (Strapoc et al., 2011; Park et al., 2016). Recently, it has been found that there is also an archaea that can directly use benthoxy in coal to produce methane (Mayumi et al., 2016).

Lower rank coal is considered to have better biogas generation potential than high rank coal (Rice and Claypool, 1981; Orem and Finkelman, 2003). The reason is explained as the weak degree of coal mineralization leaves more side chains in the coal, and these simple structures are easy to be used by methanogens to produce coalbed gas and hydrogen which is rich in chains is important in enhancing biogenic coalbed gas generation even in the high maturity stage (Strapoc et al., 2011). In recent years, there have been reports about biogenic coalbed gas generation from peat, lignite, sub-bituminous and bituminous (Ulrich and Bower, 2008; Opara et al., 2012; Haider et al., 2013; Haider et al., 2014; Bao et al., 2016; Robbins et al., 2016; Shao et al., 2018; Wang and Shao, 2019). Because of the high degree of coalescence and closer chemical structure, high-rank coal, such as anthracite, was considered as an imperfect substrate of biogenic coalbed gas. However, some scholars still believed that high-rank coal could also be anoxic degraded to produce bio-gas under appropriate conditions and they had successfully carried out experiments researches on biogenic coalbed gas from higher rank coal (Fallgren et al., 2013; Wei et al., 2014; Susilawati et al., 2015). Bao et al. (2016) summarized 83 data on biogas production in coal seams and found that biogenic coalbed gas can be generated from various coals with different coal ranks, and sub-bituminous and high volatile C-Bituminous coals have higher biogenic coalbed gas yield than peat and anthracite.

Qinshui Basin is one of the main development bases of coalbed gas industry in China. However, due to the influence of geological factors, the production of coalbed gas is low in many areas (Chen et al., 2018). The high coal rank reservoirs in the south of Qinshui basin are characterized by poor physical properties and low permeability (Qin et al., 2018; Hu et al., 2019). The generation of biogenic coalbed gas has the significance of reforming the pore structure of coal seam, increasing the permeability of coal seam, and facilitating the desorption and migration of coalbed gas (Xia et al., 2014). Therefore, if the microbial enhanced coalbed gas technology can be successfully applied to high-rank coal, it will be of great significance to increase coalbed gas production, improve coal

reservoir permeability and clean utilization of coal.

Using anthracite from Sihe Coal Mine in the south of Qinshui Basin, China, as substrate, this paper carried out the simulated experiment of biogenic coalbed gas generation and focuses on the geochemistry characteristics in the process. The results contribute to the further understanding of the generation mechanism and provide theoretical guidance for bio-gasification and clean utilization of higher rank coal.

2. Experimental materials and methods

2.1. Anthracite sample collection and the basic properties

Four samples, No. SH1, SH2, SH3 and SH4 were collected from Sihe Coal Mine, Jincheng City, Shanxi Province, China (Fig. 1). The samples collected under the mine were immediately wrapped with thin film and sealed with bags to prevent oxidation. The samples were crushed uniformly and the pure coal samples were selected manually.

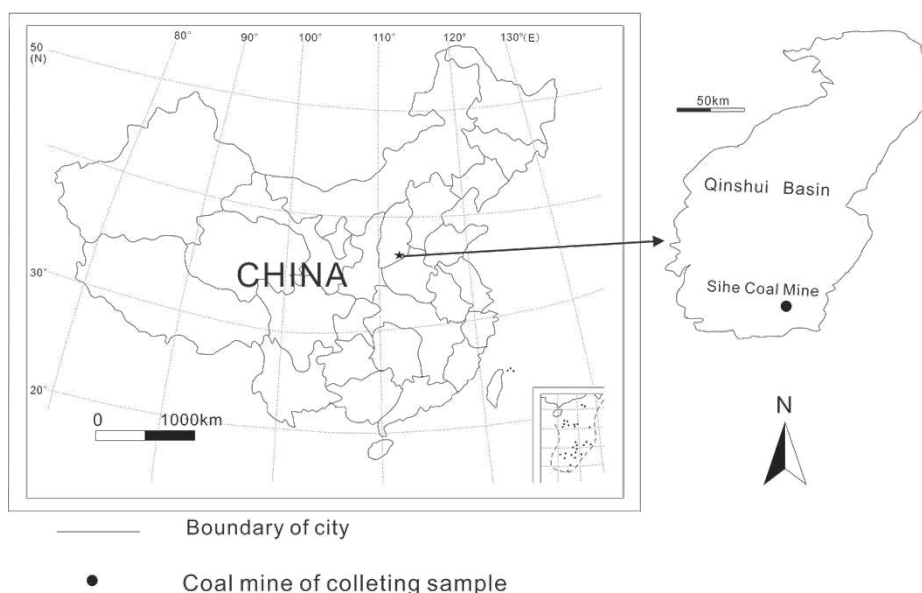


Figure 1 Location for collecting anthracite samples

A Zeiss Imager Mim microscope was used to measure maximum vitrinite reflectance ($R_{o,max}$). The proximate analysis and elemental analysis were conducted follow STM Standard D3173-11, D3175-11, D3174-11 and D5373-08. The maceral content was determined by white light photometer and Zeiss Imager Mim microscope. 500 points were recorded for each maceral. These results were shown in Table 1.

The $R_{o,max}$ values are all more than 2.28% and the average value is 2.56%, indicating that the coal have a high degree of metamorphism and belong to anthracite. The fixed carbon contents in coal samples are relatively high with an average of 82.78%. The anthracite samples are of low-volatile (7.16% to 9.97%) and low-ash (7.62% to 12.95%) content according to Chinese coal industry standard MT/T849-2000 and GB 15224.1-2004. The sulfur contents are very low and

belongs to super low sulfur coal. Among the organic macerals in coal, the vitrinite group has the highest content (74.2% to 81.1%), followed by the inerte group (16.1% to 20.2%), and the exinite has not been detected. The average mineral content is 3.8%.

Table 1 Test data of basic properties of anthracite samples (%)

Coal samples	$R_{o,max}$	Proximate analyses				Elemental analyses					Maceral		Mineral
		M_{ad}	A_d	V_{daf}	FC_d	O_{daf}	C_{daf}	H_{daf}	N_{daf}	$S_{t,d}$	V	I	
SH1	2.44	1.16	12.95	9.84	78.48	3.58	91.27	3.44	1.35	0.31	74.2	20.2	5.6
SH2	2.87	2.10	8.66	7.16	84.80	2.01	93.33	2.95	1.10	0.55	79.2	18.3	2.5
SH3	2.66	1.88	9.08	9.01	88.90	3.06	90.97	4.02	1.51	0.39	77.8	17.8	4.4
SH4	2.28	2.09	7.62	9.97	78.92	2.57	91.83	3.28	1.07	0.43	81.1	16.1	2.8
Average	2.56	1.81	9.58	9.00	82.78	2.81	91.85	3.42	1.26	0.42	78.1	18.1	3.8

$R_{o,max}$ is maximum vitrinite reflectance ; M_{ad} is moisture on air dry basis; A_d is Ash on dry basis; V_{daf} is volatile matter on dry and ash-free basis; and FC_d is fixed carbon content on dry basis. Elements were determined on a dry and ash-free basis, except for sulfur, which was on a dry basis. V is vitrinite and I is intrinite in coal maceral composition.

2.2 Process and method of simulated experiment of biogenic coalbed gas

The simulation experiment was carried out according to the experimental process of bacterial selection - medium configuration - bacterial enrichment culture –inoculation and grouping experiment- biogas production, as what shown in Fig. 2.

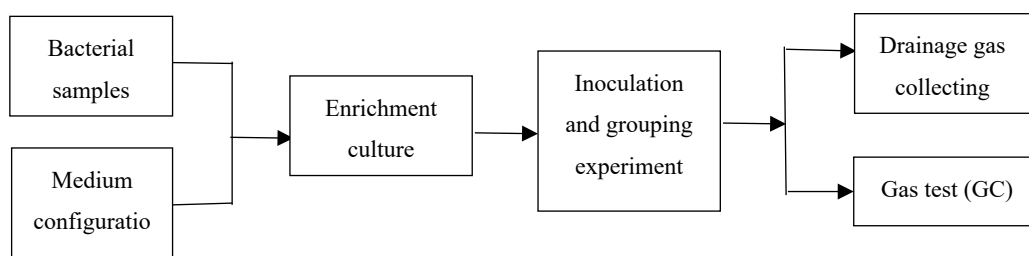


Figure 2 Flow chart of biogas generation simulation experiment

2.2.1 Natural gas release of coal samples

Anthracite samples were subjected to a natural gas release process before the simulated experiment. They are initially crushed and then placed in a flask connected to a beaker through a glass tube. Place the flask in a thermostatic water bath (60°C for 7 days). Bubbles in the water indicate that gas has been resolved, and when no bubbles in the water, the natural analysis process is considered complete.

2.2.2 Bacterial samples and the medium compositions

The source of the bacteria used in the simulation experiment was supplied by the Chinese Academy of Science and was enriched and purified in the mine water of Dananhu Coal mine of Hami coalfield, Xinjiang Province, China. The bacteria were placed in a low-temperature anaerobic

biochemical incubator and stored at a constant temperature of 7°C.

The medium consisted of K_2HPO_4 0.4g, $MgCl_2$ 2.0g, KH_2PO_4 0.4g, yeast extract 1.0g, NH_4Cl 1.0g, resazurin 0.01g, sodium acetate 2.0g, KCl 0.2g, NaCl 2.0g, trace element solution 10.0ml and deionized water 1000mL. The trace element solution was prepared follow reference of Shao et al. (2018). 1.0mol/L HCl and 1.0mol/L NaOH were used to adjust the pH value of the medium to 7.0-7.2. The prepared medium was boiled for 5-10 minutes to remove the dissolved oxygen in the solution, and sterilized at 120°C for 20 minutes and then place it in an anaerobic glove box immediately. Before inoculation, 20mL of 1% Na_2S and 5% $NaHCO_3$ mixed solution and 0.5g cysteine were injected with sterilized deoxygenation syringe to completely remove the dissolved oxygen in the liquid (Shao et al., 2018).

2.2.3 Bacterial enrichment cultivation

The bacterial source was placed in HZQ-F160 incubator with constant temperature oscillation, and incubated at 37°C for 10 hours. The whole process of inoculation and cultivation was held in SYQX - II anaerobic incubator. N_2 was used to replace the air in the anaerobic incubator. 380mL of the chilled medium solution was added to the anaerobic tank, then 3-5mL of deoxidizer was added, shaken evenly, then 6mL of 2.5mol/L sodium acetate solution was added, and finally the cultured bacteria source was added. The inoculated anaerobic flask was placed in the HZQ-F160 constant temperature oscillating incubator for enrichment culture. The temperature was set as constant temperature 37°C, the rotation speed was 50R/min, and the culture time was 30 days.

2.2.4 Inoculation and grouping experiment

A 500 mL brine bottle with a butyl rubber stopper and wax seal was selected to serve as the simulation experiment device to ensure good airtightness. The assembly of the culture-gas collection device is shown in Fig. 3. It was composed of a culture bottle, a needle, a 3-way valve, a 2-way valve, and a 10 mL screw syringe. The gas was collected by the downward drainage saturated brine method.

The experiment was divided into 10 groups, including two blank groups (BK-1, BK-2) and 8 experimental groups (all coal samples were subjected to parallel experiment, SH1-1, SH1-2, SH2-1, SH2-2...). In the 8 experimental groups, 40 g of anthracite, 40 mL of bacterial seed solution and 350 mL of culture medium were added respectively. No anthracite were added to the two blank groups. All the culture bottles were placed in HZQ-F160 constant temperature oscillation incubator. The temperature was set at 37 °C, the rotation speed was 50R / min, and the expected culture time was 80 days. The generated gases were collected on periodically during the experiment (10d, 20d, 30d, 40d, 60d, 80d). The test values below, including gas production, gas composition and stable

isotope composition, are the average values of the corresponding two parallel samples.

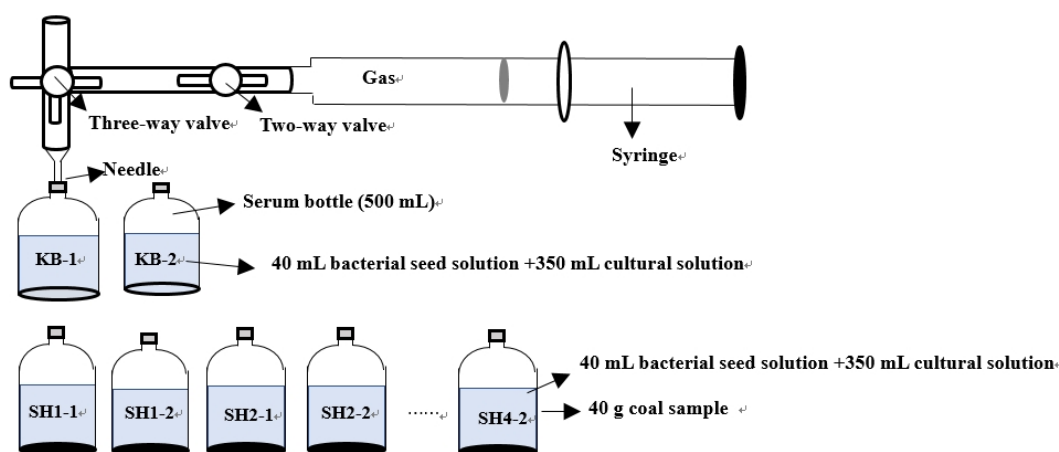


Fig. 3 Schematic diagram of the simulation experiment device

2.3 Gas analysis

The gas composition was directly determined by East West electronic chromatograph (model GC-4000A), and the analysis process have been described in a published paper (Shao et al., 2018).

Stable isotope composition of C ($\delta^{13}\text{C}$) was tested follow the Chinese standard GB/T18340.2-2010 with mass spectrometer (model DELAT V) and HP-PLOT chromatographic column. The split ratio was 15:1. The injection temperature was 40°C. $\delta^{13}\text{C} = 1000(R_1/R_2 - 1)$, where R_1 and R_2 are the $^{13}\text{C}/^{12}\text{C}$ ratios of the samples and standard, respectively.

3 Experimental results

The simulated gas productions in different days are listed in Table 2.

Table 2 Gas production during different stages (mL)

Samples	10d	20d	30d	40d	60d	80d
BK	6.7	22.8	24.6	11.2	0	0
SH1	39.5	63.4	54	27.5	13.2	7.3
SH2	38.2	66	54.7	23.5	18.6	12.5
SH3	47.5	79.8	56.9	29.1	15.4	13.7
SH4	43.2	71	52.8	24.6	16.7	10.4

According to the previous research results, the culture medium can generate biogas (Wang et al., 2017; Shao et al., 2018). The gas production results of BK group in Table 2 also verify this. Therefore, the biogas production of anthracite was obtained by deducting the gas production from culture medium, as shown in the Eq. (1).

The gas compositions are shown in Table 3. The collected gas mainly consists of N_2 , CO_2 and CH_4 , but also contains little heavy hydrocarbon, including C_2H_6 , and C_3H_8 . Previous studies have

shown that N_2 in the collected gas does not belong to the part of biogas generation (Tao et al., 2007; Shao et al., 2018). The existence of N_2 is caused by the air entering when replacing the air in the process of inoculation. The actual biogas component can be obtained after N_2 is deducted by Eq. (2).

Table 3 Relative content of biogas components and methane concentration

Gas	Time(d)	N_2 (%)	CO_2 (%)	CH_4 (%)	C_2H_6 (%)	C_3H_8 (%)
BK	10	83.89	12.32	3.91	-	0.28
	20	76.32	14.65	8.71	0.32	-
	30	21.97	11.4	65.98	0.65	-
	40	10.79	13.34	75.69	0.18	-
SH1	10	81.19	16.78	2.01	-	0.01
	20	77.88	12.21	9.91	-	-
	30	30.45	12.66	56.87	0.02	-
	40	16.79	26.78	56.42	0.01	-
	60	9.89	17.75	72.36	-	-
SH2	80	-	3.56	96.44	-	-
	10	86.12	13.56	1.29	0.01	0.01
	20	80.09	16.78	3.13	-	-
	30	25.76	13.22	61.02	-	-
	40	12.96	23.89	63.11	0.02	0.02
SH3	60	10.01	15.5	74.49	-	-
	80	-	4.22	95.78	-	-
	10	79.99	15.56	4.42	0.01	0.02
	20	73.65	18.02	8.33	-	-
	30	30.03	9.09	60.87	0.01	-
SH4	40	11.98	20.08	67.92	0.02	-
	60	12.21	12.43	75.36	-	-
	80	-	4.02	95.98	-	-
	10	84.54	13.89	1.55	-	0.02
	20	78.94	10.09	10.97	-	-
SH4	30	27.52	11.29	61.18	0.01	-
	40	12.47	19.08	68.43	0.02	-
	60	8.97	12.2	78.83	-	-
	80	-	3.98	96.02	-	-

$C_1/C_{1-n} = CH_4 / (CH_4 + C_2H_6 + C_3H_8 + C_4H_{10})$; - is below detection limit.

$$q_{net} = q(E) - q(BK) \quad (1)$$

$$q = q_t \times (100 - C(N_2)) / 100 \quad (2)$$

Notes: q_{net} is net biogenic gas generated from anthracite samples, mL; $q(E)$ is q of experimental groups, mL; and $q(BK)$ is q of blank group, mL; q is production of biogas, mL; q_t is production of collected gas, mL; $C(N_2)$ is concentration of N_2 in Table 3, %.

The calculated net biogas productions (q_{net}) of anthracite are shown in Table 4.

Table 4 Net biogas production (mL)

q_{net}	10d	20d	30d	40d	60d	80d
SH1	6.35	8.63	18.36	12.89	11.89	7.30
SH2	4.22	7.74	21.41	10.46	16.74	12.50
SH3	8.43	15.63	20.62	15.62	13.52	13.70
SH4	5.60	9.55	19.07	11.54	15.20	10.40

4 Discussion

4.1 Anthracite biogas production

According to the weight of coal and gas collection time, the net gas yield was determined by Eqs. (3).

$$R_{net} = q_{net} / (m \times \Delta t) \quad (3)$$

Notes: R_{net} is net biogas yield, $mL \cdot g^{-1} \cdot d^{-1}$; m is weight of anthracite samples, g; Δt is interval time of gas collection.

On day 60, the BK no longer produced biogas, indicating that microorganisms had used the culture solution completely then (Fig. 4. (a)). After 60 days, biogas was still produced in the experimental group, indicating that the anthracite samples in Sihe Mine could be effectively utilized by methanogenic bacteria to produce biogas. Anthracite is characterized by high degree of coalescence and tighter chemical structure, so it is considered by most scholars that it is difficult to biodegrade to produce gas. However, some scholars have successfully simulated gas production from anthracite coal in the laboratory (Xiao et al., 2013). The results of this study once again verify

this conclusion.

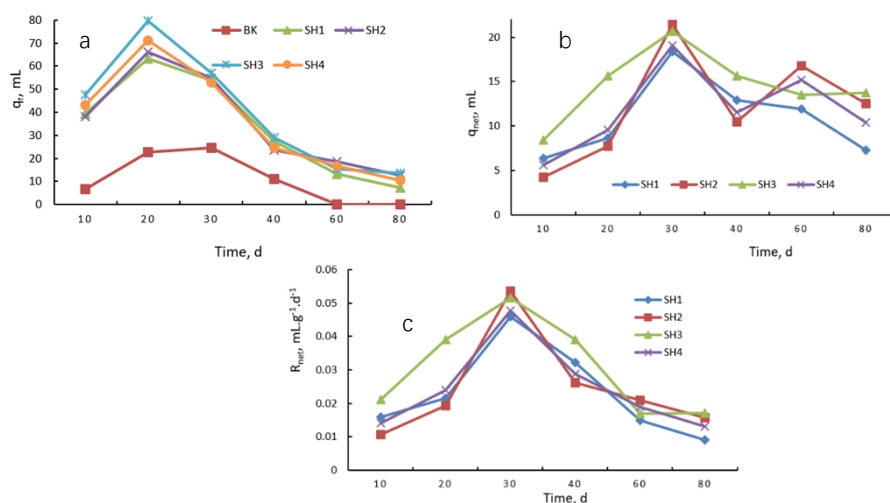


Figure 4 Biogas production from anthracite samples. (a) Change in the production of biogenic gas; (b) Change in the net production of biogenic gas; (c) Change in the net biogas yield

The total productions of net biogas generated from SH1, SH2, SH3 and SH4 were 65.42, 73.07, 87.52 and 71.63 mL, the average value was 74.34mL. This means that approximately 1.79 mL/g of biogas can be produced from anthracite in Sihe Mine, Qinshui Basin. Under the similar cultured condition, bituminous coals can produce 5.98 mL/g approximately and lignite can produce 8.4 mL/g (Shao et al., 2018). Anthracite produce less biogas than that of lower rank coal. There is no doubt that low rank coal can be easily biodegraded than high rank coal, because they have more aliphatic hydrocarbons and heteromatoms. By the way, the maceral composition was considered to influence the biogas generation rate, which could explain why high rank coal has more biogas rate than low rank coal (Haider et al., 2013; Shao et al., 2018).

The whole biogas generation process can be divided into 2 stages: a fast growth stage (0-30d) and a slow decline stage (30-80d) (As what shown in Fig.4. (b) and (c)). Similar periodic characteristics occur in almost all biogenic coal bed gas generation simulation experiments (Wang et al., 2012; Wang and Shao, 2018; Shao et al., 2019). The results in this study indicated that the biodegradation process of anthracite is similar to that of low rank coal. In the first 30 days, the nutrients were rich in organic carbon, and many small soluble organic compounds were available for biodegradation. These organisms effectively activated methanogens in this first stage. The slow decline stage resulted from the low activity of methanogens, which perhaps be due to the inhibitory compounds accumulated in the solution, such as volatile fatty acids or heavy metals (Strapoć et al., 2011; Wawrik et al., 2012; Fallgren et al., 2013; Chen et al., 2017). The amount of these substances was not sufficient to completely inhibit methanogenic activity. With the increasing activity of

methanogens, they were decomposed to produce biogas.

4.2 Simulated biogas composition characteristics

As shown in Table 3, the main components of biogas were CO₂ and CH₄, heavy-hydrocarbons were little Heavy- hydrocarbons were rarely found in biogenic gas simulated experiments of lignite or bituminous coals (Shao et al., 2018; 2019). However, they were often found in secondary biogenic coalbed gas reservoirs (Scott et al., 1994; Faiz et al., 2007; Lan et al., 2012). It is not clear why now. Some study considered that heavy-hydrocarbons might be caused by the catalysis of heavy metals (Wu, 2011; Wang et al., 2017). However, we considered that the high coalification degree and large molecular structure of anthracite were the reasons for the formation of heavy-hydrocarbons. These are all subject to further study.

The change of CO₂ concentrations can be divided into two stages: rising (0-40d) and falling (40-80d) (Fig. 5 (a)). In the first 40 days, the increase curve of CO₂ concentration was oscillatory. On the 30th day, the concentration of CO₂ showed the lowest value, but during the next 10 days, it rapidly increased to the maximum. In the falling stage, CO₂ content decreased almost linearly. CH₄ concentration increased slowly in the first 20 days, but increased rapidly in the 20-30 days. During 30-80d, it increased steadily (Fig. 5(b)). Concentrations of CO₂ and CH₄ showed an opposite alternation, suggesting that some CO₂ was used to produce CH₄ especially in 30-80 days. This means that part of biogenic CH₄ from anthracite was generated by way of CO₂-reduction in this study. The main pathway was acetic fermentation, because the contents of CO₂ were all lower than 30%, but the CH₄ content was more than 60% in the final 50days.

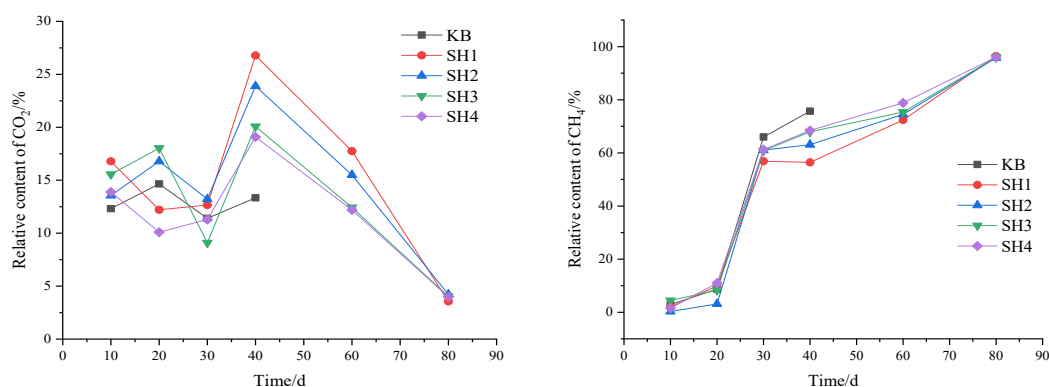


Figure 5 (a) Change of CO₂content; (b) Change of CH₄ content.

4.3 Carbon isotopic composition of simulated biogas

$\delta^{13}C$ is an important geochemical parameters of biogas, which can reflect the source and formation mechanism of biogas generation (Hayes, 1993; Conrad et al., 2011). Carbon isotope fractionation factor (α_C) is also regarded as identifiers of methanogenic pathway (Hayes, 1993). It can be calculated using Eq. (4). Isotope effect (ϵ_C), which is the difference between

C isotope composition CO₂ ($\delta^{13}\text{C}_{\text{-CO}_2}$) and CH₄ ($\delta^{13}\text{C}_{\text{-CH}_4}$), was calculated following Eq. (5). It can reflect whether the biogas is produced by acetate fermentation or CO₂ reduction (Hayes, 1993). They were all shown in Table 5.

$$\alpha_C = (\delta^{13}\text{C}_{\text{-CO}_2} + 1000) / (\delta^{13}\text{C}_{\text{-CH}_4} + 1000) \quad (4)$$

$$\varepsilon_C = \delta^{13}\text{C}_{\text{-CO}_2} - \delta^{13}\text{C}_{\text{-CH}_4} \quad (5)$$

These four anthracite samples have similar carbon isotope compositions with the average value of -22.3‰. The biogenic gas has the characteristic of light $\delta^{13}\text{C}_{\text{-CH}_4}$, which was generally considered to range from -110‰ to -50‰. However, research results in recent years showed that the $\delta^{13}\text{C}_{\text{-CH}_4}$ values of coal bed biogas generated under laboratory conditions were higher than -50‰ (Krüger et al., 2008; Wang et al., 2018; Shao et al., 2018; 2019). Moreover, acetoclastic methanogenesis can produce ¹³C-enriched CH₄ and the $\delta^{13}\text{C}_{\text{-CH}_4}$ values can reach -40‰ (Penning et al., 2006; Vavilin et al., 2008). In this study, the $\delta^{13}\text{C}_{\text{-CH}_4}$ values of gases production from anthracite ranged from -39.9‰ to -45.8‰, which can be considered as biogenic gas and mainly produced by pathway of acetic fermentation. On the 40th day, the mean $\delta^{13}\text{C}_{\text{-CH}_4}$ value was -43.6‰, which was lighter than that of 20d (-40‰). So pathway of CO₂-reduction was involved at the later stage of the simulation.

α_C and ε_C values can indicate the results above more accurately. The four experimental groups all produced $\alpha_C = 1.02$. The mean ε_C values at 20d and 40d were 20.25 and 24.13 respectively. All these values were consistent with what for acetic fermentation pathway (Penning et al., 2006; Govert and Conrad, 2009).

Table 5 Test of carbon and hydrogen stable isotopes of biogenic gas and coal samples.

Sampl es	$\delta^{13}\text{C}_{\text{-coal}}$ (‰)	20d					40d		
		$\delta^{13}\text{C}_{\text{-CH}_4}$ (‰)	$\delta^{13}\text{C}_{\text{-CO}_2}$ (‰)	α_C	ε_C	$\delta^{13}\text{C}_{\text{-CH}_4}$ (‰)	$\delta^{13}\text{C}_{\text{-CO}_2}$ (‰)	α_C	ε_C
BK	none	-46	-21.1	1.03	24.9	-42	-23.4	1.02	18.6
SH1	-22.8	-40.2	-20.2	1.02	20	-39.9	-18.7	1.02	21.2
SH2	-20.7	-39.9	-18.9	1.02	21	-42.4	-19.2	1.02	23.2
SH3	-22.3	-41.1	-20.9	1.02	20.2	-44.6	-19.7	1.02	24.9
SH4	-23.4	-39.6	-19.8	1.02	19.8	-45.8	-18.6	1.02	27.2

All carbon isotope compositions are relative to V-PDB standard.

5 Conclusions

This experiment confirmed that, the methanogenic bacteria could use anthracite as substrate to produce biogas. Approximately 1.79 mL/g of biogas can be produced from anthracite in Sihe Mine, Qinshui Basin. Although this value was lower than that of lower rank coal, it is of great significance for the clean utilization of anthracite

Through the analysis of gas production process, gas composition and gas carbon isotope composition, it can be found that, the biogas generation process can be divided into two stages.

After the rapid gas production stage (0-30d), the speed gradually slows down(30-80d). Biogas generation process from anthracite is similar to that of low rank coal, indicating that their formation process and mechanism is similar. Despite the pace was slow for the first 30 days, CH₄ contents kept increasing in the whole process. In addition to high concentrations of CH₄ and CO₂, there was little heavy-hydrocarbons production. The stable isotope geochemical characteristics showed more positive $\delta^{13}\text{C}_{\text{-CH}_4}$, compared to the previous studies on biogenic gas. These results showed that, the biogenic CH₄ is mainly produced by pathway of acetic acid fermentation, although the pathway of CO₂-reduction joined in the later stage.

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Authors' contributions

Experimental operation, Aikuan Wang, Qinghui Wang and Pei Shao; Data processing, Aikuan Wang, Qinghui Wang, Pei Shao, Tian Fu, Moran Cao; Writing original draft, Aikuan Wang, Qinghui Wang. All authors read and approved the final manuscript.

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Availability of data and materials

Data obtained from experiments in this study

Competing interests

The authors declare that they have no competing interests

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