

MICROBIAL CONVERSION OF COALS TO CLEAN FUEL FORMS

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ABSTRACT

Anaerobic cultures have been used for the production of methane and alcohols from coal. Cultures were adapted from natural inocula collected from sources such as sewage sludge and horse manure. A 1% (w/v) slurry of leonardite, lignite, or subbituminous coal was used in the incubations. Methane was produced from all cultures, including some untreated coals, to a greater extent than in control cultures. Over several months of adaptation, methane production capacity increased considerably. Volatile fatty acids (VFAs) were identified as intermediates in the conversion of coal to methane. A proposed scheme for the conversion is breakdown of the coal polymer by a series of organisms and metabolism of the fragments to methane precursors such as VFAs. A mixture of short chain alcohols was produced by cultures grown in the presence of methane inhibitors. These cultures after prolonged adaptation show potential for use in larger scale bioreactors for the production of gaseous and liquid fuels.

INTRODUCTION

Recent interest in the use of microorganisms to process coal has led to the investigation of sulfur removal from coal as well as the conversion of coal to water soluble forms. Prior work in this laboratory has focused on investigating the mechanisms of formation of these water soluble compounds from coal by microbial as well as chemical means and characterization of the resulting products (ARCTECH, Inc. 1988a). The nonvolatile nature of these coal products inhibits their use as a clean fuel even though a majority of the ash and a proportion of the sulfur has been removed. In the current work, we have investigated the use of these coal products as well as untreated coals for the production of gaseous and liquid fuels (ARCTECH, Inc. 1988b).

EXPERIMENTAL PROCEDURE

Coals--Both untreated coals and coal depolymerization products were used as substrates (1% w/v and 1% v/v, respectively) for methane, alcohol, and acid production. Two lignites were used as raw coal substrates. For the depolymerization products, three coals, North Dakota lignite, Beulah lignite, and Wyodak subbituminous, were treated with chemical or biological agents to yield water soluble products of a range of molecular weights.

Anaerobic Cultures--Anaerobic samples were collected from environmental sources and inoculated into an anaerobic medium containing coal or coal products. The procedures of Hungate, as modified by Bryant (1972) and by Balch and Wolfe (1976) were followed throughout. Serum stoppered tubes or serum bottles capped with black butyl rubber stoppers and crimp sealed were used for incubations.

Enrichment cultures were developed through successive transfers from each inoculum to fresh medium containing coal or coal depolymerization products every 28-45 days over a period of several months. Slow cultures were adapted to the coal or coal products over longer periods of time. Enrichment cultures were also developed in the presence of the methane inhibitors, 2-bromoethanesulfonic acid (BESA) and monensin, to allow the accumulation of acids and/or alcohols.

Chemical Analysis--All anaerobic fermentation products were quantified using gas chromatography. For gas analysis, a 10' x 1/8" O.D. stainless steel column packed with 100/120 mesh Carbosieve S-II was used. Methane, carbon dioxide, nitrogen, and hydrogen were determined using a thermal conductivity detector. The oven was programmed to hold at 100°C for 1 minute then to increase temperature at a rate of 20°C per minute to 200°C. Total gas production was determined by syringe displacement and was used to calculate mole % of methane in the gas phase.

Alcohol analyses were performed with either a 6' x 2 mm I.D. (1/4" O.D.) glass column packed with 1% SP-1000 on 60/80 mesh Carbopack B (first 3-4 inches 10% SP-1000 on 100/120 mesh Supelcoport) or a 2.4 M x 2 mm I.D. (1/4" O.D.) glass column packed with 0.3% Carbowax 20M on 80/100 mesh Carbopack C using a flame ionization detector. The oven was programmed from 60°C to 150°C at 20°C per minute then to 190°C at 5°C per minute and held. Analysis was performed by direct aqueous injection after centrifugation of samples to remove particulate matter.

Volatile fatty acids were primarily analyzed with an 8' x 2 mm I.D. glass column packed with 4% Carbowax 20M on 80/120 mesh Carbopack B-DA using a flame ionization detector. The oven was programmed to hold at 100°C for 1 minute then increase temperature to 180°C at 15°C per minute then to 205°C at 10°C per minute. Samples were diluted 1:1 with 0.06 M oxalic acid and centrifuged to remove particulates before injection.

RESULTS

Production of Methane From Coal and Coal Products

Figure 1 presents the time course of methane production from an untreated North Dakota coal and from Beulah lignite coal products. Methane production from samples containing coal or coal depolymerization products was higher than that of control cultures, demonstrating the conversion of coal carbon to methane. Similar results were obtained with other natural inocula, although not all cultures produced methane from every coal. A shift in the color of the reaction medium was observed during the course of incubation that was associated

with depolymerizing activity. The flattening out of the production curve indicates depletion of nutrients in the culture.

The effect of biological or chemical depolymerization of the coal on methane production was investigated with several different cultures. Data in Table 1 demonstrate increased production of methane in samples containing biologically produced coal depolymerization products. Methane is also produced from chemically depolymerized substrates although at a lower level. These experiments indicate that the products formed during biological and chemical depolymerization differ.

Identification of Alcohols and Acids in the Culture Medium

Our experiments indicated that methanogens were present and active in the adapted cultures. Methanogens are known to convert only simple organic molecules such as acetate and carbon dioxide to methane. Further experiments were initiated to determine the existence of methane precursors in the medium. To accumulate these precursors, methane inhibitors were added to enrichment cultures. Monensin serves as an inhibitor of specific enzymatic steps of methane production, whereas 2-bromoethane sulfonic acid (BESA) is an analogue of coenzyme-M which is required for methane production.

In almost all of the samples, BESA completely inhibited the production of methane. Monensin, however, inhibited methane production only from a single culture adapted to Beulah coal products. Results of analyses of culture media during methane inhibition studies are reported in Tables 2 and 3. Several short chain alcohols, including methanol, ethanol, propanol, and butanol, were produced by these cultures from either coal or coal depolymerization products. Acetone was also produced in small quantities by some cultures. No alcohols were produced in the absence of coal or coal products.

Product ratios varied depending on the inhibitor added to the medium. Ethanol was clearly the major alcohol produced by all cultures, with concentrations ranging between 757 and 2288 ppm. Methanol accumulated up to 316 ppm only in the presence of monensin. Propanol and butanol formation was favored in the presence of BESA. Total alcohol production decreased as the pH of the medium increased with no production of alcohols at pH 7.

In addition to alcohols, several short chain organic acids were detected in the culture medium (Table 3). Acetic acid was the principal organic acid detected, accumulating to a level of 1312 ppm. Small quantities of propionic, butyric, and valeric acid were also identified. Control samples without coal or coal depolymerization products produced minute quantities of acetic acid. No other organic acids were detected in these control samples.

DISCUSSION

The results reported in this paper demonstrate the feasibility of converting untreated lignite coals or depolymerized products of lignite and

subbituminous coals to methane by anaerobic cultures. Methane is produced from enrichment cultures in excess of that produced in the absence of coal or coal products. The ability of the cultures to produce methane increased as the enrichment period increased, demonstrating bacterial adaptation to use of coal or coal depolymerization products. The next step in culture development will be transfer of the most promising culture to a small bench-scale bioreactor to monitor continuous production of methane from coal or coal products.

Enrichment cultures are also capable of converting coal and coal-derived material to short chain alcohols and acids when methane production is inhibited. Although total alcohol concentration in the medium is less than one percent, the amount of alcohol produced by the cultures has steadily increased as the cultures adapted to the new substrates. Time course experiments are in progress to determine the production of alcohols and acids over an extended period.

Anaerobic enrichment cultures are capable of converting both untreated lignite coal and depolymerized coal products to methane, alcohols, and volatile fatty acids. A distinct preference for biologically derived coal products rather than chemically derived products was observed. Alterations in the coal molecule effected by microorganisms might be more conducive to further microbial attack than chemical modifications.

ACKNOWLEDGEMENTS

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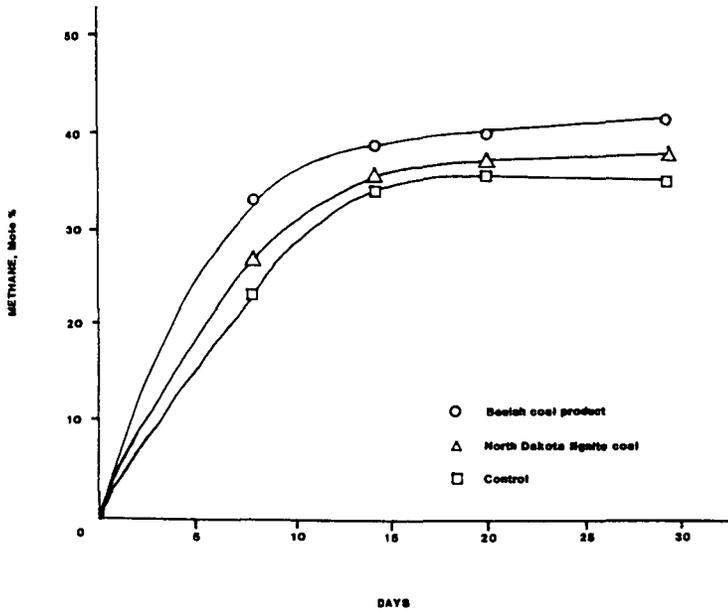


Figure 1. Production of methane from a ND Coal and Beulah Coal Product by Natural Inocula

Table 1. Direct Production of Methane from Coals by Anaerobic Bacteria

Coals	Methane Produced,** Mole %	
	2 Mos. Adaptation	6 Mos. Adaptation
Leonardite	7.8	25.6
	11.4	19.3
Texas lignite	9.1	----
	6.4	----

* 1% (w/v) coals were used.

** Methane from control samples (no coal) was subtracted.

Table 2. Production of Alcohols from Untreated Leonardite Coal and Depolymerized Products of a Beulah Coal Using Anaerobic Microorganisms

pH	Coal	Inhibitors	Alcohols Produced, ppm			
			Methanol	Ethanol	Propanol	Butanol
5.0	L	BESA	7.2	2288.2	22.3	18.6
5.0	L	Monensin	275.3	2053.3	3.9	1.9
5.0	L	Control	0	10.9	25.6	0
6.0	L	BESA	7.06	1335.9	173.5	38.3
6.0	L	Monensin	315.9	1975.5	1.7	0
6.0	L	Control	0	16.2	19.9	1.7
6.0	B	BESA	13.5	756.5	202.9	88.9
6.0	B	Monensin	129.2	911.4	10.1	8.5
6.0	B	Control	29.1	4.9	4.5	6.2

Table 3. Production of Short Chain Acids from Coals and Depolymerized Coal Products Using Anaerobic Microorganisms

Coal	Inhibitors	Acids Produced, ppm			
		Acetic	Propionic	Butyric	Valeric
L	BESA	925.8	70.9	28.8	280.7
L	Monensin	626.5	77.7	34.1	266.1
L	Control	34.7	0	0	0
L	BESA	1311.5	306.5	80.7	501.0
L	Monensin	618.9	92.6	83.8	436.5
L	Control	4.5	0	0	0
B	BESA	932.4	233.9	62.5	0
B	Monensin	805.0	261.8	57.9	0
B	Control	99.6	118.7	0	0
TXL	BESA	885.7	158.4	34.7	0

L - Leonardite
 B - Beulah lignite
 TXL - Texas lignite
 BESA - 2-bromoethanesulfonic acid