A PROGRAM FOR PARAMETRIC EVALUATION OF POLLUTANTS FROM A LABORATORY GASIFIER

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Abstract

Pollutants from gasification processes are being evaluated utilizing a small semibatch reactor. Emphasis is placed on analyzing the production of trace contaminants, especially those presenting potentially pronounced toxic or carcinogenic hazards. Research is progressing in three phases: (1) Chemical screening analyses of the scope of pollutants produced; (2) Evaluation of controlling reactor parameters to reduce specific compounds; and (3) Reactor kinetics studies of first-priority pollutants. Design and construction of the reactor facility and initial baseline tests have been completed.

INTRODUCTION

Work was begun this year at the Research Triangle Institute to investigate some particular pollution problems associated with coal conversion. The research is funded by the Environmental Protection Agency/RTP. The program has recently moved into data accumulation, and the following discussion describes, for the most part, preparation that has been made for the experimental and theoretical research to follow.

With the program still in the early stages, research goals, as determined in coordination with EPA, are being continually defined. Major priorities of this work are, however, clear at present. Emphasis will be placed upon the assessment and analysis of trace pollutants possibly associated with coal conversion processes which have received little attention in the past. This includes particularly investigation of many organic compounds which are associated with carcinogenic or highly toxic properties. Other compounds presenting potential hazards to human health, such as some of the trace elements, will also be included.

When full-scale synthetic fuels plants (e.g., 20,000 tpd of coal) are considered, even trace constituents may be present in significant amounts. Such plants are capable of producing daily (1) more than 15 railroad tank cars of tars and heavy liquids; (2) byproduct waters directly downstream from the reactor containing as much as 340,000 pounds of ammonia, 6,000 pounds of thiocyanates, and 800,000 pounds of phenol; and (3) hazardous contaminants in raw gases, liquids, or solids from the reactor that can possibly find their way into the environment or the synthetic fuel product.

The RTI research is primarily concerned with the nucleus of any coal conversion plant, the reactor, which receives and evolves most of the process streams of environmental interest. While there are certainly other pollution problems in the gas beneficiation and cleanup modules of a plant, the reactor is the major source of compounds going to both product gases and effluent streams.

As indicated in Figure 1, we are also concerneded with the ash, char, particulates, tars, and liquids in reactor outputs. These, along with reactor inputs and product gas, constitute the major mass flows at the front end of any coal conversion system. Research in this area complements (1) other efforts being directed toward environmental control for coal conversion in the Research Triangle area (discussed in other papers at this Symposium) and (2) the intensive on-site sampling and analysis, control options evaluations, and other environmental assessment and control technology development being carried out by prime contractors for EPA; see Figure 2. RTI findings will be compared with EPA analyses being done on a much larger scale, e.g., in joint programs with ERDA or at the Kosovo, Yugoslavia Lurgi gasification plant.

The research at RTI was prompted by several needs and interests of the Environmental Protection Agency:

1. There has been increased emphasis on investigation of toxic constituents in the environment which, in many cases, may be present in relatively low concentrations. This emphasis has been fostered by more extensive and successful cancer research and other related health and medical studies. The

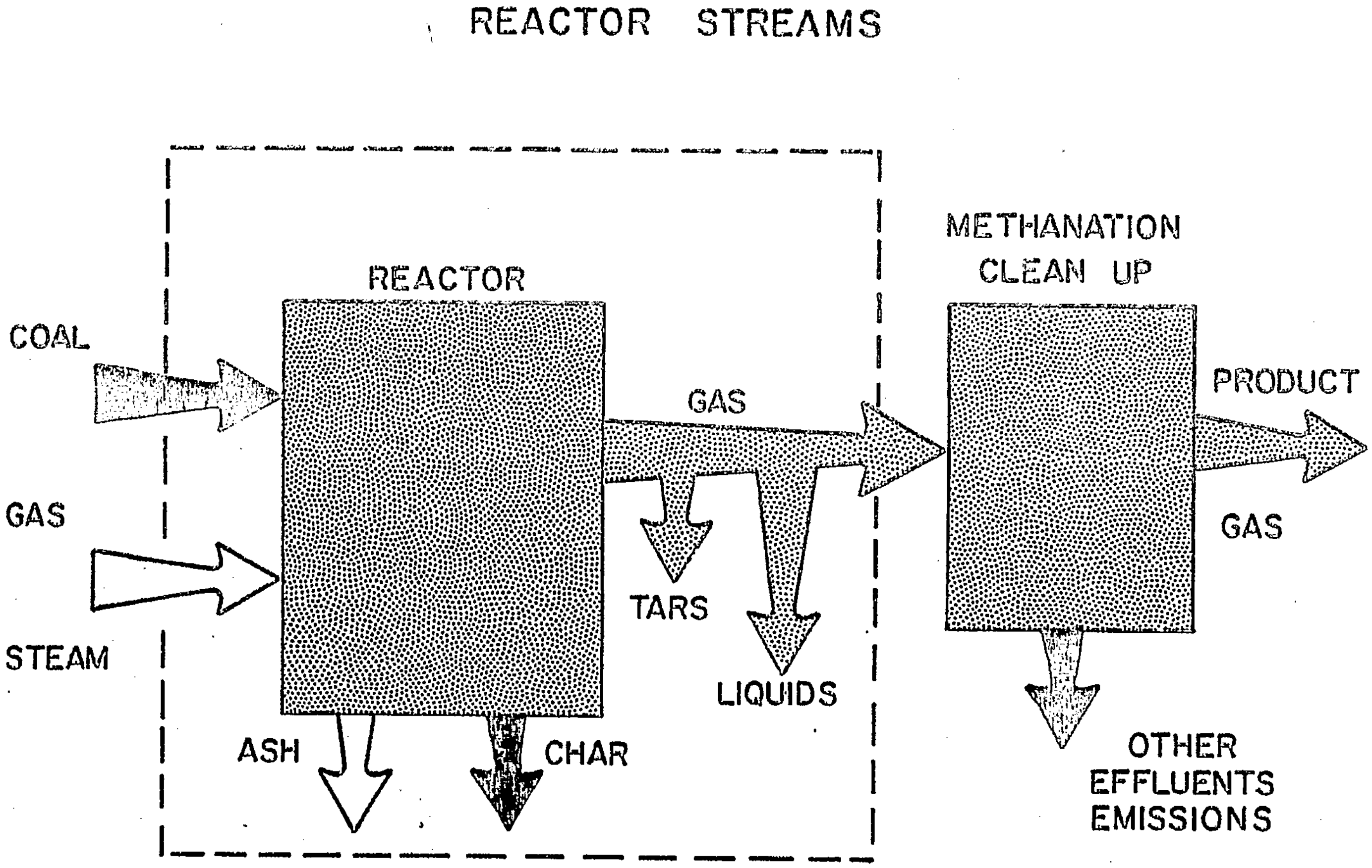


Figure 1. Reactor streams.

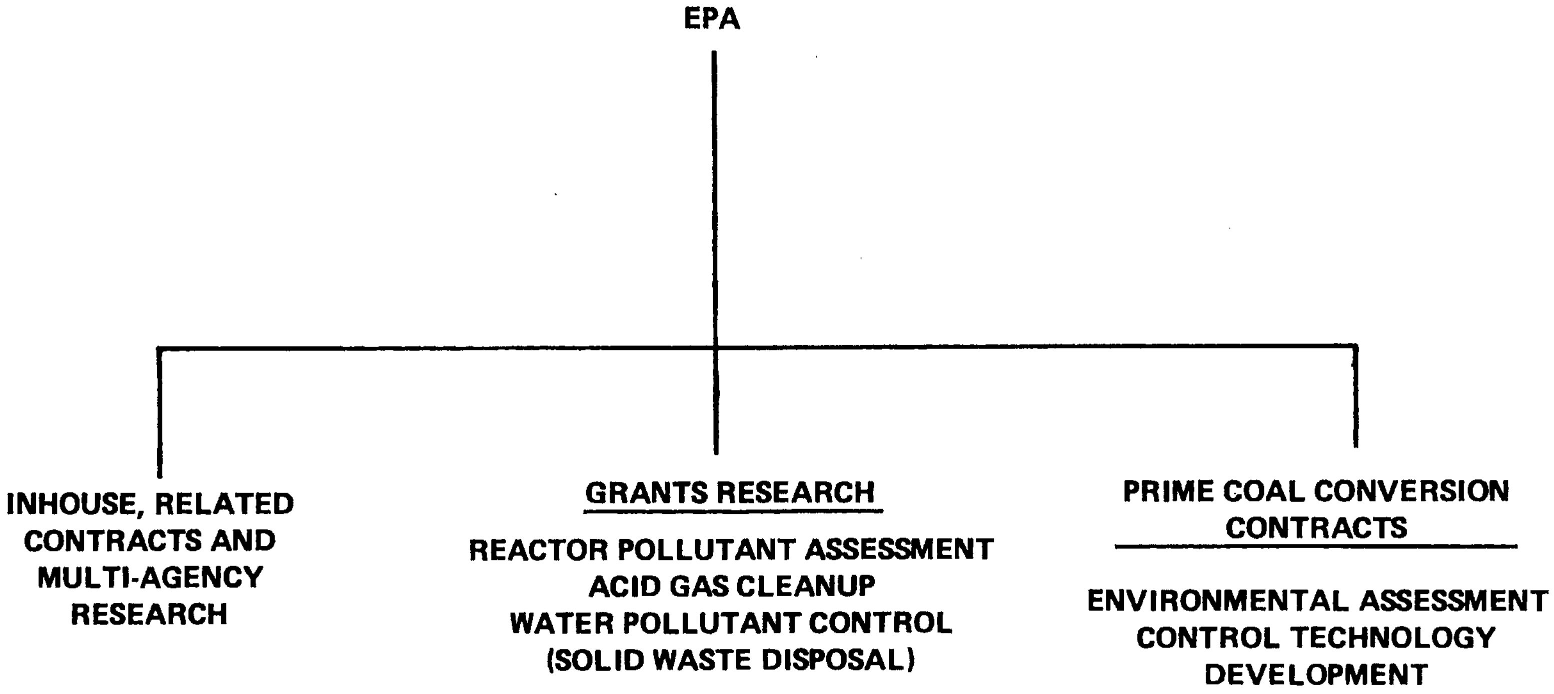


Figure 2. EPA program.

association of oncogenic activity with environmental causes is now widely accepted.

Increased environmental concern in the nation has necessarily extended into new areas of environmental problems. Improved chemical analytical techniques, which have made it possible to quantify substances at nanogram levels and parts per trillion concentrations, have influenced the increasing list of potential pollutants. Table 1 lists some potentially hazardous substances taken from an investigation of more than 200 substances.[1] These are grouped in terms of increasing hazard potential based upon both carcinogenic and toxic effects (it may be noted that some compounds, such as SO_2, are not included when considerations of *quantities* in the environment are ignored).

2. EPA recognizes that there are large information gaps concerning highly toxic substances associated with coal conversion. The problems, whether real or imagined, must be verified, or eliminated. Certainly, claims of environmental dangers associated with synthetic fuels which slow the progress of the industry must be addressed. A general example of the force of such claims is a settlement agreement resulting from litigation against EPA by various environmental organizations. The agreement sets a time table for new source performance standards, effluent guidelines and pretreatment controls for a list of more than 300 specific point source categories or industries. Commonly referred to as the Consent Decree,[2] this document now has been modified to include more than 100 substances which must be addressed for pollutant control.

3. Regulatory and standard setting processes are encompassing a larger number of pollutants. A new source performance standard under EPA review would designate control levels for sulfur species and hydrocarbons in the areas of coal gasifier lockhoppers, coal gas purification facilities, byproduct recovery, gas/liquid separation facilities, and sour water stripping facilities.[3] The fairly recent OSHA standard for hydrocarbon control in the vicinity of coke ovens (primarily concerned with carcinogenic activity) set an important precedent. This organization has also legally established threshold limits for about 500 different substances in the workroom atmosphere.[4]

4. Research on coal conversion reactors and associated toxic substances is considered an important factor in developing control technologies in these areas. Processes for direct burning of product gases from low Btu gasifiers, followed only by particulate cleanup, have been proposed. Both high- and low-Btu conversion processes often call for combustion of chars and tars for process heat and steam. These feedstocks must be analyzed to insure that incineration will accomplish complete destruction of hazardous materials.

The most important control option to be observed at the RTI experimental facility will be that of the reactor itself. The concept of utilizing the reactor for pollutant control through parametric variations is not an original one, but has received little previous development. The Environmental Protection Agency is interested in the idea of utilizing process variations or modification of process modules in order to effect environmental control. Where this is possible, of course, redundance and/or retrofitting of additional control systems is avoided. It is at the same time essential that any variations in process operation not severely limit production or result in unfavorable cost tradeoffs between process variation

TABLE 1

SUBSTANCES RECEIVING TOXIC INDICATORS

x

- 2-Chloro-2,3-epoxypropane
- Formaldehyde
- Acrolein
- Phthalic acid
- Monomethyl hydrazine
- Aminotoluenes
- 2-Aminonaphthalene
- 4-Aminobiphenyl
- 1-Aminonaphthalene
- N,N'Dimethylhydrazine
- α-Chlorotoluene
- 1-Chloro-2-Nitrobenzene
- 1-Chloro-4-Nitrobenzene
- 2,4-Dichlorophenol
- 2,4,6-Trinitrophenol
- Anthracene
- Chrysene
- Dibenzo(b,def)chysene
- Benzo(b)fluoranthene
- Pyridine
- Dibenz(a,j)acridine
- Dibenz(a,h)acridine
- Dibenz(c,g)Carbozole
- Tetraethyl lead
- Organotin
- Nickeocene
- PPAH (Collective)
- Lithium
- Lithium hydride
- Barium
- Germanium
- Bismuth
- Hydrogen sulfide
- Tellurium
- Vanadium
- Nickel carbonyl

xx

- N-Nitrosodimethylamine
- N-Nitrosodiethylamine
- Ethyleneimine
- Diazomethane
- PCB's
- 4,6-Dinitrocresol
- Benz(a)anthracene
- Dibenzo(a,i)pyrene
- 3-Methylcholanthrene
- Tetramethyl lead
- Thallium
- Lead
- Hydrazine
- Phosphorus
- Phosphine
- Antimony
- Antimony Trioxide
- Ozone
- Cobalt
- Nickel
- Silver
- Uranium

xxx

- 4-Nitrobiphenyl
- Dibenzo(a,h)anthracene
- Benzo(a)pyrene
- Alkyl Mercury
- Beryllium
- Arsenic
- Arsine
- Arsenic Trioxide
- Selenium
- Chromium
- Cadmium
- Mercury

and simply adding control technologies.

5. Benefits may accrue through operation of a small and versatile system where a number of system variations can be assessed inexpensively. The bench-scale approach developed is quite flexible, allowing changes in the course of research where indicated to be profitable. This avoids the difficulties and expense incurred in attempting the same approach with a pilot- or full-scale unit and allows rapid response to reassessed needs and prior results.

6. Finally, some facets of this program mark a continuation of an earlier project supported by EPA in the area of reaction kinetics associated with coal conversion.[5] The main emphasis of this previous work was on desulfurization kinetics and involved a nonisothermal approach which will be followed up on a broader scale. This approach holds some promise and could produce at least some predictions of probabilities of formation for compounds of interest.

RESEARCH APPROACH

The research program is intended to progress in the three complimentary phases: screening studies, parametric control evaluations, and reaction kinetics research.

The first phase of efforts, screening studies, will be first associated with broad qualitative chemical analyses of a large number of compounds produced during gasification reactions. Attempts will be made to gasify a variety of U.S. coals through a range of reactor conditions, primarily to provide the opportunity for production of practically any substance which might be associated with gasification. It is probable that up to 300 different compounds will be screened following many of these tests. Qualitative screening, which will emphasize detection of the presence of the higher molecular weight organics already mentioned and particular compounds designated as having high toxic potential. The screening will also produce relative quantifications for selection of particular compounds that are present in gross enough quantities to warrant further investigation. Work will also be concerned with the isolation of chemical groups, such as polynuclear aromatics.

Screening studies will then move into the quantitation of selected compounds which, because of their relatively high concentrations balanced with their health hazard potential, are specified as important gasification pollutants. Confidence in this approach will be built through reproduction of the same substances under similar conditions while utilizing more specific and rigorous analysis.

Figures 3a and 3b (Figure 3a is an overlay) demonstrate one approach for estimating the amount of sample which must be taken from the products or byproducts from the gasifier to insure that possibly hazardous pollutants have been detected at levels which may be environmentally significant. Parameters taken into consideration include:

1. For a full scale plant—average stack heights, average wind speeds and weather conditions within the U.S. (primarily based on the states with high coal reserves), plant production (a 20,000 ton/day of coal plant was considered here), and a maximum concentration for any specific pollutant calculated using a dispersion model.

2. For the experimental setup—test duration, amount of coal input, duration of the sampling period (variable), and the percent of product/byproduct stream sampled during the same period (variable). The latter were multiplied to form a composite variable.

3. For the potential pollutants—an estimated permissible concentration (variable) has been derived for over 200 potential pollutants from fossil fuel processes.[1] Parameters involved in the derivation of these permissible concentrations (which in this case only included EPC's for ambient air considering effects on human health) were threshold limit values, LD_{50}'s and

Benzo(a)pyrene

Dibenzo(a,h)anthracene

3-Methylcholanthrene

Dibenzo(a,i)pyrene
Alkyl mercury
9,10-Dimethyl-1,2-benzanthracene

1-Chloro-2,3-epoxypropane
Acrolein
Aminotoluenes
2-Aminonaphthalene
1-Aminonaphthalene
Ethyleneimine
Diazomethane
Monomethyl hydrazine
N-Nitrosodimethylamine
N-Nitrosodiethylamine
4,6-Dinitro-O-cresol
2,4,6-Trinitrophenol
Naphthalene
Anthracene
Phenanthrene
Naphthacene
Benz(a)anthracene
Benzo(c)phenanthrene
Chrysene
Methyl chrysene
Triphenylene
Pyrene
Dimethyl pyrenes
Benzo(g)chrysenes
1,2,3,4-Dibenzanthracene
Benzo(e)pyrene
Perylene
Picene
Dibenzo(b,def)chrysene
Dibenzo(a,l)pyrene
Benzo(ghi)perylene
Coronene
Fluorene
Benzo(b)fluoranthene
Acridine
Dibenzo(a,j)acridine
Dibenz(a,h)acridine
11 H-Indeno(1,2-b)quinoline
Dibenzo(c,g)carbazole
Tetramethyl lead -
Tetraethyl lead
Organotin

Formaldehyde
Tetramethylsuccinonitrile
4-Aminobiphenyl
N,N'Dimethylhydrazine
N,N-Dimethylhydrazine
Methyl mercaptan
Ethyl mercaptan
N-Butyl mercaptan
Biphenyl
1,4-Dichlorobenzene
PCB's
a-Chlorotoluene
Dinitrotoluene
Dinitrophenols
1-Chloro-4-nitrobenzene
Pyrrole
Thiophene
Copper-8-hydroxyquinoline

2,2'-Dichlorodiethyl ether
Phenylethanol
t-Pentanol
Ethylene glycol
Propionaldehyde
Isophorone
Formic acid
Acetic acid
Phthalic acid
Formamide
Phthalate esters
Benzonitrile
Cyclohexylamine
Aniline
4,4'-Diaminodiphenyl
Butylamines
Ethanolamine
Ethylamine
Dimethylaniline
Dimethylamine
N,N-Dimethylaniline
Hydrazobenzene
Benzenesulfonic acid
Benzene
Nitrobenzene
1-Chloro-2-nitrobenzene
Nitrotoluenes
Phenol
Cresols
Xylenols
Catechol
2-Chlorophenol
2,4-Dichlorophenol
3-Nitrophenol
4-Nitrophenol
Pyridine
Picolines
Quinoline
Isoquinoline
2-Methylquinoline
Benz(c)acridine
Indole
Carbazole
Dibenz(a,g)carbazole
Methylthiophenes
Benzo(b)thiophene
Ferrocene
Nickelocene

Methyl chloride
1,4-Dioxane
Methanol
Butanols
Pentanols
t-Butanol
Acetaldehyde
Butraldehyde
Benzaldehyde
Benzoic acid
Hydroxy acetic acid
Acetonitrile
Acrylonitrile
Toluene
Tetrahydronaphthalene
Chlorobenzene
1,2-Dichlorobenzene
2-Chlorotoluene
Phenylphenol
Indanols
2-Nitrophenol
Indan, Indene
Collidines

Figure 3a. Compounds ordered on basis of EPC and sampling required.

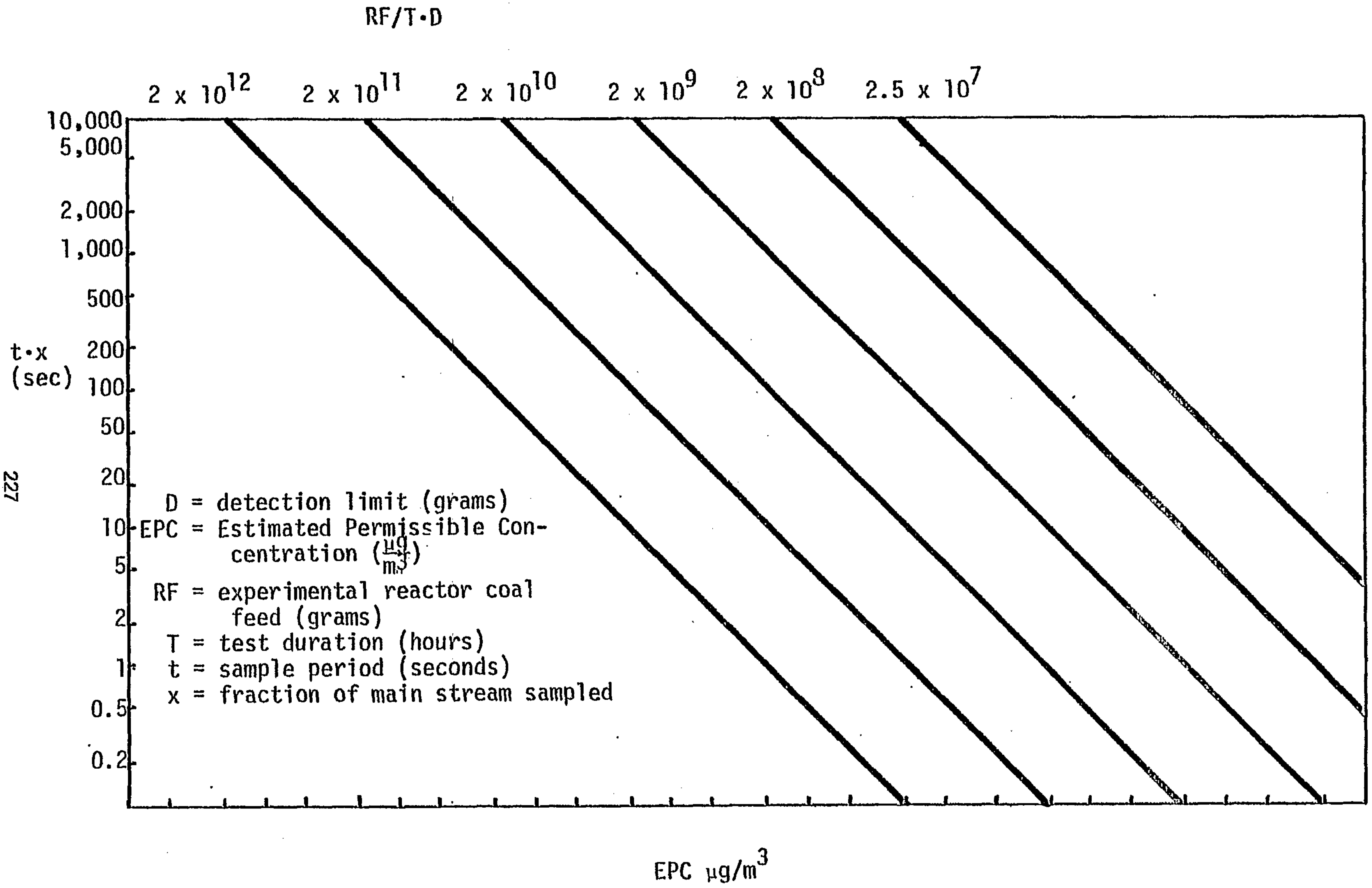


Figure 3b. Sampling required for proper environmental assessment.

human breathing rates, or in some cases, carcinogenic potential, human consumption rates, or ecological effects.

The overlay with Figure 3 shows those pollutants which fall into a specific sampling—i.e., sample percent ranges associated with their particular estimated permissible concentrations. These sampling ranges are further subdivided by the parameters of the experimental tests that are possible with the RTI synthetic fuels reaction system.

An important part of both qualitative and quantitative screening will be the development of improved analytical techniques for analysis of coal conversion products and byproducts. (Developments to date will be discussed in another paper at this Symposium.)

Throughout testing, quantitative measurements will be made on-site of fixed gases, sulfur species, and hydrocarbons up to C_6. These analyses will be made by gas chromatograph and, at a later date, continuous gas monitors for the major product gases associated with gasification.

The second phase of research, concerned with parametric studies, involves application of the gasification reactor to the control of potential pollutants. Parameters to be considered for investigation include those listed in Table 2. To these could also be added the parameters of bed type (fixed, entrained, fluidized) and reactor type (batch, semibatch, plug flow, mixed flow) which should receive attention as research progresses. A statistical approach for optimization of parametric combinations to minimize the number of tests required while investigating all possible influences is currently being undertaken.

Results from parametric testing will be continuously compared with those from chemical analyses so that influential variables can be more extensively assessed as testing progresses. It is obvious that, unless the test plan is directed by previous engineering data , the number of tests could burgeon to orders of 10^3-10^4.

Other researchers[6] have noted the influence of different reactor configurations on the production of byproducts of possible environmental significance. Results of this nature are scarce, however, and extrapolations are difficult. The literature[7,8,9,10,11] describes some established effects of the variation of reactor

TABLE 2

POSSIBLE REACTOR PARAMETERS

COAL TYPE

GRIND SIZE

GASES
  COMPOSITION
  FLOW RATE

STEAM

PRETREATMENT

CATALYST

BED DEPTH

TEMPERATURE

PRESSURE

RESIDENCE TIMES

conditions on major gasification kinetics. Some examples follow:

Pretreated chars may be several orders of magnitude less reactive in terms of oxidation than raw or mildly pretreated coals. The rate of the endothermic reaction

$$C + H_2O \rightarrow CO + H_2$$

varies widely for different coals. Char-CO_2 gasification and hydrogasification contribute little to coal conversion in low pressure steam/oxygen gasifiers. High temperatures favor CO production in the exothermic water-gas shift reaction, while hydrogen is more evident at lower temperatures. Conversion of coal sulfur to gaseous species is a rate-limited phenomenon, and is generally promoted by conditions that lead to high carbon conversion. Product distribution through pyrolysis or volatilization is a strong function of both the final reaction temperature and the time taken to reach it. For example, at high heating rates on the orders of 10,000-50,000° C/s—rates typically attained in continuous fluidized bed and entrained bed gasifiers—the yield of volatiles at a given temperature and the tar-to-gas ratio of the product are both higher than at lower heating rates. Packed beds, larger particles, and elevated gasifier pressures tend to diminish yields of tar and augment yields of char and light hydrocarbon gases during pyrolysis. Observations indicate that char, in general, is less reactive than carbon in nondevolatilized coal in reaction with such species as steam, oxygen, or hydrogen.

Another factor, which can be particularly important in an experimental nonproduction system such as the RTI reactor, is that of nonsteady state conditions. Also, steady-state production of major gases (CO_2, CO, H_2, CH_4) is not an assured indication of a steady output of trace constituents.

Possible relationships of formation probabilities to process parameters will be further evaluated in the kinetics phase of the RTI studies. Some tests in this phase will include:

1. Development of analytical methods,
2. Ascertaining appropriate level of stratification of pollutants,
3. Conducting experimental nonisothermal tests, and
4. Reduction, tabulation, and analysis of data and application to pollutant reduction.

Data obtained through the nonisothermal measurement technique is applicable to any chemical reaction. Nonisothermal techniques are somewhat controversial, and options for reverting to isothermal studies will be retained. In the analysis of coals and coke, nonisothermal measurements are advantageous because, in isothermal studies, the large effect of heating to a given reaction temperature is controlling the competing reactions and consequently the results. For the nonisothermal method, the reaction rates are to be studied at a preprogrammed rate of heating of the solid samples.

Figure 4 depicts the reaction velocity constants for the decomposition of hydrocarbons and petroleum fractions associated with petroleum refining. On this figure is superimposed the typical reaction velocity curve as a function of temperature obtained from some previous studies utilizing nonisothermal reaction kinetics. It is obvious from this simple example that if the reaction velocity can be obtained as a function of temperature, the operating conditions can be selected to favor the desired reactions and to minimize the undesired ones.

One theoretical procedure for obtaining changing concentration (for first order kinetics) as a function of temperature is given in equations below.

$$\frac{dV}{dT} = k_o \left[\exp - \frac{E}{RT} \right] (V_f - V)$$

$$\text{If } \frac{1}{T} = X, \ -dt = dX$$

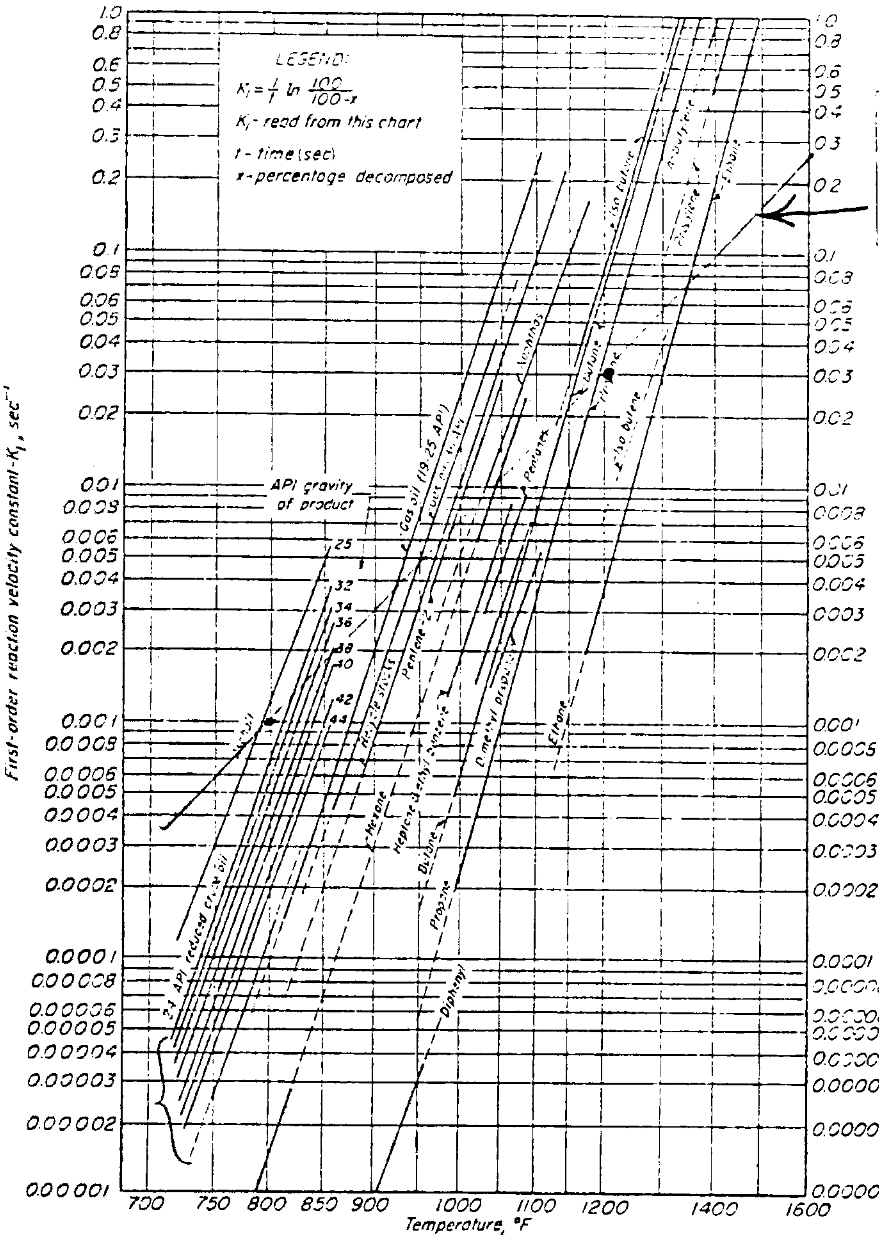
$$dt = \frac{1}{T^2} dT$$

$$t = \frac{1}{T} + c$$

$$T = \frac{1}{t\text{-}c} = \frac{K}{t_{max} - t}$$

$$\frac{dV}{V_f - V} = - k_o \exp\left(- \frac{E}{R} X\right) dX$$

THERMAL CRACKING AND DECOMPOSITION PROCESS



TYPICAL
GASIFICATION
KINETICS

$$K = 1.6 \times 10^{13}/\text{sec} \ \exp - \frac{55{,}000 \text{ cal}}{RT - {}^\circ K}$$

Figure 4. Reaction velocity constants for the decomposition of hydrocarbons and petroleum fractions into various products.

$$\ln \frac{V_f - V}{V_f} =$$

$$-\frac{k_o R}{E} \exp\left(-\frac{E}{R} X\right)\Bigg|_{\infty}^{1/T} = -\frac{k_o R}{E}\left[\exp - \frac{E}{RT}\right]$$

$$\ln\left[-\ln \frac{V_f - V}{V_f}\right] = \ln \frac{k_o R}{E} = -\frac{E}{RT}$$

This approach, properly conducted, permits the simultaneous determination of the sets of two parameters in the typical Arrhenius expressions for the reaction velocity constants for pollutants of interest. An example of a plot for a first order test is shown in Figure 5.

Knowledge of the kinetics of formation can be utilized to suggest changes in the operating conditions of a synthetic fuels conversion system to minimize pollutant formation. Such changes can then be confirmed, for example, on the RTI gasifier. The results from the use of chemical reaction theories will be related to the corresponding experimental and chemical analytical studies.

Although the thermodynamics and kinetics of coal pyrolysis, gasification and desulfurization have received attention, these areas are still not well defined. Complexities of the materials and the reactions involved make a unifying theory most elusive. Descriptions of

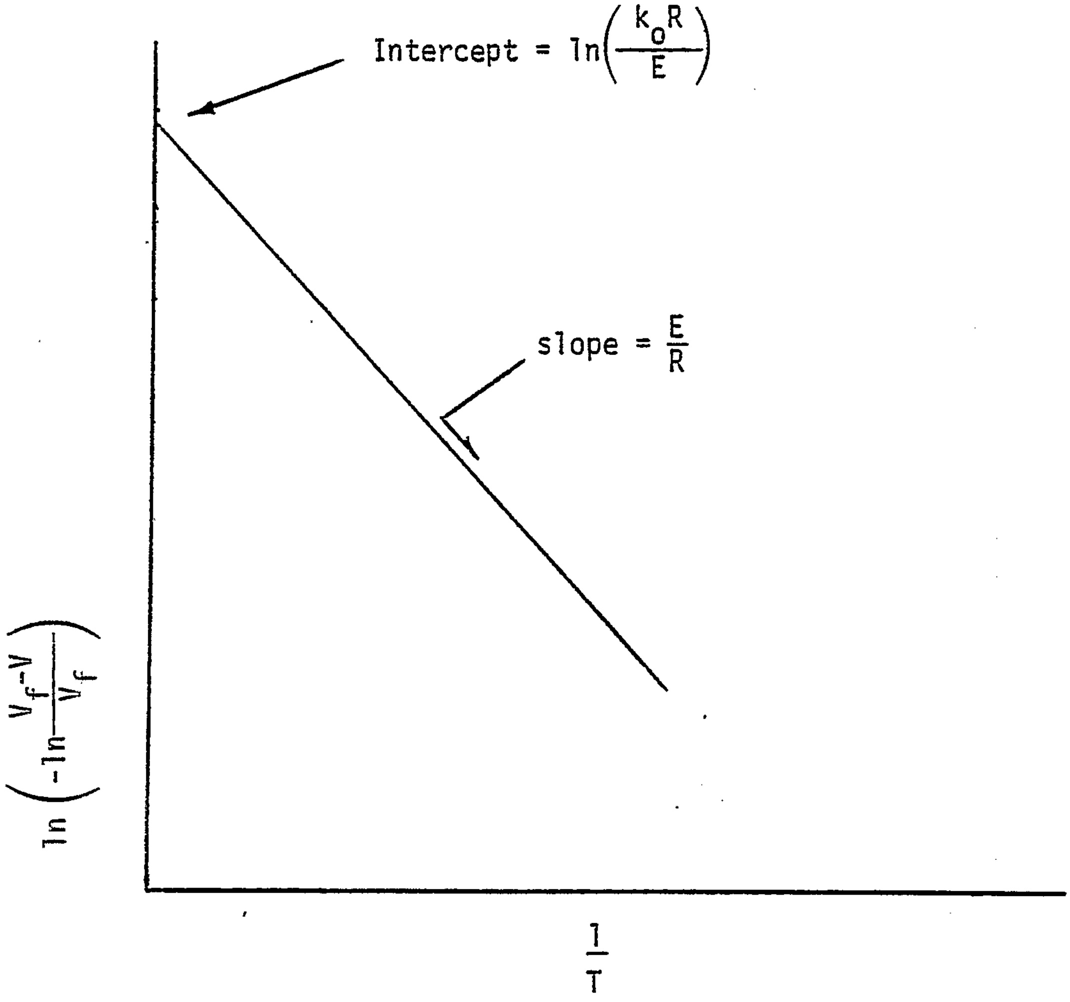


Figure 5. First-order test plot.

devolatilization have, for the most part, treated the combined volatile fractions. This necessitates such approaches as Gaussian distribution estimation of the activation energies, semi-empirical results for determining rate constants, mean activation energy and standard deviations, and some rather complicated rate expressions. Devolatilization rate may be controlled by kinetics or mass and heat transfer, and the product distribution is often provided by coupled effects. Also, reactive volatile products such as tars may undergo secondary cracking or polymerization reactions.

For gasification, mechanisms and rates of the reactions involved have been postulated. Rate laws of the Langmuir type and also more simplified forms have been proposed for the primary carbon/steam mechanism. Van-Fredersdorff and Elliott[7] have proposed a Langmuir-Hinselwood rate law given by equation

$$r = \frac{\left[k \ PH_2 PCO_2 - \frac{PCO \ PH_2O}{k}\right]}{1 + K_A PCO_2 + K_R PCO}.$$

Wen[12] uses a simpler form of the rate law, a reversible second order expression.

A literature survey has been carried out to explore these and other efforts describing coal gasification kinetics, including the reactions leading to the generation of H_2S, CS_2, and COS. While these studies provide some exemplary approaches to solving reaction kinetics problems, it is recognized that the same approaches may not be applicable to formations of trace constituents of interest and that indeed problems involved in the latter effort may be much more difficult.

IMPLEMENTATION OF APPROACH

The unique requirements of the program have demanded extensive additions of hardware, facilities, and analytical equipment. The opportunity of close coordination with the Environmental Protection Agency and familiarity through previous programs with the environmental problems of coal conversion processes have facilitated progress.

Attempts have been made initially to avoid as many problems as possible. Initial testing will investigate the gasification area of fossil fuels conversion only. A simple experimental system has been devised that is much less complex than a full-scale plant design yet, hopefully, offers good approximation of the reactor operation of such facilities.

The coal conversion reactor, Figure 6, topped by the tubular coal feed hopper, extends only approximately nine feet in height. Under operating conditions, the reactor is encased in a vertical furnace which allows preheat of internal inert gases or reactor wall heating of the coal bed and gases during reaction.

The reactor operates in a semibatch mode—i.e., the entire charge of coal to be gasified is injected into the reactor, and steam,

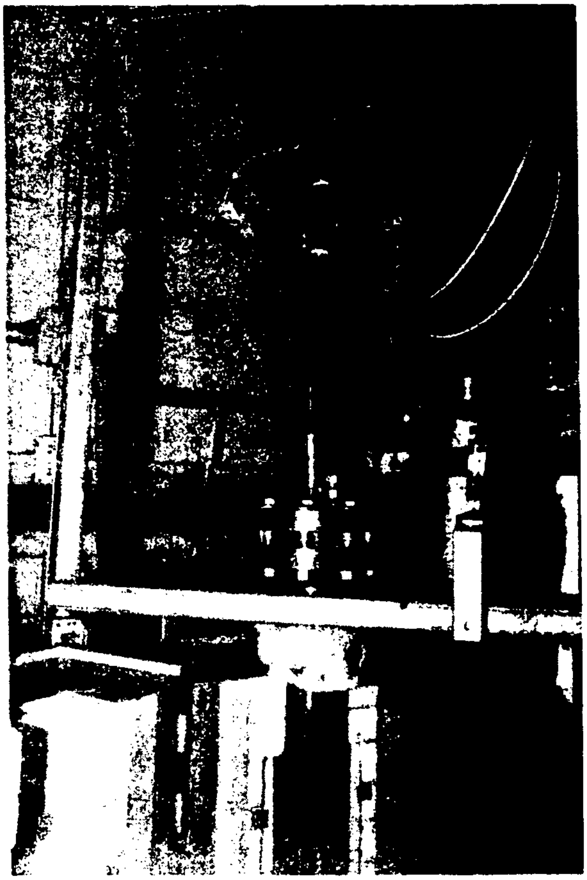


Figure 6. Gasification reactor.

along with other gases, is continuously passed through the bed during a test run. Such an approach obviously relieves the experimental work of the complications of continuous coal feed and ash/char removal. Consequently a porous,temperature-resistant ceramic flow distributor, Figure 7, which supports the coal bed in the reactor itself, is situated in the reactor. This allows a reasonably homogenous fixed bed or, on the other hand, a truly fluidized bed as opposed to many of the suspended or highly entraining beds associated with many pilot-scale processes. The flow distributor is designed to eliminate channeling around the circumference and to present a pressure drop conducive to optimized fluidization should the reactor be operated in this mode.

Coal beds in the reactor are fixed at present. It is hoped that reasonable results and simulations can be obtained with fixed bed reaction since this will eliminate the modeling difficulties associated with fluidized beds, e.g., bubbling. The primary concern is to simulate the reaction history of coal particles introduced into gasification reactors, particularly those phases which might be most closely associated with the production of contaminants. These phases include (1) surface evaporation of volatiles—probably zero order, low activation energy; (2) diffusional evaporation of volatiles—probably first order, low activation energy; (3) surface cracking—complex order, high activation energy; and (4) organic sulfur decomposition and removal—two ranges, first order, high activation energy. A comparison of the differences between continuous and batch feed in terms of coal particle history and reaction analysis is given in Table 3.

While investigating some of the fundamental questions associated with the possible production of toxic materials in this experimental gasifier, it is at the same time essential that the experimental procedures offer a real approximation of gasification processes which exist or

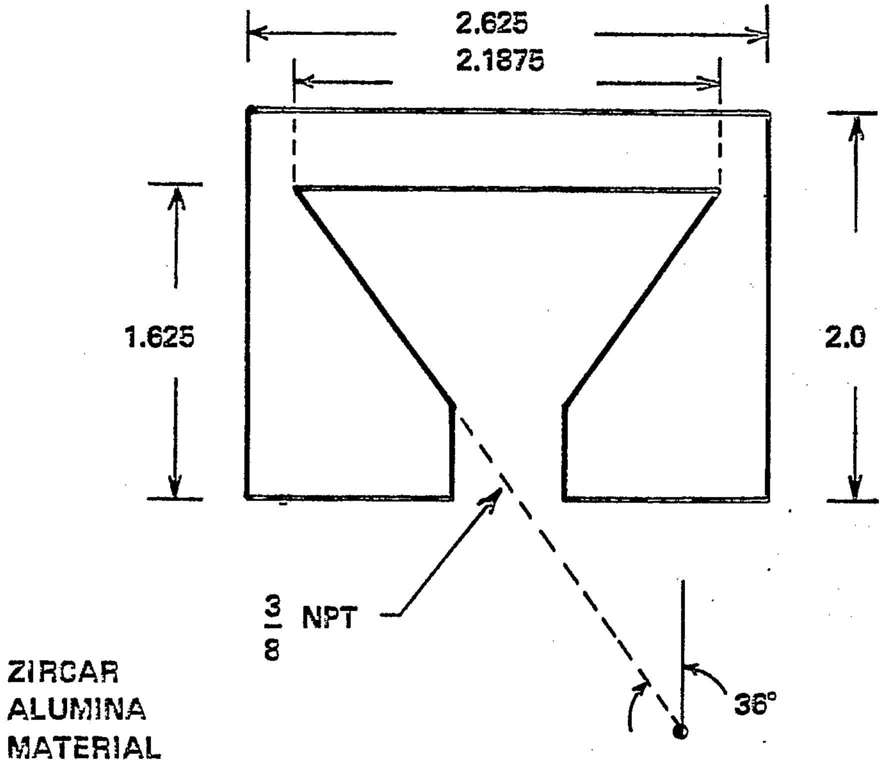


Figure 7. Flow distributor

TABLE 3

COMPARISON OF REACTOR CHARACTERISTICS

	BATCH	CONTINUOUS
FEED MATERIAL REQUIRED	ONE REACTOR VOLUME	MANY REACTOR VOLUMES
LENGTH OF RUN	ABOUT 1 REACTOR TIME	MANY REACTION TIMES
BEST APPLICATION	EXPERIMENTATION	PRODUCTION
INDEPENDENT VARIABLE (CHEMICAL REACTIONS)	TIME	DISTANCE; AND TIME UNTIL STEADY STATE
TYPICAL RATE EQUATION	$\frac{dc}{dt} = K[T(t)]\,c(t)$	$u\frac{dc}{dx} = K[T(x)]\,c(x)$
USUAL MEASUREMENTS	$c(t)$	c at $x = o$; $x = L$

have been proposed for operation in the United States. The laboratory gasifier has been designed to cover a wide range of operating conditions to provide some simulation of large-scale gasifiers. Mass ratios of gases or steam to coal ratios, internal pressures, reactor gas and coal bed temperatures, bed types, particle sizes, and other parameters can be matched. The reactor is presently intended to gasify up to two kilograms of coal (noncaking or pretreated coals), and operate in pressure ranges from ambient to 1,000 psig (depending upon temperature) and temperatures to 1950° F. Nominal testing ranges at present are 200-300 psig, maximum temperatures to 1900° F, and coal masses of less than one kilogram.

All gas flow and pressure control is maintained at a single control panel. Steam generation and steam superheating to injection temperatures (up to 1500° F) are accomplished through a series of remotely controlled furnances fed by high-pressure, low-flow metering pumps.

Temperature control within the reactor itself is accomplished in one of two ways:

1. Controlling the level of oxygen flow and, therefore, combustion within the coal bed, and/or
2. Varying current supply to the remotely controlled vertical furnace and a separate strip heater near the top flange of the reactor.

Internal temperatures are measured in the reactor in the axial direction during testing. Vertical temperature gradients scheduled for observations are quite possibly an important parameter in the generation of particular gasification contaminants. Provision has been made for remote control of the three zones of the vertical furnance utilizing a Datatrack programmer. This allows graphical inputs describing a desired temperature profile to be followed during test runs. Therefore, during nonisothermal kinetic studies, a temperature profile can be selected to eliminate nonlinearities in the solutions to proposed rate equations and allow simplified extrapolation and solution for rate constants and activation energies.

An operational schematic of the mechanics of the experimental laboratory gasifier system is shown in Figure 8.

Product gases from the gasifier pass through a series of traps designed to eliminate particulates, tars, water, and other condensates before the gases pass to the gas sampling train. Substances remaining in the traps are analyzed primarily by GC/mass spectrometry and high pressure liquid chromatography.

The RTI sampling train in use at present is shown in Figure 9. Discrete gas samples are currently being taken for on-site analyses by gas chromatography of fixed gases (N_2, O_2, CO, CO_2), sulfur species (e.g., H_2S, COS), and hydrocarbons (less than C_6). On-site continuous gas monitors will be added in the near future for fixed gases and methane. This is, of course, most important to assure reasonable simulations by the laboratory reactor of real gasification processes. Heavy organics and other constituents are being adsorbed by XAD_2 and Tenax cartridges. The XAD_2 cartridges are sufficiently large to allow passage of the entire product gas stream through them throughout a test to provide an integrated sample of all contaminants, while the Tenax cartridges are valved to be individually selectable so that sampling may also be associated with discrete test times.

The sampling system is presently constructed of stainless steel. A glass sampling system is being planned.

All sampling and analysis areas are contained under ventilated hoods. The entire reactor facility area has been well ventilated to prevent worker exposure to hazardous contaminants.

An on-site signal processing unit has been included to manage both the large amount of data from the numerous sensors included in the experimental system and that data from on-site chemical analysis. This unit includes a 64 K core with compatible disk storage. Real time functioning is included which will allow reactor and sampling system control, automatic safety shut-off and on-line analysis during test periods. All data will be processed, stored, and analyzed through this system. The signal processing unit is backed up by multipoint and analog strip chart recorders and digital displays.

INITIAL TESTING

Experimental evaluations have just begun using the reactor system. A period of pregasifica-

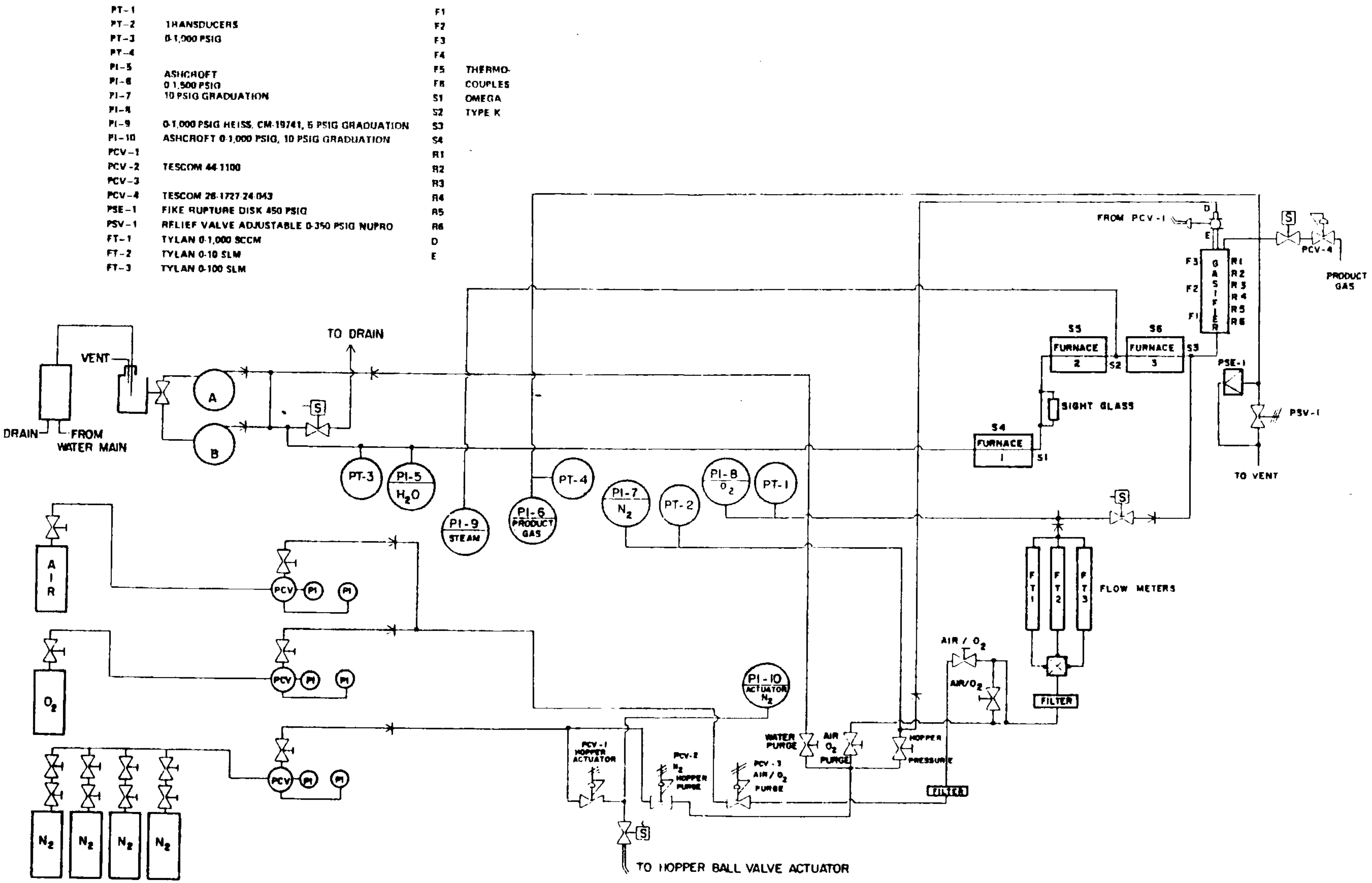


Figure 8. Process schematic

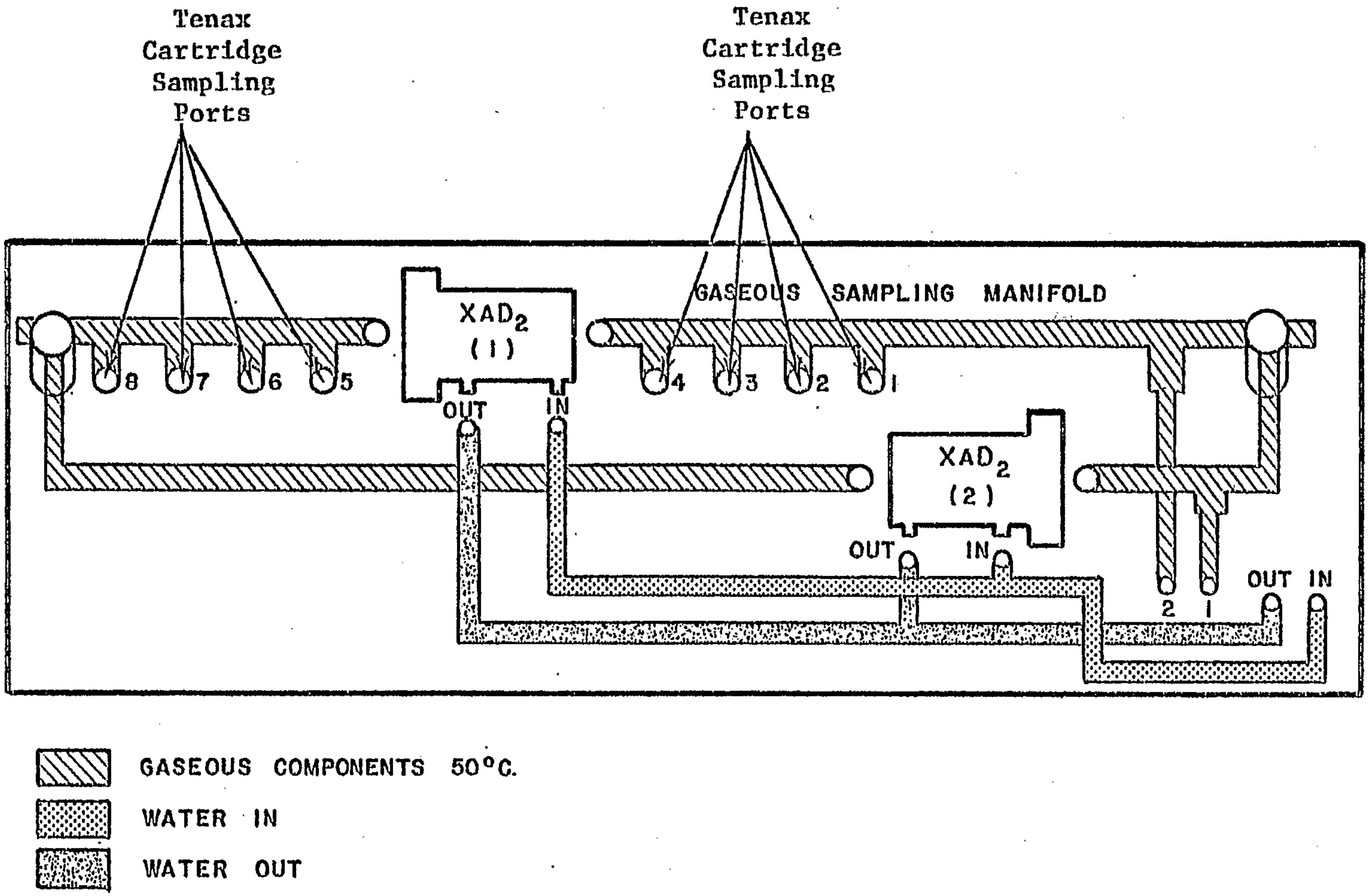


Figure 9. Gaseous sampling manifold.

tion testing has included the following:

1. Calibrations of pumps, flow meters, thermocouples, pressure transducers, gas chromatographs, temperature controllers, digital displays, strip chart recorders, furnace responses, gauges and metering valves.
2. Heat up tests for steam generation, reactor internal temperature control, and particulate, tar and condensate trap temperature control.
3. Overall system flow tests using inert gases, and pressurization of all system modules.
4. Evaluation of radial temperature profiles within the reactor at various gas flow rates and flow distributor positions.
5. Fluidization tests in a plexiglass "reactor" with various coals of different mesh sizes.

The first reactor tests have been carried out primarily to ascertain the proper functioning of the system and the logistics of the sampling and analysis techniques. To facilitate matters, a Western Kentucky FMC char, low in volatiles and free-swelling index, has been used. A first test took a 175-gram sample of this char to nearly complete combustion with about 43 grams of ash remaining at the end of the test. Char-ash analyses are given in Table 4. Both air/coal and steam/coal mass ratios were near 1:1 to begin with and, air flow was increased at discrete intervals over the two-hour test. Temperatures did not exceed 800° C. Chemical analyses were not done for the products of this test.

A second test included much less complete reaction of the char, about 67 percent. Some gross chemical analyses done on the products of this test indicated lower carbon monoxide and higher hydrocarbon yields, which would be expected to be associated with the lower reaction temperatures of this test. Gas production was still increasing at the end of the sampling period, indicating that steady state conditions for gasification were not reached. Results from these tests remain qualitative, and more detailed assessment remains to be done. One indication from these and other tests is that inter-

TABLE 4

CHAR/ASH ANALYSES

Analyzed For	Char Sample Air	Ash Sample A1C
BTU/lb.	11,090	570
Moisture, %	1.0	0.9
Ash, %	19.7	91.0
Volatile Matter, %	7.8	6.9
Fixed Carbon, %	71.5	1.2
Sulfur, %	1.8	0.2
Carbon, %	74.02	13.82
Hydrogen, %	1.48	0.82
Oxygen, %	1.7	<0.1
FSI	<1.0	<1.0
Ash Fusion Temp.	2,600	2,610
Nitrogen (TKN), %	1.3	0.3

nal reactor temperatures could be reasonably controlled by varying power input to the surrounding vertical furnace. Therefore, a more recent experiment investigated gasification of a small amount of char, 175 grams again, in the absence of combustion.

This last experiment was carried out utilizing the Datatrack programmer to provide a ramp function for control of vertical furnace temperatures. Furnance and reactor temperatures were initially increased to approximately 700° C before char was injected into the bed. Steam was continuously passed through the bed following injection. Steam flow was supplemented by a carrier gas (N_2) to improve flow and temperature stability of the injected steam.

It has been demonstrated in all tests that heat conduction and gas flow convection through the bed allow reasonably short heat-up times to increase char bed temperatures to those originally in the preheated reactor. Increased flow through the bed has been demonstrated to shorten this heat-up time. Internal reactor and coal bed temperatures were also demonstrated in the last mentioned test to closely follow the signal input for signal temperature control from the Datatrack program. These results are shown in a general fashion in Figure 10.

Few problems have been encountered to date in this simple and low risk system design. Some recognized problems, however, have included the difficulty of flow control at very low rates (for example, less than 1 standard liter per minute) and high pressures, placement of the flow distributor within the reactor which will completely prevent channeling and consequent oxygen breakthroughs, coordination of metering valve controls with back pressure regulation at very low gas flow rates, placement of sufficient thermal insulation in small spaces where high heat losses are possible, maintaining upper reactor temperatures to prevent condensation of exit gases before passage through the proper traps, and maintaining superheat steam temperatures at very low flow rates. Most of these problems have been solved, all or in part.

PLANNED RESEARCH

During the final quarter of the first year of research, several brief tests are planned which are concerned with improving system controllability as indicated by results from early gasification tests. Reevaluation of system components is also being carried out.

As soon as confidence has been developed in the capability of the RTI reactor to provide reasonable simulation of coal gasification characteristics, a second phase of gasification testing will be entered. Different coals and reactor parameters will be used, and extensive screening evaluations of all products and byproducts will be carried out. Intentions are at this time to begin with a representative eastern coal (e.g., Kentucky, Illinois, or Pittsburgh). This coal will be of a reasonably large mesh size such as the 10 by 80 char size used to date.

Testing on the eastern coal will be followed by gasification of a western subbituminous coal such as Montana Rosebud. Again, a large mesh size will be used. Both coal samples will be gasified during separate tests at two different temperatures. Future comparisons will be made with real gasification processes.

Further tests will be carried out using smaller mesh sizes. This will be done first to evaluate the coal supply system with these sizes, secondly to investigate bed flow through or fluidization problems, and finally to examine the effects upon pollutant production.

All future plans are dependent upon directions from the Environmental Protection Agency. Some likely improvements will include in-house coal preparation including grinding and screening and possibly in-house sample analyses to include proximate, ultimate, and more intensive analyses. It was mentioned previously that continuous gas monitors will be added to give real time assessment of product gases. A number of safety features and alarms are planned. Preliminary investigations have been begun into utilizing gamma ray detection for measurement of fixed or fluidized bed levels within the reactor. Hopefully, in-house pretreatment of caking coals will be added.

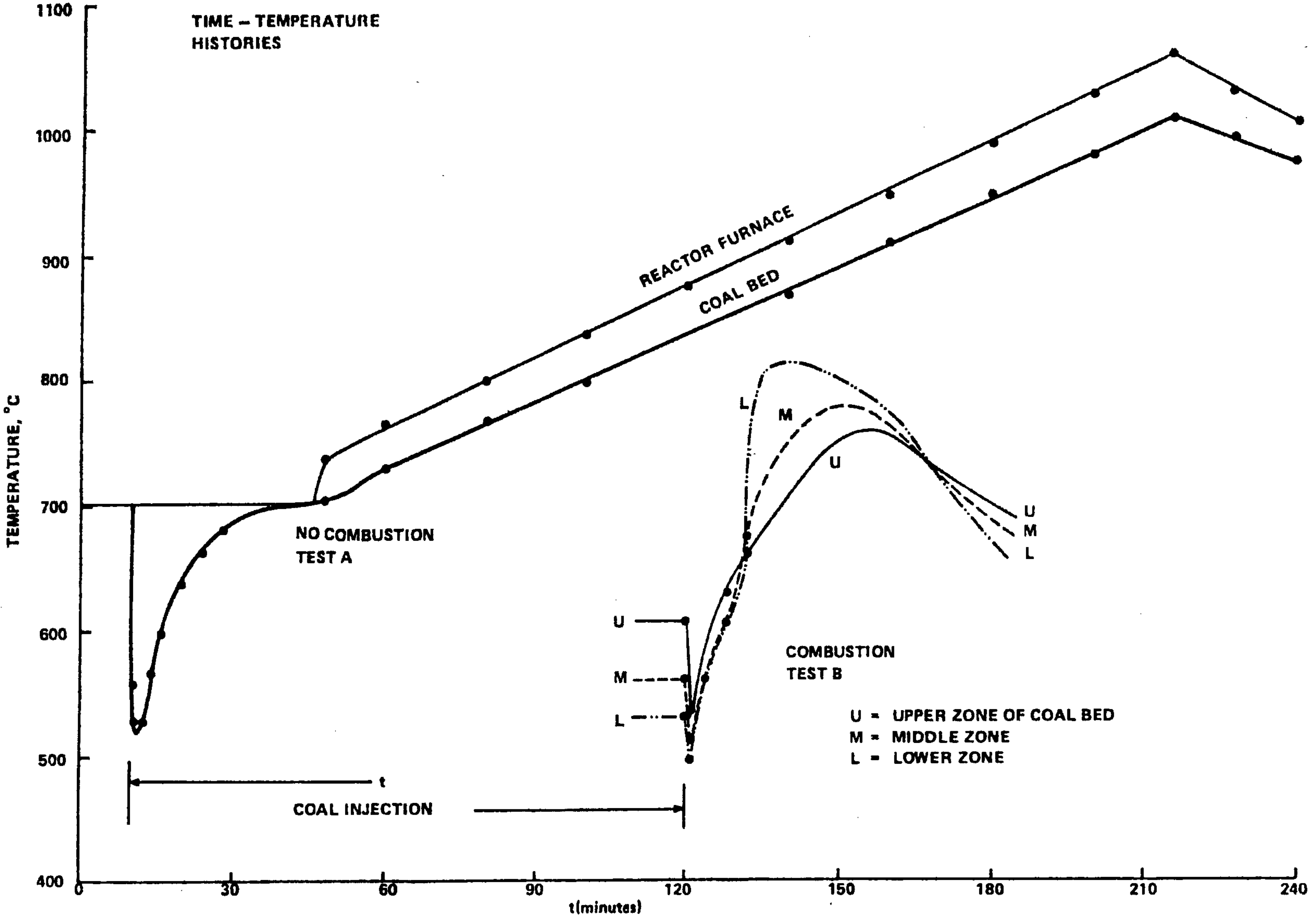


Figure 10. Early gasification tests.

Some extensions of the research discussed which seem potentially valuable:

1. Simplified experimental reactions to provide better correlation with theoretical analyses, e.g., reaction of thin coal wafers to provide a one-dimensional approximation and the observation of the action of very small coal samples in conjunction with thermogravimetric analysis tied to continuous mass spectromery.
2. Investigation of byproduct or contaminant production following the incineration of gasifier tars and chars.
3. Continuous coal feed to the reactor to evaluate discrepancies produced by this method with the results obtained during batch operations.
4. Determination of the effects of fluidization and entrainment on the production of toxic or other trace constitutents presenting health hazards.
5. Comparison of contaminants analyzed for and samples taken from different regions of the coal conversion reactor.

It is hoped that the present and future research plans described will begin to produce some profitable scientific results in the upcoming year and be made available to those interested in coal conversion. It is also hoped that these results will alleviate concern over environmental problems associated with coal utilization.

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