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STATUS REPORT: ENGINEERING CONTRIBUTIONS TO COAL GASIFICATION ENVIRONMENTAL ANALYSIS

Ninth Quarterly Report

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PROLOGUE

In July of 1976, the Department of Energy initiated a comprehensive program for environmental assessment of its high-BTU coal gasification pilot plant installations. The overall objective of the program is to develop the methodology and data base necessary for meaningful assessment of the environmental impact of the coal gasification processes. The environmental characterization efforts at each pilot plant are focused on scalable process units, with the goal of establishing rules and strategy for scaleup to commercial-size installations.

Carnegie-Mellon University, in its role as assistance, coordination and evaluation contractor for the DOE environmental assessment program, has prepared a series of technical documents in support of program objectives and activities within and across the coal gasification facilities. This report represents one in that series. Reports are also available describing the unique C-MU role and summarizing program activities.

INTRODUCTION

This report represents the third annual report of progress in the coordination of DOE Fossil Energy's environmental characterization activities at its coal gasification pilot plants. Participants in the program include Argonne National Laboratory (Hygas), Combustion Engineering (CE gasifier), the Grand Forks Energy Technical Center (slagging fixed bed gasifier), the Institute of Gas Technology (Hygas), Oak Ridge National Laboratory (gasifiers in industry), the Pittsburgh Energy Technical Center (Synthane), Phillips Petroleum (Bi-Gas), and Radian Corp. (CO_2-Acceptor). Coordination and evaluation efforts are carried out by Carnegie-Mellon University with the assistance of its sub-contractor, Environmental Research and Technology, Inc.

Substantial progress has been made by each of the listed participants during the past year; their work is extensively documented in a series of reports now available in the literature. The present report is devoted to a discussion of the evolving role of engineering in the generation of coal gasification environmental data bases. Engineering contributions to the FE program have been significant during the past year, and are highlighted here with supporting data.

ROLE OF ENGINEERING IN COAL GASIFICATION ENVIRONMENTAL ANALYSIS

Definition of the Problem

In principle, two sets of people have contrasting interests in environmental data bases for coal gasification:

(1) Process development people are concerned about the form, content, and depth of data base which they may be expected to generate at various stages in process development.

(2) Environmental assessment people are concerned about both

- The scope and adequacy of the data base, particularly with regard to trace toxic materials, and
- Proper interpretation of data bases, particularly those generated on PDU and pilot-scale equipment.

Ultimately, both groups are interested in the assessment of environmental impact of commercial-scale coal gasification processes. In those cases where process development has not advanced beyond the PDU or pilot-scale stage, projections of potential commercial-scale environmental impact can be complicated. As illustrated in Figure 1, there are a number of distinct steps associated with the projection of commercial-scale plant discharge characteristics from which an enviroinmental impact assessment is made. Chemical and bio-assay measurement and analysis techniques often must be tailored to conform to the vagaries of site-specific application. Since PDU and pilot-scale experiments are typically performed over a wide range of process conditions, the impact of these variations on environmental measurements must be addressed in any site-specific data bases. Operation of scalable state-of-the-art control technology is rarely practical in PDU and pilot-scale operations; consequently the treatability of individual raw effluent-bearing process streams must be addressed separately. Finally, since PDU and pilot-scale operations typically are not miniature replicas of future commercial-scale practice, scaling of measured data bases is required for the projection of commercial-scale environmental characteristics.

As will be apparent from data presented later in this paper, impacts of the various factors above on the generation and interpretation of data bases for environmental assessment projection are significant.

Role of Engineering

The heart of the engineering contribution to environmental assessment in coal gasification processing lies with:

(1) Site-specific data acquisition (SSDA): Scalable application of the tools of chemical and bio-assay measurement/analysis to plant-specific chracterization (see Figure 2).

(2) Process environmental analysis (PEA): Integration and analysis of raw process and environmental data for commercial-scale data base projections (see Figure 1).

(3) Raw effluent treatment analysis (RETA): Scalable determinations of the fates of significant environmental species in treatment (see Figure 1).

Actually, each of the processes of data acquisition, analysis, and treatability determination are highly iterative in nature, and involves interactions between process engineers, life science assessment people, and methods research personnel.

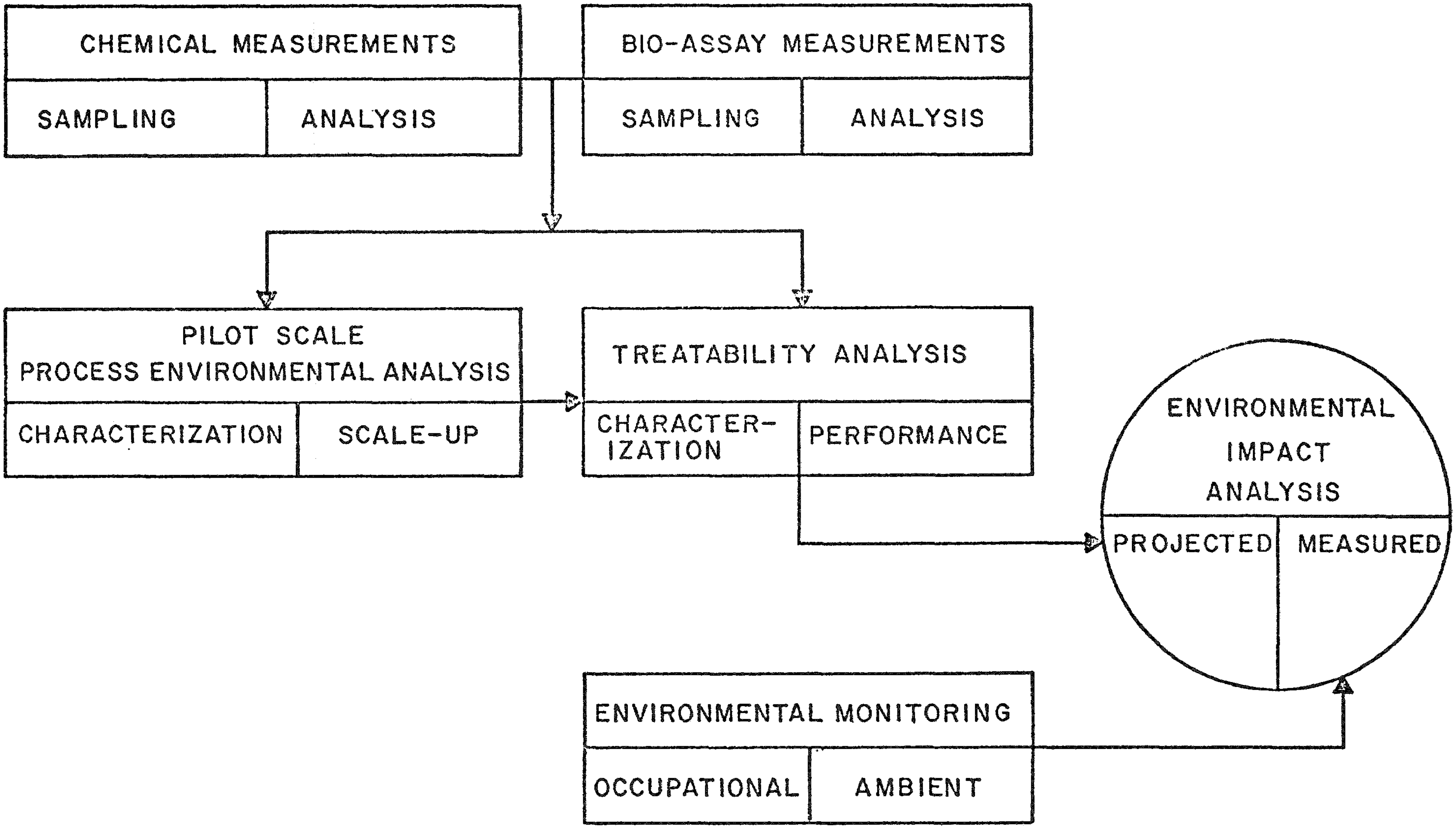

Figure 1. Sequence of Steps Associated with Environmental Impact Analysis In Coal Gasification Systems

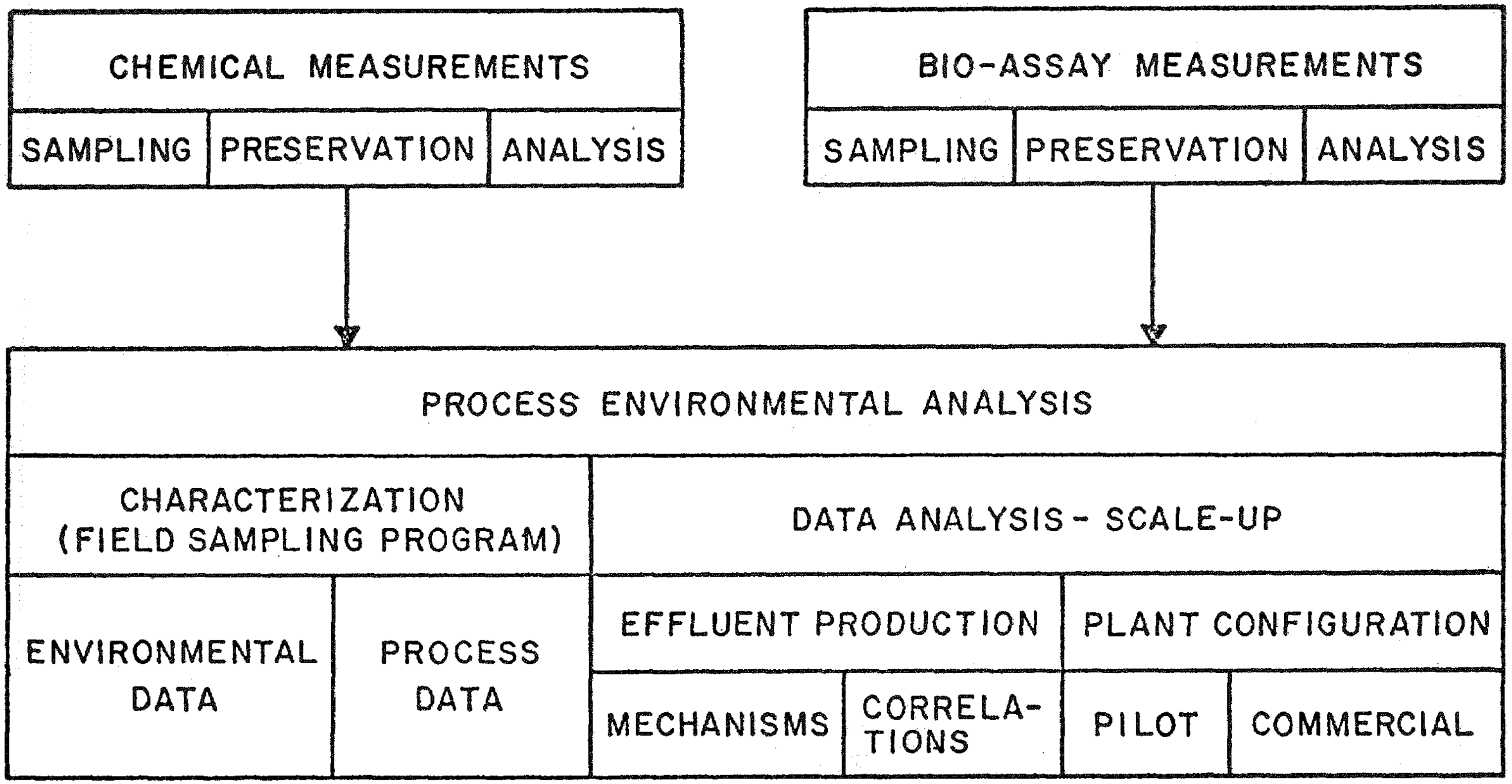

Figure 2. Interaction of Data Acquisition and Process Environmental Analysis for the Generation of Scalable Environmental Characterization Data

Significance of the Engineering Role

Experience to date in the FE program indicates that without early and extensive engineering involvement, significant errors in all three phases of environmental data base generation -- data acquisition, process environmental analysis, and raw effluent treatment analysis -- can occur. A simple example from the CO_2-Acceptor program serves to illustrate the point. For purposes of their conceptual commercial design effort, Conoco and Stearns-Roger projected environmental characteristics of raw CO_2-Acceptor gasifier product gas as shown in Table 1. They used collective experience as the basis for their projection since their work preceded field sampling efforts by Radian Corp. and C-MU. Recently completed extensive engineering analysis of all process and environmental data from the pilot plant reveals a substantially different projection of raw product gas environmental characteristics (see Table 1).* Furthermore, it is apparent from such analysis that a number of weaknesses in selected sampling/analytical methods and/or the synchronization of their application with process-related factors limit the interpretability of the final data base. This is particularly evident in the case of trace elements.

As will be apparent from data presented later in this paper, similar problems of interpretation and projection of pilot-scale environmental data have been identified in the Hygas process; the pattern can be expected to recur at other sites as preliminary data bases evolve to support such investigation. To understand the reasons for such contrasting environmental projections as those shown in Table 1 for CO_2-Acceptor raw product gas, it is necessary to examine raw environmental data first in the context of pilot plant operations and then in relation to projected commercial-scale plant operating practice. Three examples are provided here by way of illustration:

(1) Fate of coal nitrogen during gasification.

(2) Fate of environmental species (e.g., S, N, hydrocarbons) during oxidative pretreatment of agglomerating coals; effect on downstream gasifier environmental characterization.

(3) Effects of recycle systems on process environmental characterization.

FATE OF COAL NITROGEN DURING GASIFICATION

Nitrogen entering the gasification process can be retained by residual solids, or released to product gases in the form of molecular nitrogen, ammonia,

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*Results of this effort are presented in a comprehensive report(1), and are highlighted in a recent DOE symposium presentation(2).

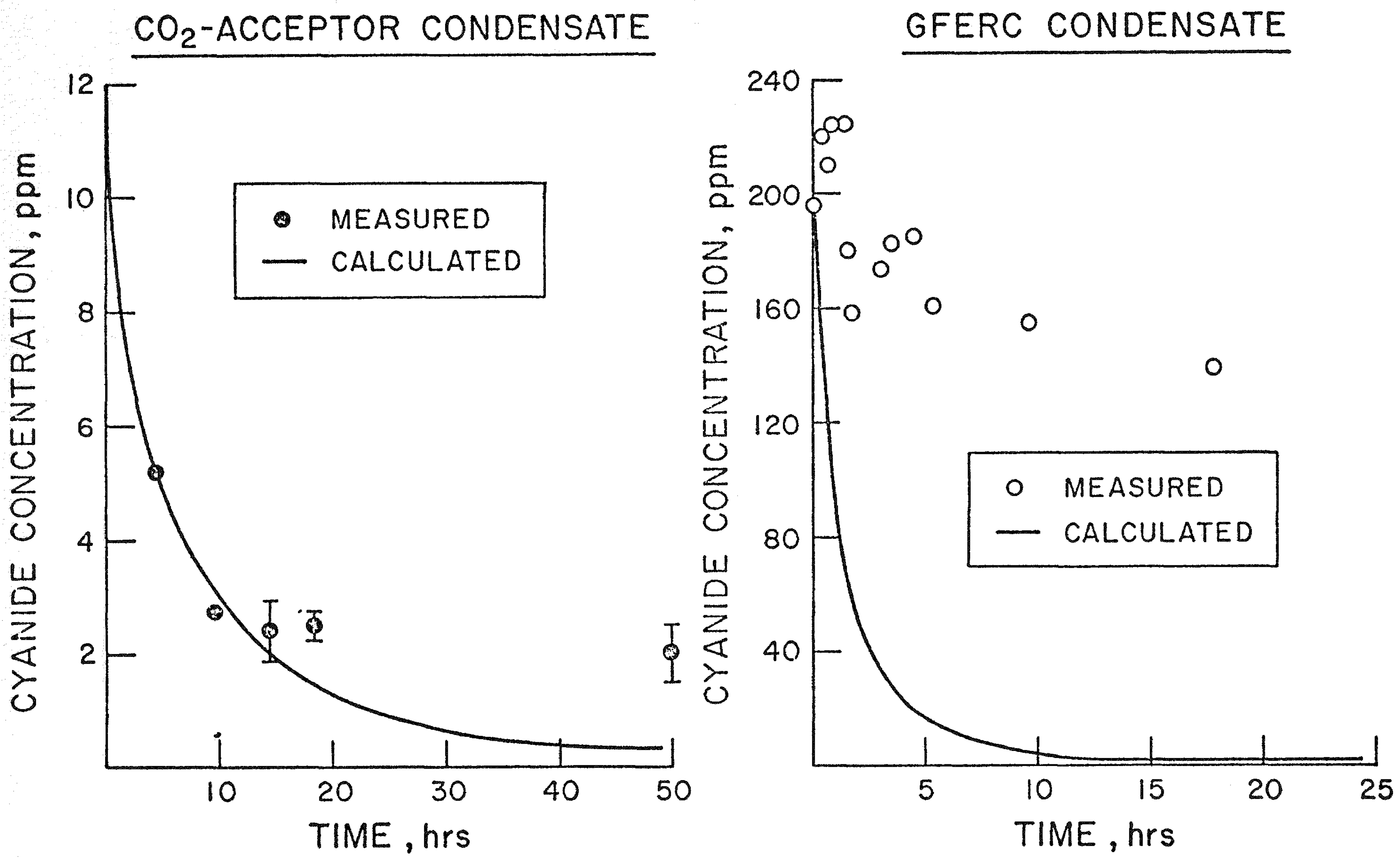

Figure 3. Measured and Calculated Degradation Characteristics of Cyanide in Unpreserved Quench Condensates from the CO_2-Acceptor and GFERC Slagging Fixed Bed Gasifier Systems$^{(4)}$

hydrogen cyanide, or a nitrogen-bearing hydrocarbon. Since substantial amounts of nitrogen are typically employed for reactor purge gas, amounts of molecular nitrogen produced from coal nitrogen cannot be measured directly. However, ammonia, hydrogen cyanide, and nitrogen-bearing hydrocarbons can be measured in product gases and related to nitrogen measured in feed coal and residual solids.

Early reported results of gas phase NH_3 and HCN and solid phase nitrogen measurements suggested negligible HCN production and approximately 50-60 percent conversion of coal feed nitrogen to NH_3. This evidence presumably formed the basis for the CO_2-Acceptor conceptual commercial design figures for NH_3 and HCN presented previously in Table 1. However, further investigation of data acquisition procedures and trends in the data indicated that:

(1) Rapid and significant degradation of aqueous HCN samples occurs unless special precautions are taken for sample preservation.

(2) Measured NH_3 production varies at times significantly, with process operating conditions.

With properly modified preservation and analytical methods, significant HCN production rates are observed in essentially all currently operating gasification systems. As discussed below, NH_3 yields from coal nitrogen appear to vary as a function of coal carbon conversion, at least for high BTU steam/oxygen gasification systems.

HCN Production and Degradation

Time series studies of HCN and SCN^- concentrations in various gasifier quench condensate indicate rapid decomposition of HCN and a corresponding increase in SCN^- with time in the absence of preservation. Examples for CO_2-Acceptor and GFERC slagging fixed bed gasifier condensate are provided in Figure 3(4). Bench-scale reaction studies indicate that polysulfide formed from H_2S in solution reacts with HCN to produce SCN^-; the rate limiting step in the process is polysulfide formation, which can be eliminated through precipitation of sulfide from solution (basis for HCN sample preservation)(5). If bench-scale kinetic data on cyanide decomposition are applied to field measurements at CO_2-Acceptor and GFERC, the results shown in Figure 3 are obtained. In the case of CO_2-Acceptor measured and calculated HCN degradation rates correspond reasonably well; furthermore, measured SCN^- levels correspond closely with projected initial sample HCN concentrations (t=0). By contrast, observed HCN degradation rates in GFERC condensate are only a small fraction of those predicted by bench-scale kinetics. In this case, polysulfide formation kinetics clearly dominate.

Table 1. Effect of Comprehensive Engineering Analysis on the Projection of Commercial-Scale Raw Product Gas Environmental Characteristics for the CO_2-Acceptor Process

Environmental Components in Gas	Projected Commercial-Scale CO_2-Acceptor Raw Product Gas Environmental Characteristics	
	Conceptual Commercial Design[(a)]	PEA Effluent Data Base[(b)]
Sulfur Species		
● H_2S	Determined by $CaCO_3/H_2S$ chemical equilibrium relationships	Determined by $CaCO_3/H_2S$ chemical equilibrium relationships
● COS	Not considered	$\gtrsim$ 2 times equilibrium
Nitrogen Species		
● NH_3	60% of feed coal N	approx. 90% of feed coal N
● HCN	None	$\sim$0.5% of feed coal N
● N_2	23% of feed coal N	Negligible
Trace Species		
● Organics	Not considered	Negligible
● Trace Elements	Not considered	Variable and uncertain, but significant

Notes:

(a) Reference 3.

(b) Reference 1.

Separate studies of the efficiency of HCN removal from raw product gases during water quenching indicate substantial retention of HCN in quenched gas, typically 50 percent of raw product gas loadings(6). Thus, accurate estimation of gasifier HCN production requires both careful attention to immediate preservation of quench condensate samples and matched measurements of HCN content of quenched product gas. Direct analysis of the HCN content of raw product gas prior to quenching represents an attractive alternative strategy, and is now being applied wherever possible(7).

Gasifier NH_3 Production

As illustrated in Figure 4 using CO_2-Acceptor and Hygas data, feed coal nitrogen gasification is a strong function of gasifier carbon conversion, and to a first approximation is independent of coal rank. Data regarding the fate of gasified coal nitrogen is less than clear. A summary of published Hygas steady state period NH_3 yields presented in Figure 5 suggests that the bulk of gasified coal nitrogen is converted to NH_3. However, scatter introduced by data available from periods of self-sustained plant operation costs at least some doubt on this conclusion. Unfortunately, available CO_2-Acceptor NH_3 and coal nitrogen data are also scattered and somewhat suspicious*. Further resolution of the yield rate of coal nitrogen to NH_3 will have to await new results from one or more carefully executed experimental investigations.

The implications of a correlation of NH_3 yield with coal carbon conversion are clear. Although the bulk of pilot plant experience and data may be gained at intermediate carbon conversions with correspondingly low NH_3 yields (the case at Hygas), at minimum proposed commercial design carbon conversion levels of 90 percent, NH_3 yields can be expected to approach 90 to 100 percent.

EFFECT OF OXIDATIVE COAL PRETREATMENT ON PROCESS ENVIRONMENTAL CHARACTERIZATION

In certain processes designed to operate on agglomerating eastern coals, mild pretreatment of the raw coal is required prior to gasification. Pretreatment consists of a partial devolatilization of the coal and an oxidation of the coal surface. As might be expected, material released from raw coal during pretreatment includes varying amounts of environmentally significant species (e.g., S, N, organics, trace metals). Material released from coal during pretreatment is of course unavailable for later release during gasification. As a consequence, events of pretreatment can be expected to alter the environmental characteristics of the gasifier. By way of illustration, three examples of

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*The nature and extent of nitrogen data scatter in the CO_2-Acceptor data base is discussed in detail in reference 1.

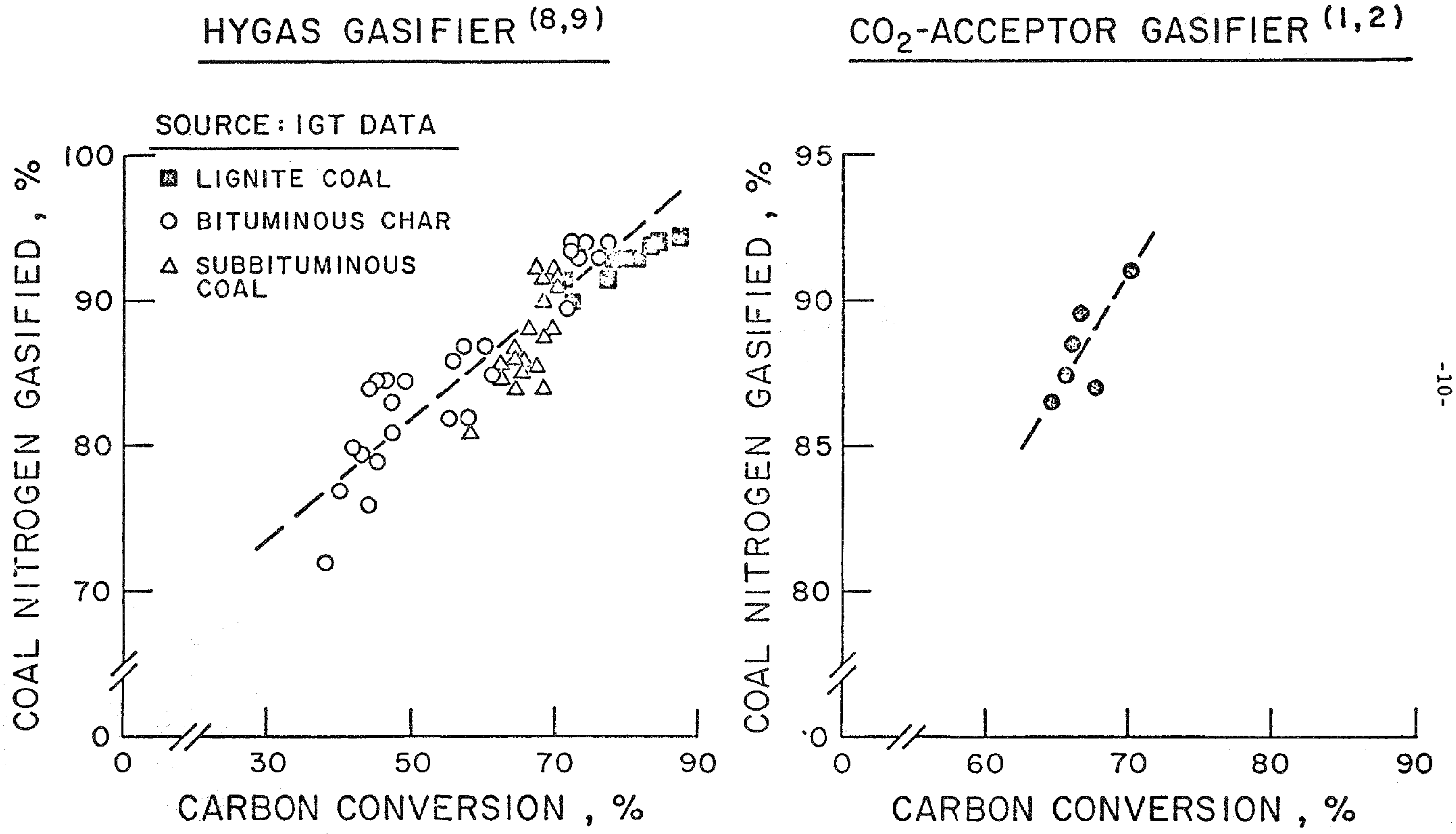

Figure 4. Steady State Hygas and CO_2-Acceptor Coal Nitrogen Conversion as a Function of Gasifier Carbon Conversion

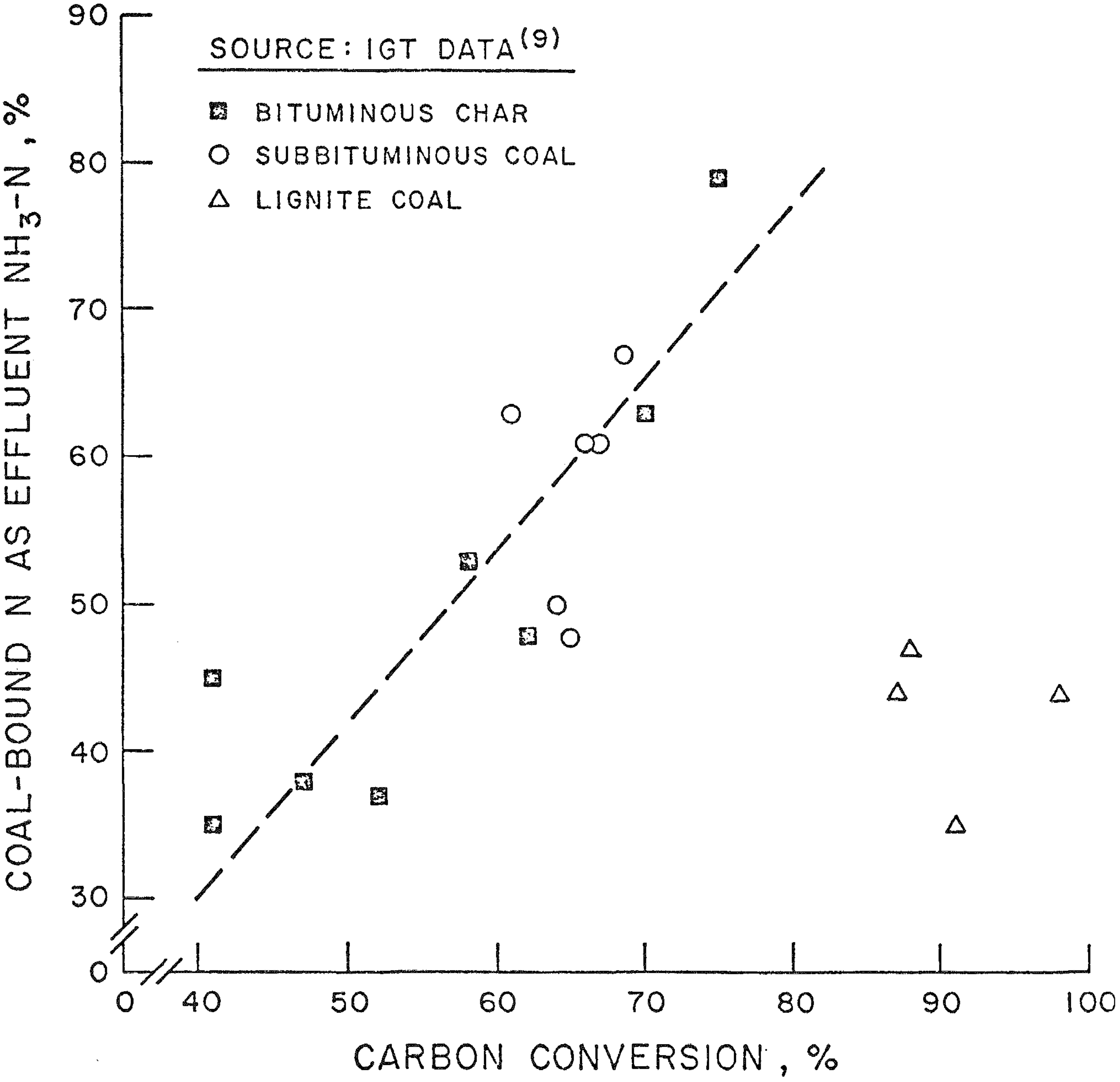

Figure 5. Variation of NH_3-N Yields with Changes in Carbon Conversion in the Hygas Gasifier

pretreater effects on the fate of environmental species are presented here based upon available IGT Hygas data. Data and format presented are drawn from a recently completed comprehensive status report by IGT of its Hygas environmental data base(9)

Influence of Pretreatment on the Fate of Coal Sulfur

As shown in Figure 6, Hygas pretreatment has a significant effect on coal total sulfur; the bulk of the change is seen to occur in the organic sulfur content of raw feed coal. As the severity of pretreatment increases, removal of organic sulfur (about 50 percent of total coal sulfur)* increases. Plant operating experience to date (50-70 percent severity) suggests a 20-30 percent release of coal sulfur at the pretreater with a corresponding 70-80 percent release to raw product gas later during gasification. However, commercial-scale pretreater severities are expected to be substantially lower than pilot plant levels. At a 20 percent severity, sulfur releases at the pretreater may be substantially reduced -- linear extrapolation of current data would suggest about a 10 to 20 percent release. Such a trend obviously would alter the quantity of sulfur released to raw product gas in the gasifier, but it might also alter the distribution of sulfur species (H_2S to COS ratio).

For purposes of commercial-scale environmental projection, it is clearly necessary to know the anticipated severity of pretreatment and to have a data base which describes the effects of pretreatment severity on both the amount of sulfur released at the pretreater and the quantity and composition of sulfur released later during gasification.

Influence of Pretreatment on the Fate of Coal Nitrogen

As shown in Figure 7, effects of pretreater severity on coal nitrogen content follow a pattern similar to that previously shown for coal sulfur. Increasing pretreatment severity increases coal nitrogen releases. While current pretreater practice (50 to 70 percent severity) results in 15 to 45 percent losses of coal nitrogen, linear extrapolation to a 20 percent severity in commercial-scale practice would suggest negligible nitrogen losses. This in turn would suggest substantially higher than measured coal nitrogen releases during gasification. The fate of any incremental nitrogen releases remains unknown at this time.

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*Pretreatment severity here is defined as the percentage reduction in coal volatile matter as measured by standard ASTM proximate analysis.

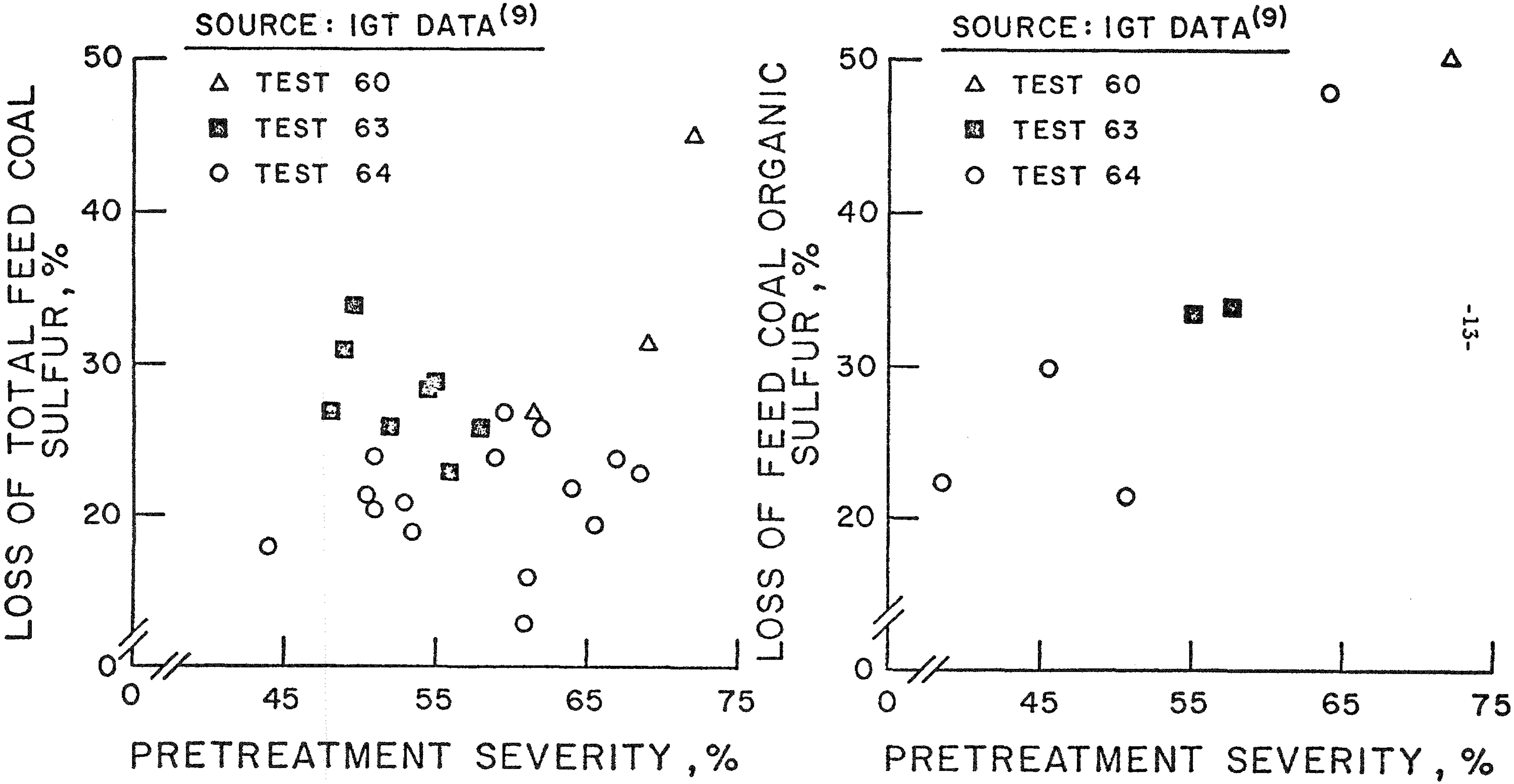

Figure 6. Effect of Hygas Pretreater Severity on the Loss of Total Sulfur and Organic Sulfur from Feed Coal

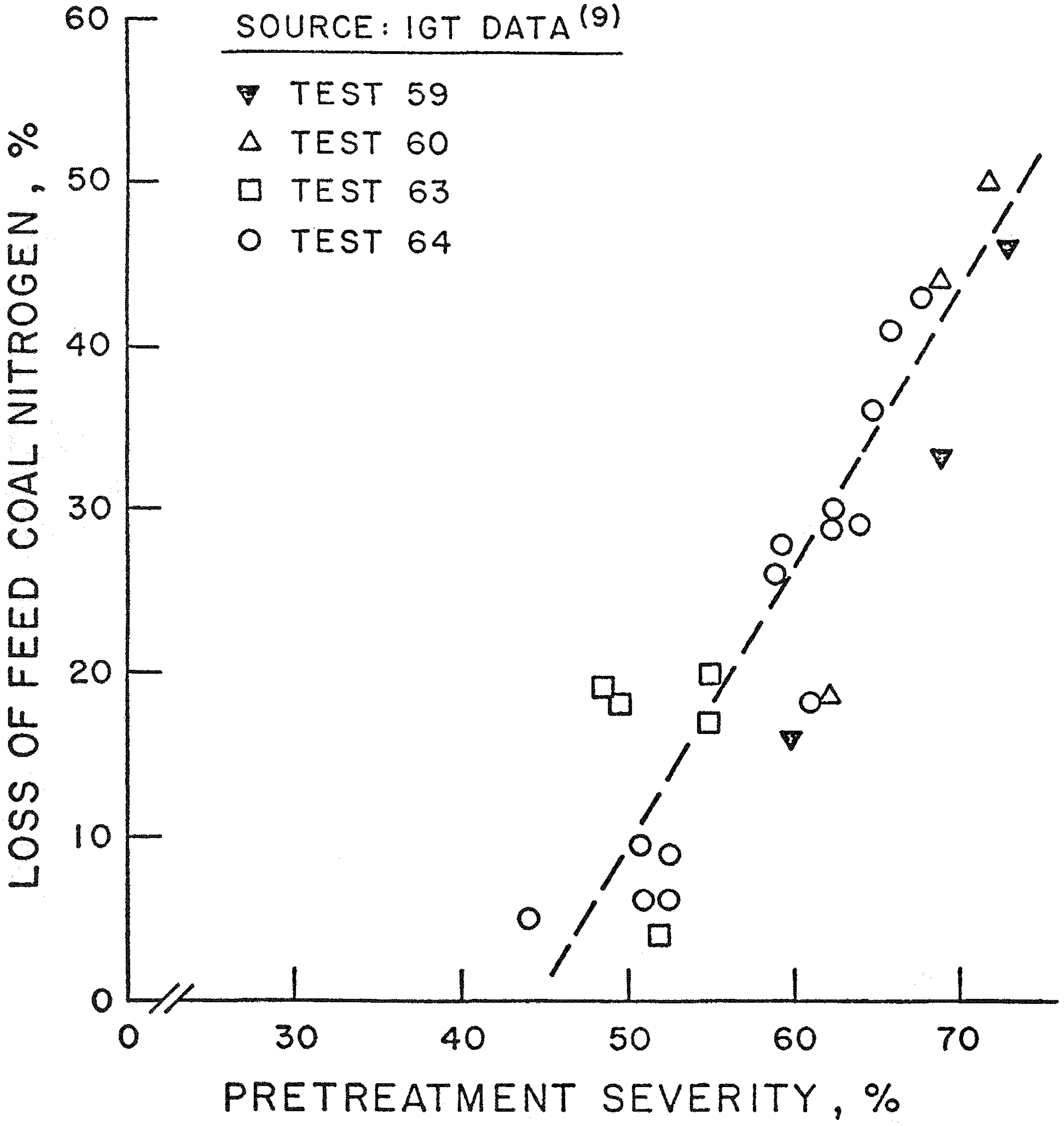

Figure 7. Effect of Pretreatment Severity on the Loss of Coal Nitrogen

Clearly, proper characterization of the fate of nitrogen for a commercial-scale projection requires knowledge of anticipated pretreater severity, an understanding of the relationship between pretreater severity and coal nitrogen loss, and some indication of the products of subsequent nitrogen gasification.

Influence of Pretreatment on the Fate of Phenols and Other Hydrocarbons

Although present data are limited (Figure 8), a significant effect of pretreatment on pretreater phenolic production is suggested. Over a range of 50 to 70 percent severity, phenolic production is seen to vary from about 2 to 6 lbs/ton MAF coal. This compares with gasifier productions of about 3 to 15 lbs/ton MAF coal as measured in cyclone and product gas quench condensate(9). On the basis of a commercial-scale pretreater severity, linear extrapolation of present data would suggest negligible phenolic production in the pretreater. Extensive C-MU studies of phenolic production patterns in coal gasification indicate that at least a portion of former pretreater phenolic production would be diverted to the gasifier, thereby altering, perhaps significantly, phenolic production patterns there(10).

Although direct data are not yet available, it is anticipated that at least gasifier oil production rates and perhaps composition are significantly affected by coal pretreatment severity. To the extent that future data bear this out, it suggests that pretreater performance and its effects on oil characterization must be taken into account in the interpretation and scaling of oil data for projection of commercial-scale environmental impacts.

EFFECTS OF RECYCLE STREAMS ON PROCESS ENVIRONMENTAL ANALYSIS

Although recycle streams can have a significant influence on the fate of materials in a process, their effect is usually transient, diminishing as a process approaches steady state operation. If circumstances interfere with the attainment of steady state, recycle loops complicate both process and environmental analysis.

Example of a Gasification Recycle Stream

As shown in the simplified flowsheet in Figure 9, Hygas represents an excellent example of a gasification process with a major recycle stream. By-product oil (toluene in the pilot plant) is mixed with feed coal to form a slurry which can be pumped under pressure to the gasifier. After reaching the

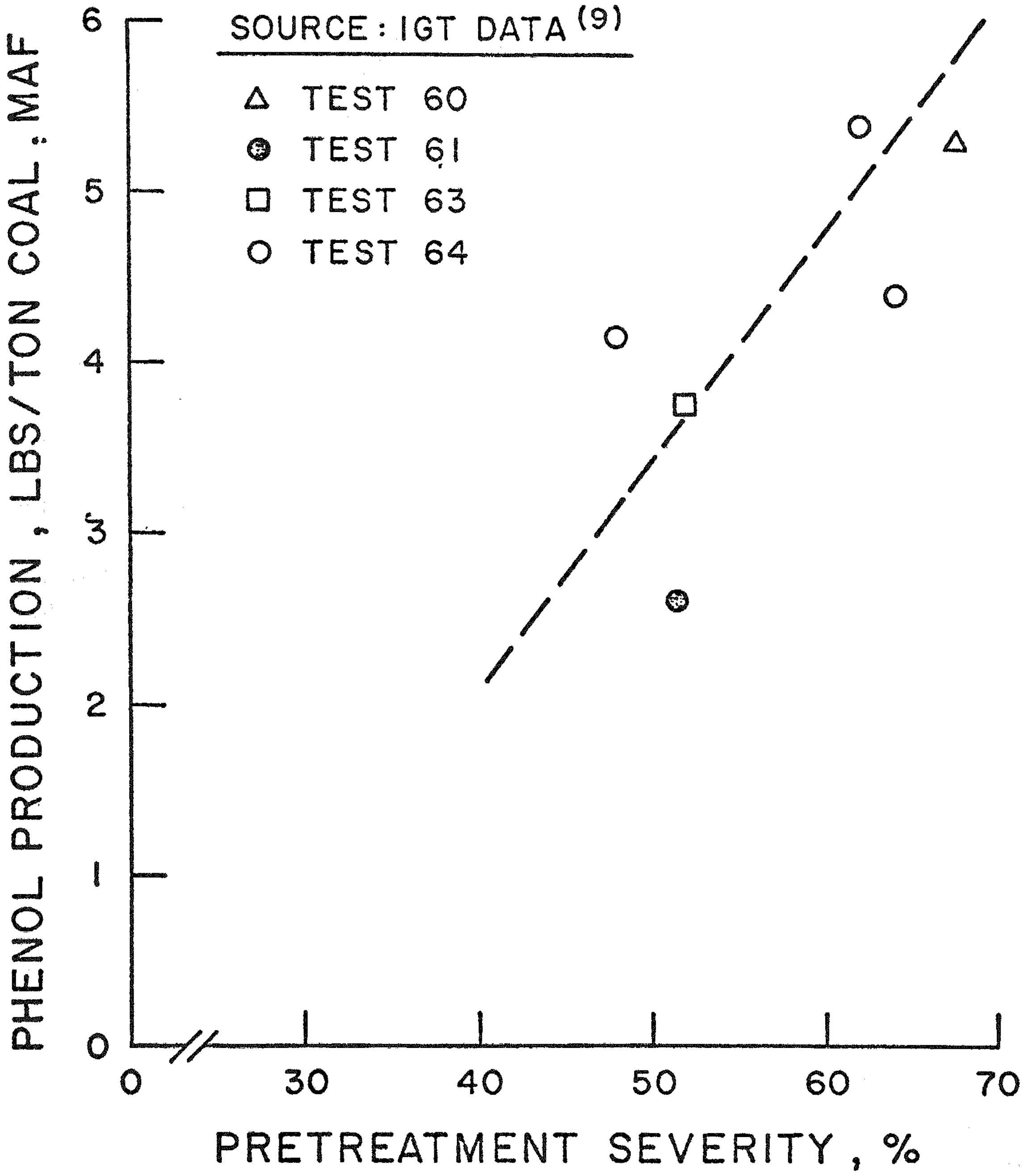

Figure 8. Effect of Pretreater Severity on the Production of Phenols in the Pretreater

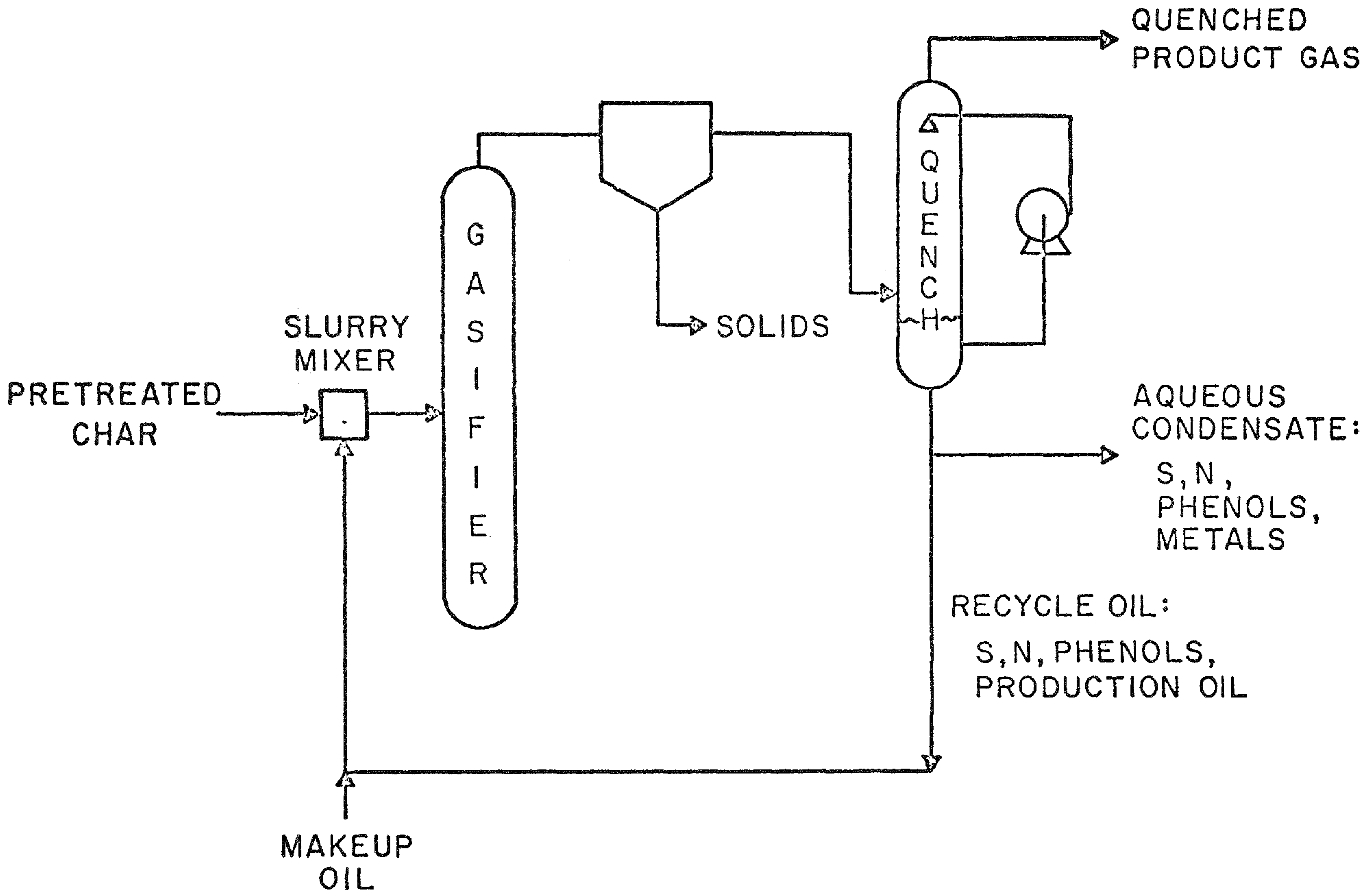

Figure 9. Simplified Hygas Schematic, Emphasizing the Oil Recirculation System

gasifier, the oil is vaporized, withdrawn from the gasifier, condensed and recycled.

In the commercial-scale design, the composition of the oil recycle loop eventually equilibrates. Recycle oil is withdrawn at the same rate that fresh oil is produced in the gasifier; recirculating oil saturates with respect to a range of soluble components. By contrast, the oil recycle loop at the pilot plant never does equilibrate. Due to various leaks in the system, there is a net loss of oil with time which must be compensated for by make-up additions of toluene. Under these conditions, recirculating oil does not reach saturation with regard to various oil soluble components.

Impact on Environmental Analysis

In the case of Hygas, most of the species of interest in environmental characterization efforts are to at least some degree soluble in recycle oil, notably HCN, H_2S, COS, phenolics, toxic organics, and gasifier oil production. As long as the recycle oil stream remains unsaturated, a portion of the environmental species produced in the gasifier will report to the oil rather than to either the quench water or the quenched product gas -- the traditional points of environmental measurement. Since recycle oil would be saturated in a commercial operation, gasifier effluent production is underestimated by a pilot plant data base derived strictly from quench water and quenched gas analysis. The extent of the possible bias can be illustrated by considering the partition coefficient for phenol between toluene (the bulk component of Hygas pilot plant recycle oil) and water. At a pH of 7.5 phenol is approximately 3.75 times as soluble in toluene as it is in water. Dropping the pH to 1.0 reduces this factor to about 2.6. Since the quench station in the Hygas pilot plant (see Figure 9) operates at a pH of about 8.5, fresh phenol production is about 4 times more likely to report to recycle oil than to quench water.

The tendency for phenol to report to recycle oil is borne out both by direct measurement of the phenolic content of the oil (see reference 9) and collection and measurement of quench condensate under different pH conditions. Data for the latter case are summarized in Figure 10. Measured phenol production can be seen to rise sharply with decreasing quench water pH, an indication of the significant absorptive capacity of recycle oil at plant operating pH.

It is interesting to note that, regardless of the pH used for quenching, phenol production in Figure 10 varies over a wide range. While it is premature to draw conclusions regarding precise causes, this variation has been observed to correlate with certain variations in gasifier process conditions. Variations in production rate and their correlation with process operating conditions are discussed extensively in a current Hygas report(9),

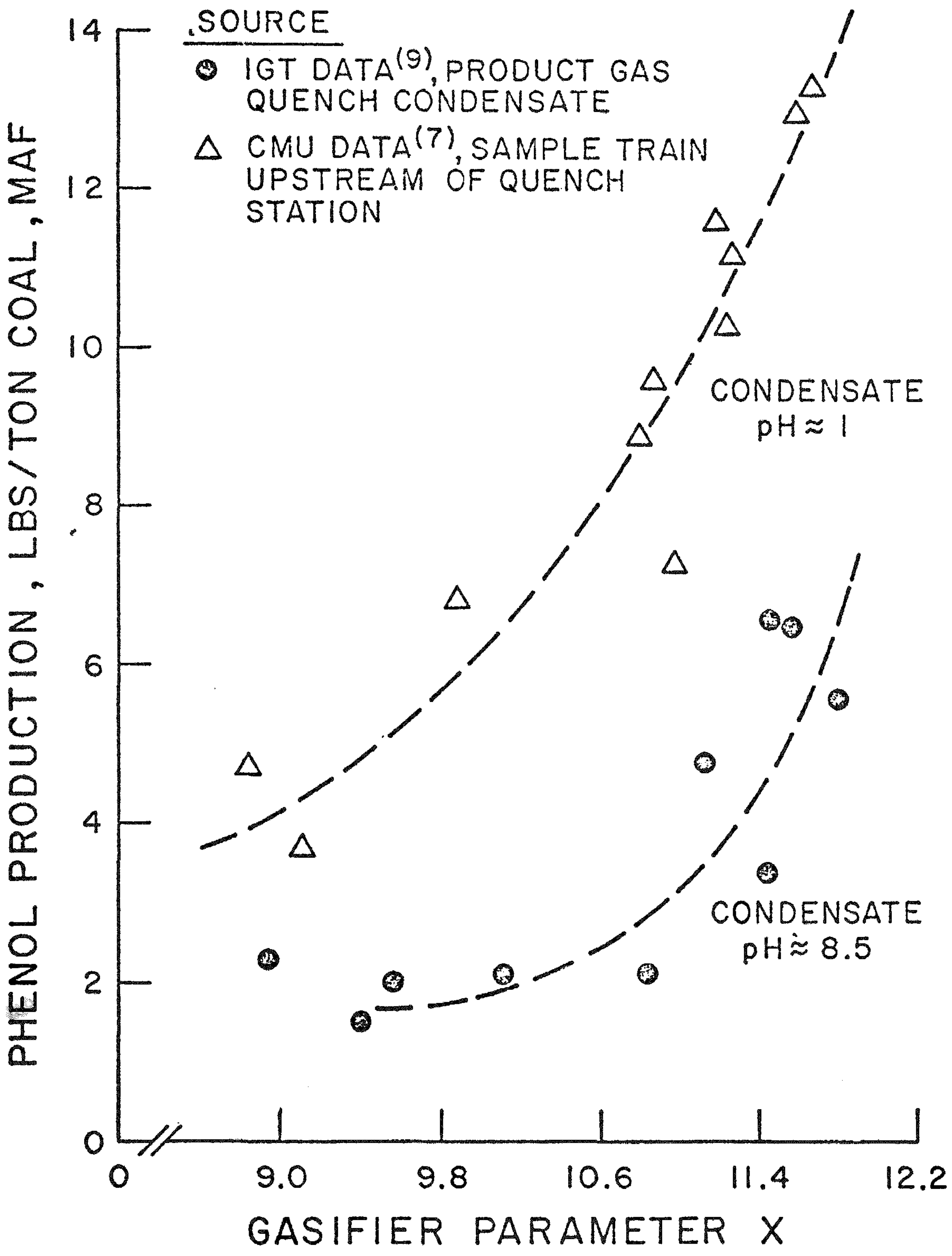

Figure 10. Effect of Gasifier Conditions and Condensate pH on Aqueous Measurements of Gasifier Phenol Production

and are the subject of intense continuing field investigation at the pilot plant.

Implications for Environmental Characterization

Where significant unsteady recycle streams exist -- typically in pilot-scale systems -- special provisions must be made in the strategy for environmental data acquisition efforts to insure the scalability of pilot-scale data. Special provisions must also be made in subsequent process environmental analysis efforts to insure proper interpretation of pilot data and the formulation of accurate scaling relationships for commercial projection. Finally, treatability studies based on raw effluent discharges taken from systems with unstable recycle streams must be suitable corrections and/or allowances for the non-representativeness of plant effluent samples.

FUTURE DIRECTIONS FOR ENGINEERING

During the past three years engineering has contributed significantly to the establishment of a firm basis for the construction of environmental data bases in coal gasification systems. In the course of this effort, useful but limited information has been generated from which comprehensive environmental assessment could be carried out by the life science community. The major role for engineering in the future must be implementation of developed environmental characterization expertise in support of the broadening of the available coal gasification environmental assessment data base. Specific activities include the following:

(1) Toxic substance characterization. Work jointly with the life science community to establish scalable data bases on trace, potentially toxic substances in coal gasification systems.

(2) Control technology assessment. Work jointly with the environmental assessment community to scalably determine the fates of major and trace environmental species in treatment.

(3) Environmental assessment support. Perform the necessary scaling of pilot plant data for projection of an appropriate commercial-scale data base for comprehensive environmental impact analysis.

There are limits, to be sure, to the environmental characterization which can be expected from current PDU and pilot-scale systems. It will take the collective wisdom of engineering and life science to establish these limits and to define future demonstration-scale environmental characterization objectives accordingly.

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