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Comparative experimental study of hydrogen and methane with coal cogeneration system and methane of single-phase production

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With low coal rank lignite as bio-gas production substrate, characteristics of single phase methane production in coal seam and cogeneration of hydrogen and methane gas at 35 ℃ were studied, with liquid phase and solid phase product during reaction analyzed for comparative mechanism study of single-phase and two-phase gas. The results showed that: (1) In single-phase and two-phase gas production with coal as substrate, single-phase methane production rate is 22.86ml / g, cogeneration production rate is 26.24ml / g, second-phase methane concentration ratio is 7.9% higher than single-phase. (2) Single-phase methane fermentation featured ethanol fermentation, while cogeneration featured butyric acid type and acetic acid type fermentation. (2)C and O contents of coal after cogeneration and single-phase production of methane declined, but H content increased. Lignin, cellulose, hemicellulose consumption rates of co-produced coal were respectively 15.2%, 18.1% and 16.6%; XRD results show that crystalline structure damage of coal was more obvious after cogeneration. (3) Single-phase production mechanism of methane gas featured carbon dioxide reduction, while cogeneration experimental hydrogen production featured hydrolysis and decomposition of macromolecules, methanogenic phase featured acetic acid fermentation. Experimental results show obvious biological effects of cogeneration of bio-hydrogen and methane, which can significantly improve the utilization of residual coal.

Keywords: cogeneration of hydrogen and methane, VFA change, coal degradation, mechanism

INTRODUCTION

Seam biogas in the United States have achieved commercial exploitation. Recently, research group [1-6] study confirmed that if there is proper control of the reaction conditions, in first period of seam biogas production, bio-hydrogen will be generated, which is consistent with traditional four-stage fermentation theory.

Coal is degraded by white rot fungi into cellulose, lignin material that can be used, which can be degraded into small molecules of acid and alcohol [7-15] by hydrolytic bacteria and syntrophic acetogenic bacteria. Hydrogen will be produced in the process which combines with carbon dioxide and produces methane under the role of methanogens. Hydrogen is a cleaner energy than methane, with yield and substrate utilization rate lower than the methane. If cogeneration of the two is realized, maximal recycling of resources can be achieved with biological residual coal mining realized[16]. Early tests confirmed feasibility of hydrogen and methane production with two-phase anaerobic fermentation. In this study, with independent methane production experiment, cogeneration experiment of hydrogen and methane as the basis, reaction conditions were adjusted before the end of the second set of experiments, methane was produced by changing the pH and adding nutrients, and analysis was done from gas production rate, fermentation period, VFA change, coal structural parameters in order to define the reaction mechanism.

MATERIALS AND METHODS

Preparation of Coal Sample

Place low rank coal sample into the crusher to be grinded into pulverized coal of 0.25mm or so. Then screen out 400g of coal sample into autoclave sterilization pot for 30min sterilization at 120 ℃ to reduce side effects of microorganism outside. Then, transfer coal sample to a sample bag, and finally place the coal sample into 60 ℃oven to be dried to constant weight for standby application.

White Rot Fungi Liquid Enrichment

Enrich white rot fungi, inoculate appropriate amount of white rot fungi into medium after sterilization and cooling of white rot fungi enriched medium. Shock and mix for 2min in a fast mixer, so that thallus is dispersed. Then culture 2d in 35°C constant temperature shaking chamber.

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Mine Water Bacterial Liquid Enrichment

Prepare hydrogenogens-rich liquid 1000ml respectively with mine water and hydrogenogens medium, and prepare hydrogenogens-rich liquid 1000ml with mine water and methanogens medium for standby application.

EXPERIMENTAL PROGRAM

Methanogenesis Experiment

20g pulverized coal + 20ml white rot fungi liquid+ 200ml methanogens mine water enrichment nutrient solution, set three parallel samples to be placed in 35 ℃ incubator, adjust p H = 7, gas production time at 35 days, and ultimately take the average value for calculation.

3.2. Cogeneration of Hydrogen and Methane

Hydrogen production stage: 20g coal + 20ml white rot fungi liquid + 200ml enriched hydrogenogens liquid, adjuste the initial pH value of the sample at about 6.8 which then receives anaerobic fermentation for about 10 days at 35 ℃. Methanogenic stage: Similarly, supplement 1 mol / L NaOH solution to hydrogen production reaction flask at anaerobic work station, adjust the pH to about 7, add methanogens nutrient solution and add a small amount of trace elements. The total gas production time is 50 days. Set three parallel samples and ultimately take the average value for calculation. Record total gas production, gas concentration of two set of experiments. Carry out pH value detection and VFA analysis of reaction liquid, perform element and XRD analysis of coal before and after the reaction, calculate lignin and cellulose, hemicellulose consumption in order to carry out comparative analysis of the two gas production mechanisms.

EXPERIMENTAL RESULTS

Analysis of Gas Production

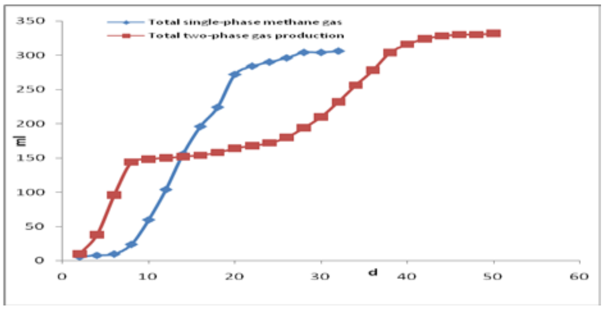

Fig. 1. Cumulative production output of methane and hydrogen.

Gas production changes show that single-phase production of CH4 lasted 36 days, with a total CH_4 volume of 306ml; two-phase hydrogen and methane gas production time was 52 days, total first-phase hydrogen production volume was 114ml, total second-phase production volume was 264ml, with total gas production at 398ml. Two-phase situation is 18.1% more than single phase.

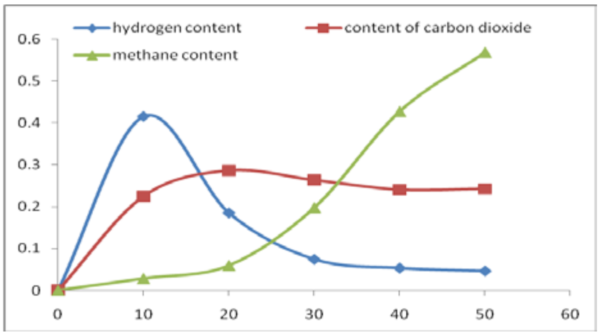

Fig. 2a. Two-phase system gas concentration variation diagram.

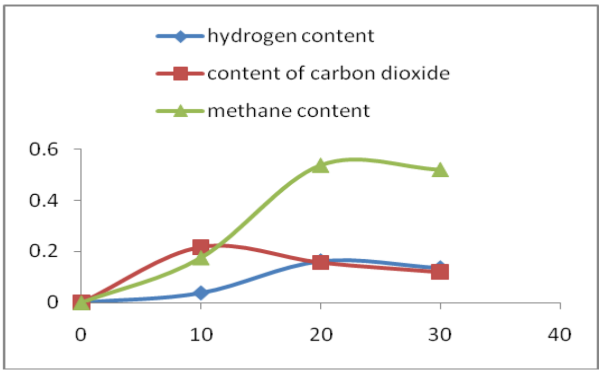

Fig. 2b. Single-phase methane gas concentration variation diagram.

Changes in gas concentrations show that in single-phase production of CH_4 system, H_2 concentration peaked at 16.3%, remaining low, while CO_2 concentration decreased after growth, reaching 21.7% on the tenth day and then reducing to 11.9%, CH_4 concentration kept growing to 50.6% at end of the experiment; cogeneration experiment shows that, H_2 content and concentration peaked at 40.6% on the tenth day, the highest value of hydrogenogens metabolic activity, and then plummeted afterwards, CO_2 concentration peaked at 28.7% on 22rd day and then maintained at around 25%. Obviously, CH_4 gas production and concentration of two-phase gas production are higher than that of single phase in gas production effect.

As can be seen from the figure, gas production lag phase of independent methane production lasted 8 days, which was because methanogens is with longer growth cycle which needs some time from growth delay to metabolism bloom phase. Hydrogenogens at hydrogen production stage in cogeneration experiment was with shorter growing cycle, and hydrogen production basically ended after about 10 days. Second-phase methanogenesis had a delay of about 10 days, delaying about two days compared with independent methanogenesis. It is mainly becuase low pH value growth environment of methanogens. After adding alkali solution, methanogens needed an adjustment period, and therefore methanogens lag phase of cogeneration experiment was longer than independent methanogens. But seen from the figure, average production rate of cogeneration system is 32% higher than average production rate of independent methanogenesis, with average methane content also increased by 7.3%, indicating that gas production performance of cogeneration hydrogen and methane is better than single-phase system.

Effect on Liquid Fermentation Products

Effect on pH

During single-phase fermentation of methanogenesis, pH value decreased to some extent, until the minimal point 6.21 throughout the reaction on the 16th day or so, but continued to increase to 7.82 afterwards. Two-phase hydrogen production and methanogenesis reached the lowest value 5.25 on the twelfth day before stabilizing at 8.25. As is apparent, lowest pH value of two phase is much lower than that of single phase with final pH higher than that of single phase.

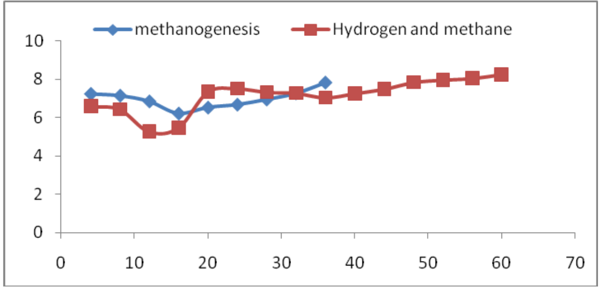

Fig. 3. pH value changing curve of single-phase and two-phase gas production.

As is seen from Figure 5, during single-phase methanogenesis fermentation, substrate degradation featured ethanol type fermentation. Peak occurred on the 18th day, about 0.35mmol / L, while acetic acid, butyric acid peaked on the 15th day, respectively 3.15mmol / L and 2.85mmol / L, whose concentration bottomed out to 0.35mmol / L and 0.21mmol / L after fermentation on the 26th day. The degradation rate of ethanol was very low throughout the experiment. After reaching the peak on the 10th day, ethanol concentration stopped significant change with only slight decrease in the later period, indicating that the acid generated thereafter was rapidly degraded and no longer accumulated in fermentation liquid.

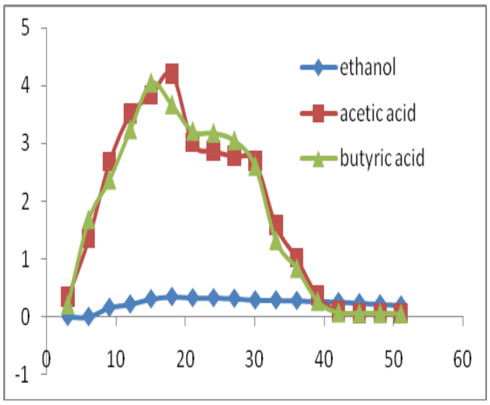

Fig. 4a. Variation of two-phase system of small molecule acid.

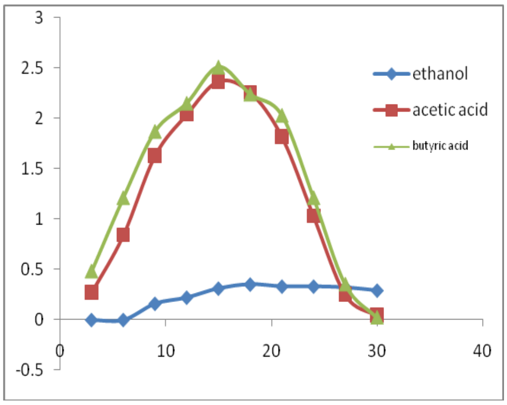

Fig. 4b. Variation of single-phase system of small molecule acid.

As is seen from the figure, first-phase substrate degradation in two-phase anaerobic fermentation featured butyric acid type fermentation. In production of butyric acid, a large amount of hydrogen was produced. At the end of hydrogen reaction, residual concentration of acetic acid was 4.21mmol / L, that of butyric acid was 3.67mmol / L, while that of ethanol was only 0.17mol / L or so. However, in the second phase, after methanogens recovered activity after 6d lag phase, butyric acid and acetic acid began to be used by methanogens. At the end of the reaction, acetic acid and butyric acid in the solution were substantially reduced to zero. From this, it can be concluded that concentration of acetic acid and butyric acid produced in two-phase and single-phase system are greatly different from each other, but final two-phase decomposition is more thorough. In analysis of the reasons, due to action of syntrophic acetogenic bacteria and fermentation bacteria, in cogeneration hydrogen production stage, more volatile fatty acids will be produced, which also provide fermentation substrate for methanogenesis. After pH adjustment and physiological lag phse of bacteria, methanogens's VFA consumption accelerated. Judging from that final acetic acid and butyric acid concentration is zero, reaction of the stage features acetic acid decomposition.

Degradation of Coal

Degradation of Coal Elements

Comparative change of coal sample elements before and after aerogenesis is shown in the following table. As can be seen from the table, C content in coal suffered from varying degrees of decline after aerogenesis, decreased most after cogeneration to final amount of 73.5%. Gas experiment mainly studied organic carbon in microbial degradable coal. In cogeneration test, it was secondary aerogenesis with large consumption of C element, and therefore degree of degradation was more thorough. H element content increased, especially after hydrogen production when H content increased to 6.37%, 22.3% over that of raw coal sample. It was mainly because hydrolysis reaction occurred during hydrogen production, microbial enzymes substance decomposed macromolecules in coal and generated water-soluble small molecule compounds, aromatic ring fractured and induced active functional group with higher hydrogen content. Therefore, H element content increased, and after methanogenesis, hydrogen elements were broken down into water-soluble small molecules acid. So after methanogenesis, H element content decreased compared with hydrogen generation. O element increase was mainly a result of hydrolysis of macromolecules in coal in hydrogen production stage.

Table 1. Analysis of elemental changes of coal.

Sample	C（%）	H（%）	O（%）
Raw coal sample	81.35	4.96	15.72
Coal sample after methanogenesis	76.35	5.45	13.64
Coal sample after hydrogen production	80.2	6.07	16.74
Coal sample after cogeneration	73.5	5.39	14.13

Coal Lignin, Cellulose, Hemicellulose Decomposition

As can be seen from the table, compared to single-phase methanogenesis system, cellulose, hemicellulose and lignin consumption rates of two-phase system were respectively increased by 3.6%, 5.8% and 6%, so degradation of two-phase system was definitely more thorough. Lignin, cellulose, hemicellulose are more easily decomposed organic compounds in low rank coals. Under the action of primary enzymes such as laccase and manganese peroxidase, lignin and cellulose-based substances were hydrolyzed to high-molecular polymers such as polysaccharide protein and fat, which were further broken down into monose, amino acid and fatty acid. As is apparent from the table, in cogeneration system, after hydrogen production, acidic environment of the system is more conducive to degradation and use of cellulose, hemicellulose, lignin and other substances in the coal. Coal degradation rate was increased, availability of intermediate products including ethanol, acetic acid, propionic acid, butyric acid and other small molecules increased correspondingly, and therefore aerogenesis efficiency of hydrogen production and methanogenesis in co-fermentation was also improved.

Table 2. Decomposition of main chemical substances in coal.

	Cellulose	Hemi-cellulose	Lignin
Single-phase methanogenesis	12.3%	10.6%	11.6%
Two-phase hydrogen production phase	10..5%	10.4%	9.7%
Two-phase methanogenic phase	7.6%	6.2%	5.5%
Two-phase system	18.1%	16.6%	15.2%

XRD Analysis of Coal Structure

Table 3. XRD structural parameters of coal.

	d_{002} （10^{-1}nm）	La （10^{-1}nm）	Lc （10^{-1}nm）
Raw coal sample	3.694	2.517	0.896
Coal sample after methanogenesis	3.876	2.426	0.862
Coal sample after hydrogen production	3.945	2.503	0.877
Coal sample after cogeneration	3.936	2.368	0.833

In cogeneration experiment, after acid production in hydrogen production stage, three-dimensional molecular structure of coal was oxidized, benzene ring was gradually opened to introduce oxygen-containing groups such as carboxyl, hydroxyl at open place, resulting in weakened bond energy, larger bond length and greater interlayer distance d002. In addition, order degree of orientation was also reduced after hydrogen production. As a result, number of plies of condensed ring aromatic layer was decreased to some extent, also height, extension and diameter of aromatic layer were obviously less than those of independent methanogenesis, and loose degree of coal structure was larger than that of independent methanogenesis, which explained why coal structure degradation of two-phase hydrogen production and methanogenesis experiment was stronger than that of independent methanogenesis experiment.

Mechanism Analysis

Based on the above gas, liquid and solid phase change results, let us explore difference in aerogenesis mechanism of single-phase methane production and cogeneration of hydrogen and methane. In single-phase methanogenesis process, various types of oxygen-containing functional groups such as methyl, etc. were degraded by microorganism and dissolved in the reaction liquid after falling off, forming small molecule compounds; pH of reaction liquid lowered, concentration of fermentation substrate such as methyl etc. in this stage first increased and then decreased. CO_2 was the main production gas, and as the reaction proceeded, acetic acid content in the fermentation liquid continuously declined. pH value kept growing, and methane concentration during the stage continued to increase, reaching a peak at 53.68%, while CO_2 continued to reduce, indicating that CO_2 was consumed. CO_2 reduction pathway for CH_4 output appeared, with $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ as the representative reaction. The stage was for main output pathway of methane. In cogeneration of hydrogen and methane, under action of syntrophic acetogenic bacteria, a large amount of H_2 and CO_2 plus many small molecule acid were generated. Methane concentration was low at this time, but after re-adjusting pH and adding nutrients, various VFA began to be degraded and utilized by methanogens. However, due to adaptation period, methanogens's utilization of degradation intermediates was lagged. After fermentation to 36d, VFA concentration was only slightly reduced and methane concentration was very low at this time. After 36d, methanogens activity increased, use rate of small molecule acid was greatly increased, concentration of various acids decreased rapidly, causing gradual increase in pH value. After reaction proceeded to about 60d, pH value of test fermentation liquid increased to 8.28, and in the process CO_2 concentration remained high, indicating that second phase methanogenesis process featured acetic acid substance fermentation, with reaction equation as $CH_3COOH \rightarrow CH_4 + CO_2$.

CONCLUSION

(1) In the case of single-phase fermentation of methanogenesis, average content of methane in gas was about 48.6%, with gas production rate at 18.7ml / g; in the case of cogeneration of aerogenesis, average content of pre-gas hydrogen reached 42.3%, with gas production rate at 9.6 ml / g, methane content in second-phase aerogenesis reached 53.6%, with gas production rate at 23.7 ml / g, respectively improving by 8.15% compared with single-phase fermentation.

(2) Degradation of substrate during single-phase methanogenesis featured ethanol type fermentation; degradation of substrate in two-phase anaerobic fermentation of hydrogen production phase featured butyric acid type fermentation, and second phase also featured ethanol type fermentation. Although higher concentrations of butyric acid and acetic acid were generated in hydrogen production phase fermentation, after pH adjustment, most of the acetic acid and butyric acid were utilized by methanogens, generating methane and carbon dioxide, which made methane amount gas produced in methanogenesis phase increased compared with hydrogen production phase.

(3) In independent methanogenesis, main elements of coal, lignin and cellulose degradation rate, aromatic parameter were lower than those of cogeneration system at the end of aerogenesis, which proved that degradation of coal in cogeneration experiment was more thorough with higher utilization of residual coal.

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