GASIFICATION PROCESS/ ENVIRONMENTAL CHARACTERIZATION FROM PILOT PLANT DATA

by

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INTRODUCTION

Now and for the foreseeable future, pilot plant-scale effluent characterization data necessarily must serve as the only resource for environmental assessment in high Btu coal gasification processing. However, meaningful collection and interpretation of such data are complicated, since little if any effluent treatment is usually performed and large sections of these plants are typically nonscalable. In the absence of a data base and any established regulatory guidelines or standards, specification of an appropriate set of effluent characterization parameters is also complicated. The challenge in coal gasification environmental assessment is therefore two-fold:

1. to identify the set of effluent monitoring parameters, sampling/preservation/analytical procedures, and control characteristics appropriate to a comprehensive environmental characterization; and
2. to develop an effluent characterization strategy (both predictive and experimental) which properly addresses both the vagaries of measurements from small-scale plant operations and the sharp contrasts in effluent characteristics from process to process.

ERDA has assembled a combination of environmental contractors (see Figure 1) and a coordination contractor (Carnegie-Mellon University) to address these issues in an environmental assessment of its high BTU coal gasification pilot plant program. Details regarding the structure and operation of the program have been published elsewhere.[1,2] In the present paper, program methodology is discussed, available field data are presented, and preliminary trends in the effluent data base are explored in relation to evolving evidence of the fundamental relationship between process variables and effluent production.

BASIC STRUCTURE OF PROGRAM ENVIRONMENTAL ASSESSMENT PLANS

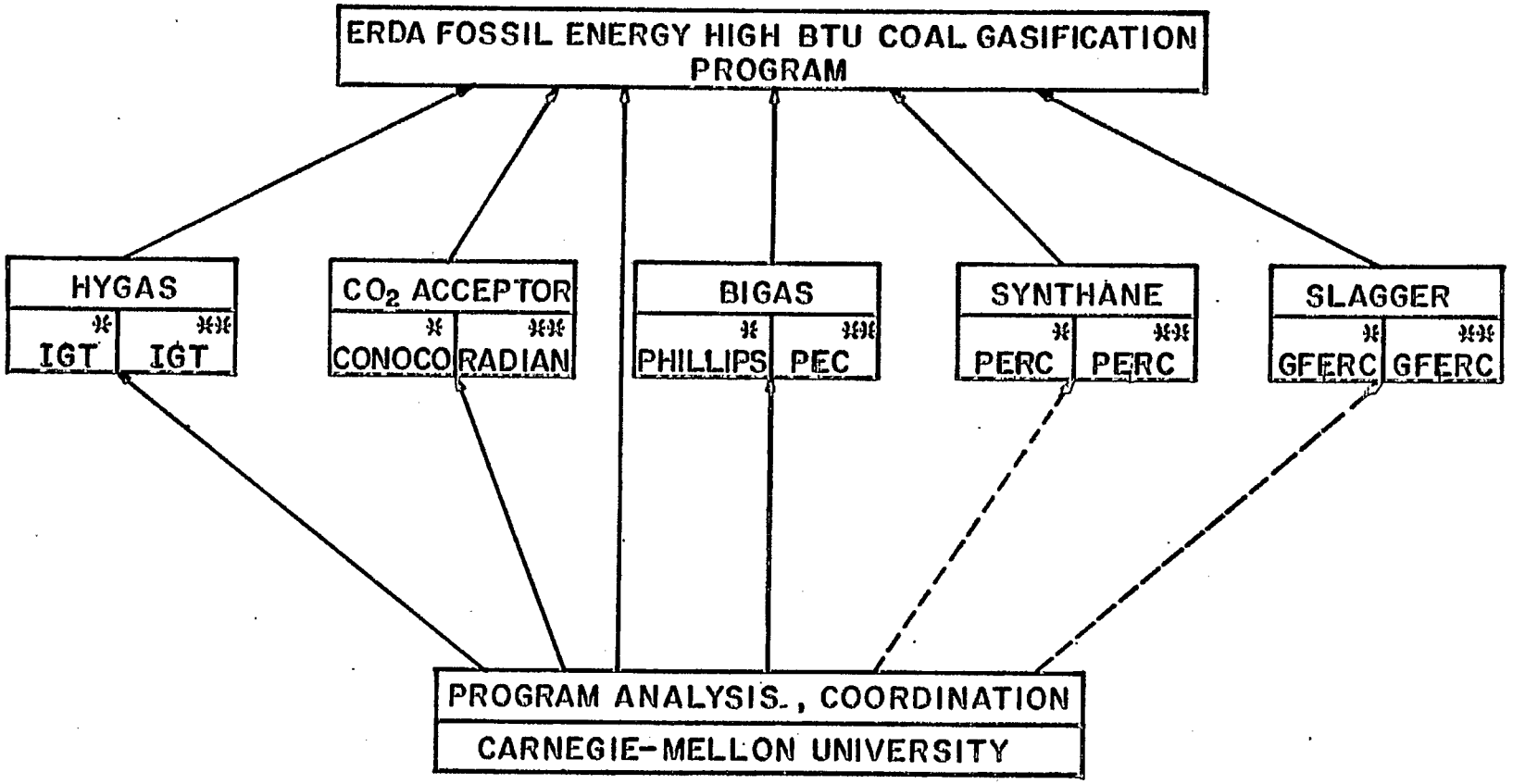
In the absence of any reference data base, assessment plans at each pilot plant are being formulated in two stages. Initially preliminary test plans have been developed to address basic issues of prioritization in stream and effluent parameter selection, alternative sampling methodologies, and validation of sample preservation and analysis techniques. Exploratory effluent characterization efforts have also been undertaken to identify significant effluent characteristics for later more comprehensive, quantitative investigations. Background analysis and preliminary test plans have been completed and documented for two pilot plants, Hygas and CO_2-Acceptor;[2,3] similar efforts are now in progress at the other participating plants.

Stream Sampling and Effluent Parameter Selections

Stream Sampling Selection

Plant streams are selected for sampling for one of three purposes (in decreasing order of importance): (1) to provide a baseline characterization of pilot plant effluent production *scalable* to larger plant sizes; (2) to provide material balances for specific effluent constituents; and (3) to determine pilot plant-specific environmental impacts. The critical issue of stream scalability is discussed below. First priority constituents for material balancing include sulfur, nitrogen, and trace metals. Stream characterization for pilot plant environmental impacts is receiving only minor attention in the program.

Pilot-scale versions of a process rarely reflect either the structural or the operational practices



* Process Developer
** Environmental Contractor

Figure 1. Structure of ERDA Pilot Plant effluent characterization program.

TABLE 1

SUMMARY OF MAJOR ENVIRONMENTALLY SCALABLE AND NONSCALABLE SECTIONS OF PARTICIPATING HIGH BTU COAL GASIFICATION PILOT PLANTS

Scalable Plant Sections	Nonscalable Plant Sections
BI-GAS PILOT PLANT	
• Coal preparation • Coal slurry dryer • Raw product gas (prior to quenching) • Gasifier ash • High pressure gas washer • Water gas shift reactor • Selexol purification system	• Atmospheric vent washer • Wastewater handling and disposal system
CO_2-ACCEPTOR PILOT PLANT	
• Raw product gas (prior to quenching) • Regenerator offgas (prior to quenching) • Product gas quench system	• Regenerator offgas quench system • Regenerator offgas SO_2-scrubber system • Coal preparation • Coal venturi scrubber system • Regenerator ash • Wastewater handling and disposal system • Product gas purification system
GRAND FORKS PILOT PLANT	
• Raw product gas (prior to quenching) • Product gas quench system (with certain modifications)	• Wastewater handling and disposal system
HYGAS PILOT PLANT	
• Coal pretreater (tar, oil, wastewater, offgas streams) • Raw product gas (prior to quenching) • Product gas quench system • Gasifier ash	• Oil stripper • Product gas purification system • Coal preparation • Wastewater handling and disposal system • Coal venturi scrubber system

of subsequent commercial versions. In the specific case of existing coal gasification pilot plants, few if any plant effluent-bearing streams are processed as they would be in a larger commercial plant. As a result, conventional environmental sampling at the outfalls (air, water, land) of gasification pilot plants does not yield meaningful information. Instead, process stream sampling must be concentrated at points where effluent stream characterizations are scalable. Note that results of such sampling reflect process effluent production not emission levels, since sampling is undertaken upstream of any effluent treatment.

As shown in Table 1 the locations of scalable effluent streams vary widely among the four participating pilot plants in the environmental assessment program. With the exception of the Bi-Gas plant, coal preparation areas yield essentially no scalable effluent streams; virtually none of the plants have scalable wastewater handling and disposal systems; only the Bi-Gas plant operates a scalable product gas purification system; and only the Hygas plant operates a scalable coal pretreatment system. As a result, first priority scalable sampling efforts are concentrated on streams immediately linked to the primary gasification step, viz., raw product gases, gasifier quench condensates, and gasifier ash. Beyond these points, sampling efforts are tailored to the special scalable features of a given plant, e.g.,

- *Coal pretreatment* effluent data are being generated at the Hygas plant.
- *Product gas purification* performance data will be generated at the Bi-Gas plant.
- *Coal slurry dryer* performance data will be generated at the Bi-Gas plant.

Effluent Parameter Selection

Procedures for the identification, grouping, and ranking of effluent parameter priorities have been published elsewhere;[2,4] a summary of current priorities is provided here in Table 2. Essentially all of the parameters listed in Table 2 either have or will be surveyed during the course of initial plant screening efforts. The subset of parameters found to be significant in this screening will be retained in subsequent more comprehensive sampling and analysis efforts.

TABLE 2

SUMMARY OF FIRST PRIORITY EFFLUENT PARAMETERS IN THE ERDA ENVIRONMENTAL ASSESSMENT PROGRAM

Wastewater Effluent Parameters [2,4]

- pH
- TSS
- BOD_5
- COD
- Phenols
- TOC
- Grease and Oil
- F^-
- $S^=$
- CN^-
- $NH_3 - N$
- $NO_3^- - N$
- $PO_4^{\equiv}$

Trace Wastewater Effluent Parameters [2,4]

- Al
- As
- Cd
- Cr
- Cu
- Fe
- Hg
- Mn
- Ni
- Pb
- Sn
- Zn

Gaseous Effluent Parameters [2,5]

- Sulfur Species: SO_2, SO_3, COS, CS_2, H_2S
- Other Acid Gases: NO_x, HCl, HCN, HF
- Other Inorganic Constituents: NH_3
- Other Organic Constituents: nonmethane HC's, e.g., C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}, C_4H_8

Stream Sampling Strategy

Major types of stream sampling methodologies include grab, composite, and continuous sampling. Typically one or more of these methods are combined to yield a working sampling strategy. Selection of the appropriate sampling strategy requires some knowledge of the nature of systematic and random variations in stream composition as well as an understanding of the use to which sample data will be put. For purposes of screening characterization, although a stream may be highly variable in composition, the large coefficient of variation of a grab sample may be adequate, and would certainly be the lowest cost sampling strategy. By contrast, sampling for material balance purposes may require a particular combination of grab and composite sampling strategy which yields a relatively lower coefficient of variation.

Use of Time Series Sampling

The systematic variability of an effluent stream composition with time can be determined by time series study of the behavior of selected effluent parameters. As illustrated in Figure 2 for three Hygas wastewater streams, the nature and the degree of variability differs significantly from stream to stream. Much of this variability (or in certain cases, the lack of it) can often be explained in terms of factors unrelated to actual effluent production. For example, operating practice accounts for a significant fraction of the variability in Hygas pretreater condensate composition.[6] Appropriate normalization of the data can often filter out some of this variability. A certain fraction of stream variability may represent actual changes in effluent production, which in turn are related to basic changes in process operating conditions.

Naturally, a sampling methodology designed to identify process variable/effluent production relationships would differ from that designed for simple screening characterization. However, given adequate time series data, statistical procedures available and described elsewhere[7,8] are adequate in either case for the selection of an appropriate combination of grab and composite sampling.

Specialized Sampling Requirements

Note that a low measured effluent stream coefficient of variation does not necessarily imply stable effluent production. For example, the large inventory (~2,000 gallons) of recirculating quench water at Hygas and its dampening effect are responsible for the low observed variability of Hygas quench condensate. Determination and correlation of the actual variability of effluent production with time requires the sampling of raw product gases prior to quenching. C-MU has developed and described elsewhere[2] an apparatus for the sampling of such raw product gases. Preliminary shakedown tests were recently completed successfully. Exploratory time series sampling is scheduled to begin in October.

Validation of Sample Preservation and Analysis Procedures

Preliminary C-MU/IGT experimentation with Hygas wastewaters at the outset of the environmental assessment program pointed to the importance of prompt sample preservation and indicated potential problems with several traditionally recommended procedures for the preservation and analysis of coal and oil processing wastewaters.[9] Subsequent investigations by C-MU/Radian and C-MU/GFERC with CO_2-Acceptor and Grand Forks condensates, respectively, revealed additional evidence of analytical problems.[2] In particular, major analytical interferences of oils in the determination of thiocyanate were observed (Table 3) as well as the simultaneous degradation of cyanide and production of thiocyanate with time in unpreserved samples of gasifier quench condensate (Figure 3). Consequently, an ongo-

TABLE 3

CNS^- OIL INTERFERENCE[2]

Procedure	No. of Tests	CNS^- Spike, mg/l	Measured CNS^- Level, mg/l Mean	Std. Dev.
Millipore Filtration Only	3	0	96.4	1.6
	3	50	151.8	2.1
Millipore Filtration and Hexane Extraction	3	0	32.3	5.4
	3	50	94.1	13.8

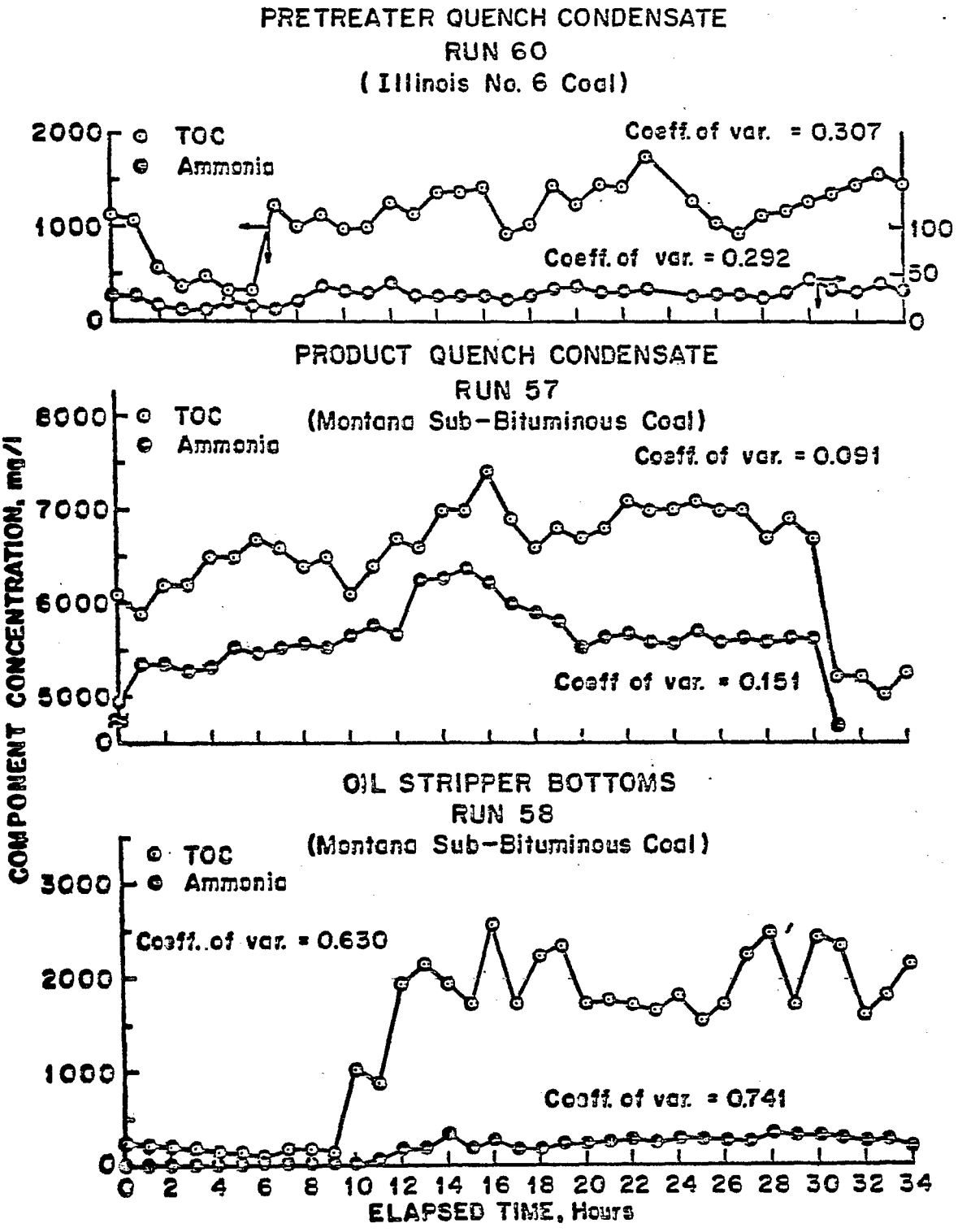


Figure 2. Time-series analysis: total organic carbon and ammonia contents of three major wastewater streams produced in the Hygas Pilot Plant.

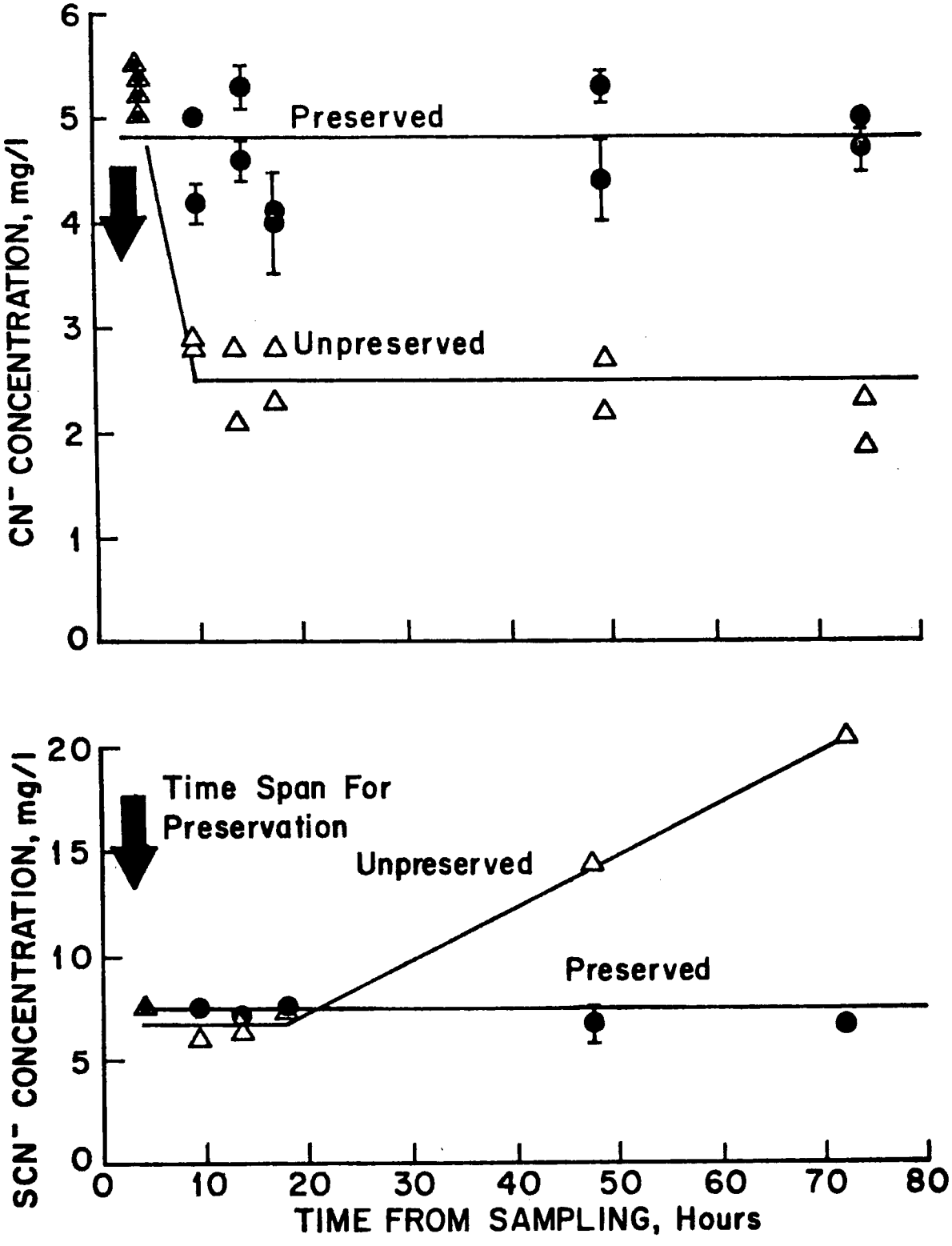


Figure 3. Time stability of cyanide and thiocyanate in preserved and unpreserved samples of gasifier quenchwater: Co_2-acceptor run 42.

ing effort of the program involves the investigation of the preservation techniques and analytical methods for the major liquid effluent parameters in coal gasification wastewaters. A set of recommended procedures for preservation and analysis has evolved from these initial investigations and is published elsewhere.[10] Research is also continuing on the complex relationships between cyanide and thiocyanate in these waters. Reaction mechanisms and kinetics for the conversion of cyanide to thiocyanate have been explored and the active sulfur species involved in the conversion has been investigated in both synthetic and actual gasification wastewaters. The results of these studies will be presented in the near future.[11]

SUMMARY OF AVAILABLE PROGRAM DATA

The major emphasis of the first year of the environmental assessment program has been on the characterization of the liquid effluents from the pilot plants. As noted, substantial work has been completed at the Hygas and CO_2-Acceptor pilot plants while initial efforts have just begun on the Bi-Gas, Synthane, and slagging fixed bed processes.

Characterization of Liquid Effluent Production

The initial characterization of the pilot plant liquid effluents, consistent with the overall program methodology, focused on those effluent streams which:

1. represent the bulk, by mass, of the total plant effluent production, and
2. have a direct and measureable linkage to the major process variables.

The liquid effluent streams in gasification which satisfy these criterion are the quench condensates of the gasification and/or pretreatment process steps. However, each pilot plant possesses liquid effluent flow patterns unique to its design and the determination of the total pilot plant effluent production may also involve other streams. The liquid flow patterns for the CO_2-Acceptor and Hygas pilot plants are shown in Figures 4 and 5, respectively, as are the major effluent streams which were sampled to yield the total liquid effluent production.

The total plant effluent production of these pilot plants for 10 major parameters (tars, oils, TSS, TOC, COD, Phenol, CN^-, CNS^-, NH_3, and $S^=$), normalized per pound of moisture and ash-free feed coal, is presented in Table 4. Also shown in Table 4 are the available normalized effluent production rates for the Lurgi-Westfield semi-plant and slagging fixed bed gasifier in Grand Forks. These normalized data are very amenable to analysis for the initial review of the effluent potential of the processes and the comparison and evaluation of these potentials among the existing plants.

Similarities and Differences in Pilot Plant Liquid Effluent Production Data

A cursory review of Table 4 reveals significant similarities and differences in the production of both organic and inorganic liquid effluents in the various pilot plants. For example, both the Lurgi and the slagging fixed bed plants exhibit quite similar tar production, ~60 to 80 lbs/ton coal, MAF; the Hygas and Lurgi processes produce similar quantities of phenol, ~11-12 lb/ton coal, MAF; the cyanide and sulfide production data for the Lurgi and CO_2-Acceptor plants are quite comparable, ranging from ~0.01 to 0.05 and 0.2 to 0.4 lb/ton coal, MAF respectively; and ammonia production is very similar for all the processes at ~15 lb/ton coal, MAF.

However, at the same time, there are also dramatic differences in the liquid effluent production data. In particular, tar, oil, and phenol production range from negligible to 80, 60, and ~15 lb/ton coal, MAF, respectively. Also, significant variations in cyanide, thiocyanate, and sulfide production are evident in Table 4, ranging from negligible to 0.04, 0.12 to 5.6, and 0.2 to 7.4 lbs/ton coal, MAF, respectively.

This large degree of variability is not surprising given the stage of development of the liquid effluent data base. Differences in coal feed type, sampling methodology, and sample preservation and analysis can possibly explain some of the variation, e.g., cyanide/thiocyanate interaction. However, some of the dramatic differences demonstrated by the hydrocarbon constituents, viz., tar, oil, and phenol, could not be accounted for in this man-

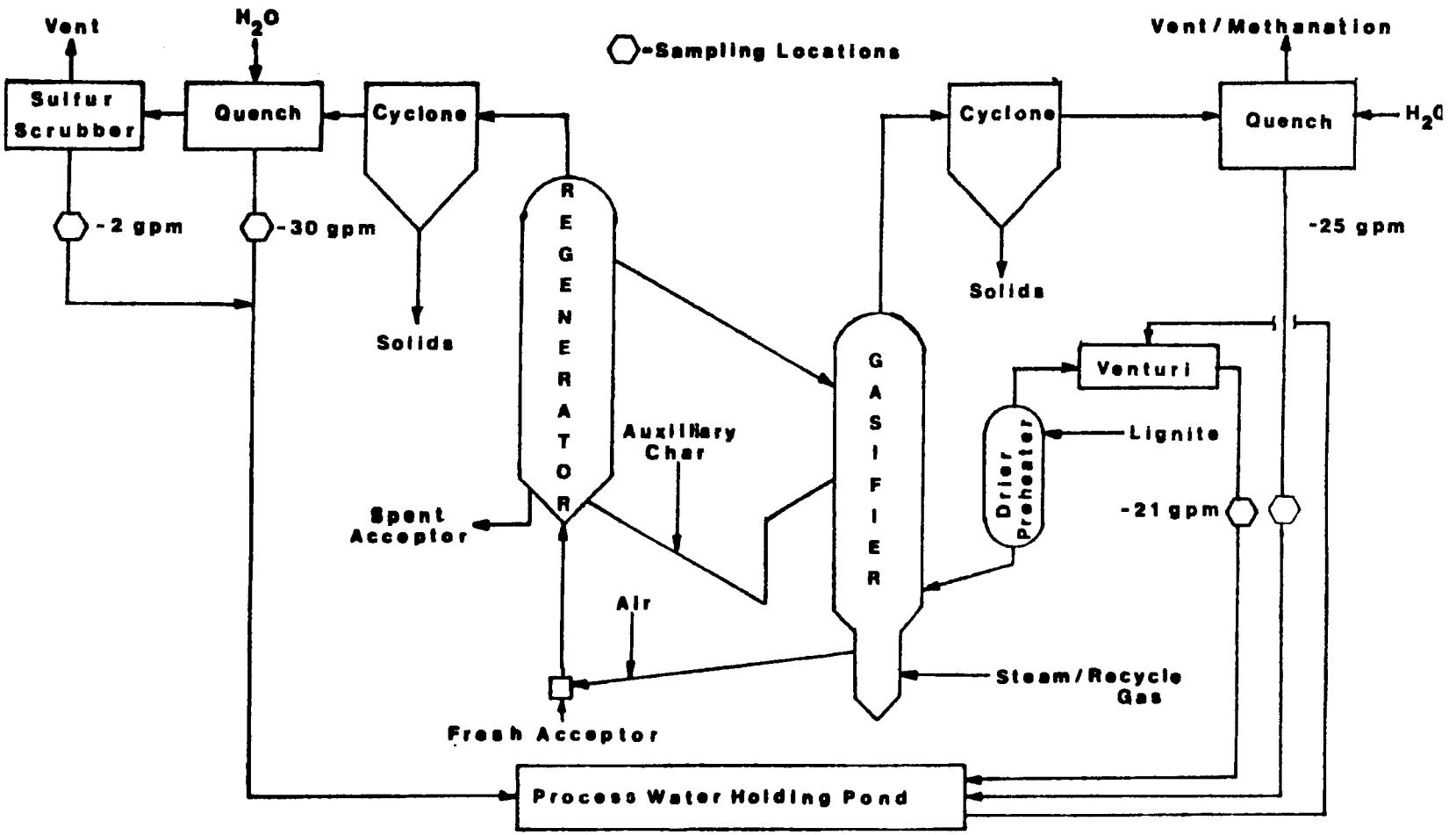


Figure 4. Liquid effluent flow patterns of the CO_2-acceptor coal gasification pilot plant.

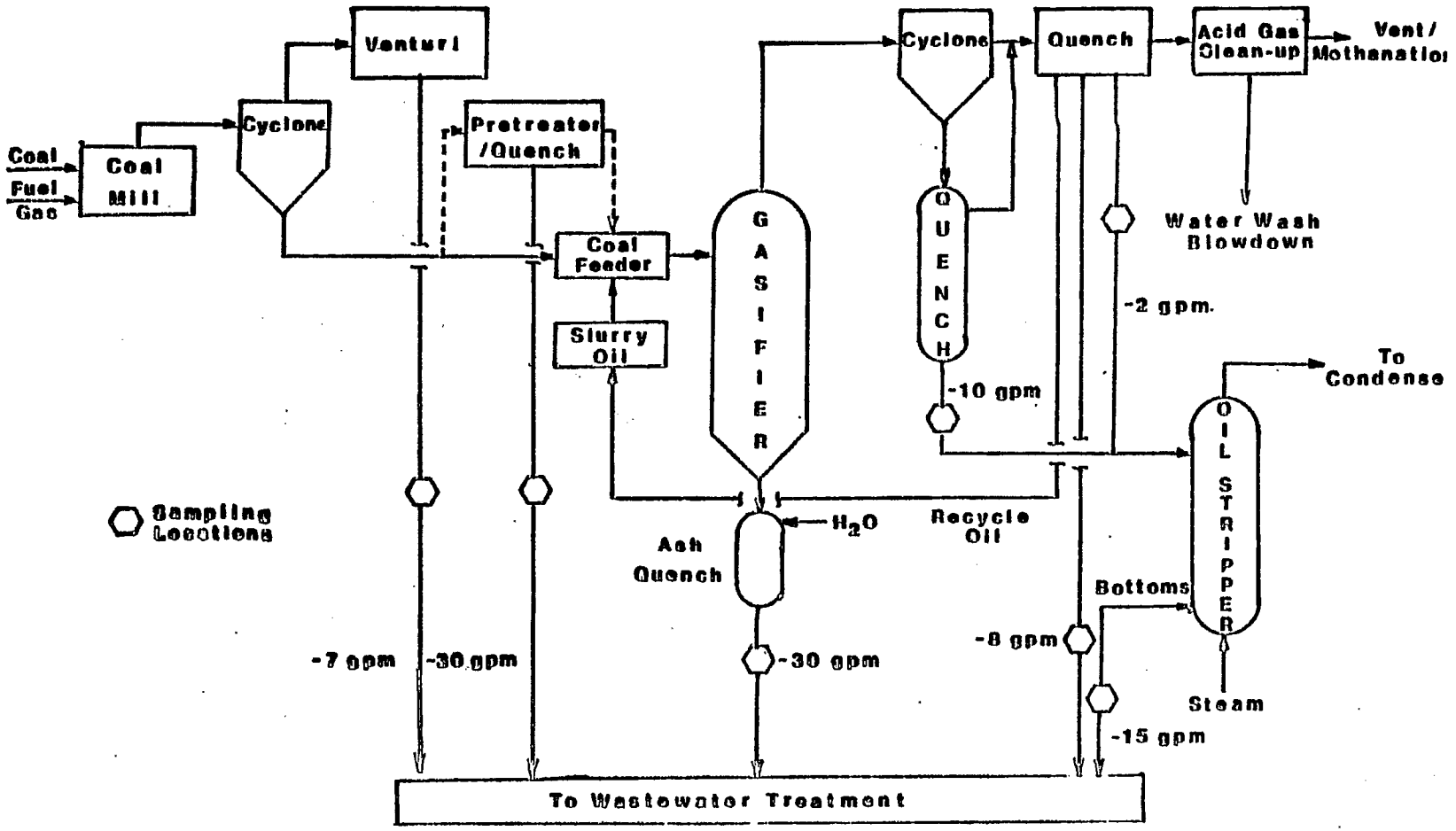


Figure 5. Liquid effluent flow patterns of the Hygas coal gasification pilot plant.

TABLE 4

SUMMARY OF NORMALIZED LIQUID EFFLUENT PRODUCTION FROM OPERATING COAL GASIFICATION PILOT PLANTS

Process[a]	Coal Type	Run No.	Normalized Liquid Effluent Production, lbs/ton coal, MAF									
			Hydrocarbons		Aqueous							
			Tars	Oils	TSS	TOC	COD	Phenol	CN	CNS	NH_3	S
CO_2-Acceptor[b]	Glenharold Lignite	39	Negl.	Negl.	45 ± 26	0.45 ± 0.25	2.9 ± 0.75	0.05 ± 0.02	0.028 ± .005	0.12 ± 0.14	23 ± 15	0.39 ± 0.21
Hygas	Montana Lignite[c]	37	Negl.	Mod.[h]	-[g]	39.1 ± 15.4		11.4 ± 2.4	Negl.	2.5 ± 0.2	13.1 ± 0.3	0.2 ± 0.1
	Montana Sub-bituminous[d]	55	Negl.	Mod.	123 ± 59	40.0 ± 11.2	-	17.3 ± 2.8	Negl.	1.9 ± 0.6	27.7 ± 13.8	7.4 ± 0.2
		58	Negl.	Mod.	376 ± 112	10.9 ± 3.0	-	15.4 ± 3.5	Negl.	0.9 ± 0.2	14.8 ± 4.2	0.5 ± 0.2
	Illinois No. 6[d]	46	Negl.	Mod.	134 ± 96	5.7 ± 1.1	-	2.8 ± 1.5	Negl.	0.8 ± 0.3	17.1 ± 7.5	1.3 ± 0.7
		54	Negl.	Mod.	64 ± 42	7.0 ± 2.3	-	4.9 ± 0.9	Negl.	3.3 ± 1.9	12.9 ± 6.0	1.4 ± 0.6
		59	Negl.	Mod.	150 ± 90	30.2 ± 5.8	-	13.3 ± 4.1	Negl.	5.6 ± 1.5	3.4 ± 2.1	2.6 ± 1.6
		60	Negl.	Mod.	153 ± 122	25.2 ± 7.3	-	11.5 ± 3.9	Negl.	4.1 ± 2.5	14.9 ± 5.4	4.7 ± 2.0
Lurgi-Westfield[e] (Dry Ash)	Montana	-	61 ± 3	60 ± 5	-	-	56 ± 15	14.6 ± 3.0	0.01 ± 0.001	0.12 ± 0.14	11.9 ± 6.7	0.4 ± 0.2
	Illinois No. 6	-	82 ± 19	10 ± 4	-	-	52 ± 2	12.6 ± 1.6	0.04 ± 0.02	0.31 ± 0.08	16.8 ± 1.8	0.3 ± 0.1
	Illinois No. 5	-	78 ± 39	14 ± 5	-	-	44 ± 3	12.4 ± 0.1	0.02 ± 0.01	0.35 ± 0.04	16.4 ± 4.2	0.4 ± 0.2
	Pittsburgh No. 8	-	82 ± 4	18 ± 14	-	-	29 ± 1	7.9 ± 0.9	0.02 ± 0.02	0.54 ± 0.12	15.4 ± 0.7	0.2 ± 0.1
Slagging Fixed Bed (CPERC)[f]	N. D. Lignite	-	74 ± 1	-	-	15.4 ± 6.4	-	-	-	-	7.3 ± 0.2	3.6 ± 0.2
	N. D. Lignite	-	56 ± 7	-	-	8.4 ± 2.9	-	-	-	-	6.6 ± 0.8	-

Footnotes

(a) The Bi-Gas and Synthane pilot plants are presently undergoing start-up operation and are not included in this table. However, substantial effluent data have been generated on the Synthane pilot development unit and are reported elsewhere; References 12, 13.

(b) Source: Reference 14.

(c) Source: Reference 3.

(d) Total plant production derived from individual effluent streams presented in References 15 and 16.

(e) Source: Reference 17.

(f) Source: Reference 18.

(g) No data.

(h) Moderate production rates.

ner. Such differences can only be explained by the inherent processing differences exemplified by each of the processes. The correlation of these process differences with the subsequent differences in effluent production is a complicated task. For example, why does the CO_2-Acceptor process simultaneously produce negligible quantities of tar, oil,[2] and phenol while the Hygas process, which also produces insignificant amounts of tar, yields significant amounts of oil and phenol? Or, why does the Lurgi process produce quantities of oil and phenol comparable to the Hygas process, yet produce much more tar? Understanding such phenomena requires the identification of the major gasification process variables which influence effluent production and subsequently, the specific relationships between these process variables and effluent production characteristics.

DEVELOPMENT OF PROCESS VARIABLE/EFFLUENT PRODUCTION RELATIONSHIPS FOR THE INTERPRETATION OF PROGRAM DATA

A combination of bench-scale, PDU-scale, and pilot scale experimental studies have been initiated to define the relationships between the process variables and liquid effluent production as an aid in interpreting the pilot plant effluent data bases.

Structure of Process Variable/Effluent Production Studies

Research initiated jointly by C-MU and the Pittsburgh Research Energy Center (PERC) in 1974 provides the framework for the comprehensive studies of the relationships between process variables and liquid effluent production.

Identification of Critical Process Variables

During a sequence of 19 controlled experiments on the Synthane pilot development unit, seven effluent production parameters (tar/oil, phenols, COD, TOC, TIC, CN^-, and CNS^-) were monitored both as a function of time and as a function of changing coal injection geometry (free fall, shallow, and deep bed-injection).[12,13] The typical response of the hydrocarbon effluents or indicators (tar/oil, phenols, TOC, COD) to the changes in feed geometry are demonstrated by the phenol production data shown in Figure 6. Note the dramatic reduction of phenol production as the coal was injected deeper into the fluidized bed. At the same time, significant changes in critical process variables also occurred as the point of fresh coal injection was altered from free fall to shallow and deep bed-injection:

1. Product gas residence time: Volatile materials evolved from the coal during its initial heatup were now forced to pass through the hotter, fluidized bed portion of the gasifier thereby increasing their residence time at conditions more conducive to attaining chemical equilibrium.
2. Gas-solid mixing: Coal injection now occurred in a region of intimate gas-solid contacting encouraging reaction of the volatilized species both with hydrogen and the highly reactive, potentially catalytic, char surfaces.
3. Mean reaction temperature: Longer residence times in the fluidized bed portion of the gasifier effectively increased the mean reaction temperature of the devolatilized coal species, and
4. Coal heat-up rate: Coal injection into the hotter fluidized bed effectively increased the heatup rate of the coal particles to their final temperature.

Table 5 summarizes the major impacts of changes in process variables on liquid effluent production demonstrated in that study. Examination of this table reveals that the largest percentage reduction in gasifier tar production, viz., 86 percent, resulted from the shift from free fall to shallow bed-injections of lignite. Accompanying this shift were major changes in coal heat-up rate, gas-solid mixing, and product gas residence time. However, increasing the depth of injection of lignite from 1-1/2 to 4-1/2 feet in the fluidized bed portion of the gasifier (deep bed-injections) and hence increasing the product gas residence time even more, resulted in an additional reduction of only 38 percent.

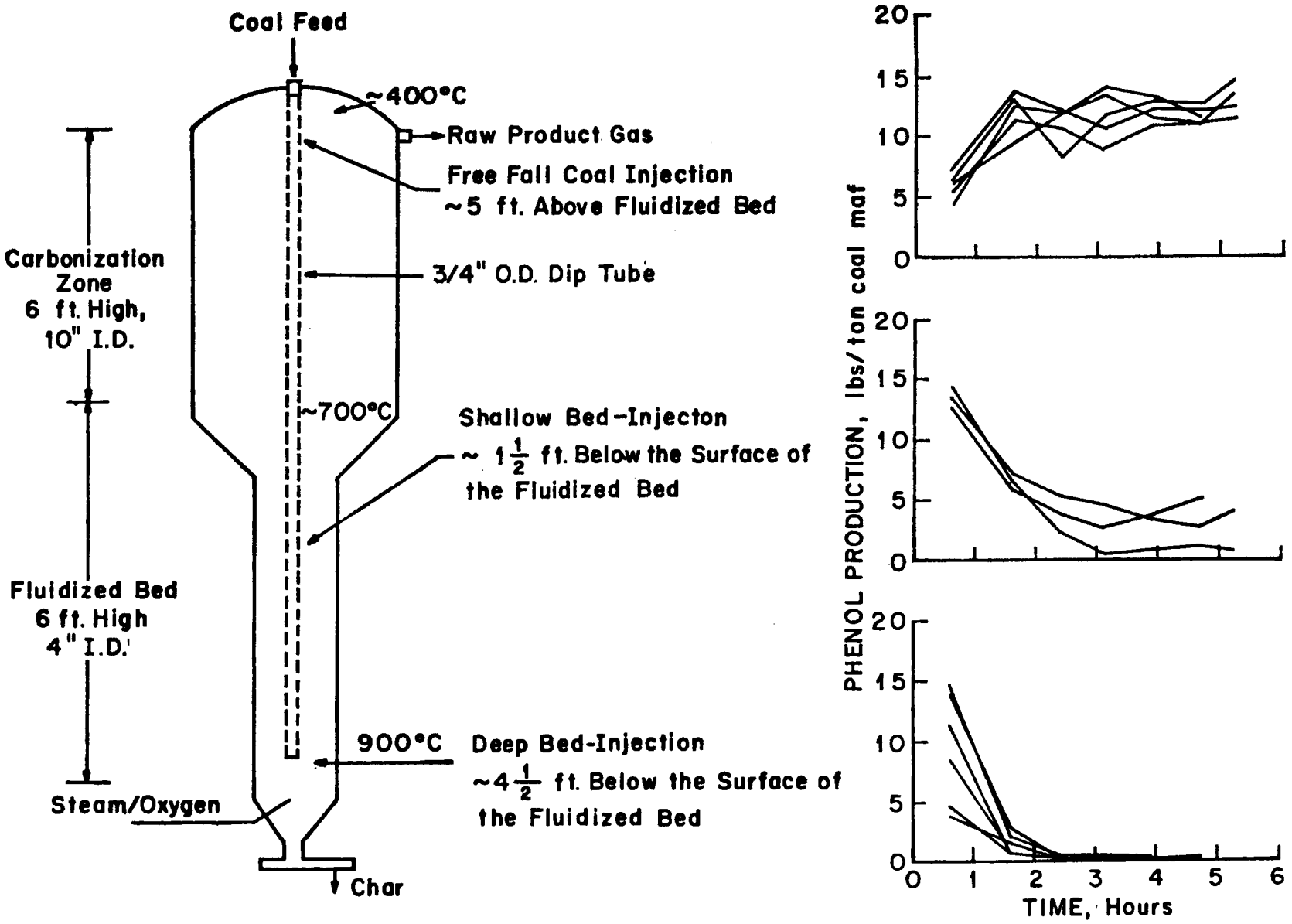


Figure 6. Influence of coal feed injection geometry on effluent production in the synthane pilot development unit.

TABLE 5

RELATIVE IMPACTS OF CHANGES IN MAJOR PROCESS VARIABLES ON SYNTHANE GASIFIER EFFLUENT PRODUCTION

Process Variables	Nature of Increase	Decrease in Effluent Production			
		Tar/Oil	TOC	Phenol	COD
SHALLOW VS FREE FALL-INJECTION					
Reaction Temperature[a]	Major				
Coal Heatup Rate	Major				
Residence Time[b]	Moderate	86%	78%	71%	85%
Gas/Solid Contacting	Major				
DEEP VS SHALLOW BED-INJECTION					
Reaction Temperature[a]	Minor				
Coal Heatup Rate	Negligible				
Residence Time[b]	Major	38%	44%	86%	69%
Gas/Solid Contacting	Negligible				

Notes:

(a) Mean reaction temperatures varied from 828° C (free fall) to 789° C (shallow bed) to 773° C (deep bed).
(b) Effective product gas residence time varied from zero (free fall) to 2.8 (shallow bed) to 6.6 seconds (deep bed).

Similar trends in chemical oxygen demand (COD) and total organic carbon (TOC) of aqueous effluents are apparent; COD's are reduced by 85 and 69 percent, TOC's by 78 and 44 percent, respectively. Interestingly, the above pattern does not hold for phenol production. Shifting from free fall to shallow bed-injections of lignite results in a 70 percent reduction in phenol production; however, increasing the product gas residence time by shifting from shallow to deep bed-injections of lignite results in a further reduction of 86 percent! Such evidence strongly suggests that different mechanisms may be responsible for observed reductions in various steady state effluent production rates with changes in fresh coal injection geometry.

Potential Mechanisms Governing Hydrocarbon Production

On the basis of the Synthane PDU test results, the following tenative mechanisms are proposed as major determinants in gasifier hydrocarbon formation and decomposition:

1. Phenols are inherently formed during the initial stages of coal heating and devolatilization, after which they are subject to decomposition by thermal cracking.
2. By contrast, tar/oil formation is strongly influenced by conditions and interactions during initial coal heat-up and devolatilization, e.g., gas-solid mixing, coal heat-up rate and hydrogen partial pressure. Formed material is then subject to decomposition by thermal cracking.

The first mechanism suggests that the determining factors in phenol production are reactor temperature and product gas residence time. The second mechanism suggests that net tar/oil production rates are the result of two contrasting process variable interactions: the first governs the extent of tar/oil formation and depends upon such variables as gas-solid contacting, hydrogen partial pressure, and coal heat-up rate; the second governs tar/oil decomposition and depends upon reactor temperature and product gas residence time.

Investigation of Hydrocarbon Formation/Decomposition Mechanisms: Experimenal Strategy

There are advantages and disadvantages to the study of the process variable/effluent production relationships at any single experimental scale. However, a judicious distribution of experiments across a range of scales affords an opportunity for maximum utilization of the advantages of each scale. Accordingly, as shown in Figure 7, a mixture of bench-scale, PDU-scale, and pilot scale experiments were designed to screen the major mechanisms influencing the formation/decomposition of hydrocarbons in coal gasification. In particular, information was sought to determine:

1. The susceptability of phenol to decomposition under gasification conditions, and
2. The relative impacts of formation phenomenon and thermal decomposition on the existence of tar/oils.

Studies of Phenol Formation-Decomposition

The postulated mechanism of intrinsic phenol production with subsequent decomposition by thermal cracking was examined on both the bench-scale and pilot plant scale.

1. Bench Scale Phenol Studies

The effect of reactor temperature and product gas residence time on the decomposition of phenolic compounds is amenable to examination using bench-scale apparatus operated under simulated gasifier conditions. C-MU and PERC recently completed initial experiments of this type on a model compound, phenol, and verified a thermal decomposition mechanism.[19]

The bench-scale experiments were conducted at atmospheric pressure in a homogeneous gas phase reactor (Figure 8) in which the reaction gas temperature, residence time, and composition were varied and the rate of phenol decomposition and the nature of the decomposition products were monitored. The range of conditions covered in these experiments included:

- Nominal reactor temperatures from 300 to 975° C, with primary emphasis on the range from 750 to 950° C,
- Nominal reaction gas residence times from 2 to 4 seconds, and
- Nominal hydrogen partial pressures of 0.0, 0.2, and 0.5 atmospheres, water partial pressure of approximately 0.5 atmospheres.

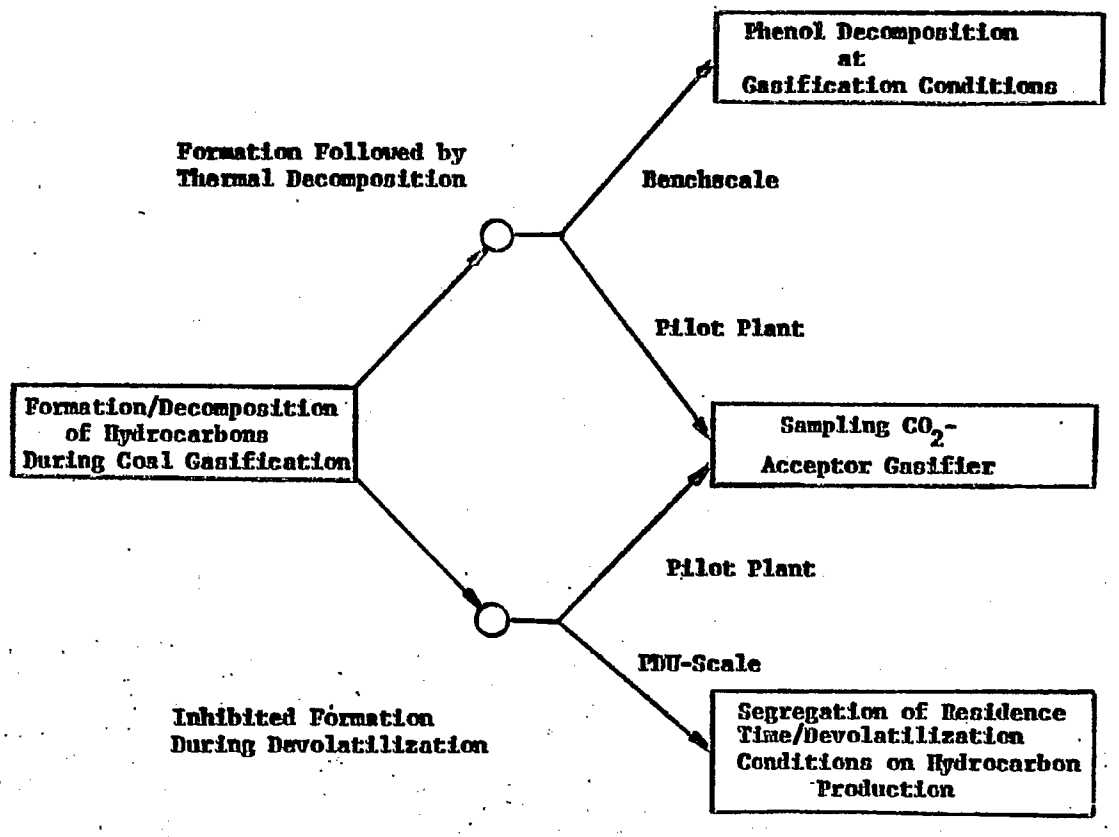
In addition to the homogeneous tests, two heterogeneous tests were also completed using gasifier char from the previous Synthane PDU tests. From this mixture of homogeneous and heterogeneous tests it was demonstrated that:

1. Phenol decomposition proceeds rapidly (2 to 4 seconds) by thermal cracking, at rates which are independent of reaction gas composition, particularly hydrogen partial pressure (Figure 9),
2. Phenol decomposition product distribution is a strong function of system hydrogen partial pressure, tar production increasing with decreasing partial pressure, and
3. The presence of solid surfaces reduces by at least 200° C (975 to 775° C) the reaction gas temperature required to accomplish rapid and essentially complete phenol decomposition (see Figure 9).

Future experiments are in progress to explore the decomposition kinetics of other prominant phenolic compounds (e.g., cresols) found in gasifier quench condensates. Additional atmospheric and possibly higher pressure experiments under heterogeneous reaction conditions will also be conducted.

2. Pilot Plant Phenol Studies

Very small amounts of phenol are produced in the CO_2-Acceptor process (Table 4). If phenol behaves as postulated, increasing phenol levels would be expected as process gas is sampled closer and closer to the coal injection point at the base of the gasifier. C-MU designed a sample probe to complete this experiment and it has been described in a previous document.[14] Preliminary sampling results have identified the presence of phenols at the point of coal injection in the CO_2-



- Phenol susceptible to thermal decomposition in homogeneous gas phase at 700 to 900°C and 2-4 seconds residence time
- 99% Decomposition observed at 970°C and a residence time of 2 to 4 seconds
- Char catalyzes decomposition of phenol: 99% decomposition at 750°C and a residence time of 2 to 4 seconds

- Preliminary results indicate the presence of phenol and other organics at the point of coal feed injection; however, quantitative analysis not yet available

- Heavy hydrocarbons (80% boil over 400°C) are very sensitive to gas/solid mixing and temperature at the point of devolatilization: 95% reduction by increasing both parameters on PDU gasifier
- Oil (boiling point 100-400°C) and phenol not influenced by gas-solid contacting and temperature at point of devolatilization

Figure 7. Preliminary screening of major mechanisms influencing the formation/decomposition of hydrocarbons in coal gasification.

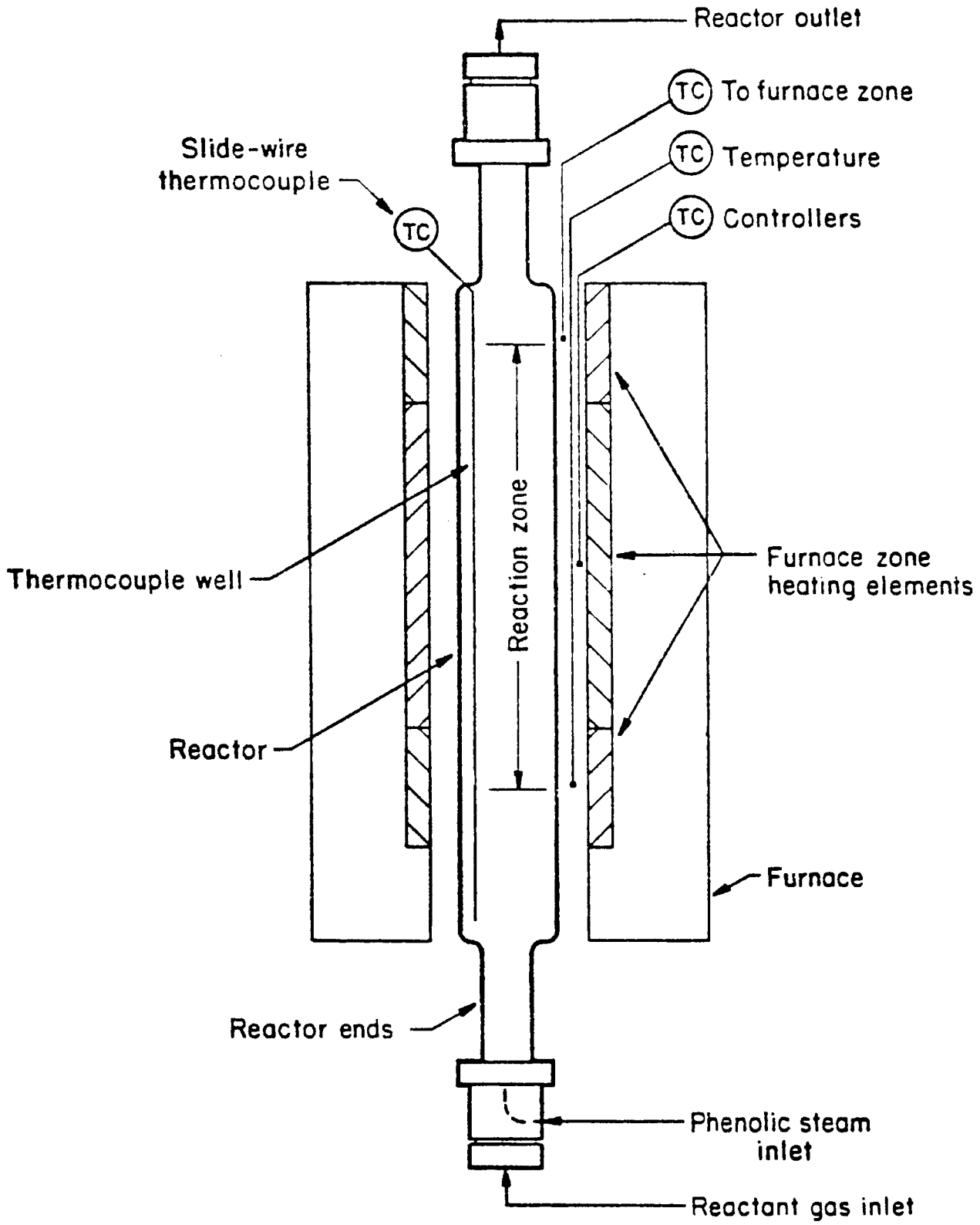


Figure 8. Thermal decomposition reactor and furnace configuration for phenol decomposition studies.

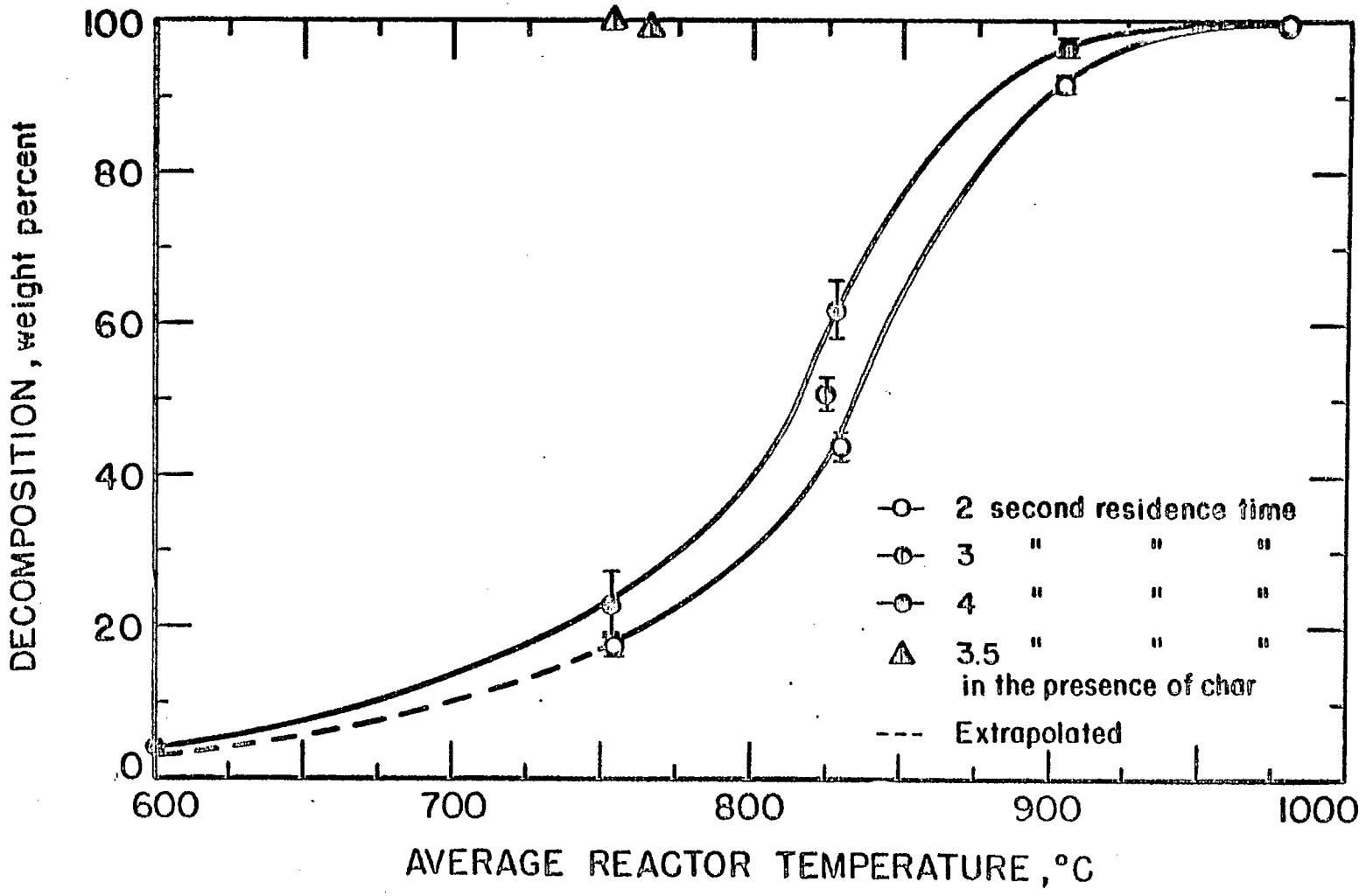


Figure 9. Measured phenol decomposition as a function of average reactor temperature for 2, 3, and 4 second nominal residence times.

Acceptor gasifier; however, further results are required before an extensive quantitative analysis can be done.

Studies of Tar/Oil Formation-Decomposition

It is believed that both formation and decomposition phenomena play an integral part in dictating the production of hydrocarbons produced during the thermal processing of coal. Bench-scale equipment are not adequate for the segregation of these formation/decomposition interactions since (1) the multicomponent nature of the tars and oils make it difficult to simulate these compounds for bench-scale decomposition studies and (2) studies based on simulated materials preclude the effects of process variables on the formation of tar/oils during devolatilization. Larger scale systems, operating on fresh coal and capable of examining both the effects of devolatilization conditions and thermal decomposition on tar yields, are required. This led to the initiation of two experimental programs - one on the Synthane PDU and the other on the CO-Acceptor pilot plant gasifier - to segregate the relative impacts of tar/oil formation and thermal decomposition on the existence of tar/oils under gasification conditions.

1. PDU-Scale Tar/Oil Studies

The use of a PDU-scale equipment train for the examination of process variable effects on tar/oil production and composition has some obvious advantages and disadvantages. While it provides a scale sufficient to preserve material balance capabilities and flexibility regarding changes of process conditions, it is very difficult to totally decouple individual process variables effects. However the purpose of the study was not to specifically isolate the effects of individual process variables; but rather, to dissociate the impact of tar/oil formation phenomenon and tar/oil decomposition on the existence of tar/oils. While the result of such a study may not yield quantitative mechanisms to explain the observed phenomenon, it should provide semi-quantitative empirical relationships which are quite amenable to scale-up and extrapolation.

The isolation of the decomposition and formation phenomenon in the Synthane PDU was accomplished by injecting the feed coal of the Synthane PDU gasifier directly onto the top of the fluidized bed (Figure 10). This provided devolatilization conditions similar to the shallow and deep bed-injection trials of the previous studies, e.g., gas-solid contacting, final reaction temperature, and coal heat-up rate, and at the same time essentially eliminated the residence time of the devolatilized species in the hot, fluidized bed.

Preliminary effluent production rates for these PDU trials have been summarized in a previous document[20] and are shown in Table 6 for tars (80 percent with boiling point >400° C), oils (boiling point between 100 and 400° C) and phenols:

Trial Description	Mean Particle Size (Micron)	Hydrocarbon Production (lbs/ton Coal, MAF) Tars	Oils	Phenols
Free Fall-Injection	50	13±4 (6)[a]	48±10 (2)	8±2 (6)
Top Bed-Injection	50	0.6±0.3 (3)	49±38 (6)	9±6 (8)

[a]Number of Observations

These data are significant since they suggest that the tar reductions observed during the previous shallow and deep bed-injection trials were largely a result of the enhanced gas-solid contacting and temperature at the point of coal devolatilization. This statement results from the fact that a 95 percent reduction in heavy tar was accomplished with negligible product gas residence time in the fluidized bed (top bed-injection trials provide effectively no residence time for the product gas in the hot fluidized bed).

The mechanisms responsible for the tar reduction during coal devolatilization are not discernable from the PDU trials. However, enhanced gas-solid contacting and temperature during devolatilization have the potential to influence the secondary reactions of the devolatilized species. In particular, tar production could be reduced by (1) enhancing the reaction of the devolatilized species with

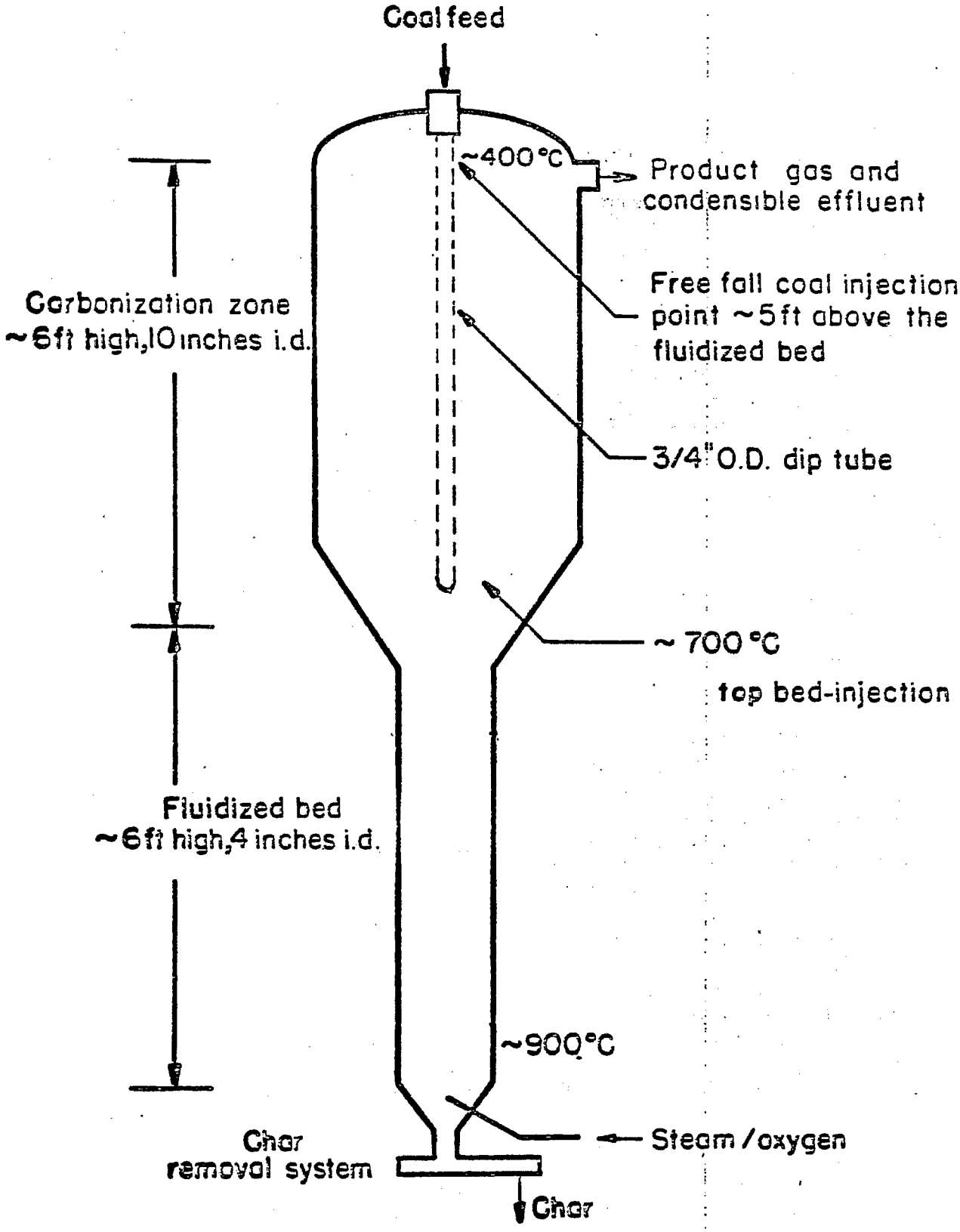


Figure 10. Synthane PDU gasifier: top bed-injection of feed coal.

TABLE 6

PROCESS VARIABLE AND EFFLUENT PRODUCTION PATTERNS FOR SELECTED COAL GASIFICATION PROCESSES

Process	Process Variable: Gas-Solid Contacting During Devolatilization	Process Variable: Residence Time at Temperature	Analogous Synthane PDU Coal Feed Geometry	Effluent Production: Tars	Effluent Production: Oils	Effluent Production: Phenol
Lurgi-Westfield	Minimal	Minimal	Free Fall-Injection	High	High	High
Hygas	Extensive	Minimal	Top Bed-Injection	Negl.	High	High
CO_2-Acceptor	Extensive	Extensive	Deep Bed-Injection	Negl.	Negl.	Negl.

hydrogen, thereby reducing repolymerization, or (2) providing additional surface area of the potentially catalytic char solids which may serve as sites for tar deposition/decomposition. Enhancing the stabilization of the devolatilized species by reaction with hydrogen would be expected to increase the quantity of lighter oils produced. Examination of the oil production reveals no such change (48 ± 10 versus 49 ± 38 for the 50 micron free fall and top bed-injection trials, respectively). Hence, deposition and/or decomposition of the tar species on the char surfaces may be the dominate mechanism of tar reduction. However, there is no data to verify or refute this hypothesis. Regardless of the mechanism, an empirical relationship has been identified between heavy tar production and gas-solid contacting during coal devolatilization at gasification temperatures (700° C). Thermal cracking or decomposition beyond this initial devolatilization point appears to contribute very little to the overall yield of heavy tar in gasification.

Not surprisingly, phenol production was statistically invariant (95 percent confidence level) for the change in injection geometries incorporated in this study. Both of the coal injection geometries used in the experiments provided no gas residence time in the fluidized bed and accordingly, phenol production for all the tests were aproximately equivalent. These data, combined with the previous bench-scale results, strongly support the original postulate that phenol is inherently formed during gasification and its destruction occurs via thermal decompositon.

2. Pilot-Scale Tar/Oil Studies

As with phenol, the CO_2-Acceptor pilot plant produces essentially no tar/oil effluent. Consequently, using the gasifier sample probe discussed earlier for sampling at the point of coal injection in the CO_2-Acceptor gasifier could also provide information concerning the relative impacts of formation and decomposition phenomenon on tar/oil existence. Preliminary data indicate the presence of some heavier hydrocarbons; however, the specific indentification of these components has not yet been completed nor have their production rates been determined.

Preliminary Interpretation of Pilot Plant Liquid Effluent Data

Based on the bench-scale, PDU-scale, and pilot scale experimental studies completed at this time, it would appear that:

1. Phenol is indeed inherently formed during the heat-up and devolatilization of coal. Consequently, phenol production during gasification is directly related to the extent of thermal decomposition that occurs in the gasifier. This in turn, is influenced by residence time and temperature in the gasifier, and the presence of char solids, and
2. Heavy tar production, on the other hand, is dramatically influenced by devolatilization conditions, particularly

gas-solid contacting, and does not appear to be influenced by thermal decomposition phenomenon.

These semi-quantitative observations are quite useful in understanding the liquid effluent production of the various pilot plants presented earlier in Table 4 as well as providing the initial tools for the prediction of liquid effluent production levels for full scale commercial plants.

The relationships between process variables and liquid effluent production identified in the bench-scale and PDU-scale experiments are also demonstrated by the major gasification pilot plants. The free-fall, top bed-injection, and deep bed-injection coal feed geometries of the PDU effectively simulated the devolatilization conditions, i.e., gas-solid contacting and temperature, and product gas residence time conditions of the Lurgi, Hygas, and CO_2-Acceptor gasifiers, respectively. Accordingly, these pilot plants demonstrated qualitatively the same liquid effluent production characteristics as the equivalent feed geometries in the PDU (Table 6):

- Minimal gas-solid contacting/ temperature and product gas residence time - high tar, oil, and phenol production,
- Extensive gas-solid contacting/ temperature and minimal product gas residence time - low tar, high oil, and high phenol production, and
- Extensive gas-solid contacting/ temperature and product gas residence time - low tar, oil, and phenol production.

The ability to correlate these process variables to liquid effluent production on the pilot plant scale represents a significant first step for the interpretation and prediction of liquid effluent production in full scale commercial facilities. In addition, this initial screening has indicated the direction for more detailed experimental work which will further define the critical relationships identified at this point. Perhaps more importantly, the methodology used to identify these process variable/effluent production relationships, that is, the process engineering approach to the collection of environmental data, may prove to be an invaluable tool necessary for the simultaneous development of new technologies and environmental regulatory policies in the United States.

FUTURE WORK

In the initial year of the ERDA coal gasification environmental assessment program, primary emphasis has been placed on activities which should lead to well-designed environmental test plans at each pilot facility. In field work at the pilot plants, this has led to an emphasis on wastewater studies, due to the lack of factual information concerning coal gasification wastewaters and the potential importance of such wastewater effluents. Although these studies are not yet completed, initial efforts have developed and verified wastewater sampling and analytical methods, and have produced a preliminary data base. Comprehensive environmenal assessment test plans for the ERDA pilot plants can now be based on the preliminary information obtained in these wastewater studies, as well as on information available from related and previous studies characterizing gas/liquid/solid waste streams from coal gasification.

With the completion of activities closely related to test plan formulation, emphasis in the next year can shift to the following priorities:

- Media emphasis will be refocused from wastewater studies to a balanced emphasis on all the media. In particular, characterization of gas streams and waste solid streams is seen as a priority. The characterization work includes efforts to measure the distribution and form of sulfur in coal gasification effluents, as well as efforts involving characterization of selected trace metals in effluent streams.
- Emphasis in planning activities will shift from environmental and process-related parameters (e.g., SO_2 in gas streams, COD in liquid effluents) to those parameters useful for characterization of potential occupational health problems in coal gasification (e.g., trace organics, hydrocarbon condensates). Efforts will be made to develop and verify basic methods for characterization of these parameters

as well as carry out screening analyses in typical pilot plant streams.

- Data-gathering programs at the pilot plants are to emphasize the characterization of effluent streams which will have a counterpart in larger-scale facilities, for a range of important gaseous, wastewater, and waste solid components.

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