CHEMICAL ENGINEERING TRANSACTIONS

VOL. 59, 2017

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Zhuo Yang, Junjie Ba, Jing Pan

ISBN 978-88-95608- 49-5; **ISSN** 2283-9216

DOI: 10.3303/CET1759002

The Effect of Different Mineral Materials on Preparation of CH4 from Sodium Acetate

Keke Chen

College of Chemistry and Chemical Engineering, Xinxiang University, Xinxiang 453003, China
lisa820928@126.com

As a renewable energy source, methane can not only improve ecological benefits and save energy, but also bring good economic benefits. In order to enhance the efficiency of methane preparation, the author used sodium acetate as the base material to study the effect of various mineral materials on microbial methane preparation. The results showed that mineral materials with good conductivity play a positive role in anaerobic microbial methane preparation, which is of referential meanings to highly-effective CH4 preparation.

1. Introduction

With the rapid development of various industries and the economy, the resultant problems of environmental pollution and energy shortage are increasingly serious. As a countermeasure, renewable energy sources are strongly promoted. Among them, CH_4 acts as a kind of renewable energy that plays an important role (Bardi et al., 2016). The main components of biogas are methane and hydrogen, and the former one accounts for about 60% to 70%. Since biogas can replace natural gas as the fuel needed for people's life, biogas promotion can not only improve ecological benefits and save energy, but also bring good economic benefits (Iorio, 2016; Carotenuto et al., 2016; Rongwang et al., 2017; Hoo et al., 2017).

CH4 can be prepared by the metabolism of known anaerobic microorganisms of over 200 species (Ettwig et al., 2008). These microorganisms survive in an anaerobic environment and eventually produce CH4 by decomposition of organic matter (Wang et al., 2009). In synthesizing CH_4, acetic acid decomposition is one of the main accesses to methane (Murray and Berg, 2010). At present, microbial methane production has been applied to real life, albeit low in production efficiency and utilization rate (Thauer and Shima, 2008). Documents (Leloup Et al., 2007; Thauer, 2010) show that the efficiency of microbial methane production can be improved with such additives as sodium bicarbonate (Ağdağ and Sponza, 2005), iron and other trace elements (Zhang and Jahng, 2012), goethite (Tan et al., 2015), and enzymes (Quiñones Et al., 2012).

In order to enhance the efficiency of methane preparation, the author used sodium acetate as the base material to study the effect of various mineral materials on microbial methane preparation and to analyse its working principle.

2. Experimental design

2.1 Experimental materials

The anaerobic microbial fermentation experiment was carried out in a 250 ml volumetric flask in which there is sludge of a concentration of 0.165 gVS/L, sodium acetate of a concentration of 1.65 g/L, and 1 mL/L vitamin solution. The PH value is controlled at 7.0. After exhausting air from the flask, we sealed the flask and placed it into a 35°C incubator. The experiment had 1 control group and 7 test groups with mineral materials of goethite, hematite, magnetite, ferrihydrite, dolomite, activated carbon, and graphite, respectively, at the ratio of 1: 1. Every test was repeated for 3 times. The related properties of each mineral material are shown in Table 1:

Please cite this article as: Keke Chen, 2017, The effect of different mineral materials on preparation of ch4 from sodium acetate, Chemical Engineering Transactions, 59, 7-12 DOI:10.3303/CET1759002

Table 1: The property of mineral materials

Mineral Material	Goethite	Hematite	Magnetite	Ferrihy-drite	Dolomite	Activated carbon	Graphite
Specific surface area (m^2/g)	14.5	92.6	19.921	198.77	5.851	20.368	6.54
Resistivity (Ω·cm)	10^3–10^6	10^{-3}–10^2	10^{-2}–10^{-1}		10^{11}–10^{14}	10^{-2}–10^1	10^{-6}–10^{-2}
Density (g/cm^{-3})		5.02~5.31	5.15~5.18		3.00~3.20	1.80	2.26
Grain size	60~100	60~100	60~100	60~100	200	8~20	100

2.2 Experimental measurement

Gas chromatography FID was used to gauge the contents of methane and acetic acid. Here are some parameters: 25*m*×0.25*mm* capillary columns, detector temperature 300 ° C, vaporization temperature 250 °C, nitrogen gas as the carrier gas. The total carbon, total organic carbon, total inorganic carbon, carbon dioxide gas concentration, and carbon content in the solid were measured by a *JenaC/N* 2100 TOC analyser.
The modified Gompertz equation was used to simulate methane preparation in this paper and has been widely applied to the simulation of the production of similar products to methane (Adam et al., 2011; Roy et al., 2012). The equation is: 10^3–10^6

$$P = P_{\max} \exp\{-\exp[R_{\max} e / P_{\max} (\lambda - t) + 1]\} \tag{1}$$

Where P is the amount of methane prepared, P_{max} is the maximum methane produced during the anaerobic reaction, R_{max} is the highest rate of methane production in the anaerobic reaction process, λ is the time lag in reaction, e is a constant equal to 2.71828, t is the accumulated time of anaerobic reaction.

3. Experimental results and analysis

3.1 Methane and carbon dioxide production

The contents of methane and carbon dioxide were measured in each group in a daily basis, and the data results are shown in Figure 1 and Figure 2:

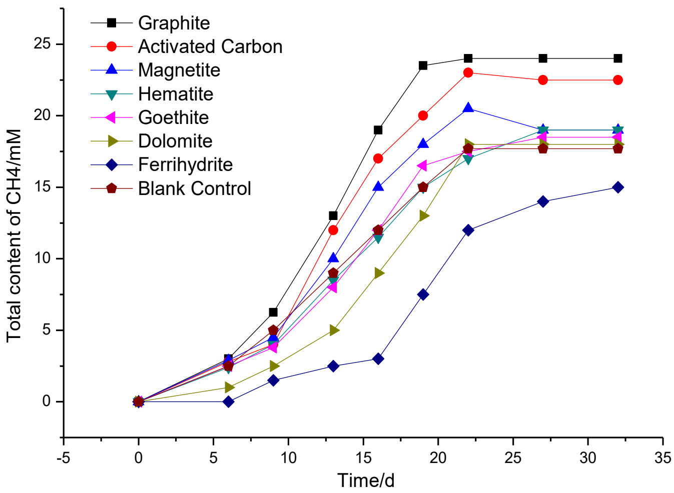

Figure 1: The change of total content of CH4

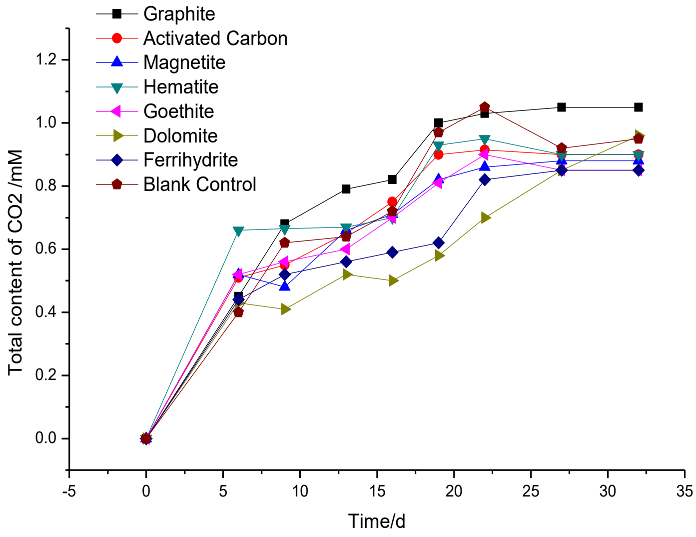

Figure 2: The change of total content of CO_2

It can be seen from Figure 1 that the CH_4 content in each group increases over time. In terms of the CH_4 increment, the graphite group ranks the first, followed by the activated carbon group and the magnetite group. The CH_4 content in these groups is much higher than that of the control group. The CH_4 contents in the hematite group and the goethite group are slightly higher than that of the control group. The CH4 contents in the dolomite group and the ferrihydrite group are lower than that of the control group, reflecting the inhibitory effect on CH4 preparation.

If we compare Figure 1 with Figure 2, we will find that CO_2 content is much smaller than CH_4 content, and the reason is that some of the CO_2 gas dissolves in water. Through comparison, the content of CO_2 produced in the dolomite group and the hydrothermal group is also smaller than that of the control group due to the same reason.

For further analysis, we fitted the CH_4 production data in each group according to the formula (1), and the fitting data are listed as follows:

Table 2: Fitting data of Gompertz equation

Mineral Material	P_{max}	R_{max}	λ	R^2
Graphite	24.69352	2.09251	6.14872	0.98389
Activated Carbon	23.47294	2.00017	6.69032	0.99252
Magnetite	20.89245	1.78895	6.41096	0.98973
Hematite	21.06163	1.31874	5.86149	0.98721
Goethite	20.89371	1.40973	6.07730	0.98913
Dolomite	19.52407	1.48037	8.99358	0.98995
Ferrihydrite	17.73129	1.10258	11.35999	0.97986
Blank Control	20.09785	1.51204	8.97783	0.99504

It can be seen from Table 2 that the experimental data of each group are well fitted and the fitting coefficients are above 0.97. The maximum CH_4 content P_{max} and the maximum production rate R_{max} are the largest in the graphite group but the smallest in the ferrihydrite group. Considering the mineral property parameters shown in Figure 1 and Table 1, that phenomenon is linked to the conductivity of mineral materials. The lower the resistivity is, the better the conductivity is, and the higher value P and R have. Graphite is such an example. Minerals with stronger conductivity are better at electron storage in the process of anaerobic fermentation reaction, and thus stimulate electron transfer between micro-organisms. In terms of the time lag data listed in Table 2, the λ value of minerals with better conductivity is around 6 days, and the λ value in the control group is about 9 days, indicating that minerals with better conductivity can have CH_4 production accelerated to reach the maximum methane amount as fast as possible.

3.2 PH value change in each experimental group

The time-varying change of PH value in each group is detected and listed in Figure 3:

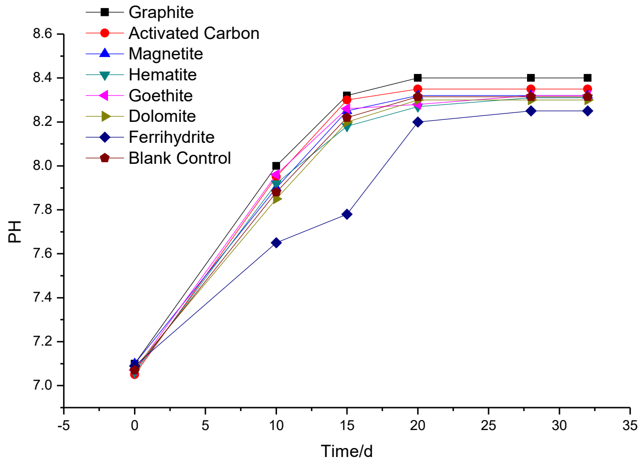

Figure 3: The change of PH value in each group

As can be seen from the curves of PH value change, the change trends are similar to each other. Specifically speaking, the PH value increases fast at the beginning of the reaction, slows down and remains basically unchanged at the 15th day. The increment in PH value for minerals with better conductivity is higher than that in the control group. For example, the PH value reaches 8.4 in the graphite group and 8.35 in the activated carbon group, while the PH value in the control group is 8.3; correspondingly, the PH value of the ferrihydrite group with poor conductivity is significantly lower than that of the control group (which is 8.25). With respect to the overall trend, the PH value increases over time, which means the alkalinity of the solution increases. Accordingly, CO_2 solubility is enlarged, and the CO_2 gas content is much smaller than methane content. The reason why the solution is more alkaline is that: on the one hand, due to the existence of microbes, the reaction in formula 2 happens in the solution, leading to the production of HCO_3^-; on the other hand, CO_2 gas dissolves in the solution, reacts and generates HCO_3^-. The production of HCO_3^- increases the PH value of the solution.

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \qquad (2)$$

3.3 The concentration changes of sodium acetate

With microorganisms, sodium acetate is decomposed into methane and carbon dioxide. As the reaction prolongs, sodium acetate is gradually consumed, and its concentration change is shown in Figure 4:

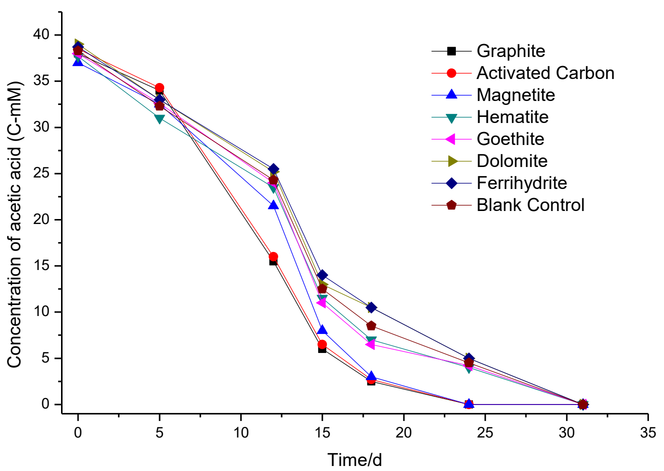

Figure 4: The change of acetic acid concentration

It can be seen from Figure 4 that the concentration of acetic acid is decreasing and approaches zero after a month, indicating that all of the microorganisms have been decomposed. The rate of concentration incline is high in the first 15 days and then lowers down, which accords with the change law of methane content in Figure 1. In the initial stage, microbes have high activity and a high metabolic rate, and thus the acetic acid consumption is fast; what is more, minerals of good conductivity can enhance microbial activities because they provide surfaces for microbial growth. Therefore, the decrement in acetic acid concentration in groups with minerals of good conductivity is much higher than that in the control group, which also applies to methane content change.

3.4 Carbon balance in each group

The carbon distribution before and after the anaerobic fermentation reaction in each group is shown in Table 3:

Table 3: Distribution of carbon before and after reaction

Mineral Material	At the beginning (C-mM)		Carbon in gas phase(C-mM)		Carbon in liquid phase (C-mM)		solid carbon (C-mM)	Recovery (%)	Proporti-on of CH_4 (%)
	Organic	Inorga-nic	CH_4	CO_2	Orga-nic	Inorga-nic			
Graphite	56.2	0	24.11	1.05	2.61	21.5	2.34	91.83	42.90
Activated Carbon	56.38	0	22.51	0.92	3.29	22.11	3.37	92.59	39.93
Magnetite	55.04	0	19.32	0.88	2.03	23.49	2.36	87.04	35.10
Hematite	55.61	0	19.03	0.95	2.85	22.92	2.49	86.75	34.22
Goethite	56.09	0	18.54	0.85	2.32	23.58	2.43	85.08	33.05
Dolomite	56.15	0	17.87	0.93	2.5	24.39	2.56	85.93	31.83
Ferrihydrite	55.57	0	15.28	0.85	2.41	24.51	2.54	82.04	27.50
Blank Control	55.78	0	17.75	0.96	2.48	23.62	2.2	84.28	31.82

Table 3 is a collection of carbons contained in the gas, liquid and solids in each experimental group. After the reaction is finished, the total carbon content in each group is found to be below 100%, which is inevitable as there are natural carbon losses in sampling, measurement and other operations. As can be seen from table 3, the inorganic carbon content in the solution is high, most of which higher than the carbon content in methane. There are two reasons that cause this phenomenon: 1. CO_2 produced from anaerobic fermentation dissolves in the solution and is converted into CO_3^-; 2. there are other unbeneficial bacteria among microbes that can decompose acetic acid and produce inorganic carbons of other forms. In the presence of methane, the proportion of carbon is the highest in the graphite group (42.9%), which is 11% higher than that of the control group. Therefore, in the descending order, graphite, activated carbon, and magnetite have significant effects on the production of methane by microbial anaerobic fermentation.

4. Conclusion

In this paper, the effects of different mineral materials on the production of methane from sodium acetate were studied. The results showed that the mineral materials with better conductivity can enhance the activity of microorganisms and increase the methane content and production speed of metabolites. Among these mineral materials, graphite achieves the best effect, followed by activated carbon and magnetite.

Reference

Adam N.R.B., Elahee M.K., Dauhoo M.Z., 2011, Forecasting of peak electricity demand in mauritius using the non-homogeneous gompertz diffusion process. Energy, 36(12), 6763-6769. DOI: 10.1016/j.energy.2011.10.027.

Ağdağ O.N., Sponza D.T., 2005, Effect of alkalinity on the performance of a simulated landfill bioreactor digesting organic solid wastes. Chemosphere, 59(6), 871-9. DOI: 10.1016/j.chemosphere.2004.11.017.

Bardi U., Perissi I., Csala D., Sgouridis S., 2016, The Sower's way: a strategy to attain the energy transition. International Journal of Heat and Technology, 34(2), 263-265. DOI: 10.18280/ijht.34S211.

Carotenuto C., Guarino G., Morrone B., Minale M., 2016, Temperature and pH effect on methane production from buffalo manure anaerobic digestion. International Journal of Heat and Technology, 34(2), 425-429. DOI: 10.18280/ijht.34S233.

Ettwig K.F., Shima S., Pas-Schoonen K.T.V.D., Kahnt J., Medema M.H., Camp H.J.M.O.D., 2008, Denitrifying bacteria anaerobically oxidize methane in the absence of archaea. Environmental Microbiology, 10(11), 3164-3173. DOI: 10.1111/j.1462-2920.2008.01724.x.

Hoo P.Y., Hashim H., Ho W.S., Tan S.T., 2017, Potential biogas generation from food waste through anaerobic digestion in peninsular malaysia, Chemical Engineering Transactions, 56, 373-378, DOI:10.3303/CET1756063

Iorio S.D., 2016, Diesel/methane dual fuel strategy to improve environmental performance of energy power systems. International Journal of Heat and Technology, 34(2), 581-588. DOI: 10.18280/ijht.34S254.

Leloup J., Loy A., Knab N.J., Borowski C., Wagner M., Jørgensen B.B., 2007, Diversity and abundance of sulfate-reducing microorganisms in the sulfate and methane zones of a marine sediment, black sea. Environmental Microbiology, 9(1), 131-42. DOI: 10.1111/j.1462-2920.2006.01122.x.

Murray W.D., Berg L.V.D., 2010, Effect of support material on the development of microbial fixed films converting acetic acid to methane. Journal of Applied Microbiology, 51(2), 257-265. DOI: 10.1111/j.1365-2672.1981.tb01240.x.

Quiñones T.S., Plöchl M., Budde J., Heiermann M., 2012, Results of batch anaerobic digestion test - effect of enzyme addition. Agricultural Engineering International: The CIGR e-journal, 4(1), 38-50. DOI: 10.1016/j.fuel.2014.12.087.

Rongwang C., Polprasert S., Kanchanasuta S., 2017, Effect of partial ozonation and thermal pretreatment on biogas production from palm oil decanter cake, Chemical Engineering Transactions, 57, 1987-1992, DOI: 10.3303/CET1757332

Roy D., Kumar V., Acharya K.K., Thirumurugan K., 2012, Estimating the parameters of a gompertz-type diffusion process by means of simulated annealing. Applied Mathematics & Computation, 218(9), 5121-5131. DOI: 10.1016/j.amc.2011.10.077.

Tan J., Wang J., Xue J., Liu S., Peng S., Ma D., 2015, Methane production and microbial community analysis in the goethite facilitated anaerobic reactors using algal biomass. Fuel, 145, 196-201. DOI: 10.1016/j.fuel.2014.12.087.

Thauer R.K., 2010, Functionalization of methane in anaerobic microorganisms. Angewandte Chemie, 49(38), 6712. DOI: 10.1002/anie.201002967.

Thauer R.K., Shima S., 2008, Methane as fuel for anaerobic microorganisms. Annals of the New York Academy of Sciences, 1125(1), 158. DOI: 10.1196/annals.1419.000.

Wang Y., Zhang Y., Wang J., Meng L., 2009, Effects of volatile fatty acid concentrations on methane yield and methanogenic bacteria. Biomass & Bioenergy, 33(5), 848-853. DOI: 10.1016/j.biombioe.2009.01.007.

Zhang L., Jahng D., 2012, Long-term anaerobic digestion of food waste stabilized by trace elements. Waste Management, 32(8), 1509-1515. DOI: 10.1016/j.wasman.2012.03.015.