

Biokinetics of Activated Sludge Treatment of SYNTHANE
Fluidized Bed Gasification Wastewaters

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Introduction

The SYNTHANE process, developed at the Pittsburgh Energy Research Center, is a second generation fluidized bed gasification process capable of producing a high-Btu substitute natural gas product. This process differs from fixed bed or slagging processes in that the coal is kept in a fluidized state, the fluidizing media consisting of steam and pyrolysis gases. Ground coal, which may be pretreated to destroy its agglomerating properties, is fed to the gasifier where it reacts with steam and oxygen. Bed temperatures and product gas composition may be varied within limits by the steam to coal and oxygen to coal ratios employed. Due to overall thermal balance considerations, about 70% of the carbon in the coal is gasified, while the remaining carbon and an inorganic residue is removed from the gasifier bottom as a char product which will be burned in a commercial plant. While much of the coal carbon is converted to CO, CO₂, and CH₄, a small fraction, amounting to about 4% to 6% of the feed carbon, appears as liquid effluent tars and potential water pollutants from the scrubbed product gas. This value as found for SYNTHANE is similar in magnitude to that reported by Ellman et al. (1) for the slagging fixed bed gasification at the Grand Forks Energy Research Center. It further appears that, for fluidized bed gasification, this fraction of liquid phase carbon may be further reduced via alteration in coal injection geometry (2) and via alterations in gasification conditions (3). However, such alterations extract an economic toll in terms of thermal efficiency and have not been fully evaluated.

While characterization of components and concentrations of coal gasification wastewater has been reported (4,5,6), little published data exists regarding normalization of components of pollutants produced per unit coal gasified. Table 1 presents effluent production data for the SYNTHANE gasification of Montana Rosebud coal (37 gasification runs), Illinois #6 coal (27 gasification runs), and North Dakota lignite (9 gasification runs) in terms of pounds of pollutants produced per ton of coal gasified, moisture and ash free (MAF). These data were collected from the 40 lb coal per hour SYNTHANE PDU gasifier located at the Pittsburgh Energy Research Center. All environmental analyses were conducted in accord with Standard Methods (7). Data on the same basis from the literature for fixed bed Lurgi, slagging fixed bed, and Hygas gasifier effluents are also presented in Table 1.

This table shows that the effluent pollutant component production is of a consistent order of magnitude for the SYNTHANE gasification of Montana Rosebud, Illinois #6, and North Dakota lignite coals with the exception of thiocyanate and cyanide production. These components appear to be about one order of magnitude greater for the gasification of the Illinois #6 coal than for the other coals considered.

Comparison of published data for the Lurgi, Hygas, and GFERC gasification facilities indicates that the Lurgi gasification of Rosebud coals in the existing Lurgi first generation facility at Westfield, Scotland produced more of each pollution

Table 1. - Normalized Production of Gasifier Wastewater Pollutants (lb/ton of coal (MAF) + coefficient of variation if available)

Parameter	SYNTHANE		North Dakota Lignite	LURCI (8)		GFERC (1)		HYCAS (9)	
	Montana Rosebud	Illinois #6		Montana Rosebud	200 psi Lignite	400 psi Lignite	Run #37 Lignite		
BOD	27.1 ± 34%		66.5	7					
TOC	22.1 ± 69%	21.1 ± 23%	40.7 ± 24%	13.9	8.3				39.1
COD	55.5 ± 64%	64.2 ± 12%	70.6 ± 33%	103					
PHENOL	8.72 ± 79%	9.12 ± 22%	10.8 ± 36%	21.8	6.8				11.4
OIL & TAR	1.77 ± 44%	1.96 ± 34%		3.2	0.78				
ACETONE SOL. ^{a/}	1.98 ± 62%	2.26 ± 36%							
THIOCYANATE	0.067 ± 105%	0.67 ± 40%	0.053 ± 71%	0.08					2.5
CYANIDE ($\times 10^{-4}$)	2 ± 225%	7.8 ± 89%	2.1 ± 110%	200					0.287
H ₂ S	0.033 ± 95%			0.57					
TOTAL SULFUR	0.449 ± 22%			1.31					0.2
FREE + FIXED NH ₃	14.0 ± 29%			72.1	6.6				13.1
ALKALINITY	3.95 ± 33%			219	13.3				
TOTAL TAR + OIL PRODUCTION ^{b/}	30.4 ± 83%	77.6 ± 50%		210	70.1				55.5
WASTEWATER PRODUCTION	2740 ± 46%	3920 ± 19%	3300 ± 42%	2976	916				736

a/ Acetone Soluble Tars: A measure of high molecular weight organics precipitated from pretreated gasifier water by pH depression, an analytical technique developed at PERC

b/ Measured prior to settling and hence is not part of the wastewater.

component than did each of the improved or second generation domestic experimental gasification facilities. Comparison of the data for SYNTHANE and Hygas indicates a degree of similarity; however, the SYNTHANE data is an averaged composite of many runs while the data collected to date for Hygas is from one specific run. Thus, such comparisons, at this time, must be considered as preliminary.

Results and Discussion

Initial evaluation of raw gasifier water indicated a need for partial removal of ammonia and floating oily materials prior to biological processing. An overview of linkages of suitable SYNTHANE wastewater processing steps with preliminary process proof of principle data is discussed by Johnson, et al. (4). In this experimental approach, ammonia is reduced from 10,000 mg/l to about 500 mg/l via batchwise air stripping at an elevated pH. This treatment also results in an 80% reduction of the alkalinity of the wastewater reducing the chemical requirements of future pH manipulations.

The removal of trace suspended oils and tars is accomplished by pH depression with sulfuric acid and alum coagulation. About 20% of the influent soluble TOC and about 50% of the wastewater oils, grease and tars are removed in this step. Filtration of the treated effluent assures no particulate carry-over to the biological reactor. In larger scale installations, this filtration step would be replaced by sedimentation, sand bed filtration or dissolved air flotation.

Experimental Protocol

Continuously operated 7-liter biological reactors were designed with adjustable internal clarifiers to provide recirculation of settled bio-sludge. Pumping was accomplished via micro-bellows pumps. The prepared feed for each reactor was kept at about 4°C via a large chilled water bath. Appropriate levels of mono and dibasic potassium phosphate were then added as nutrients to the feed so that the influent TOC/N/P ratios were about 60/6/1 with a buffered pH of about 7.5. However, both phosphate and nitrogen were periodically monitored to assure ample supply. Influent and effluent samples of each bioreactor were monitored for pH, suspended solids, volatile suspended solids (used as a monitor of biomass level), phenolics, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC). Both sludge volume index and specific oxygen consumption were monitored once steady state was achieved. Prepared feed to the biological reactors was diluted with tap water for appropriate kinetic determinations. In most cases, the hydraulic detention time was kept at about 1 day while the sludge age and applied organic loading varied as independent parameters.

Biological growth kinetic analysis indicates that the net growth rate of biomass follows the relationship:

$$\frac{dX}{dt} = uX - bX \quad 1)$$

where: u = specific growth rate (day^{-1})

X = volatile suspended solids (mg/l, a measure of concentration of biological solids)

b = endogenous decay coefficient (day^{-1})

t = time

The specific growth rate (u) is a kinetic function, and is therefore related to the nature of the organic substrate, pH, temperature, toxicant levels, limiting nutrients, etc. Thus, for conditions where only the organic substrate (S) ambient to the organisms is allowed to vary, with all other parameters essentially constant, we may write:

$$u = \frac{dX}{dt} \cdot \frac{1}{X} = f(S) \quad 2)$$

where $f(S)$ is a derived kinetic equation expressing the rate of biomass growth as a function of substrate concentration.

The growth of organisms (dX/dt) is also related to the rate of substrate utilization (dS/dt) by the relationship:

$$dX/dt = a(dS/dt) - b X \quad 3)$$

where a = yield coefficient (wt biomass/wt substrate used)

Equation 2 may be written in terms of the specific utilization rate of substrate as:

$$\frac{dS}{dt} \frac{1}{X} = f'(S) \quad 2a)$$

For aerobic systems such as those utilized in this research, the utilization of oxygen is related to the oxygen required for substrate bio-oxidation, and to the oxygen required for maintenance of the cellular biomass. Thus, an oxygen utilization equation may be written of the form:

$$\frac{dO_2}{dt} = a' \frac{dS}{dt} + b' X \quad 4)$$

where: a' = oxygen utilization coefficient (wt O_2 /wt substrate)

b' = endogenous constant (wt O_2 used/wt biomass-day)

The approach used in this research is to evaluate the constants of Equations 3 and 4, and determine the functional form of Equation 2a, the governing kinetic equation, for several measures or bases of organic substrate in SYNTHANE gasifier wastewater.

Test Results

Each "run" for the continuous biological reactors lasted a period of several weeks to months, during which time steady state was achieved and sustained.

During each run, the feed to the majority of the reactors was diluted with tap water to 15% \pm 5% concentration of gasifier condensate, the exact value depending on the TOC level of the specific wastewater sample. Thus, each data point on Figures 1 and 2 represents a sustained steady state condition with influent feed being composed of effluent from a series of Montana coal gasification runs, the overall influent TOC being held constant. Three experimental runs, however, were conducted with undiluted gasifier water in order to determine potential deviations from developed bio-kinetics and to illustrate "worst case" conditions for effluent quality stability. These points are also identified on Figures 1 and 2.

Analysis of data from the diluted gasifier feeds indicated that a first order relationship of the form:

$$\frac{\Delta TOC}{\Delta t} \frac{1}{X} = K (TOC) \quad 5)$$

did not go through the origin. This indicated the existence of a non-degradable fraction of TOC in gasifier water. For the 15% concentrations used, this value

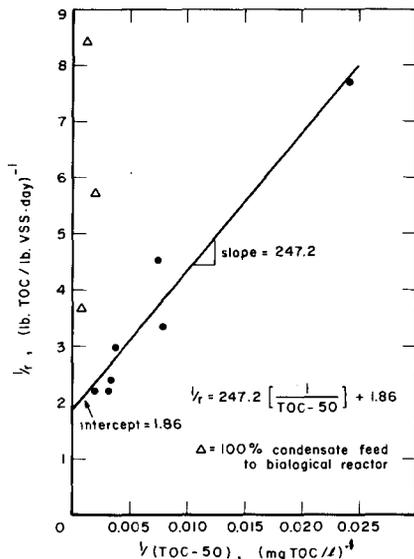


Figure 1 - Lineweaver - Burk plot of TOC data corrected for non-degradable TOC. SYNTHANE gasifier water, Montana Coals.

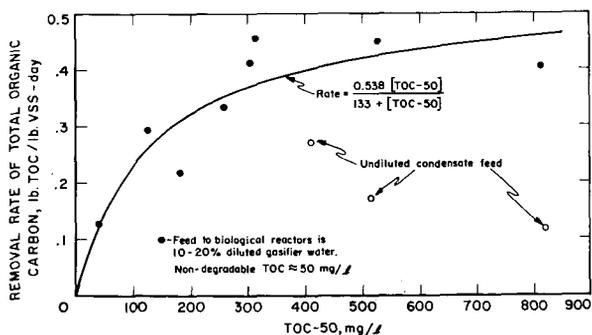


Figure 2 - Biokinetics of TOC removal. SYNTHANE gasifier water, Montana Coals.

appeared to be on the order of about 50 mg/l. The set of observed data was found to fit a classical Monod relationship (10), modified to reflect the non-degradable TOC fraction, of the form:

$$r = \frac{\Delta \text{ TOC } \frac{1}{X}}{\Delta t} = \frac{r' (\text{TOC}-50)}{k + (\text{TOC}-50)} \quad 6)$$

where: r' = maximum specific rate of TOC utilization (lb TOC/lb VSS-day)

r = measured specific rate of TOC utilization (lb TOC/lb VSS-day)

(TOC-50) = biodegradable level of soluble TOC ambient to biomass (mg/l)

k = constant (mg/l)

The values of r' and k may be graphically determined, using linear regression techniques, by noting the inverted or Lineweaver-Burk (10) linear form of the equation as:

$$1/r = \frac{k}{r'} \frac{1}{(\text{TOC}-50)} + \frac{1}{r'} \quad 7)$$

A plot of $1/r$ against $1/(\text{TOC}-50)$ should yield a straight line if the functional form of the kinetic equation fits Monod type kinetics. Figure 1 illustrates the graphical determination of such constants from slope and intercept analysis, yielding the result:

$$\frac{\Delta \text{ TOC } \frac{1}{X}}{\Delta t} = \frac{0.538 (\text{TOC}-50)}{133 + (\text{TOC}-50)} \quad 8)$$

This equation is plotted on Figure 2 with data points for comparison. It should be noted that the three steady state values for TOC utilization for the reactors with undiluted condensate feed do not fit the overall kinetics obtained. One possible explanation for these phenomena is that some toxic inhibitor exists in SYNTHANE plant wastes in concentrations which become significant only at SYNTHANE condensate concentrations stronger than the 15% value used for kinetic determinations. Also, one should note that the nonbiodegradable portion of the undiluted condensate would be larger than the 50 mg/l value cited. Investigations are underway to quantify the non-biodegradable TOC concentration of the wastewater and to determine if toxic inhibition does exist.

The functional form of the kinetic equation for BOD utilization did not similarly correlate in accord with Monod kinetics. Figure 3 indicates that, for the range of BOD from 2 mg/l to 130 mg/l, the BOD utilization data best fit the relationship:

$$\frac{\Delta \text{ BOD } \frac{1}{X}}{\Delta t} = 0.182 (\text{BOD})^{0.186} \quad (\text{lb BOD used/lb VSS-day}) \quad 9)$$

Some scatter exists in this correlation, however, it should be noted that BOD measurements are, by nature of the test, subject to considerable error and scatter (7).

Development of a suitable correlation for specific phenol utilization rates from gasifier water is difficult since phenol, as measured by Standard Methods (7), is a colorimetric test sensitive to phenol, cresols, and other aromatic hydrocarbons to various degrees. For phenol levels of less than 5 mg/l, Figure 4 shows that the specific utilization rate best appears to fit the relationship:

$$\frac{\Delta (\text{Phenol})}{\Delta t} = 0.423 (\text{Phenol})^{0.58} \quad (\text{lb phenol used/lbVSS-day}) \quad 10)$$

This relationship does not appear to properly model phenol utilization over an expanded range of phenol concentrations as shown on Figure 5. A better fit was found

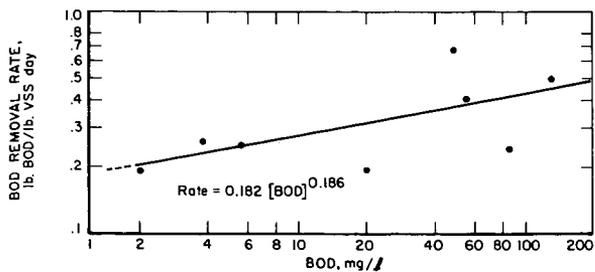


Figure 3 - Biokinetics of BOD removal from SYNTHANE gasifier condensate, Montana Rosebud Coal.

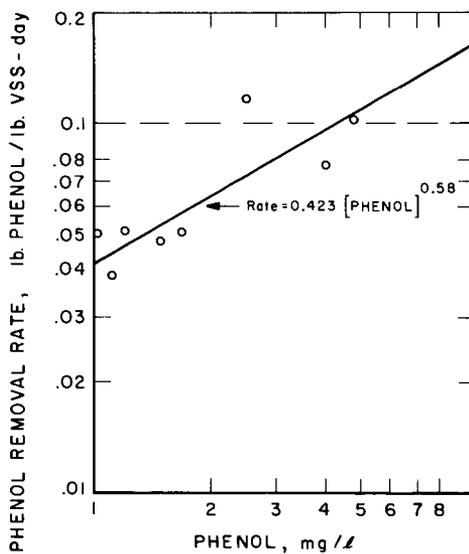
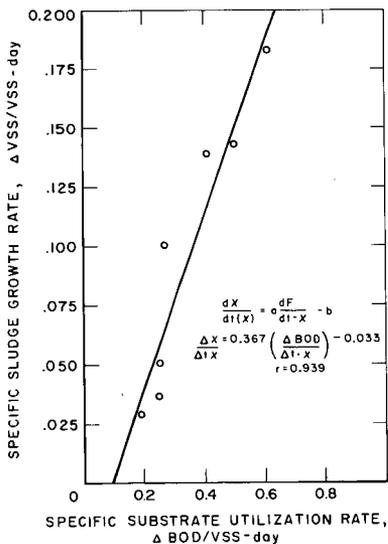
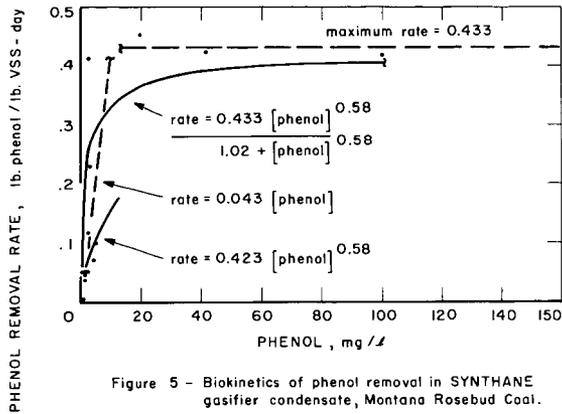


Figure 4 - Biokinetics of phenol removal in SYNTHANE gasifier condensate, Montana Rosebud Coal, low phenol concentrations.



using a continuous equation of the form of modified Monod kinetics:

$$\frac{\Delta (\text{Phenol})}{\Delta t} \frac{1}{X} = \frac{0.433 (\text{Phenol})^{0.58}}{1.02 + (\text{Phenol})^{0.58}} \quad (11)$$

Figure 5, however, also indicates that over the wider range of phenol levels, the governing kinetic equation for specific rates of phenol utilization may be best approximated by a zero order relationship of the form:

$$\frac{\Delta (\text{Phenol})}{\Delta t} \frac{1}{X} = 0.433 \quad (\text{lb phenol used/lb VSS-day}) \quad (12)$$

for phenol levels ambient to the organisms greater than 10 mg/l, and a first order relationship for lower phenol levels. As indicated above, due to the non-specificity of the Standard Methods (7) phenol test, a mixed model for phenol utilization may be expected. It should also be anticipated that similar models based on pure phenol bio-degradation would give different numerical results.

Parameters fitting the biomass production equation (Equation 3) are developed as shown in Figure 6. From this figure, it may be seen that: $a = 0.367$ lb biomass produced/lb BOD removed; and the decay coefficient is: $b = 0.033/\text{day}$.

Similar curves shown on Figure 7 were developed for oxygen consumption in accord with Equation 4, yielding the following results for "a'" and "b'".

<u>Substrate</u>	<u>a'</u>	<u>b'</u>
<u>Basis</u>	<u>lb O₂ used/lb substrate removed</u>	<u>endogenous respiration coefficient lb O₂/lb VSS-day</u>
BOD	0.747	0.110
TOC	1.680	0.090
COD	0.562	0.093

With biokinetic parameters for substrate utilization rates and necessary sludge production and respiration parameters for the degradation of SYNTHANE wastes, process design computations for a suspended film biological reactor of the activated sludge type become rote (11).

Process Stability Observations

While kinetic and stoichiometric data obtained from laboratory-size reactors are applicable to larger-size facilities, similar extrapolations regarding process stability should not be made. Laboratory-size reactors demonstrate both effluent quality and quantity fluctuations due to slight deviations in pumping rates, minor laboratory temperature variations, etc. Such unavoidable deviations in small equipment is of a relatively greater magnitude than that found in larger-scale operations. As a "worst case" example of the process stability that might be found in a large-scale treatment plant, Figure 8 illustrates a probability plot of effluent TOC for a one-stage biological reactor with undiluted Montana condensate as feed. For example, the effluent TOC from this reactor was less than 448 mg/l 50% of the time, while the influent TOC was 3979 mg/l, indicating a process efficiency of 89% or better 50% of the time.

An asymptote of about 415 mg/l is evident in this figure, indicating that this is the approximate level of non-biodegradable TOC in these samples of SYNTHANE Montana condensate. This value is in fair agreement with the data shown in Figure 2, indicating about 50 mg/l in a 10% to 20% concentration of gasifier wastewater as being the non-biodegradable fraction.

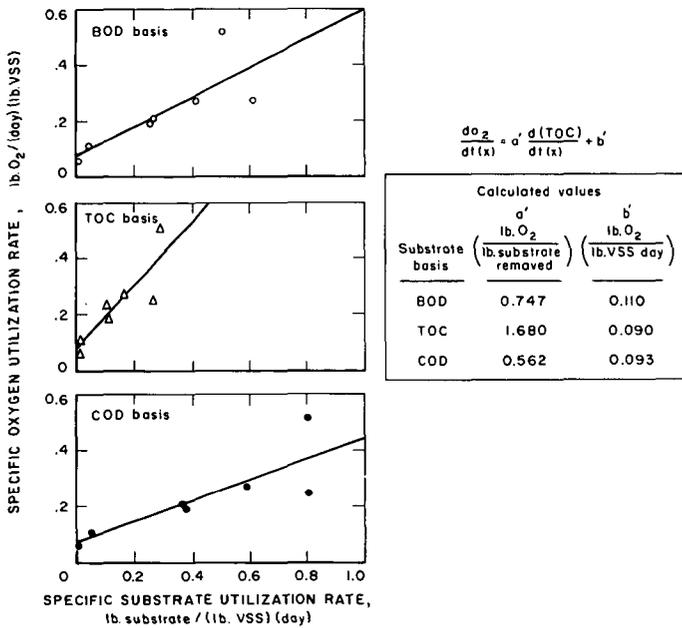


Figure 7 - Oxygen consumption as a function of biological substrate utilization.

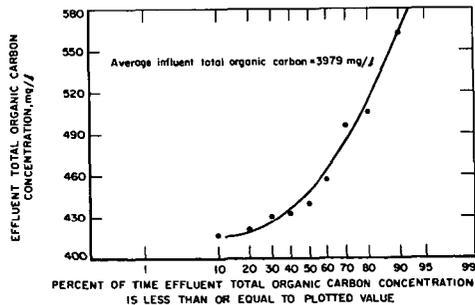


Figure 8 - Effluent quality - probability plot.

Summary and Conclusions

1) Data is presented on a normalized basis for key pollutant parameters from the SYNTHANE gasification of Montana Rosebud, Illinois #6, and North Dakota lignite coals. These values are of the same order of magnitude as existing limited published data from other second generation gasification facilities, and less than that from the Westfield, Scotland Lurgi gasification of Rosebud coals.

2) Biological kinetic parameters, sludge production parameters, and oxygen utilization parameters are established for the activated sludge treatment of wastewater from the SYNTHANE gasification of Montana Rosebud coal. The following represent equations of best fit for the biokinetics of activated sludge treatment of diluted wastewaters from the SYNTHANE gasification of Rosebud coal:

a) <u>Basis for Specific Utilization (r)</u>	<u>Equation</u>	<u>Comments</u>
1b TOC/lb-VSS-day	$r = \frac{0.538(\text{TOC}-50)}{133 + (\text{TOC}-50)}$	TOC < 800 mg/l
1b BOD/lb-VSS-day	$r = 0.182 (\text{BOD})^{0.186}$	BOD < 130 mg/l
1b Phenol/lb-VSS-day	$r = \frac{0.433 (\text{Phenol})^{0.58}}{1.02 + (\text{Phenol})^{0.58}}$	Phenol < 80 mg/l

b) BOD sludge yield coefficient of 0.37 lb VSS/lb BOD and decay coefficient of 0.033/day.

c) Oxygen utilization coefficients are: 1.68 lb O₂/lb TOC, 0.747 lb O₂/lb BOD, and 0.562 lb O₂/lb COD with an endogenous respiration coefficient of 0.093 lb O₂/lb VSS-day.

3) About 12% of the TOC in the feed to biological reactors from Montana gasifier condensate is not biologically degradable. This may correspond to about 400 ± 100 mg/l TOC for such wastewaters.

4) Based on experimental observations from the biological treatment of Montana Rosebud condensates, a one-stage aerobic biological reactor with sludge age of 10 days and hydraulic detention time of about 1 day is capable of treating SYNTHANE by-product wastewater.

5) Biological processing should have a major role in the water pollution abatement of SYNTHANE gasifier water, and is probably applicable to other first and second generation gasification wastewaters. Biological processing cannot, however, completely remove all organics from gasifier wastewater. Research seeking answers to questions of the chemical nature and potential processes for further treatment of the biologically treated effluent is an area of high priority.

References

1. Ellman, R. C., B. C. Johnson, H. H. Schobert, L. E. Paulson, and M. M. Fegley. "Current Status of Studies in Slagging Fixed-Bed Gasification at the Grand Forks Energy Research Center", Presented at the 9th Biennial Lignite Symposium, May 18-19, 1977, Grand Forks, ND.
2. Nakles, D. V., M. J. Massey, A. J. Forney, and W. P. Haynes. "Influence of SYNTHANE Gasifier Conditions on Effluent and Product Gas Production", ERDA/PERC/RI-75/6, December, 1975.
3. Energy Research and Development Administration, Internal Quarterly Technical Progress Report, ERDA/PERC/QTR-76/4, Oct.-Dec., 1976, pp. 70-72.
4. Johnson, G. E., R. D. Neufeld, C. J. Drummond, J. P. Strakey, W. P. Haynes, J. D. Mack, and T. J. Valiknac. "Treatability Studies of Condensate Water from SYNTHANE Coal Gasification", DOE/PERC/RI-77/13, November, 1977.
5. Singer, P. C., et al, "Composition and Biodegradability of Organics in Coal Conversion Wastewaters", Presented at the Symposium on Environmental Aspects of Fuel Conversion Technology III, EPA, Hollywood, FL, Sept., 1977.
6. Neufeld, R. D. and A. A. Spinola, "Ozonation of Coal Gasification Plant Wastewater", to appear in Environmental Science and Technology.
7. APHA, AWWA, WPCF, "Standard Methods for the Examination of Water and Wastewater", 14 ed., American Public Health Association, Washington, D.C., 1976.
8. "Trials of American Coals in a Lurgi Gasifier at Westfield, Scotland", ERDA R & D Report, FE-105, Dec., 1972-Nov., 1976.
9. Massey, M.J., R. W. Dunlap, F. C. McMichael, and D. V. Nakles, "Characterization of Effluents from the Hygas and CO₂-Acceptor Pilot Plant", FE-2496-1, Interim Report July-September 1976, November 1976.
10. Bailey, J. E. and D. F. Ollis, "Biochemical Engineering Fundamentals", McGraw-Hill, NY, 1977.
11. Metcalf & Eddy Inc., "Wastewater Engineering: Collection, Treatment, Disposal", McGraw-Hill, NY, 1972.