RGNZ/MGPB

The Effect of Rumen Fluid Application on Various Coal Types in Methane Production

Rudarsko-geološko-naftni zbornik
(The Mining-Geology-Petroleum Engineering Bulletin)
UDC: 620.3
DOI: 10.17794/rgn.2025.1.12

Original scientific paper

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Abstract

Indonesia is one of the largest coal producers in the world. The conversion of coal into coalbed methane (CBM) by involving methane-producing microbes appears to be a potential alternative to utilizing coal for energy resources. One possible source of methanogens is rumen fluid collected from slaughterhouse waste. Previous studies have reported the possibility of employing rumen fluid to produce methane from coals. To sustain field application, microbiological testing of rumen fluid in CBM reservoir circumstances is required. Therefore, various water formations and coals were involved in the present study. The present study aims to identify methane production by combining rumen fluid as methane-producing microbes, formation water, and various coal types (A: lignite, B: sub-bituminous, C: bituminous, and K: control) at room temperature. The results suggest that supplying microbes from rumen fluid and formation water can produce methane from different types of coal. Microbial activity in all treatments is denoted by pH changes and observing living microbes. Bacilli are the predominant type of microorganism. Due to coal organic compound breakdown, the presence of methanogenic microbial activity is denoted by volatile fatty acids (VFA). The total VFA in all treatments demonstrated a similar declining tendency. It was found that all treatments produce volatile fatty acids in different amounts up to 60 days of incubation. These acids included acetic, propionic, butyric, iso-butyric, iso-valeric, and valeric acids. Acetic acid is the most commonly produced partial VFA, the primary, intermediate compound in methane formation. Treatment A with lignite coal had the maximum gas production. The cumulative gas volume reached 16,400 mL after 60 days of incubation. In contrast, the highest cumulative methane production occurred in treatment C with bituminous coal, amounting to 100.60 mL after 60 days of incubation.

Keywords:
coal bed methane, rumen fluid, formation water, microbes, coal types

1. Introduction

The world's energy demand continues to increase, and according to the International Energy Agency (IEA), until 2030, the world's energy demand will experience an increase of up to 45% or an annual increase of 1.6%. Fossil fuels will supply most or almost 80% of these energy demands.

Coal is an abundant energy source and will play an essential role in the future, replacing the decreasing trends in oil and gas availability. In addition to its role as an energy source, coal can also be utilized to produce methane (**Strapoc et al., 2011**). Executive Director of IEA, Nobue Tanaka, stated that coal currently ranks second in the energy supply after oil. Coal consumption is predicted to increase three times in 2030.

Coal, in general, can produce more gas that is later absorbed and stored. A basin can contain between 500 and 600 standard cubic feet (SCF) of methane per ton, and it is considered to be a significant amount for commercial production as long as the permeability and desorption rate of the reservoir are sufficient (**US DOE, 2004**) According to **Gou et al. (2003)**, coalbed methane is a non-conventional natural gas consisting of methane in the majority and other hydrocarbon gases in the minority that are trapped in the coalbed seam. Coalbed methane is primarily stored in the pore structure of coal

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seams. The primary structure of coal seam pores consisted of matrices and cleats.

Based on the study performed by **Shi and Durucan (2003)**, the matrix consisted of micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). The micropores of the matrix layer have low permeability properties and can store gas with a large capacity. A diffusion is a phenomenon affected by concentration changes in the coal seam matrix. Cleats are fractures that form naturally during the coal formation process. Cleats have more excellent permeability properties than the micropores of the matrix layer. The phenomenon occurring along the fracture is Darcy laminar flow, which is affected by pressure differences. The process of extracting methane from coalbed methane is conventionally initiated by dewatering, resulting in the reduction of reservoir pressure (**Reznik et al., 1984**).

The coalbed methane formation process begins during coalification and is trapped in the coal seam. The coalbed methane formation process involves decomposing bacteria during coalification, which occurs in the initial and final phases, known as the biogenic processes. Meanwhile, the temperature factor due to pressure and loading during coalification is known as the thermogenic process (**Speight, 1994**).

Coalbed methane production can be increased by biological means, such as biostimulation and bioaugmentation. These two methods can be carried out in situ or ex situ (**Colosimo et al., 2016; Park and Liang., 2016; Ritter et al., 2015**). Biostimulation is the process of stimulating the population of indigenous coal microorganisms by adding nutrients to the reservoir. In contrast, bioaugmentation is inoculating a consortium of microorganisms into the reservoir. These two methods are commonly employed to reactivate unproductive and in situ reservoirs (**Strapoc et al., 2008**). The ex-situ application involves the utilization of mined or weathered coal to produce methane in a bioreactor through methanogenic microorganisms. Indonesia has the potential to develop coal resources as methane bioreactors, which may provide renewable energy resources for future energy needs (**Rita et al., 2015**). The formation of biogenic methane from coal is highly demanded in research because the final product is considered to be clean energy (**Jones et al., 2010**).

Livestock waste is generally rich in nitrogen (N) content but deficient in carbon (C) (**Shuler and Kargi, 2002**). According to **Tamara (2008)**, cattle feces have a C/N ratio of 22:12. Cow dung is used as a source of nitrogen and methane gas-producing bacteria, naturally found in the rumen of ruminants. One of the characteristics that must be considered in the production of methane is the C/N ratio (the ratio between the amounts of C and N in one material). Microbes that play a role in the anaerobic fermentation process require nutrients to grow and develop in the form of a carbon source (C) and a nitrogen source (N) (**Yani and Darwis, 1990**). Therefore, efforts to utilize a combination of livestock and agricultural waste as biogas are expected to address the future scarcity of fossil-sourced energy. This will be in line with environmental conservation efforts.

In the present study, coalbed methane production is increased through a combination of rumen microbial injection and CO_2 gas. Rumen fluid contains a microbial consortium of bacteria, protozoa, fungi, and methanogenic microbes (**Hungate, 1990**). Methanogenic microbes are expected to have the potential to degrade coal. In addition, the rumen microorganisms can digest lignite made from plants (**De Ondarza, 2000**). Plants themselves serve as the primary raw material in coal formation. Rumen fluid will be used as a microbial source during the application of in situ bioaugmentation.

The results of bioaugmentation to increase coalbed methane production on a laboratory scale at surface conditions suggested that all coal types can produce methane by utilizing microbial sources of rumen fluid combined with formation water. The highest gas volume production occurred in lignite coal, with a cumulative gas volume of 12,910 ml/kg (456 cf/ton) after 60 days of incubation. However, the highest cumulative methane production occurred in sub-bituminous coal at 2,135 ml/kg (75 cf/ton) after 60 days of incubation (**Kosasih et al., 2014**). The study later confirmed the possibility of supplementing rumen fluid to increase methane production and provided guidelines on applying rumen fluid to increase coal methane.

2. Methods

2.1. Materials and equipment

The material in the present study included coals collected from the Sumatra Basin, South Sumatra (see **Figure 1**). Sampling was carried out manually using the **ASTM D 2234/D2234-19** method, and samples were prepared at 31.5 mm (pebble) using the **ASTM D 4749-87** method (2019).

Cattle rumen fluid samples were collected from the Bogor Slaughterhouse, West Java (see **Figure 2**), considering that the ruminants in this slaughterhouse only fed on forages and that the slaughterhouse site is quite close to the research sites.

The primary equipment and tools are a simple fermenter, a water bath, a thermal gravity analyzer (TGA), Elemental CHN analyzer, fourier transform infrared (FTIR) spectroscopy, a pH meter, a camera-mounted microscope, and gas chromatography-mass spectrometry (GCMS).

2.2. Coal preparation

Before incubating coal samples, coal types are identified by crushing and pulverizing the coals using a Raymond mill (**ASTM 2013/2013M-2020**). **Figure 3a** is then sieved with 250μm mesh sieve (size 60). **Figure 3b** shows the procedure of the **ASTM D 4749-87 (2019)**. Samples were subjected to proximate analysis using

Figure 1: Coal sampling

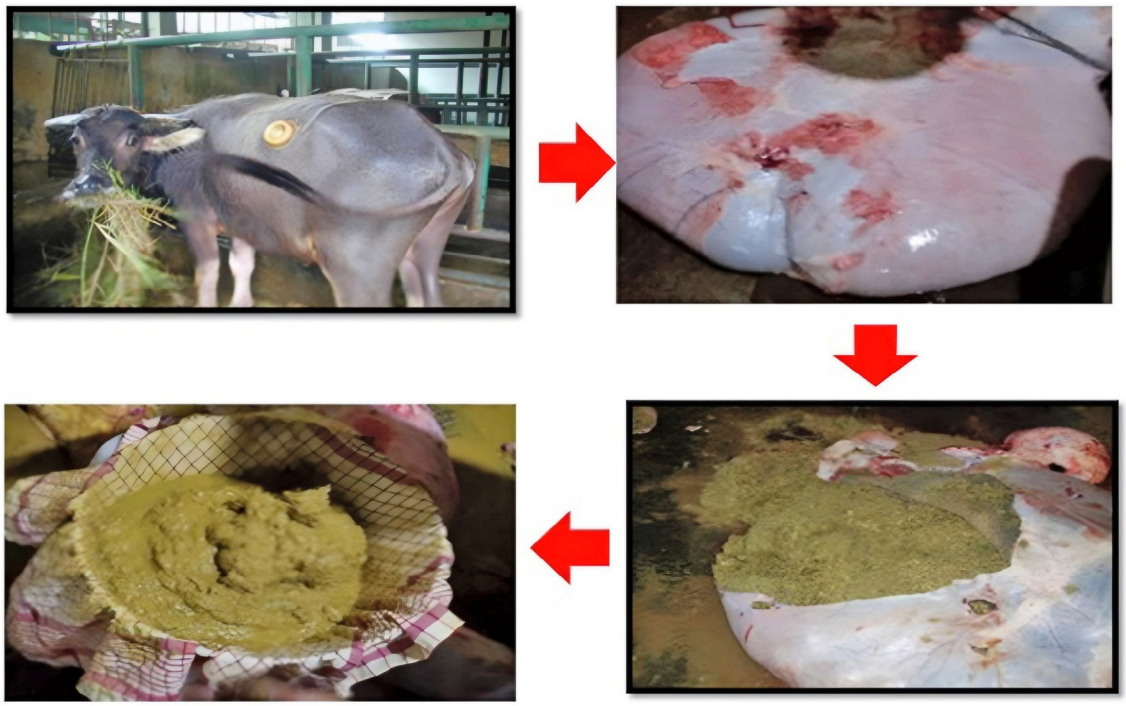

Figure 2: Rumen fluid sample collection at Bogor slaughterhouse, West Java, Indonesia

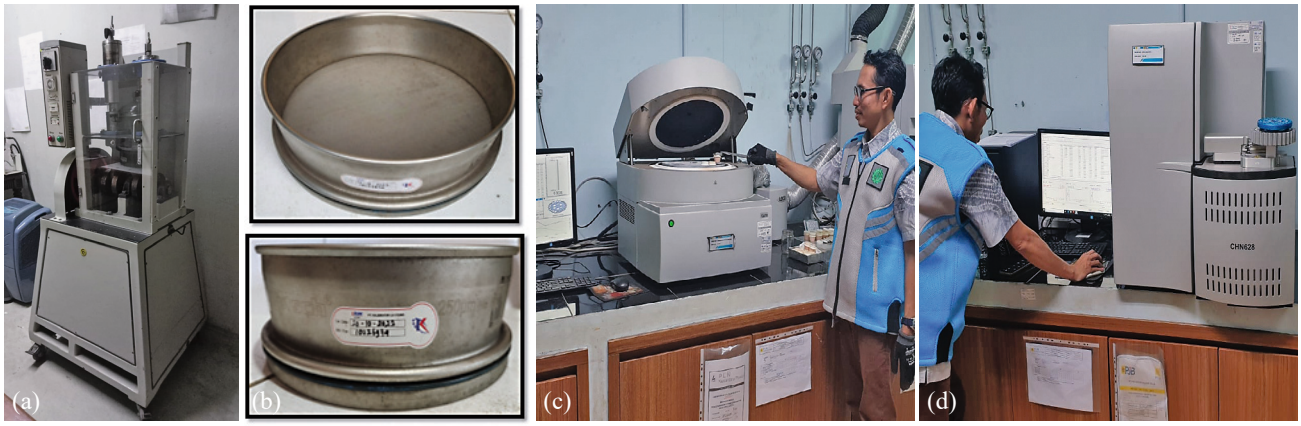

Figure 3: a) Raymond mill, b) 250 µm mesh sieve (Size 60), 3c) proximate analysis, 3d) ultimate analysis.

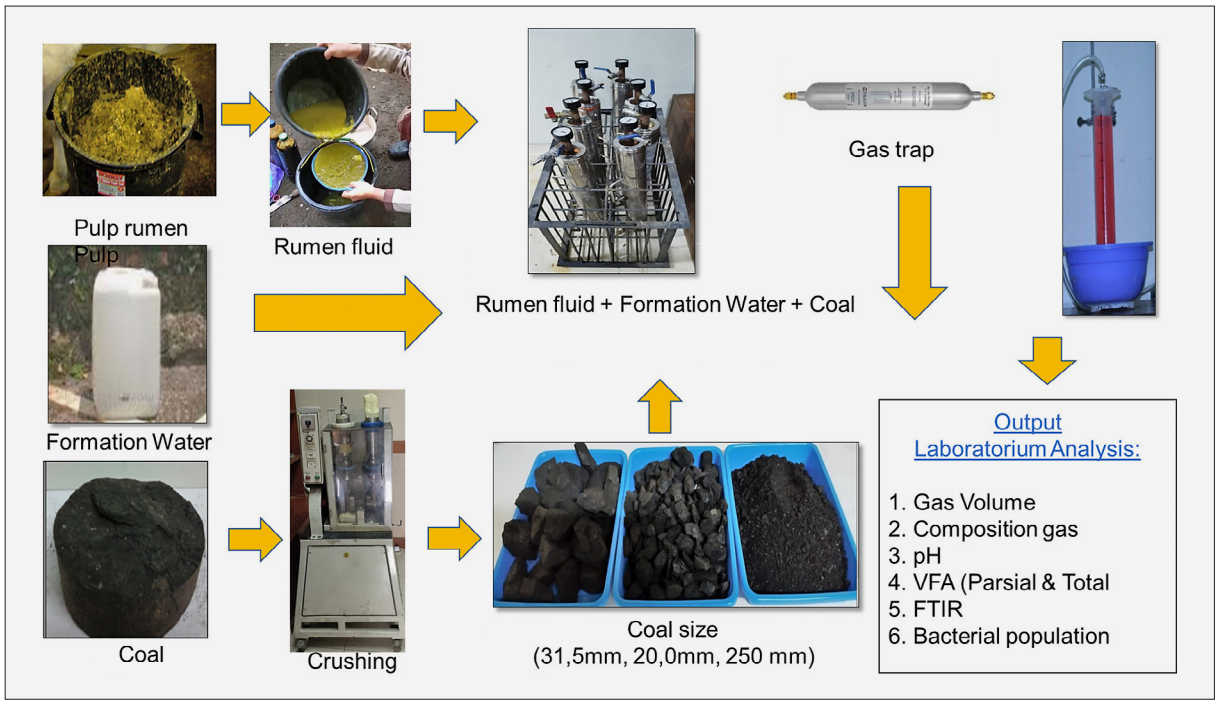

Figure 4: Research flow chart

Table 1: Composition of treatment media

Treatment	Coal Types (g)			Rumen Fluid	Formation Water
	lignite	Sub Bituminous	Bituminous	(mL)	(mL)
A	500	0	0	500	500
B	0	500	0	500	500
C	0	0	500	500	500
K	0	0	0	500	500

ASTM D 7528 using TGA-type 701, as can be seen from **Figure 3c**. These instrumental test methods cover the determination of moisture, volatile matter, and ash, as well as the calculation of fixed carbon in the analysis of coal and coke. The working principle of the thermogravimetric method (TGA) involves heating a material at a specific temperature and time. Meanwhile, the parameters for ultimate analysis use **ASTM D 5373**, Standard Test Methods for Determination of Carbon, Hydrogen, and Nitrogen in Analysis Samples of Coal and Carbon in Analysis Samples of Coal and Coke. This information can be seen in **Figure 3d**.

2.3. Coal scanning stages

From the results on proximate, ultimate, and ASTM D 388 analysis, the samples can be classified as lignite (calorific value: 8,300 Btu/lb Moist MMFB), sub-bituminous (calorific value: 9,400 Btu/lb Moist MMFB) and bituminous (calorific value: 11,500 Btu/lb Moist MMFB).

2.4. Coalbed methane production

Coal, rumen fluid, and formation water were combined in the fermenter (see **Figure 4**) at a composition comparison of the treatment media, as shown in **Table 1**. After that, the mixture was incubated at room temperature for 60 days. Observations and analysis were conducted on media pH, microbial images, total VFA, partial VFA, gas volume, and gas composition.

3. Results and discussion

3.1. Proximate and ultimate analysis

Data obtained from research results of proximate and ultimate analysis of coal samples is presented in the following **Table 2**. **Figure 5** shows the results of proximate and ultimate analysis of research coal.

In sample A, B is sample C. Sample C coal has a high carbon content of 84.16%, while sample B's carbon content is 82.70%, and sample A's carbon content is 69.02%. In general, the analysis of the proximate and ultimate results for the three samples reveals significant differences. Coal sample C is superior to coal samples B and A. This is attributed to the proximate and ultimate analysis of sample C, which shows an inherent moisture content of 16.47%, ash content of 1.33%, volatile matter of

Table 2: Result of proximate and ultimate analysis

ID Sampels	Proximate analysis					Ultimate analysis				
	Inh. moisture (% wt)	Ash content (% wt)	Fixed carbon (% wt)	Volatile (% wt)	Fixed carbon (%wt)	C (%)	H (%)	N (%)	O (%)	S (%)
A	22.22	6.96	28.57	59.65	40.35	69.92	4.96	0.26	16.60	0.65
B	21.60	1.67	37.41	51.25	48.75	82.70	3.40	1.22	3.58	0.97
C	16.47	1.33	44.95	45.33	54.67	84.16	4.42	1.48	2.61	0.70

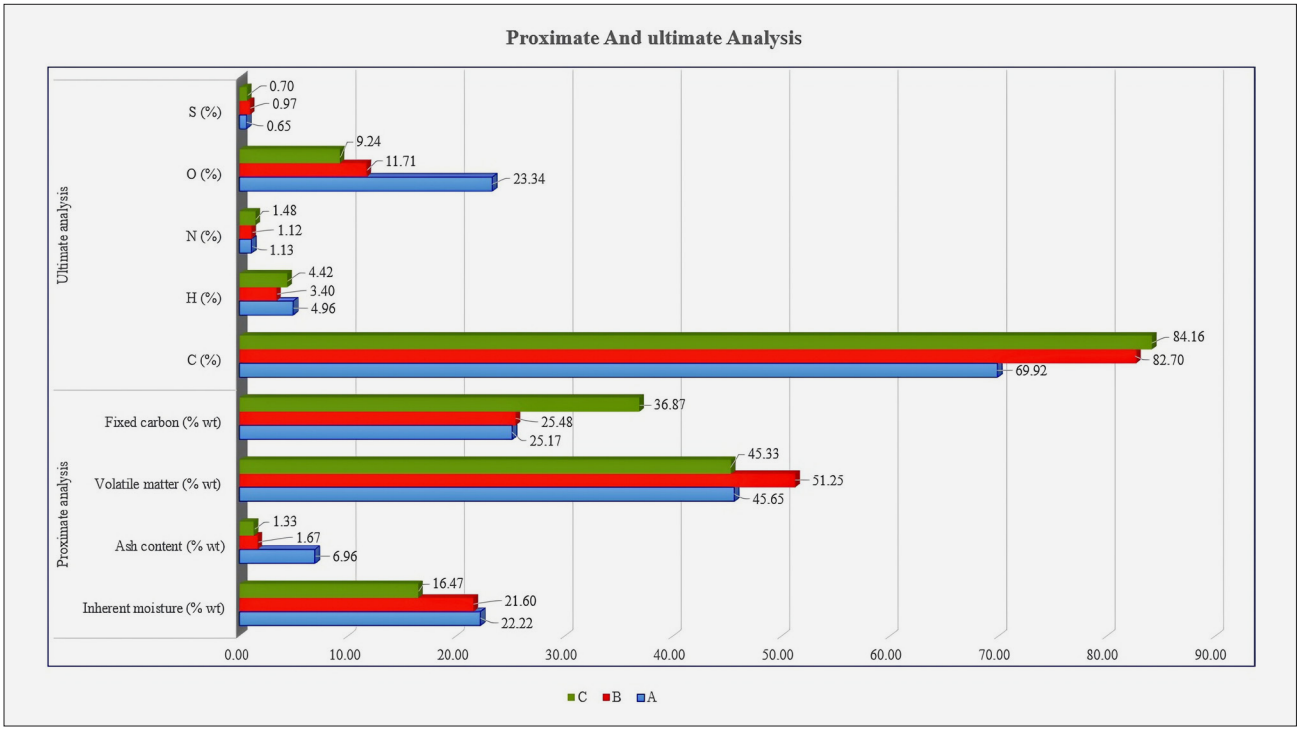

Figure 5: Proximate and ultimate analysis of samples A, B and C

45.33%, hydrogen content of 4.42%, nitrogen content of 1.48%, and oxygen content of 9.24%. In contrast, sample B has an inherent moisture content of 21.60%, ash content of 1.67%, volatile matter of 51.25%, hydrogen content of 3.40%, nitrogen content of 1.12%, and oxygen content of 11.71%. Sample A has an inherent moisture content of 22.22%, ash content of 6.96%, volatile matter of 45.65%, hydrogen content of 4.96%, nitrogen content of 1.13%, and oxygen content of 23.34%. These differences indicate variations in coal classification, which are influenced by the coal formation process in situ, originating from the fossils of living organisms in the surrounding area. Consequently, the primary factor contributing to these differences is the longer deposition period for sample C compared to samples B and A.

3.2. pH media

Changes in the media pH indicated microbial growth from the water formation, rumen fluid, and coal mixture. The formation water had a pH of 8.12, while the rumen fluid pH was 6.34. After being added to coal, the media pH values in each treatment differed, ranging from 6.30 to 6.55 (see **Figure 6**). Such a difference in pH occurred due to differences in the coal types (lignite, sub-bituminous, and bituminous) and coal concentration. After mixing the media, the coal released inorganic sulphur and organic acid compounds such as humic and fulvic acids, resulting in an acidic pH. The media pH was still within the working range of methanogenic bacteria at a pH of 3–9, while the most optimal working range was at a pH of 7.

After incubation for 60 days, the media pH in all treatments demonstrated different pH values. This shows that formation water, rumen fluid, and indigenous coal microbes can grow to degrade coal and produce higher amounts of organic acids. A decrease in the pH value was observed after 14 days of incubation from all treatments except the control treatment (K). The pH kept increasing to the end of incubation, except for treatment A (lignite coal), which demonstrated a decrease to the end of the incubation period. The pH value of the control treatment (K) also changed and was higher after day 14

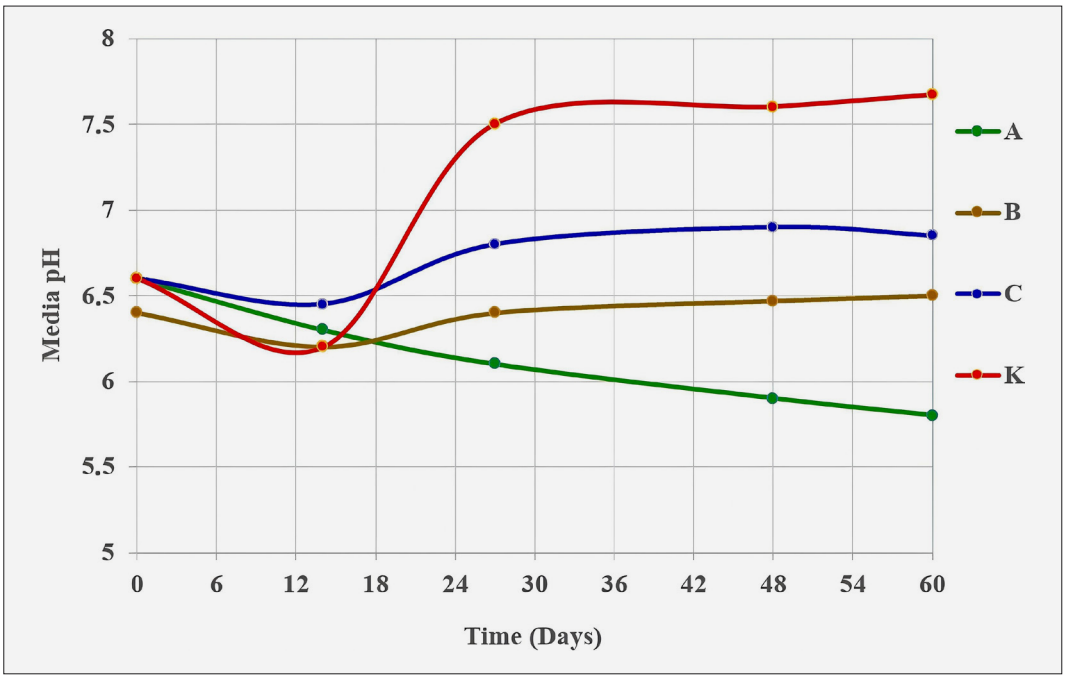

Figure 6: Changes in media pH containing formation water, rumen fluid, and coal (A: lignite, B: sub-bituminous, C: bituminous, and K: control) at room temperature

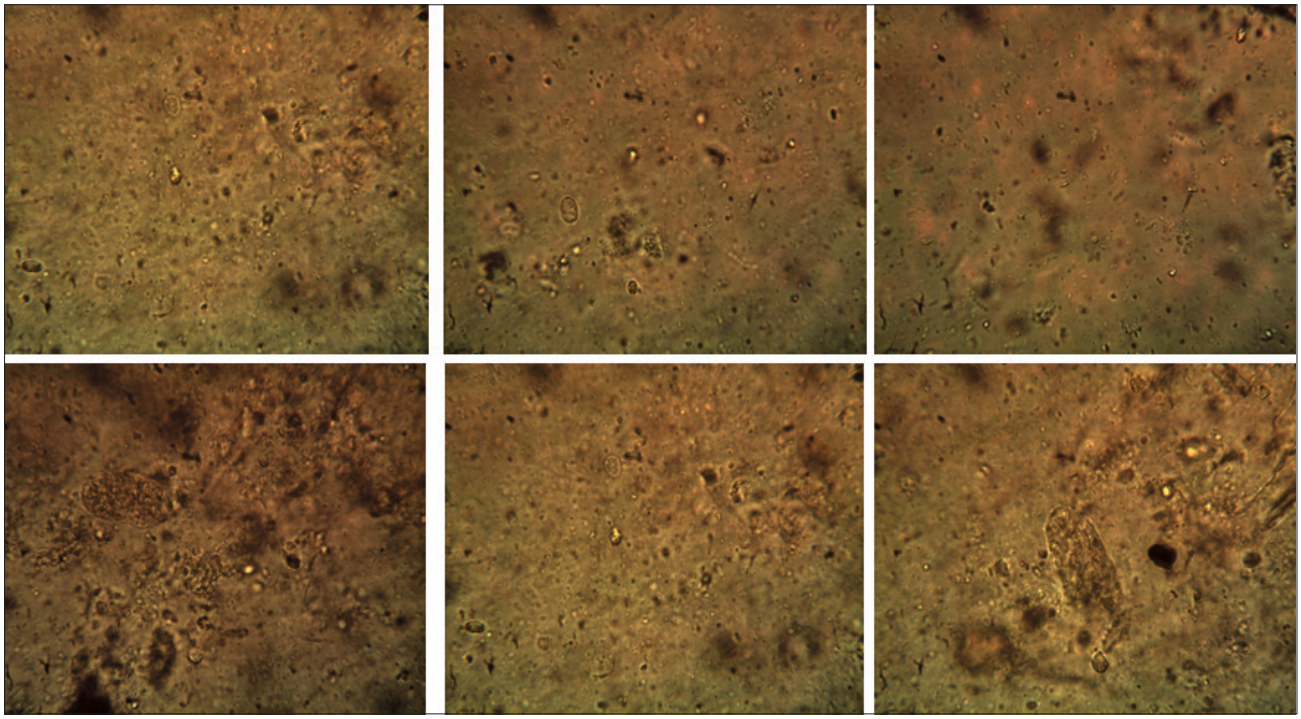

Figure 7: Results on microbial image analysis on treatment media containing water formation, rumen fluid, and coals (A: lignite, B: subbituminous, C: bituminous, and K: control) at room temperature

than the other treatments. This is due to the microbial activity from the formation of water and the absence of coal.

A decrease in pH could be promoted by producing volatile fatty acids (VFA) such as acetic, propionic, and butyric acids introduced by rumen fluid, formation water, or coal microbes. Thus, there was a direct correlation between a decrease in pH and an increase in VFA production. A reduction in pH promotes high H^+ levels in the media. The generated organic acids from coal degradation in coals included phenols, aldehydes, and ketones (**Shi et al., 2009**). Biodegradation of coal causes desulfurization, or the dissolution of sulfur into the liquid medium in the form of sulfate ions (SO_4^{2-}). As a result, sul-

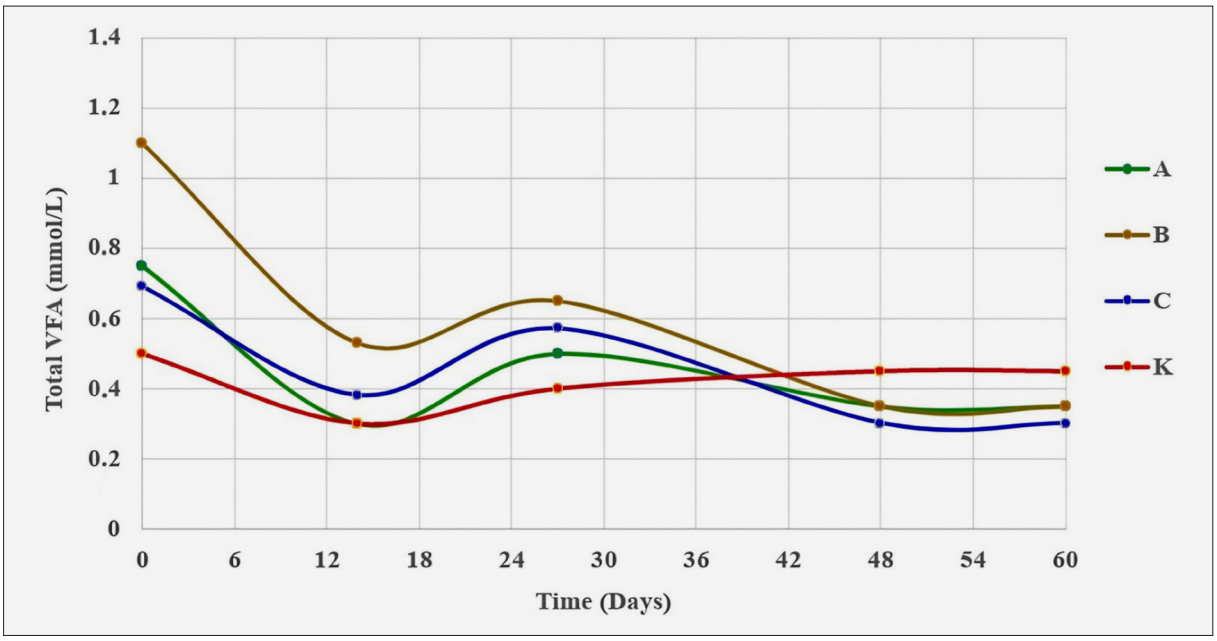

Figure 8: Variations in the overall VFA value of treatment media at room temperature contain coal (A: lignite, B: sub-bituminous, C: bituminous, and K: control), rumen fluid, and formation water

furic acid is formed (**Hammel, 1996**) and creates acidic media conditions.

The increasing pH occurs due to the production of ammonia compounds from the degradation of pyridine in coals. Ammonia is produced by the pyridine ring opening that forms pentanol and ammonia (**Du et al., 2010**). **Ying et al. (2010)** and **Kirk (1993)** also mentioned a similar explanation, where the ammonia compound formation causes the increase in medium pH due to pyridine biosolubilization in lignite coal. In addition, during the methanogenesis stage, organic acids are broken down into methane and carbon dioxide, and the possibility of NH_3 formation could also lead to the solution increasing pH (**Kresnawaty, 2008**). Most of the protein hydrolysis products undergo further catabolism (deamination), resulting in the production of ammonia (NH_3) (**Arora, 1995**).

3.3. *Images of microbes*

The evidence of the changing media pH due to microbial activity was confirmed by identifying present microbes in all samples with different coals involving British Standard EN 12353:2013 that supersedes BS EN 12353:2006 (see **Figure 7**). The analysis of microbial identification indicated that the bacteria were the most prevalent. Another identified microorganism is the protozoa, which appears in the rumen fluid. The most dominant bacteria in the treatment media were rod-shaped bacteria or bacilli. These bacteria are believed to have originated from the coals and can survive due to their ability to create spores. A study by **Sugoro (2012)** reported supporting findings where common bacteria found in coal are strains of *Bacillus* from the *Bacillus* genus.

On the other hand, several cocci-type bacteria were identified in the formation water. The identified protozoa belonged to the Ciliata. They were not found again after the incubation period that exceeded 14 days, possibly because they could not adapt to a medium containing coal.

3.4. *Total VFA*

Volatile fatty acid (VFA) analysis was conducted to measure the extent of coal organic compound degradation and the conversion of total VFA into gases, such as methane and carbon dioxide. Total VFA was observed at the beginning of incubation due to its presence in rumen fluid, formation water, and coal (see **Figure 8**). Throughout the incubation period, the levels of volatile fatty acids (VFAs) in the media experienced changes in all treatments with various coal types and the control group. The pattern of changes in VFA values was consistent across all treatments. However, this contradicts the control treatment, which does not include coal.

Microbial activity from coal, formation water, or rumen fluid causes changes in the media VFA levels. The decline in VFA levels occurs due to microbes using VFA as a carbon or energy source, producing methane and carbon dioxide. The rise in VFA levels is a result of bacterial metabolism under anaerobic circumstances, where coal is broken down as the primary substrate. A correlation exists between the VFA value and the degree of acidity (pH), where the pH value will correspondingly induce changes in the VFA value. According to **Jones et al. (2010)**, the breakdown of long-chain alkanes, long-chain fatty acids, and single-aromatic ring intermediates produces the VFA. Methanogenic microbes subsequently use the created VFA to produce methane. When VFA

Table 3: Partial VFA compound concentration in the treatments

Treatment Code	Time	Acetic Acid (C2)	Propionic Acid (C3)	Isobutyric Acid (iC4)	N-butyric Acid (nC4)	Isovaleric Acid (iC5)	N-Valeric Acid (nC5)
A	0	18.70	4.35	0.17	1.46	0.18	0.24
	14	14.77	5.19	0.24	2.05	0.24	0.16
	60	1.83	1.60	0.10	0.08	0.13	0.17
B	0	23.19	9.04	0.20	2.31	0.22	0.16
	14	26.10	7.50	0.30	2.72	0.37	0.35
	60	2.36	2.31	0.30	0.46	0.29	0.55
C	0	34.85	10.27	0.29	3.62	0.32	0.28
	14	39.34	12.75	0.47	4.60	0.53	0.32
	60	2.49	11.95	0.36	0.09	0.35	0.22
K	0	26.10	7.12	0.20	2.46	0.20	0.17
	14	15.56	4.69	0.27	1.50	0.34	0.11
	60	2.56	4.69	0.30	0.10	0.31	0.12

(volatile fatty acids) levels are high, there is an expectation of increased conversion of organic acids into gas (**Plummer, 1971**). The VFA production process is a result of hydrocarbon fermentation in the glycolysis pathway and the Krebs cycle, affecting the pH level and making it more acidic (**Pelczar and Chan, 1992**).

Rumen microbes may immediately utilize the generated VFA as it serves as the primary energy source and carbon for their growth and sustains the microorganism community. This will cause a minor pH decrease (**Preston and Leng, 1987**). The rapid generation of volatile fatty acids (VFAs) in rumen is promoted by the early utilization of simple compounds, such as amino acids, in the coal substrate. Rumen bacteria transform these amino acids into alpha-keto acids (**Jeffries, 1990**).

The decline in volatile fatty acid (VFA) production may be attributed to complex compounds in the coal substrate. Therefore, energy is required to break the lignocellulose linkages, which are the main components of the coal substrate. Changes in total volatile fatty acid (VFA) production are attributed to microbes using VFA as an energy source for their survival. The energy generated by the VFA formation will be used for vital life processes and the synthesis of microbial proteins, after which the microbes begin reproduction (**McDonald et al., 2002**).

The decrease in total VFA is due to the slow processes of acidogenesis and acetogenesis. A reduction in pH is directly correlated with increased VFA production and high gas production (**McDonald et al., 2002**). An increased total VFA indicates greater solubilization because the degraded compounds are converted into VFA and gas, leading to increased gas production. The total VFA value decreases because VFA is synthesized into methane (**Leuschner et al., 1990**).

3.5. Partial VFA

The results of partial VFA analysis showed that all treatments produced volatile fatty acids, such as acetic,

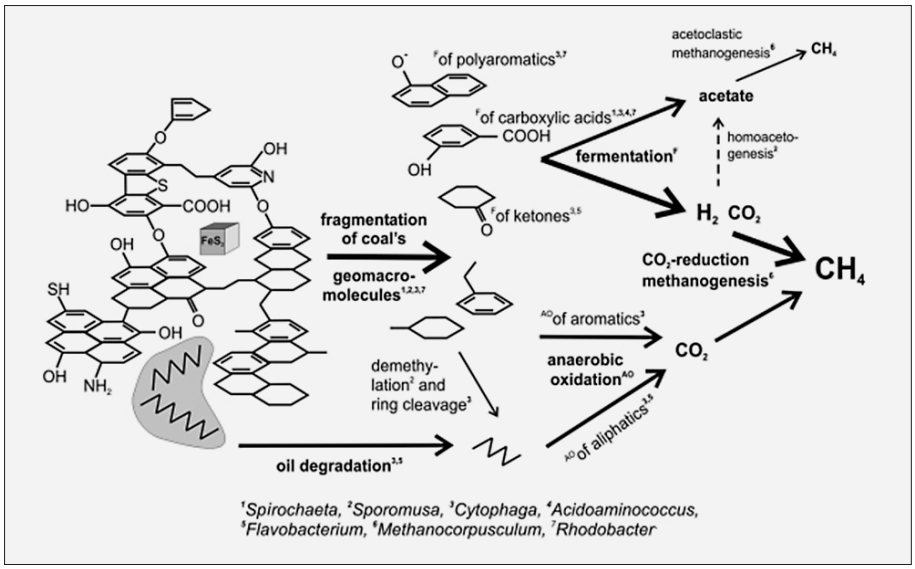

Figure 9: Reaction path model of coal conversion into methane (**Strapoc et al., 2008**)

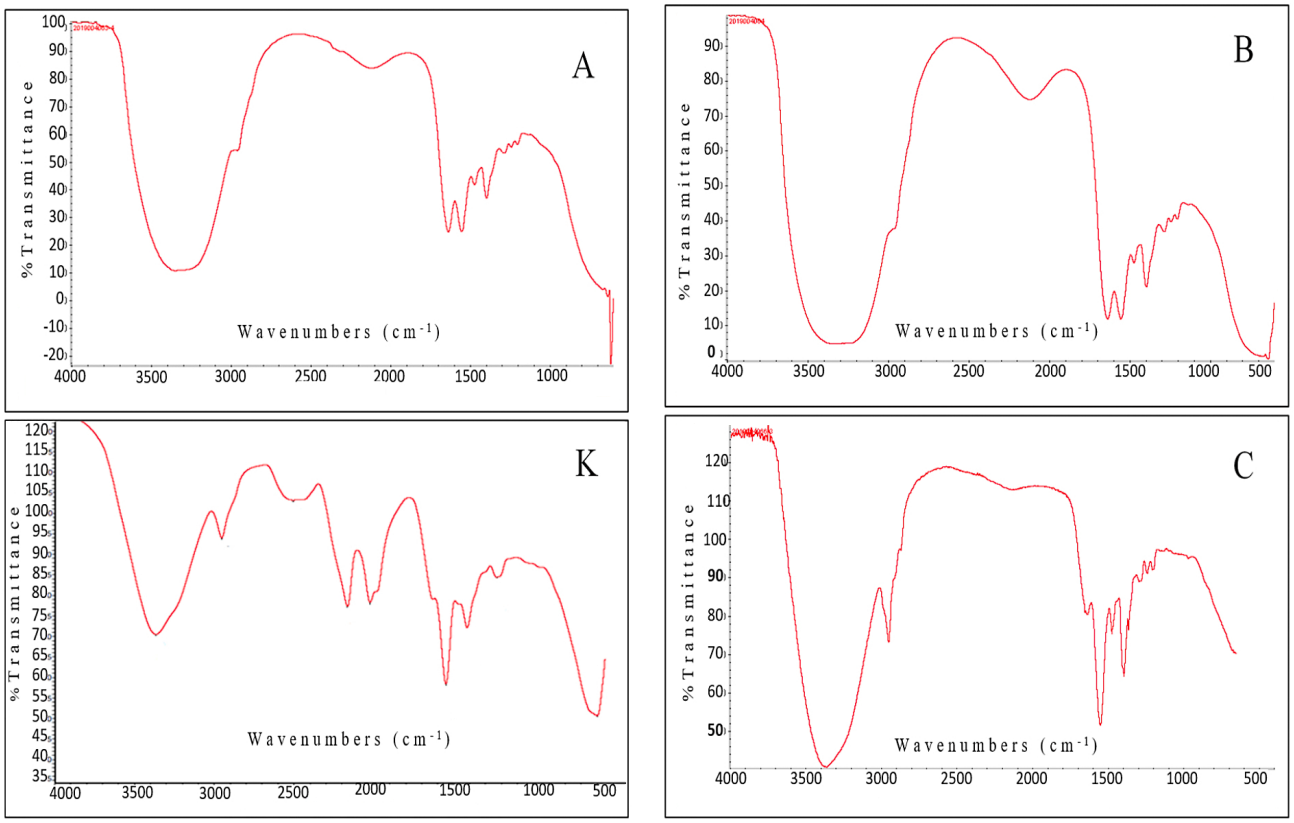

Figure 10: Results of FTIR spectroscopy analysis on the intensity of the coal functional group

propionic, butyric, iso-butyric, iso-valeric, and valeric acids, after 60 days of incubation at different concentrations (see **Table 3**). The highest fatty acid concentration produced is acetic acid, an intermediate compound before the methane formation. This is because acetic acid is the end product of the glycolysis process, which occurs when complex carbohydrates are broken down. The media may also contain homoacetogenic bacteria, converting the produced CO_2 and H_2 during fermentation into acetic acid compounds and causing its concentration to be higher. This acetic acid can be utilized by methanogenic bacteria to produce methane (**Thalib et al., 2004**).

The acetate accumulation can be caused by propionic and butyric acids that are degraded by acetogenic bacteria into acetic acid (**Manurung, 2004**). Propionate is a glucogenic VFA because it can be catabolized into glucose. At the same time, acetate and butyrate are non-glucogenic VFAs. Therefore, the amount of propionate is lower due to the conversion by bacteria contained in the media (**Astuti et al., 2007**). The isobutyric and isovaleric acids are lower than butyrate and valerate because these two compounds are carbon sources for amino acid biosynthesis (**Husnajat, 1998**). The reaction pathway model that occurs during incubation is presented in **Figure 9**.

3.6. Coal functional group analysis

In FTIR spectrometer testing, the employed samples were coal deposits. Control treatment as a comparison in this analysis used coals before treatment application. A study performed by **Saika et al. (2008)** concerning subbituminous coals in India found C-S bond at 690 cm¬-1, long-chain aliphatic bond in the absorption area of 2920-2850 CM, and minerals, such as kaolinite (1031 cm 1) and pyrite (420 cm¬-1). Profile analysis of the sub-bitumen coal function group in Nigeria showed the existence of NO2 bonds of nitro compounds at 1500-1300 CM¬-1 in the region and the hydrogen atom replaced the benzene ring. Furthermore, Manoj et al. (2009) analyze pure coal and identify aromatic bonds in the area between 700 and 900 cm-1. The increase and decrease in coal functional groups observed in all samples imply that microbial degradation carried out by microbes from rumen fluid, water formation, or coal itself has resulted in structural change. Microbial activity in coal involves transformation of coal structures into phenolic compounds, aliphatic lignin, and ring break. These compounds are then converted into volatile acids, causing a decrease in pH of the media and the total increase in VFA (**Scott, 1990**). This can be seen from the FTIR spectrum indicating a long chain aliphatic bond in the absorption area of 2920-2850 CM¬-1, and minerals such as kaolinit (1031 cm¬-1), the bond of the benzene ring in the region 1680-1530 CM¬-1 and minerals, like kaolinit (1031 cm¬-1).

In FTIR spectrometer testing, the employed samples were all types of coal deposit samples. Control treatment for comparison in this analysis is the coal before treat-

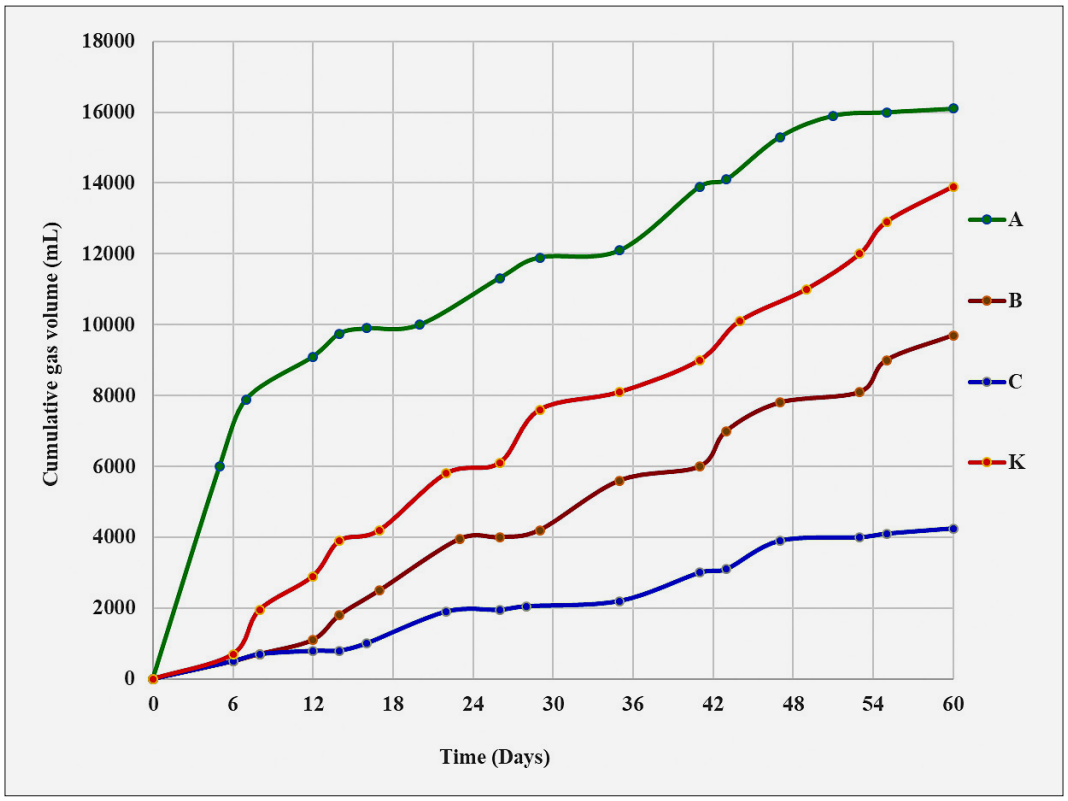

Figure 11: Cumulative gas volume in treatments containing formation water, rumen fluid, and coals (A: lignite, B: subbituminous, C: bituminous, and K: control) at room temperature

ment application. A study performed by **Saikia et al. (2008)** on sub-bituminous coal in India found that there were C-S bonds in the region at 690 cm^{-1}, long-chain aliphatic bonds in the absorbance region at 2920–2850 cm^{-1}, and minerals such as kaolinite (1031 cm^{-1}) and pyrite (420 cm^{-1}). The functional group profile analysis of sub-bituminous coal in Nigeria demonstrated the presence of NO_2 bonds from nitro compounds at 1500–1300 cm^{-1} in the region and hydrogen atoms substituted for benzene rings. Furthermore, **Manoj et al. (2009)** analyzed pure coal and identified aromatic binding in the region between 700 and 900 cm^{-1}.

The observed increase and decrease in coal functional groups across all samples imply that microbial degradation performed by microbes from rumen fluid, formation water, or coal itself has resulted in structural changes. Microbial activity on coal involves transforming coal's structure into phenolic compounds, aliphatic lignin, and the breakdown of rings. These compounds are subsequently turned into volatile acids, leading to a drop in the media pH and a rise in the total VFA (**Scott, 1990**).

3.7. Cumulative gas volume

The results of gas production measurements show that all treatments can produce gas at different volumes and rates (see **Figure 11**). The gas formed is the result of coal biodegradation. Increased gas production indicates that rumen microbes can utilize the coal substrate. The highest gas production occurred in treatment A, namely lignite coal, followed by control, then treatments B (subbituminous coal) and C (bituminous coal).

The results of gas production measurements show that all treatments can produce gas at different volumes and intensity, along with the ability of bacteria from rumen fluid which outline and produce methane gas in each of the samples. The gas formation is the result of coal biodegradation, while the control (k) producing extra formed gas was due to the continuation of the substrate residue of rumen fluid. Increased gas production shows that rumen microbes can use coal substrates. Based on the obtained data, the highest produced cumulative gas production was in the type of lignite coal (see **Figure 9**). This might occur because the lignite coal structure is softer and is not subbitaluminous and bituminous coal substrate that are easier to degrade by microbes.

The gas formed from coal biodegradation produces simpler intermediate compounds, such as aromatic rings, long-chain alkanes, and long-chain fatty acids. This biodegradation can be seen from changes in the coal functional group profile (see **Table 3**). Furthermore, these compounds will be broken down into H_2, CO_2, and Volatile Fatty Acid (VFA), namely volatile fatty acids such as acetic acid, propionic acid, and butyric acid (**Jones et al., 2010**), resulting in a decrease in pH accompanied by an increase in total VFA. The increase in gas volume in the four treatments occurred due to the dominance of methanogenic microbial activity by utilizing VFA, CO_2,

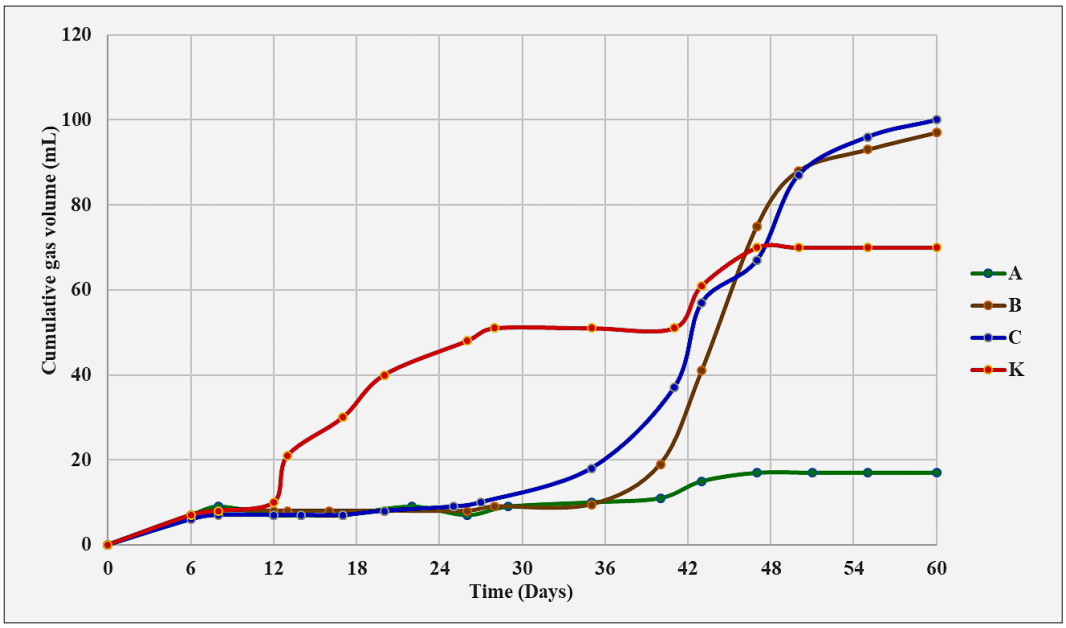

Figure 12: The cumulative methane volume among the treatments containing formation water, rumen fluid, and coals (A: lignite, B: sub-bituminous, C: bituminous, and K: control) at room temperature

and H_2 to produce methane (**Manurung, 2004**). Methane is also produced from methanol conversion (**Ikbal and Rudi Nugroho, 2006**).

3.8. Methane

Methane can be produced by all treatments containing different coal types with a similar pattern (see **Figure 12**). Methane production in the control group exceeded all treatments after day 48. After that, higher gas production occurred in treatments C (sub-bituminous) and B (bituminous) until day 60. The lowest methane production occurred in treatment A with lignite coal. Such a result contrasts the cumulative gas volume production (see **Figure 10**). This could be due to the production of several compounds other than methane, as their structure is more simply broken down.

Generally, the production of methane by fermentation involves a series of phases. One of these processes is hydrolysis, which breaks down the complex coal polymer into monomers. This process leads to a change in the composition of the coal functional groups. Next, these compounds will undergo degradation into H_2, CO_2, and volatile fatty acids (VFA), such as acetic acid, propionic acid, and butyric acid (**Jones et al., 2010**). Then, acetogenic bacteria break down propionic acid and butyric acid into acetic acid, CO_2, and H_2, leading to a drop in the media pH and increasing total volatile fatty acids (VFA).

During the methanogenesis process, microorganisms involved in homoacetogenesis and acetoclastic methanogenesis utilize H_2, CO_2, and acetate to produce methane (CH_4). The homoacetogenesis bacteria in coal sources utilize H_2 and CO_2 to produce acetate. Acetate produced through fermentation and gas conversion reactions can be transformed into CH_4 by acetoclastic methanogenesis bacteria (**Jones et al., 2010**). **Whitford et al. (2001)** reported that methanogenesis-acetoclastic bacteria contained in rumen encompass Halobacterium halobium, Methanosarcina barkeri, Methanosarcina mazei, Methanococcoides burtonii, Methanolobus taylorii, Methanomicrobium mobile, Methanobacterium bryantii, Methanobrevibacter smithii, Methanobrevibacter ruminantium, and Methanosphaera stadtmanae that produce methane during the incubation. In addition, methane is produced from methanol conversion (**Ikbal and Rudi Nugroho, 2006**).

The methane produced in this study is relatively small compared to coalbed methane produced in nature, which accounts for 80–95% of the total gas available (**Susilawati, 2008**). This was due to several influential factors, including substrate availability, where the optimum substrate ratio for rumen microbes is C/N between 20:1 to 30:1. Meanwhile, the C/N ratio in coal can reach more than 100:1, causing the coal substrate degradation process to take a long time. Livestock waste is generally rich in N content but deficient in C. On the other hand, agricultural waste is usually rich in C content but deficient in N (**Shuler and Kargi, 2002**).

The anaerobic condition factor is where the decomposition of organic compounds in aerobic conditions produces CO_2, whereas in anaerobic conditions, it produces methane (**Mazumdar, 1992**). Oxygen can kill all anaerobic bacteria that produce methane. Methanogenic bacteria are anaerobic microorganisms and are very sensitive to oxygen. It is also generally known that microbial growth will be inhibited at a dissolved oxygen concentration of 0.01 mg/L (**Yani and Darwis, 1990**). The degree of acidity (pH) factor has been explained in the discussion of media pH.

In addition, the temperature factor, in which bacteria are active in the fermenter to produce gas, depends on the environmental temperature. However, gas can be made at temperatures that range from 20-40°C. Faster decomposition will be obtained by increasing the fermenter temperature to 40-60°C. The optimum temperature for methane-producing microbes is 30-35°C (**Yani and Darwis, 1990**). Inhibitory Factor: The capacity of a compound to inhibit process activity in the fermenter depends on its concentration. The toxic compounds at high concentrations included sulfides, soluble metals, antibiotics, alkaline earth (sodium, magnesium, calcium), and ammonia. Some of these compounds are soluble and are toxic at low pH (**Wise, 1987**).

5. Conclusions

The results of the present study suggested that all types of coal can produce methane by utilizing microbial sources from rumen fluid and formation water. The highest gas production occurred in treatment A with lignite coal, Factors affecting methane include substrate availability, where the optimal substrate ratio for rumen microbes ranges from C/N 20:1 to C/N 30:1, while the C/N ratio of coals can exceed 100:1, resulting in the coal substrate degradation process, which requires quite a long period, followed by control, treatments B (sub-bituminous coal) and C (bituminous coal). Methane production in the control group exceeded all treatments until the 48th day. After that, higher gas production occurred in treatments C (sub-bituminous) and B (bituminous) after day 60. The lowest methane production occurred in treatment A with lignite coal.

Both increasing and decreasing coal functional groups were observed from all samples, indicating that structural changes had occurred due to degradation by microbes from rumen fluid, formation water, and coal. Biodegradation of lignite coal will be easier because it is softer and less complex than sub-bituminous and bituminous coal.

This method can be implemented in unproductive coalbed methane reservoirs, as proven by the rumen fluid's bacteria for surviving at a temperature of 50 psi and coalbed methane reservoir pressure (400 psi).

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SAŽETAK

Učinak primjene fluida iz buraga na proizvodnju metana iz različitih vrsta ugljena

Indonezija je jedan od najvećih proizvođača ugljena u svijetu. Drugi način korištenja ugljena kao izvora energije jest pretvaranje ugljena u metan korištenjem metanogenih mikroorganizama. Inovativno korištenje klaoničkoga otpada kao izvora metanogenih mikroorganizama za proizvodnju metana iz ugljena predstavlja nov pristup diverzifikaciji energije dobivene iz ugljena na ekološki prihvatljiviji način. Kako bi se navedeno moglo primijeniti u praksi, potrebno je provesti ispitivanje mikrobiološkoga djelovanja fluida iz buraga na proizvodnju metana iz ugljena u uvjetima koji vladaju u bušotini za proizvodnju metana iz ugljena (engl. *coalbed methane* (CBM) *well*), te su u ovome istraživanju korištene različite vrste ugljena. Prethodno provedena istraživanja potvrdila su mogućnost korištenja fluida iz buraga za proizvodnju metana iz ugljena. Kako bi se potvrdila primjena navedenoga u praksi, potrebno je provesti ispitivanje mikrobiološkoga djelovanja fluida iz buraga u uvjetima CBM ležišta. Stoga je ovo istraživanje provedeno na različitim geološkim formacijama koje sadržavaju vodu i ugljen. Cilj je istraživanja ispitati proizvodnju metana kombinacijom fluida iz buraga kao izvora metanogenih mikroorganizama, slojne vode i raznih vrsta ugljena (A: lignit, B: subbitumenski, C: bitumenski i K: kontrolni) na sobnoj temperaturi. Rezultati provedenoga istraživanja upućuju na to da je dodavanjem slojne vode i mikroorganizama iz tekućine iz buraga moguće proizvesti metan iz različitih vrsta ugljena. Mikrobiološka aktivnost tijekom istraživanja praćena je mjerenjem promjene pH vrijednosti i promatranjem živih mikroorganizama. Bacili su dominantna vrsta mikroorganizama. Zbog razgradnje organskih spojeva ugljena prisutnost metanogene mikrobne aktivnosti praćena je hlapljivim masnim kiselinama (engl. *volatile fatty acid*, VFA). Ukupni VFA u svim je slučajevima pokazao sličnu tendenciju smanjenja. Istraživanjem je utvrđeno da u svim slučajevima do 60 dana inkubacije dolazi do stvaranja hlapljive masne kiseline u različitim količinama. Navedene masne kiseline uključuju octenu, propionsku, maslačnu, izomaslačnu, izovalerijansku i valerijansku kiselinu. Najčešće proizvedeni djelomični VFA, kao primarni međuspoj u stvaranju metana, jest octena kiselina. Slučaj A s lignitskim ugljenom imao je najveću proizvodnju metana. Ukupni volumen plina u tom je slučaju nakon 60 dana inkubacije dosegnuo 16 400 mL. Nasuprot tome, najveća kumulativna proizvodnja metana dogodila se u tretmanu C s bitumenskim ugljenom, u iznosu od 100,60 mL nakon 60 dana inkubacije.

Ključne riječi:
metan proizveden iz ugljena, fluid iz buraga, slojna voda, mikroorganizmi, vrste ugljena

Author's contribution

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