

**Session III: ENVIRONMENTAL ASSESSMENT:  
GASIFICATION AND INDIRECT LIQUEFACTION**

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ENVIRONMENTAL TEST RESULTS

FROM

COAL GASIFICATION PILOT PLANTS

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Environmental awareness and the world oil situation are having a profound impact on the U.S. Electric Power Industry. "Environmental acceptability" has been redefined and it is emerging as one of the major criteria for selection of a power generation process to satisfy increasing load demand or to replace retired units. Furthermore, the fact that the cost of fuel has risen in real terms dictates that more fuel efficient plant configurations will be deployed. Fuel efficiency and environmental tolerability come only at the expense of increased monetary cost.

These fundamental changes certainly are creating problems for the power industry but they are also creating opportunities for new and more appropriate power generation processes.

EPRI has high expectations that combined cycle power systems fueled by gas from coal will be cleaner and more efficient than the competing processes for equivalent capital cost. Advantages accrue to these Gasification-Combined Cycle (GCC) systems primarily from the relative ease of cleaning fuel gas, the benign nature of the waste products, and the inherent and proven high thermodynamic efficiency of the combined cycle configuration.

These and other advantages will be discussed. Coal gasification processes will be identified which most effectively capitalize on these advantages. Environmental test results on these processes will be summarized. Finally, the plans for commercial scale demonstration of a GCC system will be reviewed. This demonstration will be a critical milestone since no technology can be considered to be a real option until it has been operated at an appropriate scale.

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INTRODUCTION

The combined circumstances of rapidly escalating oil prices, reduced availability of oil and natural gas, strict plant emission standards and the prospect of continued delays in nuclear implementation plans, provide the electric power industry with urgent incentives to develop economically competitive and environmentally acceptable new methods of power generation based on our most plentiful fossil fuel resource - coal.

Of all these motivations, it is probably the environmental aspects which constitute the major incentive for coal gasification based power systems, since without the requirement for post-combustion clean up of the flue gases it would clearly be less costly to simply burn coal directly.

Coal gasification based systems offer distinct environmental advantages over conventional direct coal fired plants with flue gas clean up, since emission forming constituents are removed prior to the combustion process. When coupled with combined cycle power generation the resultant Integrated Gasification Combined Cycle (IGCC) plants will be more efficient and use less water than direct coal fired units. Studies show that such IGCC plants when designed to current emission standards and using currently commercial combustion turbines are economically competitive with direct coal firing. If emission standards become more restrictive the competitive position of IGCC technology will be further enhanced. There are also considerable prospects for future improvements in both coal gasification and combustion turbine technology, which will enable the industry to resume its historic learning curve for more efficient less costly systems.

EPRI CLEAN GASEOUS FUELS PROGRAM

The overall goal of the EPRI Clean Gaseous Fuels Program is to develop economically competitive and environmentally acceptable coal gasification-based generating systems.

The principal technical objective of the EPRI program is to design and operate an integrated Texaco entrained gasification-combined cycle demonstration plant of about 100 MW by 1985. A second demonstration plant based on another gasifier is also planned. The program also includes work to improve gasifiers, gas clean-up technology, heat recovery boilers, fuel gas combustors and other components of gasification-based generating systems.

Coal gasifiers react coal, steam and air or oxygen to produce a gaseous fuel, primarily carbon monoxide and hydrogen. The sulfur in the coal is converted to hydrogen sulfide ( $H_2S$ ), which can be removed from the gas and converted to elemental sulfur by processes currently used widely in the natural gas, chemical and petroleum industries. The mineral matter is withdrawn primarily as ash or slag from the gasifier or from the gas stream as part of the gas cleaning process. The coal nitrogen is converted either to ammonia, which can readily be scrubbed from the gas, or to nitrogen itself.

Gasifiers are also important components of other coal conversion technologies of potential benefit to utilities. The CO-H<sub>2</sub> product gas can be catalytically converted to methanol for use in peaking or intermediate service. Gasifiers can be used to provide hydrogen for use in Exxon, H-Coal or SRC coal liquefaction plants by gasifying the liquefaction residues.

#### ECONOMIC ATTRACTIVENESS OF GCC PLANTS

EPRI studies show that integrated gasification combined cycles using commercially available combustion turbines (2000°F inlet temperature) and based on Texaco or BGC/Lurgi slagging gasifiers are competitive with conventional coal-fired power plants with stack gas cleanup. Table 1 shows a performance comparison between conventional coal firing and gasification-based power systems. The data presented in this table reflect 1978 environmental control regulations. Cost estimates are included for cycles with advanced high temperature turbines to illustrate the further performance improvement potential of this technology. As environmental control regulations become more stringent, the economic advantages of gasification combined cycle (GCC) power plants will increase markedly. Table 2 shows estimated costs for more stringent projected mid-1980s standards. GCC systems offer better efficiency, lower emissions, reduced water consumption and land requirements, less fuel and chemicals consumption, and reduced solid waste volume. The solid waste from the Texaco, BGC/Lurgi slagger, and Combustion Engineering gasifiers is in the form of extremely inert slag which should be readily disposable at lower cost than solid waste from a coal-fired plant.

Gasification may also offer fuel for retrofit to existing gas and oil-fired boilers, combined cycles and combustion turbines. Gasifiers might be installed in an existing plant or in some cases remotely, with fuel distributed by pipeline. Gasification may allow repowering existing boilers with combustion turbines to reduce the heat rate and provide increased generation capacity in convenient increments at an existing site with probably reduced permitting periods.

#### ENVIRONMENTAL ADVANTAGES OF GASIFICATION-BASED POWER PLANTS

The potential environmental advantages of gasification-combined cycle power plants over direct coal fired plants with flue gas cleanup are summarized in Table 3. GCC plants offer better resource utilization - more kilowatts per ton of coal mined, less water usage per kilowatt, and less land since sludge disposal is not required. They are also capable of achieving markedly reduced emissions compared to direct coal fired units. Each of these aspects is discussed in more detail below.

##### Resource Utilization

GCC systems utilizing currently available combustion turbines offer a minor but measurable improvement in heat rate over conventional coal plants with scrubbers. However, better efficiencies projected for GCC plants with higher temperature turbines currently being developed, i.e., machines capable of operating at firing temperatures above 2000°F upwards to 2600°F, should result in significant reductions in coal use versus direct coal-based units of similar capacity as reflected in the range of coal consumption estimates for GCC plants in Table 3.

Table 1 SUMMARY OF PRESENT AND PROJECTED  
GCC SYSTEM PERFORMANCE  
1978 FEDERAL EMISSION CONTROL REQUIREMENTS

	<u>Coal Fired Plant</u>	<u>Texaco GCC 2000°F Turbine</u>	<u>Texaco GCC 2600°F Turbine</u>	<u>BGC Slagger GCC 2600°F Turbine</u>
Heat Rate, Btu/kWh	9900	9500	8460	7920
Capital Require- ment, \$/kW	900	860	830	690
30-Year Levelized Cost of Elec- tricity, mills/kWh	57.5	51.1	47.9	41.3

Basis: mid-1978 dollars; high-sulfur Illinois coal; coal cost \$1.00/million  
Btu; 70% capacity factor.

Table 2 ECONOMIC COMPARISON OF TEXACO GASIFICATION-BASED  
 POWER SYSTEMS USING CURRENT (2000° F) COMBUSTION TURBINES  
 WITH CONVENTIONAL COAL-FIRED STEAM PLANTS  
 EMPLOYING WET SCRUBBING OF STACK GASES.

	1978 Federal		Projected mid-1980's	
	<u>Emission Controls</u>		<u>Emission Controls</u>	
	<u>Coal Fired</u>	<u>Texaco GCC</u>	<u>Coal Fired</u>	<u>Texaco GCC</u>
Heat Rate, Btu/kWh	9900	9500	9950	9680
Capital Requirement, \$/kW	900	860	1180	900
30-Year Levelized Cost of Electricity, mills/kWh	57.5	51.1	69.0	52.9

Basis: mid-1978 dollars; high-sulfur Illinois coal; coal cost  
 \$1.00/million Btu; 70% capacity factor.

<u>Emission Controls</u>	<u>1978</u>	<u>mid-1980's</u>
sulfur	85% removal	95% removal
particulates	0.03 lbs/10 <sup>6</sup> Btu	0.02 lbs/10 <sup>6</sup> Btu
NO <sub>x</sub>	0.6 lbs/10 <sup>6</sup> Btu	0.2 lbs/10 <sup>6</sup> Btu
waste water	---	zero discharge
coal ash	---	special handling

Table 3: RELATIVE ENVIRONMENTAL EFFECTS/RESOURCE REQUIREMENTS

1000 MW POWER PLANTS

	<u>PC Boiler with Wet Scrubber</u>	<u>GCC Plant</u>
Coal Consumption - lbs./kWh	0.80	0.64-0.77
Limestone Required - lbs./kWh	0.12-0.15	-
SO <sub>2</sub> Emissions - ppm	80-400	50-225
NO <sub>x</sub> Emissions - ppm	300-500	40-90
Particulate Emissions - lbs./10 <sup>6</sup> Btu	0.03	<0.02
Make-up Water - gal./kWh	0.6-0.65	0.45-0.55
Land Required - acres	1200-2400	200-500

Note: Solid wastes, consisting of sulfur and inert slag, produced in GCC plants in significantly lower quantity than troublesome scrubber sludge produced in coal fired unit.

Also, while power produced in conventional coal plants is derived from steam turbine generators, a large part of the electricity output of GCC plants is developed directly from fuel combustion energy with the remainder being produced in a steam cycle. Accordingly, make-up water requirements (by far the major part of which supports the cooling water system for the steam turbine generator condenser) are significantly less in GCC plants.

#### Sulfur Emissions and Disposal Land Required

The range of sulfur emissions cited in Table 3 is based on single stage sulfur removal from high and low sulfur coal based systems for both the coal fired boiler and gasification combined cycle power plant. Sulfur emissions can be reduced at additional expense by adding a second stage of stack gas scrubbing to the coal fired boiler plant or by several mechanisms in the coal gasification based plant. EPRI economic evaluations have shown that incremental sulfur removal from gasification based systems is less expensive than from coal fired boiler plants. Additionally, gasification based systems will produce elemental sulfur and inert slag, potentially saleable byproducts, while the coal fired boiler produces a much larger volume of waste sludge which contributes significantly to the additional disposal land required for the latter option.

#### NO<sub>x</sub>

In coal or oil combustion, NO<sub>x</sub> is produced by two mechanisms, the oxidation of nitrogen in the fuel (fuel NO<sub>x</sub>), and oxidation of nitrogen in the combustion air (thermal NO<sub>x</sub>). Fuel NO<sub>x</sub> can account for up to 75% of the total NO<sub>x</sub> emissions from a coal fired plant. This is not the case with coal gasification based power plants because the coal-bound nitrogen leaves the gasifier as either N<sub>2</sub> or NH<sub>3</sub> which is scrubbed out in all commercial or proposed processes. The issue then becomes one of controlling thermal NO<sub>x</sub> by limiting temperature via steam/water injection and/or phased combustion techniques. At Texaco's Montebello pilot plant, EPRI has burned medium Btu gas in existing and developmental gas turbine combustors with promising results<sup>1</sup> (at atmospheric pressure). A 70 to 80% reduction in NO<sub>x</sub> emissions over conventional pulverized coal fired power plants should be achievable with gasification-combined cycle power plants.

#### Particulates

There will be for various reasons, minimal particulate emissions to the atmosphere from gasification based power plants. Gasification systems, specifically those supported by EPRI, propose at least two sequential intensive gas scrubbing steps. Isokinetic sampling at Texaco's Montebello pilot plant and the Westfield Development Centre of the British Gas Corporation has failed to detect any significant particulates after scrubbing. For combined cycle systems, particulate levels in gas turbine fuel must be minimized to prevent erosion or deposition on gas turbine blades. For mechanical integrity of these systems, if for no other reason, particulates will be minimized.

Soot formation can occur in pulverized coal fired systems and oil fired systems, especially during transients or upsets. Soot formation is not expected to be a problem with coal gas based systems because of the burning characteristics of the gas and better controllability of the fuel/air ratio.

## Non-Leachable Slag

EPRI actively supports 3 gasifiers, all of which are slagging gasifiers, that is, they are operated above the melting temperature of the coal mineral matter so it is extracted in the form of a glassy inert frit. This slagging mode of operation has two distinct advantages:

1. Operating at higher temperature speeds the gasification reactions leading to greater throughput per reactor and reduced waste of reactants (e.g., gasification steam).
2. Slag is environmentally more acceptable than ash.

The EPA proposed Waste Extraction Procedure (among several others) has been performed on the slags produced in all three gasifiers which EPRI supports, BGC/Lurgi Slagger, Texaco, and Combustion Engineering. Although the slags were produced from a variety of coals, the maximum concentrations of toxic elements in the leachate, or often the minimum limits of detection with the available equipment, are shown in Table 4. In no case did the trace element concentration in the leachate approach the EPA proposed criteria for hazardous wastes which is 100 times the drinking water standard. When more sensitive detection equipment was used, the actual concentrations were most often much lower than those shown in the table. Those elements with proposed limits greater than 5000 ppb have been omitted from the table since in all cases, their concentrations in the leachate actually comfortably met the drinking water standard.

One preliminary comparison has been made between a gasifier slag and fly ash from a coal fired boiler based on coals with similar ash compositions. This effort was conducted by Oak Ridge National Laboratory under contract to EPRI and examined the leachates on solid wastes from a conventional wet bottom slagging boiler and the Combustion Engineering pilot plant gasifier. The fly ash leachate generally had 10 to 1000 times greater concentrations of toxic elements than the gasifier slag leachate (the narrowest margin was 2 times). The slag from slagging gasifiers therefore appear to be environmentally tolerable, certainly more so than fly ash.

## GASIFIER SELECTION FOR ELECTRIC POWER APPLICATIONS

Coal gasification is almost as old as the industrial revolution itself, serving a wide variety of industrial applications from steel, refining, chemicals, to fuel and power production. Perhaps it is for this reason there are so many coal gasification processes currently under development. A recent Oak Ridge National Laboratory survey lists almost 100 such projects.

A first priority at the outset of the EPRI gasification program was the establishment of criteria for selection of those processes most likely to meet the requirements of the power industry. Coincidentally, objective criteria were required to evaluate the status of process development for each concept and to assess the risk and benefit involved at each scaleup stage. The attached Table 5 summarizes EPRI Program Criteria for scaleup to the demonstration size of 1000 tons/day of coal per unit, a size judged sufficient for subsequent commercial deployment.

The electric power industry emphasizes the need for plant reliability and availability. Therefore, simplicity of design with inherent ease of maintenance is very desirable. The preferred gasification process should be

Table 4 GASIFIER SLAG LEACHING TESTS

	Proposed EPA Limit ppb	Gasifier Slag Leachates ppb
As	5000	< 200
Cd	1000	< 10
Pb	5000	< 140
Mn	5000	< 250
Hg	200	< 2
Se	1000	< 80
Ag	5000	< 20
Cr	5000	< 20

Table 5 CRITERIA USED IN COAL GASIFICATION  
TECHNOLOGY SELECTION FOR SCALE UP  
TO DEMONSTRATION SIZE (=1000 TPD COAL)  
IN THE ELECTRIC POWER INDUSTRY

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- Simplicity
  - Feedstock flexibility
  - Complete carbon conversion
  - Absence of troublesome byproducts
  - Compatibility with power generation requirements
  - Existence of an operating pilot plant of greater than 100 tpd coal capacity
  - Proof (direct experimental evidence) of all essential aspects of the process with regard to the above criteria including waste heat recovery and gas clean up
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flexible with regard to coal feed properties and should be able to convert all the carbon to gas. Incomplete conversion or the formation of byproduct tar gives rise to additional processing complications, disposal problems and the potential for greater environmental intrusion. The process must also be compatible with the power generating system needs. This implies a rapid response rate for ease of load change, a wide operating range, and a relatively constant heating value of the product gas throughout the operating range and during transients. For scaleup to demonstration size, all essential aspects of the process should have been experimentally proven on a large pilot plant of 100 tons/day capacity (so that eventual scaleup is less than tenfold). Since the gasifier is only one part of a large system, such a pilot plant should also verify the technical concepts for the waste heat recovery and gas clean up systems.

When these criteria of simplicity, flexibility, cleanliness, etc. are examined against the known characteristics of the three main types of gasifier - moving bed (both dry ash and slagging), fluid bed and entrained systems, it is clear that entrained systems come closest to meeting the desired criteria. Coincidentally three such systems - the Texaco, Shell-Koppers and Combustion Engineering, have each progressed to an advanced state of development and pilot plants greater than 100 tons/day coal capacity are currently being operated for each of these technologies. Each of these developments is able to draw on a background of commercial gasification experience, and each of these organizations plans to scale up the pilot plant to commercial size demonstration units of about 1000 tons/day coal capacity.

Each of these three entrained systems offer distinct environmental advantages in their demonstrated complete carbon conversion, production of a dense inert slag, and absence of tar and other troublesome byproducts.

The currently commercial Koppers-Totzek process has similar environmental advantages although low throughput, as yet incomplete carbon conversion and atmospheric pressure indicate higher costs than the other three entrained systems referred to above.

The current commercial Lurgi moving bed gasifier operates with dry ash removal, and excess steam is injected at the bottom to keep the ash below slagging temperature. This excess steam requirement reduces the thermal efficiency and produces large volumes of contaminated water which require treatment. The British Gas Corporation (BGC) is developing a slagging version of the Lurgi gasifier at Westfield, Scotland. By operating at the higher slagging temperature, essentially only the steam for the gasification reaction is required. The steam consumption and overall efficiency is greatly improved, and the waste water treatment requirements markedly reduced.

Both dry ash and slagging versions, being countercurrent devices, operate at lower outlet temperatures and the outlet gases thereby contain tars, oils and phenols. The slagging version provides a means for their subsequent gasification by injection into the slagging region, so no net tar production will result. Lurgi is also working on various recycle schemes to consume the tars and liquors.

The existence of tars does create additional processing and increased safety and housekeeping requirements. However, such a choice can be justified if the overall economics justify the extra costs for environmental acceptability. Processes operating in the slagging region do offer the opportunity

for recycle and consumption of streams with fuel value, and a means of recycle of contaminated water streams (perhaps with coal added as a slurry) so as to capture the minerals in the slag.

The only currently commercial fluid bed gasifier, the Winkler, has historically suffered from four problems - feeding caking coal, tar production (with bituminous coals), high carbon in the ash, and inability to consume fines. The 'U' Gas and Westinghouse small pilot plants (< 1 ton/hour) seem to have been able to solve the caking coal and tar production problems at least in short runs. By operating with a specially designed ash - agglomerating zone at the bottom, ash low in carbon has been observed, however, full consumption of fines has yet to be demonstrated. With the smaller scale of current experimentation, we judge the scale-up risks, particularly with the ash agglomerating zone, to be greater than with the entrained systems. In addition there is still some concern as to whether tar formation can be avoided during the load change and start up conditions expected for a gasifier operating in a power plant.

#### EPRI TEST RESULTS FROM COAL GASIFICATION PILOT PLANTS

The tests conducted to date on coal gasification pilot plants give reason for optimism that environmentally acceptable commercial power plants can be designed to economically meet current and proposed emission standards. However, it must be admitted that in many cases the configuration of the pilot plants and the short run lengths inevitably associated with pre-commercial facilities, do not lead to results directly translatable to larger continuously operating plants with full economic use of recycle steams

At EPRI the overall program is aimed at obtaining process and environmental data on several gasification processes judged to be at a stage of development where commercial deployment can reasonably be projected in the 1980's. These studies are planned, wherever possible, at larger pilot plants (e.g., BGC/Lurgi at Westfield, Texaco at Oberhausen, and Combustion Engineering at Windsor, Connecticut) during runs of sufficient length to accommodate appropriate recycle of process streams.

Comparison of the environmental impact of various coal technologies in the trace element area is particularly difficult.

Coal is variable, not only from mine to mine in a large deposit, but even within a given mine, particularly with regard to variation in the mineral matter content.

To obtain consistent comparisons of direct coal firing, fluid bed combustion and coal gasification presents a great challenge requiring an extremely rigorous set of long term tests on the technologies with careful monitoring of feedstocks. Too often comparisons are made with different coals, unrepresentative plants, short runs, etc.

EPRI has supported and is supporting test programs on the BGC/Lurgi, Combustion Engineering and Texaco technologies. We are also working with Shell-Koppers. All of these processes produce the ash as a dense slag and offer recycle opportunities.

## BGC/Lurgi Slagging Gasifier

Being a slagging gasifier, the BGC/Lurgi Slagger produces all the coal mineral matter as an inert glassy frit. Under the DOE's high Btu demonstration program, tests on U.S. coals were conducted at BGC's Westfield pilot plant to determine performance and to characterize emissions. Based on the slag leaching test results, the EPA in Ohio (proposed site of the Demonstration Plant) has agreed that the slag is a non-hazardous waste.

The Slagger is a countercurrent moving bed gasifier, and therefore tars are present in the raw product gas. As indicated by the Kosovo tests (the subject of a paper to be presented later in this meeting), the presence of tars dictates that a great deal of attention must be paid to plant design and procedures to prevent worker exposure to these compounds. The Slagger can in all cases easily accommodate complete gasification (destruction) of these tars as successfully demonstrated under the EPRI test program (on Pittsburgh No. 8 coal) at the Westfield 350 tpd pilot plant in late 1979. The tars are therefore only a plant internal recycle stream and need not intrude into the outside environment. Another advantage of the Slagger over the dry ash Lurgi type gasifiers tested at Kosovo is that the Slagger normally consumes 80-90% less steam, dramatically reducing the hydrocarbon-saturated wastewater stream. Conventional wastewater treatment of this stream to acceptable limits hence becomes a much more manageable endeavor. Also, since this stream is so small the possibility exists of using it to slurry finely ground coal to an entrained gasifier such as Texaco thus utilizing all the hydrocarbon content of the feed coal and further simplifying the task of water treatment.

EPRI's economic evaluations of the BGC Slagger show it to be very promising and therefore worth the extra effort needed to deal with the tars in an environmentally acceptable manner. The Pipeline Gas Demonstration Plant planned for Ohio will hopefully verify this acceptability without reducing its economic viability. An extensive environmental program has already been specified for this project.

## Combustion Engineering

The C-E gasifier has most of the previously cited environmental advantages of entrained gasifiers over coal fired boilers including non-leachable slag, no detected hydrocarbon production, minimum particulate,  $\text{NO}_x$ ,  $\text{SO}_2$  effluents, and reduced waste disposal land requirements. Since it operates at atmospheric pressure, the C-E gasifier is economically attractive for oil or natural gas fired boiler retrofit to conserve these valuable resources. In such applications, however, water consumption would be as great as that in a conventional coal-fired boiler plant. Combined cycle power plants based on the C-E gasifier also appear competitive with direct coal firing, with advantages of reduced water consumption and relatively low cost sulfur removal.

A comprehensive program is planned under EPRI sponsorship to measure gaseous emissions plus liquid and solid effluents from the Process Development Unit (PDU) gasifier at Windsor, Connecticut. At a design capacity of 120 tons of coal per day, it is currently the largest operating gasifier in the U.S.

An effort is underway by Oak Ridge National Lab (ORNL) to compare wastes from the gasification process with those of a direct coal-based power plant using similar coal feedstock. The first results are very tentative because the gasifier has not achieved well-balanced full-scale operation; nevertheless,

they are very encouraging. For example, solids leaching tests on gasifier slag point to very low concentrations of selected metals relative to proposed standards. Results of combustion plant bottom ash were comparable. However, the fly ash showed 10 - 1000 times the concentration of some toxic elements. This appears consistent with expectations of an environmentally acceptable solid waste from high temperature, entrained-flow gasifiers, i.e., in the form of chemically inert slag particles.

In the EPRI-funded effort Radian Corporation is preparing to conduct an extensive sampling program to assess both organic and inorganic emissions, with emphasis on potentially hazardous components. The methodology developed here may also form the basis for future environmental assessment of other prominent gasification technologies.

#### Texaco Process - Montebello Pilot Plant

In the wake of the 1973 oil embargo, Texaco undertook a concerted effort to advance the development of its coal gasification process. This technology had been first tested in the 1950's as an outgrowth of Texaco's successful partial oxidation process for producing synthesis gas from heavy oils and natural gas. In the last 5 or 6 years a large number of coals and other solid feedstocks, including petroleum coke and coal liquefaction residue, have been tested with considerable success in a 15 tpd pilot plant at the Montebello Research Laboratory near Los Angeles. Among these tests, particularly in the most recent 2 year period, have been efforts which have emphasized in significant detail the environmental aspects of the process. The equipment configuration at Montebello is shown in the attached flow sketch, Figure 1.

In a continuing set of EPRI-sponsored runs at the Montebello unit utilizing Illinois No. 6 coal as the feed and employing as the oxidant both oxygen and, alternatively, oxygen-enriched air (35% O<sub>2</sub>), very encouraging operational and environmental results have been obtained. The Texaco gasifier was shown to be particularly responsive, reacting essentially instantaneously to rapid changes in throughput. The product gas composition remained virtually unchanged at various load levels and even during fast transients. One major inherent environmental advantage of the Texaco process over most other gasifiers was confirmed as expected in that no undesirable liquors or tars were produced. These byproducts, when formed in other processes, usually appear in the waste water streams, creating a substantial removal and disposal problem. At the high reaction temperature of the Texaco gasifier (2300 to 2800°F), such condensable materials are unstable and are destroyed.

The Selexol<sup>®</sup> sulfur removal system, when operating within its design specification, removed upwards of 98 percent of the H<sub>2</sub>S in the gas. The only other significant sulfur species present was COS, measured in the feed gas to the Selexol<sup>®</sup> unit at about 5 percent of the H<sub>2</sub>S level, and 50 percent of this COS was removed. It is believed that if required, the COS level could be further reduced by catalytic hydrolysis to H<sub>2</sub>S ahead of the acid gas absorber.

It should be noted that the Selexol<sup>®</sup> process installed at Montebello is among the acid gas removal alternatives likely to be preferentially applied in eventual commercial gasification-combined cycle plants due to its selectivity in removing H<sub>2</sub>S versus CO<sub>2</sub>. For gas turbine applications the latter compound, CO<sub>2</sub>, can remain in the gas and contribute, in the form of increased mass flow, to the total energy developed.

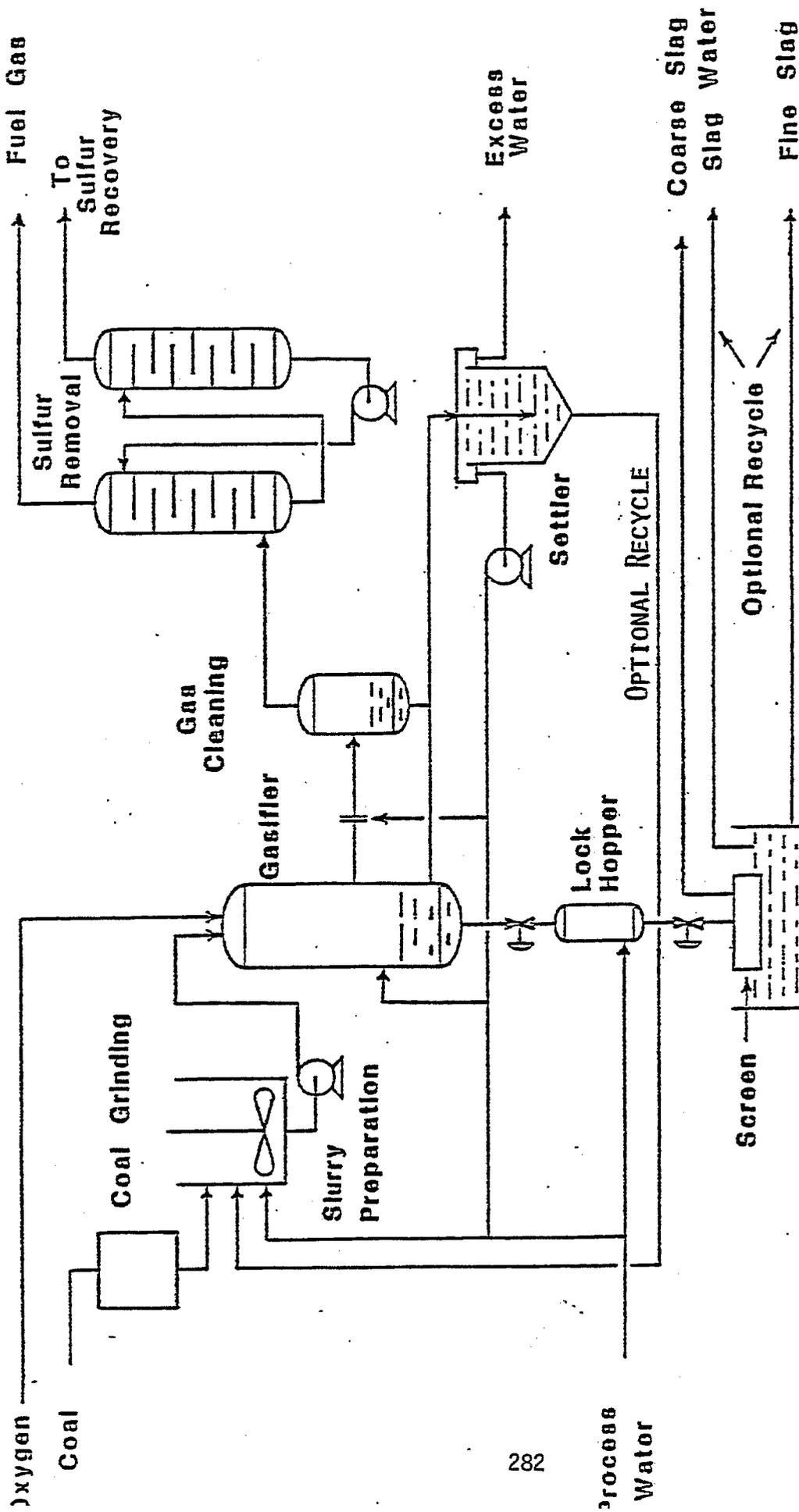


Figure 1 Schematic flow diagram - Texaco Coal Gasification Process - Montebello 15 tpd pilot plant.

In the EPRI-funded test runs, particulate levels in the product gas were essentially negligible, i.e., less than 0.1 mg per normal cubic meter. The ammonia level in the gas was less than 1 ppm. In addition to the product gas, analytical data were gathered in the EPRI runs to determine the constituents of various other plant streams, including the presence and nature of trace materials. With the exception of benzene, organic compounds on the EPA priority pollutant list were not detected in the effluent and recycle water streams at the 10 ppb level. Benzene was detected at a level of less than 20 ppb in the recycle water. No polynuclear aromatics (PNA's) which appear on the EPA priority pollutant list were found in the slag or particulates. Leaching tests conducted on the slag indicated all trace metals found in the leachate fell at least an order of magnitude below the one hundred times EPA drinking water standard proposed for implementation of the Resource Conservation and Recovery Act. In fact, all but three trace metals actually met the drinking water criteria, and these three were present at less than ten times the drinking water standard.

A similar level of environmental analysis and testing to that discussed above has been conducted by Texaco at the Montebello facility on a western coal, Kaiparowits. Reference No.2 in the list at the end of this paper contains a detailed discussion of coal, gas, water, slag, and slag leachate compositions in both the EPRI-sponsored Illinois No. 6 coal tests and the Kaiparowits coal tests.

#### Larger Texaco Pilot Scale Facilities

Extensive testing, including substantial environmental analysis, is planned to be carried out in larger Texaco gasification facilities now operating or scheduled to commence operation soon. EPRI is proceeding with plans to conduct during the next few months testing of Illinois No. 6 coal in a 150 tpd Texaco unit in West Germany. These runs will be of similar scope to the oxygen-blown runs performed at Montebello and the coal has been procured from the same mine. This larger unit, operated at Oberhausen by Ruhrchemie (a European chemical firm) to produce synthesis gas for a chemical feedstock, has achieved considerable success in a planned test program on German coals since its start-up in early 1978. Unlike the Montebello pilot plant, the Ruhrchemie facility is equipped with a waste heat boiler, a key component required for efficient gasification-combined cycle power applications. This factor (versus direct water quench for cooling of the gas as employed at Montebello), along with the larger equipment sizes in the German unit, should increase the relevancy of the environmental measurements taken to the projected performance of commercial scale Texaco-based GCC plants. It is intended to perform a careful analysis of the EPRI results from Oberhausen when available to clearly identify the reasons for any significant difference from the Montebello tests, i.e., effects of scale-up, dissimilarities in equipment design or configuration, differing operating conditions, etc.

Another Texaco gasifier, having a capacity of about 200 tpd of coal is being readied for start-up by TVA at Muscle Shoals, Alabama. This plant, designed to produce a medium-Btu gas as feedstock for ammonia synthesis, was the subject of a paper presented earlier at this meeting. It is understood that a comprehensive environmental program is planned for the TVA unit, which utilizes a direct water quench for cooling of the product gas and, accordingly, should be reasonably representative of a number of other industrial applications of the Texaco gasifier.

## COOL WATER DEMONSTRATION PROJECT

A number of major energy technology developers and supporters, including EPRI, are proceeding with a project to design, construct, and operate a demonstration scale (commercial size equipment) GCC power plant at Southern California Edison's existing Cool Water generating station. The demonstration unit will integrate a 1000 tpd Texaco coal gasifier with a 100 MW combined combustion turbine-steam turbine electric generating system. The plant flow scheme is depicted in Figure 2 and the project is presently in the beginning stages of detailed design. A preliminary estimate of the product gas composition based on the conceptual design of the Cool Water facility<sup>3</sup> is provided in Table 6. The makeup of the clean gas presented in the table reflects the design criteria of 97 percent removal of the sulfur in the raw gas based on a feed coal containing 0.7% sulfur by weight. Similar (and higher) levels of sulfur removal are quite readily achievable in plants feeding higher sulfur coals through appropriate selection of design options within one of several commercially available acid gas removal processes.

The preliminary expected emissions from the Cool Water plant are shown in Table 7. The projection of SO<sub>2</sub> emissions is based on the clean gas composition in the previous table. It should be noted that the NO<sub>x</sub> emissions shown, which correspond to approximately 43 ppm, reflect compliance with the plant permit conditions which apply to the area in California where the plant is to be situated. This criteria is significantly more strict than the federal New Source Performance Standard for stationary gas turbines which limits NO<sub>x</sub> emissions to 75 ppm. To achieve the required low NO<sub>x</sub> emissions level the project intends to employ gas saturation/steam injection prior to combustion, along with the use of advanced combustor design undergoing development concurrent with the design effort for the plant facilities.

The good performance anticipated regarding particulate emissions is a result of effective water scrubbing of the product gas which is carried out as an integral part of the Texaco gasification process. The use of enclosed storage and dustsuppression techniques in the coal receiving, transfer, and preparation areas will, in addition, provide appropriate control of potential emissions from these areas.

In the gasifier process section all but a relatively small amount of the water will be recycled internally. The small amount of process blowdown will be routed along with cooling tower blowdown and other minor power plant aqueous effluents to a lined evaporation pond located on-site. The slag produced will also be stored on-site in an impervious lined storage area, at least until such time as sufficient data has been collected to confirm that, as expected, this material is non-hazardous and alternate off-site disposal (or practical use) can be pursued.

Sulfur produced in the plant as a by-product will be stored at the facility unless and until an application has been developed for it.

The Cool Water project has already received the required State environmental permit from the California Energy Commission (CEC). The conditions of the permit granted by the CEC require that an extensive environmental monitoring and surveillance plan be carried out during the plant operations and test period. The details of this plan are currently being developed.

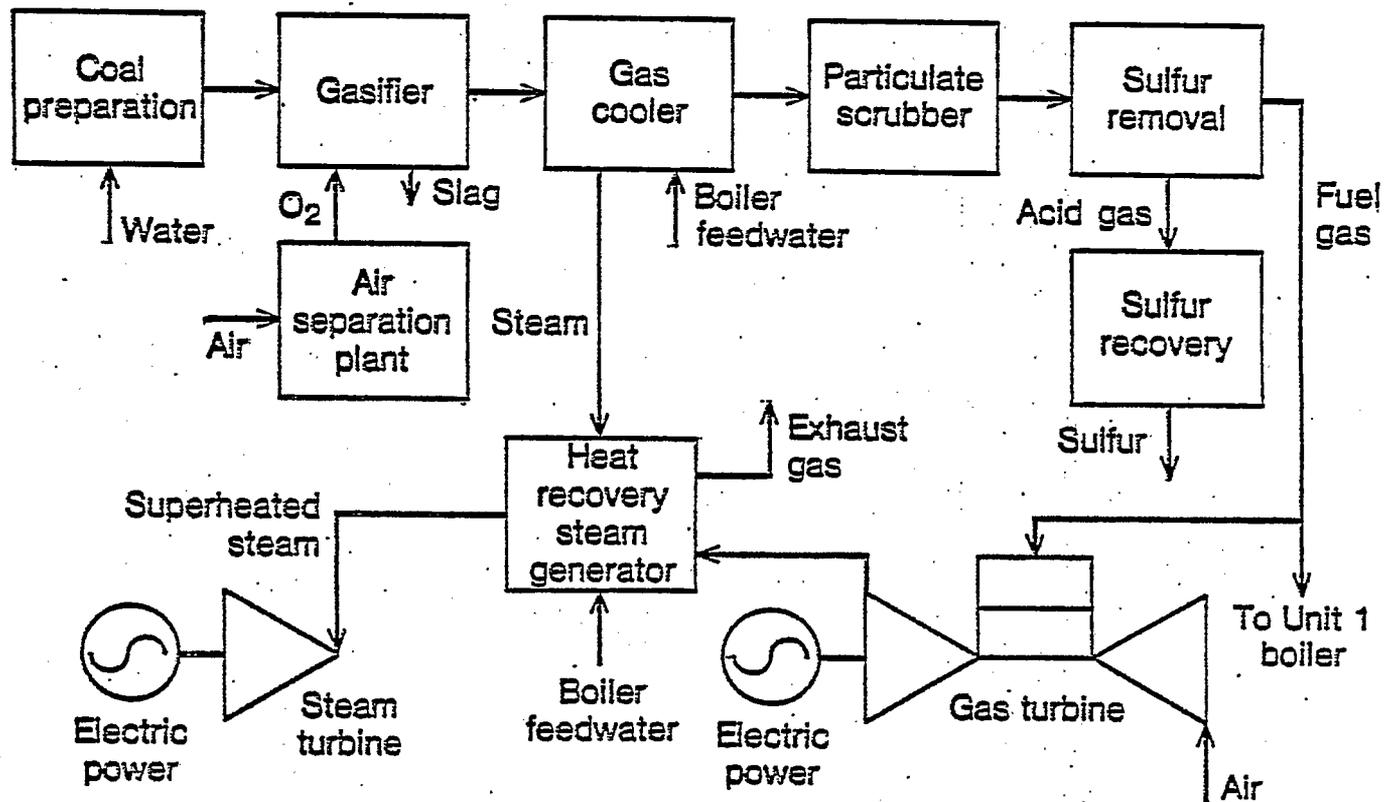


Figure 2 Block flow diagram for Cool Water project

Table 6 COOL WATER GCC DEMONSTRATION PROJECT

PRELIMINARY ESTIMATED GAS COMPOSITIONS (DRY)

FROM A CANDIDATE WESTERN DESIGN COAL

<u>Component</u>	<u>Vol. Percent</u>	
	<u>Raw Gas</u>	<u>Clean Gas</u>
H <sub>2</sub>	33.61	35.94
CO	48.22	51.51
CO <sub>2</sub>	17.38	11.86
CH <sub>4</sub>	0.09	0.10
N <sub>2</sub> + Ar	0.54	0.58
H <sub>2</sub> S	0.15	13 ppmv
COS	0.01	40 ppmv

Table 7 COOL WATER EXPECTED EMISSIONS

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	<u>Lbs./10<sup>6</sup> Btu (Coal)</u>
SO <sub>2</sub>	0.04
NO <sub>x</sub>	0.14
Particulates	0.005

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Notes:

1. Emissions based on performance calculations for a candidate (western) design coal.
  2. Aqueous effluent intended to be routed to lined evaporation pond.
  3. Solid wastes (slag) to be stored at site.
-

A one-year monitoring program to provide additional data regarding the present local environment in the vicinity of the plant site is nearly complete. The data from this effort, undertaken to comply with regulations promulgated for implementation of the Prevention of Significant Deterioration (PSD) provisions of the Clean Air Act Amendments, will be submitted to the EPA to support the recently prepared project application for a PSD permit.

#### SUMMARY

The data from existing pilot plants enables us to identify the species, i.e., compounds, present in the various gasification process streams. These species would not be expected to change in scaled-up commercial facilities. What remains unclear, however, is the concentration at which these substances will appear in commercial plants employing recycle of certain materials and other design dissimilarities for continuous economic operation.

The promise of the data obtained so far strongly suggests that process schemes to meet present and future emissions and effluent standards can be economically achieved with coal gasification combined cycle power plants. Nevertheless the detailed long term environmental impacts and full achievement of the above promise can only be obtained by continuous long term operation of a commercial sized (and configured) demonstration plant. It is with this very much in mind that EPRI together with Southern California Edison, Texaco, G.E. and Bechtel have commenced engineering the 100MW gasification combined cycle demonstration plant at Cool Water.

#### REFERENCES

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2. W. G. Schlinger and G. N. Richter, Texaco Montebello Research Laboratory, paper entitled "An Environmental Evaluation of the Texaco Coal Gasification Process", presented at The First International Gas Research Conference, Chicago, Illinois, June 9-12, 1980.
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COS-H<sub>2</sub>S RELATIONSHIPS IN PROCESSES PRODUCING  
LOW/MEDIUM-BTU GAS\*

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ABSTRACT

The chemical aspects of the distribution of sulfur between H<sub>2</sub>S and COS in the product gas from the gasification of coal are examined. Comparing actual gasifier measurements with equilibrium computations we find that the gas stream becomes frozen corresponding to equilibrium values at high temperature, most likely corresponding to the reactor exit. This implies a sulfur distribution with a higher COS concentration than one may expect. The conversion of COS to H<sub>2</sub>S occurs mainly by COS hydrolysis, which is very slow at low temperatures. Finite rate studies indicate that an effective catalytic COS hydrolysis rate constant of  $10^{-17}$  to  $10^{-16}$  cm<sup>3</sup>/mol. sec will allow the reaction to reach >95% equilibrium in small enough residence time to allow reasonable reaction vessel sizes.

It is found that the achievable H<sub>2</sub>S/COS equilibrium ratio is determined from the product of the locally frozen H<sub>2</sub>O/CO<sub>2</sub> ratio and the COS hydrolysis equilibrium constant. The governing parameters for the H<sub>2</sub>O/CO<sub>2</sub> equilibrium ratios are the temperature, pressure, and the gas stream (H/C) and (O/C) ratios. The higher the (H/C) ratio and the lower the (O/C) ratio the larger the H<sub>2</sub>O/CO<sub>2</sub> ratio and thus the larger the H<sub>2</sub>S/COS ratio. Moreover, raising the (H/C) ratio and lowering the (O/C) ratio also increases the achievable CH<sub>4</sub> equilibrium concentration from a catalytic methanation module.

\*Supported by the Environmental Protection Agency, Industrial Environmental Research Laboratories/Research Triangle Park under contract EPA 68-02-3137.

## COS-H<sub>2</sub>S RELATIONSHIPS IN PROCESSES PRODUCING LOW/MEDIUM-BTU GAS

### I. INTRODUCTION

The production of gaseous and liquid fuels from domestic coal has a high priority in the overall U.S. energy policy. Of the technologies used to produce these fuels from coal, gasification and indirect liquefaction are commercially available, and therefore, will be the first generation plants constructed in the U.S.

One of the largest process and environmental concerns associated with gasification and indirect liquefaction technologies is the removal and ultimate fate of sulfur compounds formed during the gasification of coal. Sulfur compounds will poison downstream methanation and synthesis catalysts and will present a potential environmental and health problem if emitted to the atmosphere at certain levels.

The two primary sulfur compounds formed during coal gasification are H<sub>2</sub>S and COS. Of these, the amount of COS in relation to H<sub>2</sub>S is of primary concern because of the following reasons:

- Gaseous sulfur compounds are usually removed by an acid gas removal (AGR) process (i.e., Rectisol, Selexol, etc.). COS is less soluble than H<sub>2</sub>S in physical AGR solvents; therefore, more energy is required to remove COS from the product gas stream to levels required for downstream processes (i.e., <5 ppm reduced sulfur).
- Because of the relative solubility, when a selective AGR operation is used, COS will distribute itself differently than H<sub>2</sub>S in the AGR tail gases.
- Certain sulfur recovery processes (e.g., Stretford) will not remove COS from AGR tail gases and more expensive sulfur recovery processes may be required to reduce sulfur emissions from the plant.

Based on the above reasons, COS can be removed from gas streams; however, it is more difficult to remove than H<sub>2</sub>S. In order to design AGR and sulfur recovery systems it is important to identify and understand the effect of the parameters which control the distribution of sulfur between H<sub>2</sub>S and COS in gasifier technologies.

The conversion of COS to H<sub>2</sub>S is limited by the hydrolysis reaction,



This reaction is sufficiently slow that equilibrium levels cannot be achieved. However, catalysts exist<sup>2-4</sup> which increase the rate of (I) and test modules are being prepared. The scope of the present study is to investigate the relationship of H<sub>2</sub>S and COS in various gasifier technologies. Comparisons between model computations and actual gasifier measurements lends an understanding of the systematics to aid in future designs. Both equilibrium and finite rate considerations are included.

The data base<sup>5-11</sup> used for comparison is characterized in Table 1. As can be seen the gasifiers represent a wide diversity in gasifier technology, coal classification, and operating conditions. Table 2 shows the measured concentrations of the major species as well as the H<sub>2</sub>S and COS levels contained in the raw product gas stream. These are the values to be used in comparisons with model calculations.

## II EQUILIBRIUM COMPUTATIONS

The equilibrium concentration of molecular species at a given temperature and pressure may be calculated by minimizing Gibbs Free Energy constrained by the conservation of mass for each element. We have performed such calculations for each gasification system using as input the amounts of total carbon, hydrogen, oxygen, nitrogen, and sulfur present from the measurements of the product gas streams. The data base consists of the Gibb's Free Energy of over 70 molecular species from the JANAF handbook.<sup>12,13</sup>

Figures 1 and 2 show typical results from such calculations. Figure 1 corresponds to the CO<sub>2</sub> Acceptor<sup>9</sup> and Figure 2 to the Wilputte-Chapman<sup>8</sup>. The bars on each plot show the measured levels (with 10% uncertainty) of each of the species. Figure 1 illustrates that the CO<sub>2</sub> Acceptor is able to maintain its equilibrium as the gas cools to about 1000K where the reactions become frozen. Although the Wilputte-Chapman results show a similar effect, the agreement is not as definitive. The CO, H<sub>2</sub>, and CH<sub>4</sub> are in equilibrium corresponding to approximately 900K while the H<sub>2</sub>O is not in the same temperature range. This is most likely due to an imprecise H<sub>2</sub>O measurement. Of the H<sub>2</sub>S and COS, the COS measurement is much higher than equilibrium would predict at any temperature. However, this difference is only a factor of 3 and for these small concentrations, the deviation is considered to be reasonable. In general, we conclude that at least the major gaseous species (H<sub>2</sub>O, CO<sub>2</sub>, CO, H<sub>2</sub>, and CH<sub>4</sub>) are frozen at equilibrium values corresponding to temperatures in the 900-1300K range.

TABLE 1. GASIFIER CHARACTERIZATIONS

Site	Type	Technology	Coal	Gas	Pressure (atm)	Flowrate (scfs)	Identifier
Glen Gery	Wellman-Galusha	Fixed-Bed (Thick)	Anthracite	Low-Btu	1	45	GG
Fort Snelling	Wellman-Galusha	Fixed-Bed (Thick)	Lignite	Low-Btu	1	30	FS
Riley Morgan	Riley Stoker	Fixed-Bed (Thin)	Lignite	Low-Btu	1	80	RS
Holston	Wilpette-Chapman	Fixed Bed (Thin)	Subbituminous	Low-Btu	1	390	WC
Rapid City	CO2 Acceptor	Fluidized Bed	Sublignite	Med-Btu	10	20	CA
Montebello	Texaco	Entrained Bed	Subbituminous	Med-Btu	24	800	T
Hanna	UCG	In-Situ	Subbituminous	Low-Btu	5	55	UCG

TABLE 2. PRODUCT STREAM COMPOSITIONS<sup>a</sup>

Gasifier <sup>b</sup>	N <sub>2</sub> (vol %)	H <sub>2</sub> (vol %)	CO (vol %)	CH <sub>4</sub> (vol %)	H <sub>2</sub> O (vol %)	CO <sub>2</sub> (vol %)	H <sub>2</sub> S (ppmv)	COS (ppmv)
GG	48.5	15.3	24.0	0.22	5.9	5.2	649	87
FS	37.6	12.4	21.1	0.77	19.6	7.6	892	115
RS	33.9	13.2	20.3	0.77	25.6	5.3	860	95
WC	50.9	13.2	17.9	1.4	7.0 <sup>c</sup>	7.7	228	25
CA	6.0	40.7	11.7	8.8	24.7	7.1	1000	7.5
T	0.3	34.0	43.8	0.029	0.47 <sup>d</sup>	21.1	1264	48
UCG	47.1	14.4	11.4	2.6	11.7	11.8	2584	84

<sup>a</sup>Only major species, H<sub>2</sub>S and COS compositions given.

<sup>b</sup>Identifier from Table 1.

<sup>c</sup>Estimated from partial data.

<sup>d</sup>Assumed value corresponding to saturation at 100F. This value is a lower bound to the H<sub>2</sub>O level in the gas stream. The actual value is probably much higher.

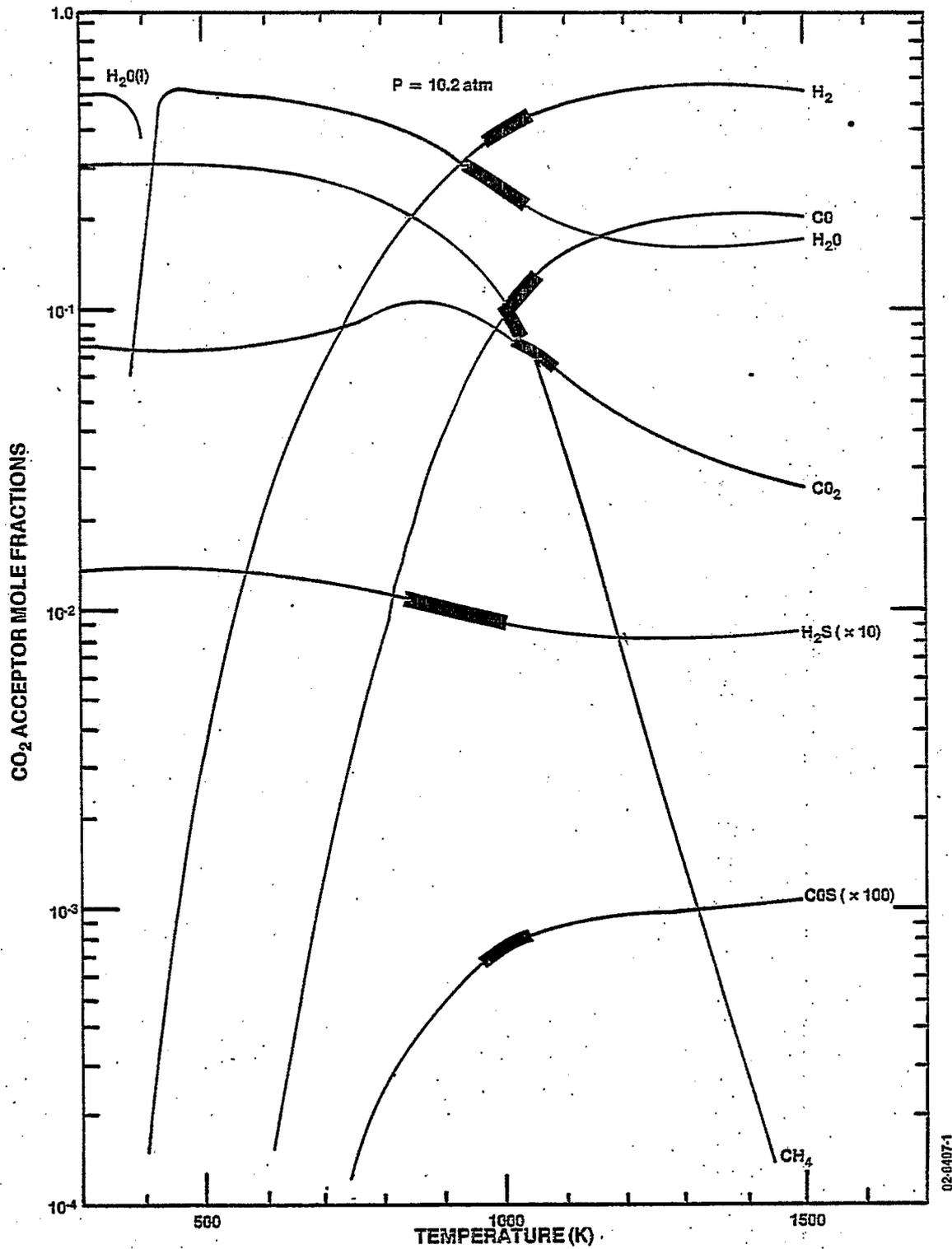


Figure 1. Plot of the Calculated Equilibrium Major Gas Species and the H<sub>2</sub>S-COS Distributions as a Function of Temperature for the CO<sub>2</sub> Acceptor Gasifier. Bars indicate actual measured levels (with 10% uncertainty).

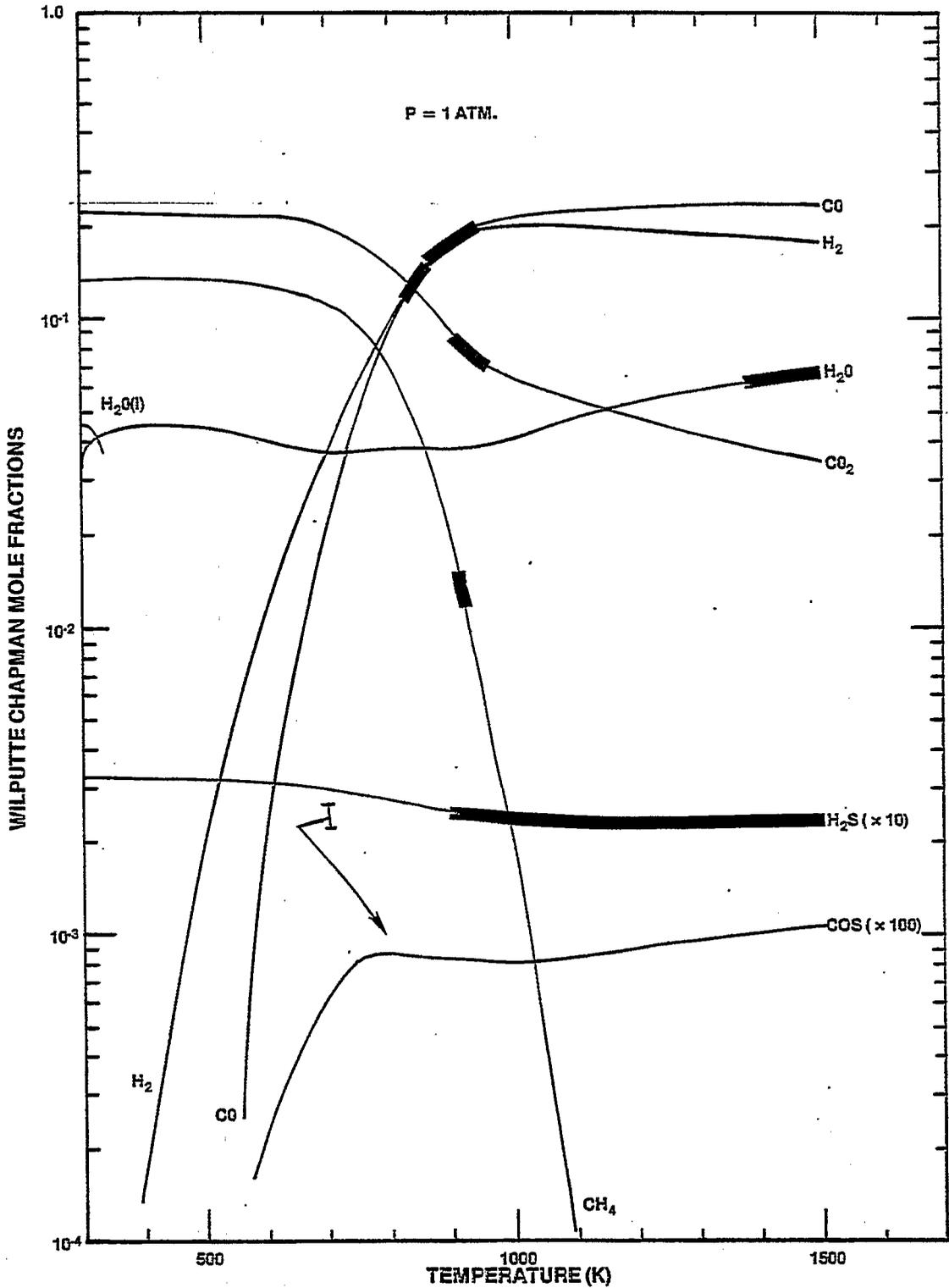


Figure 2. Plot of the Calculated Equilibrium Major Gas Species and the H<sub>2</sub>S-COS Distributions as a Function of Temperature for the Wilputte-Chapman Gasifier. Bars indicate actual measured levels (with 10% uncertainty).

Figure 3 gives the calculated values for the H<sub>2</sub>S/COS ratio (by volume) for each of the gasifiers as a function of temperature assuming the system maintains equilibrium at all temperatures. It should be noted that the measured H<sub>2</sub>S/COS ratios for only the CO<sub>2</sub> Acceptor (CA) and the in-situ (UGG) gasifiers correspond to H<sub>2</sub>S-COS equilibrium at any temperature; all others show actual levels much lower than their equilibrium level. This is a clear indication that if equilibrium could be achieved between H<sub>2</sub>S and COS much more of the sulfur would be in the form of H<sub>2</sub>S, especially at lower temperatures.

If H<sub>2</sub>S and COS were at equilibrium then reaction I shows that the H<sub>2</sub>S/COS ratio is directly related to the H<sub>2</sub>O/CO<sub>2</sub> ratio by the equilibrium constant, K<sub>I</sub>, namely,

$$\left(\frac{\text{H}_2\text{S}}{\text{COS}}\right) = \left(\frac{\text{H}_2\text{O}}{\text{CO}_2}\right) K_I \quad (1)$$

Since K<sub>I</sub> is monotonically increasing with decreasing temperature as shown in Figure 4, the larger the H<sub>2</sub>O/CO<sub>2</sub> ratio is the larger the H<sub>2</sub>S/COS ratio will be. Figure 5 shows the behavior of the equilibrium H<sub>2</sub>O/CO<sub>2</sub> ratio with changing temperature. Again bars indicate the actual measurements. Note that the H<sub>2</sub>O/CO<sub>2</sub> ratios form a family of curves related by the H/C ratio by weight. As may be expected, the higher the H/C ratio the greater the H<sub>2</sub>O/CO<sub>2</sub> ratio.

Now, if a catalytic module were added to increase the rate toward equilibrium of reaction I, and since the H<sub>2</sub>S and COS are present in very low concentrations compared to H<sub>2</sub>O and CO<sub>2</sub>, H<sub>2</sub>S/COS equilibrium would be obtained without significantly affecting the H<sub>2</sub>O and CO<sub>2</sub> concentrations. Here the equilibrium H<sub>2</sub>S/COS ratios will not be as in Figure 4 but will have the form

$$\left(\frac{\text{H}_2\text{S}}{\text{COS}}\right) = (\text{constant}) K_I \quad (2)$$

where the constant in Equation (2) is the frozen value of H<sub>2</sub>O/CO<sub>2</sub>. Figure 6 shows the possible equilibrium values achievable for the gasifiers studied here. These are simply K<sub>I</sub>(T) multiplied by the actual (H<sub>2</sub>O/CO<sub>2</sub>) ratio of each gasifier. The equilibrium values of H<sub>2</sub>S/COS ≡ R\* are plotted on the left hand axis. If only 90% of equilibrium were reached, i.e., H<sub>2</sub>S/COS = 0.9R\*, then the fraction of sulfur as H<sub>2</sub>S is H<sub>2</sub>S/(H<sub>2</sub>S + COS) = 0.9R\*/(0.9R\* + 1). The right hand axis is scaled to this fraction. Therefore, if the module achieved 90% equilibrium at 500K nearly all gasifiers would yield >99.9% of all sulfur as H<sub>2</sub>S.

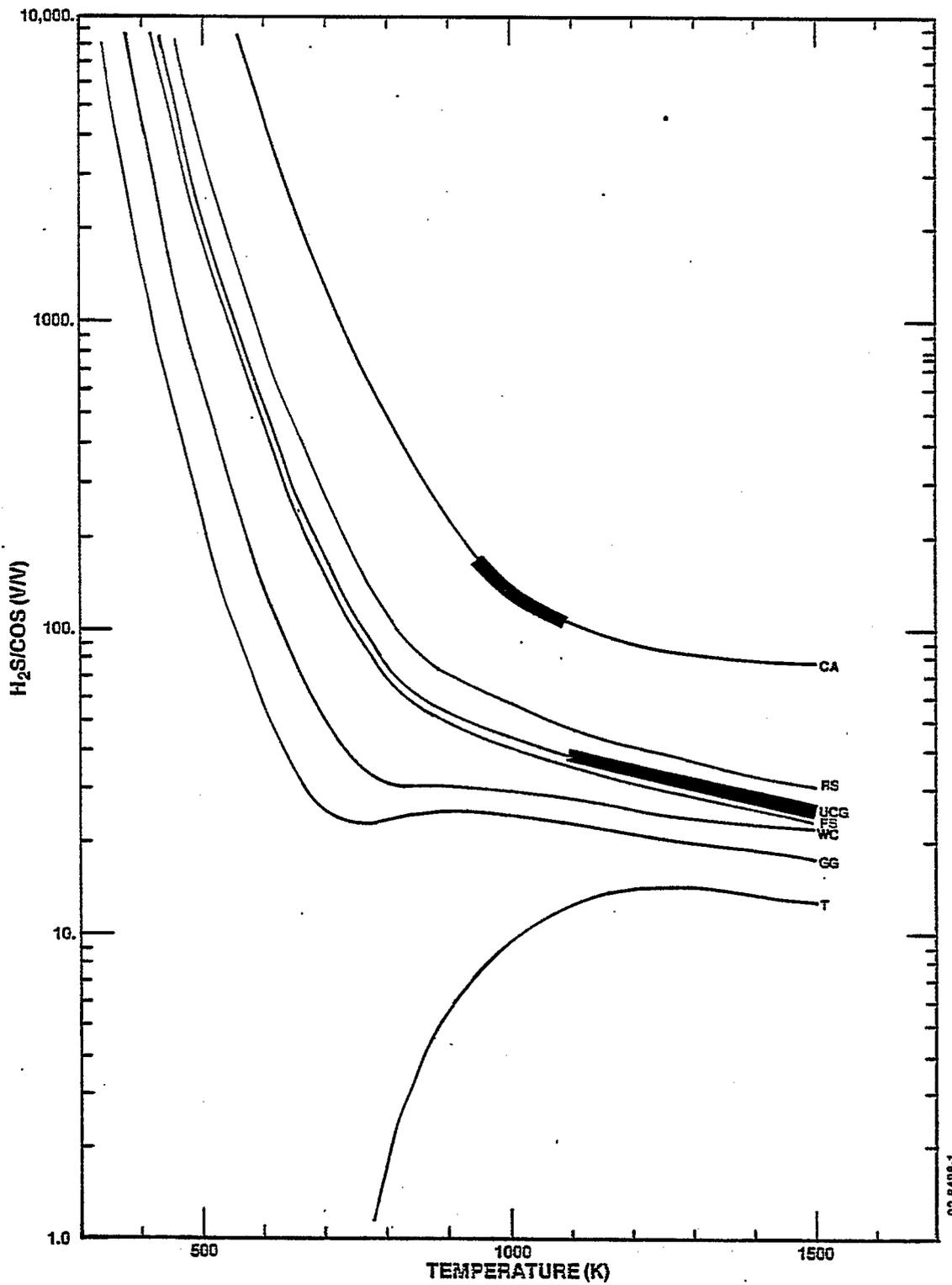


Figure 3. Plot of the Calculated H<sub>2</sub>S-COS (by volume) Ratio Corresponding to Total System Equilibrium for Each Gasifier. Identifiers are as in Table 1. Bars indicate actual measured levels (with 10% uncertainty).

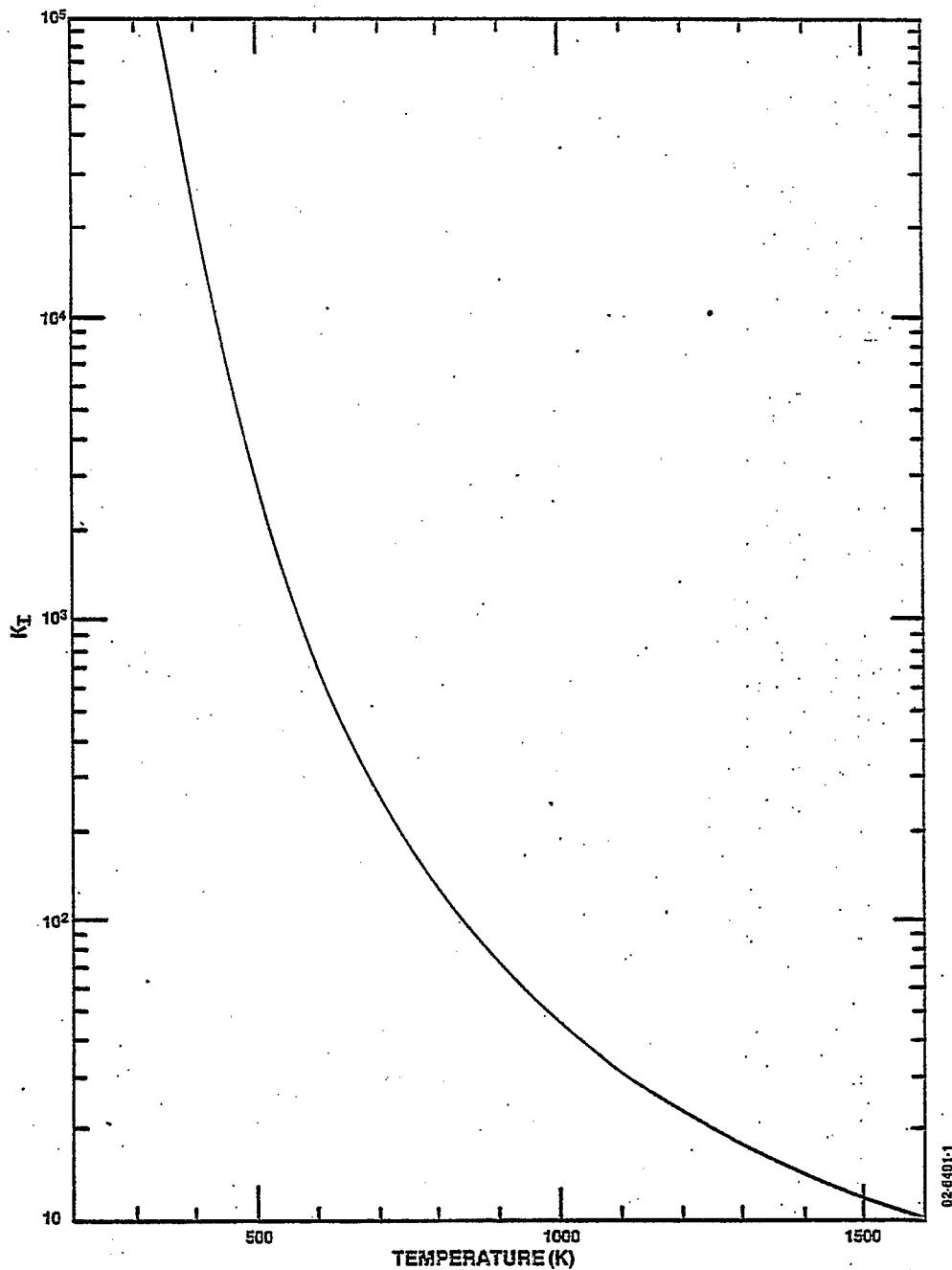


Figure 4. Plot of the COS Hydrolysis Equilibrium Constant as a Function of Temperature.

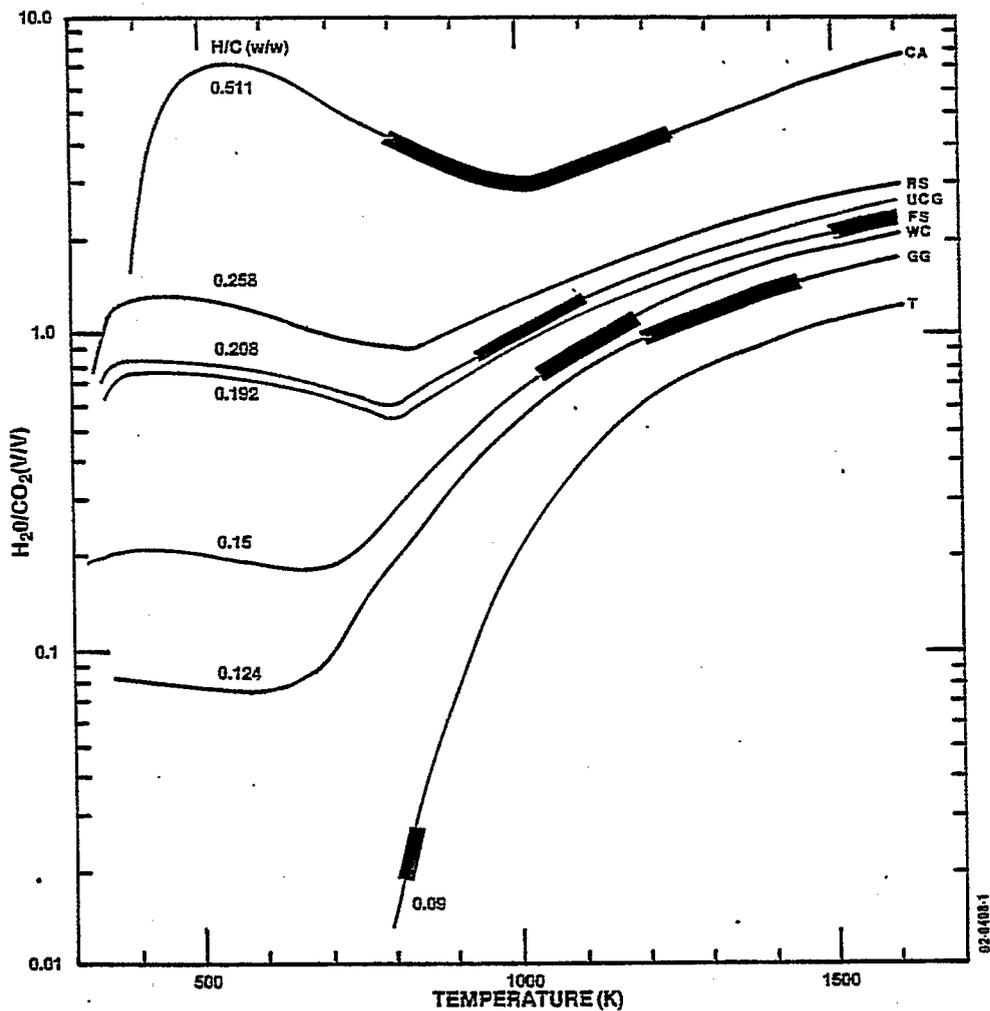


Figure 5. Plot of the Calculated H<sub>2</sub>O/CO<sub>2</sub> (by volume) Equilibrium Ratio for Each of the Gasifiers. Identifiers are as in Table 1. Bars indicate actual measured levels (with 10% uncertainty).

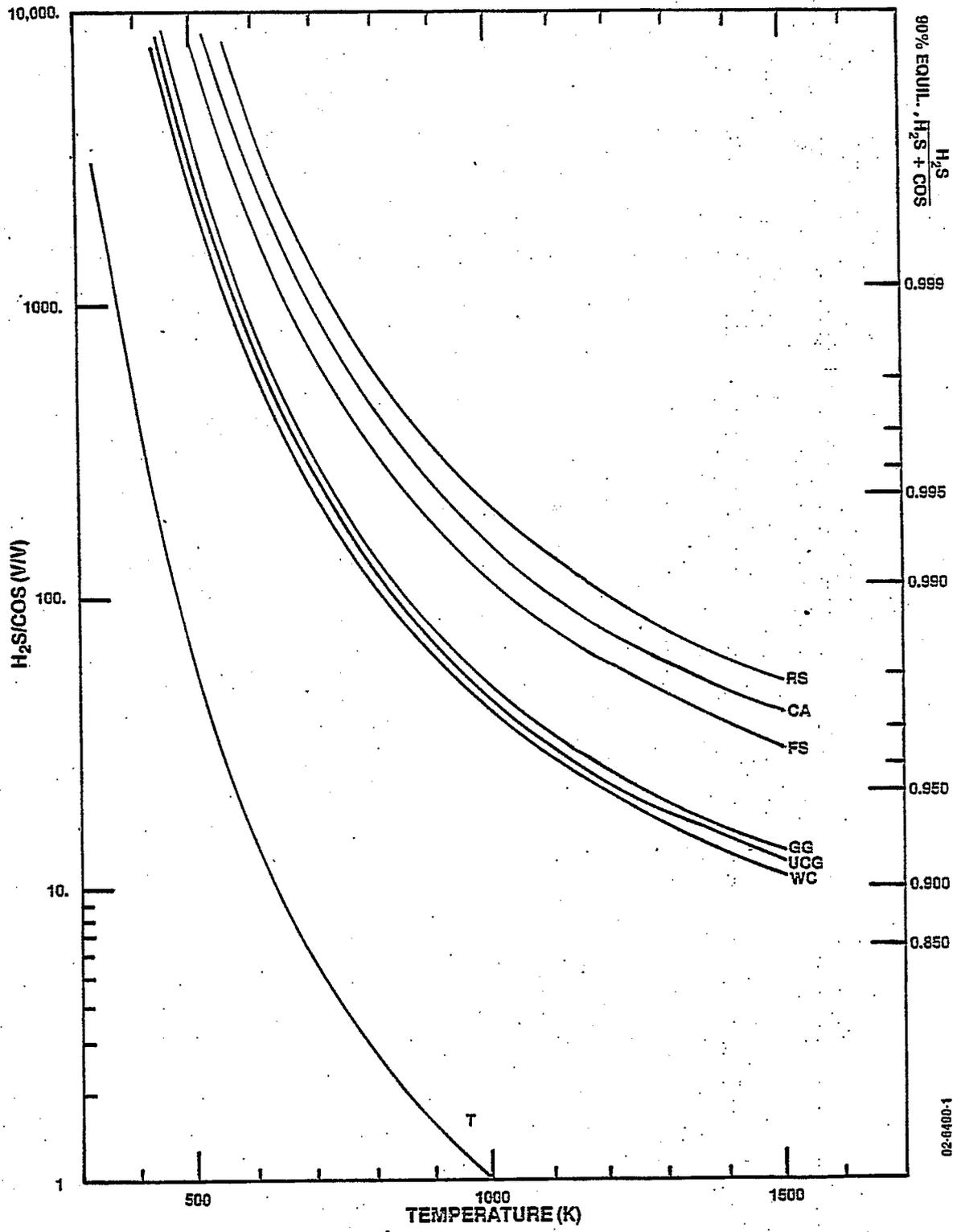


Figure 6. Plot of the Achievable H<sub>2</sub>S/COS (by volume) ratio for Each of the Gasifiers Assuming a Frozen H<sub>2</sub>O/CO<sub>2</sub> Ratio Corresponding to Measured Levels and COS Hydrolysis Equilibrium. Identifiers are as in Table 1.

It is clear that the greater the  $H_2O/CO_2$  ratio the greater the achievable  $H_2S/COS$  ratio. Therefore, it is worth considering which parameters determine the  $H_2O/CO_2$  ratio. Both  $H_2O$  and  $CO_2$  are major species in the gas phase and as such they will only be affected by the other major species. Of the major elements present (C, H, O, and N) only the C, H, and O will affect the  $H_2O/CO_2$  ratio. Moreover, since we are only interested in a ratio, only the (total H/total C) and (total O/total C) ratios in the gas stream are important to the equilibrium. Figure 7 shows the correlation of the gasifiers between the O/C and H/C ratios by weight, designated  $(O/C)_w$  and  $(H/C)_w$ , respectively. The  $(O/C)_w$  ratio for each gasifier (except the  $CO_2$  Acceptor) is empirically related to the  $(H/C)_w$  ratio by

$$(O/C)_w = 7.6 (H/C)_w + 0.88 \quad (3)$$

The  $(O/C)_w$  ratio is much lower in the  $CO_2$  Acceptor due to the removal of  $CO_2$  to form  $CaCO_3$  in the fluidized bed, and the absence of  $O_2$  in the input stream.

Using the relationship of Equation (3) the  $H_2O/CO_2$  equilibrium ratio is uniquely determined from the  $(H/C)_w$  ratio. Separate equilibrium computations were performed for atmospheric pressure considering only H, C, and O with various  $(H/C)_w$  ratios and Equation (3). The result for the  $H_2O/CO_2$  ratio are presented in Figure 8. Comparing Figure 8 to Figure 5, we find the  $H_2O/CO_2$  equilibrium ratio to be identical when conditions are the same. Moreover, even when conditions are very different, such as the  $CO_2$  Acceptor, the  $H_2O/CO_2$  ratio is in agreement within approximately 25% for temperature greater than 800K. Therefore, if one knew the  $(H/C)_w$  ratio and approximated the temperature at which the  $H_2O/CO_2$  becomes frozen (in most cases 1000-1200K) the achievable  $H_2S/COS$  equilibrium ratio could be estimated from Figures 4 and 8 using Equation (2).

### III. FINITE RATE CONSIDERATIONS

From the previous section, it is clear that at lower temperatures nearly all of the sulfur would exist as  $H_2S$  if equilibrium for reaction I could be obtained. If a catalyst is used, the equilibrium is unaltered, only the rate at which the equilibrium is attained is increased. Several catalysts have been partially investigated<sup>2-4</sup> which enhance the hydrolysis of  $COS$ ; however, rates are ill-defined and catalytic poisoning has not been well characterized. Nevertheless, it is useful to understand the effect of various rate constants on the design of catalytic  $COS$  hydrolysis process modules.

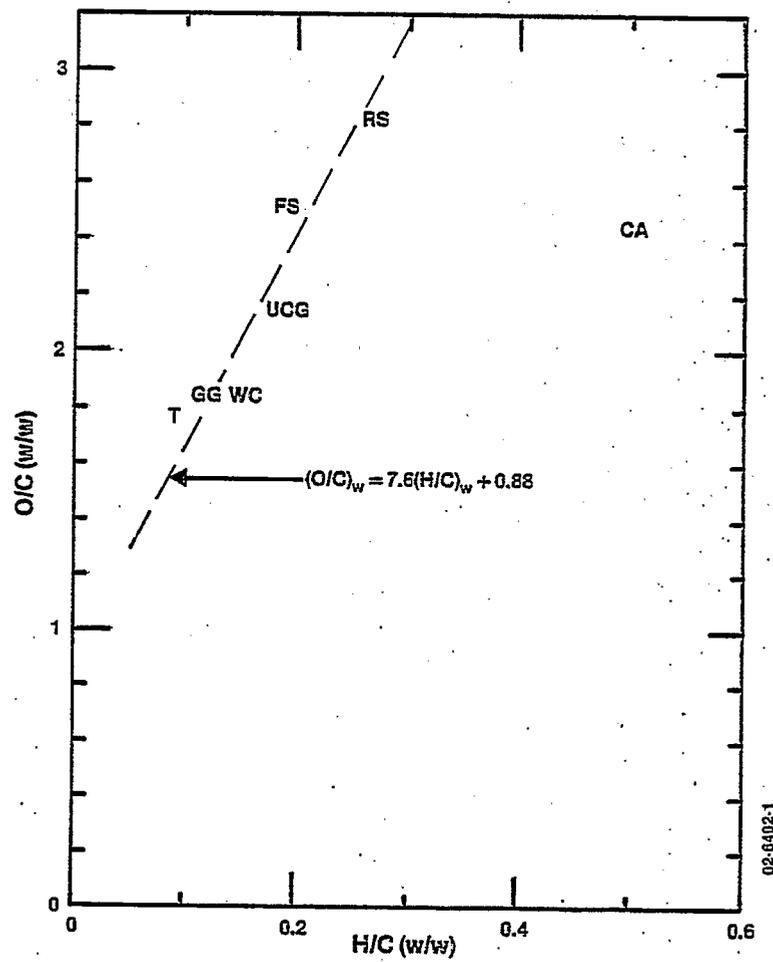


Figure 7. Plot of the Gas Stream  $(O/C)_w$  to  $(H/C)_w$  Correlation for Each of the Gasifiers. Identifiers are as in Table 1.

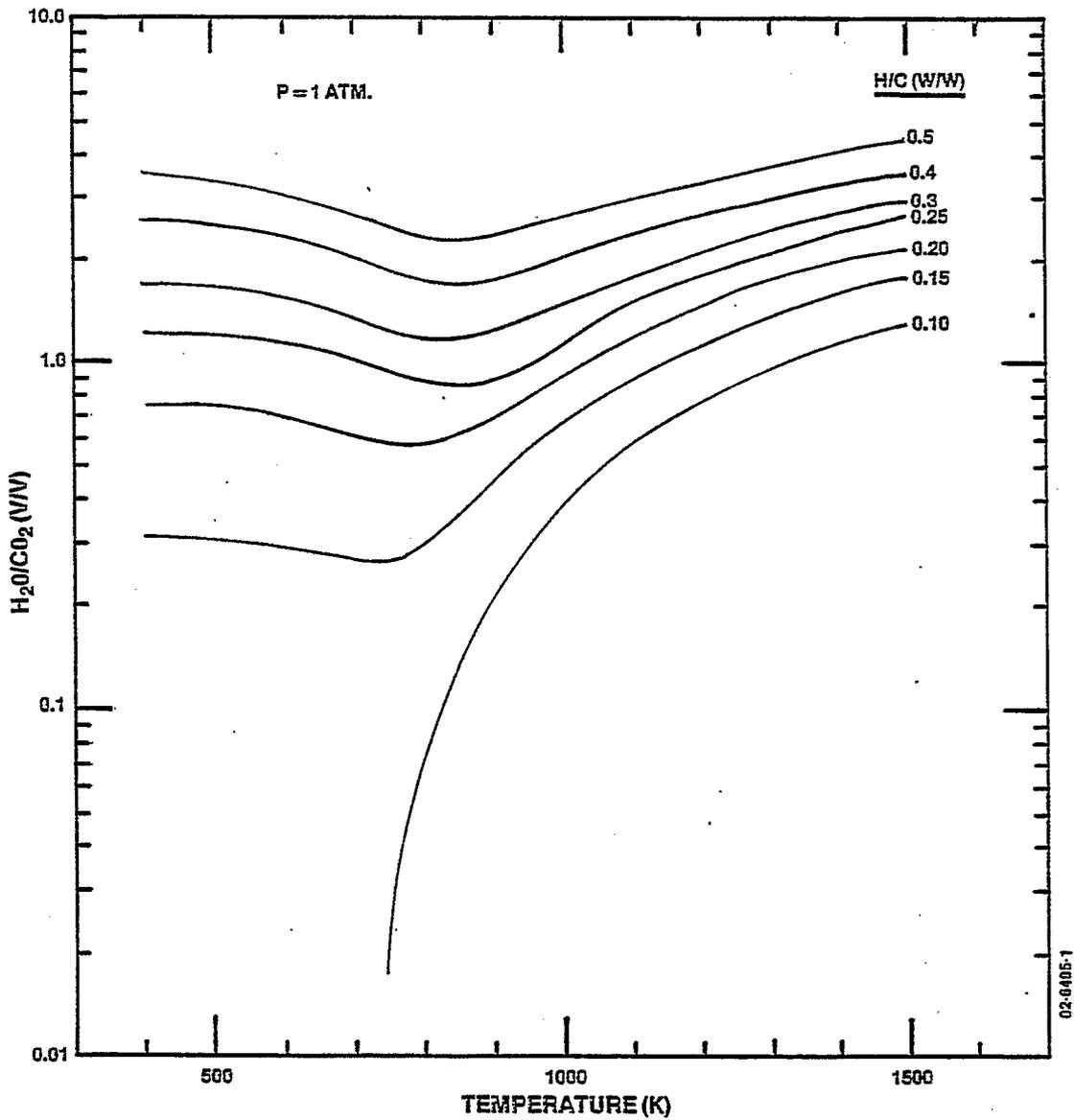


Figure 8. Plot of the Calculated Equilibrium H<sub>2</sub>O/CO<sub>2</sub> Ratio as a Function of Temperature and at 1 atm. for Several (H/C)<sub>w</sub> Ratios. (O/C)<sub>w</sub> Ratios determined from Equation (3).

Consider  $k_f$  and  $k_r$  as the effective forward and reverse rate constants for Reaction I, respectively. Then the rate of change of COS is given by

$$\frac{dn_{\text{COS}}}{dt} = -k_f n_{\text{H}_2\text{O}} n_{\text{COS}} + k_r n_{\text{CO}_2} n_{\text{H}_2\text{S}} \quad (4)$$

where  $n_i$  is the density of the  $i$ th species in moles/cm<sup>3</sup>. Now, by conservation of sulfur species

$$n_{\text{total,S}} = n_{\text{COS}}^o + n_{\text{H}_2\text{S}}^o = n_{\text{COS}} + n_{\text{H}_2\text{S}} = n_{\text{COS}}^* + n_{\text{H}_2\text{S}}^* \quad (5)$$

where the superscript "o" and asterick indicate, respectively, the initial and equilibrium values. Using Equation (5) in Equation (4) and recognizing that  $K_I = k_f/k_r$ , Equation (4) may be rewritten

$$\frac{dn_{\text{COS}}}{dt} = -\alpha n_{\text{COS}} + \beta \quad (6a)$$

where

$$\alpha = k_f n_{\text{H}_2\text{O}} \left( 1 + \frac{n_{\text{CO}_2}}{K_I n_{\text{H}_2\text{O}}} \right) \quad (6b)$$

and

$$\beta = k_r (n_{\text{H}_2\text{S}}^o + n_{\text{COS}}^o) n_{\text{CO}_2} \quad (6c)$$

As discussed in Section II, H<sub>2</sub>O and CO<sub>2</sub> are major species and remain unchanged by any redistribution of sulfur species, e.g., reaction I. Therefore, the H<sub>2</sub>O/CO<sub>2</sub> ratio will be constant during the approach to the H<sub>2</sub>S-COS equilibrium. Using this,  $\alpha$  is time independent and may be written as

$$\alpha = k_f n_{\text{H}_2\text{O}} \left( 1 + \frac{1}{R^*} \right) \quad (6b')$$

where  $R^*$  is the equilibrium ratio,  $n_{\text{H}_2\text{S}}^*/n_{\text{COS}}^* \equiv \text{H}_2\text{S}^*/\text{COS}^*$ . Finally, the solution to Equation (6a) is given by

$$n_{\text{COS}} - n_{\text{COS}}^* = (n_{\text{COS}}^o - n_{\text{COS}}^*) e^{-\alpha t} \quad (7)$$

with  $\alpha$  given by Equation (6b').

Defining an extent of equilibrium,  $\gamma$ , by

$$\gamma \equiv \frac{R}{R^*} = \frac{n_{H_2S}/n_{CO_2}}{n_{H_2S}^*/n_{CO_2}^*}, \quad (8)$$

and after considerable manipulation, we find

$$\gamma = \frac{\gamma_0 + R^* - R^* (1 - \gamma_0)e^{-\alpha t}}{\gamma_0 + R^* + (1 - \gamma_0)e^{-\alpha t}}, \quad (9)$$

where  $\gamma_0$  corresponds to the initial value of  $\gamma$ .

Toward obtaining residence times to reach a given extent of equilibrium, Equation (9) may be rearranged as

$$\alpha t = \ln \frac{(\gamma + R^*)(1 - \gamma_0)}{(\gamma_0 + R^*)(1 - \gamma)}. \quad (10)$$

Now using the ideal gas relationship for the total gas phase density ( $n$ ), and  $n_{H_2O} = X_{H_2O}n$ , where  $X_{H_2O}$  is the  $H_2O$  mole fraction,  $\alpha$  [cf. Equation (6b')] is given by

$$\alpha = 7.34 \times 10^{21} X_{H_2O} k_f \left(\frac{P}{T}\right) \left(1 + \frac{1}{R^*}\right), \quad (11)$$

where  $P$  and  $T$  are the pressure and temperature, respectively. Substituting Equation (11) into Equation (10), we find

$$X_{H_2O} k_f P\tau/T = 1.36 \times 10^{-22} \frac{R^*}{1 + R^*} \ln \frac{(\gamma + R^*)(1 - \gamma_0)}{(\gamma_0 + R^*)(1 - \gamma)} \quad (12)$$

If  $t=\tau$  is the time to reach 90% of equilibrium then  $\gamma = 0.9$  and the right hand side is a given value depending on the achievable equilibrium ratio  $R^*$  and the initial value  $\gamma_0$ .

Table 3 presents these values for a wide range of  $\gamma_0$  and  $R^*$  for  $\gamma = 0.85, 0.90, 0.95$ . As can be seen, the entries are relatively independent of  $\gamma_0$  and  $R^*$ , and all entries are well represented by

$$X_{H_2O} k_f P\tau/T = \begin{cases} 1.5 \pm 1 \times 10^{-22} & \gamma = 0.85 \\ 2.0 \pm 1 \times 10^{-22} & \gamma = 0.90 \\ 3.0 \pm 1 \times 10^{-22} & \gamma = 0.95 \end{cases} \quad (13)$$

In fact, all three categories may be summarized by

$$X_{H_2O} k_f P\tau/T = 2.0 \pm 2 \times 10^{-22} \quad (14)$$

or, for a given process with a given rate constant, the reaction time necessary to achieve >95% of equilibrium is

$$\tau_R \geq 4 \times 10^{-22} T/X_{H_2O} P k_f \quad (15)$$

Here, we have used the conservative upper limit for the constant. The fact that these constants are all very similar in magnitude is just a reflection of the nature of first order kinetics. That is, these constants represent the driving force toward equilibrium and the further the system is from equilibrium initially, the faster the approach to equilibrium, providing similar times to reach the desired extent of reaction. Now, the required residence time in a reactor (reaction time) is related to the reactor volume,  $V$ , and the actual gas flowrate,  $F$ , by

$$\tau_R = V/F = 300 V P/F_0 T \quad (16)$$

where  $F_0$  is the flowrate at 300K and 1 atm. Therefore, Equation (15) may be rewritten

$$\frac{V}{F_0} \geq 1.33 \times 10^{-24} T^2/X_{H_2O} P^2 k_f \quad (17)$$

TABLE 3. EQUILIBRIUM DRIVING FORCES<sup>a</sup>

$\gamma_0 \backslash R^*$	$10^0$	$10^1$	$10^2$	$10^3$	$10^4$
<u><math>\gamma = 0.85</math></u>					
$10^{-4}$	1.71	2.45	2.57	2.58	2.58
$10^{-3}$	1.71	2.45	2.56	2.58	2.58
$10^{-2}$	1.69	2.43	2.55	2.56	2.56
$10^{-1}$	1.57	2.30	2.42	2.44	2.44
0.5	0.96	1.53	1.63	1.64	1.64
0.7	0.53	0.87	0.94	0.94	0.94
<u><math>\gamma = 0.90</math></u>					
$10^{-4}$	2.00	2.95	3.11	3.13	3.13
$10^{-3}$	2.00	2.95	3.11	3.13	3.13
$10^{-2}$	1.99	2.94	3.10	3.12	3.12
$10^{-1}$	1.87	2.81	2.97	2.99	2.99
0.5	1.26	2.04	2.17	2.19	2.19
0.7	0.82	1.38	1.48	1.49	1.49
<u><math>\gamma = 0.95</math></u>					
$10^{-4}$	2.49	3.82	4.05	4.07	4.07
$10^{-3}$	2.49	3.81	4.05	4.07	4.07
$10^{-2}$	2.48	3.80	4.03	4.06	4.06
$10^{-1}$	2.35	3.67	3.90	3.93	3.93
0.5	1.74	2.90	3.11	3.13	3.13
0.7	1.31	2.24	2.42	2.43	2.43

<sup>a</sup>Entries correspond to  $10^{22} X_{H_2O} k_F P \tau / T$ .

Equation (17) may be thought of as a design criterion for a process module. It relates the necessary volume of the module to the governing parameters, Figure 9 shows a log-log plot of  $V/F_0$  vs  $k_f$  for each of the gasifier conditions with a process module temperature of 500K.  $V/F_0$  values above the line correspond to a sufficiently sized process module for a given effective rate constant to achieve 95% equilibrium. The two horizontal dashed lines correspond to large scale systems (flowrates of 3000 SCF/sec) with modules of 1000 and 100 ft<sup>3</sup>. For these parameters, the catalytic rate must be  $k_f \sim 10^{-17}$ - $10^{-16}$  cm<sup>3</sup>/mol-sec to handle all gasifiers. The noncatalytic gas phase rate constant is not known but is estimated to be  $10^{-26}$ - $10^{-24}$  cm<sup>3</sup>/molsec at 500K. This would correspond to an activation energy of approximately 15000K. Since catalytic enhancement is thought to reduce the activation energy to approximately 3000K, this type of catalytic module would appear encouraging.

#### IV. EQUILIBRIUM REVISITED

In the previous section the governing parameters and their relationship to the process module were determined. With them, once the effective hydrolysis rate constant is determined, an optimal module may be designed. This model presents the parameters necessary to reach a desired fraction of the equilibrium H<sub>2</sub>S/COS ratio. This ratio is determined by the gasifier operating conditions. As noted earlier, the H<sub>2</sub>S/COS equilibrium ratio is directly related to the COS hydrolysis equilibrium constant by the frozen H<sub>2</sub>O/CO<sub>2</sub> ratio in the gas stream. Since the value of the H<sub>2</sub>S/COS ratio is so important to the attainable sulfur redistribution in the process module, a few points should be noted regarding this ratio and any effect on the gaseous product fuel.

Although the minimization of Gibbs Free Energy is a numerically efficient and general method of obtaining the equilibrium compositions, often the more explicit method of solving equilibrium constant expressions can lead to insights obscured by the above technique. In a gasifier, the major molecular participants are H<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>O, and CO<sub>2</sub>. Therefore, there are only five conditions necessary to determine the concentrations of these species. These are the three elemental conservation equations and two additional chemical equilibrium equations. Namely



The two chemical equations are the water-gas shift (V) and methanation (VI) reactions.

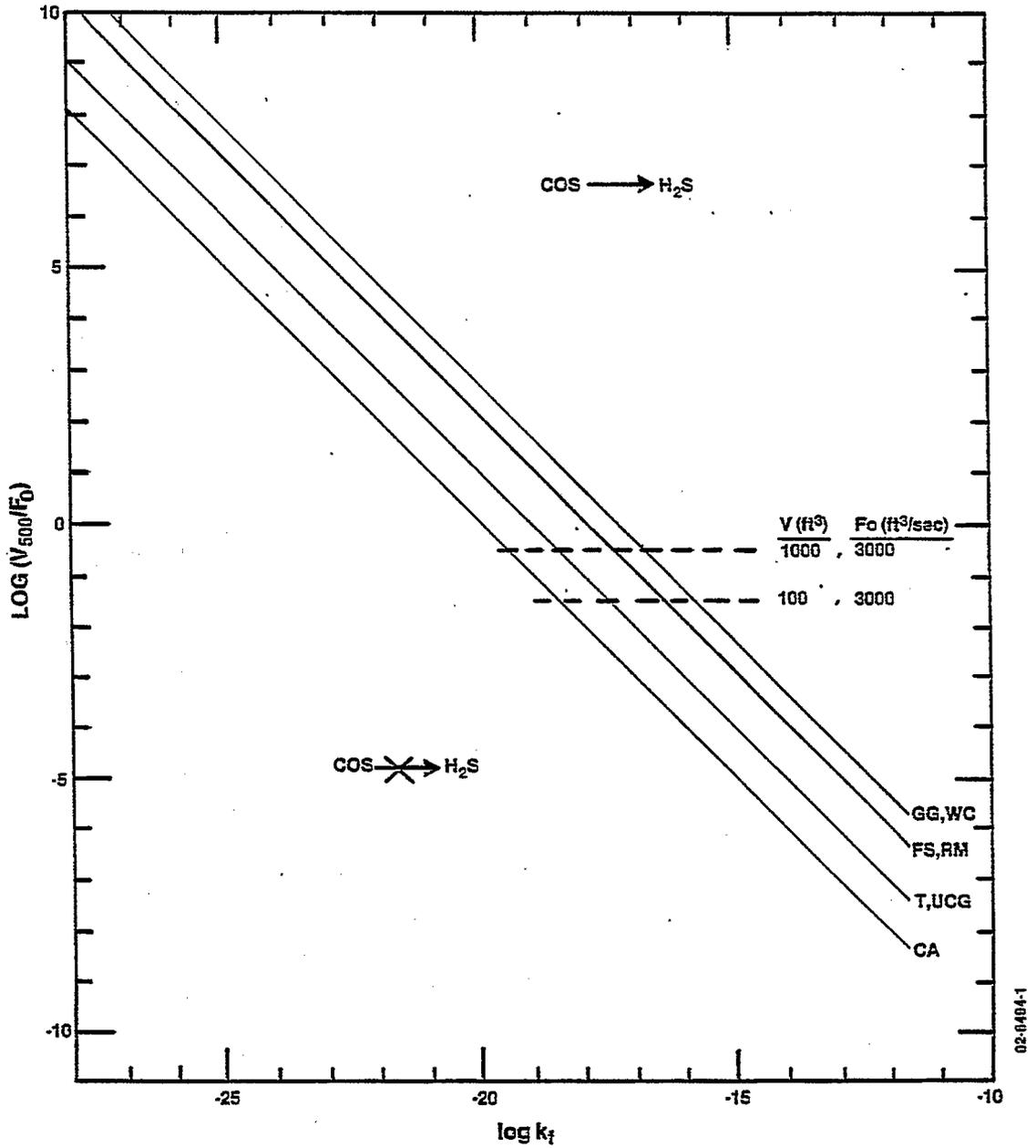
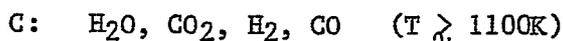
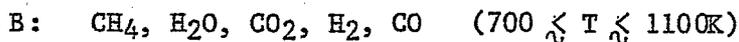
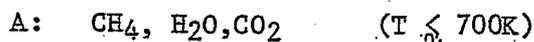


Figure 9. Log-Log Plot of  $V/F$  vs.  $k_f$  for Each of the Gasifiers Corresponding to a Process Module<sup>o</sup> Temperature of 500K. Area above the Lines Corresponds to Conditions such that the Reaction will Achieve Equilibrium. Below the lines the ratio is too slow for the reaction to proceed.

Now, the equilibrium of the methanation reaction is such that at high temperatures the equilibrium is totally shifted to the left, with no CH<sub>4</sub> present. At lower temperatures, equilibrium is with the CH<sub>4</sub> formation, however, rates became too slow to achieve the equilibrium. Since CH<sub>4</sub> is a more economical fuel, often a methanation module is added to convert the H<sub>2</sub> and CO to CH<sub>4</sub>. Therefore, it is important to understand the equilibrium over the entire range of temperatures.

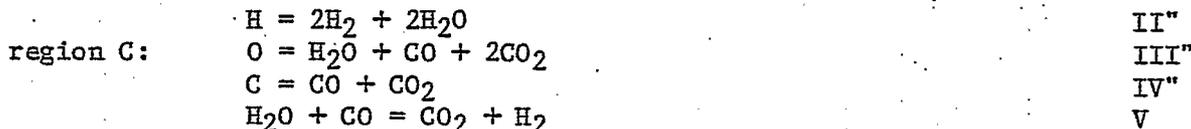
The equilibrium is naturally divided into three temperature regions denoted by A, B, and C. Only in region B are all five molecular species present. The molecular distribution of major species within the regions are:



Therefore, since the molecular species are reduced in regions A and C, only B requires the entire (II-VI) set of equilibrium conditions. In regions A and C, the conditions become



and



In region A the molecular distribution of major species is trivially determined from the conservation equations.

The solution (per mole of carbon) in region A is

$$\left(\frac{\text{CH}_4}{\text{C}}\right) = \frac{3}{2} \left(\frac{\text{H}}{\text{C}}\right)_w - \frac{3}{16} \left(\frac{\text{O}}{\text{C}}\right)_w + \frac{1}{2} \quad (18a)$$

$$\left(\frac{\text{H}_2\text{O}}{\text{C}}\right) = 3 \left(\frac{\text{H}}{\text{C}}\right)_w + \frac{3}{8} \left(\frac{\text{O}}{\text{C}}\right)_w - 1 \quad (18b)$$

$$\left(\frac{\text{CO}_2}{\text{C}}\right) = \frac{1}{2} - \frac{3}{2} \left(\frac{\text{H}}{\text{C}}\right)_w + \frac{3}{16} \left(\frac{\text{O}}{\text{C}}\right)_w \quad (18c)$$

Therefore, as  $(\text{H}/\text{C})_w$  is increased, the yield of  $\text{CH}_4$  and  $\text{H}_2\text{O}$  is increased and  $\text{CO}_2$  is decreased, while as  $(\text{O}/\text{C})_w$  is increased the yield of  $\text{CH}_4$  is decreased with  $\text{H}_2\text{O}$  and  $\text{CO}_2$  being increased. Note that there is no pressure or temperature dependence within this region.

Region C has a temperature dependence due to the addition of the water gas reaction (V). However, since there is no change in the number of moles during this reaction there is no pressure dependence throughout this region. The solution for the molecular species within this region is

$$\left(\frac{\text{H}_2\text{O}}{\text{C}}\right) = \frac{3}{4} \left(\frac{\text{O}}{\text{C}}\right)_w - 1 - \left(\frac{\text{CO}_2}{\text{C}}\right) \quad (19a)$$

$$\left(\frac{\text{CO}}{\text{C}}\right) = 1 - \left(\frac{\text{CO}_2}{\text{C}}\right) \quad (19b)$$

$$\left(\frac{\text{H}_2}{\text{C}}\right) = 6 \left(\frac{\text{H}}{\text{C}}\right)_w - \frac{3}{4} \left(\frac{\text{O}}{\text{C}}\right)_w + 1 + \left(\frac{\text{CO}_2}{\text{C}}\right) \quad (19c)$$

with 
$$\left(\frac{\text{CO}_2}{\text{C}}\right) = G(T) [ H^{\frac{1}{2}}(T) - 1 ] \quad (19d)$$

where 
$$G(T) = [ 6 \left(\frac{\text{H}}{\text{C}}\right)_w - \frac{3}{4} (1-K_V) \left(\frac{\text{O}}{\text{C}}\right)_w + 1 ] / 2(1-K_V) \quad (19e)$$

and 
$$H(T) = 1 + \frac{K_V}{(1-K_V)G^2} \left[ \frac{3}{4} \left(\frac{\text{O}}{\text{C}}\right)_w - 1 \right] \quad (19f)$$

Table 4 gives the values of  $K_V$  for several temperatures.

TABLE 4. EQUILIBRIUM CONSTANT FOR  $\text{H}_2\text{O} + \text{CO} = \text{CO}_2 + \text{H}_2$

T (K)	$K_V = \frac{(\text{CO}_2)(\text{H}_2)}{(\text{H}_2\text{O})(\text{CO})}$
1600	0.3360
1500	0.3899
1400	0.4645
1300	0.5718
1200	0.7337
1100	0.9936
1000	1.445
900	2.315
800	4.246
700	9.472
600	28.44
500	138.0

As seen from Figures 1 and 2, the  $H_2O/CO_2$  ratio is most likely to become frozen at temperatures corresponding to region C (or perhaps region B). In region C the  $H_2O/CO_2$  ratios is given by,

$$\left(\frac{H_2O}{CO_2}\right) = \frac{\left[\frac{3}{4}\left(\frac{O}{C}\right)_w - 1\right]}{(CO_2/C)} - 1 \quad (20)$$

Here, an increase in  $(H/C)_w$  [with constant  $(O/C)_w$ ] implies an increase in  $H_2O$  at the expense of  $CO_2$  and thus an increase in the  $H_2O/CO_2$  equilibrium. Another useful simplification within this region is obtained when  $K_V = 1$ . This condition corresponds to a temperature of approximately 1100K. Here the  $H_2O/CO_2$  ratio is easily found from

$$\left(\frac{H_2O}{CO_2}\right) = 6 \left(\frac{H}{C}\right)_w \quad T \approx 1100K \quad (21)$$

Region B is the only one which requires the full set of equilibrium conditions, namely the addition of the methanation reaction. Since this reaction decreases the total number of moles, the corresponding equilibrium constant carries a factor of  $P^2$ . Therefore this is the only region which will show a pressure dependence as well as a temperature dependence.

Figure 10 shows a replotting of Figure 9 with the three temperature regions indicated by vertical dashed lines. The accuracy of Equations (18-21) is related by the plotted points within each region. The open circles correspond to Equation (18), the solid circles correspond to Equations (19 and 20), and the open squares correspond to Equation (21). This figure and the above discussion illustrate that for most temperatures and pressures in the gasification of coal, the equilibrium distribution of the major species may be predicted without the need for more elaborate computations. Examining these relationships, the governing parameters are found to be the temperature, pressure, and the  $(H/C)_w$  and  $(O/C)_w$  ratio. Moreover, using Equations (18-21) it is possible to obtain a set of conditions which will give a desired equilibrium distribution of the sulfur species. In the following section, we will examine the gasifier as a whole and discuss the effect of these parameters on the overall quality of the product gas.

#### V. CONCLUDING REMARKS

The gas phase chemistry of a gasifier has been studied with particular attention to the major species and their influence on the equilibrium distribution of sulfur between  $H_2S-COS$  and the size of the process module needed to achieve the desired extent of equilibrium. One important conclusion is that the

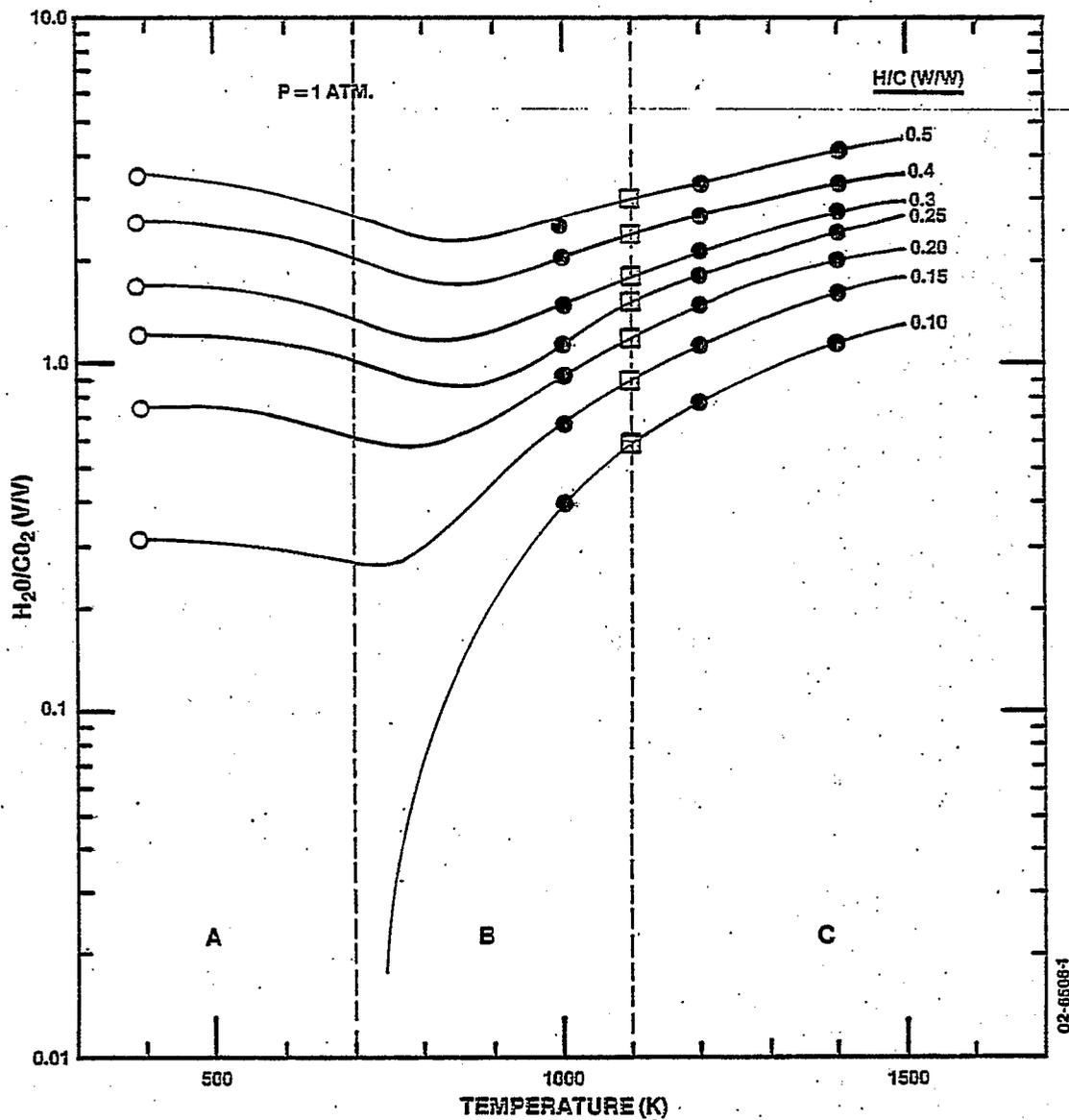


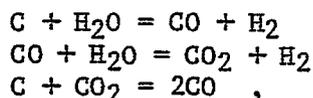
Figure 10. Plot Similar to Figure 9 Showing the Three Temperature Regions (see text). Open circles correspond to the analytical expressions of Equation (18), solid circles correspond to Equations (19 and 20), while open squares correspond to Equation (21).

residence time is essentially independent of the initial and final H<sub>2</sub>S/COS ratios. Therefore, there are no module design criteria which depend on the desired sulfur redistribution. The attainable H<sub>2</sub>S/COS ratio is completely determined by the local H<sub>2</sub>O/CO<sub>2</sub> ratio and the COS hydrolysis equilibrium constant.

The H<sub>2</sub>O/CO<sub>2</sub> ratio is controlled by the water-gas reaction at high temperatures (>1100K) and by the water-gas and methanation reactions at intermediate temperatures (700-1100K). As the gas stream is quenched upon exiting the gasifier reactor these reactions become very slow and the H<sub>2</sub>O/CO<sub>2</sub> ratio becomes frozen corresponding, most likely, to its equilibrium value at the temperature of the reactor exit. Although, this temperature may be between 700 and 1100K, (i.e., the pressure dependent region), the adjoining temperature regions are pressure independent. Therefore, we expect that the H<sub>2</sub>O/CO<sub>2</sub> ratio is not strongly dependent on pressure. This has been born out for the gasifiers considered in the present study.

Apart from temperature and pressure, the parameters which govern the H<sub>2</sub>O/CO<sub>2</sub> equilibrium ratio are the (H/C)<sub>w</sub> and (O/C)<sub>w</sub> ratios. In general, increasing the (H/C)<sub>w</sub> and decreasing the (O/C)<sub>w</sub> ratios increases the H<sub>2</sub>O/CO<sub>2</sub> ratio which in turn increases the H<sub>2</sub>S/COS equilibrium ratio. It is important to note that the affect of increasing the (H/C)<sub>w</sub> and decreasing the (O/C)<sub>w</sub> ratios also increases the equilibrium CH<sub>4</sub> yield. Therefore, attempting to improve the sulfur distribution not only does not lower the attainable CH<sub>4</sub> yield from the methanation module but actually increases it.

Although, from the above discussion, it would appear that every effort should be made to increase the (H/C)<sub>w</sub> ratio and decrease the (O/C)<sub>w</sub> ratio, this is only true within bounds. The gasification of coal requires fairly high temperatures. Moreover, the overall gasification reactions,



are endothermic. Thus, if heat is not continually supplied the temperature will drop and gasification will cease. This heat is produced from the combustion zone where some of the carbon is oxidized to CO<sub>2</sub>. Now, the (H/C)<sub>w</sub> ratio may be increased by introducing more steam but this will increase the (O/C)<sub>w</sub> ratio as well. In order to decrease the (O/C)<sub>w</sub> ratio the air (or oxygen) flowrate must be decreased. However, decreasing the air will cause less combustion and therefore lower the reaction zone temperature. In actuality, increasing the steam flowrate, will increase the endothermic gasification reactions, resulting in lower temperature. Therefore, an increase in steam flowrate must be accompanied by an increase in air (or oxygen) flowrate to maintain temperature.

In summary, the major points of this study are:

- A process module with an effective catalytic COS hydrolysis rate constant of approximately  $10^{-17}$  to  $10^{-16}$   $\text{cm}^3/\text{mol-sec}$  will reach >95% of the equilibrium  $\text{H}_2\text{S}/\text{COS}$  ratio in small enough residence times to allow reasonable reaction vessel sizes.
- This residence time is essentially independent of initial and final  $\text{H}_2\text{S}/\text{COS}$  ratios.
- The achievable  $\text{H}_2\text{S}/\text{COS}$  equilibrium ratio at a given temperature is completely determined from the product of the locally frozen  $\text{H}_2\text{O}/\text{CO}_2$  ratio and the COS hydrolysis equilibrium constant for that temperature.
- The  $\text{H}_2\text{O}/\text{CO}_2$  ratio becomes frozen at approximately 900-1200K, probably near the reactor exit temperature.
- The governing parameters for the  $\text{H}_2\text{O}/\text{CO}_2$  equilibrium ratios are the temperature, pressure, and the gas stream  $(\text{H}/\text{C})_w$  and  $(\text{O}/\text{C})_w$  ratios.
- The higher the  $(\text{H}/\text{C})_w$  ratio and the lower the  $(\text{O}/\text{C})_w$  ratio, the larger the  $\text{H}_2\text{O}/\text{CO}_2$  equilibrium ratio and thus the larger the  $\text{H}_2\text{S}/\text{COS}$  equilibrium ratio.
- Raising the  $(\text{H}/\text{C})_w$  ratio and lowering the  $(\text{O}/\text{C})_w$  ratio also increases the achievable  $\text{CH}_4$  equilibrium concentration.

#### ACKNOWLEDGMENTS

The authors would like to thank Mr. Robert V. Collins and Dr. Gordon C. Page for many stimulating discussions during this work. The equilibrium computations were performed using the PACKAGE CODE which was developed and extended by many people (including Michael B. Faist) at Aerodyne Research, Inc.

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## BEHAVIOR OF A SEMIBATCH COAL GASIFICATION UNIT

by

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### ABSTRACT

This paper describes the transient behavior of a laboratory scale fixed-bed gasifier operated in a semibatch mode. The operation is batch with respect to the coal feed and continuous with respect to gas flows. Various coals ranging from lignite to bituminous were gasified using steam-air mixtures at 1.4 MPa (200 psia) and approximately 900°C. The transient behavior of the reactor temperature at various coal bed depths was examined. Test results from nine tests involving five coals are reported. The data presented include the rate of production of various gasification products. These include CH<sub>4</sub>, CO, H<sub>2</sub>, benzene, toluene, xylene, H<sub>2</sub>S, COS, and thiophene, as a function of run time. It was found that the majority of the CH<sub>4</sub>, the minor hydrocarbons, and sulfur species were evolved during coal devolatilization. These data were analyzed using a simple kinetic model which assumes that the rate of production of a compound at any time is proportional to the (potential) amount of that compound remaining in the coal. This model explains the data reasonably well during the devolatilization period. It was found that the specific rate of production of individual species was practically the same for all coals and gasification products considered; the ultimate yield was dependent on coal type. The ultimate yield of (a) CH<sub>4</sub> or benzene, and (b) sulfur species roughly paralleled the volatile and sulfur contents of the coals, respectively.

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## BEHAVIOR OF A SEMIBATCH COAL GASIFICATION UNIT

### INTRODUCTION

The Research Triangle Institute (RTI) has performed over 40 gasification tests in a laboratory scale gasifier using a variety of coals.<sup>[1,2]</sup> During these tests, RTI has developed procedures for the sampling of the various gasifier process streams and for identifying and quantifying potential environmental pollutants found in these streams.<sup>[3]</sup>

The coal gasification tests were performed in a semibatch reactor where the experiments are batch with respect to the coal and continuous with respect to gas flows. The gasifier is approximately 6.6 cm I.D. and its 60 cm active length is surrounded by a three zone furnace. During a gasifier run, the gasifier was initially heated electrically to the desired gasification temperature of about 950°C with the desired air and steam flow passing through the gasifier. The air flows varied from 5.0 to 15.0 standard liters per minute (slpm) and steam varied from 5.0 to 18.0 slpm. After reaching gasification temperatures, the coal was batch-fed to the gasifier with the charge ranging from approximately 1.2 to 1.6 kg. The coal size was 8 x 16 mesh, and the charge was supported by a porous ceramic plate which also acted as the gas distributor.

The coal was charged to the gasifier at room temperature and, consequently, cooled the gasifier well below the initial temperature. This behavior is shown in Figure 1. Recovery of the temperature took about 30 minutes, and the rate of increase in the average bed temperature after coal drop appeared to be proportional to the difference between the average final temperature and instantaneous average bed temperature. It was found that after the recovery period, the temperature profiles in the coal bed closely matched the initial temperature profile and were dominated by the furnace except in the combustion zone of the bed.

The gasification tests were characterized by two distinct periods of operation: (1) the initial stage after the coal drop during which devolatilization of the coal occurred (surge period), and (2) a steady-state period which followed the surge and was the stage where coal gasification took place resulting in a fairly steady product gas composition.

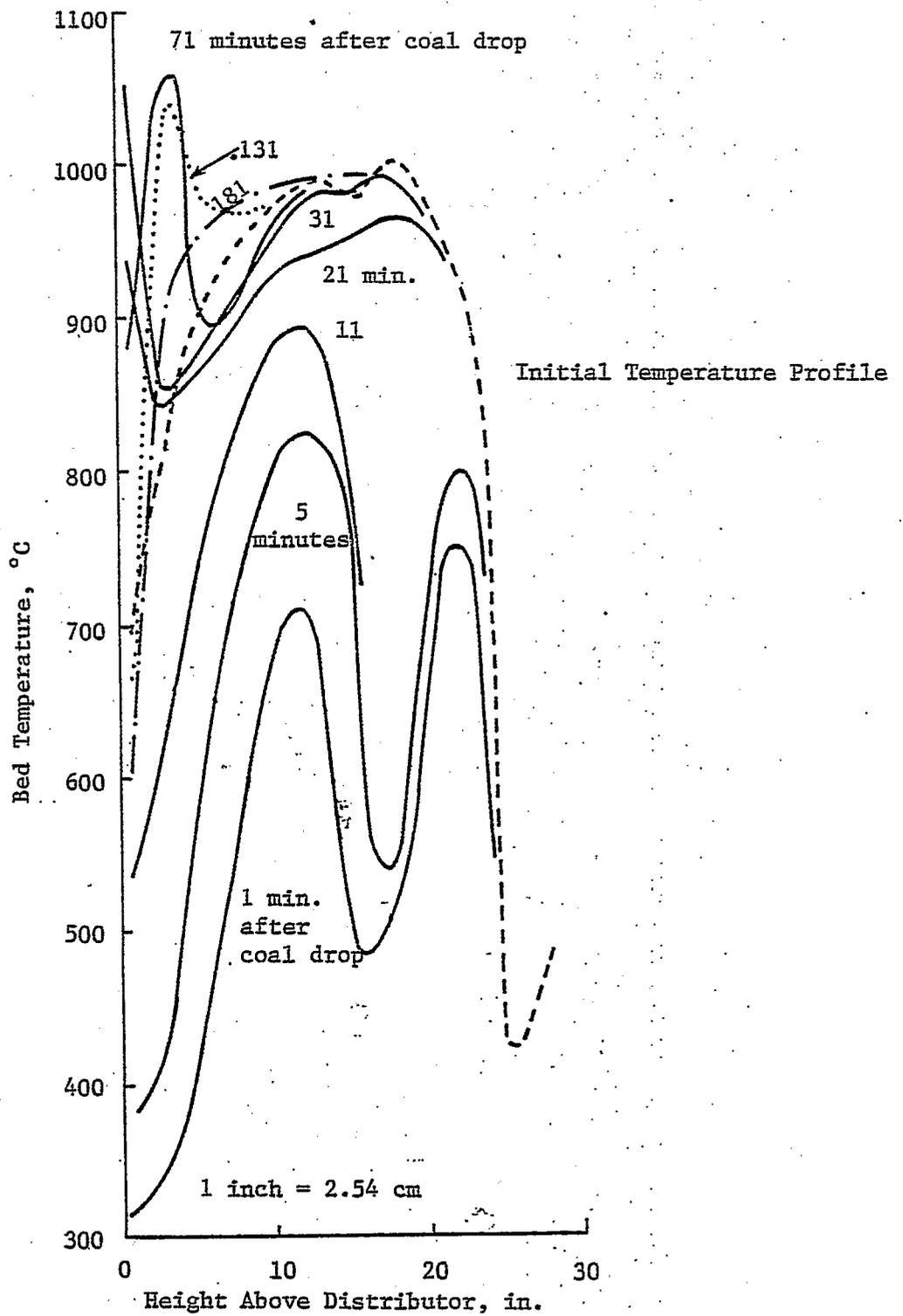


Figure 1. Temperature Profile in the Batch Gasifier - Run 25.

Figures 2, 3, and 4 show the time-dependent nature of a typical gasifier test in which Illinois No.6 bituminous, Wyoming subbituminous and North Dakota lignite coals were gasified. The composition of the coals and gasification conditions are shown in Tables 1 and 2, respectively. It can be seen from these figures that production of methane and other minor hydrocarbons is greatest during the initial stage of the gasification test or during coal devolatilization. The production rate of these components fall almost two orders of magnitude from their initial rates during the surge period. A more complete description of the production rate-time characteristics of the semibatch gasification of the five coals in nine tests have been presented elsewhere. [4]

Based on the data in Figures 2, 3, and 4 and additional data presented by McMichael et al., [4] the following observations can be made about the rate of pollutant and product production as a function of time:

1. The production of pollutants and  $\text{CH}_4$  in the product gas usually surges to a high rate just after the coal drop, and drops quickly as the bed temperature rises. A majority of the minor components and  $\text{CH}_4$  are formed in the first 25 to 30 minutes of the run. After this time the product rate decreases.
2. For the bituminous coals and the Montana subbituminous coal the rate of  $\text{H}_2$  production increases during the initial stages of gasification during devolatilization. This could be a consequence of (a) increasing bed temperatures at the beginning of the run resulting in increasing  $\text{H}_2$  formation from the steam-carbon reaction, and (b) decreased availability of reactive carbon as coal devolatilization proceeds, thus more  $\text{H}_2$  appears in the gas. Hydrogen formation peaks early in the run, and the rate of formation decreases fairly steadily over the remainder of the run. This steady decrease is probably due to the decrease in the density of carbon in the bed with time.
3. For a steady flow of steam and air, the rate of production of CO approximately parallels the  $\text{H}_2$  production.
4. For Illinois No.6 bituminous coal, the rate of  $\text{CO}_2$  production reaches a maximum in the initial stage of the gasification run and then decreases or remains fairly constant. The Western Kentucky coal also shows this trend except the production rate increased sharply at oxygen breakthrough. For the subbituminous and lignite coals,  $\text{CO}_2$  production reaches a maximum during devolatilization and then quickly drops to a minimum at about 25 minutes into the run. After this minimum the production rate increases steadily over the length of the run. The  $\text{CO}_2$  increase is usually accompanied by a slow decrease in the rate of CO production. The reason for this could be that as the density of carbon in the bed decreases through gasification, more CO is burned in the gas phase.

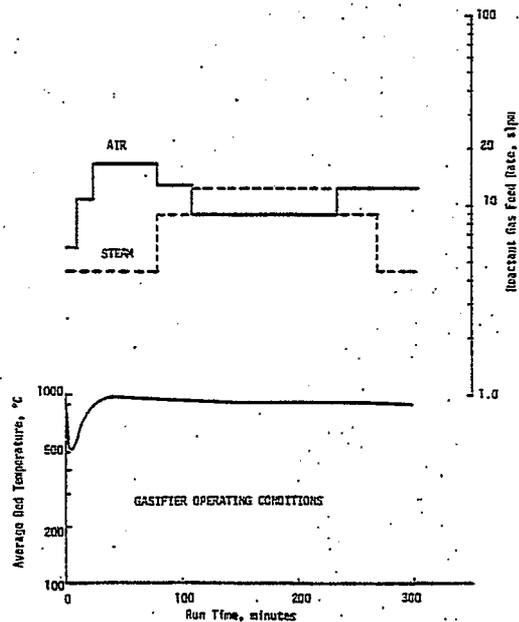
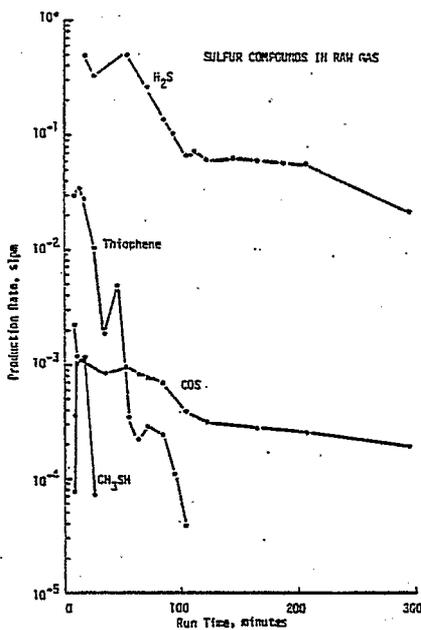
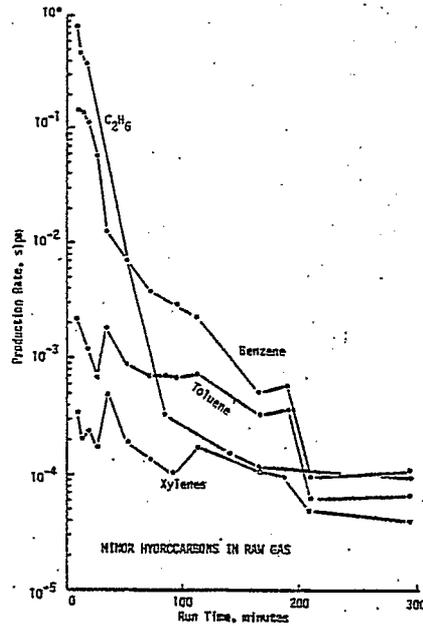
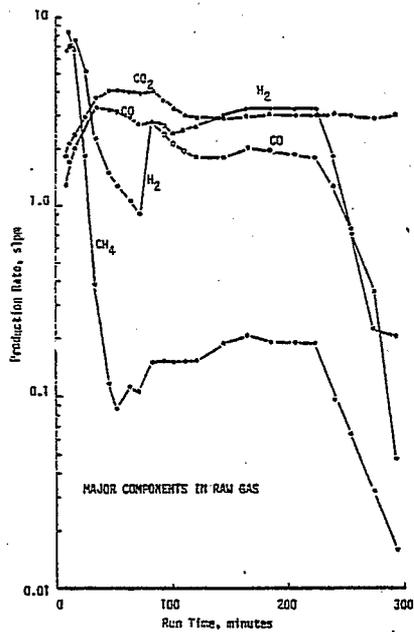


Figure 2. Gasifier operating conditions and production rate of various compounds as a function of run time - Run 23, Illinois No.6 bituminous coal.

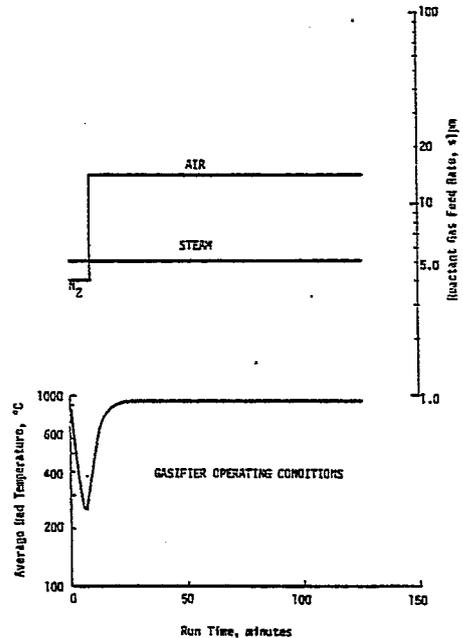
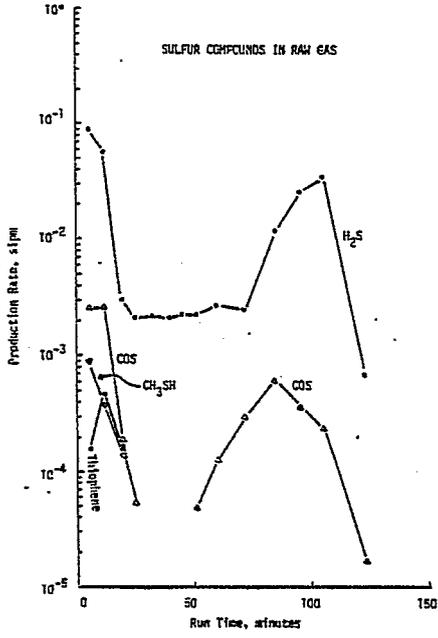
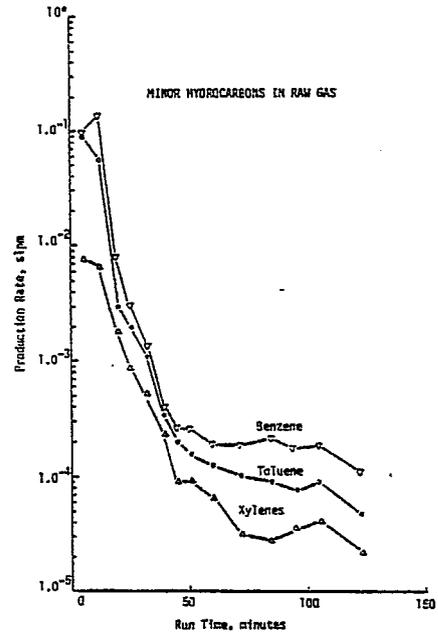
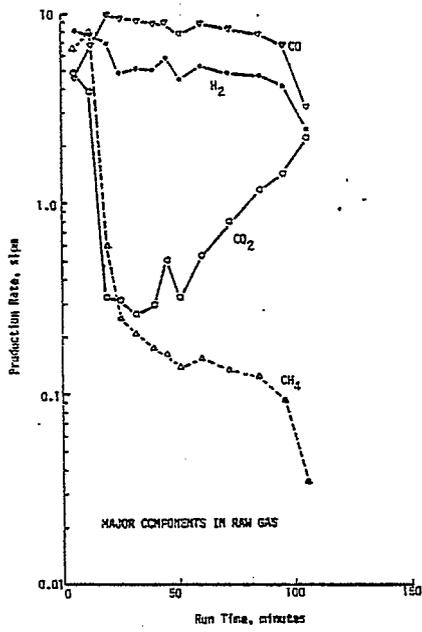


Figure 3. Gasifier operating conditions and production rate of various compounds as a function of run time - Run 33, Wyoming subbituminous coal.

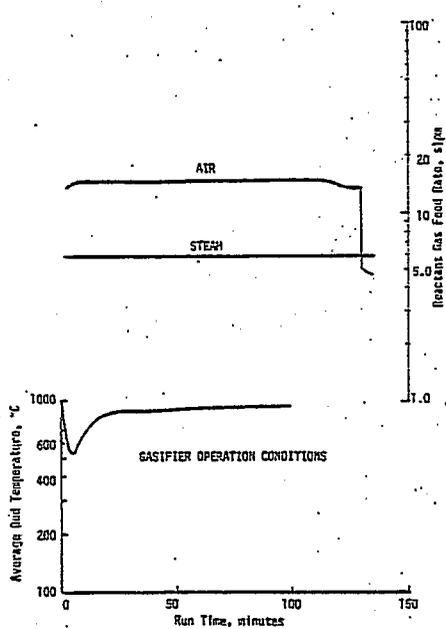
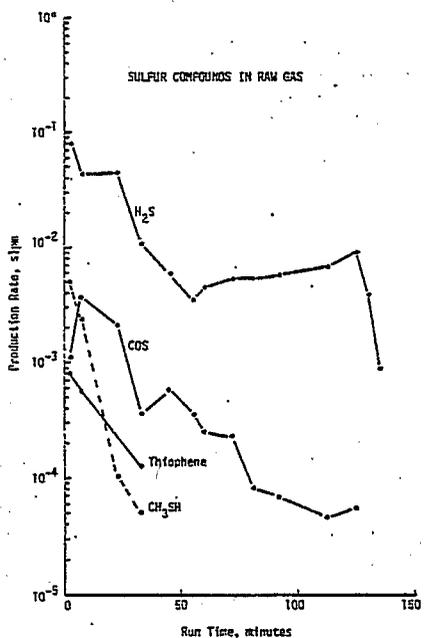
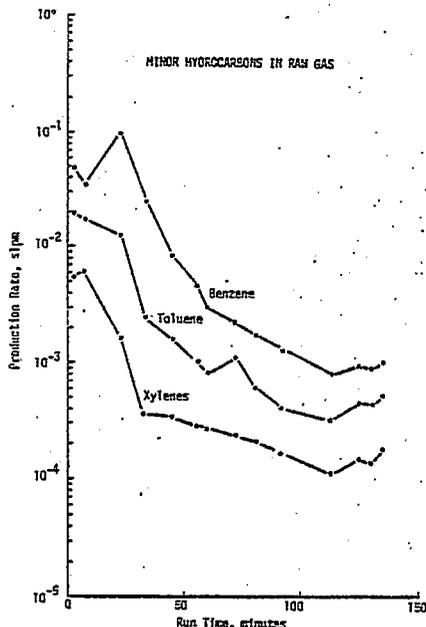
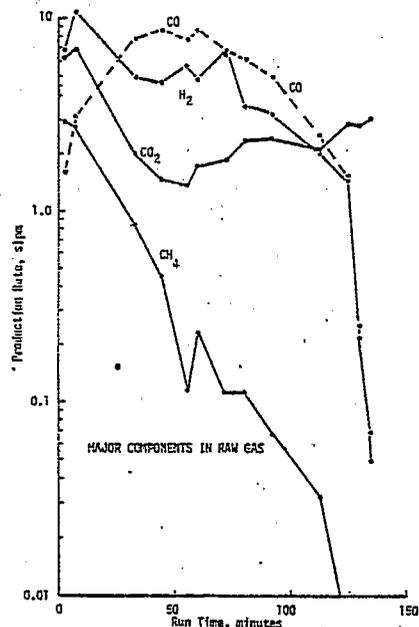


Figure 4. Gasifier operating conditions and production rate of various compounds as a function of run time - Run 36, North Dakota lignite.

TABLE 1. ANALYSIS (AS RECEIVED) OF FUELS GASIFIED

Fuel	Moisture %	Ash %	Volatile Matter %	Fixed Carbon %	Sulfate Organic Pyritic Total S'	Carbon %	Hydrogen %	Oxygen %	Nitrogen %	FSI
Illinois No.6 Bituminous	5.31	11.03	34.16	49.50	0.00	66.35	5.32	12.71	1.525	3.5
					1.83					
					1.24					
Montana Rosebud Subbituminous	21.19	8.86	31.56	38.39	0.17	53.95	6.87	28.53	1.20	0.0
					0.21					
					0.21					
Wyoming Subbituminous	15.56	6.31	38.30	39.83	0.07	56.80	5.94	30.02	0.38	0.0
					0.08					
					0.40					
North Dakota Lignite	29.63	6.39	28.57	35.41	0.01	46.82	9.85	35.65	0.73	0.0
					0.54					
					0.01					
Western Kentucky No.9 Bituminous	7.03	7.83	38.78	46.36	0.05	67.36	5.58	13.71	1.08	4.0
					2.69					
					1.70					
					4.44					

TABLE 2. SUMMARY OF OPERATING CONDITIONS FOR THE RTI SCREENING TESTS

	16	21	23	41	25	33	35	36	43
	Illinois No.6	Illinois No.6	Illinois No.6	Western Kentucky	Montana	Wyoming	Wyoming	North Dakota	North Dakota
Steam (g)	3704	4713	1952	1390	748	500	527	639	422
Air (g)	1350	1720	3288	3060	2482	2097	2461	1939	2022
Coal (g)	1569	1543	1594	1250	1491	1396	1420	1444	1458
Air/Coal	0.86	1.1	2.1	2.5	1.7	1.5	1.7	1.3	1.4
Steam/Coal	2.4	3.1	1.2	1.1	0.50	0.36	0.37	0.44	0.29
Air/Steam	0.35	0.35	1.8	2.2	3.4	4.2	4.6	3.1	4.8
T <sub>max</sub> * °C	941	984	1020	1034	1006	1010	790	916	914

\*Time averaged maximum bed temperature.

5. The rates of production of benzene, toluene, and xylenes parallel each other. In general, benzene has the highest rate of production and the xylenes the lowest. Each has a high initial production rate. The rate decreases rapidly during devolatilization by one to two orders of magnitude.
6. The production of  $H_2S$  and  $COS$  is at a maximum during devolatilization and falls off rapidly near the end of this period. After devolatilization,  $H_2S$  and  $COS$  appear to follow the production of  $CO_2$ . This is probably due to two modes of sulfur release from the coal. The first is during devolatilization when sulfur-containing compounds are being rapidly evolved from the coal. Decomposition of these compounds results in  $COS$  and  $H_2S$ . In the second mode after devolatilization, sulfur is released by oxidation of the char matrix. Upon release the sulfur species react with  $H_2$ ,  $CO$ , or  $CO_2$  giving rise to  $H_2S$  and  $COS$ . Thus the production rate of  $H_2S$  and  $COS$  follows that of  $CO_2$  since it is indicative of oxidation.
7. Methanethiol and thiophene are produced primarily during coal devolatilization. For each compound the production rate starts at a high initial value and falls below detection limits within 25 to 50 minutes after the coal drop.

The yield of potential environmental pollutants in the gasifier product gas over the length of the gasification runs has been computed for the RTI gasifier by integrating the rate of production with respect to time. These yields have been compared by Green, et al. [5] to yield data reported in the literature for larger scale, continuous gasifier. An example of this is shown in Table 3. It can be seen that for a majority of the components reported that the data from the RTI gasifier appears to bracket the data from the continuous gasifier even though the continuous gasifiers represent a range of gasifier operation from fixed- to fluidized-bed. Analysis of data from semibatch operation is difficult due to the unsteady nature of operation. Recently RTI has been operating its gasifier in a continuous feed mode and analysis of this data is now underway.

The initial production rates of methane and minor hydrocarbons during the devolatilization of the coal as shown in Figures 2, 3, and 4 can be interpreted in several ways. One way is in terms of the Gregory-Littlejohn equation. [6] For a constant heating rate this equation predicts a straight line on a semilog graph of rate of production of volatiles versus time. This equation could perhaps be applied to the individual components making up the total volatile yield.

TABLE 3. POLLUTANT PRODUCTION IN RAW MOISTURE-FREE PRODUCT GAS FROM GASIFICATION OF NORTH DAKOTA LIGNITE

Pollutant	Air-Blown Synthane (Mercer County) µg/g coal	CO <sub>2</sub> Acceptor (Velva) µg/g coal	GFETC (Velva) µg/g coal	RFI Range Beulah Zap (Mercer County) µg/g coal
Hydrogen Sulfide	9.4E3	2.1E3	1.5E3	1.7E3-2.6E3
Carbonyl Sulfide	7.6E2	9.7E1	1.3E2*	1.7E2-2.9E2
Thiophene	<3.8E1	NA	NA	3.8E0-5.7E2
Methylthiophene	<4.4E1	NA	NA	1.3E1-3.7E1
Dimethylthiophene	<5.0E1	NA	NA	1.3E0***
Methanethiol	3.4E1	NA	8.5E1**	1.3E1-7.8E1
Benzene	4.8E3	NA	NA	2.0E3-5.3E3
Toluene	5.8E2	NA	NA	1.1E3-2.1E3
Xylene	1.9E2	NA	NA	2.4E2-7.6E2
Ammonia	NA	5.5E3	NA	5.3E1-1.7E2

\*Includes CS<sub>2</sub>.

\*\*"thiols."

\*\*\*C<sub>2</sub>-thiophenes.

Another way to interpret data of the type shown in Figures 2, 3, and 4 involves the use of a rate expression. The most commonly used kinetic approach is to assume that the rate of evolution of a volatile species is proportional to the potential amount of that species remaining in the coal. [7]

$$\frac{dV_i}{dt} = k_i (V_{\infty_i} - V_i) \quad (1)$$

where  $k_i$  = the rate constant,  $\text{min}^{-1}$ .

$V_i$  = the yield of the  $i$ th volatile component,  $\text{sl/kg}$  coal.

$V_{\infty_i}$  = the ultimate yield of the  $i$ th volatile component,  $\text{sl/kg}$  coal.

$t$  = time,  $\text{min}$ .

Assuming isothermal conditions, Equation (1) can be integrated subject to  $V_i = 0$  at  $t = 0$  to give

$$V_{\infty_i} - V_i = V_{\infty_i} e^{-k_i t} \quad (2)$$

Substituting Equation (2) into (1) gives

$$\frac{dV_i}{dt} = k_i V_{\infty_i} e^{-k_i t} \quad (3)$$

Taking the log of Equation (3) yields

$$\ln \frac{dV_i}{dt} = \ln (k_i V_{\infty_i}) - k_i t \quad (4)$$

Equation (4) predicts that a semilog plot of the rate of production of a volatile species versus time should yield a straight line with the slope equal to the negative of the rate constant and the intercept equal to the product of the ultimate yield and the rate constant. A substantial number of product rate-time curves determined in RTI's gasification experiments can be interpreted in terms of Equation (4) if the rate constant,  $k_i$ , is viewed as an average constant over the period of the linear data. This can be done if the rate constant is not a strong function of temperature such as would be the case in diffusion-controlled processes.

A kinetic analysis has been made of the rate data for nine gasification tests using Equation (4). The results of this analysis are shown in Table 4. This table presents average results for individual species for an initial rate period for each type coal gasified. The ultimate yield values shown have been normalized to a unit coal basis.

The following observations can be drawn from Table 4.

1. The average ultimate yield of  $\text{CH}_4$  for Illinois No.6 coal is approximately 2.7 scf  $\text{CH}_4$ /lb coal maf which is in good agreement with a value of 2.4 scf  $\text{CH}_4$ /lb coal maf which would be obtained by extrapolating the data for the SYNTHANE gasifier to 200 psig.
2. The kinetic parameters for the initial rate period are for the most part fairly consistent within a given coal type. For example, for Wyoming coal the rate constants range from 0.149 to 0.173  $\text{min}^{-1}$ . In the worst case (Illinois No.6 coal), the rate constants vary by a factor of four which is still in fair agreement considering the assumptions made in the analysis and errors involved in computing production rates. Wyoming subbituminous coal appeared on the average to have the highest specific rate of product formation (i.e., largest rate constants) of any of the coals tested.
3. The values of the rate constants for the different coals and each component are close to each other with a simple average constant being approximately 0.10  $\text{min}^{-1}$ .
4. Examination of the average ultimate yields for the various coals in Table 4 shows that the bituminous coals have the greatest potential for the production of  $\text{CH}_4$  and  $\text{C}_6\text{H}_6$  as well as the sulfur-containing species. The potential for sulfur species production appears to roughly parallel the sulfur content of the coal except for COS in the case of Illinois No.6. However, only one value of the ultimate COS yield could be computed out of the three Illinois runs, and this may not be representative. Of the lower ranked coals, the Wyoming subbituminous coal had the highest potential for  $\text{CH}_4$  and  $\text{C}_6\text{H}_6$  product with ultimate yields of these components approximately on the same order as the Illinois No.6 bituminous coal.

## CONCLUSIONS

Screening tests in which several types of coal were gasified have been considered in this paper. Major emphasis has been placed on the analysis of temperature histories in the gasifier bed and transient production rates of the major gas products, minor hydrocarbons, and selected sulfur-containing species.

The temperature in the bed was found to be dominated by the gasifier furnace when the furnace was in operation. The rate of increase in the average bed temperature in the gasifier after the coal drop appeared to be

TABLE 4. AVERAGE KINETIC PARAMETERS FOR THE INITIAL RATE PERIOD

Volatile Species	Kinetic Parameters									
	Illinois No.6 Coal $k_1$ , $\text{min}^{-1}$	$V_\infty$ , sl/kg coal	Western Kentucky* $k_1$ , $\text{min}^{-1}$	$V_\infty$ , sl/kg coal	Montana* $k_1$ , $\text{min}^{-1}$	$V_\infty$ , sl/kg coal	Wyoming $k_1$ , $\text{min}^{-1}$	$V_\infty$ , sl/kg coal	Zap North Dakota $k_1$ , $\text{min}^{-1}$	$V_\infty$ , sl/kg coal
CH <sub>4</sub>	0.080	141.0	0.155	243.0	0.103	63.3	0.149	121.0	0.064	67.8
C <sub>6</sub> H <sub>6</sub>	0.088	3.05	0.095	4.28	0.092	1.32	0.165	2.55	0.108*	0.70*
H <sub>2</sub> S	0.047	11.5	0.101	10.2	0.104	0.93	0.164	1.80	0.087	1.16
COS	0.036*	0.027*	0.107	0.17	0.062	0.13	0.173	0.071	0.057	0.077
Thiophene	0.130	0.47	0.192	0.17	0.104	0.015	0.149	0.0093	0.046	0.0057

\*Data available for only one gasification test.

k = rate constant for the initial kinetic period.

V<sub>∞</sub> = ultimate yield.

be proportional to the difference between the average final temperature and the instantaneous average bed temperature.

According to the Gregory-Littlejohn equation, the coal bed temperature should have a significant effect on evolution of total volatile material. At a constant heating rate the Gregory-Littlejohn equation predicts that a semilog graph of the devolatilization rate as a function of time should be linear during the initial stages of the gasification test. This behavior was observed for the evolution of individual components such as methane, benzene, minor hydrocarbons, and sulfur species indicating the possibility of developing a Gregory-Littlejohn type of equation for each volatile species.

A simple kinetic model, which has been widely used in the literature in one form or another, was applied to rate-time data for selected chemical components. This model assumes that the rate of formation of a species is proportional to the potential amount of that species remaining in the coal. The model involves two parameters: (1) the ultimate yield of the species, and (2) a proportionality (kinetic rate) constant. It was found that the kinetic rate constant was roughly the same for all species and all coals with a simple average of the constants being  $0.10 \text{ min}^{-1}$ .

The average ultimate yield for each coal for a given species was dependent on the chemical species and coal type. The ultimate yield of methane and benzene approximately paralleled the volatile content of the coal and yield of sulfur-containing components paralleled the sulfur content of the coal. The potential for the evolution of sulfur-containing compounds into the gas was found to be an order of magnitude less for the subbituminous and lignite coal than for the bituminous coals.

#### ACKNOWLEDGEMENT

Support of this work from the U.S. Environmental Protection Agency, Fuel Process Branch, Research Triangle Park, North Carolina, under Grant No. R804979 is gratefully acknowledged.

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CARBON CONVERSION, MAKE GAS PRODUCTION,  
AND FORMATION OF SULFUR GAS SPECIES  
IN A PILOT-SCALE FLUIDIZED BED GASIFIER

by

M. J. Purdy, J. K. Ferrell,  
R. M. Felder, S. Ganesan, and R. M. Kelly

ABSTRACT

The steam-oxygen gasification of a pretreated Western Kentucky No. 11 bituminous coal was carried out in a pilot-scale fluidized bed gasifier. This paper describes the experiments and summarizes measured carbon conversions, sulfur conversions, make gas production rates, and the results of material balance calculations on total mass and major elements (C, H, O, N, and S). The development of a single stage kinetic model for the gasifier is outlined, and correlations of the experimental results using this model are presented. Quantities of sulfur gas compounds formed in the gasifier at different operating conditions are summarized and a first analysis of these results is presented.

## INTRODUCTION

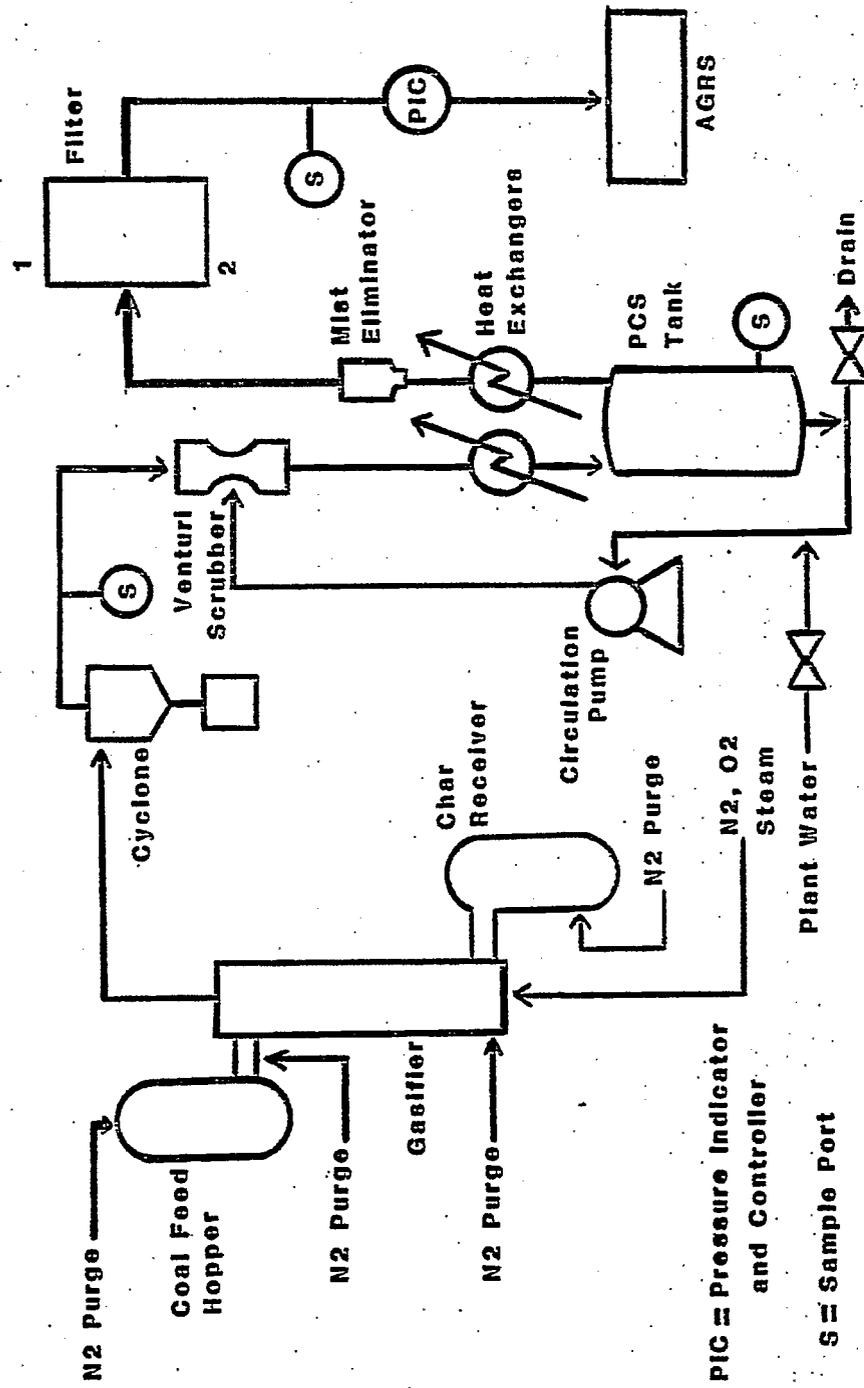
Since 1976, the Department of Chemical Engineering at North Carolina State University has been engaged in a research project on coal gasification sponsored by the U. S. Environmental Protection Agency. The facility used for this research is a small coal gasification-gas cleaning pilot plant. The overall objective of the project is to characterize the gaseous and condensed phase emissions from the gasification-gas cleaning process, and to determine how emission rates of various pollutants depend on adjustable process parameters. Specific tasks to be performed are:

1. Identify and measure the gross and trace species concentrations in the gasifier product streams.
2. Correlate measured emission levels with coal composition and gasifier operating variables.
3. Perform material balances around the gasifier, raw gas clean-up system, and acid gas removal system, and determine the extent to which selected species are removed from the synthesis gas in each subsystem.
4. Correlate measured extents of conversion and removal efficiencies for various species with system operating variables.
5. Evaluate and compare the performance characteristics of alternative acid gas removal processes.
6. Use results to develop models for the gasification and gas cleanup processes.

A complete description of the facility and operating procedures is given by Ferrell et al., Vol I, (1980), and in abbreviated form by Felder et al. (1980). A schematic diagram of the Gasifier and Particulates, Condensables, and Solubles (PGS) removal system is shown in Figure 1. The Acid Gas Removal System (AGRS) is an integral part of the facility, but will not be discussed here.

In the initial series of runs on the gasifier, a pretreated Western Kentucky No. 11 coal was gasified with steam and oxygen. A computer program was written to reduce the operating and analytical data for a run to manageable proportions and to perform material balance calculations. In addition, a single-stage model for the gasifier was formulated and used to correlate the results of the char gasification runs. This paper outlines the data processing program, describes the modeling and model parameter estimation procedures, presents the char gasification results and comparisons with model predictions, and presents a preliminary analysis of the formation of sulfur gases in the gasifier.

FIGURE 1  
GASIFIER - PCS SYSTEM



## DATA REDUCTION COMPUTER PROGRAM

A complete description of the data reduction program is given by Ferrell et al., Vol II, (1980). The program takes as input the reactor temperature profile and pressure, bed dimensions, solid feed properties (sieve analysis, density, settled bed density, proximate and ultimate analyses), feed rates of coal, steam, oxygen and nitrogen, removal rate of char, reactor leak rate, gas flow rate at the PCS system outlet, masses of coal fed, spent char collected, cyclone dust collected, ultimate analyses of the spent char and cyclone dust, chromatographic analyses of the gases exiting the cyclone and the PCS system, pressure drop across a 20-inch segment of the bed, various feed and effluent flow meter calibration temperatures and pressures, and results of trace element and wastewater constituent analyses.

The output of the program contains the following components:

1. Reactor specifications, including the average bed temperature and pressure, the apparent bed density and void fraction, and the bed expansion factor.
2. Solid feed properties, including coal type, solid particle and settled bed densities, as-received moisture content, average feed particle diameter, and proximate and ultimate analyses.
3. Feed rates of coal, steam, oxygen, and nitrogen, selected feed ratios and inlet conditions, superficial gas velocity, solids holdup, and space times for both gases and solids.
4. The make gas flow rate and chemical composition.
5. Production rates of fuel components and the heating value of the make gas.
6. Carbon, steam, and sulfur conversions.
7. Material balances on total mass, and on carbon, hydrogen, oxygen, nitrogen, and sulfur.
8. An energy balance.
9. Results of water analyses.
10. Results of trace element analyses and trace element material balances.

An example of the partial output for a run made on January 22, 1980, is shown in Table 1.

Table 1

```

*****
*
* NCSU DEPARTMENT OF CHEMICAL ENGINEERING *
*
* FLUIDIZED BED COAL GASIFICATION REACTOR *
*
*****
    
```

RUN GO-44B 1/22/80 11:15-14:30

REACTOR SPECIFICATIONS

PRESSURE = 101.6 PSIG ( 801.7 KPA)  
 TEMPERATURE = 1699.8 DEG.F ( 926.5 DEG.C)  
 BED HEIGHT = 38.0 IN. (0.97 METERS)  
 BED DIAMETER = 6.0 IN. (0.152 METERS)  
 ESTIMATED BED VOIDAGE = 0.74  
 SOLIDS HOLDUP = 18.4 LB ( 8.3 KG)

FEED RATES AND RATIOS

COAL = 34.69 LB/HR (15.74 KG/HR)  
 STEAM = 55.85 LB/HR (25.33 KG/HR)  
 OXYGEN = 10.10 LB/HR ( 4.58 KG/HR)  
 NITROGEN = 6.32 LB/HR ( 2.87 KG/HR)  
 PURGE N2 = 14.16 LB/HR ( 6.42 KG/HR)  
 STEAM/CARBON = 1.31 MOLES STEAM/MOLE C  
 O2/CARBON = 0.13 MOLES O2/MOLE C  
 N2/O2 = 0.71 MOLES N2/MOLE O2

ELEMENTAL MATERIAL BALANCES : FLOWS IN LB/HR

	MASS	C	H	O	N	S
COAL	34.7	28.44	0.16	1.37	0.05	0.918
GASES	86.4	0.00	6.25	59.70	20.47	0.000
TOTAL INPUT	121.1	28.44	6.41	61.06	20.52	0.918
CHAR	21.8	18.10	0.08	0.53	0.08	0.412
DUST	1.8	1.20	0.01	0.23	0.01	0.029
GASES	96.2	8.99	6.43	59.88	20.43	0.426
WASTEWATER	0.0	0.00	0.00	0.00	0.00	0.000
TOTAL OUTPUT	119.8	28.29	6.52	60.64	20.52	0.866
% RECOVERY	98.9%	99.5%	101.8%	99.3%	100.0%	94.3%

EXPERIMENTAL MODEL

CARBON CONVERSION (PERCENT)		
COMBUSTION		14.0
GASIFICATION		18.7
TOTAL	31.6	32.7
DRY MAKE GAS FLOW RATE (SCFH)	11.7	12.0
HEATING VALUE OF SWEET GAS (BTU/SCF)	296.0	286.1
EFFLUENT FLOW RATES (LB/HR)		
CO	8.48	8.67
H2	0.94	1.00
CH4	0.66	0.41
CO2	17.79	19.33
N2	20.43	20.48
H2S	0.434	0.297

## GASIFIER MODEL

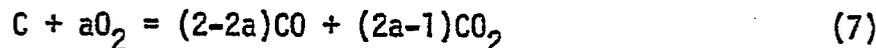
To aid in the analysis of the char gasification runs, a mathematical model of the fluidized bed gasifier was developed. The model takes as input the average reactor bed temperature and pressure; bed dimensions, feed rates of coal, steam, oxygen, nitrogen, and purge nitrogen, solids holdup, ultimate analysis of the feed coke and spent char, and values of three adjustable model parameters, the relative reactivity of the coke, the CO/CO<sub>2</sub> distribution coefficient, and the water gas shift reactivity parameter.

### MODEL DEVELOPMENT AND ASSUMPTIONS

The model treats the gasifier as a single perfect mixer, with the following six reactions taking place:



Reactions 5 and 6 are the oxidation steps required to supply heat for the remaining reactions. These two reactions are assumed to occur instantaneously in a zone of negligible volume separate from the gasification zone. All oxygen in the feed gas is assumed to be consumed to form CO and CO<sub>2</sub> according to the relation



where "a", the combustion product distribution parameter, is an adjustable parameter. A value of  $a = 0.5$  indicates that all CO is formed, while a value of  $a = 1.0$  indicates that only CO<sub>2</sub> is formed.

Reactions 1, 2, and 3 are the reactions by which Johnson (1974) at the Institute of Gas Technology correlated gasification kinetics. Reaction 1 is the conventional steam-carbon reaction. Reaction 3 is assumed to be an independent reaction, although it is attainable as a linear combination of 1 and 2.

The correlation used by Johnson to describe the carbon conversion is given by

$$r = f_L k_T (1-f_c)^{2/3} \exp(-bf_c) \quad (8)$$

where  $r$  is the rate at which the carbon is gasified,  $k_T$  is the sum of the rate constants for Reactions 1, 2, and 3,  $f_c$  is the fractional carbon conversion and  $b$  is a kinetic parameter which depends on gas composition and pressure. Expressions for  $k_1$ ,  $k_2$ , and  $k_3$  are presented by Ferrell et al., Vol II. (1980).

The relative reactivity factor  $f_L$  is determined from

$$f_L = f_0 \exp(8467/T_0) \quad (9)$$

where  $T$  is the maximum temperature to which the char has been exposed prior to gasification. The relative reactivity factor,  $f_0$ , which is an adjustable parameter whose values depend on the particular char used, has values ranging from 0.3 for low-volatile bituminous coal chars to about 10 for North Dakota lignites (Johnson, 1974).

Reaction 4 is the water gas shift reaction, often assumed to be at equilibrium in gasification processes. Results to be described indicate this may be a bad assumption, leading to the necessity of incorporating shift kinetics into the model. The rate expression used is that given by Wen and Tseng (1979)

$$r_4 = 1.6652 \times 10^4 V (1-e) f_{wg} \exp(-25147/T) P G \quad (10)$$

where

- $V$  = bed volume
- $G$  =  $[CO] - [H_2][CO_2]/[H_2O][K_4]$
- $e$  = bed void fraction
- $f_{wg}$  = adjustable shift reactivity parameter  
(varies from char to char)
- $K_4$  = equilibrium constant

The equilibrium constants for the water gas shift reaction and for reactions 1, 2, and 3 were taken from Lowry (1963), and were fit to the equation

$$\ln(K_E) = (a_0/T) + a_1 \quad (11)$$

by least-squares analysis (Alexander, 1978).

A complete description of the model development and the reactor simulation computer program is given by Ferrell et al., Vol II, (1980).

## CHAR GASIFICATION RESULTS

A total of 56 runs have been completed using a Western Kentucky No. 11 coal char as feed stock. The first 13 of these runs were used primarily for the development of operating and sampling procedures, and refinement of analytical methods. The data from gasifier runs G0-14 through G0-56 have been collected and reviewed, and a complete analysis of these runs is presented by Ferrell et al., Vol II, (1980).

### MASS BALANCES

An example of a single page output from the previously described data processing program is shown as Table 1. Criteria for acceptance of a run were arbitrarily chosen following inspection of the mass balance results. A run is judged acceptable if the total mass recovery is within 5% of 100%, and if the worst of the recoveries of elements C, H, and O are within 8%. Based on these criteria, 22 of the 34 runs reviewed are acceptable, and are designated by crossed circles in the figures. Points with filled circles are for runs with total mass recoveries within 5% and worst element recoveries within 6%. Open circles are used for all other runs.

### TEMPERATURE EFFECTS

The effect of the average bed temperature on the dry, nitrogen-free make gas flow rate is shown in Figure 2. For the points shown, the molar steam to carbon ratio varied from 0.92 to 1.15. The plot indicates that the make gas flow rate is highly sensitive to the average bed temperature, with scatter due mainly to the small steam to carbon ratio differences and differing feed rates. The high sensitivity makes determination of the average bed temperature crucial for good model predictions.

### STEAM TO CARBON EFFECTS

The effect of the steam to carbon ratio on the make gas flow rate is shown in Figure 3. At any given temperature the effect of increasing the steam rate at a given carbon input is to increase the make gas flow rate. A side benefit to operating with relatively high steam to carbon ratios in the fluidized bed gasifier is a reduced tendency for the char to clinker.

### SULFUR CONVERSION

Measured sulfur conversion, assumed to equal the carbon conversion by the model, is plotted vs carbon conversion in Figure 4. In most cases the sulfur conversion is greater than the carbon conversion. Studies are currently under way to put the sulfur gas evolution

FIGURE 2

THE EFFECT OF THE AVERAGE BED TEMPERATURE  
ON THE MAKE GAS FLOW RATE (DRY, N<sub>2</sub> FREE)

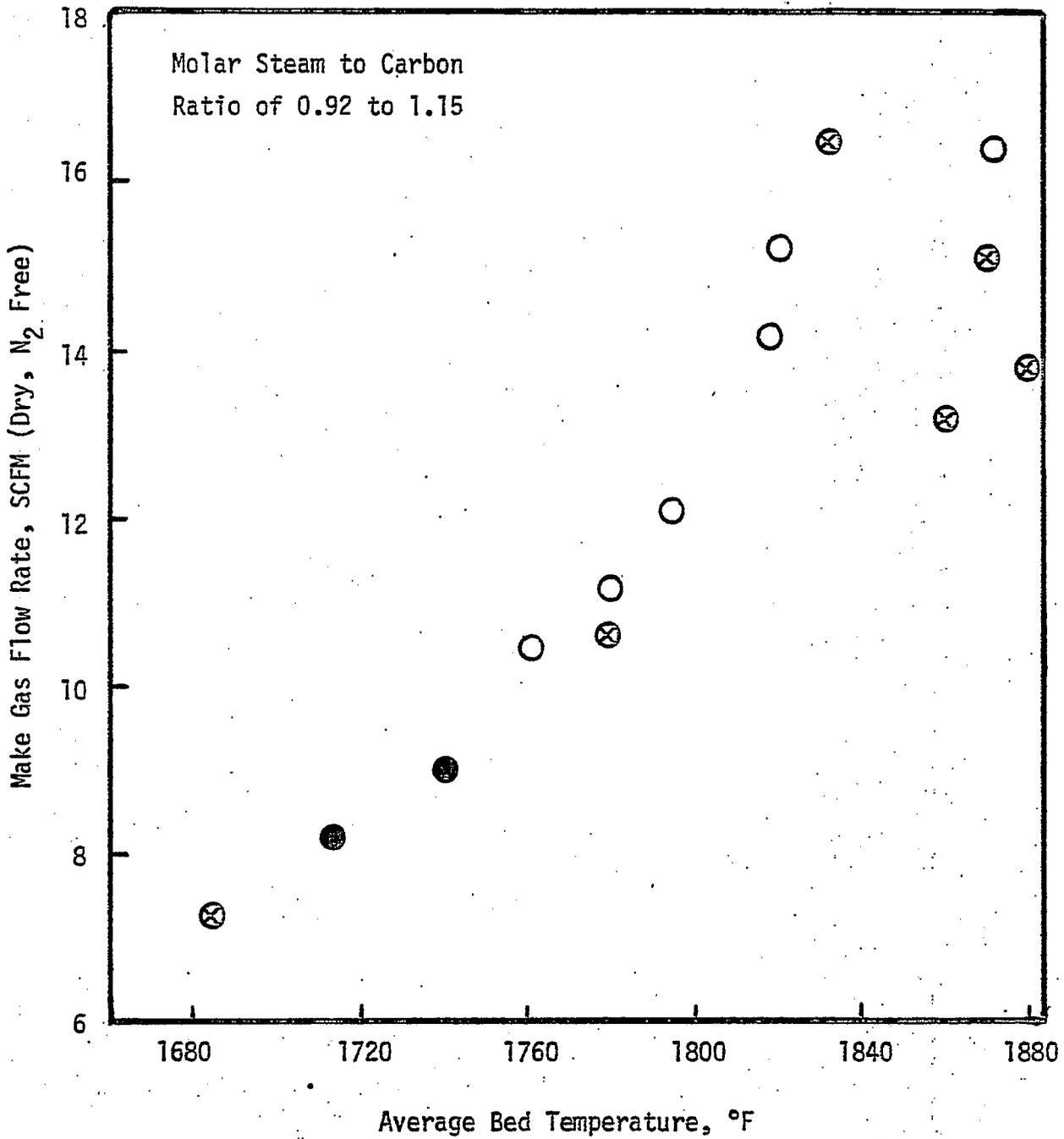


FIGURE 3

THE EFFECT OF THE STEAM TO CARBON RATIO  
ON THE MAKE GAS FLOW RATE (DRY, N<sub>2</sub> FREE)

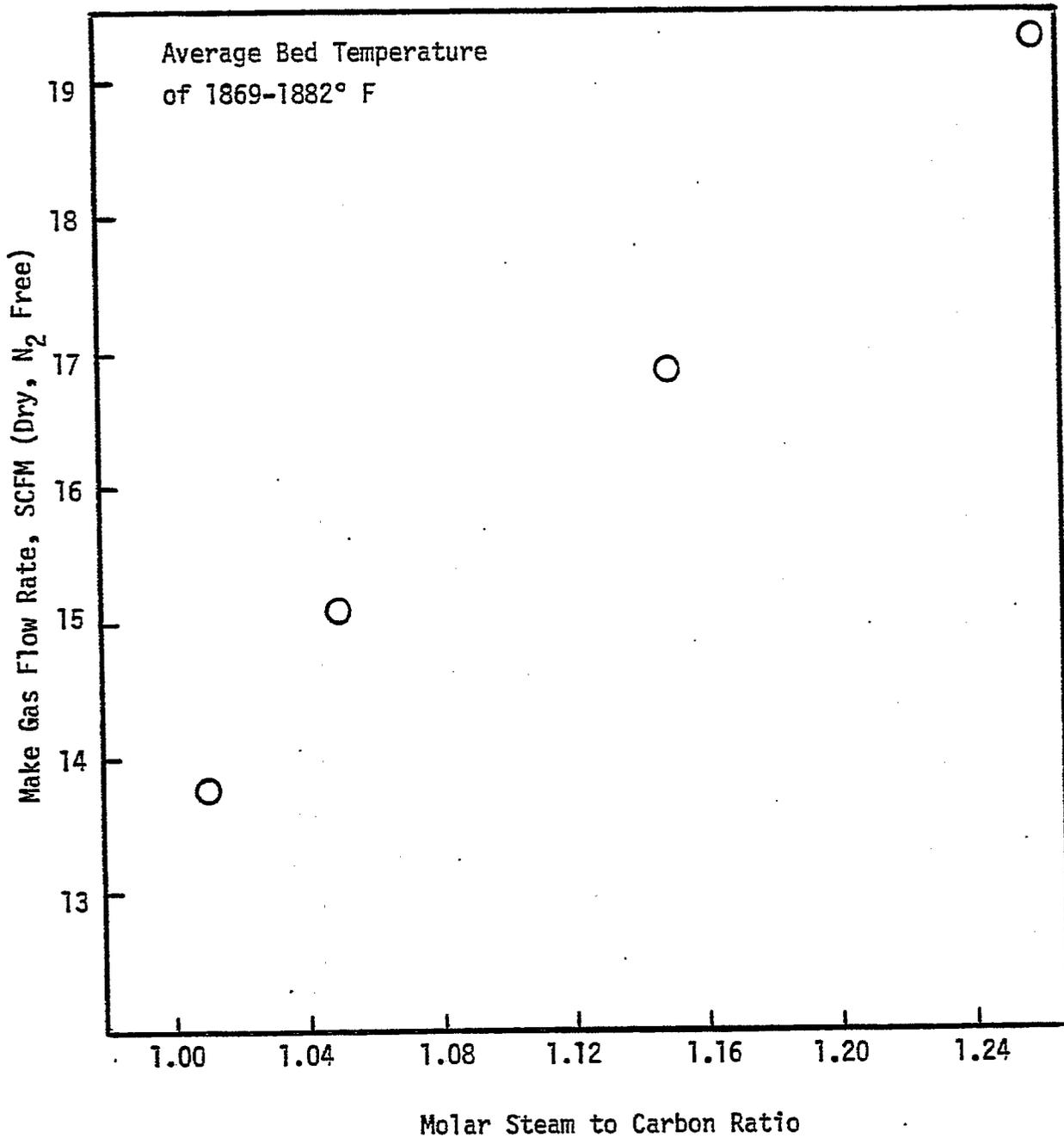
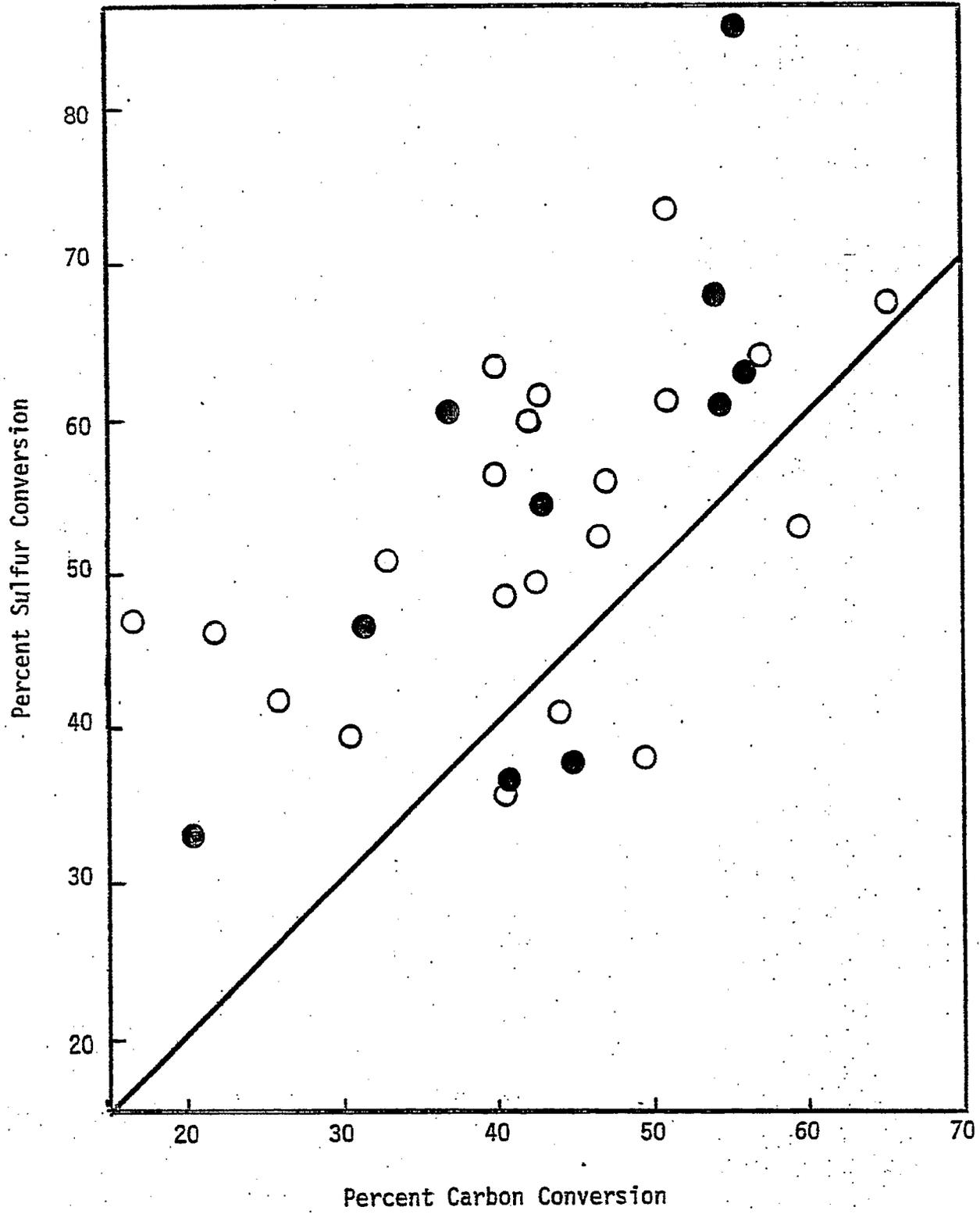


FIGURE 4  
COMPARISON OF PERCENT SULFUR CONVERSION  
TO PERCENT CARBON CONVERSION



on a firmer theoretical foundation.

#### EVALUATION OF MODEL PARAMETERS

In its present form, the model has three adjustable parameters:

1. the char reactivity,  $f_0$
2. the combustion product distribution parameter,  $a$ , which specifies the split between CO and CO<sub>2</sub> in the products of the combustion stage of the gasification
3. the water gas shift reactivity parameter,  $f_{wg}$ .

These parameters were evaluated by using a Pattern Search algorithm to minimize a function of the sum of squared deviations between predicted and measured values of gasifier performance variables. This analysis gave the following values:

1.  $f_0 = 0.50$
2.  $a = 0.95$
3.  $f_{wg} = 0.0000099$

The value of  $a$ , when substituted into Eq. 7, indicates that 90% of the carbon oxidized forms CO<sub>2</sub> and 10% forms CO. An equation by Arthur (1951) predicts values of 0.57 at 1400 F to 0.52 at 2000 F, while several gasification studies have assumed  $a = 1.0$ .

Johnson (1975) developed a correlation for char reactivity

$$f_0 = 6.2 y (1-y) \quad (12)$$

where  $y$  is the dry, ash free carbon fraction in the original raw coal. Eq. 12 predicts a value of  $f = 1.1$ , which is larger than that determined in this study. The difference may be due to the differences in the microbalance used by Johnson and the fluidized bed of this study.

The value of  $f_{wg} = 0.0000099$  indicates that the shift reaction rate is approximately five orders of magnitude less than the rate obtained in catalytic shift reactors. Wen and Tseng (1979) used a shift reactivity value of 0.00017 in modeling the gasification of a bituminous coal by the SYNTHANE process. The larger value used by Wen and Tseng may be attributed to the differences between the coal of their study and the char used in this study.

Due to the simplicity of the model, it is also likely that the effects of factors not specifically accounted for in the model have influenced the optimal values of the three model parameters. The va-

lues of the parameters found as described above appear to be reasonable, and are probably a fair representation of what actually happens in the fluidized bed gasifier.

#### MODEL RESULTS

Using the optimal parameter values, the model was run for gasifier runs GO-14 through GO-56. A representative model output is shown for run GO-44B in Table 2. Plots of predicted vs measured values of carbon conversion, dry make gas flow rate, and sweet gas heating value are shown in Figures 5 - 7. The reasonably close proximity of most points to the 45 degree line is gratifying in view of the crudeness of the model. The proximity of the points corresponding to the "best" runs (from the standpoint of satisfying mass balances) is even more satisfying.

For each run, the ratio

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} \quad (13)$$

was calculated, where [ ] is the mole fraction of the evaluated species in the product gas. This quantity would equal the water-gas shift equilibrium constant at the reactor temperature if this reaction proceeded to equilibrium. A plot of the predicted vs experimental values of this ratio, K, is given in Figure 8. The substantial degree of scatter may be attributed to the simplicity of the model, and equally to the fact that the mole fractions which are the constituents of K are interdependent, so that an experimental error in one of them affects the values of the others.

The significance of this plot emerges when it is compared with Figure 9, which shows the values of K predicted assuming shift equilibrium. This assumption leads to the overprediction of K by as much as a factor of two, and lends support to the conclusion that the shift reaction should not be assumed to proceed to equilibrium.

#### FORMATION OF SULFUR GASES

One of the objectives of gasifier runs GO-43 through GO-59 was to investigate the production of sulfur gas species in the fluidized bed reactor. A summary of results is given in Table 3.

The coal char used in this study has a very low volatile matter, less than 2%, and it is very likely that most of the sulfur is present as pyritic sulfur. For this case, it has been postulated that during

Table 2

```

*****
*
* WELL-MIXED CHAR GASIFICATION *
*
* MODEL RESULTS *
*
*****
    
```

60-448 1-22-80 11:15-14:30

REACTOR SPECIFICATIONS

BED PRESSURE(PSIG)	101.60
BED TEMPERATURE(F)	1699.80
SOLIDS HOLDUP(LB)	18.40
BED HEIGHT(IN)	38.00
BED DIAMETER(IN)	6.00
BED VOIDAGE	0.74

FEEDRATES(LB/HR)

INLET CHAR	34.69
STEAM	55.85
OXYGEN	10.10
NITROGEN	6.32
HYDROGEN	0.00
PURGE N2	14.16

MODEL PARAMETERS

PRETREAT TEMP(F)	2000.00
CHAR REACTIVITY	0.5000
COMBUSTION EXTENT	0.9500
SHIFT REACTIVITY	9.900E-06

FEED CHAR ANALYSIS(WT PERCENT)

CARBON	82.00
HYDROGEN	0.50
OXYGEN	3.99
NITROGEN	0.10
SULFUR	2.60
ASH	10.80

	MODEL	EXPERIMENTAL
DRY GAS FLOW RATE (SCFH)	12.04	11.73
STEAM CONVERSION	0.171	0.153
CARBON CONVERSION		
COMBUSTION	0.140	
GASIFICATION	0.187	
TOTAL	0.327	0.316
ASH CONTENT OF CHAR	15.24	12.00
CHAR REMOVAL RATE (LB/HR)	23.07	21.80

GAS COMPOSITION (MOLE PERCENT)

	MODEL	EXPERIMENTAL
CO	6.76	6.60
H2	10.85	10.11
CH4	0.56	0.89
CO2	9.59	8.82
N2	15.96	15.91
H2S	0.19 *	0.28
COS	0.00	0.01
H2O	56.08	57.38

(\* ESTIMATED)

FIGURE 5  
PREDICTED VS. EXPERIMENTAL CARBON CONVERSION

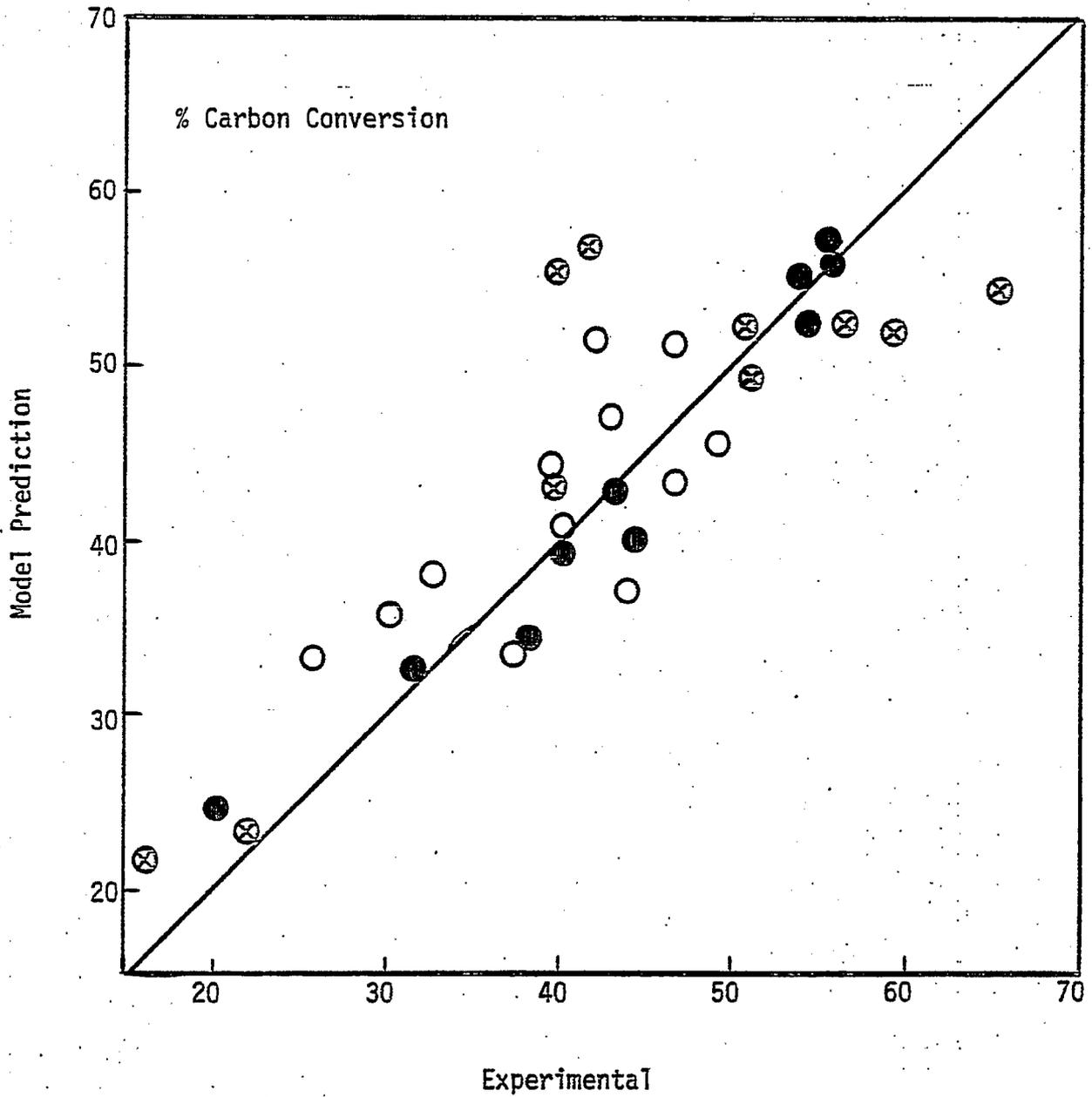


FIGURE 6

PREDICTED VS. EXPERIMENTAL DRY MAKE GAS FLOW RATE

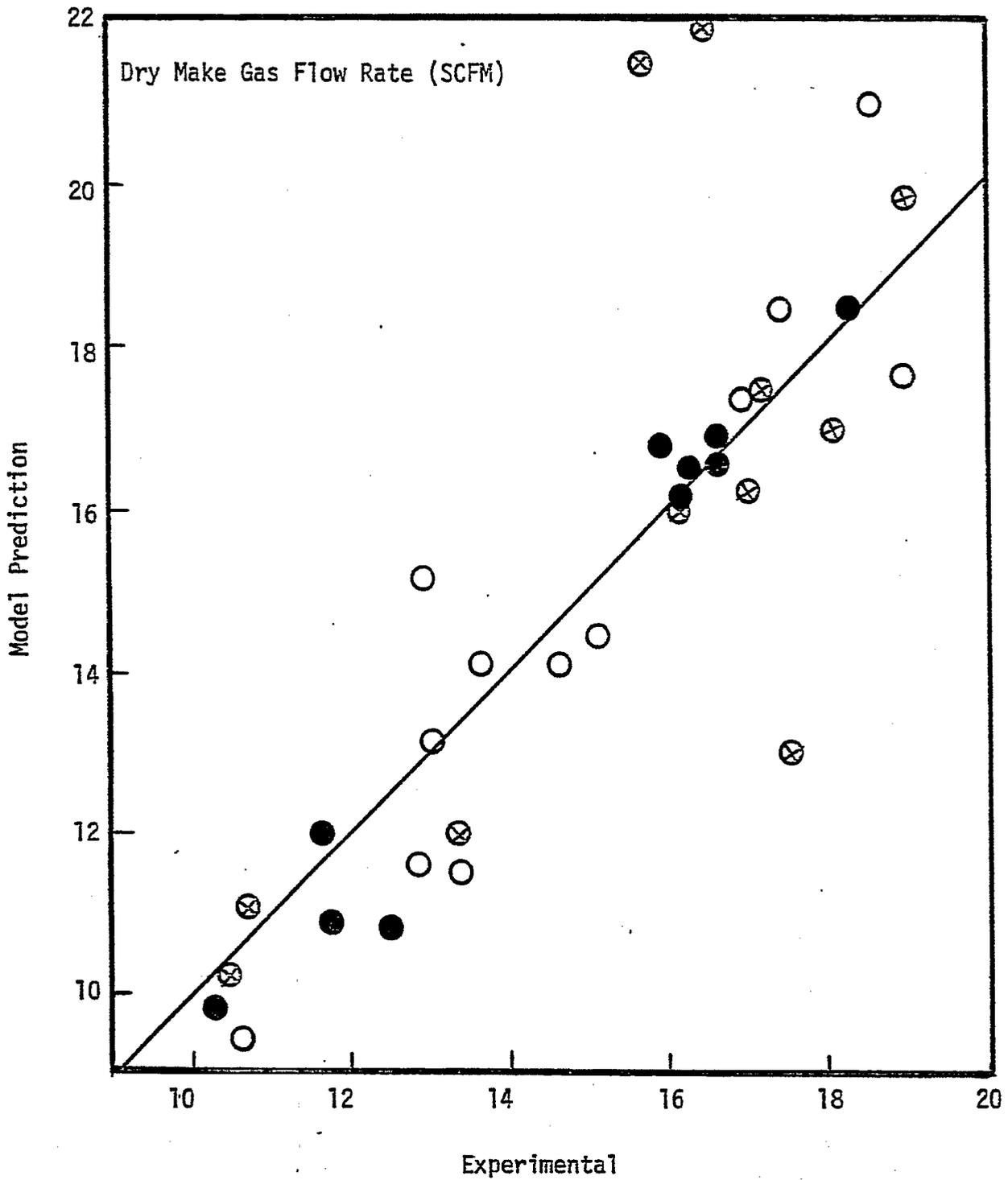


FIGURE 7

PREDICTED VS. EXPERIMENTAL HEATING VALUE OF SWEET GAS

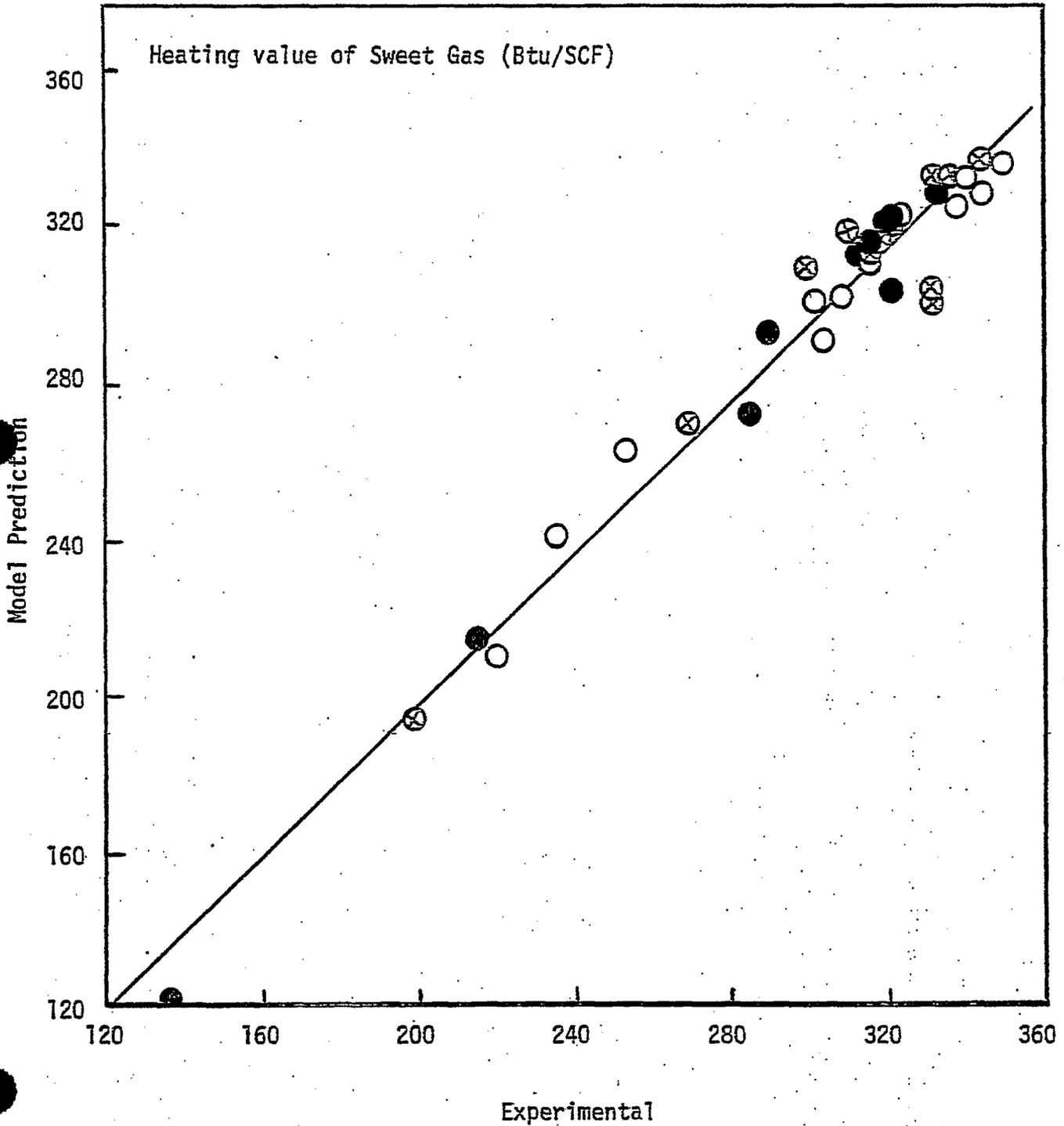


FIGURE 8

PREDICTED VS. EXPERIMENTAL K VALUE

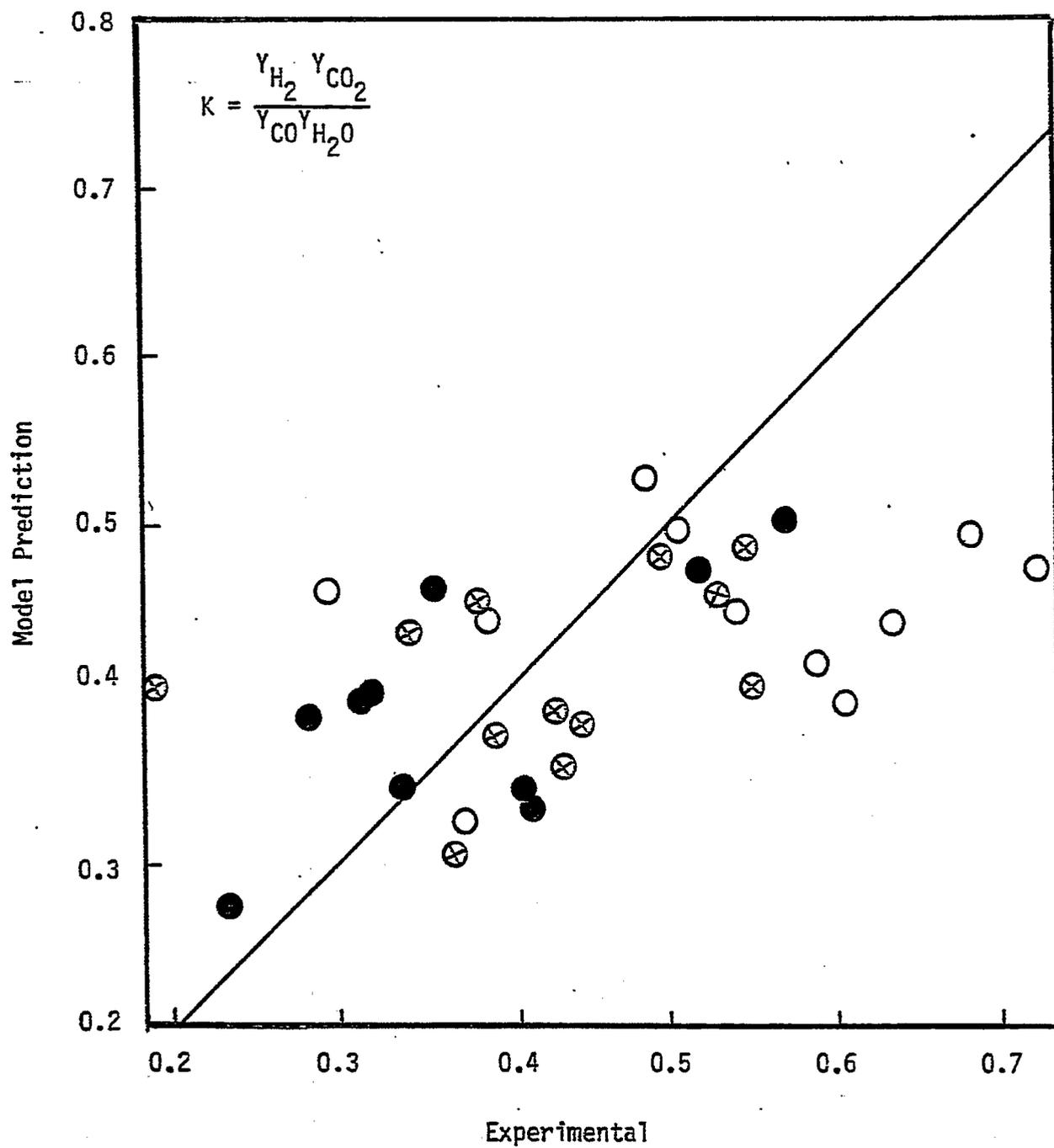


FIGURE 9

PREDICTED VS. EXPERIMENTAL K VALUE

ASSUMING SHIFT EQUILIBRIUM

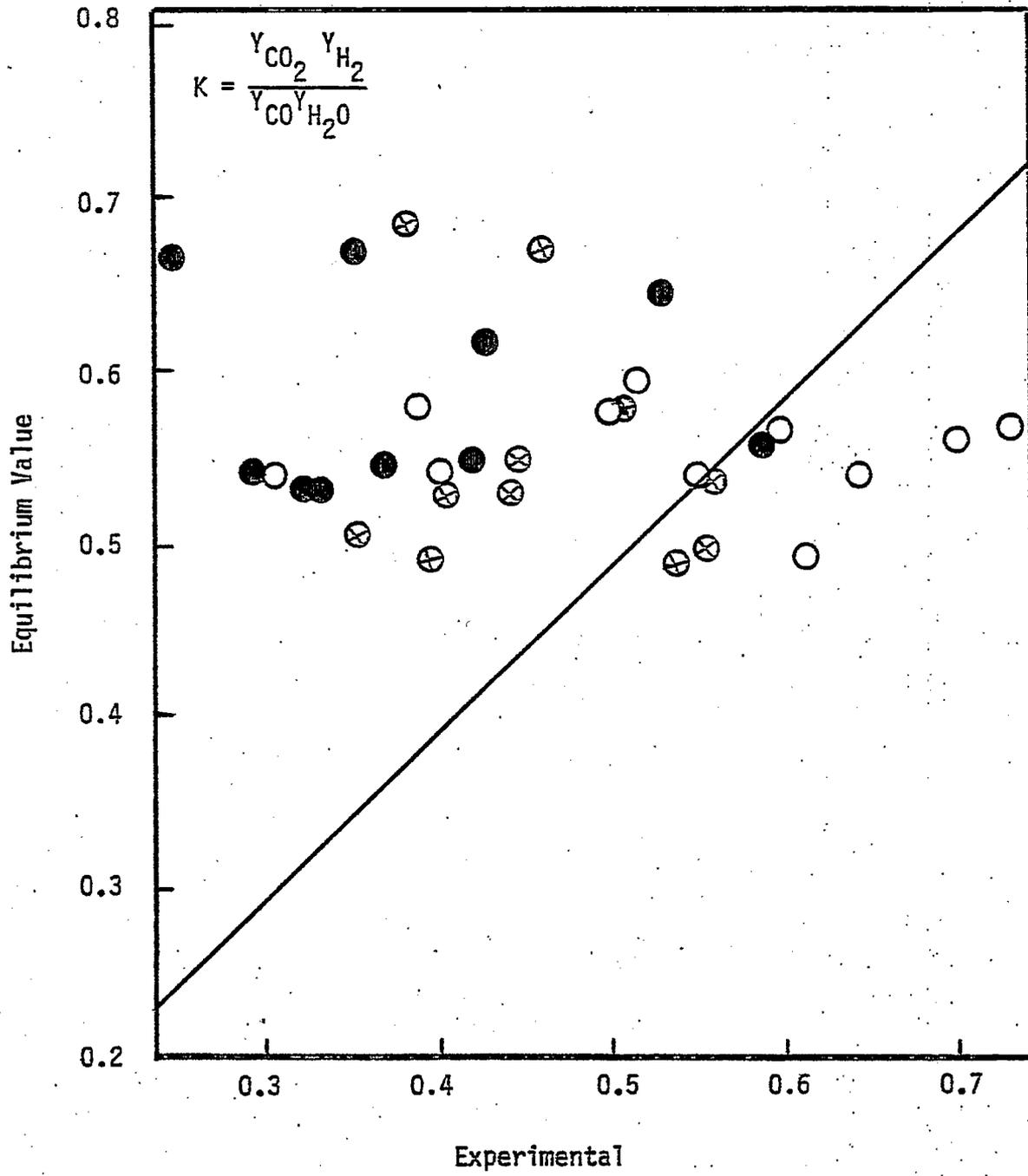


TABLE 3  
CONCENTRATIONS OF SULFUR GASES IN REACTOR EFFLUENT

Run No.	Bed Temp. F	Reactor Effluent Concentrations ppm				
		H <sub>2</sub> S	COS	CS <sub>2</sub>	Methyl Mercap-tan	Thiophene
43	1794	6229	277	2.27	x	x
44	1678	6510	283	2.44	x	N.D.
45	1671	3433	266	7.92	x	x
46	1790	5478	222	1.56	x	x
47	1785	5071	272	1.97	x	x
48	1778	6912	312	3.30	x	x
49	1799	7052	403	3.80	x	x
51	1777	6711	299	1.56	x	x
55	1708	8931	465	2.95	x	N.D.
56	1800	8924	410	1.58	x	x
57	1778	8098	388	1.58	x	x
58	1771	5111	362	1.36	x	x
59	1803	8470	306	1.61	x	x

x - Less than 1 ppm

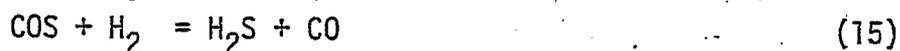
N.D. - Not detected

TABLE 3 CONTINUED  
EQUILIBRIUM CONSTANTS FROM EXPERIMENTAL DATA

Run No.	Reactor Effluent Concentrations				Equilibrium Constants	
	CO	CO <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> O	K <sub>1</sub>	K <sub>2</sub>
43	16.80	12.36	11.21	43.60	6.4	33.7
44	6.60	8.82	10.11	57.38	3.5	15.0
45	4.22	6.81	8.27	39.27	2.2	6.6
46	12.77	9.08	13.82	33.14	6.8	22.8
47	13.89	9.86	15.16	29.89	6.2	17.1
48	12.88	10.79	15.77	46.62	5.1	18.1
49	15.42	16.03	13.68	36.25	7.7	19.7
51	10.98	15.11	19.06	41.49	8.2	12.9
55	9.28	12.61	15.24	50.05	4.8	11.7
56	10.73	12.75	16.98	48.95	5.7	13.8
57	12.74	14.87	18.05	41.92	7.4	14.7
58	11.68	15.80	19.84	38.38	5.8	8.3
59	10.10	14.60	17.15	47.68	8.5	16.3

steam-oxygen gasification the gas-solid reactions form mainly hydrogen sulfide. The gas phase reactions then tend to bring the compounds CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, H<sub>2</sub>S, and COS to an equilibrium mixture.

The two gas phase reactions of most importance involving H<sub>2</sub>S and COS are:



The equilibrium constants for these two reactions are defined as follows:

$$K_1 = [\text{H}_2\text{S}][\text{CO}_2]/[\text{COS}][\text{H}_2\text{O}] \quad (16)$$

$$K_2 = [\text{H}_2\text{S}][\text{CO}]/[\text{COS}][\text{H}_2] \quad (17)$$

where, due to the stoichiometry of the reactions, the brackets may indicate any convenient concentration. Ideal gas behavior is assumed.

A survey of the literature yielded several sets of equilibrium data for the above reactions, and several predictions based on thermodynamic data. Since there were substantial differences among the sources of data, predictions of the two equilibrium constants as functions of temperature were derived from the data given in Reid et al. (1977). A least squares fit of the literature data, and the predicted curve from the data of Reid are shown in Figures 10 and 11.

Also shown on Figures 10 and 11 are calculated values of the equilibrium constants from the data in Table 3. Figures 12 and 13 show the experimental data on an expanded scale and a comparison of our data with the literature values given in Kohl and Riesenfeld (1979).

Although there is considerable uncertainty in determining the correct value of the equilibrium constants, and some inaccuracy in the experimental data, it appears that the sulfur compounds H<sub>2</sub>S and COS are in equilibrium with the major gases at the exit of the fluidized bed, and that the distribution of the sulfur gases between H<sub>2</sub>S and COS can be predicted if the sulfur conversion is known.

FIGURE 10  
THE EQUILIBRIUM CONSTANT  $K_1$

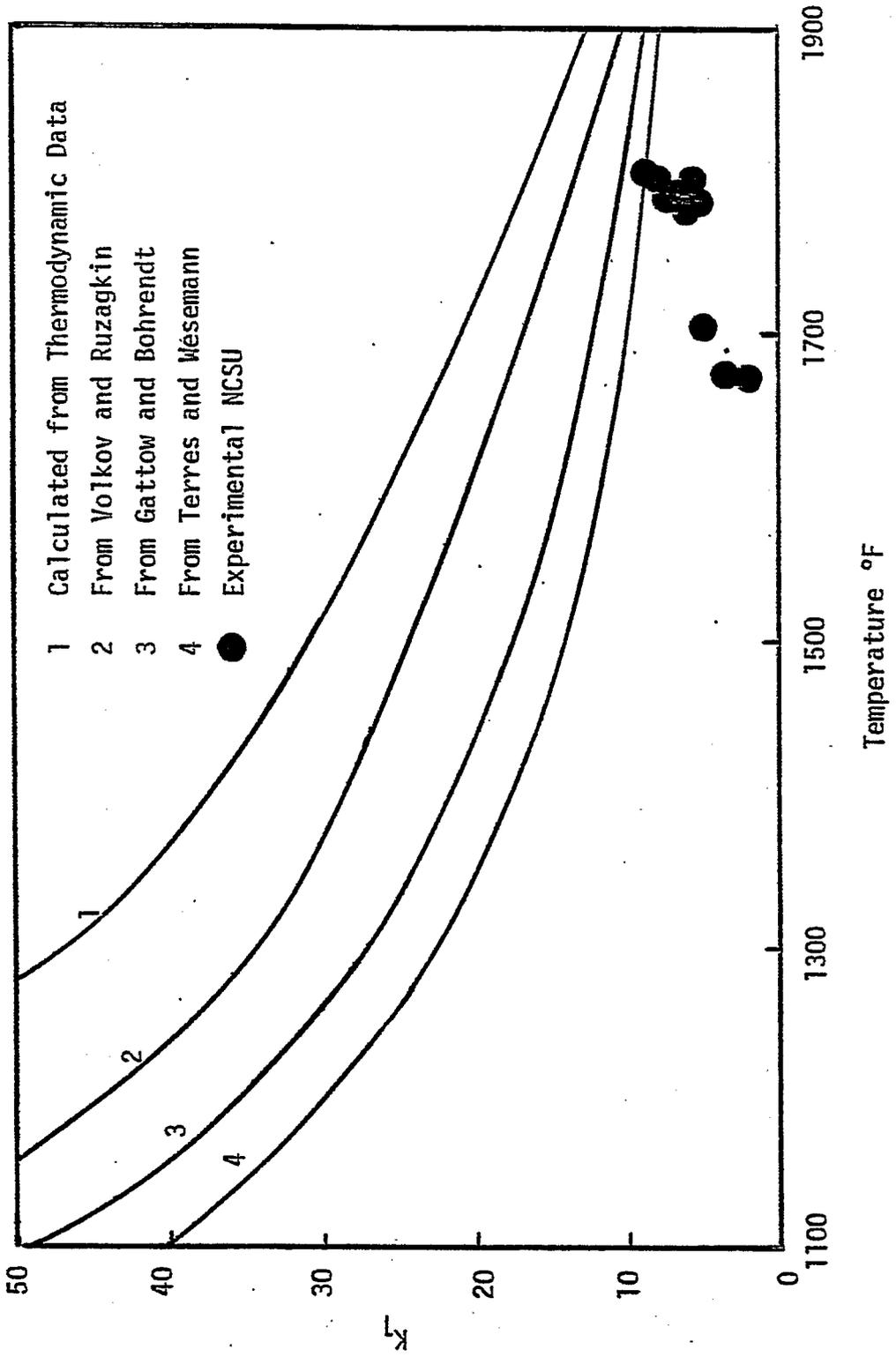


FIGURE 11  
THE EQUILIBRIUM CONSTANT  $K_2$

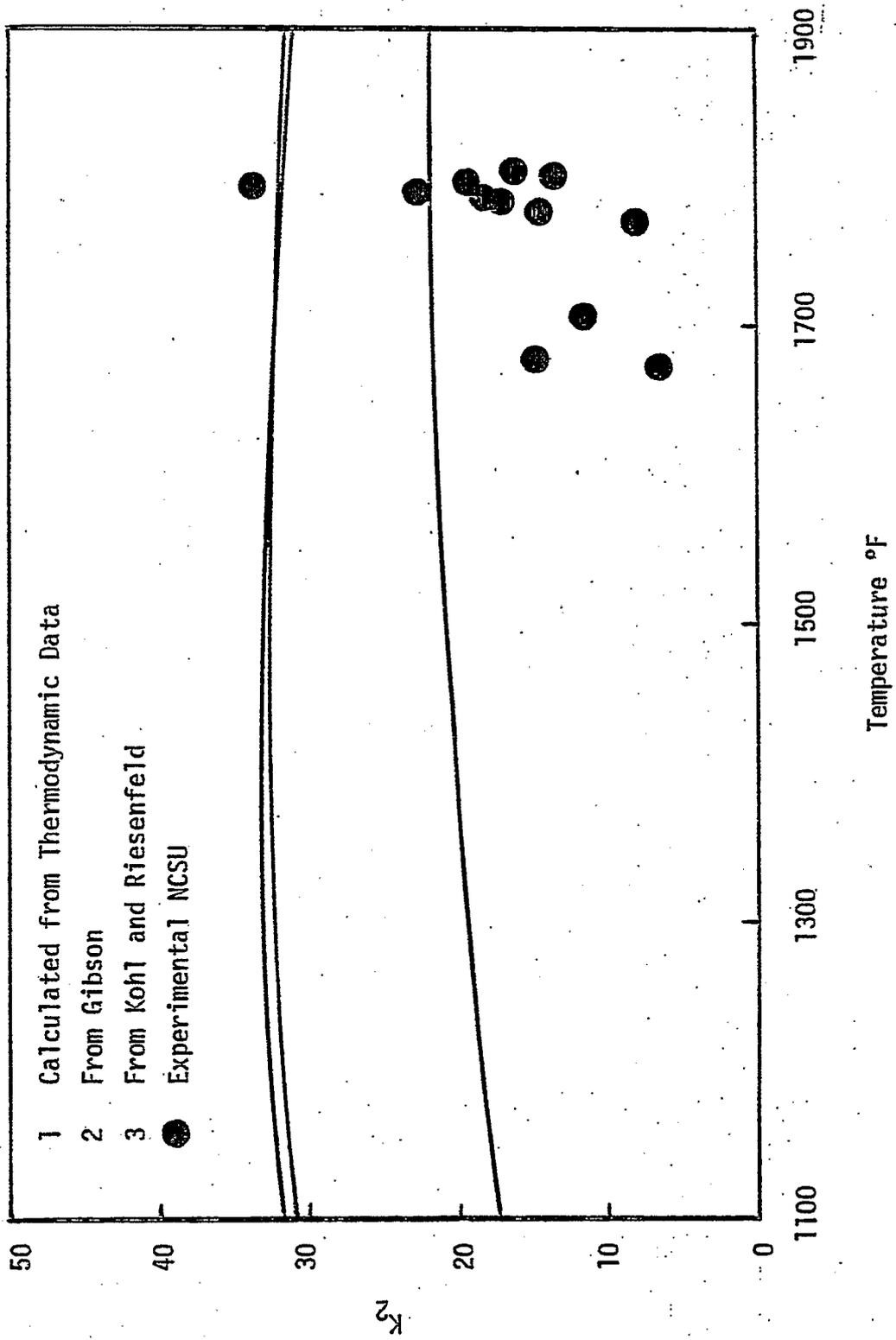
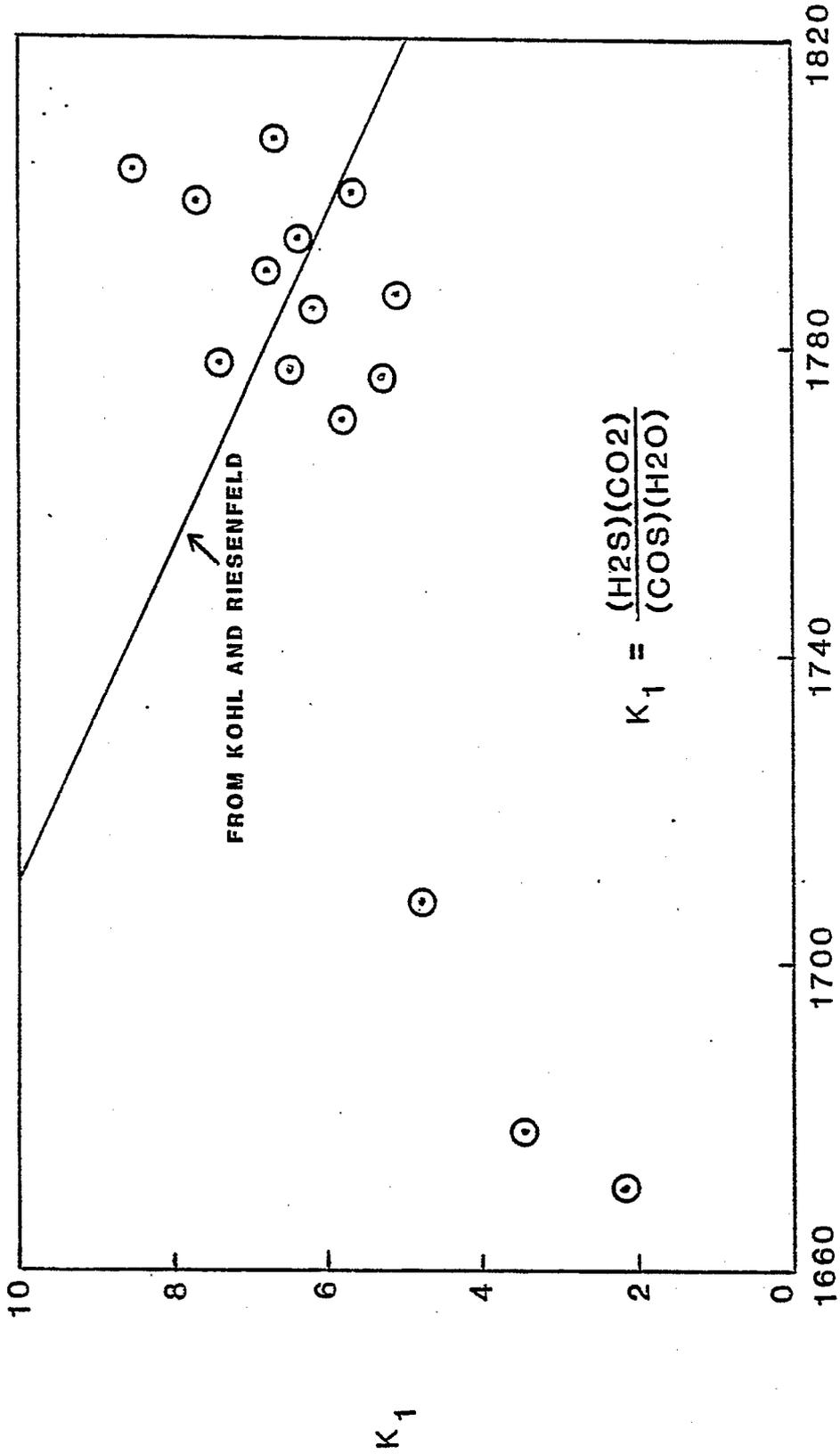


FIGURE 12

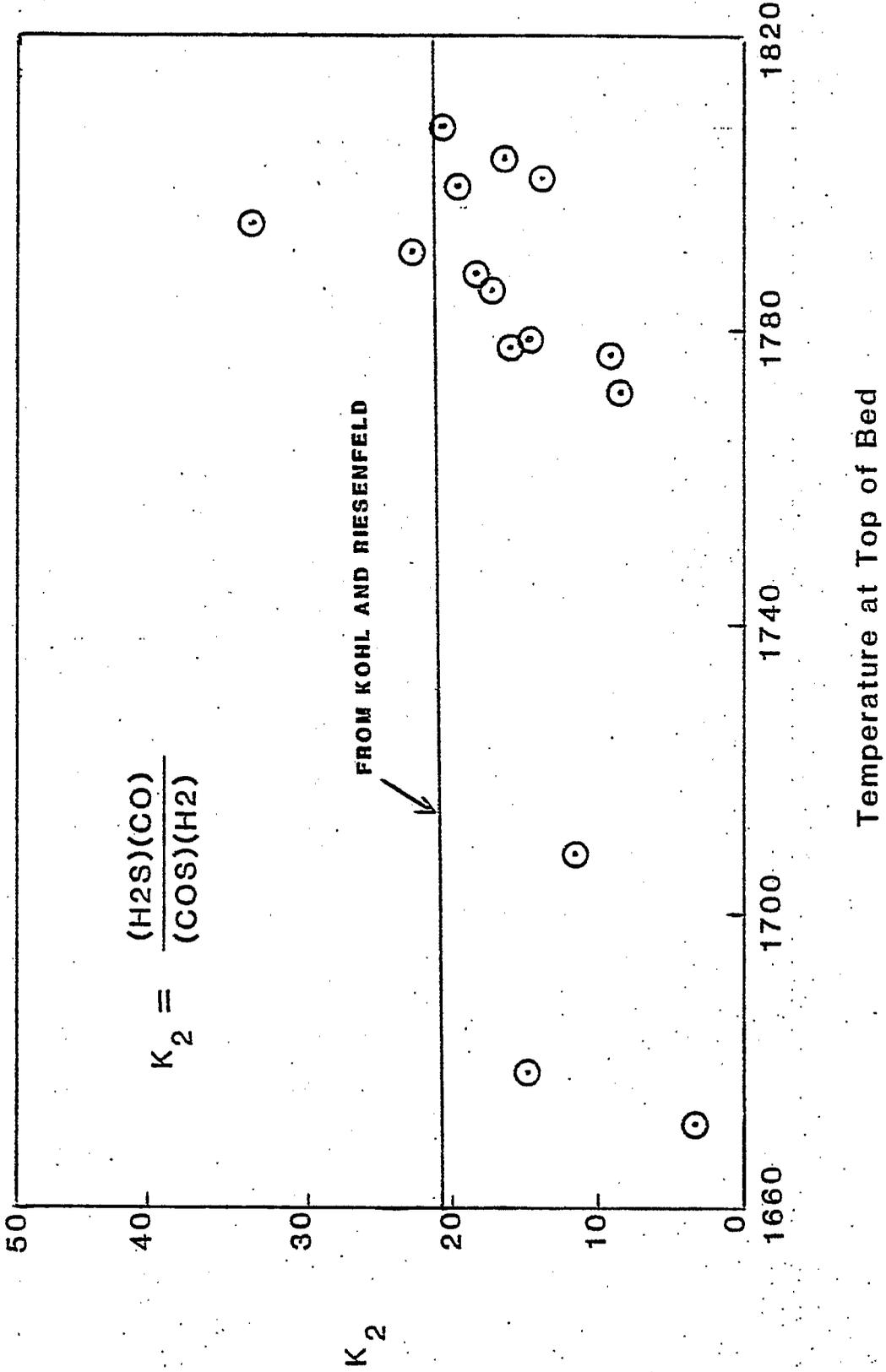
COMPARISON OF EXPERIMENTAL VALUES OF  $K_1$  WITH DATA OF KOHL AND RIESENFELD



Temperature at Top of Bed °F

FIGURE 13

COMPARISON OF EXPERIMENTAL VALUES OF  $K_2$  WITH DATA OF KOHL AND RIESENFELD



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