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DEVELOPMENT OF BIOLOGICAL COAL GASIFICATION (MicGAS PROCESS)

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CONTRACT INFORMATION

Contract Number DE-AC21-90MC27226

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Period of Performance May 25, 1990 to March 26, 1996

Schedule and Milestones

FY 93-94 Program Schedule

Tasks/ Subtasks	FY 93	Months in FY 1994											
		O	N	D	J	F	M	A	M	J	J	A	S
1.1 NEPA Compliance	done												
1.2 Work Plan	done												
2. Enhancement of Methane Production													
2.1 Strain Improvement													
2.2 Effect of Co-substrates													
2.3 Nutrient Amendment													
3. Effect of Substrates on Microbes													

OBJECTIVES

The overall goal of the project is to develop an advanced, clean coal biogasification (MicGAS) Process. The objectives of the research during FY 1993-94 were to: (1) enhance kinetics of methane production (biogasification, biomethanation) from Texas lignite (TxL) by the Mic-1 consortium isolated and developed at ARCTECH, (2) increase coal solids loading, (3) optimize medium composition, and (4) reduce retention time.

BACKGROUND INFORMATION

State-of-the-art thermal coal gasification technologies, utilizing the abundant U.S. resource of low-rank coals, operate at high temperatures and pressures and require extensive synthesis gas clean-up for power generation. These technologies require not only high capital and operating costs, but also have to comply with increasingly stringent environmental regulations to control air, water and land pollution. Advanced coal conversion technologies, such as coal gasification are being developed to enhance the conversion efficiency as well as be economical for the abatement of emissions.

Low rank coals are more amenable to microbial conversions at near ambient conditions and thus a biological conversion technology could provide a comparatively economical system for utilizing low rank coals. Consequently, ARCTECH is developing the MicGAS Process as an integrated systems approach. This Process is being developed within ARCTECH's broad vision of the "Coal Biorefinery Concept" to enhance the economic value of coal and to develop additional markets for the usage of low-rank coals . Illustrated in Figure 1, the coal refinery concept involves the biological conversion of low-rank coals to value added products with minimal disposable waste (Figure 1). This concept envisions that all the three types of matter; namely, gas, liquid and residual solids will generate value added chemicals as co-products. These include:

1. clean burning fuel (biogas), as a gaseous product that will be used for advanced power generation, in fuel cell and in industrial applications,

2. the liquids will provide value added products, such as biopesticides and oxygenated chemicals (short-chain fatty acids and higher alcohols),

3. the residual coal mixed with process liquids will be converted into an organic soil amendment product - ACTOSOL™, that ARCTECH is currently marketing in domestic and international markets.

The Coal Biorefinery Concept is based on anaerobic microbial conversion of a variety of organic substrates to methane according to the schemes presented in Figure 2. Biomethanation can be hydrogenotrophic or aceticlastic depending upon the substrate (Figure 2A and B). In the case of a complex organic substrate, such as coal, the aceticlastic biomethanation is preceded by either acetogenesis only (Figure 2C), acedo-, and acetogenesis (Figure 2D), or a series of reactions involving hydrolysis, fermentation, acedo- and acetogenesis (Figure 2E), or any combination thereof. Initial studies conducted at ARCTECH [1-4] have established that despite the complexity of coal structure and variability among types of coals, low rank coals can be bioconverted to coproducts and methane under near ambient gasification conditions of temperature and pressure by a variety of unique anaerobic microbial consortia (eg. Mic-1, Mic-2, Mic-3, Mic-4)[1]. This

bioconversion has been confirmed by other scientists[cf.5,6-7]. The work at ARCTECH has demonstrated the specificity of a certain anaerobic microbial consortium to a given lignite[1]. For example, while Mic-1 consortium worked more efficiently with TxL, Mic-4 was more effective on Neyveli lignite. ARCTECH's strategy for the direct anaerobic bioconversion of low rank coals is based on the higher availability of coal carbon for the production of CH_4 and volatile fatty acids (VFAs) rather than the formation of CO_2

An independent economic study[8], based on the laboratory scale reactor data on biomethanation of TxL and conceptual process design, demonstrated the process to be commercially attractive. The study recommended, however, that a cheaper organic nitrogen source, reduced retention time, and higher solids loading were essential to make the process profitable. In subsequent studies[2], a low-cost nutrient amendment, Sheftone-T™, was substituted for the originally used yeast extract + trypsoy mixture. This substitution brought about a ten fold reduction in the cost of the culture medium. In addition, three fold reduction in residence time was achieved and the solids loading were increased at least 10 fold. Despite these achievements, however, it became apparent that in order to successfully achieve the goals recommended by the Fluor Daniel study[8] further enhancement of methane production and reduction in residence time was necessary for the process to become commercially viable. Thus, a better understanding of the mechanism of coal biomethanation became imperative to the enhancement of the biomethanation of TxL.

It is generally agreed that coal consists of two fractions, a macromolecular and a lower molecular weight fraction. Based on the general empirical formula of a German lignite (brown coal)[9], it is also recognized that the micromolecular fraction of coal is more amenable to microbial attack than the macromolecular one. Furthermore, if the micromolecular fraction can be removed, upon long term incubation of micro-organisms with the macromolecular fraction, the latter fraction will also be bioconverted to added value products. Recent results[4] on the biomethanation studies of chemically and biologically pretreated TxL indicate that microbially pretreated TxL gave higher methane production even at higher solids loadings of 5%. Nevertheless, it also was apparent that at 10% solids loading, the pH of the culture medium dropped drastically which lead to inhibited methane production compared with that observed at lower solids loading of 0.1 and 1.0%.

A close examination of the schematics in Figure 2E indicates that the mechanism of coal biomethanation is similar to the one observed during biomethanation of lignocellulosic substrates. Similar to the constituents (cellulose and hemicellulose) of lignocellulose, TxL is also a water insoluble substrate. Literature indicates that microbial attachment to complex insoluble substrates[10] and biofilm formation[11] play an important role in efficient microbial utilization of such substrates. Consequently, the hypothesis that higher biomethanation of TxL is directly related to better attachment of Mic-1 consortium to TxL particles was tested. In a recent study, Srivastava and Manolov[12] demonstrated that a number of factors, such as sequestrants, solids loading, H^+-donors etc., that enhanced methane production, were also the ones that demonstrated higher attachment of microbial cells to TxL particles. The knowledge thus gained has been used to further address the recommendations of the Fluor Daniel Study[8] for the enhancement of methane production in the MicGAS Process. This is a report of recent laboratory findings to further enhance the MicGAS Process.

PROJECT DESCRIPTION

Biomethanation of coal (MicGAS Process) is a phenomenon carried out by the synergistic metabolism of at least four groups of anaerobic microorganisms that constitute a mixed population or consortium. In this respect, the process can be considered analogous to that of anaerobic digestion of municipal waste. The exception is that unlike municipal waste, coal is a much more complex and difficult substrate to degrade. This project was focussed on studying the factors that can result in consistent enhancement of methane production at higher than hitherto used solids loading (0.1-1.0%) and reduction of retention time in the regime (7-10 days) closer to that of anaerobic municipal digestion.

RESULTS

Biomethanation of coal is a multi-step process requiring distinct simultaneous metabolic activities of different groups of anaerobic bacteria. These steps explained in Figure 2E occur in syntrophy, rather than in a stepwise fashion. A closer analysis of the results described here indicate that biomethanation of TxL at >5% solids loading is feasible through appropriate development of nutrient medium and further adaptation of the microorganisms involved in this process. Further understanding of the inhibitory factors and some biochemical manipulations to overcome those inhibitions will hasten the process considerably.

Products of Biomethanation

Biomethanation of TxL resulted in gaseous, liquid, and solid products. While the major gaseous products were methane and CO_2 the liquid product was composed of a number of volatile fatty acids and some other compounds. The solid phase was composed of residual coal mixed with minimal biomass. A preliminary analysis of the residual solids indicated about 23% ash content in contrast to 16% ash content in the untreated TxL. Furthermore, preliminary results indicate that the carbon in the residue could be converted to humic acids. Humic acids are the major components of ARCTECH's ACTOSOL^R product which is being sold in the domestic and international markets for agricultural applications.

Enhancement of Methane Production

Several parameters were studied to enhance the production of methane from TxL.

Bacterial adaptation. Bacterial enrichment, a technique to manipulate growth and specific substrate conversion was applied to develop the Mic-1 consortium to utilize TxL as the sole source of carbon. The adapted Mic-1 consortium showed an increase in methane production from 10 to 50 mole% reaching up to 71-78 mole % - a 7.5 fold increase during the adaptation period (Table 1). Furthermore, as a result of this adaptation, the methane production from 5% TxL (as compared to 0.01% and 1% initial concentration) started at day 3 and reached a maximum of up to 230 cc/g coal, a 5 fold increase within 11-15 days compared to approximately 2 months time in initial experiments (Task 2). The maximum rate of methane production was observed to occur between 11-14 days (Table 1). These results indicate that the culture has the ability to adapt to the coal carbon and has improved significantly during the adaptation period. This is a positive indication for further improvement in the process research.

Effect of nutrient amendment substitutes. A variety of commercially

available nutrient amendments as the sources of organic nitrogen were tested to replace the expensive yeast extract(YE)/Tryptic soy broth (TSB) mixture used in the original culture medium. Results indicated that Sheftone-T™ enhanced methane production by 15.3% (Figure 3).

Effect of Solids Loading. The Fluor Daniel Study[8] also recommended that TxL solids loading should be increased in order to make the process economical. Consequently, biomethanation of TxL was studied at solids loading of 0.1, 1, 5 and 10 (% w/v). An inverse relationship was observed between increased solids loading and methane production (Figure 4). Furthermore, with the increase in solids loading (from 0.1 to 5%), the methane production was inhibited but remained more or less the same at 5% and 10% solids loading. Nevertheless, significantly higher methane production was observed at 5% solids loading than at 10% when upflow fluidized bed reactors (UFBR) were used (Figure 5).

Effect of initial pH of the culture medium. The relationship between the initial pH of the medium and biomethanation of TxL by the Mic-1 consortium is presented in Figure 6. Data from another study[12] clearly indicate that the reason for the inhibition of methane production at 10% TxL is poor microbial attachment to TxL particles at pHs lower than 7.8 (Figure 6). The data from Figure 6 also demonstrate that the optimum initial pH of the culture medium for biomethanation of TxL at 10% solids loading is 7.8.

Effect of Hydrogen (Proton, H^+) Donors. Having determined the pH that provided better microbial attachment and greater biomethanation of TxL, the next step was to further enhance the kinetics of methane production at the higher solids loading of >5%. Literature data[13-15] on biomethanogenesis indicate that hydrogen (H) plays an important role. However, lignites typically contain 6-7.5% hydrogen[16] and studies conducted with ^3H demonstrated that the additional H^+ required for the biomethanation of TxL is derived from the water in the culture medium[17].

Nevertheless, further supplementation of H^+ was critical to the enhancement of MicGAS Process. Therefore, the SNTM was supplemented with citrate, formate, lactate, methanol and succinate as potential H^+-donors. Among these, citrate, lactate and succinate enhanced the methane production with the highest effect being that from citrate addition (Figure 7). Analysis of VFAs demonstrated that acetate is in highest concentration until day 7, but sharply drops thereafter (Figure 8). This is the period when the methane production increases (Figure 7). Higher methane production was also observed at 5% solids loading in the presence of 0.5% (v/v) methanol (Figure 9). The biomethanation of TxL in serum vial cultures remained approximately the same despite the addition of 10 mM citrate (Figure 10). Nevertheless, in bench scale upflow fluidized bed bioreactors (UFBR) at 5% TxL solids loading, the methane production was drastically enhanced (Figure 11) reaching up to 78 mol% by day 8 (arrow, Figure 11). VFAs analysis indicated that the methane production is directly related to the amount of acetate produced during the metabolism of Mic-1 consortium (Figure 12) on TxL. These data also indicate that perhaps the accumulation of propionic acid in the culture medium, and the inability of members of Mic-1 consortium to metabolize this VFA into acetate may be one of the limiting steps in the continued bioconversion of TxL to methane. The results presented in Figure 13, however, demonstrate that the reduction in the retention time and higher methane production even at 5% solids loading are

reproducible in another independent experiment using 3 separate bioreactors.

Carbon Balance

An analysis of the carbon in the untreated TxL and the resulting residue, together with the carbon coming from medium components (such as Sheftone-T™) and the analysis of carbon in the products shows a process efficiency (for methane) of 20% at 5% solids loading (Table 2) and a 91% carbon recovery.

FUTURE WORK

Significant advancements were made in enhancing the biomethanation of low rank coals, especially TxL by the Mic-1 consortium. However, for this process to be viable at a larger scale more research is needed. The programmed research plan includes: (A) further development of a culture medium with reduced cost, (B) identification of inhibitors, such as phenols, that might be produced from TxL as a result of microbial metabolism and in turn inhibit further microbial metabolism, (C) biochemical manipulations to modify the physiological characteristics of the microorganisms, and (D) evaluation of known and novel reactor designs. These tasks shall be accomplished through: (1) metabolic characterization of microorganisms, (2) further biochemical manipulation of the Mic-1 consortium for higher methane yields at (a) increased coal solids loadings, (b) reduced retention times, and (c) studying the effects of medium component on methane production.

ACKNOWLEDGEMENTS

ARCTECH is developing the MicGAS technology jointly with Houston Lighting and Power. This research was supported by the Department of Energy-METC.

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CONCEPT OF COAL BIOREFINERY

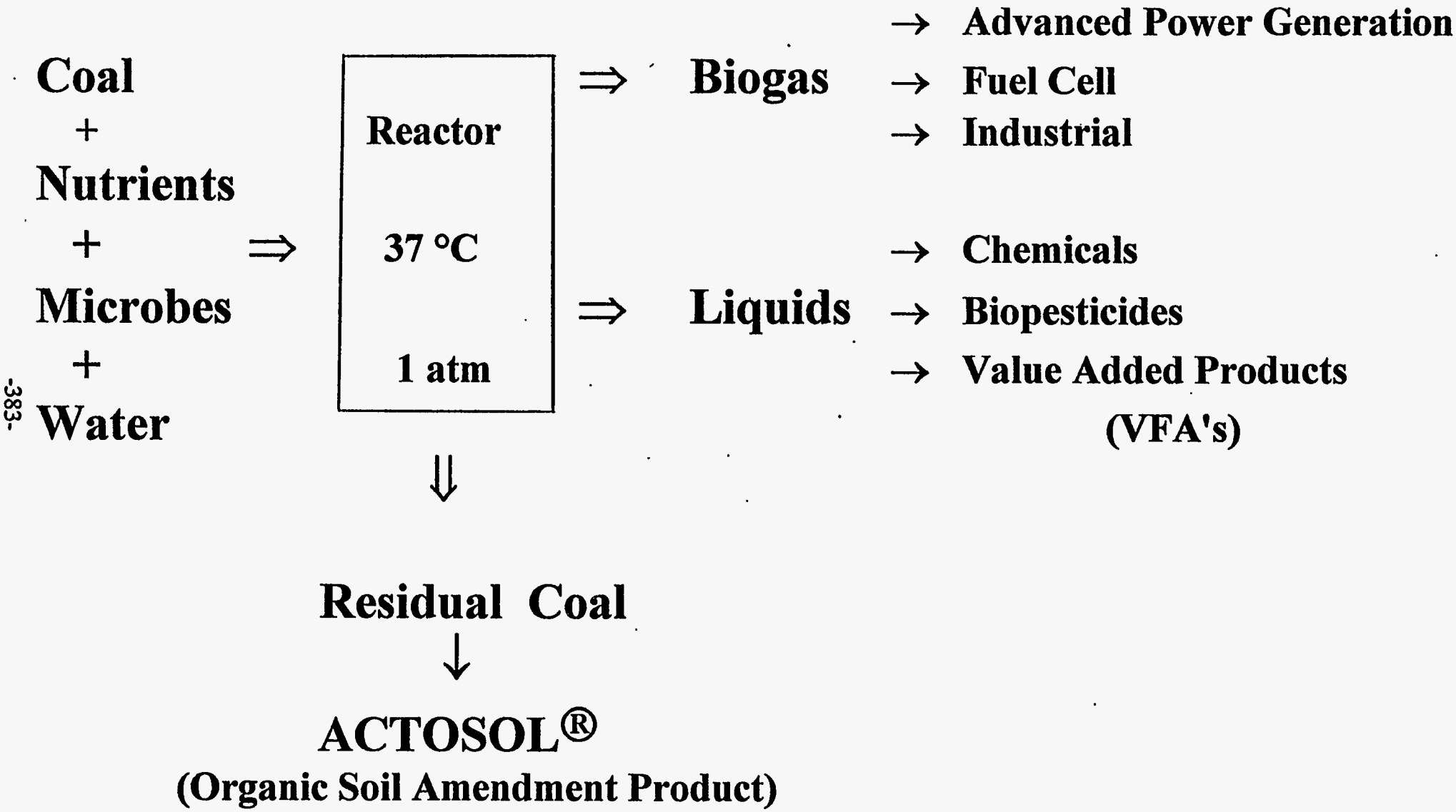


Figure 1

CONVERSION OF ORGANIC FEEDSTOCKS TO CH_4 IS A MULTISTEP PROCESS

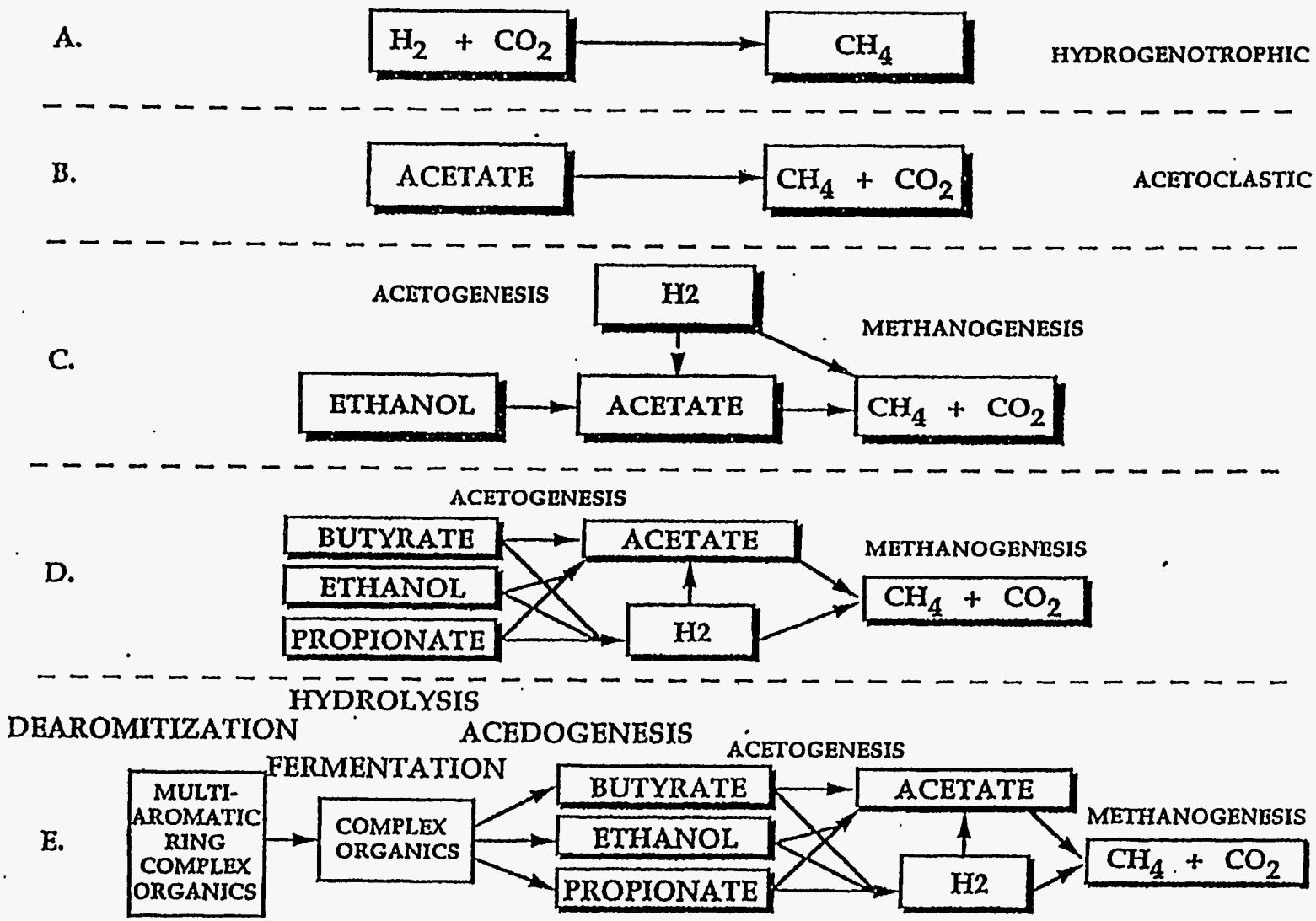


Figure 2

EFFECT OF NITROGEN SOURCE ON BIOMETHANATION OF TEXAS LIGNITE (1% w/v) BY Mic-1 CONSORTIUM

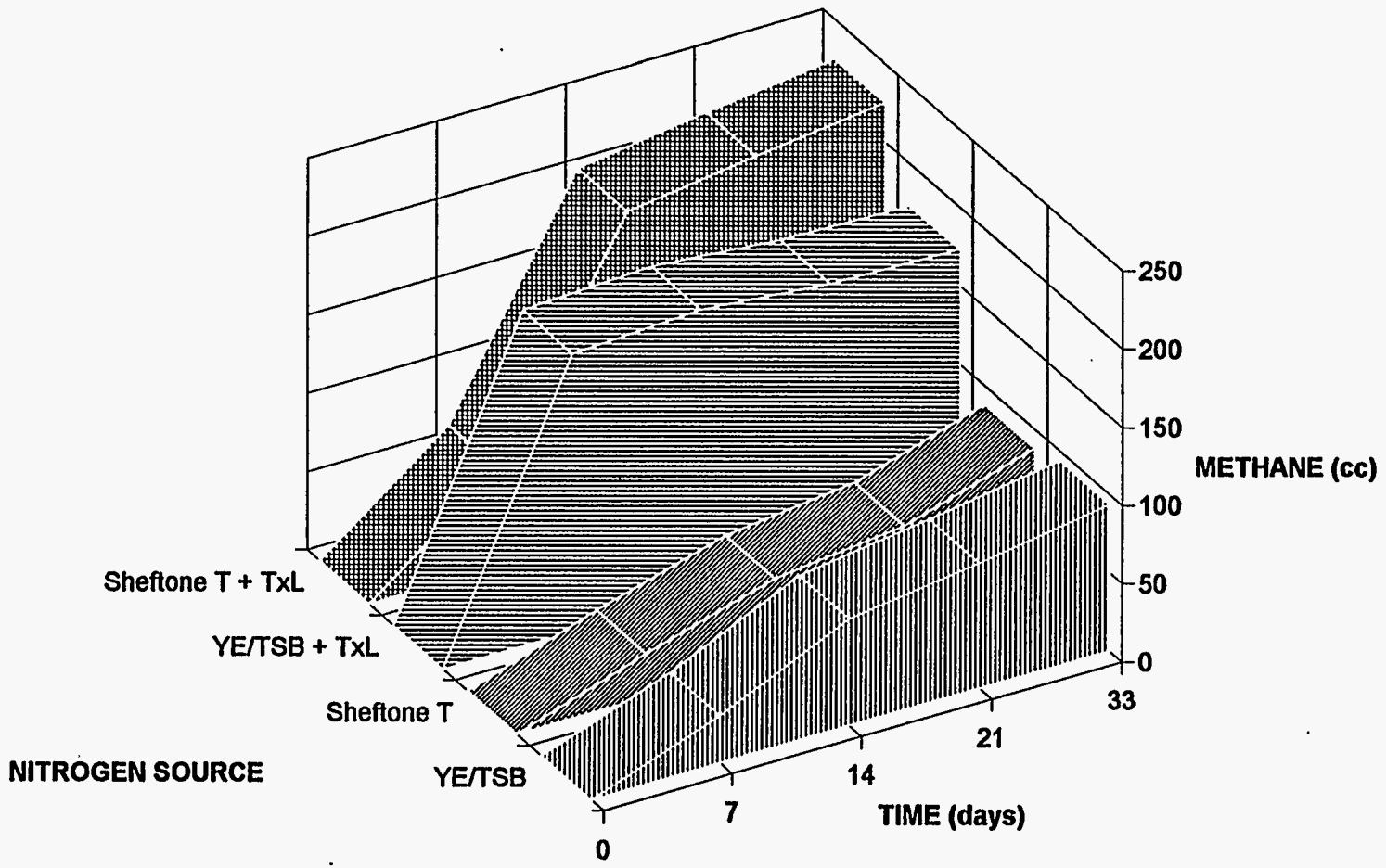


Figure 3

EFFECT OF DIFFERENT SOLIDS LOADING ON BIOMETHANATION OF TEXAS LIGNITE BY Mic-1 CONSORTIUM

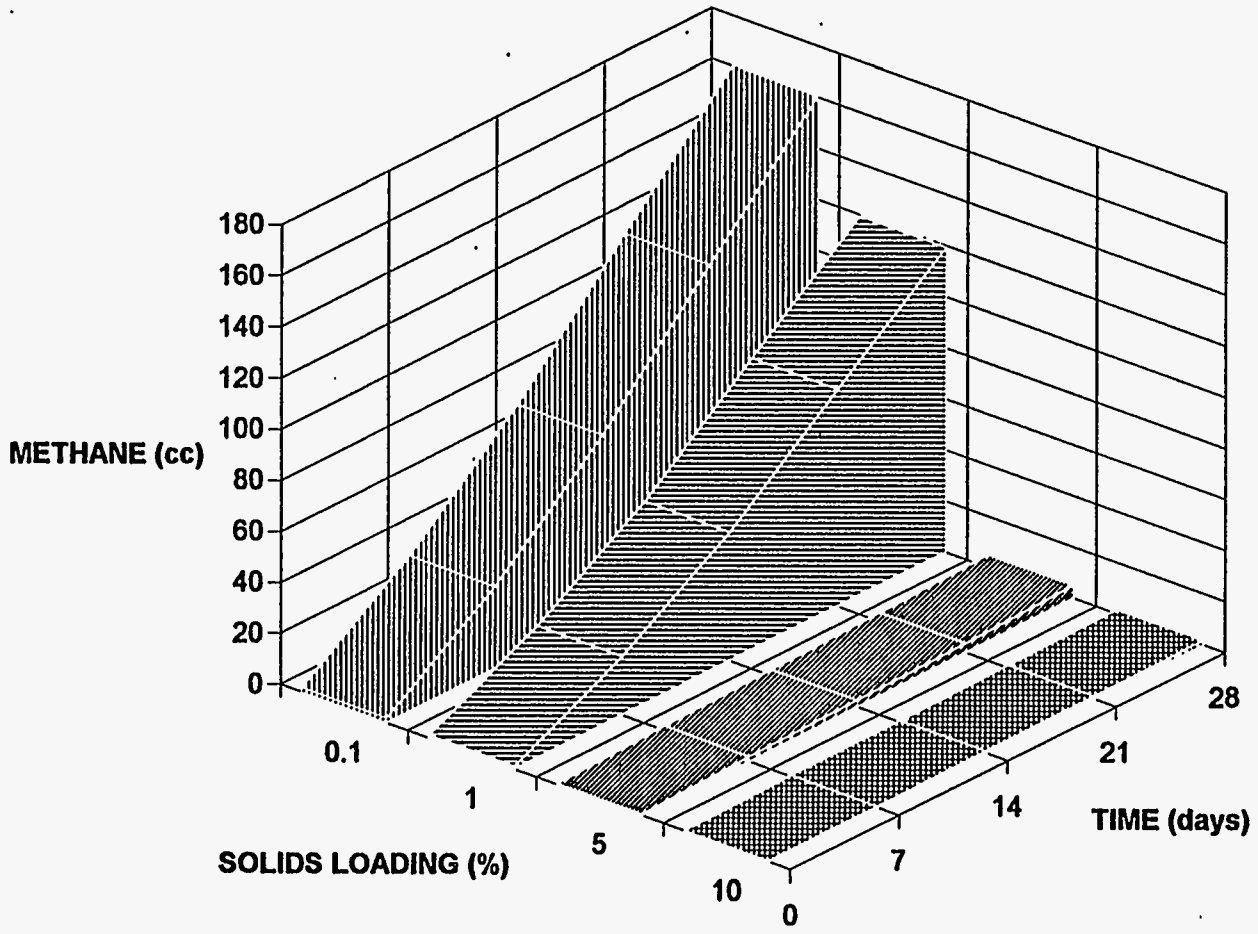
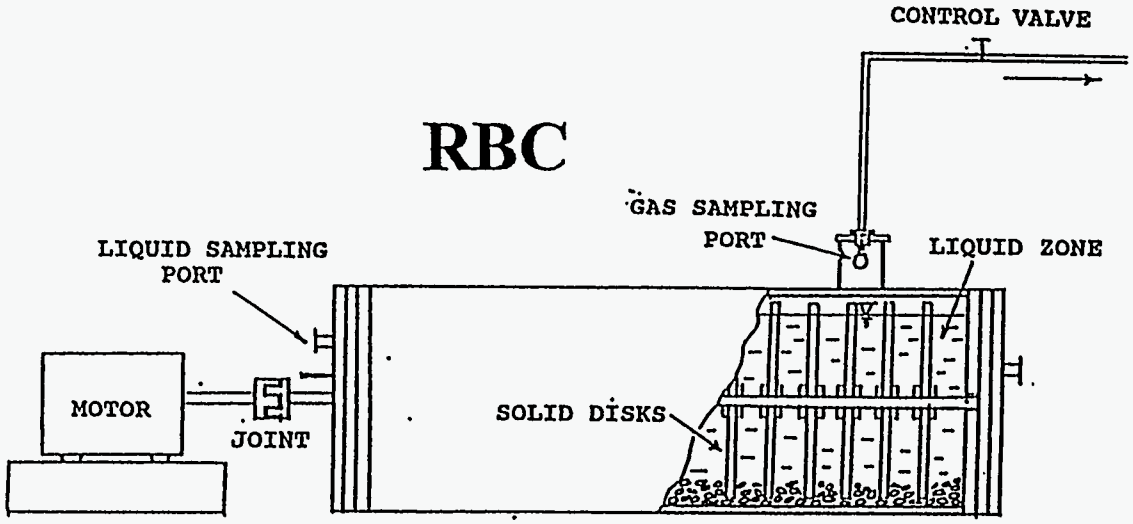
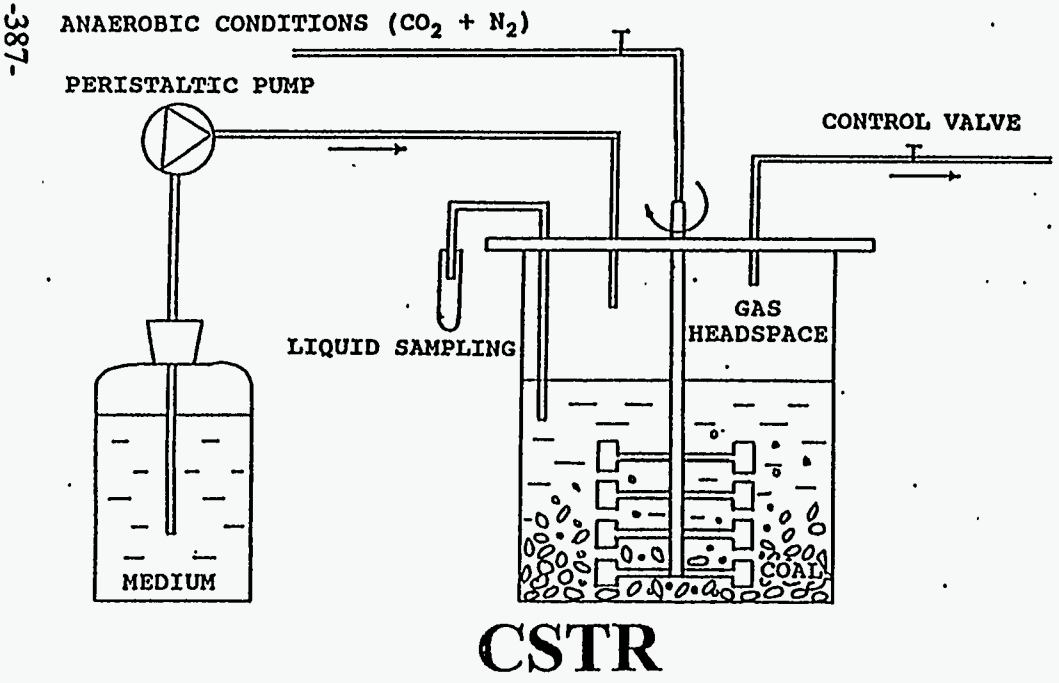


Figure 4

Bench Scale Bioreactors





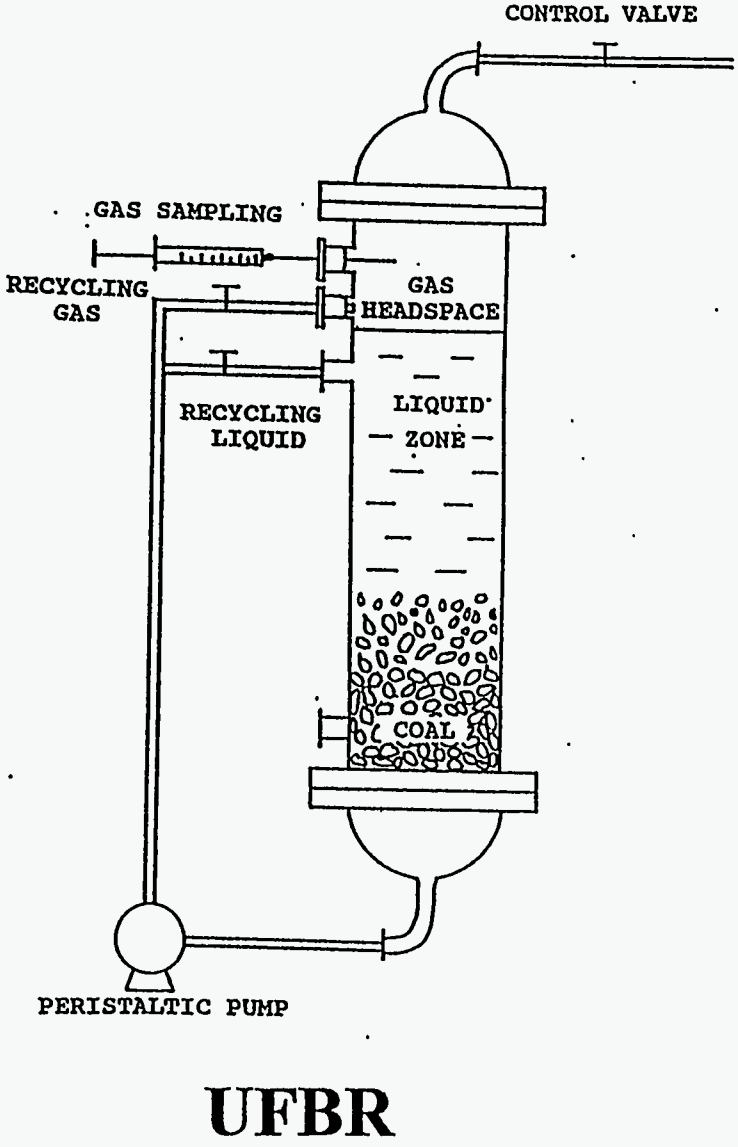


Figure .5

EFFECT OF DIFFERENT INITIAL pH OF THE MEDIUM ON BIOMETHANATION OF TEXAS LIGNITE (10% w/v) BY Mic-1 CONSORTIUM

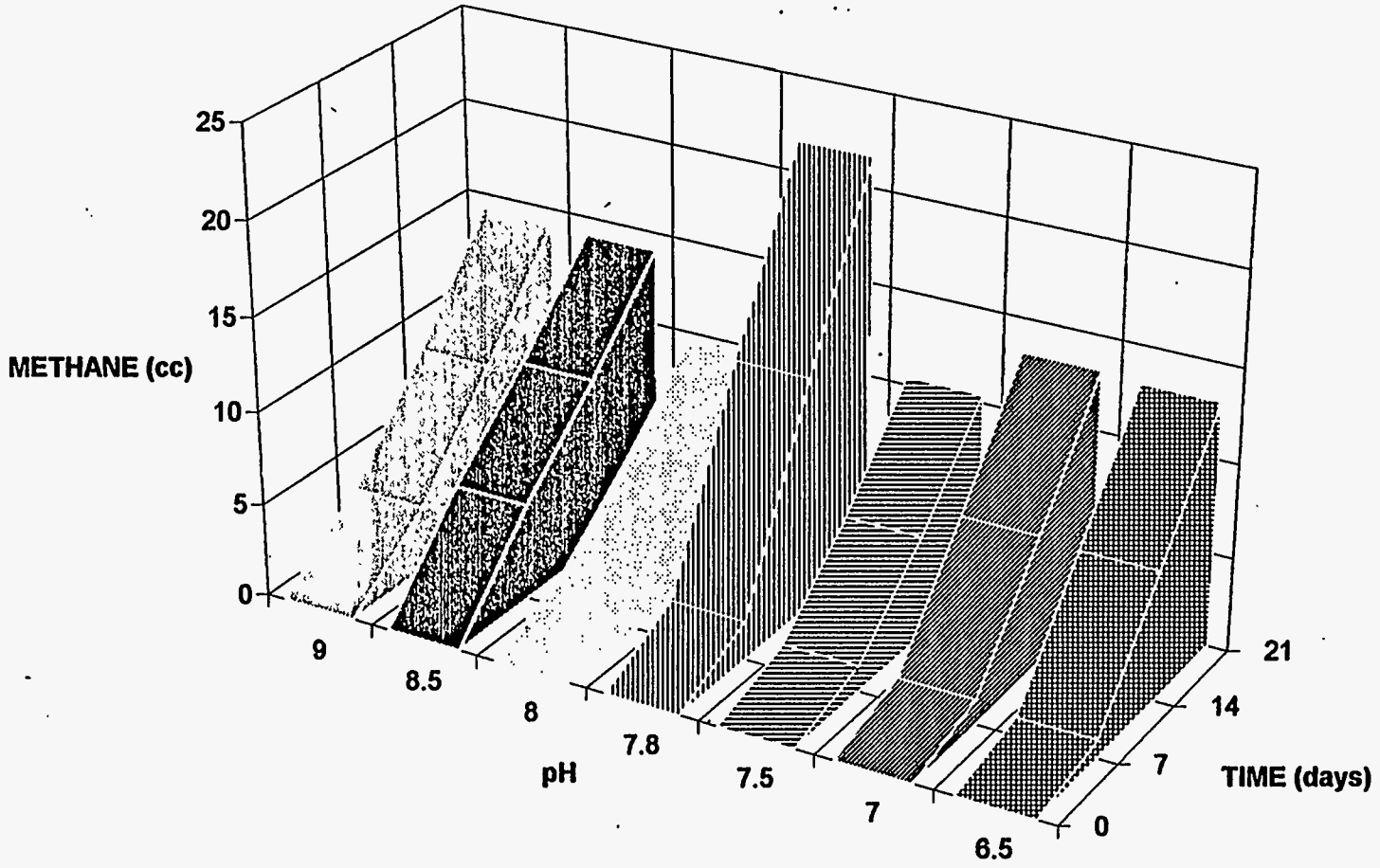


Figure 6

EFFECT OF HYDROGEN DONORS (10 mM) ON BIOMETHANATION OF TEXAS LIGNITE (1% w/v) BY Mic-1 CONSORTIUM

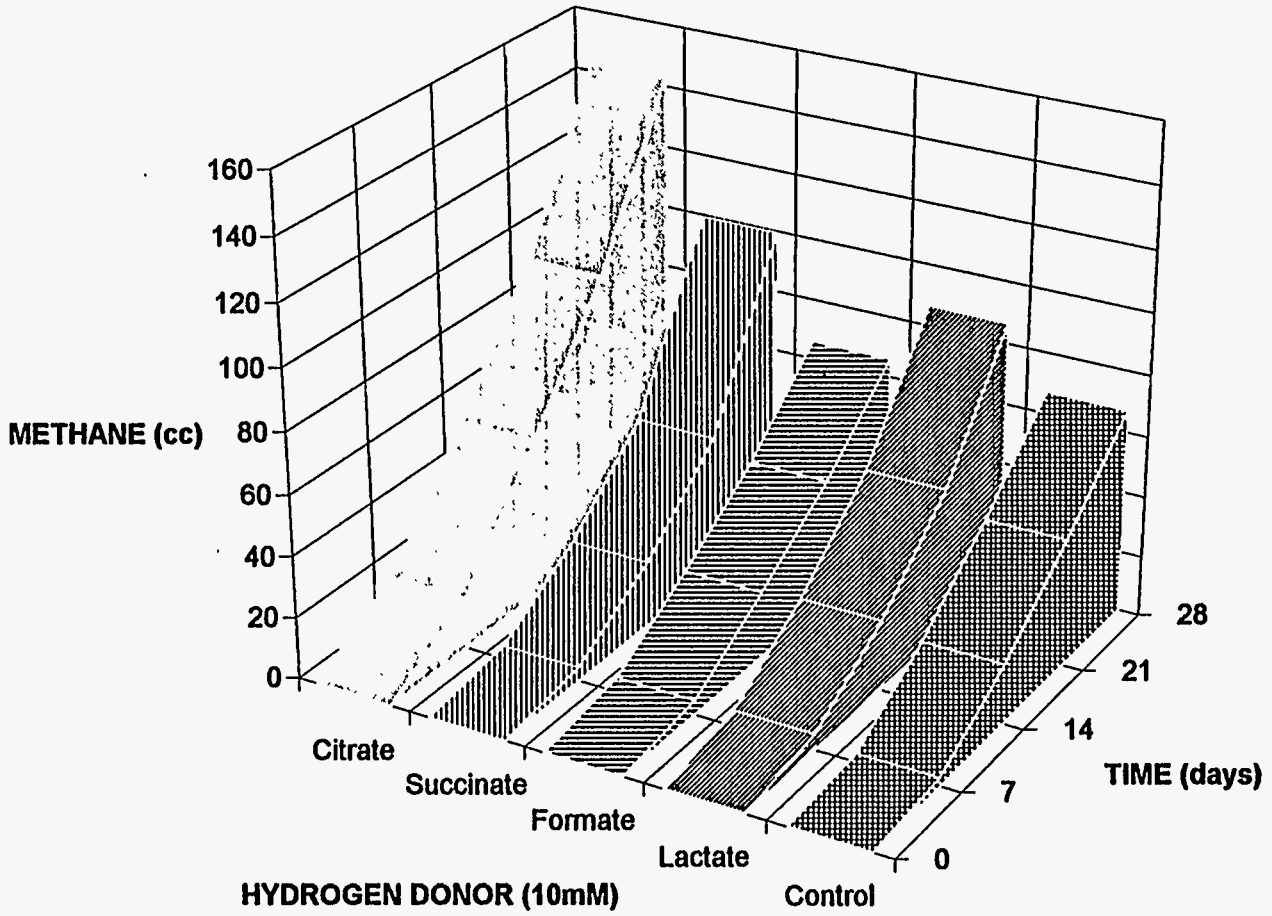


Figure 7

EFFECT OF HYDROGEN DONORS (CITRATE, 10 mM) ON BIOMETHANATION OF TEXAS LIGNITE (1% w/v) BY Mic-1 CONSORTIUM - VFA's CONCENTRATION

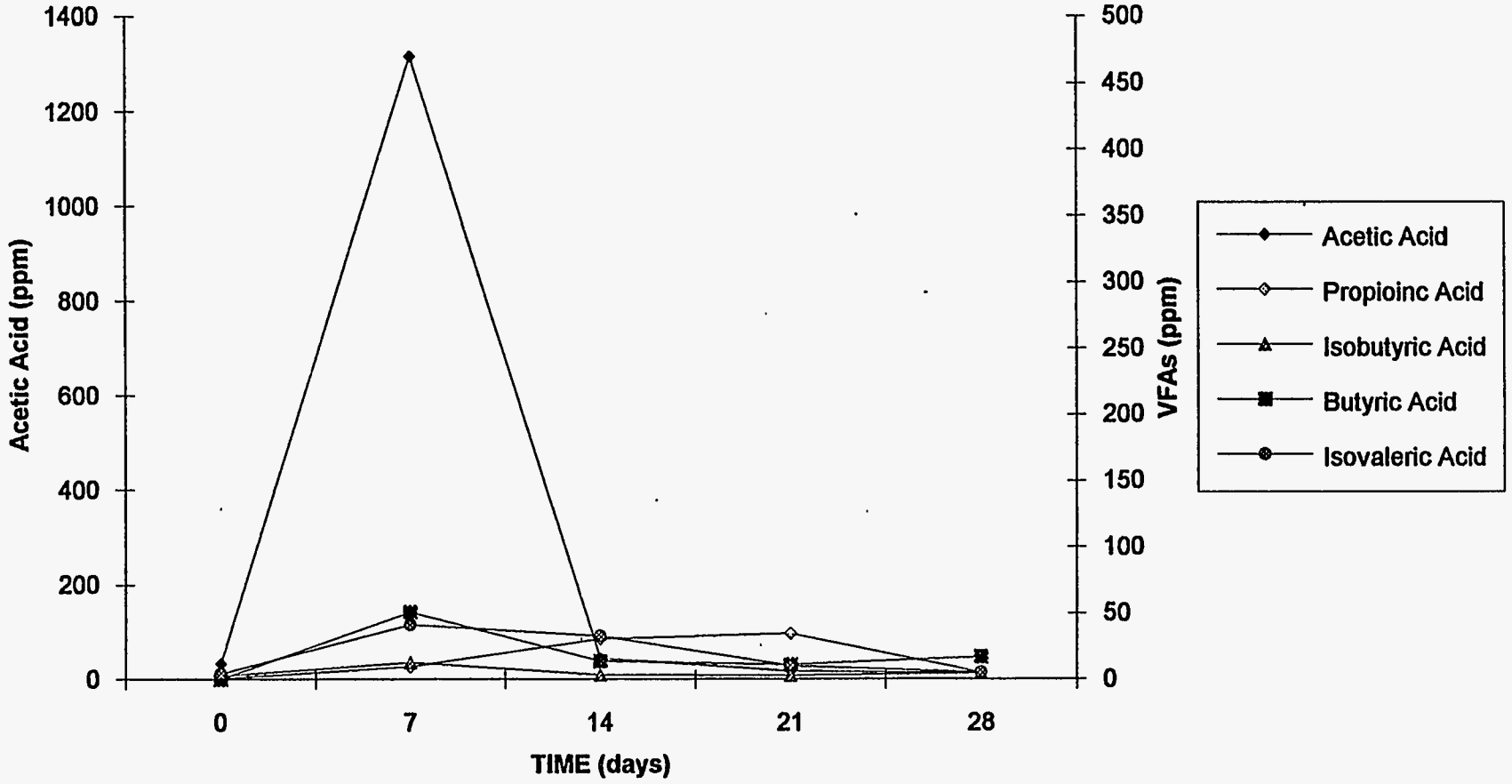


Figure 8

EFFECT OF HYDROGEN DONORS ON BIOMETHANATION OF TEXAS LIGNITE (5% w/v) BY Mic-1 CONSORTIUM

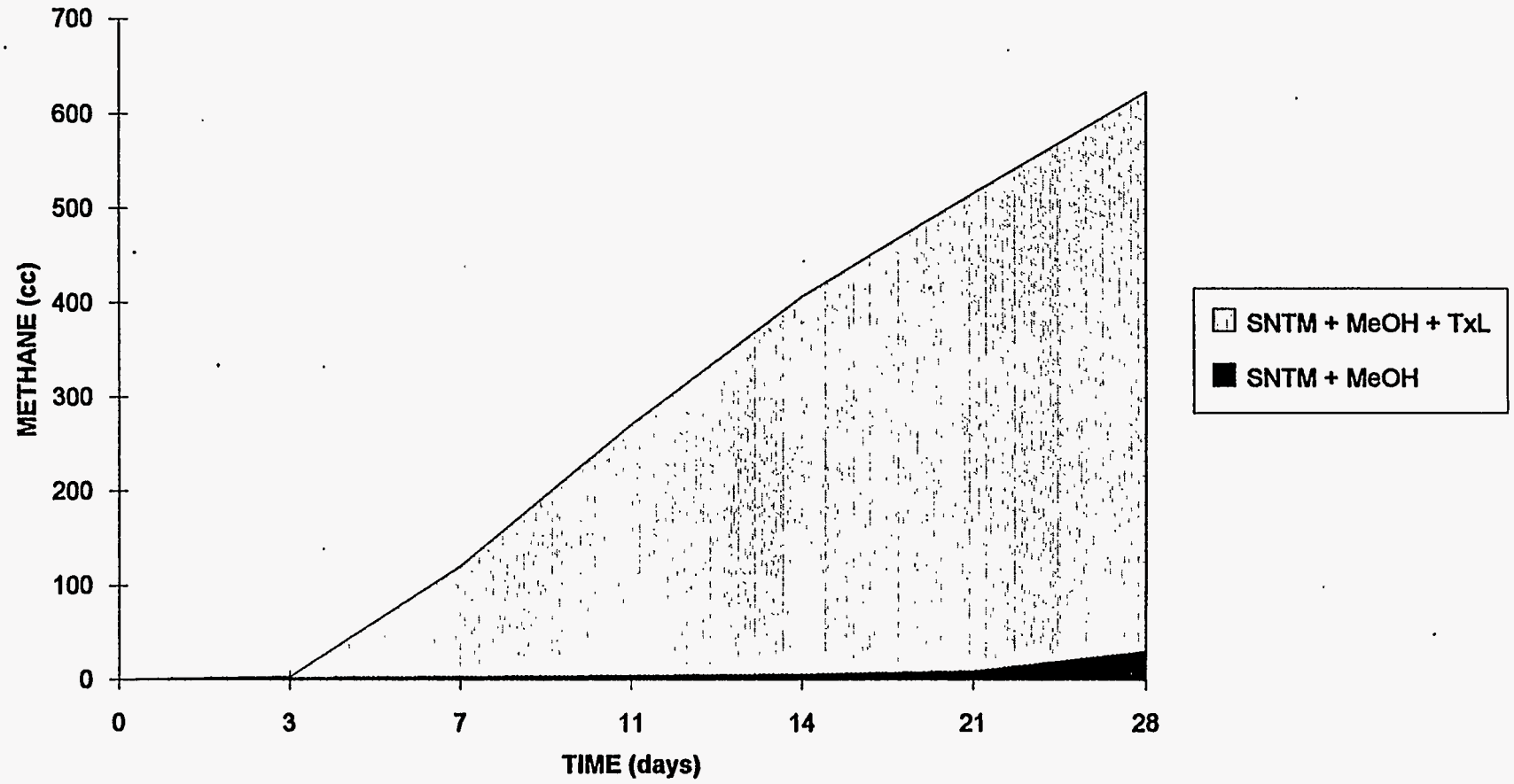


Figure 9

EFFECT OF HYDROGEN DONORS ON BIOMETHANATION OF TEXAS LIGNITE (5% w/v)

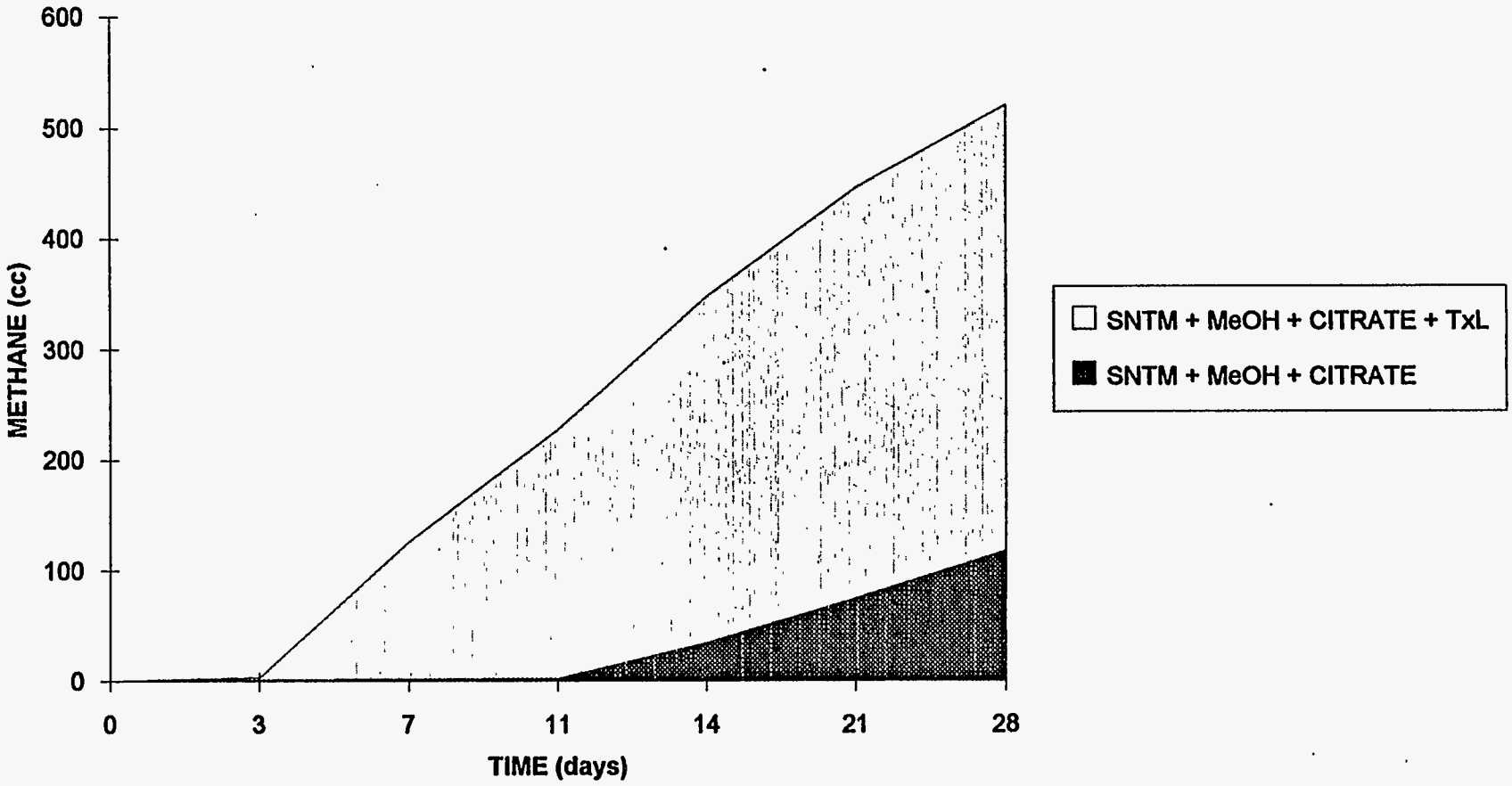


Figure 10

BIOMETHANATION OF TEXAS LIGNITE IS SIGNIFICANTLY ENHANCED IN AN UPFLOW BIOREACTOR

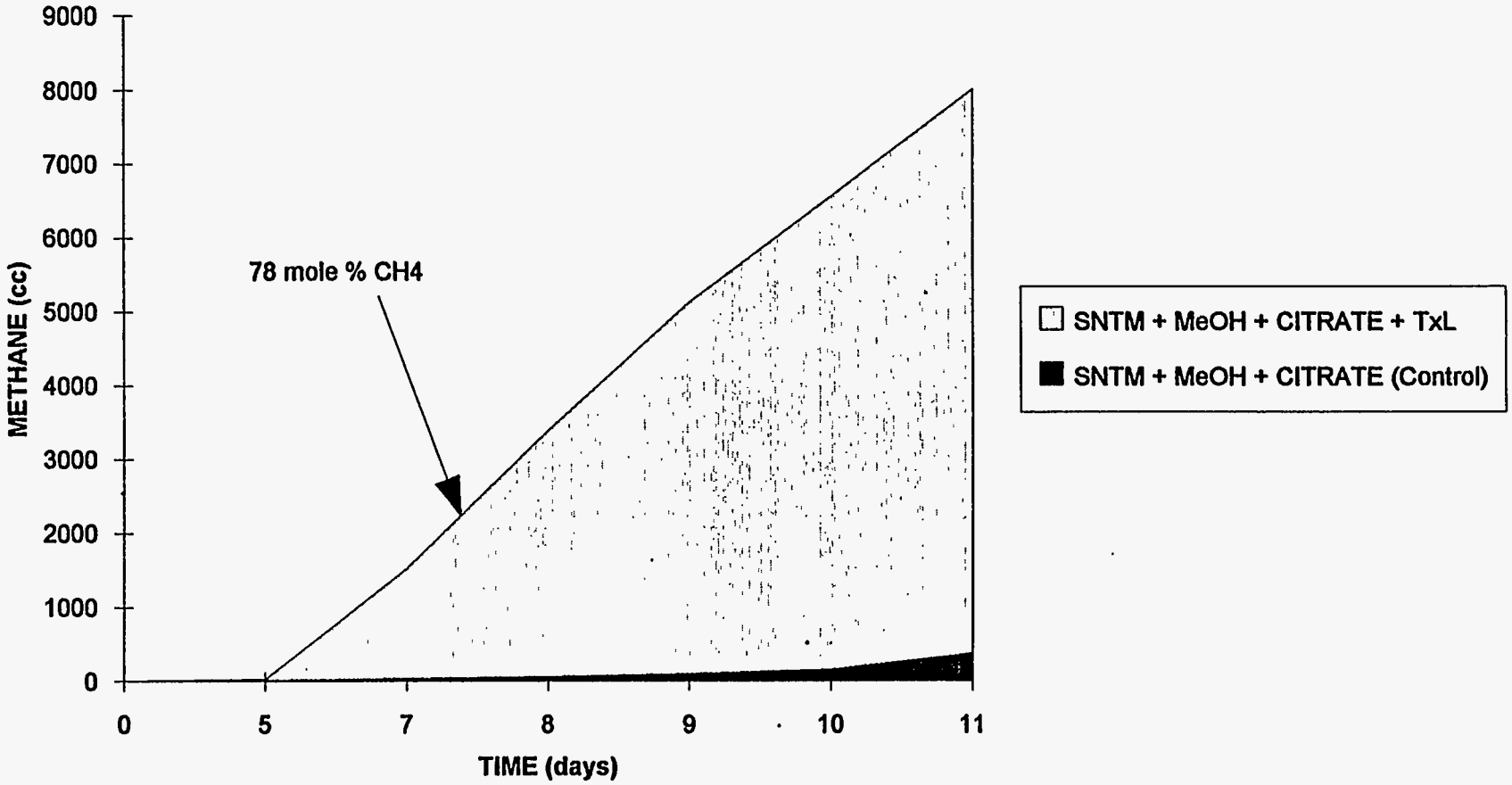


Figure 11

BIOGASIFICATION OF TEXAS LIGNITE IS DIRECTLY RELATED TO ACETATE CONCENTRATION

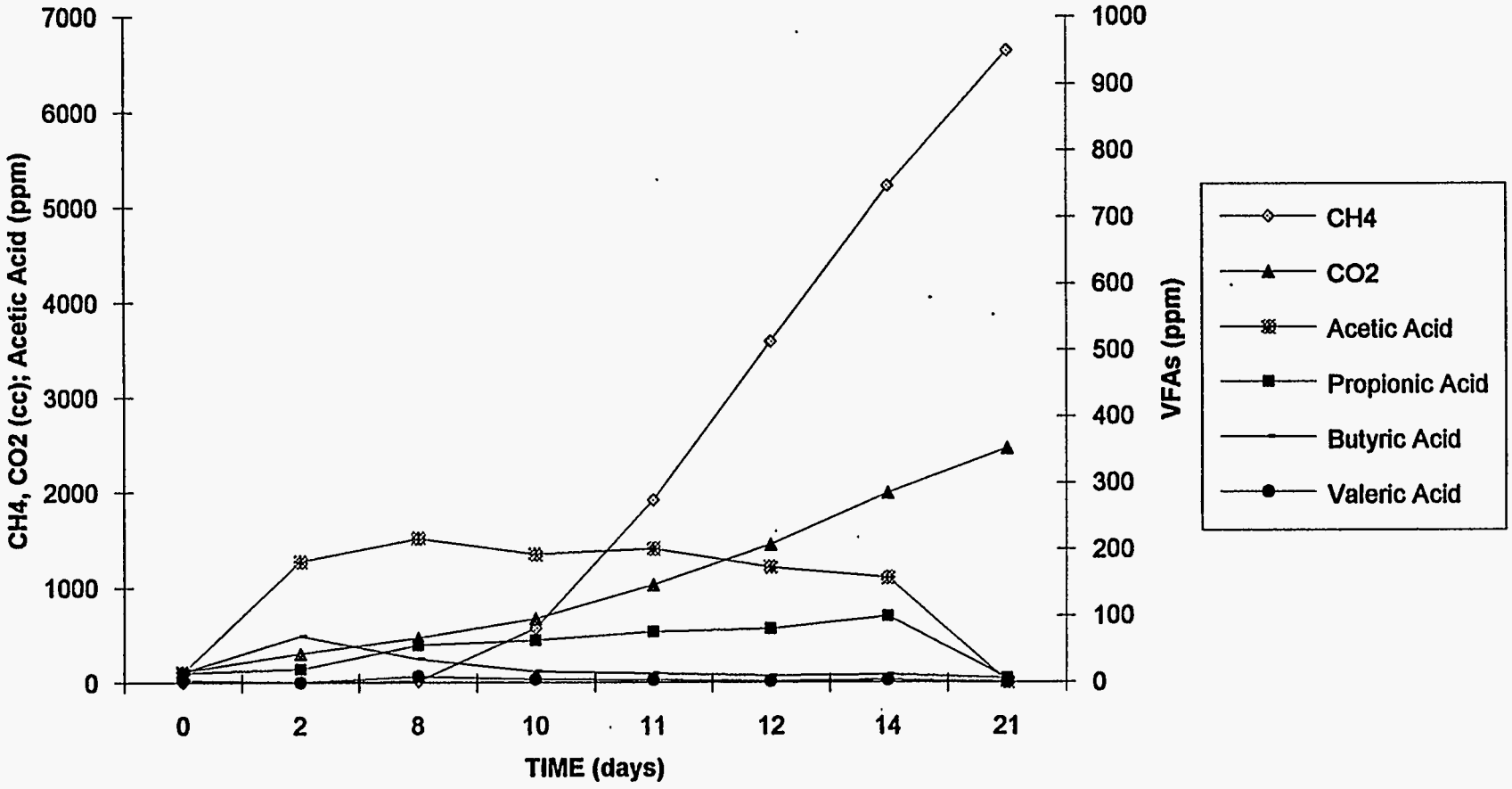


Figure 12

BIOMETHANATION OF TEXAS LIGNITE IS REPRODUCIBLE

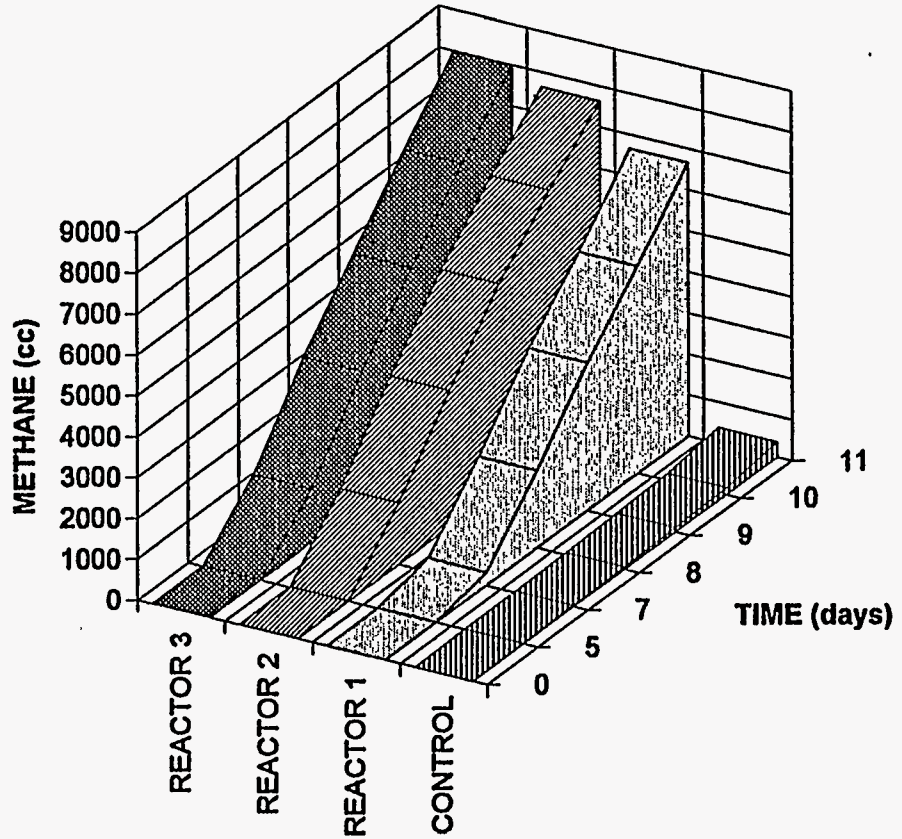


Figure 13

Table 1

Methane Production by Mic-1 Consortium Before and After Adaptation to Higher Coal Solids Loadings					
Parameters	Adaptation				Fold Increase
	Before	After			
Coal Solids (%)	0.01	0.1 - 1	5	5*	500
CH_4 (mole %)	10	40 - 50	48 - 52	71 - 78	7.5
CH_4 (cc/g coal)	40	96 - 193	134 -198	200 - 230	5
Time (days)	60	21 - 28	7 - 14	7 - 8	8**

* Bioreactor Studies

** Reduction in Residence Time

Table 2

CARBON BALANCE

CARBON IN	(%)	CARBON OUT	(%)
COAL	90	Biogas CH_4 - 20 CO_2 - 4	24
Media Components	10	Chemicals (VFAs)	2
		Humic Acid (ACTOSOL®)	74
TOTAL	100		100