



室蘭工業大学

学術資源アーカイブ

Muroran Institute of Technology Academic Resources Archive



## バイオガスの濃縮による残炭,ハサミ(低品位炭)の分解に関する研究

メタデータ	言語: eng 出版者: 室蘭工業大学 公開日: 2010-03-31 キーワード (Ja): キーワード (En): Enrichment, Gangue, Nitrogen, Methane content 作成者: DENG, Yinsheng, TANG, Min, HUANG, Yan, SHEN, Zhe メールアドレス: 所属:
URL	<a href="http://hdl.handle.net/10258/480">http://hdl.handle.net/10258/480</a>

# Research on the Degradation of Residual Coal and Gangue in the Mine by the Enrichment of Biogas

Yinsheng DENG \*, Min TANG \*, Yan HUANG \* and Zhe SHEN\*\*

(Received 27 May 2009, Accepted 20 November 2009)

In this paper, simulation study is carried out focusing on both enrichment of biogas and regulating the value of C/N, which are the effect on the degradation of residual coal and gangue by enrichment of biogas. The paper comes to the conclusions that : (1) Microorganisms in bacterial liquid is rich through enrichment of biogas, and results show that it is feasible according to degradation effect. (2) Application of nitrogen provides ample sources of nitrogen ( $\text{NH}_4^+$ ) for microorganisms. The available nitrogen ( $\text{NH}_4^+$ ) content increases, and microorganisms grow well, which are benefit from anaerobic fermentation. (3) The reduction rate of organic matter is basically consistent with gas production, furthermore the quantity of microorganisms determines the utilization degree of organic matter. (4) Considering both gas production and organic matter content, organic matter in gangue is indeed degraded by microorganisms.

Keywords : Enrichment, Gangue, Nitrogen, Methane content

## 1 INTRODUCTION

Coal is the main energy in China, but the recovery rate of coal resources has been always low. "2007 China Energy Blue Book" shows that the average recovery rate is 30% at present, and less than half of advanced level in the world; while the average recovery rate in township coal mine is only 10% -15%. A large number of residual coal can not be produced in the mine. Coal gangue is the rock containing low-carbon content in the coal-forming process, which is associated with coal seam, which is the mixture that consists of carbonaceous shale, mudstone, sandstone mudstone, sandstone and limestone rocks, etc. According to sustainable development, the treatment and resource

utilization of gangue have been solved in the course of the development of coal industry. Filling into abandoned mine, gangue and residual coal in the ground are degraded by microorganisms in closed environment, and then occurs a series of complex biochemical reacts.

Methanogenic bacteria<sup>(1)</sup> are mainly distributed in the anaerobic environment including rich organic matter, such as swamps, lake mud, hot springs, sewage and waste disposal plant, animal rumen and digestive tract as well as the methane fermentation tank. Zhao Fuling<sup>(2,3)</sup> regarded long flame coal, gangue, mine water as the research object and studied the gas production and methane content under the condition of adding inoculum. Carbon isotope value of produced methane in the course of the experiment was nearly similar with gangue, which proved that microorganisms played a certain role of gangue. However, the ammonia index in the fermentation broth can not reached class I

\* Henan Polytechnic University, Jiaozuo454000, China.

\*\* China University of Mining and Technology, Xuzhou 221003, China.

of Groundwater Environmental Quality Standard. Therefore, to further study the degradation rate of organic matter and protect ammonia from overproof, the author improves inoculum to make research on the degradation of residual coal and gangue by enrichment of biogas.

## 2 ENRICHMENT OF BIOGAS

### 2. 1 Inoculum

Biogas for enrichment in the test is derived from small-scale biogas digesters of village families in Jiaozuo.

### 2. 2 Choice of media

Medium is the manual prepared nutrients for providing microorganisms, plants and animal tissue for growth and maintenance, and generally contains carbohydrates, nitrogen-containing substances, inorganic salts (including trace elements), as well as vitamins and water. Medium applied of chemicals and identified the components are known as synthetic medium or comprehensive media, which needs to be added a certain amount of trace elements and such on.

In accordance with the literature<sup>(4)</sup>, the formulation of synthetic media is as follows: 1g NH<sub>4</sub>Cl, 1g MgCl<sub>2</sub>, 0.4g K<sub>2</sub>HPO<sub>4</sub>, 0.4g KH<sub>2</sub>PO<sub>4</sub>, 2g protein casein trypsin solution, 1g yeast extract, 50ml salt solution, 10ml trace element solution, water 1000ml, pH value 7.0. Inorganic salt solution is as follows: 6g K<sub>2</sub>HPO<sub>4</sub>, 6g KH<sub>2</sub>PO<sub>4</sub>, 6g (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 12g NaCl, 2.6g MgSO<sub>4</sub>, 0.16g CaCl<sub>2</sub>, distilled water 1000ml; trace element solution is as follows: 0.5gMnSO<sub>4</sub>, 3.0g MgSO<sub>4</sub>, 0.1g FeSO<sub>4</sub>, 1.0g NaCl, 0.1g CoCl<sub>2</sub>, 0.1g CaCl<sub>2</sub>, 0.01g CuSO<sub>4</sub>, 0.1g ZnSO<sub>4</sub>, 0.01g AlK(SO<sub>4</sub>)<sub>2</sub>, 0.02g NiCl<sub>2</sub>, 0.01g Na<sub>2</sub>MoO<sub>4</sub>, distilled water 1000ml. NH<sub>4</sub>Cl and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> provide nitrogen for the microorganisms; K<sub>2</sub>HPO<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>, MgSO<sub>4</sub>, NaCl and other inorganic salts are mineral elements for the provision of microorganisms; FeSO<sub>4</sub> and NiCl<sub>2</sub> provide trace elements; yeast extract provides growth factors, and mainly regulates B

vitamins for microbial metabolism.

Liquid medium is made by a variety of nutrients and water, which components are homogenous. It is suitable for all kinds of microorganisms growth. Hence, it is widely used in experimental research and large-scale industrial production, and beneficial to have access to a large number of cell. This experiment is equipped with a kind of synthetic liquid medium for enrichment. After preparation in accordance with document<sup>(5)</sup>, sterilization, cooling liquid medium, species can be directly introduced: 100ml biogas are added to the 1000ml synthesis medium under atmosphere of nitrogen, and then cultured isothermally for bacteria solution (at 35°C, for five days).

## 3 THE IMMERSION AND ANAEROBIC FERMENTATION TEST ON RESIDUAL COAL AND GANGUE

### 3. 1 The immersion test of residual coal and gangue

Test materials are residual coal and gangue, which sampled from Twelve Mine in Ping Dingshan Coalmine, crushed, screened below 2mm. After mixed coal and gangue are divided to 5Kg using “quartering method”, which have been drying 2h in the oven(at 105°C), reserved. Water in the test is also from the twelve Mine.

Portions of 30g coal and 120g gangue are weighed, and packed in 9 glass containers respectively, then added 300ml mine water. Solid-liquid ratio is 1:2. That is stirred once every 24h, and all soaked for 24 days.

### 3. 2 Anaerobic fermentation test

Elemental analysis for Gangue and coal is to determ-

items	C	N	P	H <sub>2</sub> O	H
gangue	9.71	1.46	0.009	2.62	1.20
coal	71.41	0.68	0.002	3.38	4.07

Table 2. Designs of the experiment

groups	solid-liquid ratio is 1:2	regulating the value of C/N		additives (g)		bacterial liquid(ml)
		original C/N	total nitrogen	chicken manure	sludge	
blank				0	0	300
A1				20	-	0
A2			chicken manure (g/kg)19.3297	20	-	300
A3	gangue 120g			10	-	300
A4	coal 30g	16.9		5	-	300
B1	mine water 300ml			-	20	0
B2			sludge (g/kg)	-	20	300
B3			26.8802	-	10	300
B4				-	5	300

ine the proportion of carbon nitrogen and phosphorus, such as Table.1. From Table.1, we can see the ratio of carbon and nitrogen in coal is 105:1, 6.65:1 in gangue, 16.9:1 in mixed coal and gangue (the ratio of coal and gangue is 2:8). Nitrogen sources provide nitrogen element for microorganisms. The available nitrogen in anaerobic fermentation is generally  $\text{NH}_4^+$  used by microorganisms, and most species can also use amino acids. However, available  $\text{NH}_4^+$  is insufficient in test materials, nitrogen sources are added in order to meet the requirements. Chicken manure and sludge for regulating the ratio of carbon and nitrogen were collected respectively from farms in villages and urban sewage treatment plant.

Chicken manure and sludge are added in the 24 days. Bacterial liquid through enrichment of biogas is inoculated to the container according to the experimental program (Table.2), sealed and placed in the incubator at  $35^\circ\text{C}$ . Observe its situation.

#### 4 THE RESULTS AND THE DISCUSSION

##### 4. 1 Gas production and methane content

Gas produced in the course of the experiment is collected by the drainage method. After the test, methane content is measured by Agilent 6890 gas chromatograph. The results of methane content and gas production are seen Table.3 and Fig. 1,2.

From Table.3 and Fig. 1, 2, conclusions are as follows:

(1) Adding nitrogen resource contained rich  $\text{NH}_4^+$  can speed up the effect of microorganisms, then speed up the gas production. 300ml bacteria liquid is added in the blank, and methane content is 0.89%. The growth of microorganisms requires not only a certain amount of carbon and nitrogen, but requires the suitable ratio of carbon and nitrogen, which influences directly the rate of decomposition of organic matter. Nitrogen sources provide nitrogen element for microorganisms. The available nitrogen in anaerobic fermentation is

generally  $\text{NH}_4^+$  used by microorganisms, and most species can also use amino acids. However, available  $\text{NH}_4^+$  is insufficient in test materials, which lowers the microbial activity, even microorganisms is not impossible to survive, ultimately unable to carry out anaerobic fermentation.

(2) In the case of adding same amount of chicken manure(sludge), 300ml bacterial liquid is added in A2, but A1 not (in B2 300ml, B1 not). Total gas production is 164.1ml in A2, while 11.5ml in A1(gas production is 92.7ml in B2, B1 29.5ml). It is considered that: ① Due to itself microorganisms, bacterial liquid is not

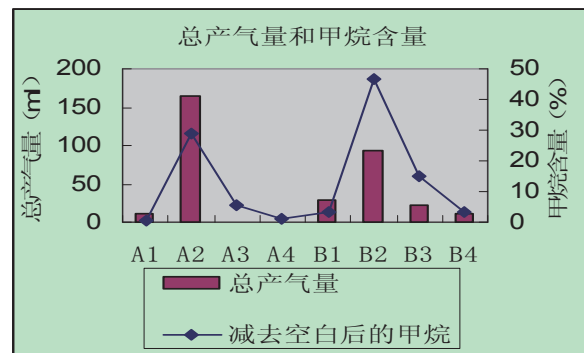


Fig. 1. Total gas production

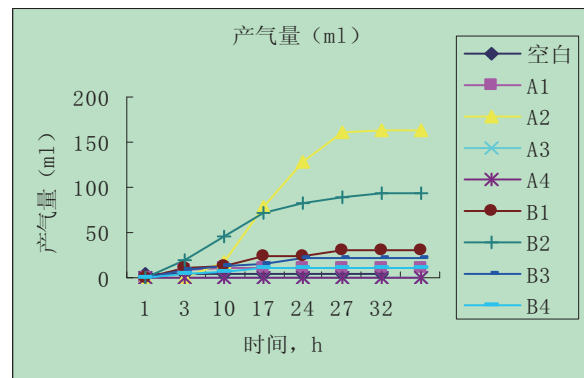


Fig. 2. Total gas production and methane content

Table 3. Gas production(ml) and methane content(%) of all groups

groups	total gas production (ml)								methane content (%)	subtracted the blank (%)
	1d	3d	10d	17d	24d	27d	32d	32d		
blank	4.6	4.6	5.0	5.1	5.1	5.1	5.1	5.1	0.89	0
A1	9.7	11.5	11.5	11.5	11.5	11.5	11.5	11.5	1.59	0.70
A2	0	17.1	78.7	127.3	159.9	164.1	164.1	164.1	29.80	28.91
A3	0	0	0	0	0	0	0	0	6.40	5.51
A4	0	0	0	0	0	0	0	0	1.96	1.07
B1	10.2	12.4	23.8	24.6	29.5	29.5	29.5	29.5	4.49	3.60
B2	18.9	45.1	72.0	83.5	89.8	92.7	92.7	92.7	47.64	46.75
B3	9.6	12.2	15.8	22.0	22.1	22.1	22.1	22.1	16.00	15.11
B4	5.0	7.3	10.7	10.7	10.7	10.7	10.7	10.7	4.24	3.35

added, while chicken manure and sewage sludge produce a certain amount of gas with its own microorganisms. However, adding bacterial liquid, its own microorganisms and microorganisms are adaptive well, and is helpful to methane production for methanogen. ② Microorganisms in bacterial liquid is rich through enrichment of biogas, and results show that it is feasible according to degradation effect. ③ It can be also suggested: organic matter in coal and gangue were actually depredated by microorganisms.

(3) Adding the same amount of bacterial liquid, but different content of chicken manure and sludge, gas production in A2 and B2 is the largest with adding respectively 20g chicken manure and sludge. That are 164.1ml and 92.7ml, and their corresponding methane content are 29.80% and 47.64%, the largest methane amount. While, gas production in A3 and A4 adding respectively 10g, 5g chicken manure (sludge) are 0ml (in B3 and B4, gas production is 22.1ml and 10.7ml). Through analysis, we can know that: Owing to adding different nitrogen resource, available nitrogen in anaerobic fermentation is gradually consumed and not to meet the need of microorganisms, which delays methane production for methanogen, until not.

#### 4. 2 Changes of organic matter

After anaerobic digestion, organic matter content of residues is determined (using weight loss on ignition method at 550°C, volatile solids), seen Table 4 and Fig.3.

From Table 4 and Fig. 3, it shows that the consumption of organic matter is in line with the laws of gas production, namely:

(1) Those that gas production in blank group is very low, and changes of organic matter is the lowest among all groups suggest that the reduction of organic matter may result in the effect of microorganisms. Available nitrogen source is not added, and can not meet the needs of microorganisms, so the activities become weak, organic matter is used less.

(2) Besides the blank, the content of organic matter

in each group decreased significantly. Contacting with Table 3, that can be drawn: the higher gas production, the more reduction of organic matter, such as A2 and B2. Though having no gas production in A3 and A4, the content of organic matter is also reduced, because of adding nitrogen and bacterial liquid, its own microorganisms and microorganisms are possible to consume organic matter.

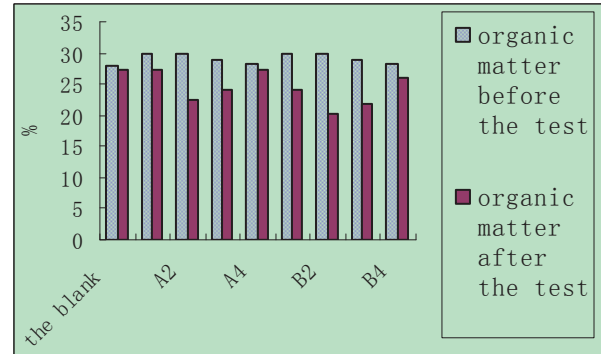


Fig. 3. Changes of organic matter before and after anaerobic fermentation

## 5 CONCLUSION AND OUTLOOK

In this paper, simulation study is carried out focusing on both enrichment of biogas and adding nitrogen, conclusions are as follows:

(1) Comparison A1 with A2, B1 with B2, it can be seen that microorganisms in bacterial liquid is rich through enrichment of biogas, and results show that it is feasible according to degradation effect.

(2) Comparison the blank with other groups, adding nitrogen source for microorganisms can provide available nitrogen ( $\text{NH}_4^+$ ), can make full use of the  $\text{NH}_4^+$ , and microorganisms grow well, are helpful to anaerobic fermentation.

(3) The changes of organic matter in residue show the existence of degradation by microorganisms. The reduction of organic matter is basically in line with the laws of gas production. Though having no

Table 4. Changes of organic matter before and after anaerobic fermentation

Groups	organic matter before anaerobic fermentation (%)		Total organic matter	organic matter after anaerobic fermentation (%)	changes (%)
	original organic matter	organic matter of additives			
blank			27.80	27.39	0.41
A1			29.76	27.30	2.46
A2		chicken manure 44.49	29.76	22.50	7.26
A3			28.84	23.97	4.87
A4			28.34	27.19	1.15
B1	27.80		29.86	24.20	5.66
B2			29.86	20.23	9.63
B3		sludge 45.29	28.89	21.76	7.13
B4			28.36	25.89	3.47

gas production in A3 and A4, the content of organic matter is also reduced, because of adding nitrogen and bacterial liquid, its own microorganisms and microorganisms are possible to consume organic matter. All can prove that the amount of microorganisms determines the reduction degree of organic matter.

(4) From both gas production and the content of organic matter, organic matter in gangue indeed can be degraded by microorganisms.

From adding enrichment of biogas and nitrogen, the research on the degradation in residual coal and gangue suggests that future research should be further carried out as follows:

(1) Further considered of the species of microorganisms after enrichment of biogas, selected dominant microorganisms for degradation in favor of residual coal and gangue, as to enhance its degradation rate of organic matter.

(2) From the utilization point of view, further consider how to enhance gas production and methane

content.

## REFERENCES

- (1) Susheng YANG, Junchu ZHOU. Microorganism biology. Beijing: Science Press, 2004.
- (2) Fuling ZHAO, Yinsheng DENG. The affection with groundwater by zymotic fluid caused by the microbe in the process of using gangue packed for mine [J]. Environmental science and management, 2007, 32 (9): 44-46.
- (3) Yinsheng DENG, Fuling ZHAO. The biogas research caused by the action of microorganisms in the process of using gangue packed for mine [J]. Journal of China Coal Society, 2008, 33 (9): 1045-1048.
- (4) Anna DING, Liwen LIAN, Hui ZHANG. Studies on the enriched cultivation of methanogen and fermentation experiment by using 1854 to 2608m gas source rocks [J]. Journal of Sedimentary, 1995, 13 (3): 117-123.
- (5) Deqing ZHOU. Microbiology course (the second edition). Beijing: Higher Education Press, 2002.

---

バイオガスの濃縮による残炭、ハサミ（低品位炭）の分解に関する研究

Yinsheng DENG \*, Min TANG \*, Yan HUANG \* and Zhe SHEN\*\*

### 概要

本論文では、バイオガスの濃縮による残炭、ハサミの分解に影響を与える C/N 値およびバイオガスの濃縮に関してシミュレーション実験を行った。その結果、以下のことがわかった。

(1) バクテリア溶液内の微生物はバイオガスの濃縮に有効であり、分解効果が結果として認められた。(2) 窒素の供給は微生物へのアンモニウムイオン (NH<sub>4</sub><sup>+</sup>) の供給源になる。アンモニウムイオンの濃度が増せば、微生物は生長し、嫌気性の醗酵を促す。(3) 有機物の減少割合は基本的にガスの生成と対応しており、微生物の量が有機物の分解を左右する。

(4) ガスの生成量と有機物の濃度を考えると、ハサミ内の有機物は微生物によって明らかに分解されている。

キーワード : Enrichment, Gangue, Nitrogen, Methane content

\* Henan Polytechnic University, Jiaozuo454000, China.

\*\* China University of Mining and Technology, Xuzhou 221003, China.