THE CATALYZED LIQUEFACTION AND GASIFICATION OF COAL

by

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ABSTRACT

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A study of one-step processes for the liquefaction of coal with water has been made at temperatures of 350 to 465°C and pressures up to 8000 psig with and without catalysts and a deliberately added liquid phase. The coal (30 grams) used was a Pittsburgh Seam coal (H/C = 0.803). The catalysts were commercial catalysts selected because their known catalytic functions were possibly desirable for promoting the water-coal reaction. Either phenanthrene (30 grams), Decalin (60 ml) or Tetralin (60 ml) was the deliberately added phase. Experiments were made in a 300 ml rocking autoclave. Usual reaction times were two hours (not including heating and cooling times). Coal conversion was defined as the coal charge less the benzene-extracted residue divided by the coal charge, all on the dry basis, times 100.

Coal conversions were 16 to 20% in the water-coal system vis à vis 10 to 11% when coal was heated with nitrogen present. Catalysts such as cobalt molybdate on alumina and cobalt-thoria on kieselguhr had no apparent effect on the water-coal reaction.

An improvement (to 25% w/w) in coal conversion occurred when phenanthrene was added to the water-coal system. Again catalysts had no appreciable effect. Coal conversions increased to 30 to 34% w/w when Decalin was added to the water-coal system. Catalysts, such as nickel tungsten on alumina and cobalt molybdate on alumina may have increased coal conversion slightly in the latter system. Tetralin liquefied about 65 to 67% of the coal. When coal was treated with Tetralin and water, coal conversion dropped to 59 to 61% and when catalysts were also used, coal conversions were 49 to 51%.

These results were satisfactorily explained by two kinetic models. One model assumed that stabilization of the coal-derived active fragments (produced via thermal cracking) to benzene solubles occurred chiefly by rearrangement reactions, and to benzene insolubles by polymerization. The other kinetic model assumed stabilization to benzene solubles occurred mainly by hydrogen transfer from a liquid donor agent and to benzene insolubles by polymerization. The model without hydrogen transfer was applicable to the water-coal and phenanthrene-water-coal systems. The model with hydrogen transfer was applicable to the Tetralin-coal and Tetralin-water-coal systems. Both hydrogen transfer and rearrangement reactions were probably important in the Decalin-containing runs.

Subsequently, a study was made to determine if the residual cokes would gasify at a practical rate at 1000°F (538°C) and atmospheric pressure using potassium and cesium salts as catalysts in the ratio of 0.002 g.-atom alkali cation per g. coke. Experiments were made in a 1" I.D. tubular reactor, operated continuously with respect to steam (downflow) and batch in carbon.

Gasification rates (R_I) generally first increased as the fraction carbon gasified (FCG) increased, then decreased. The exact shapes of the R_I curves varied depending on the catalyst and its initial distribution in the bed. When cesium acetate was mixed with the top third of the bed, R_I increased at higher FCG values. The gaseous products (dry basis) were hydrogen (70%) and carbon dioxide (29%).

Maximum R_I values at 1000°F obtained with the catalysts, cesium acetate, potassium acetate and potassium carbonate were 8.95×10^{-4}, 4.7×10^{-4} and 5×10^{-4} g.C/(min.)(g.C), respectively. These are about 20 and 10%, respectively, of the commercially feasible rate at 1500°F (50×10^{-4} g.C/(min.)(g.C)). The R_I drop with FCG for the volatile cesium and potassium acetates was attributed to catalyst loss; the R_I drop for potassium carbonate was attributed to its low mobility.

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Professor David B. Ralston
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Dear Professor Ralston:

In accordance with the regulations of the Faculty, I herewith submit a thesis, entitled "The Catalyzed Liquefaction and Gasification of Coal" in partial fulfillment of the requirements for the degree of Doctor of Science in Chemical Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

George T. Wildman

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I. SUMMARY

A. MOTIVATION

United States projected demands for energy to the year 2000 indicate that there will soon develop a shortage in the United States of our present major energy sources, petroleum and natural gas. Coal reserves, however, are enormous, constituting about 85% of the known recoverable fossil fuel in the United States. Nuclear power, now supplying a small fraction of the total energy demand, will become a much larger factor. But, as long as the basis of the United States economy remains the internal combustion engine, liquid fuels will continue to be essential. Thus, the time is approaching in the United States when coal will need to be converted on a gigantic scale, as it was in wartime Germany, to synthetic fuels.

A coal-based synthetic fuels industry has never been established in the United States simply because it has always been cheaper to convert crude petroleum, rather than coal, to oil and gasoline. The expense in coal conversion processes results from several factors, chief of which are the hydrogen deficiency of coal relative to petroleum and the fact that coal, a solid having a high ash content, is inherently difficult to handle and process.

Low cost hydrogen is currently available from natural gas. However, this situation will not continue far into the future because of the rapid depletion of the natural gas reserves. It will probably become necessary to produce the hydrogen required for coal liquefaction by coal gasification which is normally a high temperature (800 to 1000°C), highly endothermic process. Since the synthesis step in the two-step coal conversion processes is a low temperature (250 to 450°C) exothermic process, the thermal efficiency of the combined gasification-synthesis steps is low, since the second law of thermodynamics prohibits the direct utilization of low temperature heat at a higher temperature.

B. OBJECTIVES

The objectives of this thesis were to develop solutions to these two fundamental problems in coal to synthetic fuels processes, the coal hydrogen deficiency relative to crude petroleum and the low thermal efficiency of the two-stage coal conversion processes. This thesis is divided into two sections, the first section, which represents the major portion of the present effort, is devoted to the study of methods for liquefying coal. The second section is concerned with studies on coal gasification.

The primary objective of the work described in the Liquefaction Section of this thesis was to find a set of conditions of temperature and pressure under which coal and water, with a suitable catalyst would react to produce liquids. The primary objective of the work described in the Gasification Section of this thesis was to determine if the char by-products from the liquefaction studies would gasify at a practical rate at 1000°F using certain potassium and cesium salts as catalysts.

It is clear that the direct reaction of water (the cheapest potential source of hydrogen) and coal to liquids would solve both of the fundamental process problems, coal hydrogen deficiency and the low thermal efficiency of combined gasification-synthesis processes. Low temperature gasification only faces the thermal efficiency dilemma (hydrogen costs via coal gasification, however, would be reduced).

C. CATALYZED LIQUEFACTION OF COAL WITH WATER

1. Background

The thermodynamic analysis of the β-graphite-steam system presented in the text shows that it is possible below 500°C to produce methane and the higher hydrocarbons from reactions between carbon and water. Although, at equilibrium, the concentrations of the individual hydrocarbons are extremely low, there are an infinite number of hydrocarbons and oxygenated hydrocarbons that could form. Thus, in the thermodynamic sense, formation of an "oil" from the reaction of carbon and water is feasible. Examples of these direct gasification-synthesis reactions are listed below.

1. Aliphatic hydrocarbon production

$$\begin{array}{ccccccc} 2C & + & 2H_2O & = & CH_4 & + & CO_2 \\ 7C & + & 6H_2O & = & 2C_2H_6 & + & 3CO_2 \\ \vdots & & \vdots & & \vdots & & \vdots \end{array}$$

2. Olefinic hydrocarbon production

$$\begin{array}{ccccccc} 3C & + & 2H_2O & = & C_2H_4 & + & CO_2 \\ 9C & + & 6H_2O & = & 2C_3H_6 & + & 3CO_2 \\ \vdots & & \vdots & & \vdots & & \vdots \end{array}$$

3. Aromatic hydrocarbon production

$$\begin{array}{ccccccc} 15C & + & 6H_2O & = & 2C_6H_6 & + & 3CO_2 \\ 9C & + & 4H_2O & = & C_7H_8 & + & 2CO_2 \\ \vdots & & \vdots & & \vdots & & \vdots \end{array}$$

Kinetically, carbon and water have proven to be extremely nonreactive towards each other below 500°C, thus this route to cheap hydrocarbons does not appear practical. However, it is misleading to consider the amorphous carbon form coal to be in the same category, in the kinetic sense, as the other forms of amorphous carbons, such as charcoals and carbons, or in the same category as β-graphite, the soft crystalline carbon. Coals, unlike the other carbon forms, possess very complex organic structures and have high hydrogen to carbon atomic ratios, typically 0.3 to 0.7, relative to the other carbon forms. The opportunity for direct reaction with water could be postulated as being more apt to occur in the case of coal, because of its multiplicity of bond types and energies, than in the cases of other amorphous carbonaceous substances or β-graphite which have only one or a few kinds of chemical bonds. Furthermore, the chemical reactivity of coal varies remarkably depending on rank, such as anthracite, bituminous or lignite, and source.

The three major existent coal liquefaction processes: (1) Bergius process, (2) pyrolysis, and (3) liquid phase hydrogen donor agent are applicable only to coals and not to the other carbon forms having much lower hydrogen to carbon atomic ratios. These latter carbon forms must first be gasified and the resulting synthesis gas mixture (largely carbon monoxide and hydrogen) then converted to hydrocarbons via the Fischer-Tropsch process. These three major coal liquefaction processes listed above all involve a partial breakdown or decomposition of the original coal structure into fragments followed or accompanied by some type of stabilization of these fragments. All three processes thus produce liquids from coal which somewhat resemble in structure the original coal.

By analogy to the mechanisms of the known coal liquefaction processes, it is possible to visualize or develop a framework of possible reactions between coal and water which are unique to coal because of its complex organic structure. Examples of these reactions are listed below.

1. Water serving as a hydrogen donor to coal.

$$\text{Coal} + x\,H_2O = \text{"oils"} + \frac{x}{2}\,CO_2$$

2. Water serving as a hydrogen and oxygen donor to coal.

$$\text{Coal} + x\,H_2O = \text{"oils"}$$

3. Water serving as a hydrogen donor to the thermal decomposition products of coal.

$$\text{Coal} + \Delta = \text{"Active Fragments"}$$

$$\text{"Active Fragments"} + x\,H_2O = \text{"oils"} + \frac{x}{2}\,CO_2$$

4. Water serving as a hydrogen and oxygen donor to the thermal decomposition products of coal.

$$\text{Coal} + \Delta = \text{"Active Fragments"}$$

$$\text{"Active Fragments"} + x\,H_2O = \text{"oils"}$$

In essence, what is desired is an efficient process, using water as a hydrogen donor, to convert the complex organic substance coal to liquids which are amenable by further processing to desirable hydrocarbons. This process can consist of reactions involving water which are applicable to all carbonaceous solids and/or it can consist of reactions involving water which are unique to coal.

2. Program for Present Investigation

a. Reaction Conditions

Hydrocarbon formation from carbon and water, as discussed in the text, is thermodynamically favored at temperatures less than 500°C and by high pressures. A review of the commercial coal conversion processes shows that very little reaction of coal occurs, even with hydrogen, until the temperature that coal begins to thermally crack, 350 to 375°C, is attained. Further, it is probably not practical to consider pressures above 8000 to 10,000 psi for coal conversion plants unless tremendous gains can be realized. Therefore, the temperature and pressure regions selected for study in the present investigation, on both theoretical and practical grounds, were 350 to 475°C and less than 8000 psi, respectively.

b. Selection of Catalysts for Evaluation

No catalyst is known which will promote the reaction of coal and water to form liquids below 500°C. The right catalyst would possess the ability to activate the water molecule and combine it with coal or coal-derived active fragments. Other possible desirable catalytic functions include the ability to:

1. Promote carbon oxides formation.
2. Retard the polymerization reactions.
3. Facilitate the cracking reactions.
4. Catalyze the water-gas shift reaction.
5. Act as a conventional hydrogenation catalyst.
6. Catalyze desulfurization and denitrogenation reactions.

The approaches taken to the problem of catalyst selection were to (1) consider known catalysts or catalyst mixtures possessing one or more of the possible desired catalytic functions, and (2) consider catalysts used in reactions in which water is a reactant or product. The latter makes the assumption that a catalyst for the forward reaction is a catalyst for the reverse reaction which probably is not generally true. Table I is a partial listing of typical catalysts possessing certain of the possible desired catalytic functions.

TABLE I

POSSIBLE DESIRED CATALYTIC FUNCTIONS FOR COAL-WATER SYSTEM

Function	Typical Catalysts
Cracking	Silica-Alumina
Water-Gas Shift	Iron Oxides
Hydrogenation	Nickel, Cobalt, Noble Metals
Hydrodesulfurization Hydrodenitrogenation	Cobalt Molybdate/Alumina Nickel Molybdate/Alumina Nickel Tungstate/Alumina
Gasification	Alkali Metal Salts

c. Added Liquid Phase

It seems reasonable to assume that a deliberately added liquid phase could prove to be of considerable value in the water-coal system. Three polycyclic hydrocarbons were selected for inclusion in this study:

(1)	1,2,3,4-Tetrahydronaphthalene	"Tetralin"
(2)	Decahydronaphthalene	"Decalin"
(3)	Phenanthrene	

Tetralin, a hydroaromatic substance, is widely used in coal solubilization because of its hydrogen donor properties. Decalin, a saturated hydrocarbon, has been used to prepare coal extracts which closely resemble the original coal in ultimate analysis. Phenanthrene, an aromatic compound, has often been used as a coal solvent; the aromatic clusters in coal are believed to be arranged in the phenanthrene type configuration. These polycyclic hydrocarbons owe much of their effectiveness to the broad principle that "like dissolves like".

3. Experimental

a. Equipment

A 300 milliliter (nominal volume) rocking stainless steel 316 autoclave operated in the batch mode was used as the reactor in the coal liquefaction studies. The reactor was provided with a pressure gauge and two thermowells, a rupture disc assembly, and a heating mantle controlled by a West temperature controller.

b. Description of Coal

The coal used in the liquefaction studies was a Pittsburgh Seam coal from the Ireland Mine in Northern West Virginia and was supplied by the Consolidation Coal Company. Table II gives the analysis of this sample of Ireland Mine coal. The coal sample was stored under water and aliquots dried *in vacuo* just prior to use.

c. Procedure

In a normal run, thirty grams of dried coal along with 40 to 160 milliliters of deionized water was charged to the reactor. Then, if desired, sixty milliliters of Decalin or Tetralin or thirty grams of phenanthrene were added. Heterogeneous catalysts were added next in the powdered form, usually 6 grams of catalyst were used (20% w/w based on dried coal).

The reactor was then sealed, mounted in the heating mantle clamped to the rocking assembly, thermocouples inserted in the thermowells and the service line connected. Air was displaced from the reactor by five successive pressurizations using 1500 psi nitrogen. After this purging operation, the reactor was either left with a slight pressure of nitrogen or pressurized to 1500 psig with nitrogen, carbon dioxide or carbon monoxide.

Heating and rocking then commenced. The heatup time varied between sixty and ninety minutes depending on the desired reaction temperature. The reactor was then

TABLE II

ULTIMATE ANALYSIS OF IRELAND MINE COAL[+]

	Weight Percent (Dry Basis)
Carbon	66.05
Hydrogen	4.45
Nitrogen	1.15
Sulfur	4.67
Ash	12.32
Oxygen (by Difference)	11.36
Atomic $^{H}/_{C}$	0.803

[+] Analyses performed by the Physical and Analytical Department of Merck & Co., Inc., Rahway, N.J.

held at the desired temperature (± 2°C) for two hours. Cooldown times were of the order of one hour.

After cooling, the reactor was carefully vented; the service line was disconnected and the reactor placed in a vise and opened. The reactor contents, liquids and solids, were then essentially all removed using spatulas to scrape all the solids from the reactor walls and internals. Benzene was liberally used during this operation. The solids and liquids were separated via vacuum filtration and the solids, partially dried on the filter, placed in a Soxhlet thimble and then extracted exhaustively for sixteen to twenty-four hours (normally the benzene extract was almost colorless after four hours of Soxhlet extraction). The Soxhlet thimble with the solids intact was then placed in a fume hood and air-dried to constant weight.

In the present experimental work, coal conversion is defined by the equation:

$$\begin{matrix}\%\text{ Coal}\\ \text{Conversion}\end{matrix} = \frac{\text{Coal Charge, g} - \begin{matrix}\text{Dried Extracted}\\ \text{Residue, g}\end{matrix}}{\text{Coal charge, g}} \times 100$$

The coal conversion, as defined, is the difference between the dry solid coal charged to the reactor and the dried, benzene extracted carbonaceous residue recovered (corrected for any solid catalysts used) divided by the coal charged. Since the gas phase usually represented a small fraction of the coal converted, the coal conversion is essentially the extent of liquefaction.

4. Results of Coal Liquefaction Studies

The significant results of the coal liquefaction studies are summarized in Figures 1 and 2. Figure 1 is a plot of coal conversion as a function of temperature for the chief reaction systems studied. Figure 2, a bar graph of the coal conversions at 410°C for various reaction systems, provides additional information on the effects that heterogeneous solid catalysts had on the various systems.

Briefly, when coal was treated with water at high pressures (4000 to 7000 psi) and in the temperature range of 390 to 415°C, coal conversions were about 16 to 20% w/w, as compared to 11 to 12% w/w when coal was heated with just nitrogen present. Catalysts, such as iron oxide and cobalt molybdate on alumina, appeared to have little or no effect on the coal conversion in the water-coal system (not shown in Figures 1 and 2).

Phenanthrene, a frequently used extraction solvent for coal, caused an increase in coal conversion over the water-coal system, at corresponding temperatures and pressures, of three to four percentage points. Again, the catalysts had no effect.

When Decalin (decahydronaphthalene) was used with water and coal, coal conversions improved over the water-coal and phenanthrene-water-coal systems. Coal conversions obtained with the Decalin-water-coal system were in the 30 to 34% w/w range. Catalysts, such as cobalt molybdate

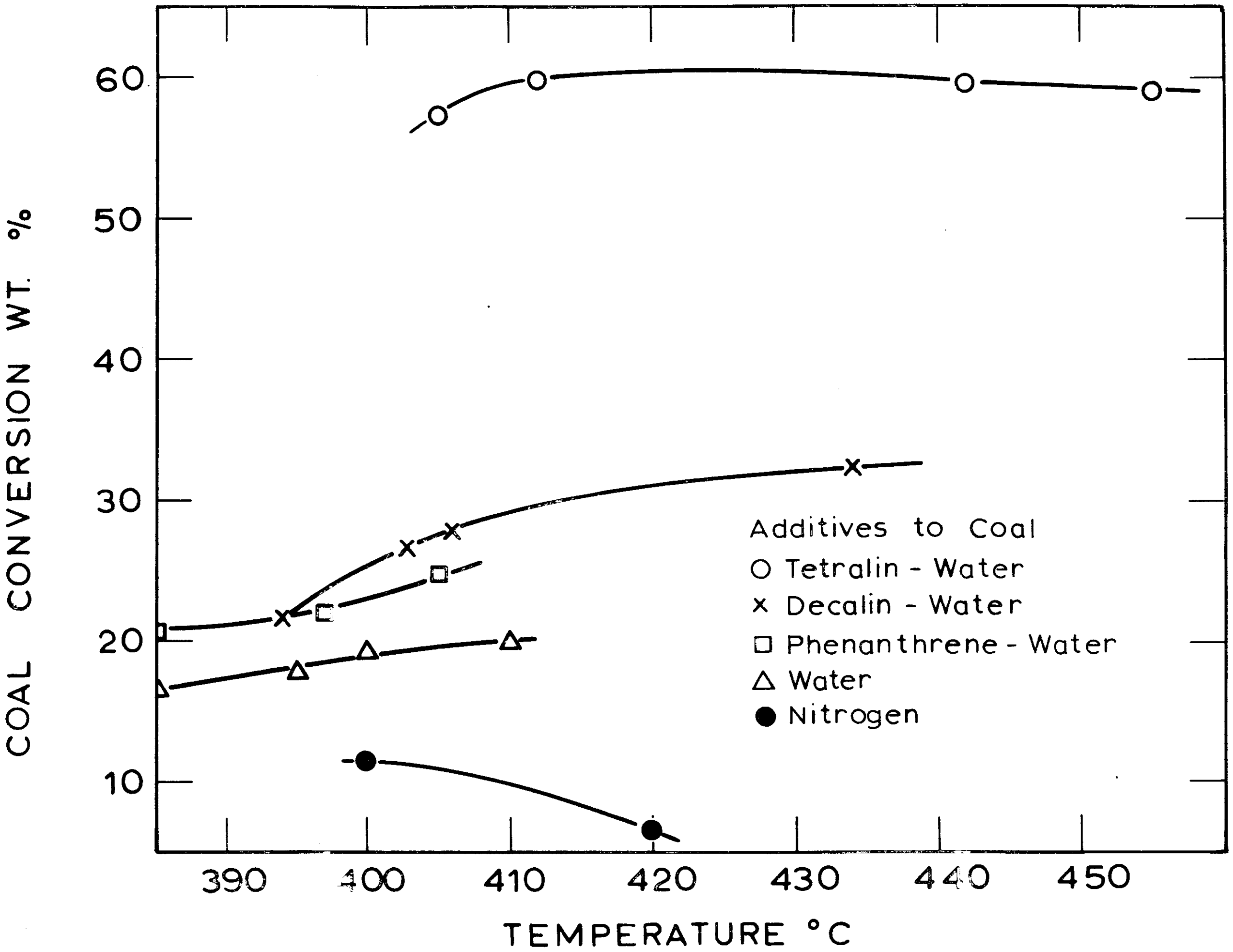


Figure 1 Effect of Water and Polycyclic Hydrocarbons on Coal Conversion

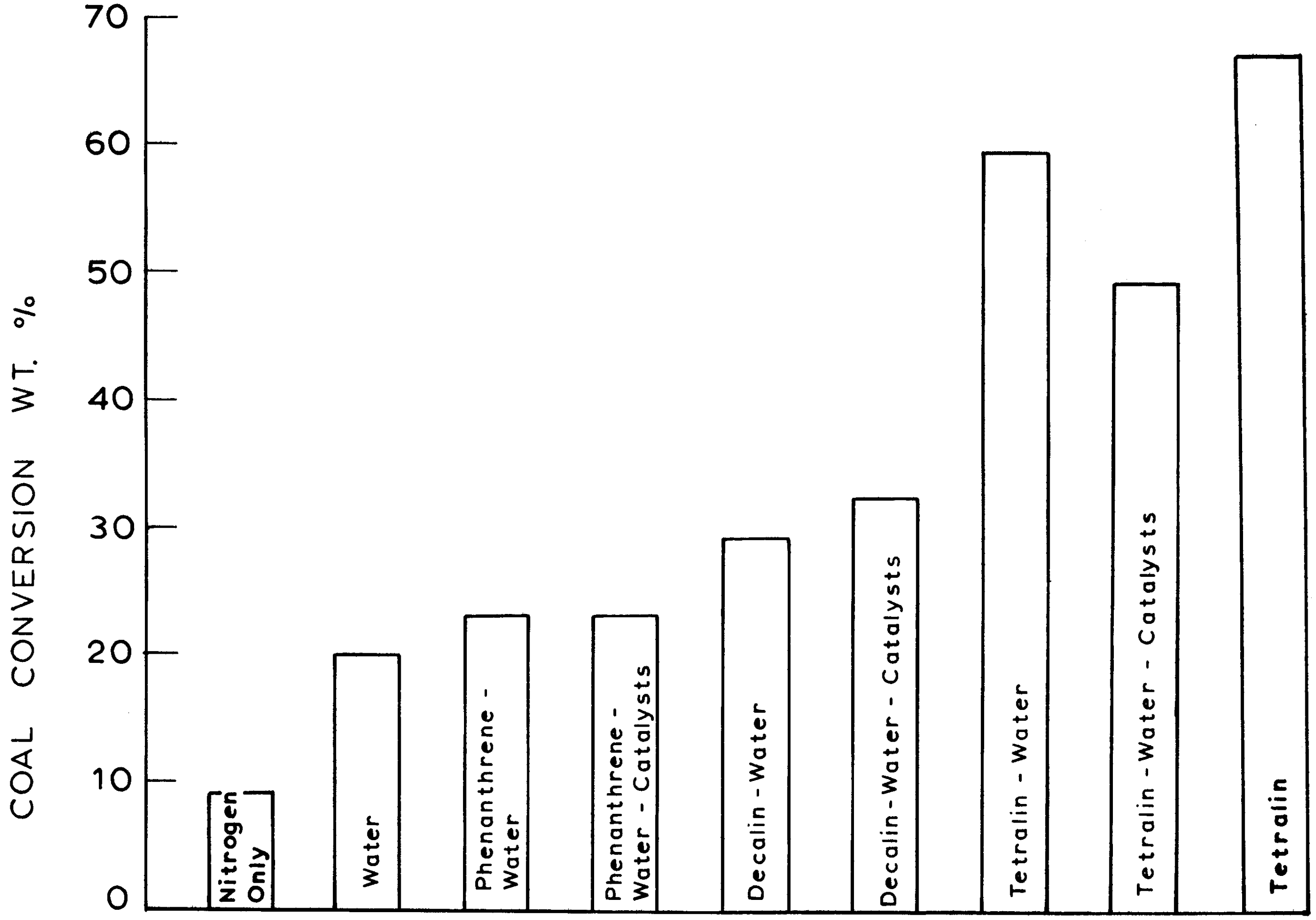


Figure 2 Effect of Water, Polycyclic Hydrocarbons and Heterogeneous Catalysts on Coal Conversion at 410°C

on alumina and cobalt-thoria on kieselguhr may have helped marginally.

Tetralin (1,2,3,4-tetrahydronaphthalene), a hydroaromatic compound known to solubilize coal by acting as a hydrogen donor agent, liquefied about 65 to 67% w/w of the coal at these conditions. Addition of water to the Tetralin-coal system lowered the coal conversion to 59 to 62% w/w; addition of water and catalysts, such as cobalt molybdate on alumina and chromia on alumina lowered coal conversions to 49 to 51% w/w.

5. Interpretation of Coal Liquefaction Results

There are undoubtedly several kinetic models which could probably satisfactorily explain the experimental observations in these complex reaction systems involving coal and the various added liquid phases and catalysts. The approach taken was to select the simplest possible logical reactions, write generalized rate equations and then combine them to give rate expressions and cumulative amounts as a function of time for benzene solubles and insolubles (coke); then show how these models do or do not agree with the data. Any kinetic model proposed must be consistent not only with the present experimental observations but also should be compatible with previously known facts or equally valid experimental observations.

a. Kinetic Model without Hydrogen Transfer

For the water-coal system the reaction sequence postulated involves thermal cracking of coal to reactive fragments (free radicals), followed by subsequent stabilization of these active fragments to either 1) benzene-soluble stable fragments or molecules formed via rearrangement-type reactions, or 2) benzene insoluble polymers or coke formed via secondary polymerization reactions.

Previous workers have shown by electron spin resonance spectroscopy (esr) that coal-derived liquids (from coal pyrolysis) contain large free radicals. These active fragments form by the rupture of several or more covalent bonds in the coal mass and thus have a number of unpaired electrons (Tschamler and De Ruiter, 1963).

Certain assumptions can be made about the kinetics of the reactions postulated to be occurring in the water-coal system. Thermal cracking of coal can be assumed to be first order. Stabilization of active fragments to benzene solubles via internal rearrangement reactions can also be assumed to be first order. Polymerization reactions are always higher than first order; for the present purpose, they were assumed to be second order. With these assumed kinetics, the rates of stabilization of the active fragments to either benzene solubles or insolubles can be derived. These rate equations are:

$$-\frac{dF}{d\theta}\Bigg)_{\substack{\text{benzene}\\ \text{solubles}}} = k_2\, V \left(\frac{a + \sqrt{a^2 + \frac{c}{V}}}{b} \right) \tag{1}$$

$$-\frac{dF}{d\theta}\Bigg)_{\substack{\text{benzene}\\ \text{insolubles}}} = k_3 \left(\frac{a + \sqrt{a^2 + \frac{c}{V}}}{b} \right)^2 \tag{2}$$

where

θ = time

C = amount of coal at any time

F = amount of active fragments at any time

k_1 = rate constant for thermal cracking of coal

k_2 = rate constant for formation of benzene solubles

k_3 = rate constant for formation of benzene insolubles

a, b and c are constants involving the rate constants and the coal amount

This simple model predicts that as dilution of the coal-derived active fragments increases, the rate of polymerization, equation (2), decreases and the rate of formation of benzene solubles, equation (1), increases. This model, which assumes the only effect of water to be simple dilution of the free radicals, can satisfactorily explain the enhancement in coal conversion obtained in the water-coal system _vis à vis_ the nitrogen-coal system, as shown in Figures 1 and 2. The possibility that water reacts with coal or coal-derived active fragments still exists, however.

Treatment of coal with phenanthrene or phenanthrene and water resulted in slightly higher coal conversions (about three to four percentage points) than those obtained in the water-coal system at corresponding temperatures and pressures. These results suggest that the same types of reactions are occurring in both of these reaction systems and that the postulated model for the water-coal system is equally valid for the phenanthrene-water-coal systems.

Phenanthrene, a high boiling (340°C) polycyclic aromatic, is not a hydrogen donor agent unless it becomes partially hydrogenated *in situ* by hydrogen from coal, coal-derived fragments or water. However, phenanthrene has been recovered quantitatively from coal extracts prepared by high temperature extraction of coal with phenanthrene. The observed extent of coal liquefaction (as measured by Soxhlet extraction with benzene) resulting from the phenanthrene treatment was about 20% (Orchin *et al.*, 1951). The latter result (20% w/w) is very similar to the present results which indicates that phenanthrene probably does not function as a hydrogen donor agent to any great extent. These observations imply that water, like phenanthrene, does not act as a hydrogen donor agent to coal to any appreciable degree and that phenanthrene, like water, functions as a diluting agent for the active fragments, thereby retarding the polymerization reactions, and allowing more time for the desirable rearrangement reactions to occur.

b. Kinetic Model with Hydrogen Transfer

Models were developed which are consistent with the experimental findings that both water and catalysts lowered the coal conversion when added to the Tetralin-coal system at corresponding temperatures and pressures. The model to explain the adverse effect of water in the Tetralin-coal system consists of: 1) thermal cracking of coal to reactive free radical fragments, 2) stabilization of these active fragments to stable molecules (benzene solubles) by hydrogen atoms donated by Tetralin, or 3) polymerization of these active fragments to coke. Stabilization of reactive fragments via rearrangement-type reactions were ignored in the Tetralin systems, since Tetralin is known to be an effective coal liquefaction agent via a hydrogen donor mechanism.

Again thermal cracking of coal was assumed to be first order, and stabilization via polymerization reactions to be second order. The reaction of Tetralin with the active fragments was also assumed to be second order.

With these assumptions about the kinetics of the reactions the generalized rate equations for the formation of benzene solubles and insolubles are:

$$-\left.\frac{dF}{d\theta}\right)_{\substack{\text{benzene}\\ \text{solubles}}} = k_2\left(-a+\sqrt{b+dV}\right)\frac{T}{V} \tag{3}$$

$$-\left.\frac{dF}{d\theta}\right)_{\substack{\text{benzene}\\ \text{insolubles}}} = k_3\left(-a+\sqrt{b+dV}\right)^2\frac{1}{V} \tag{4}$$

where,

θ = time

C = coal amount at any time θ

F = amount of active fragments from coal cracking at any time θ

T = amount of Tetralin at any time θ

V = volume of reacting species

k_1 = rate constant for coal thermal cracking

k_2 = rate constant for stabilization of active fragments to benzene solubles with Tetralin

k_3 = rate constant for stabilization of active fragments by polymerization to benzene insolubles (coke)

$$a = \frac{k_2 T}{2k_3}\,; \qquad b = \left(\frac{k_2 T}{2k_3}\right)^2\,; \qquad d = \frac{4k_1 k_3 C}{(2k_3)^2}$$

This model predicts that dilution of the hydrogen donor agent (Tetralin) with a nonhydrogen donor agent (water) decreases the rate of formation of the benzene solubles, equation (3), and increases the rate of polymerization to benzene insolubles, equation (4) in agreement with the experimental facts (Figure 2).

The adverse effects of catalysts on the apparent coal conversion in the Tetralin-water-coal system is explainable by postulating that irreversible adsorption of the coal-derived active fragments occurred on the catalytic surfaces. After adsorption, these reactive fragments polymerized to benzene insolubles.

c. Combined Model for Decalin-containing Systems

Decalin is capable of serving as a hydrogen donor agent to coal, however, its hydrogen donor activity appears to be only one-fourth that of Tetralin (Curran *et al.*, 1967). The experimental results of the Decalin-water-coal systems can be satisfactorily explained by a combination of the kinetic model without hydrogen transfer and the kinetic model with hydrogen transfer. Thus, the model for the Decalin containing systems would comprise three modes of stabilization of the active fragments produced by the thermal coking of coal. These stabilization modes are: 1) rearrangement-type reactions, 2) hydrogen transfer from Decalin, and 3) polymerization to coke.

6. Conclusions from the Coal Liquefaction Studies

a. Water does not react with coal or coal-derived liquids to any great extent in the temperature range of 390 to 460°C and pressures up to 8000 psig even in the presence of various heterogeneous catalysts and polynuclear hydrocarbons (hydrogen donor agents and non-hydrogen agents).

b. The higher observed coal conversions in the water-coal system (16 to 20% w/w) as compared to the nitrogen-coal system (11% w/w) at corresponding temperatures were probably due to the dilution of the active free radical fragments produced via the thermal cracking of coal by the water. This dilution retarded the higher than first-order polymerization to benzene insolubles and allowed more time for benzene solubles to form by various rearrangement reactions.

c. The enhancement in coal conversion with phenanthrene-containing systems *vis à vis* the nitrogen-coal system was probably also related to dilution of the active coal fragments since phenanthrene, an aromatic, possesses no hydrogen donor agent capabilities.

d. The initial mechanism of coal liquefaction in the 400°C temperature region is thermal cracking of coal to reactive fragments. Subsequently, these active fragments are converted to 1) benzene solubles by hydrogen transfer from active hydrogen donor agents such as Tetralin or by internal rearrangement-type reactions, and 2) benzene insolubles by secondary polymerization reactions.

e. The coal-derived liquids from the Tetralin-coal systems are more reactive than those produced in the Decalin, phenanthrene or water-alone systems. This is evidence for long-lived large radicals which are stable because of stereochemical reasons. Further, this implies that less recombination of radicals occur in the Tetralin system and that the hydrogen donor agent has to be active and present when bond rupture occurs.

f. The implications of the water and catalyst effects in the Tetralin-coal system confirm that solubilization via hydrogen donor agents is a homogeneous liquid-phase process.

7. Recommendations for Future Work

a. This study should be expanded to include lower rank coals and additional heterogeneous catalysts.

b. Homogeneous catalysts which could possibly activate the water molecule should be evaluated.

D. CATALYZED GASIFICATION OF COAL

1. Background

Normally, industrial coal gasifiers are operated at temperatures of 800 to 1000°C. In this temperature range, the principle gaseous products are carbon monoxide and hydrogen; the overall gasification process is represented by the equation:

$$C + H_2O = CO + H_2$$

The overall process of gasification is quite endothermic and since hydrocarbon formation via either the Bergius or Fischer-Tropsch processes require temperatures less than 450°C, the thermal efficiency of the combined gasification-synthesis sequence is low. Thus, it would be desirable to carry out the gasification step at lower temperatures which means that catalysts have to be employed in order to attain commercially feasible rates.

2. Program for the Present Investigation

Previous workers at M.I.T. and elsewhere have studied carbon gasification at 1000° to 1200°F using various alkali metal salts as catalysts (Hipkin, 1951; Tung, 1953). Both Hipkin and Tung used Disco char, a devolatilized coal, as the carbon source. As part of the present study, the residual cokes remaining from certain of the high pressure coal liquefaction runs, and considered to be similar to devolatilized coal, were gasified at 1000°F using potassium and cesium acetates, potassium carbonate and cesium nitrate as catalysts.

3. Experimental

a. Equipment

The gasification experiments were carried out using a semi-continuous flow reacter (1.084 inches inside diameter) operated at atmospheric pressure. Steam was continuously passed in the downflow mode through a fixed bed of the carbon source (described in the next section). The reactor was constructed of Type 304 stainless steel. A central thermowell, 0.25 inches outside diameter, extended from the top of the reactor column to just below the fixed coke bed. A sliding Chromel-Alumel thermocouple inside this thermowell measured the temperature at any point along its length. The reactor was heated by two electric furnaces individually controlled by Variacs.

Upstream of the reactor, auxiliary equipment included a deionized water reservoir, and the water vaporizor, a vertically mounted length of 3/4 inch schedule 40 pipe packed with stainless steel wool. During gasification, water was metered via Brooks flowmeter to the vaporizer using 25 psig nitrogen pressure in the reservoir.

Downstream of the reactor was located a water-cooled condenser, a condensate receiver, a Drierite column and finally a wet test meter. Provisions were made to sample the dried off-gases before the wet test meter by passing the gases through a Carle gas chromatographic sampling valve.

A Fisher-Hamilton Model 29 gas chromatograph measured the gaseous products, carbon dioxide, carbon monoxide and methane. Hydrogen was determined by difference.

b. Description of Cokes

Carbon sources for the present gasification experiments were composites of residual cokes from 1) water-coal and 2) Decalin-water-coal high pressure liquefaction runs. These two coke varieties are referred to in the discussion as water coke and Decalin-water coke, respectively. Since these cokes originated from Ireland Mine coal which had been solubilized by its treatment to the extent of at least 18% w/w (based on the original coal charged to the liquefaction reactor), they were considered to be similar to a devolatilized coal. The reason composites were prepared was to ensure that enough of each coke type was available for the planned gasification experiments. None of the residual cokes used in the compositing came from liquefaction runs in which a catalyst had been added. The hydrogen to carbon atomic ratios of water coke and Decalin-water-coke were 0.62 and 0.55, respectively, and their ash contents were 14.6 and 18.3 w/w, respectively.

c. Procedure

Eighteen grams of coke having a particle size of about forty mesh was admixed with alkali metal salt catalyst (about the same mesh size as the coal) and charged to the reactor. Typically, about 2.5 to 7.3 grams of catalyst were used; enough to give about 0.0021 grams atoms of the alkali cation per gram of coke. The bed of coke and catalyst, supported by quartz and steel wool plugs, was about 1 3/4 inches high and occupied about 8.6×10^{-4} cubic feet (24.3 milliliters) of the annulus between the reactor wall and the thermowell.

A devolatilization step was incorporated in the procedure to ensure that remaining volatile matter was removed from the cokes. The normal devolatilization procedure consisted of heating the reacter at a rate of about 10 to 11°F per minute to 1150°F while maintaining a small nitrogen flow through the system. Since it was necessary, for calculational purposes, to know the weight of carbon in the bed at the onset of gasification, i.e., after devolatilization, experiments were made in which only the devolatilization step was carried out. From the weight and ultimate analyses of these recovered devolatilized cokes it was determined how much of each coke variety had evolved during devolatilization. These numbers were 9.5% w/w and 9.1% w/w for the water coke and Decalin-water coke, respectively, meaning that of the original coke charged (18 grams) only about 16.3 grams remained after devolatilization of which only about 11.3 grams were actually carbon.

After reaching 1150°F, the heaters were turned off and the reactor allowed to cool to 1000°F (still maintaining the nitrogen flow). When the desired temperature of 1000°F was reached, nitrogen flow was discontinued and steam flow to the reacter was started; typical steam rates used were 0.8 to 1.1 grams per minute. The temperature was maintained by Variac adjustments at 1000 ± 10°F. Periodic readings were taken of the wet test meter, condensate volume, temperature and pressure. Samples of the dried off-gases were injected into the chromatograph at fifteen to twenty minute intervals.

After the gasification period, the reactor was allowed to cool and the carbon-catalyst bed removed and weighed to determine total weight loss over the devolatilization-gasification sequence.

4. Results of Coal Gasification Studies

The significant experimental findings of the gasification study are presented in the text as an instantaneous rate of carbon gasification, R_I, grams of carbon gasifying per minute per gram of carbon remaining in the bed at time t, versus the fraction of the original carbon gasified by time t, FCG.

a. Comparison of Coke Reactivities

Experiments were carried out to determine the relative reactivities of the water coke and the Decalin-water coke using potassium acetate as the catalyst. Initially, the water coke was approximately twice as reactive as the Decalin-water coke and whereas the maximum gasification rate for the Decalin-water coke occurred around a FCG value of 0.04, the maximum rate for the water coke occurred around a FCG value of 0.075. The observed rate dropoff was more pronounced for the Decalin-water coke than for the water coke. The maximum rates observed in these cases were 4.6×10^{-4} g.C/(min.)(g.C) for the water coke and 2.3×10^{-4} g.C/(min.)(g.C) for the Decalin-water coke.

b. Gasification of the Water Coke

Figure 3 is the comparison between potassium carbonate, potassium acetate, cesium nitrate and cesium acetate — all initially distributed uniformly in the coke bed, at 1000°F, atmospheric pressure and a catalyst concentration of 0.0021 gram-atoms alkali cation per gram coke. Figure 4 presents the same comparisons for the cases where the catalyst was initially distributed only in the top third of the coke bed.

Inspection of Figures 3 and 4 reveals the general characteristic that the gasification rate first increases as the FCG increases, then maximizes and

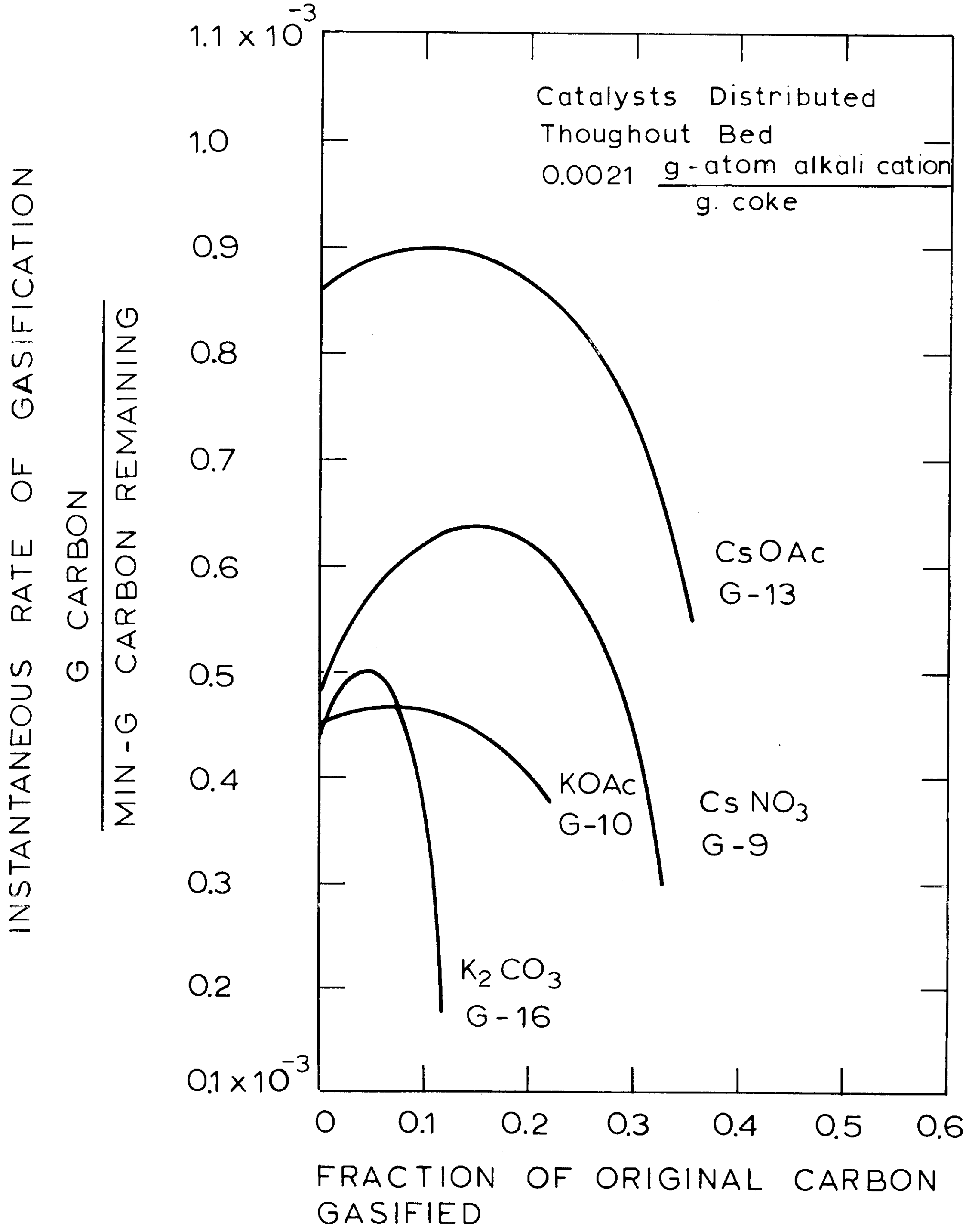


Figure 3 Comparison of Alkali Salts for Water Coke Gasification at 1000 °F

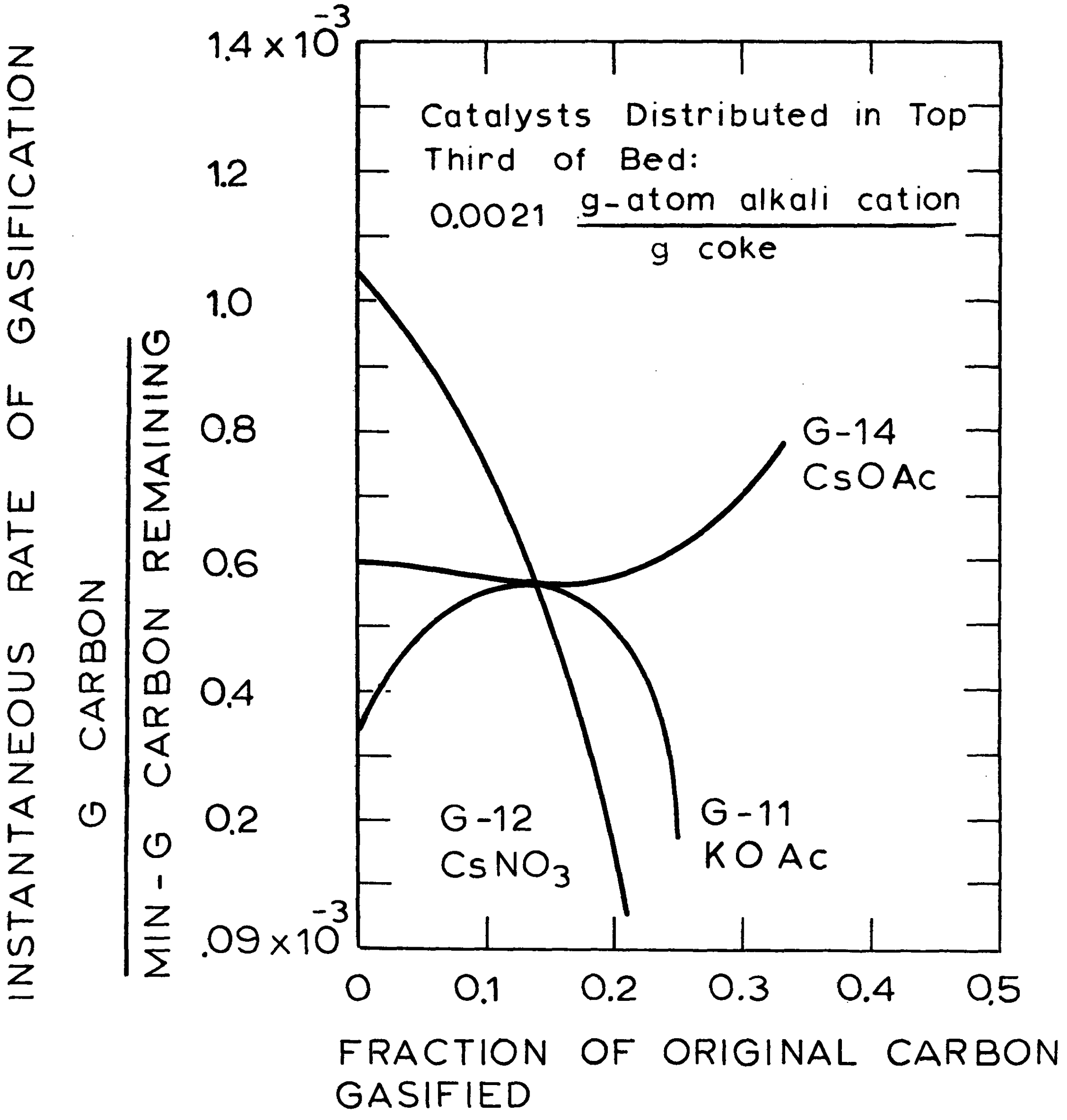


Figure 4 Comparison of Alkali Salts for Water Coke Gasification at 1000°F

commences a steady decrease. The exact shape of the R_I versus FCG curves varies depending on the catalyst and its initial distribution in the bed. Run G-14 (Figure 4) exhibited a different kind of behavior probably related to the initial distribution of cesium acetate.

Figure 3 illustrates clearly that cesium acetate is superior to potassium acetate as a gasification catalyst. The maximum gasification rate observed with cesium acetate, 8.95×10^{-4} g.C/(min.)(g.C) occurred at a FCG value of 0.12, while the corresponding values for the potassium acetate were 4.7×10^{-4} g.C/(min.)(g.C) at 0.07 to 0.08, a difference of a factor of 1.9. It is also apparent from Figure 3 that at comparable levels in this experimental system, potassium acetate is superior to potassium carbonate because with the former catalyst, the gasification rate dropoff with bed burnoff is much less than with the latter catalyst. Both potassium acetate and potassium carbonate possessed virtually the same initial and maximum rates.

5. Interpretation of the Gasification Results

Equilibrium and kinetic considerations govern the composition and relative magnitudes of the exit gases from the gasification reactor. The exit gases in the present case, on a dry basis, consisted almost entirely of hydrogen and carbon dioxide, with <1% methane and carbon monoxide.

a. Thermodynamic Considerations

Determination of the approach to equilibrium values (R values), for the possible reactions

Primary Gasification

$G_1 \quad C + H_2O = CO + H_2$

$G_2 \quad C + 2H_2O = CO_2 + 2H_2$

Carbon Oxides Interchange

$S_1 \quad C + CO_2 = 2CO$

$S_2 \quad CO + H_2O = CO_2 + H_2$

establishes that all reactions are thermodynamically possible and proceed from left to right as written.

The common features of the R values for the primary gasification reactions, G_1 and G_2, and the gasification reaction, S_1, are:

1. These gasification reactions show a very marked deviation from equilibrium, their R values are three to six orders of magnitude below unity.

2. All the reactions show a deviation on the carbon-steam side of equilibrium.
3. Catalysts and their initial distribution affect the deviation from equilibrium.
4. This deviation from equilibrium increased as the fraction of the original carbon gasified increased when the catalyst was uniformly distributed initially.
5. When cesium acetate, in particular, and potassium acetate were initially distributed in the top third of the bed certain R values increased with time.

Consideration of the R values for reaction S_2, the water-gas shift reaction showed the following:

1. Reaction S_2 is near to equilibrium.
2. Equilibrium is being approached from the carbon-monoxide-water side.
3. The nearness to equilibrium suggests that reaction S_2 is rapid.
4. In all runs except the run with cesium acetate in the top third of the bed, the deviation from equilibrium increased.
5. Runs having the catalyst initially in the top third of the bed suffered a greater R_{S_2} drop with time, except for the cesium acetate catalyzed run.

6. Cesium acetate is superior to both potassium acetate and potassium carbonate as a water-gas shift catalyst.
7. Potassium acetate and potassium carbonate are nearly identical as catalysts for the water gas shift reaction.
8. Doubling the potassium carbonate level increased R_{S_2} values about 50%.
9. Cesium nitrate was generally intermediate in activity towards reaction S_2, i.e., it lies between cesium acetate and potassium acetate in catalytic activity.

These observations suggest that a large part of the drop in the R values for the cases with initial uniform catalyst distribution is related to catalyst loss.

Some typical R values are listed below along with the K_p at 1000°F (Run G-13 at 150 minutes).

Reaction	R	K
G_1	1×10^{-4}	0.0653
G_2	0.8×10^{-4}	0.2768
S_1	1×10^{-4}	0.0188
S_2	0.7	4.26

The large value of R for reaction S_2 relative to those for reactions G_1, G_2 and S_1 suggests it is rapid compared to the others, but this is not conclusive. If reaction G_2 were more rapid than reactions G_1 and S_1, then the same result could be obtained. As long as the rate for reaction G_2 was less than 100 times greater than the rate for reaction G_1, then reaction S_2 would not have a value of R greater than 1.0 at the low water conversions involved.

Evaluation of the approach to equilibrium of the following reactions

$$\begin{array}{lcccccl}
M_1 & C & + & 2H_2 & = & CH_4 \\
M_2 & 2CO & + & 2H_2 & = & CH_4 + CO_2 \\
M_3 & CO & + & 3H_2 & = & CH_4 + H_2O \\
M_4 & CO_2 & + & 4H_2 & = & CH_4 + 2H_2O \\
GM & 2C & + & 2H_2O & = & CH_4 + CO_2
\end{array}$$

showed that reaction M_1 was near equilibrium, R_{M_1} values being generally less than 1.0. Reactions M_2, M_3 and M_4 show very large positive deviations from equilibrium which means that if these reactions are operative, they consume methane. Reaction GM showed a large negative deviation from equilibrium (10^{-3} to 10^{-6}) which generally decreased further with time, except when potassium and cesium acetates were initially in the top of the bed.

b. Catalysis

Examination of Figures 3 and 4 shows that when cesium acetate was admixed only with the top third of the bed (Run G-14), the gasification rate R_I, increased at higher FCG values rather than declining as in the case where the cesium acetate was initially uniformly admixed (Run G-13). This observation suggests that cesium acetate migrates through the coke bed and further suggests that a large part of the observed rate drop in Run G-13 is probably due to catalyst loss.

Figure 3 shows that the runs with potassium acetate and potassium carbonate, at comparable levels, exhibited nearly identical initial and maximum rates of gasification, but the rate drop with potassium carbonate was much greater than with potassium acetate. In another experiment, it was observed that when the potassium carbonate concentration was doubled the rate drop with time was more like that of potassium acetate even though the latter was only present in half the concentration of the former on a gram atom alkali metal basis.

Consideration of the melting points of the three catalysts:

	M.P., °C
Potassium Carbonate	891
Potassium Acetate	292
Cesium Acetate	194

leads to the conclusion that under the experimental conditions of devolatilization and gasification that two of the catalysts are present as liquids while the third, potassium carbonate exists as a solid. The catalyst with the highest activity, cesium acetate, has the lowest melting point and presumably the highest volatility. The catalyst with the highest melting point, potassium carbonate, while initially as effective as potassium acetate which has a much lower melting point, also exhibited the sharpest drop in gasification rate with time.

It is possible to visualize another mechanism which would explain the shape of the observed R_I versus FCG curves. As the carbon reacts, it becomes more porous and thus its surface area per unit weight increases with time or FCG. At the same time, the coke reactivity per unit area is decreasing and thus a maximum in the R_I versus FCG curve occurs because of this balance between the change in unit area per time and the change in reactivity per unit area.

6. Conclusions from the Coal Gasification Studies

a. Gasification Catalysis and Coke Reactivity

(1) Cesium acetate is superior to potassium acetate as a gasification catalyst at 1000°F.

(2) Potassium acetate is superior to potassium carbonate as a gasification catalyst at 1000°F because at comparable levels the rate drop with time is less. Initial and maximum gasification rates with these catalysts are the same.

(3) Alkali salt catalysts, such as cesium and potassium acetates, having lower melting points and hence more volatility and/or mobility (liquid or gas phase) are superior to a catalyst such as potassium carbonate which has a very high melting point and hence little mobility.

(4) Observed gasification rate drop with time was probably directly related to catalyst loss in the case of the volatile or mobile catalysts, potassium and cesium acetates, and probably related to very slow migration of the catalyst in the case of the non-volatile catalyst, potassium carbonate.

(5) Maximum observed gasification rates at 1000°F with cesium acetate are about 20% of the minimum feasible industrial gasification rate which is about 50×10^{-4} lb.C/(min.)(lb.C)

inventory. Potassium acetate catalyzed gasification rates at 1000°F are about 10% of the feasible industrial gasification rate.

(6) The coke from water-coal high pressure runs is more reactive than the coke from the Decalin-water-coal runs.

b. <u>Mechanisms</u>

(1) <u>Primary Gasification and Carbon Oxides Interchange</u>

(a) With two components, carbon monoxide and carbon dioxide, and four equations, G_1, G_2, S_1 and S_2, the same result can be obtained by a number of different combinations of sequential and parallel reactions.

(b) All the primary gasification reactions, G_1, G_2 and GM have R values far less than one so apparently all these reactions, if operative, are going to the right.

1. Carbon dioxide must be produced from reactions G_2 and/or S_2.
2. Carbon monoxide must be produced from reactions G_1 and/or S_1.
3. R_{S2} being close to one suggests that the water-gas shift reaction is rapid relative to the other reactions, but this is not conclusive.

(2) Methanation

It has not been possible to decide on the exact mode of methane formation. Several possibilities exist:

(a) Formation via the hydrogenation of carbon, reaction M_1. This reaction is close to equilibrium, R values being near 1.0; this suggests that this reaction may be rapid.

(b) Formation via the primary gasification reaction GM, shown to be thermodynamically possible but far from equilibrium.

(c) Evolution as volatile matter via the mechanism of thermal coking.

(d) Formation via hydrogenation of carbon-hydrogen linkages in the coal structure.

Methane has been shown not to be produced by the hydrogenation of carbon oxides, reactions M_2, M_3 and M_4. These reactions, if operative, proceed from right to left to consume methane.

(3) Overall

The overall rate of carbon gasification is the sum of the rates of: the primary gasification reactions G_1, G_2 and GM; the carbon oxides interchange reaction S_1; and the methanation reaction M_1. All these reactions could be operative. In addition, methane can be produced from the coke via coking or hydrogenation. Methane may be consumed by the reverse of reactions M_2, M_3 and M_4.

7. Recommendations for Future Work

Potassium acetate, because of its mobility, is clearly superior to potassium carbonate as a gasification catalyst. The use of cesium acetate may not be practical because of the scarcity of cesium. However, if catalyst losses were very minimal then cesium acetate should be at least considered.

a. Potassium acetate (and cesium acetate) should be evaluated at 1000°F with a more reactive carbon form such as a devolatilized coal like Disco coke.

b. Potassium acetate should be evaluated at 1100 and 1200°F with either the water coke or with a more reactive carbon form. A commercially acceptable rate would probably then be obtained.

c. The higher maximum rates obtained for the acetates could perhaps be maintained by engineering ingenuity — i.e., reversal of steam flow or in a continuous unit feeding coke countercurrent to the steam flow. The simpler unit to initially investigate would be the former. This unit would be a fixed bed reactor with the ability to reverse steam flows periodically. This feature would probably reduce catalyst loss — postulated to be the reason for the rate drop with time.

d. A better picture of the mechanism could be obtained if tests were made with each of the product gases, H_2, CO, CO_2, added individually with the water and the results compared with runs with water alone.

II. INTRODUCTION

A. "THE ENERGY CRISIS"

United States energy consumption in 1970 and demands forecasted to the year 2000 are shown below expressed in quadrillion (10^{15}) Btu's (Mills, 1972).

	1970	1975	1985	2000
Petroleum	30	36	47	66
Natural Gas	23	29	39	51
Coal	14	16	22	26
Hydropower	2.6	2.8	3.5	5
Nuclear	0.2	4.8	21	43
	69.8	89	133	191

The known recoverable energy reserves in the United States are (Mills, 1969):

Source	Quadrillion Btu's
Petroleum	300
Gas	300
Uranium	300
Coal	4600

Presently 77% of all energy consumed in the United States comes from the combustion of oil and gas. By the year 2000, although the demands for oil and gas are projected to be more than double the 1970 demands, oil and gas are estimated to be supplying only 61% of the energy, reflecting the forecasted tripling in the United States energy demands during this thirty year period.

It is clear from the two preceding tables that United States petroleum and natural gas reserves are insufficient to meet energy demands very far into the future and that coal constitutes the largest reserve of fossil fuel in the United States. Another incentive for the development of substitutes for oil and gas is the desire to be less dependent on foreign supplies both for political and balance-of-payments reasons.

Nuclear power, presently supplying a small fraction of the total energy demand, is on the increase. Non-conventional sources of energy, such as geothermal and solar energy, are receiving considerable attention. However, development of these non-conventional sources is far in the future.

In the transportation sector of the energy demand, liquid fuels will continue to be a necessity unless there are technologic breakthroughs in the development of electric-powered vehicles. Thus, for the near term, it is necessary to consider the manufacture of synthetic oil and gas from other fossil fuel sources. These other sources are coal, the bituminous tar sands and oil shale.

B. UTILIZATION OF COAL

The United States has tremendous coal reserves, substantial oil shale acreage, but only a limited amount of bituminous tar sands. Alberta, Canada is the site of substantial reserves of tar sands.

Coal conversion to liquid fuels is not new. A synthetic fuels industry based on coal, established for geopolitical reasons, existed for many years in Germany prior to and during World War II. As a result, there are several technically sound and proven coal conversion processes. The principal processes developed in Germany for converting her plentiful reserves of brown and bituminous coal to synthetic fuels are:

1. Bergius Process - synthetic oils via high pressure catalytic hydrogenation of coal.
2. Fischer-Tropsch Process - synthetic oils via catalytic hydrogenation of carbon monoxide.
3. Coal Pyrolysis - thermal decomposition of coal in the absence of oxygen yielding coal tars, gases and coke.
4. Pott-Broche Process - coal liquefaction via hydrogenation with process-derived liquids possessing hydrogen donor capabilities.

The conversion of coal to liquid and gaseous fuels also has an extensive technical history in the United States. Both the Bergius and the Fischer-Tropsch processes have been studied by the U.S. Bureau of Mines in large-scale pilot plants. However, until the present, there have never been economic incentives to develop a synthetic fuels industry in the United States.

Coal gasification was carried out extensively for many years in the United States for the manufacture of: (1) producer gas, a cheap, low-Btu fuel used for industrial purposes; and (2) water gas (blue gas), a relatively low-Btu gas used for heating coke ovens. For domestic consumption, oil was atomized into the water gas to raise its heating value. The resulting mixture was called carbureted water gas. As natural gas became available because of pipeline construction the gas producers and generators were for the most part phased out. In Europe, improved gasification processes such as the Winkler and Lurgi processes are still widely used.

In addition to the enormous reserves and the proven technology, several other factors favor the conversion of coal to synthetic fuels. These factors include:

1. Wide geographic distribution of coal in the United States.
2. Much of the coal reserves in the United States are in private hands, unlike the oil shale lands and the tar sand reserves.

3. Environmental
    a. Nuclear power plants are being delayed by public opposition.
    b. Desulfurization is more easily accomplished on liquids (as opposed to solid coal).
4. Developed mining technology.
5. Much of the coal reserves are recoverable by today's mining technology.

Strip mining of coal causes severe land damage. Efforts to restore the land will inevitably result in higher coal prices. This environmental factor may retard the development of coal conversion processes. On the other hand, exploitation of oil shale and tar sands reserves will encounter similar types of environmental problems. Oil prices will rise as the cost of finding and developing petroleum reserves increases.

The Office of Coal Research (OCR), United States Department of the Interior, was established in 1960 to stimulate coal utilization by contract research. It is of interest that the OCR has funded three major processes for converting coal to synthetic crude oils suitable for refinery feedstocks. These are:

1. Project H-Coal
2. Project COED (Char-Oil-Energy-Development)
3. Project Gasoline or Consol Process

Project H-Coal is a high pressure catalytic hydrogenation process carried out in an ebullating bed reactor; Project COED is coal pyrolysis or distillation to produce coal tars, gases and char in staged fluidized beds; Project Gasoline (recently renamed the Consol Process) involves coal liquefaction by process-derived hydrogen donor agents. The Fischer-Tropsch process has not received serious consideration in recent years in the United States and appears to be a relatively high cost approach.

Several coal gasification processes for synthetic pipeline gas are being developed by industrial groups under contract with the OCR. A comprehensive summary has recently appeared (Hottel and Howard, 1971a).

C. PROBLEMS IN COAL CONVERSION

Coal is a carbonaceous substance consisting chiefly of carbon and hydrogen with smaller amounts of oxygen, nitrogen, sulfur and inorganic material called ash. Table III gives the chemical composition of some coals and petroleum.

Coal has several disadvantages relative to petroleum. These may be classified as chemical or physical problems.

Chemical Problems

1. Coal is deficient in hydrogen; crude petroleum hydrogen content is 11 to 14 wt.%, while that of coal is typically 5 wt.%.
2. Presence of heteroatoms such as oxygen, sulfur and nitrogen. Crude petroleum contains no oxygen and only 0.2 wt.% nitrogen, as contrasted to 2 to 20 wt.% oxygen and 1 to 2 wt.% nitrogen in coals. Both coal and crude petroleum contain about 1 wt.% sulfur, that in coal being partly iron pyrites and partly organic.

Physical Problems

1. Solids are inherently more difficult to handle than liquids.
2. High ash content, 3 to 15 wt.%; crude petroleum has almost negligible ash.

TABLE III

CHEMICAL COMPOSITION OF SOME COALS AND PETROLEUM ‡

		Bituminous Coals						
	Anthracite	Medium Volatile	High Volatile A	High Volatile B	Lignite	Crude Petroleum	Gasoline	Toluene
C	93.7	88.4	84.5	80.3	72.7	83 - 87	86	91.3
H	2.4	5.0	5.6	5.5	4.2	11 - 14	14	8.7
O	2.4	4.1	7.0	11.1	21.3			
N	0.9	1.7	1.6	1.9	1.2	0.2		
S	0.6	0.8	1.3	1.2	0.6	1.0		
H/C atomic ratio	0.31	0.67	0.79	0.82	0.69	1.76	1.94	1.14

Coal analysis, weight %, on moisture and ash free basis (MAF).

Ash content of coal 3 to 15%.

‡ (Mills, 1969)

The fundamental problem, both chemical and economic, is the hydrogen deficiency of coal. Hydrogen manufacture is expensive; realistically the only viable sources of hydrogen are the coal itself and water. Coal hydrogenation requires high pressure; the nature of the coal introduces additional complexity in the processing. Thus, facilities are required both for coal gasification to produce hydrogen and for coal conversion to oils and gases. Estimates for coal refineries (Consol process) range up to $633 million for a 250,000 barrel per day production rate (Parsons (Ralph M.) Company, 1969).

Toluene is included in Table III to show that the hydrogen content of aromatics lies between those of coal and petroleum. It is more advantageous, from the standpoint of hydrogen costs, to convert coal to aromatic fractions rather than saturated compounds. Those processes which partially conserve the existent aromatic structures of the original coal during the liquefaction step are thus inherently superior to those that do not.

It is generally agreed that five processing steps are necessary to convert coal to gasoline (Mills, 1969). These are:

1. Liquefaction.
2. Ash removal.
3. Removal of the heteroatoms, S, N and O, and asphaltene (polynuclear aromatic structures) transformation.

4. Cracking to reduce molecular size.
5. Reforming to raise octane.

Liquefaction is the problem step. Techniques developed in the petroleum refining industry have already been found fairly applicable to steps 3, 4 and 5 above. Certainly some of these steps will overlap to a certain extent; these overlaps are particularly dependent on the processes used. For pollution control, prevention of corrosion, and because cracking catalysts are poisoned by sulfur and nitrogen containing compounds, it is imperative that the heteroatoms, sulfur and nitrogen, be removed from the liquid coal. Because coal contains considerably more nitrogen than crude petroleum, and because the nitrogen atoms are predominately located in the ring structures of the coal and not in side chains, denitrogenation is also expected to be a difficult step to accomplish.

D. THERMAL EFFICIENCY OF THE TWO-STAGE PROCESSES

Coal-to-oil processes are generally characterized by an endothermic gasification step at high temperature followed by an exothermic step at low temperature. This is shown schematically in Fig. 5 for the cases of the Bergius and Fischer-Tropsch processes.

The Bergius process (see Section II-F) involves the catalytic hydrogenation of coal, suspended in a process-derived liquid (known as the vehicle), at 400 to 450°C and 3000 to 4000 psi. The hydrogen required for the Bergius process is usually produced by coal or char gasification at 800 to 1000°C. The gasification step is endothermic, while the hydrogenation or synthesis step is exothermic. Thus, the overall thermal efficiency of the Bergius process is poor (see Section II-L), since the second law of thermodynamics prohibits the direct utilization at a higher temperature of heat produced at a lower temperature.

While more elegant, the Fischer-Tropsch process is also poor from the standpoint of thermal efficiency for the same reason as the Bergius process. In the Fischer-Tropsch process, so-called synthesis gas, a mixture of hydrogen and carbon monoxide, is produced

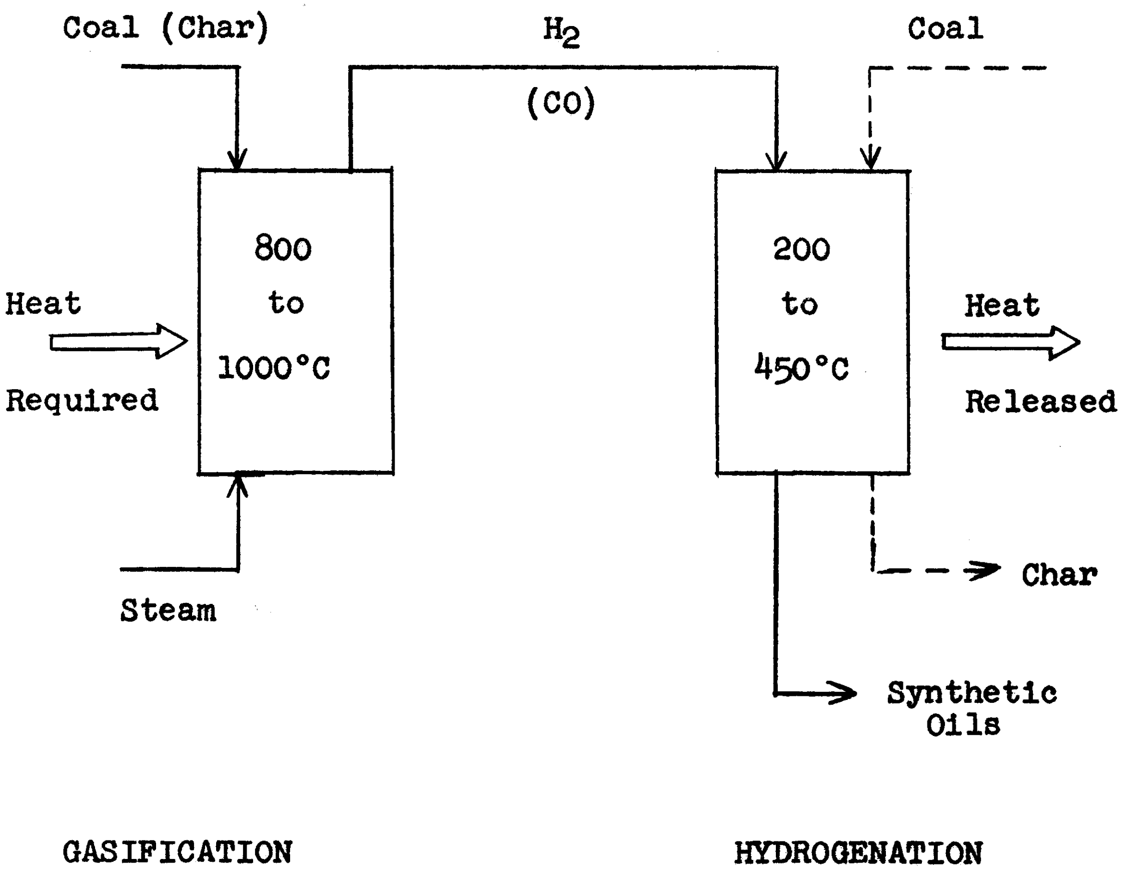


Figure 5 SCHEMATIC OF THE TWO-STAGE PROCESSES

via coal gasification, purified, and then passed over a contact catalyst at 200 to 250°C to form hydrocarbons and oxygenated hydrocarbons. Again the gasification step is endothermic and the synthesis step, the hydrogenation of carbon monoxide, is exothermic.

It is apparent that maximum thermal efficiency would be achieved in a gasification-synthesis coal conversion process if the gasification and synthesis steps were conducted at approximately the same temperature. If these steps occurred simultaneously then a single reactor perhaps would suffice; if not, then the conventional two-stage reaction system (Figure 5) could be used.

E. CHEMICAL STRUCTURE OF COAL

Considerable insight into the structure of coal has resulted from experimental studies carried out over the last seventy years, in particular since the late 1940's. This discussion will summarize the prevailing views on the chemical structure of high volatile bituminous (HVB) coal, the rank of coal most commonly used in coal conversion processes. The combination of modern instrumental analytical techniques and selective chemical reactions, chiefly oxidations, together with polarography of coal extracts and ultimate analyses have given quantitative information about the C-H structure of coal. This information has been summarized in Table IV.

A molecular model for HVB coal proposed by Hill and Lyon suggests that coal consists of large heterocyclic nuclei monomers with alkyl side chains held together by three dimensional C-C groups, and includes functional oxygen groups, and ether bonds. Sulfur and oxygen atoms are mainly present in linking units and may be interchangeable with one another, whereas nitrogen atoms occur primarily in the ring structures.

Long-chain, simple aliphatic and alicyclic hydrocarbon groups predominate in many HVB coals. Polycondensed aromatics are not common in coals containing below 88% carbon but from 88 to 93% carbon, a great increase occurs. The connecting structures are considered to be

TABLE IV

ESTIMATED AVERAGE PARAMETERS FOR COAL‡

Parameter	Vitrinite	
% C, pure coal (Parr basis)	82.5	90
% Volatile matter	39	24.5
H/C (Atomic)	0.76	0.65
$H_{aromatic}/H_{aliphatic}$	0.23	0.54
H_{CH_3}/H_{al} (IR, oxidation)	0.21(0.1-0.3)	0.23(0.1-0.3)
CH_2 bridges: $C_{ar}-CH_2-C_{ar}$	Absent	Absent
% Substitution on aromatic periphery	50+	30
R_a (aromatic rings per cluster)	>3	~4
C_{ar} (aromatic C atoms per cluster)	>13	16
Average stacking number of parallel aromatic clusters	1.3	1.8
O as hydroxyl, % of coal	7.0	2.0
O as carbonyl, % of coal	2.3	0.9
Carbon atoms per free radical	~8000	~3000
f_a (fraction of carbon as aromatic) derived from above	0.69 - 0.70	0.79 - 0.80

‡ (Ode, 1963).

principally aliphatic (methylene) bridges. Tetrahedral bonds are the cross-linking units. Little evidence for methylene bridge carbons exist (Hill and Lyon, 1962).

The high degree of substitution of the aromatic structures in coal can be seen from Table IV by comparing the fraction of the carbon in coal that is aromatic (0.70) and the ratio of hydrogen atoms attached to aromatic carbon atoms to the hydrogen atoms attached to aliphatic carbon atoms (0.23).

A slightly earlier molecular structure for coal (82% carbon) proposed by Given, conforms to the parameters in Table IV except for the assumption that the aromatic nuclei are arranged in an anthracene-type structure rather than the phenanthrene-type, the latter which better fits the experimental observations (Given, 1960; Dryden, 1963a).

A Bureau of Mines researcher, Henry C. Howard, provides considerable insight into the nature of the chemical bonding in coal by inferences from coal pyrolysis studies, stoichiometry and analogy. His contributions are summarized briefly below (Howard, 1963a).

Organic compounds are nonvolatile before thermal decomposition due to two types of bonding. There may be covalent bonding throughout large masses of the substance. Alternatively, or in addition, there may be strong secondary bonding between smaller covalently bonded masses.

The high yield of nonvolatile residue obtained when coal is pyrolyzed indicates either extensive covalent bonding, strong secondary bonding, or both. There are examples in chemistry of both types of organic structures. Glucose is an extreme example of nonvolatility due to hydrogen-bonding, a form of secondary bonding. When glucose is methylated the hydrogen-bonding is destroyed and the resulting compound exhibits the normal volatility expected in this molecular weight range.

Secondary valence forces are associated with oxygen and nitrogen containing functional groups. Since carbohydrates, which exhibit strong hydrogen-bonding, have oxygen to carbon atomic ratios near one and 85% carbon bituminous coal has oxygen to carbon atomic ratios of 0.05 to 0.07, the inference is drawn from stoichiometry that the nonvolatility of coal is not due to hydrogen-bonding of the small units of coal. Howard also noted that the ease of dispersion of coal in hydrogen-bonded solvents is evidence that large masses of coal are held together by hydrogen-bonding type forces.

Howard therefore concluded that the nonvolatility of coal arises from extensive covalent bonding throughout the coal masses and that only the large masses are hydrogen bonded.

All coal contains "mineral matter" or ash. These are heterogeneous mixtures of inorganic compounds. The ash, ranging from 3% to 15% by weight of the coal, arises from three sources: (1) minerals associated with the initial plant growth; (2) minerals which entered the coal seam during or after coalification; and (3) rocks from the mining process.

Table V lists the minerals in coal ash. The first four groups comprise about 95% of the mineral matter (Ode, 1963).

TABLE V

MINERALS ASSOCIATED WITH BITUMINOUS COAL[‡]

Group	Typical Species and Approximate Formula
Shale	Muscovite (common potash mica), $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$
	Illite (soda mica), $Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$
	Montmorillonite (clay), $(Mg,Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$
Kaolin	Kaolinite (clay), $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
	Metahalloysite, $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$
Sulfide	Pyrite and Marcasite, FeS_2
Carbonate	Calcite (limestone), $CaCO_3$
	Dolomite, $CaCO_3 \cdot MgCO_3$
	Ankerite, $2CaCO_3 \cdot MgCO_3 \cdot FeCO_3$
Chloride	Halite (common salt), NaCl
	Sylvite, KCl

Accessory Minerals - Occurring in minor quantities associated with the Shale group

Quartz, SiO_2
Felspar, $(K,Na)\,O \cdot Al_2O_3 \cdot 6SiO_2$
Garnet, $3CaCO_3 \cdot Al_2O_3 \cdot 3SiO_2$
Hornblende, $CaO \cdot 3FeO \cdot 4SiO_2$
Gypsum, $CaSO_4 \cdot 2H_2O$

Apatite, $9CaO \cdot 3P_2O_5 \cdot CaF_2$
Zircon, $ZrSiO_4$
Diaspore, $Al_2O_3 \cdot H_2O$
Magnetite, Fe_3O_4
Hematite, Fe_2O_3

[‡] (Ode, 1963).

F. COAL LIQUEFACTION PROCESSES, COMMERCIAL

Discussed in this section are (1) Coal Pyrolysis, (2) Coal Hydrogenation, and (3) Coal Liquefaction via Liquid-Phase Hydrogen Donor Agents. Most of the older literature originated from work in Germany and at the U.S. Bureau of Mines. Recently, the various OCR sponsored projects have produced a large number of articles.

1. Coal Pyrolysis

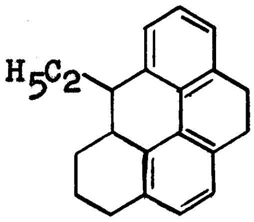
Coal exhibits a more or less definite decomposition temperature as evidenced by melting and rapid evolution of volatile matter. The terms carbonization, destructive distillation, and pyrolysis all refer to the thermal decomposition of coal at or above this temperature. This temperature is 350 to 450°C depending on the rank of the coal (Burgess and Wheeler, 1926; Berkowitz, 1949).

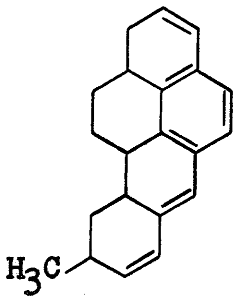
Project COED, Char-Oil-Energy-Development, is the modern version of the old German coal pyrolysis processes. Project COED utilizes four staged fluidized beds operating at 600 to 650°F, 800 to 850°F, 1000°F and 1600°F, respectively, to pyrolyze pulverized coal to oil, gas and char (Jones et al., 1964; Jones et al., 1966). The following table gives the reported pilot plant performance; yield is weight percent based on dry coal feed (Hottel and Howard, 1971b):

	Pilot Plant Yield (wt.%)
Char	56
Oil	18.7
Gas	16.9 (9000 SCF/ton)

The reported char yield is about the same as obtained via the ASTM proximate analysis procedure for fixed carbon plus ash.

Pyrolysis carried out at reduced pressures has given information about the nature of the primary decomposition products of coal. So-called short path stills are used, the principle of which is that the gap between heating surface and condenser is short. Usually the condenser is liquid nitrogen-cooled. In one study, the higher molecular weight fraction of the volatile products from pyrolysis of a bituminous coal was a semi-transparent, lacquer-like material which on exposure to light turned from yellowish-orange to black. The infrared spectra of this material was similar to that of the original coal. The condensate was assigned possible structures as illustrated (Howard, 1963b).





These asphaltene-like compounds are not considered to be the primary decomposition products of coal. Dryden expresses this viewpoint as follows: "Since coal must have a macromolecular structure, most of the fragments released are likely to have been attached to other parts of the coal skeleton, before pyrolysis, by more than one bond; in general, the larger the fragment, the greater the number of bonds. The release of large fragments involving the fission of many bonds will therefore be much less probable than the release of small fragments." (Howard, 1963b).

Coal pyrolysis in the presence of a known inhibitor of free radicals, nitric oxide, indicated that (1) thermal decomposition of coal was retarded and (2) secondary polymerization of tar was reduced if the nitric oxide were present at the onset of pyrolysis but nitric oxide had no effect if initially admitted to the retort above the temperature of coal decomposition (Berkowitz and Dammeyer, 1955).

The above points indicate that if the primary products are fairly small free radical fragments as theorized by Dryden, then the formation of the asphaltene-like materials that are obtained in vacuum pyrolysis must occur before the free radicals escape from the coal particles (Howard, 1963b).

2. Catalytic Hydrogenation of Coal

Bergius's process for coal hydrogenation to synthetic fuels is one of the most famous processes in industrial chemistry. In 1911, Bergius first hydrogenated coal to oil at 300 to 350°C without a catalyst. In 1913, commercial development of the Bergius process began, culminating in 1927 with the first commercial plant for coal hydrogenation using molybdenum oxide as catalyst and German brown coal as feedstock.

The Bergius process is essentially as follows: A coal paste, consisting of equal proportions of 80-mesh coal and the vehicle, a heavy recycle oil, is pumped, after the addition of 0.1 to 0.5 wt.% catalyst, into the reactor which operates at 400 to 450°C under hydrogen pressure of at least 3000 psig. The recycle heavy oil contains hydroaromatic, hydroxylated compounds that readily dissolve the coal at the hydrogenation temperature and transfer sufficient hydrogen to its thermal decomposition products to block condensation reactions that would result in coke deposition (Wu and Storch, 1968).

Storch commented, "It is probable that in the liquid phase hydrogenation of coal the saturation of the unsaturated molecules produced by the thermal decomposition of coal is accomplished mainly by reaction with hydroaromatic compounds, and to only a very minor extent by reactions with dissolved or catalytically adsorbed hydrogen. Hence the chief function of high hydrogen pressures and of catalysts is probably the rapid regeneration of hydroaromatics. The slow step in such regeneration may be the diffusion of one or both reactants to the catalyst surface." (Storch, 1941).

Coal can be hydrogenated effectively (using greater than 0.5 wt.% catalyst) without the vehicle being present probably because the production of primary liquid product is rapid enough so that it serves as vehicle for the remainder of the coal substance (Storch, 1941).

The postulated mechanism of coal hydrogenation (Bergius Process) then involves first, hydrogen transfer via hydroaromatic hydrogen donors to the active fragments produced via the thermal cracking of coal. The postulated second step is catalytic hydrogenation of either (1) these partially stabilized, and mobile, coal fragments to oils and/or (2) the hydroaromatic hydrogen donor molecules (*in situ* regeneration).

Catalysts and reaction conditions that have been used in coal hydrogenation are given chronologically in Table VI.

TABLE VI

CATALYSTS AND REACTION CONDITIONS FOR COAL HYDROGENATION‡

1925 to 1953

Author or Group	Temp. °C	Pressure Atm.	Vehicle	Catalyst	Yield	Date
Bergius	465	200	Heavy recycle oil	Iron oxide	80	1925
I.C.I.	450	250	Hydrocarbon oil	Tin	70	1935
I.G. Farben	435	200	Recycle oil	--	70	1935
Brit. Fuel Res. Sta.	400	215	Heavy oil	$Sn(OH)_2$	--	1938
U.S.Bureau Mines	440	250	Tar oil	SnS	90	1941
Germany	440	700	Recycle oil	Iron oxide	--	1943
Japanese	410	123	None	$ZnCl_2$	--	1946
U.S.Bureau Mines	440	700	Recycle oil	Iron oxide	--	1949
Union Carbide	500	240-420	Recycle	--	--	1953

‡ (Mills, 1969).

3. Coal Liquefaction via Liquid-Phase Hydrogen Donor Agents

Studies on the solvent extraction of coal led to the observation that certain solvents, such as Tetralin, liquefied coal in abnormally high yield. The workers, Pott and Broche, theorized that these particular solvents converted the "highly molecular coal constituents into less highly polymerized soluble bodies" (Pott and Broche, 1934). The Pott-Broche process which operated in Germany from 1938 to 1944 was the first commercialization of this concept. Described below is the Pott-Broche process.

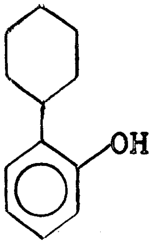
Pott-Broche Process

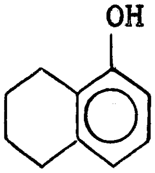
Coal, dried to less than one percent water, was ground so that 60 to 70% would pass through a sixty mesh screen and then mixed with two parts middle-oil from coal-tar pitch hydrogenation. The resulting coal paste was pressurized to 1500 psi, heated to 425°C and fed to a batch reactor in which the residence time was one hour. After the reaction time had elapsed, the reactor was vented, the contents cooled to 150°C and filtered through ceramic cartridge filters at 150°C using pressures of 45 to 60 psi. It was necessary to separate the residual solids from the extract solution rapidly to avoid polymerization of the extract. The filtrate was distilled *in vacuo* to recover the solvent. On a moisture- and ash-free basis, the coal liquefaction extent was about 80%; the extract yield was 66 to 69% (Dryden, 1963b).

Hydrogen donor processes are carried out at high temperatures, 350°C to about 450°C, in pressure vessels. The operating pressure (300 to 2000 psig) is caused by the vapor pressure of the hydrogen donor agent and gaseous products from coal breakdown. There is usually no added gas phase.

By at least the early 1940's, it had been realized that the particular effectiveness of hydroaromatic compounds in coal extraction was due to simultaneous hydrogenation via the hydroaromatic portion of the compounds (Storch, 1941).

Pott and Broche reported that a ternary mixture of Tetralin, phenol and naphthalene in a weight ratio of two to one to two was the best liquefaction agent they found for bituminous coal (Pott and Broche, 1934). Bureau of Mines workers later tested the idea that the essential features of structure deemed responsible for the peculiar effectiveness of the above ternary mixture could be combined in one pure compound. They evaluated the compounds o-cyclohexylphenol and 1,2,3,4-tetrahydro-5-hydroxy-naphthalene, both of which contain all the structural characteristics of the Pott-Broche solvent system and indeed found that these hydroaromatic phenolic group-containing compounds were superior coal liquefaction agents (Orchin and Storch, 1948).





Orchin and Storch made the following observations in their work: Under solvation conditions, a hydrogen-donor vehicle is superior to a completely aromatic vehicle. A high boiler such as naphthalene will liquefy about 20 to 30% of the coal, while its hydroaromatic partner, Tetralin, will liquefy about 50% of the coal. The hydroaromatic, phenolic group-containing compound will liquefy about 80% of the coal. A weight ratio of four parts of the agent to one part coal was used in these experiments, carried out at 400°C for one-half hour.

These workers also found that above 20% coal liquefaction there is a linear relationship between liquefaction and oxygen removal from the undissolved coal. (It was possible to liquefy 20% of the coal without any oxygen removal.) This correlation held with all the agents used, whether aromatic, hydroaromatic, hydroaromatic phenols, or aromatic phenols. The oxygen assay was by difference.

Orchin and Storch concluded that at 400°C, hydroxylated hydroaromatic solvents liquefy coal by mild hydrogenolysis of carbon to oxygen linkages by the hydrogen available from the hydroaromatic solvent and dissociation of the coal or primary products from the coal due to hydrogen bonding. The effectiveness of the hydrogen-bonded solvents suggest that one of the forces holding the reactive, unsaturated fragments of the coal structure together is the associative force resulting from hydrogen bonding (see Section II-E). A hydroxylated substance would be expected to dissociate a hydrogen bonded polymer, because the fragments of the polymer would attach themselves to the solvent by hydrogen bonding. An alternate reason for the effectiveness of a hydrogen bonded solvent may be that the primary liquefaction products are hydroxylated and hydrogen bonded and that an excess of a similar solvent keeps these fragments dissociated.

Orchin and Storch also evaluated hydrogen transfer systems in the presence of hydrogen pressure and a known coal hydrogenation catalyst. Three aromatic-hydroaromatic pairs were tried. These were, naphthalene-Tetralin, diphenyl-dicyclohexyl and o-phenylphenol-o-cyclohexylphenol. The results of these hydrogenation experiments are compared with their solvation experiments in Table VII.

The hydrogenation experiments were carried out at 400°C, maximum hydrogen pressure of 2500 psig, for one hour using a tin catalyst. The solvation experiments were 400°C for one-half hour. Their conclusions were that under hydrogenation conditions, the gaseous hydrogen is the source of the hydrogen for liquefaction and the hydroaromatic nature of the vehicle does not matter, since they obtained high percent liquefaction with all the various species. They attributed the higher hydrogen consumption observed with the aromatic partner of each pair as due to hydrogenation of the aromatic vehicle.

Orchin and Storch's results may be interpreted to show that while the gaseous hydrogen may be the source of the hydrogen for liquefaction, the mechanism may still involve hydroaromatics. Since the aromatic compounds are hydrogenated _in situ_, hydroaromatics are probably produced which then can function as hydrogen donor agents to liquify coal. Bureau of Mines workers also claim in an earlier work that tin sulfide with Tetralin had an important effect on the rate of hydrogen transfer (Storch _et al_.,

TABLE VII

EFFECT OF VEHICLE IN HYDROGENATION AND IN SOLVATION OF COAL ‡

	Hydrogenation		Solvation
Vehicle	Liquefaction[1] %	Hydrogen Consumption[1] %	Liquefaction[1] %
Tetralin	82.8	2.6	49.4
Naphthalene	80.4	4.1	22.2
Dicyclohexyl	80.8	2.6	27.2
Diphenyl	78.1	4.5	19.4
o-cyclohexyl-phenol	90.7	2.5	81.6
o-phenylphenol	91.0	3.7	19.6

‡ (Orchin and Storch, 1948).

[1] Based on weight of moisture-ash-free coal.

1943). Again, this is probably related to in situ hydrogenation of the reacted Tetralin (naphthalene) back to Tetralin.

Investigators at the Consolidation Coal Company have found that the rate of hydrogen transfer from Tetralin is not affected by hydrofining catalysts such as cobalt molybdate on alumina or cracking catalysts such as silica-alumina (Curran *et al.* 1967). No hydrogen pressure was used in these latter studies.

The evidence presented above indicates strongly that the mechanism of coal liquefaction *via* liquid-phase hydrogen donor agents involves transfer of hydrogen from the donor to the reactive fragments of coal produced by the thermal cracking of coal. The hydrogen donor process appears to be a homogeneous process, since it is not affected by catalysts. Enhanced coal liquefaction rates occur when a hydroaromatic (hydrogen donor) agent is used with high pressure hydrogen and a hydrogenation catalyst because *in situ* regeneration (hydrogenation) of the reacted hydroaromatic takes place, thus maintaining the concentration of the hydrogen donor agent at a high level.

Another observation made by Orchin and Storch was that the amount of hydrogen transferred in liquefying coal to the extent of 80 to 85% was about 2.6% w/w (based on the weight of the moisture and ash free coal). This number of 2.6% w/w has recently been confirmed by Curran who states that this is the maximum amount of hydrogen that can be transferred to the coal during the process of liquefaction by a hydrogen donor agent such as Tetralin (Curran *et al.*, 1967).

Three molecular weight fractions in coal extract using Tetralin as the hydrogen donor agent have been characterized. These were, a cyclohexane soluble oil, benzene soluble and cyclohexane insoluble asphaltenes, and a benzene insoluble, cresol soluble fraction. These fractions had average molecular weights of approximately 400, 750 and 1500, respectively (Curran *et al.*, 1967).

G. COAL LIQUEFACTION PROCESSES, EXPERIMENTAL STUDIES

1. Reaction of Coal with Water at High Pressure

The previous work on the carbon-steam system has been primarily concerned with the gasification of various forms of carbon but there are a few early references on reacting coal and water at high pressures and temperatures. The literature on both of these subjects have been reviewed by the previous M.I.T. investigators through 1960 (Boston, 1949; Jensen, 1950; Bartholomew, 1950; Hipkin, 1951; Harriott, 1952; Tung, 1953; Yen, 1960).

Boston and Hipkin treated a German Brown Coal with water in a non-agitated reactor at pressures of 400 to 4000 psi at 750°F. They found that the benzene solubles from the treated coal were less than that from the untreated coal up to 3000 psi. Above 3000 psi the benzene solubles increased over that from untreated coal. They obtained a maximum of 5.7% benzene solubles based on the original coal at 4000 psi. The benzene solubles of the untreated coal (under 4000 psi nitrogen pressure) was 1.65%. No analyses other than the amount of benzene solubles were given (Boston, 1949; Hipkin, 1951).

Yen carried out studies on the reaction between various forms of coal and water in the temperature range 650 to 1000°F, and at pressures up to 8000 psi, with and without catalysts. A rocking autoclave was used as the reactor. Three sources of carbon were used: charcoal, anthracite and bituminous coal. The charcoal and anthracite were virtually non-reactive even with catalysts present. The bituminous coal used by Yen was a high volatile coking bituminous coal known as Wharton coal originating from the Hernshaw Seam in Boone County, West Virginia. The maximum yield of benzene solubles from the reaction between this coal and water was 18% obtained at 775° and 4700 psi. Without water present, and under corresponding reaction conditions the yield of benzene solubles was c. 6%. With potassium hydroxide and iron as catalysts, the maximum percent yield of benzene solubles was 28.5% (Yen, 1960).

Yen studied the effects of time, temperature and pressure on the catalyzed and uncatalyzed reaction of Wharton Coal and water The uncatalyzed runs give the following results: The effect of time on the percent benzene solubles was negligible above reaction times of one hour and up to times of five hours. Pressure had a significant effect. At 780°F, below 3000 psi the yield of benzene solubles was about constant at 5% and above 4500 psi the yield was almost constant at 15%. Temperature was also a significant variable. In runs carried out at a constant pressure of 4700 psi, the maximum yield was 17 to 18% at 775°F and dropped rapidly above and below this temperature.

Yen used the following catalysts in his study: Potassium hydroxide, sodium chloride, sodium hydroxide, potassium carbonate, calcium oxide, tin chloride, thallium chloride, potassium acetate, iron, ferric oxide, and potassium hydroxide with iron. A normal charge of Wharton coal was 10 grams, the usual amount of catalyst was 2 grams, and the water charged varied from 40 ml to 180 ml.

2. Reaction of Coal with Carbon Monoxide and Water at High Pressure

A process is being developed by the U.S. Bureau of Mines for the liquefaction of coal and lignite by treatment at high pressure with carbon monoxide and water, but without the use of molecular hydrogen or added catalyst. The liquefaction appears dependent on temperature, pressure, and the presence of certain solvents. The combination of carbon monoxide and hydrogen has given consistently more coal liquefaction than molecular hydrogen under similar reaction conditions. The rate of liquefaction is also higher with carbon monoxide and water than it is with molecular hydrogen (Appell and Wender, 1968a,b).

Appell and Wender report that bituminous coal, in a 1:1 weight ratio with phenanthrene solvent and 1:0.5 weight ratio with water was converted in 70 to 75% yields (maf) in two hours at 425°C and 1000 to 2000 psig initial (room temperature) carbon monoxide pressure. In the absence of solvent the conversion was 50 to 58% (Appell and Wender, 1968a).

These workers found that lignites were more reactive than bituminous coal towards the combination of carbon monoxide and steam and that, in fact, this combination solubilized lignite more rapidly and completely than did hydrogen itself under the same reaction conditions. The conditions used were 380°C, 1:1 α-naphthol-phenanthrene solvent, 1500 psi initial carbon monoxide pressure, and a reaction time of 2 hours. One part lignite was used to one part mixed solvent and one part water. After ten minutes at 380°C, the conversion was 89% for carbon monoxide and water compared to 42% for hydrogen at the same conditions. With the combination of carbon monoxide and water the ultimate conversion of 92% was achieved within 30 minutes, while with hydrogen alone the ultimate conversion of 83% was achieved within 110 minutes. The sulfur content was reduced from 0.7 in the original lignite to 0.29 wt.% in the benzene-soluble tar. The oxygen content decreased from 21.7 to 5.6 wt.% and the nitrogen content remained about the same. The yield of benzene solubles was less when phenanthrene was used without α-naphthol (Appell and Wender, 1968b).

Sodium and potassium carbonate increased the conversion of bituminous coal but had only a small effect on the conversion of lignite and subbituminous coal. An examination of the water gas shift reaction occurring over these three ranks of coal showed that the lower rank coals had sufficient naturally-occurring catalyst to correspond to the addition of 1% alkali carbonate to the coal

3. Reaction of Coal and Iron with Water at High Pressure

The U.S. Bureau of Mines recently reported a "novel" liquefaction experiment in which Pittsburgh Seam bituminous coal was extensively hydrogenated to liquids by reacting coal, admixed with powdered electrolytic iron, with high pressure steam. At 5000 psig steam pressure and 800°F and a coal to iron weight ratio of one to twelve, the yield of benzene soluble oils was 79% and the net yield of gaseous hydrocarbons was 6%. In later experiments, carried out with a coal to iron weight ratio of one to eight, it was found that in order to obtain coal conversions of 85% or higher, the temperature had to be at least 750°F and the pressure had to be at least 3000 psig. The liquid products were mainly asphaltic oils of low volatility.

These same workers also demonstrated that the reaction of coal, hydrogen and massive amounts of iron using similar reaction conditions gave coal conversions and oil yields approximately the same as those obtained with steam. They concluded from these experiments that the hydrogen generated <u>in situ</u> from the steam-iron reaction is perhaps more reactive than molecular hydrogen, since its partial pressure in the latter case is much lower than in the case of the experiments with molecular hydrogen, and that iron in massive amounts will serve as a hydrogenation catalyst. This method offers the prospect of coal liquefaction without a hydrogen plant which is the most expensive unit of a conventional coal hydrogenation system (Spencer, 1968; Spencer, 1969). The hydrogen generated *in situ* is probably more reactive than molecular hydrogen not because it exists as atomic or "nascent" hydrogen but because as it forms on the iron surface, it is probably present in a dissociated chemisorbed type of structure.

4. Reaction of Coal with Aqueous Alkali

The action of aqueous alkali on coal has been studied by several investigators (Dryden, 1963c). At 350°C, using 5N NaOH and a 24 hour reaction time, subbituminous B coal was converted to a mixture of phenols, fatty acids, nitrogen bases, hydrocarbon oils and gases, and carbon dioxide in about 65% MAF yield. Elemental balances showed that the overall reaction is approximately the addition of oxygen and hydrogen in the proportions contained in water (Parker *et al.*, 1955).

Heating a bituminous coal at 350°C with 5N NaOH resulted in the formation of a coke-like residue in 75 to 80% MAF yield and an increase in the amount of benzene solubles from 6 to 8% of the carbon in the coal to 21.5% of the carbon in the coal. Products again included phenols, acids, neutral oils, hydrocarbon gases and carbon dioxide. From the carbon dioxide yield and oxygen balances, it appeared that carbon dioxide was formed by two reactions, one in which both oxygen atoms per carbon dioxide molecule came from the water and one in which one oxygen atom came from the water and the other from the coal (Kasehagen, 1937).

H. MECHANISMS OF COAL CONVERSION PROCESSES

1. Introduction

It is clear that there are fundamental differences among the coal conversion processes. The success of certain processes results from coal being a carbonaceous substance; the success of others are due to the organic structure of coal. This section is intended to unify the discussions on the nature of coal and the various processes for coal liquefaction and gasification.

2. Coal versus β-Graphite

Coals, cokes, charcoals, carbons and β-graphite are all carbonaceous substances. By definition, carbonaceous substances always contain carbon, usually hydrogen and often, in lesser amounts, sulfur, oxygen, nitrogen and inorganics. It is wrong, though, to think of coal and the other carbonaceous substances as if they are the same physical and chemical entity. Earlier, it was emphasized that coal is an amorphous, extremely complex organic substance, containing condensed heterocyclic, aromatic, hydroaromatic and alicyclic rings. β-Graphite, by contrast, is crystalline and contains only carbon. Cokes, charcoals and carbons, all amorphous substances, tend progressively in the order listed to be less organic-like in structure and more like inorganic substances.

3. Processes Common to Carbonaceous Substances

If the temperature is sufficiently high, all carbonaceous substances will react with steam, hydrogen or oxygen. Gasification reactions are those reactions which produce gases from carbonaceous solids. Examples of gasification reactions are:

$$C + H_2O = CO + H_2$$

$$2C + 2H_2O = CH_4 + CO_2$$

$$nC + mH_2 = C_nH_{2m}$$

$$C + O_2 = CO_2$$

Carbonaceous solids possess widely different reactivities. Harriott has determined from data on rates of oxidation of various carbonaceous substances with carbon dioxide or oxygen their relative reactivities (Harriott, 1952).

Substance	Relative Reactivity
β-Graphite	0.01
Coke	1
Anthracite	4
Wood charcoal	300
Deposited carbon	20,000

The differing reactivities are related to the bond strengths and the surface areas of the respective substances.

4. Conversion Processes Unique to Coal

Three major coal liquefaction processes, (1) Bergius process, (2) hydrogen donor solvent and (3) pyrolysis, are applicable only to coals and not to other carbonaceous solids such as cokes, charcoals, carbons and β-graphite. All three processes produce liquids from coal which somewhat resemble in structure the original coal. These processes involve a partial breakdown or decomposition of the original coal structure into fragments followed or accompanied by some type of stabilization of these fragments.

5. Fischer-Tropsch Process

The synthesis step of the Fischer-Tropsch process is not dependent on the structure and reactivity of the carbonaceous raw material; this hydrocarbon producing process is unique in this respect compared to the other coal liquefaction processes. The hydrocarbon structures formed in the synthesis step of the Fischer-Tropsch process are dependent on the catalyst and the reaction conditions.

I. RECAPITULATION

1. What are the major problems in coal-to-oil processes?
   a. All coal-to-oil and coal-to-gasoline processes require that the hydrogen content of coal be increased. Hydrogen manufacture is expensive and coal is consumed to produce this hydrogen.
   b. The two-step processes, the Bergius and the Fischer-Tropsch, possess low thermal efficiency since the highly endothermic step is high temperature; the moderately exothermic step is low temperature.

2. What are the alternatives?
   a. Water is reactive with carbonaceous materials at high temperatures, 800 to 1000°C. The ultimate in coal-to-oil processes would be the direct reaction of water, perhaps via a hydrogenation type reaction, with coal or coke under conditions of temperature and pressure favorable for the formation of liquids. As will be seen, thermodynamics requires that the synthesis step, i.e., the formation of hydrocarbons or hydrocarbon-like materials, be conducted at temperatures less than 500°C if carbon is the starting material. High pressures also favor hydrocarbon production.

Since carbon and water are extremely unreactive below 500°C, a catalyst would be necessary for this synthesis step.

b. Another approach is to attempt to improve the thermal efficiency of the two-step processes. Since thermodynamics requires that the exothermic step be less than 500°C, the logical course of action is to conduct the gasification at a lower temperature. Previous workers at M.I.T. have succeeded in gasifying carbon at 1000°F (538°C) using potassium salts (Hipkin, 1951; Tung, 1953).

The practicality of the two alternatives listed above have been explored in the present research effort.

J. REACTIONS BETWEEN CARBON AND WATER

Although the carbon-water system comprises only the three elements, carbon, hydrogen and oxygen, there are an infinite number of possible reaction products, including every conceivable hydrocarbon and oxygenated hydrocarbon. Listed below with examples are most of the general classes of reactions possible in the carbon-water system. These reactions neglect the carbon source: the carbon could originate from coal or it could originate from β-graphite.

1. Gasification

a. $C + H_2O = CO + H_2$

b. $C + 2H_2O = CO_2 + 2H_2$

c. $C + CO_2 = 2CO$

2. Gasification Synthesis

a. $7C + 6H_2O = 2C_2H_6 + 3CO_2$

b. $3C + 4H_2 = C_3H_8$

3. Gas-Phase Synthesis

a. $4CO + 2H_2O = CH_4 + 3CO_2$

b. $2CO + 2H_2 = CH_4 + CO_2$

c. $3CO + 7H_2 = C_3H_8 + 3H_2O$

d. $CO_2 + 4H_2 = CH_4 + 2H_2O$

4. Carbon Oxides Interchange

   a. $CO + H_2O = CO_2 + H_2$

   b. Reaction 1(c)

   c. Reactions of types 3(a), 3(b)

It should be noted that the gas-phase reactions listed above do not necessarily occur in the gas-phase; the solid phase present is usually providing a catalytic surface for the adsorption, surface reaction and desorption processes.

K. DESIRED REACTIONS BETWEEN COAL AND WATER

It is convenient to consider the direct gasification-synthesis reactions, examples of which are listed below, as the desired reactions between coal and water.

1. Aliphatic hydrocarbon production

$$\begin{array}{ccccccccc} 2C & + & 2H_2O & = & CH_4 & + & CO_2 \\ 7C & + & 6H_2O & = & 2C_2H_6 & + & 3CO_2 \\ \vdots & & \vdots & & \vdots & & \vdots \end{array}$$

2. Olefinic hydrocarbon production

$$\begin{array}{ccccccccc} 3C & + & 2H_2O & = & C_2H_4 & + & CO_2 \\ 9C & + & 6H_2O & = & 2C_3H_6 & + & 3CO_2 \\ \vdots & & \vdots & & \vdots & & \vdots \end{array}$$

3. Aromatic hydrocarbon production

$$\begin{array}{ccccccccc} 15C & + & 6H_2O & = & 2C_6H_6 & + & 3CO_2 \\ 9C & + & 4H_2O & = & C_7H_8 & + & 2CO_2 \\ \vdots & & \vdots & & \vdots & & \vdots \end{array}$$

For carbonaceous solids such as chars and carbons the above reactions are both desired and appropriate.

There are other reaction possibilities for the coal-water system which could perhaps be more desirable than these direct gasification-synthesis reactions. Earlier, a distinction was made between the coal conversion processes common to carbonaceous solids and those unique to coal because of its complex organic structure. Similarly, reactions can be postulated between coal and water which would not be applicable to other carbonaceous substances. Examples of these reactions are listed below.

1. Water serving as a hydrogen donor to coal

$$\text{Coal} + x\,H_2O = \text{"oils"} + \frac{x}{2}\,CO_2$$

2. Water serving as a hydrogen and oxygen donor to coal

$$\text{Coal} + x\,H_2O = \text{"oils"}$$

3. Water serving as a hydrogen donor to the thermal decomposition products of coal

$$\text{Coal} + \Delta = \text{"Active Fragments"}$$

$$\text{"Active Fragments"} + x\,H_2O = \text{"oils"} + \frac{x}{2}\,CO_2$$

4. Water serving as a hydrogen and oxygen donor to the thermal decomposition products of coal

$$\text{Coal} + \Delta = \text{"Active Fragments"}$$

$$\text{"Active Fragments"} + x\,H_2O = \text{"oils"}$$

There is little reason to assume, considering their chemical and physical differences, that it would be equally as facile to synthesize hydrocarbons from carbonaceous solids such as charcoals or carbons and water as it would be to produce hydrocarbons from coal and water. Formation of liquids could be visualized as perhaps being more apt to occur in the case of coal and water, because of its multiplicity of bond types and energies, than in the cases of β-graphite or the other amorphous carbonaceous substances which have only one or a few kinds of chemical bonds and water.

What is desired is an efficient process, using water as a hydrogen donor, to convert the complex organic substance coal to liquids which are amenable by further processing to desirable hydrocarbons. This process can consist of reactions involving water which are applicable to all carbonaceous solids and/or it can consist of reactions involving water which are unique to coal.

L. THERMODYNAMICS

1. Introduction

a. Theoretical Background

Thermodynamics deals with systems in equilibrium and offers insight into the rates or mechanisms of reactions only in extremely simple situations such as those in which the principle of microscopic reversibility can be applied. A thermodynamic analysis does provide insight into which reactions may be promising, which reactions are not promising and the equilibrium yields of various products. In addition, thermodynamics permits the calculation of heats of reactions. If a system not at equilibrium is subjected to a thermodynamic analysis, discrepancies will appear between theory and experimental data which can be used to determine the extent of departure of the system components from equilibrium.

Determination of the standard free energy change, ΔG°, for a reaction at a given temperature allows an assessment of whether or not the reaction should be considered feasible. The thermodynamic equilibrium constant, K, is related to the standard free energy by the equation:

$$\Delta G^\circ = -RT \ln K$$

The following table, due to Dodge, is intended to serve only as a guide since there is no value of ΔG° that can completely eliminate a reaction from occurring (Dodge, 1944).

$\Delta G°$	ln K	Reaction Feasibility
Less than zero	Positive	Promising
Greater than zero, but less than + 10,000	Negative	Doubtful promise, but warrants further study.
Greater than + 10,000	Negative	Very unfavorable. Feasible only under unusual conditions such as high pressure.

b. Carbon-Steam Thermodynamics vs. Coal-Water Thermodynamics

A rigorous thermodynamic analysis of the carbon-steam system is possible using as a basis the free energy of carbon in the form of β-graphite. How applicable is the information provided by this analysis to the coal-water system? This question can be answered by consideration of what information thermodynamics generally provides and a comparison of the possible reactions in the carbon-steam system, that is, those reactions carbonaceous solids have in common with the postulated reactions unique to coal and water.

Thermodynamics may be used to determine the regions of temperature and pressures where reactions are favored or unfavored. The equations subjected to the thermodynamic analysis need not represent the molecular events that actually occur because thermodynamics concern is only with the equilibrium end states.

Comparison of the desired unique reactions between coal and water with certain of the possible reactions in the carbon-steam system shows that the compared reactions possess the same equilibrium end states.

Water serving as a hydrogen or hydrogen and oxygen donor to coal is analogous to the gasification-

$$\text{Coal} + x\, H_2O = \text{"oils"} + \frac{x}{2}\, CO_2$$

$$\text{Coal} + y\, H_2O = \text{"oils"}$$

synthesis type reactions, an example of which is

$$8C + 6H_2O = C_5H_{12} + 3CO_2$$

Reactions involving the "active fragments" produced via coal thermal cracking and water can be treated as:

$$\text{Coal} \xrightarrow{\Delta} \text{"Active Fragments"}$$

$$\frac{\text{"Active Fragments"} + x\, H_2O = \text{"oils"} + \frac{x}{2}\, CO_2}{\text{Coal} + x\, H_2O = \text{"oils"} + \frac{x}{2}}$$

again analogous to gasification-synthesis type reactions.

The conclusions drawn from a thermodynamics analysis of the β-graphite-steam system will therefore be generally applicable to all carbonaceous substances, although the actual reaction pathways may be completely dissimilar.

2. Equilibrium Constants

Fig. 6 is a plot of the common logarithm of the equilibrium constant as a function of temperature over the range 300 to 1500°K for ten of the possible reactions in the carbon-steam system. These equilibrium constants were determined from the free energy changes for the various reactions and thus are functions of temperature only. The free energy changes were calculated from the free energy values of carbon in the form of β-graphite (Rossini, 1953). It has been shown via equilibrium studies that the carbon in amorphous substances such as coals, cokes and charcoals possess free energy values perhaps as much as 1500 to 2600 calories per gram atomic weight higher than graphitic carbon (Harriott, 1952; Hottel and Howard, 1971c). Free energy changes of reactions calculated based on the free energy values of carbon in amorphous substances would then be lower than those calculated based on the free energy values of carbon in the form of β-graphite. Since the free energy values of carbon in common industrial fuels are usually not known, the free energy values of β-graphite are customarily used in thermodynamic analyses. Later in this section the impact of the carbon form on the equilibrium gas compositions is described in detail.

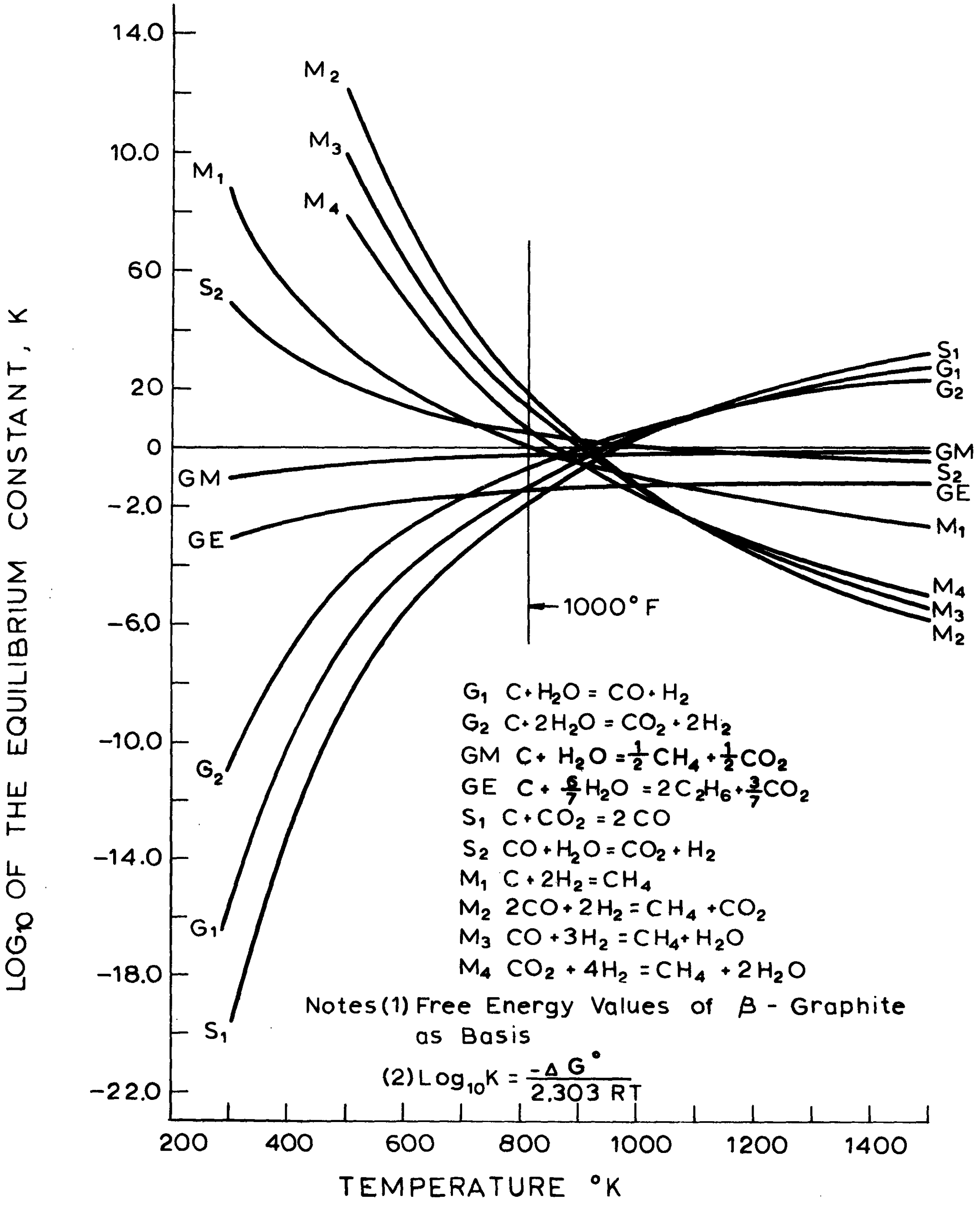


Figure 6 Equilibrium Constants for Possible Reactions in Carbon - Steam System

The ten reactions considered are:

Gasification Reactions

$G_1 \qquad C + H_2O = CO + H_2$

$G_2 \qquad C + 2H_2O = CO_2 + 2H_2$

$GM \qquad C + H_2O = \frac{1}{2} CH_4 + \frac{1}{2} CO_2$

$GE \qquad C + \frac{6}{7} H_2O = \frac{2}{7} C_2H_6 + \frac{3}{7} CO_2$

CO-CO_2 Interchange

$S_1 \qquad C + CO_2 = 2CO$

$S_2 \qquad CO + H_2O = CO_2 + H_2$

Methane Producing Reactions

$M_1 \qquad C + 2H_2 = CH_4$

$M_2 \qquad 2CO + 2H_2 = CH_4 + CO_2$

$M_3 \qquad CO + 3H_2 = CH_4 + H_2O$

$M_4 \qquad CO_2 + 4H_2 = CH_4 + 2H_2O$

The standard states of the components, other than β-graphite at one atmosphere, were taken as gases at one atmosphere. By definition, the free energy of formation of an element in its standard state at any temperature is zero.

Fig. 6 shows the following:

1. Methane formation via hydrogenation of carbon and carbon oxides, reactions M_1, M_2, M_3 and M_4, is thermodynamically favored at temperatures below 800°K. All the other reactions except the water gas shift, reaction S_2, are not favored in this temperature region.
2. Reactions M_2 and M_3, the simplest of the Fischer-Tropsch type reactions, illustrate well why the synthesis step of the Fischer-Tropsch process is carried out at 200 to 250°C.
3. The gas-phase methane producing reactions, M_2, M_3 and M_4, have large negative slopes. A moderate change in temperature produces a large change in the values of the respective equilibrium constants.
4. Reaction GM, which produces methane by direct carbon gasification, is not very temperature dependent, its K value lies between 0.1 and 1 in the temperature range 300 to 1500°K.
5. Reaction GE, the gasification-synthesis reaction for the higher hydrocarbon, ethane, has a smaller equilibrium constant than reaction GM; its K behavior with temperature is similar to the K behavior of reaction GM.

6. All the hydrogenation reactions except for the reverse of reaction S_2, the water gas shift, are exothermic. Thus their equilibrium constants decline with increasing temperature.
7. Reaction S_2, the water gas shift, is favored thermodynamically below 800°K; reaction S_1 is highly unfavored. At equilibrium in the low temperature region a high ratio of carbon dioxide to carbon monoxide would be predicted.
8. About 900°K, all the reactions, except the direct synthesis of the higher hydrocarbons, have approximately the same equilibrium constant, meaning these reactions are all equally favored.
9. Above 900°K, methane formation via the gas phase reactions is thermodynamically unfavorable.
10. Above 900°K, thermodynamics favors the gasification reactions G_1, G_2 and S_1. At these high temperatures the equilibrium gas mixture will then be largely carbon monoxide and hydrogen.

3. Equilibrium Gas Compositions as Functions of Temperature and Pressure

Equilibrium gas compositions for the β-graphite-steam system have been calculated as functions of temperature and pressure (Bartholomew, 1950; Hipkin, 1951; Jensen, 1950; Tung, 1953). The gaseous components considered were the carbon oxides, hydrogen, methane and water over the temperature range 400 to 1800°F and the pressure range 0 to 1100 psig. In these calculations it was assumed that only methane would be formed in significant quantities, equilibrium being so unfavorable for the higher hydrocarbons. Figures 7 to 14 show the effect of pressure on the equilibrium gas composition at 400, 600, 800, 900, 1000, 1200, 1400 and 1800°F (Tung, 1953). Figures 15 to 17 show the effect of temperature on the equilibrium gas composition at 14.7, 100 and 1000 psig (Tung, 1953).

Again it should be remembered that these calculations are based on carbon as β-graphite. The free energy values of carbon in coals and other amorphous carbons are considered to be higher than the free energy value of β-graphite, thus the equilibrium compositions will vary correspondingly.

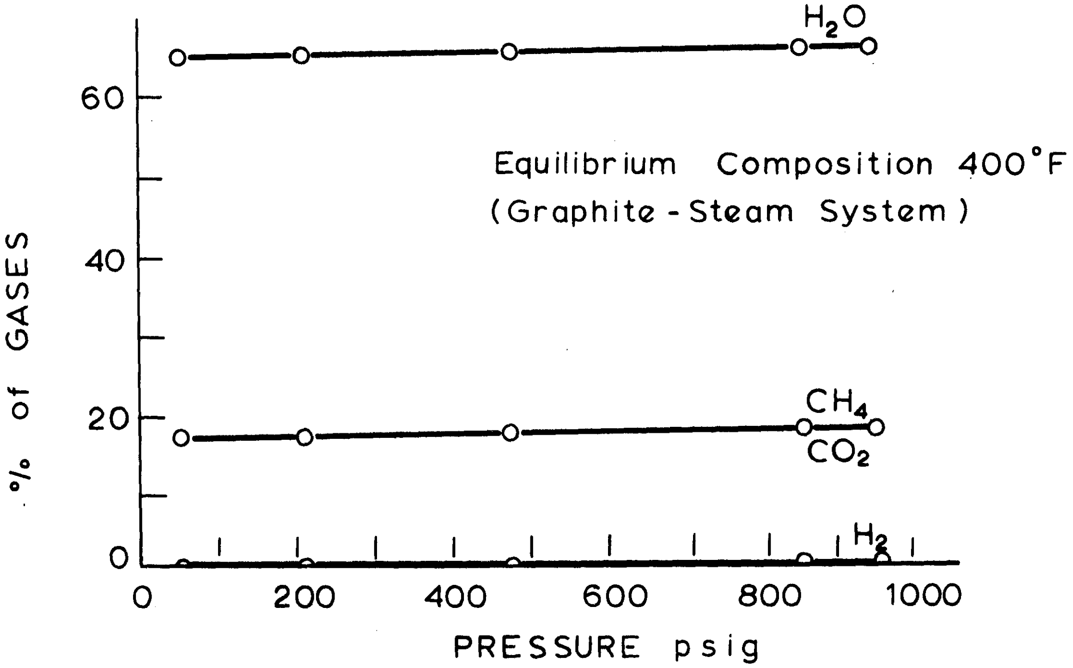


Figure 7

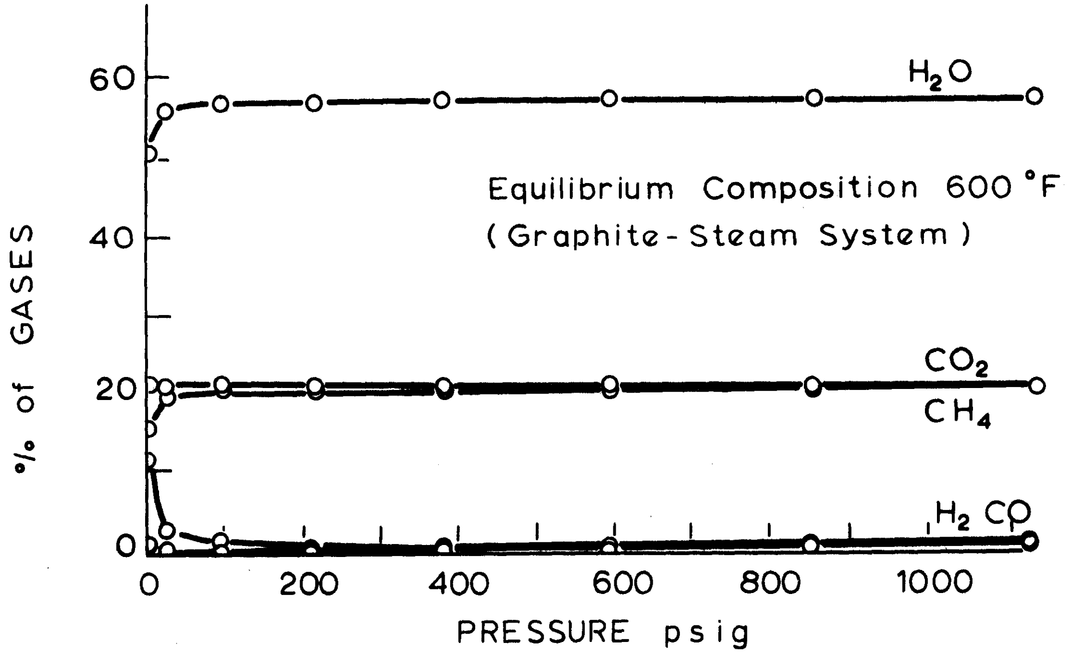


Figure 8

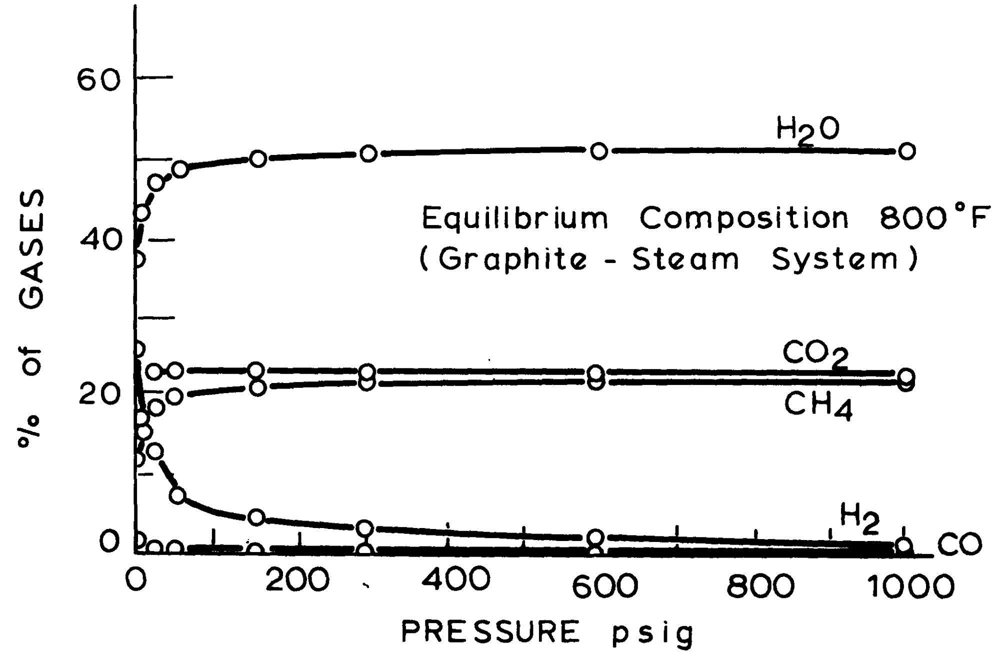


Figure 9

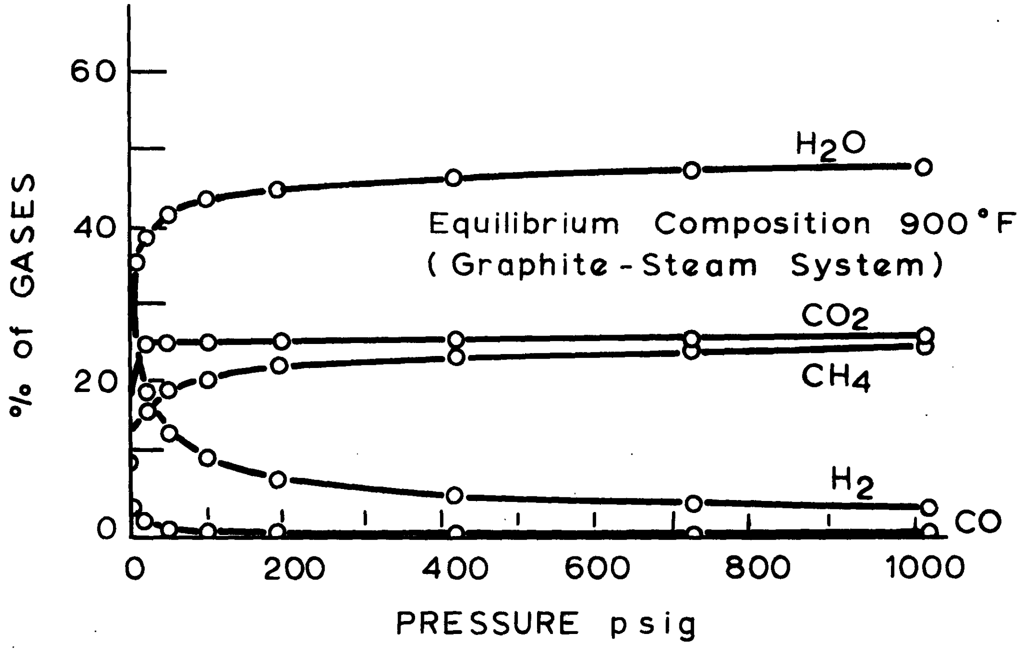


Figure 10

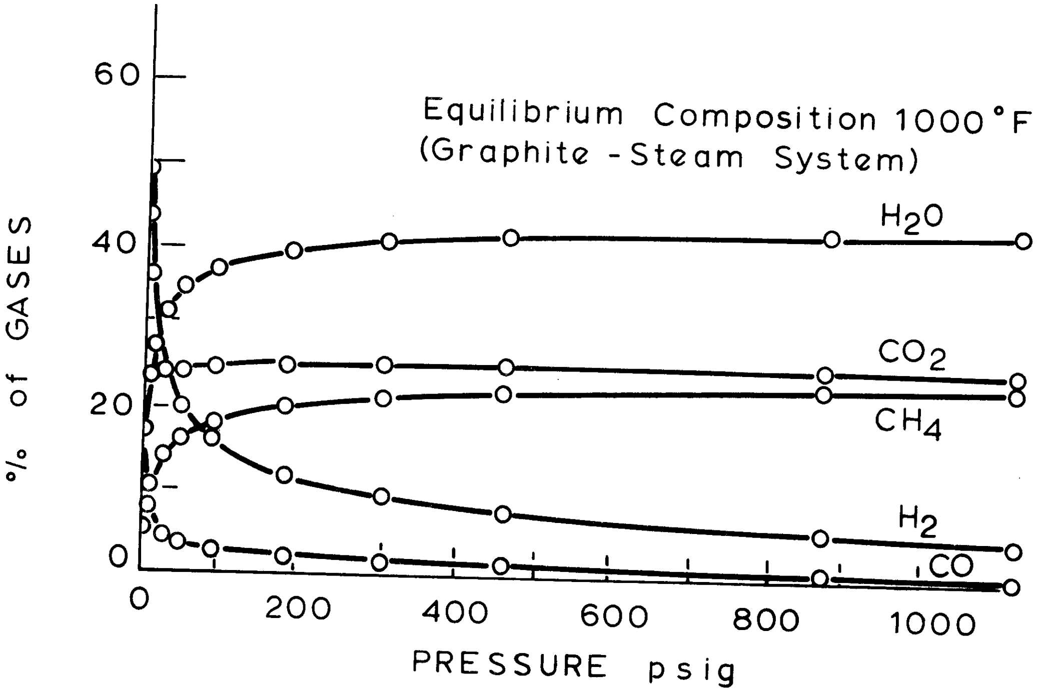


Figure 11

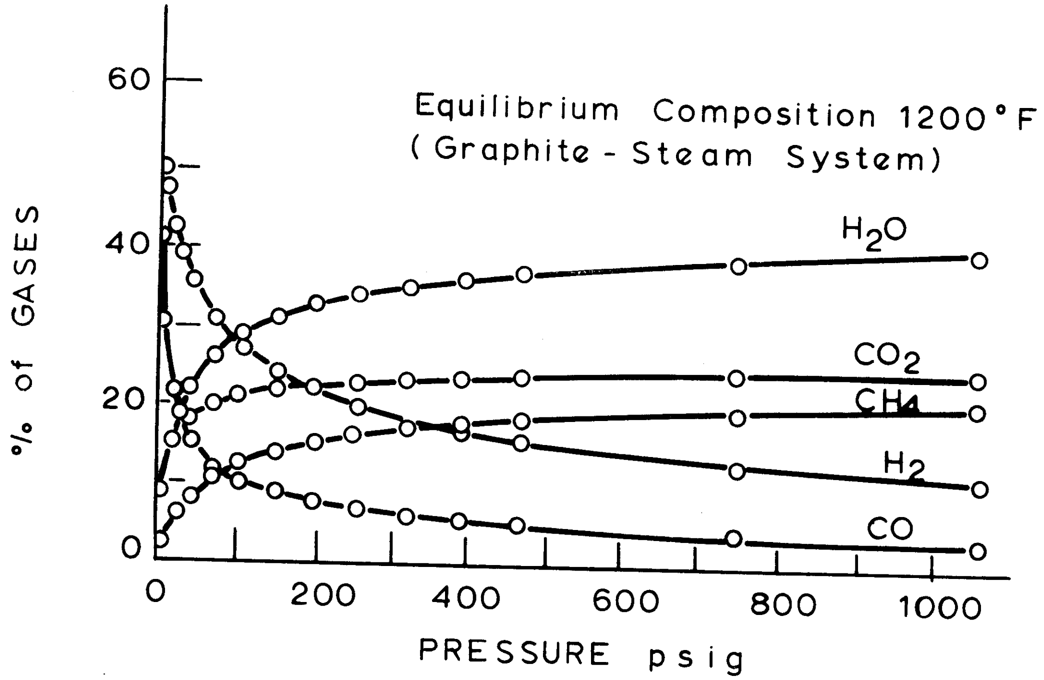


Figure 12

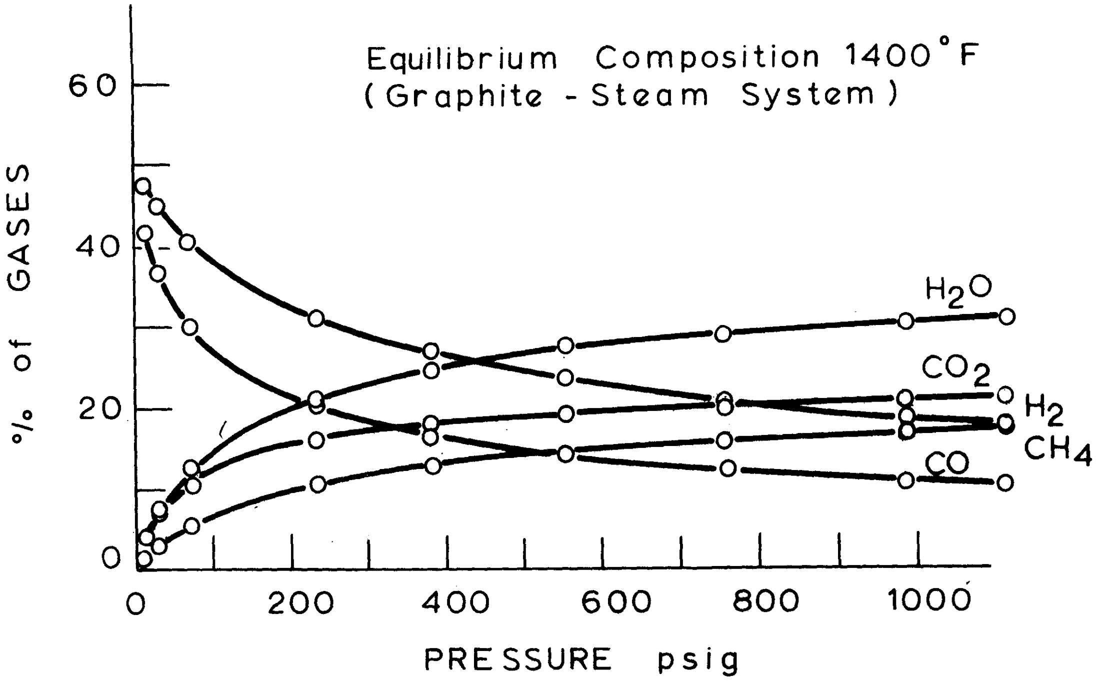


Figure 13

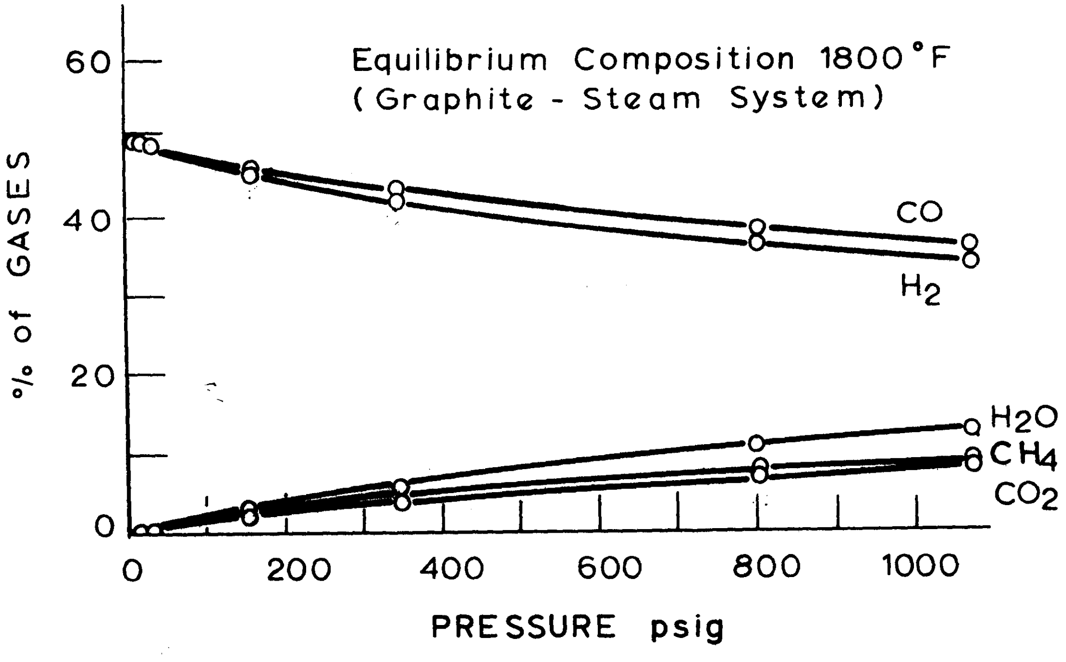
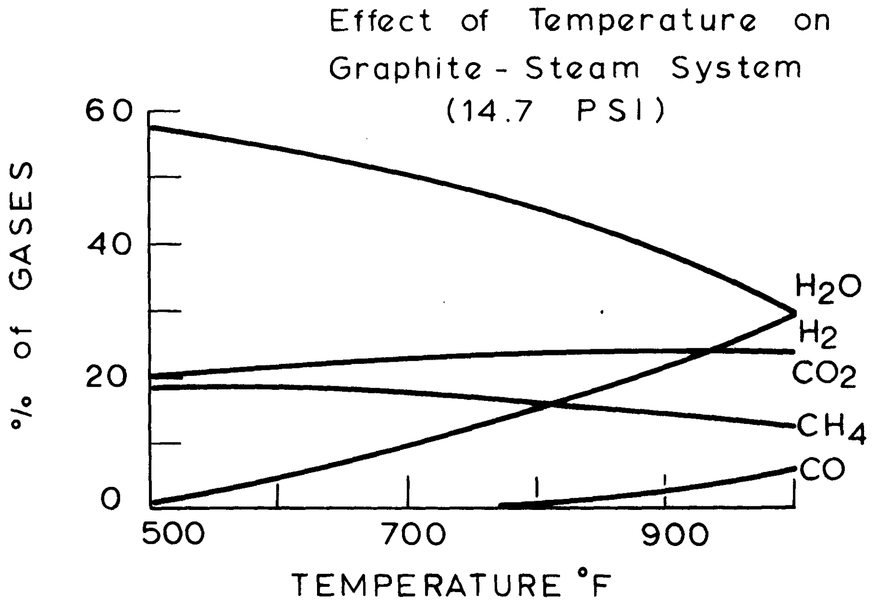
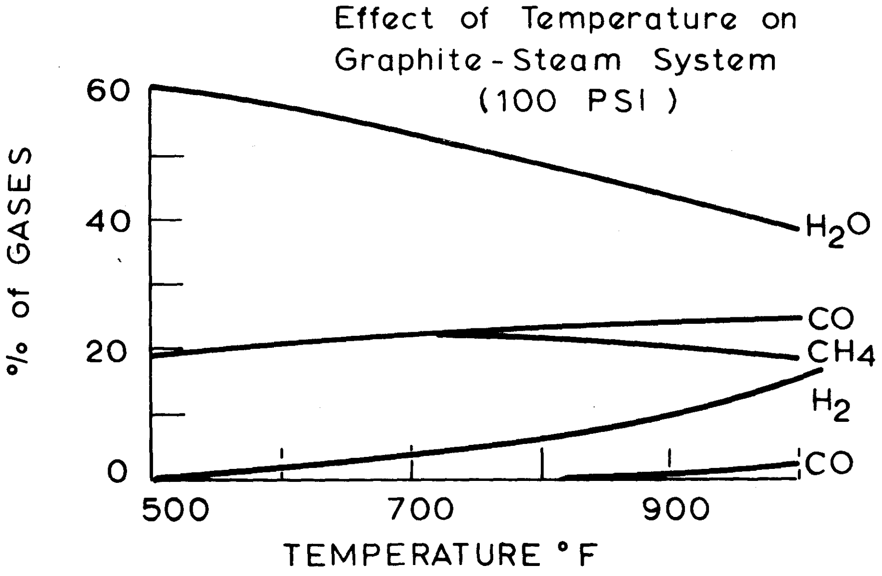


Figure 14



Effect of Temperature on Graphite - Steam System (14.7 PSI)

Figure 15



Effect of Temperature on Graphite-Steam System (100 PSI)

Figure 16

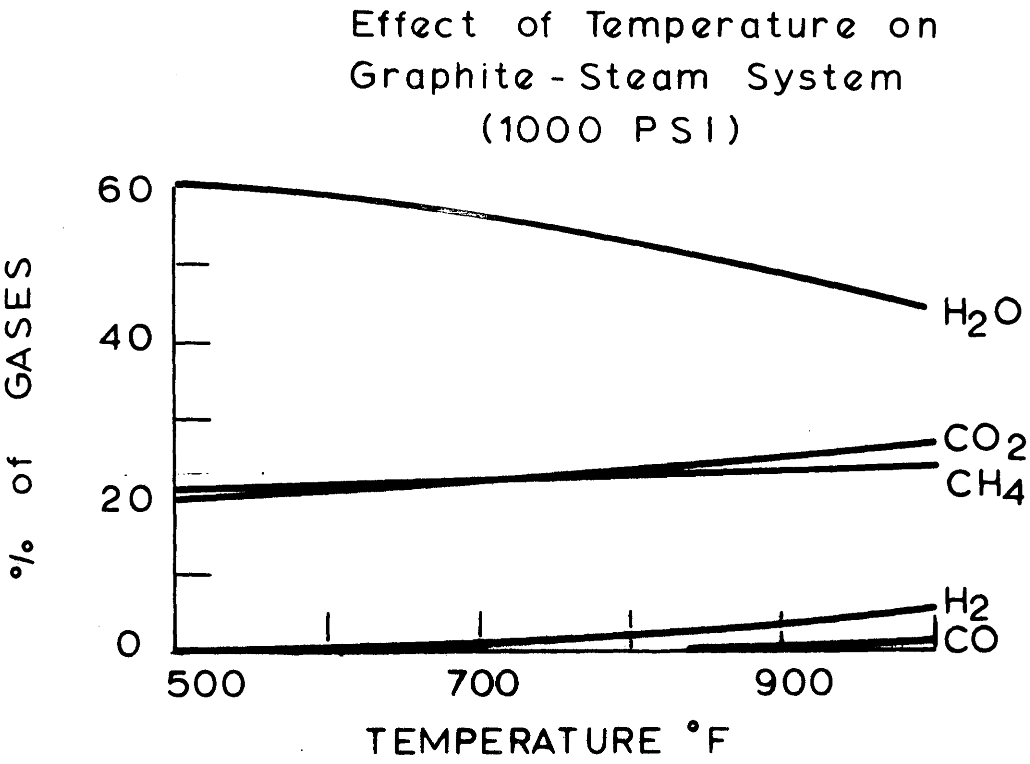

Effect of Temperature on
Graphite - Steam System
(1000 PSI)
60
40
20
0
% of GASES
500
700
900
TEMPERATURE °F
H_2O
CO_2
CH_4
H_2
CO

Figure 17

These figures provide the following information:

1. Steam conversion increases markedly with increasing temperature as shown by the decrease in the equilibrium steam content. Increasing pressure decreases steam conversion, this manifests itself by an increase in the equilibrium steam content.
2. Methane formation is favored by increased pressure. Pressure becomes increasingly more important as the temperature is increased.
3. Methane formation is adversely affected by increasing temperature, especially at low pressures. At 15 psig, a temperature rise of 400°F reduces the equilibrium methane content from 11% to 2%; at 1000 psig the same temperature rise reduces the equilibrium methane content from 22% to 20%.
4. At low temperature, the carbon dioxide to carbon monoxide ratio is high. At high temperatures the carbon monoxide to carbon dioxide ratio is high.

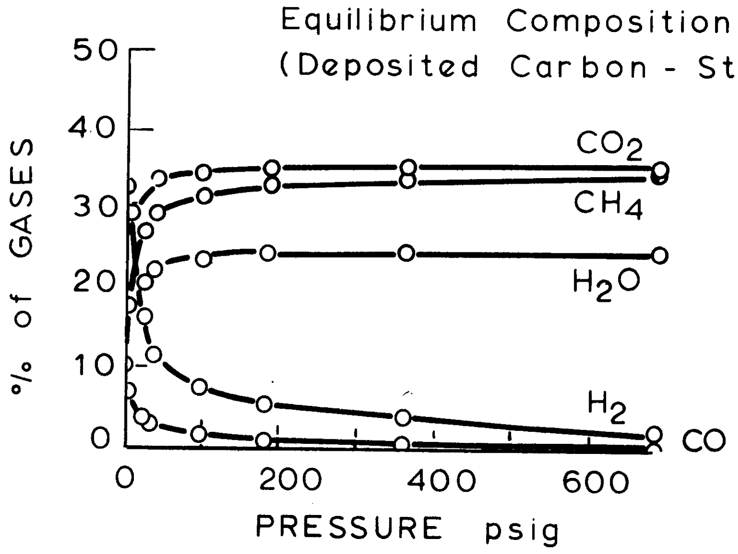


Figure 18

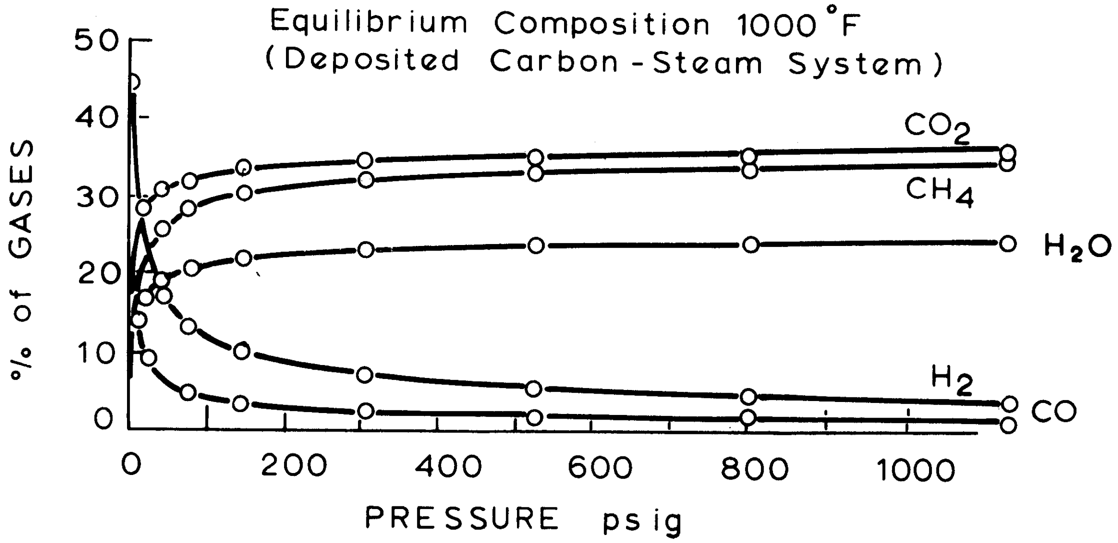


Figure 19

From Figure 6 , it does not appear that methane formation is favored above 900°K. For example, in this temperature region the equilibrium constant for reaction GM, the direct gasification-methanation reaction, is near but under one; the gas phase methanation reactions, M_2, M_3 and M_4, have very small equilibrium constants with strong negative temperature coefficients as does to a lesser extent, reaction M_1, the hydrogenation of carbon. In spite of these observations the equilibrium methane content even at 1800°F (Fig. 14) is considerable: At 1100 psig, the methane content is 10%; at very low pressures, however, it is insignificant.

4. Effect of Carbon Form on Equilibrium Gas Composition

In his study of methane decomposition over silica gel, Harriott found from equilibrium studies that the carbon deposited on the catalyst possessed a free energy value 1.5 kcalorie per gram mol above that of β-graphite (Harriott, 1952). Tung calculated the equilibrium gas compositions for the deposited carbon-steam system at 900°F and 1000°F; his results are reproduced in Figures 18 and 19. Comparison of these latter figures with Figures 10 and 11 shows the differences between the β-graphite-steam and the deposited carbon-steam systems. Table VIII makes this comparison at 1000°F.

TABLE VIII

PERCENTAGE OF METHANE IN PRODUCT GAS AT EQUILIBRIUM AT 1000°F ‡

(Graphite-steam system compared with
Deposited carbon-steam system)

Pressure (psig)	Percent Methane in Equilibrium Mixture Graphite-steam	 Deposited Carbon-steam
50	16%	26%
100	18.5%	29.2%
200	20.5%	32%
500	22.5%	33.2%
1000	24.0%	34.5%

‡ (Tung, 1953).

It could be expected from the observations on relative reactivities of carbonaceous substances (see Section II-H) that coals and cokes would possess free energy values higher than β-graphite but lower than carbon deposited by catalytic cracking of methane. The equilibrium gas compositions arising from coals and cokes would lie then somewhere between those of the β-graphite-steam and the deposited carbon-steam systems. Both the Bergius coal hydrogenation and the hydrogen donor agent processes produce more higher hydrocarbons and less methane than correspond to equilibrium for either the β-graphite-steam or the deposited carbon-steam systems.

This observation teaches that coal liquefaction via hydrogenation probably involves breakdown of the organic structure of coal into smaller units rather than stepwise synthesis of hydrocarbons from hydrogen and carbon. While it does not require a thermodynamic analysis to arrive at the foregoing conclusions, it is interesting that some mechanistic insight is derivable from thermodynamic analysis.

5. Thermodynamically Favored Regions for Hydrocarbon Production

It is theoretically possible to form oil from carbonaceous substances even though the equilibrium concentrations of the higher hydrocarbons and the oxygenated hydrocarbons are extremely low because there exists an infinite number of possible products from reactions between water and the carbon source.

This thermodynamic analysis of the β-graphite-steam system shows that hydrocarbon formation is favored by high pressures and low temperatures. High pressures mean substantially above atmospheric, 100 psi and upwards, and low temperatures mean less than 800°K or 1000°F. At high temperatures, 900 to 1500°K, the beneficial effect of pressure on the equilibrium methane content of the reaction gases (and the equilibrium content of the higher hydrocarbons) is more pronounced than at the low temperatures. At low pressures, less than 100 psi, the detrimental effect of temperature on the equilibrium hydrocarbon content of the reaction gases is the greatest.

6. Enthalpy Considerations

In Table IX are listed the standard enthalpy changes at 25°C for the reactions considered in the carbon-steam system. These enthalpy changes were calculated from heats of formation (Rossini, 1953).

Earlier, the observation (see Section II-D) was made that the maximum thermal efficiency would occur in the two-stage coal conversion processes if the gasification and synthesis steps were conducted at the same temperature levels. Using the standard enthalpy changes in Table IX, the thermal loads on the reactor(s) can be calculated for various reaction combinations assuming gasification

TABLE IX

STANDARD ENTHALPY CHANGES OF POSSIBLE REACTIONS IN THE CARBON-STEAM SYSTEM ‡

	Reaction	$\Delta H_R{}^\circ$ at 25°C kcal/g mol
G_1	$C + H_2O = CO + H_2$	31.38
G_2	$C + 2H_2O = CO_2 + 2H_2$	21.55
G_M	$C + H_2O = \frac{1}{2} CH_4 + \frac{1}{2} CO_2$	1.92
G_E	$C + \frac{6}{7} H_2O = \frac{2}{7} C_2H_6 + \frac{3}{7} CO_2$	3.46
S_1	$C + CO_2 = 2CO$	41.21
S_2	$CO + H_2O = CO_2 + H_2$	-9.83
M_1	$C + 2H_2 = CH_4 + CO_2$	-17.71
M_2	$2CO + 2H_2 = CH_4 + CO_2$	-58.92
M_3	$CO + 3H_2 = CH_4 + H_2O$	-49.09
M_4	$CO_2 + 4H_2 = CH_4 + 2H_2O$	-39.26

Reference State: All elements and compounds in the ideal gaseous state at 1 atm., except solid carbon as β-graphite at 1 atm.

‡ (Rossini, 1953).

and synthesis occurring at the same temperature. For these calculations the enthalpy changes at 25°C will be used; a rigorous approach would be to determine the enthalpy changes at an assumed reaction temperature. Further complications develop if the reactor(s) are operated at pressures other than atmospheric; in the latter case the enthalpy changes would have to be corrected for pressure. To demonstrate the concept of equal temperatures for the two stages, the Table IX enthalpy changes are sufficiently accurate, however.

Three situations will be considered. These are combinations of: (1) Low temperature gasification with a Fischer-Tropsch synthesis; (2) Low temperature gasification with a Bergius-type synthesis; and (3) Direct gasification-synthesis.

		ΔH_R at 25°C kcal/g mol
Case I		
Gasification:	$C + H_2O = CO + H_2$	+31.38
Synthesis:	$2CO + 2H_2 = CH_4 + CO_2$	-58.92

Reactor Heat Requirements = 2 (31.38) - 58.92 = 3.84 kcal/g mol CH_4

Case II		
Gasification:	$C + 2H_2O = CO_2 + 2H_2$	+21.55
Synthesis:	$C + 2H_2 = CH_4$	-17.71

Reactor Heat Requirements = 21.55 - 17.71 = 3.84 kcal/g mol CH_4

Case III

Gasification-Synthesis:

$$C + H_2O = \frac{1}{2} CH_4 + \frac{1}{2} CO_2 \qquad +1.92$$

Reactor Heat
Requirements = 2 (1.92) = 3.84 kcal/g mol CH_4

These calculations show that about 4 kilocalories of heat are necessary to produce one gram mol of methane if the gasification and synthesis steps are conducted at the same temperature. Industrial gasifiers normally operate at 800 to 1000°C and synthesis reactors at 250°C. In the latter case, to produce one gram mol of methane requires the addition of about 64 kilocalories of heat in the gasifier at 800 to 1000°C; the heat release in the synthesis step, about 59 kilocalories at 250°C, is available only to provide latent heat to vaporize water and sensible heat up to near 250°C. Therefore the difference in endothermic heat between normal industrial gasification-synthesis and the equal temperature gasification-synthesis is of the order of 50 to 60 kilocalories per gram mol of methane.

Similar comparisons using the model reactions for the higher hydrocarbons would also show the heat economy of equal temperature gasification-synthesis. It is also apparent that proportional improvements in heat economy ensue the nearer the gasification temperature approaches the synthesis temperature.

M. OBJECTIVES

1. The primary objective of the work described in the Liquefaction Section of this thesis was to find a set of conditions of temperature and pressure under which coal and water, with a suitable catalyst would react to produce liquids.

2. The primary objective of the work described in the Gasification Section of this thesis was to determine if the char by-products from the liquefaction studies (thought to be similar to a devolatilized coal) would gasify at a practical rate at 1000°F using alkali salts as catalysts.

N. PROGRAMS FOR PRESENT INVESTIGATION

Included in this section are the experimental programs developed to satisfy the primary objectives of this thesis: (1) Direct reaction of water and coal to produce liquids and (2) Low temperature gasification of coal.

1. Coal Liquefaction Program

The questions to be answered were:

a. What regions of temperature and pressure should be examined?
b. What kinds of catalysts should be evaluated?
c. Is there an advantage to an added liquid phase, and if so, what?
d. What should the experimental reactor configuration be?

a. Reaction Conditions

Thermodynamic considerations have shown that hydrocarbon formation from carbonaceous substances is favored at temperatures less than 500°C and by high pressure. The review of the commercial coal conversion processes has shown that very little reaction of coal even with hydrogen occurs until the temperature that coal begins to thermally crack, 350 to 375°C, is attained.

In industry, pressures of 3000 to 5000 psi are considered to be high pressures. Pressures above 10,000 psi are considered to be super high pressures and there are very few processes operated in this pressure region. Coal conversion plants, by their nature, will be very large installations. It would probably not be practical to consider for coal conversion plants pressures above 8000 to 10,000 psi unless tremendous gains could be realized.

Thus, for the present investigation of a possible direct synthesis of oils from coal and water, the temperature and pressure regions that seem to offer the most promise, both on theoretical and practical grounds, are 350 to 500°C and less than 8000 to 10,000 psi, respectively.

b. Selection of Catalysts for Evaluation

A catalyst must be found which will promote the reaction of coal and water at temperatures below 500°C. The essential functions that this catalyst must possess are:

1. Activation of the water molecule.
2. Ability to combine the hydrogen from water with coal or active fragments therefrom.

Other catalytic functions, desirable but less essential are the ability to:

1. Promote carbon oxides formation.
2. Retard the coking reactions.
3. Facilitate the cracking reactions.
4. Catalyze the water gas shift reaction.
5. Act as a conventional hydrogenation catalyst.
6. Promote desulfurization and denitrogenation reactions.

With the exception of (2) in the latter group above, catalysts are known which possess one or more of the listed functions; no catalyst is known which will produce liquids by direct reaction of coal and water.

The approaches taken to the problem were to:

(1) Compile the known catalytic processes in which water appears or can appear as a reactant or product and then consider the catalysts used in these processes (Table X); and

(2) Consider known catalysts or mixtures of catalysts possessing one or more of the desired catalytic functions (Table XI).

There has been considerable work recently on the hydrogen processing of coal-derived liquids to hydrocarbon oils. Most of the catalysts being used in this service are included in Tables X and XI.

TABLE X

CATALYTIC PROCESSES IN WHICH WATER APPEARS AS REACTANT OR PRODUCT

Process	Typical Catalysts
Steam Reforming	- Nickel
Hydrogenation/Dehydrogenation	- Cobalt, Nickel, Chromia-Alumina
Fischer-Tropsch	- Cobalt-Thoria/Kieselguhr Iron, Nickel
Hydration/Dehydration	- Alumina, Tungsten Oxide/Alumina
Water Gas Shift	- Iron Oxides
Hydrodesulfurization Hydrodenitrogenation	- Cobalt-Molybdate/Alumina Nickel-Molybdate/Alumina Nickel-Tungstate/Alumina

TABLE XI

POSSIBLE DESIRED CATALYTIC FUNCTIONS FOR COAL-WATER SYSTEM

Function		Typical Catalysts
Cracking	-	Silica-Alumina
Water-Gas Shift	-	Iron Oxide
Hydrogenation	-	Nickel, Cobalt, Noble Metals
Hydrodesulfurization Hydrodenitrogenation	-	Cobalt-Molybdate/Alumina Nickel-Molybdate/Alumina Nickel-Tungstate/Alumina
Gasification	-	Alkali Metal Salts

c. Added Liquid Phase

A basic problem in the water-coal system as in the hydrogen-coal system is achieving intimate contact between the catalyst surface, coal, and the hydrogen donor agent be it hydrogen, a hydroaromatic molecule, or water. In the Bergius coal hydrogenation process the initial step in coal liquefaction involves hydrogen transfer to the coal or coal fragment via a process-derived, hydroaromatic hydrogen donor agent. The coal fragments, now solubilized, are then able to migrate to the catalyst to receive additional hydrogen.

It seems reasonable to assume that an added liquid phase could prove to be of considerable value in the water-coal system. Three polycyclic hydrocarbons were selected for inclusion in this study:

(1) Phenanthrene
(2) Decahydronaphthalene "Decalin"
(3) 1,2,3,4-Tetrahydronaphthalene "Tetralin"

Phenanthrene, an aromatic compound, has often been used as a coal solvent; the aromatic clusters in coal are believed to be arranged in the phenanthrene-type configuration.

Decalin, a saturated hydrocarbon, has been used to prepare coal extracts which closely resemble the original coal in ultimate analysis.

Tetralin, a hydroaromatic substance, is widely used in coal solubilization because of its hydrogen donor properties.

d. Experimental Reactor Configuration

For simplicity, considering the extreme temperatures and pressures involved in this coal liquefaction study, a batch reactor was selected. A continuous setup would be too elaborate and would lack the flexibility of a batch setup for an exploratory investigation of this nature.

2. Residual Cokes Gasification Program

a. Reaction Conditions

A temperature of 1000°F (538°C) and atmospheric pressure was selected for the present effort, since these were the reaction conditions used in a previous study at M.I.T. of the low temperature gasification of carbon (Tung, 1953).

b. Selection of Catalysts for Evaluation

Previous workers at M.I.T. have studied carbon gasification at 1000 to 1200°F using primarily potassium carbonate and acetate as catalysts (Hipkin, 1951; Tung, 1953). The present study, intended to determine if the residual cokes from the liquefaction experimental programs would gasify at a practical rate at 1000°F, selected also as catalysts these potassium salts and for comparative purposes, the salts of cesium, another alkali metal.

c. Experimental Reactor Configuration

A vertically mounted tubular reactor containing a fixed bed of the residual coke and operating with a constant steam flow in the downflow mode was selected for this study, primarily because it is a facile system to construct and operate.

III. LIQUEFACTION

A. APPARATUS AND PROCEDURE, LIQUEFACTION RUNS

1. Description of Liquefaction Equipment

The liquefaction setup built and operated in this study is shown schematically in Figure 20. Details of the reactors and the rocker assembly appear in Appendix I. All of the equipment with which the process streams came into contact were stainless steel type 316, nickel or silver.

Reactions were carried out batchwise in a high pressure reactor agitated about its axis in a rocker assembly. The working volume of the reactor was approximately 100 to 150 milliliters. The reactor was heated electrically by a mantle type heater; temperature was monitored by a Chromel-Alumel thermocouple inserted in a thermowell extending to near the bottom of the reactor. The rate of heatup of the reactor was regulated by a Variac. Another Chromel-Alumel thermocouple inserted in a second thermowell served as the control thermocouple, or sensing element, for a West temperature controller. The reactor was completely insulated with asbestos and fiberglass. Calibrated Bourdon tube type pressure gauges were used to measure the reactor pressures.

For alkali-coal runs, a nickel-lined reactor was designed and built. This reactor is also shown in Appendix I.

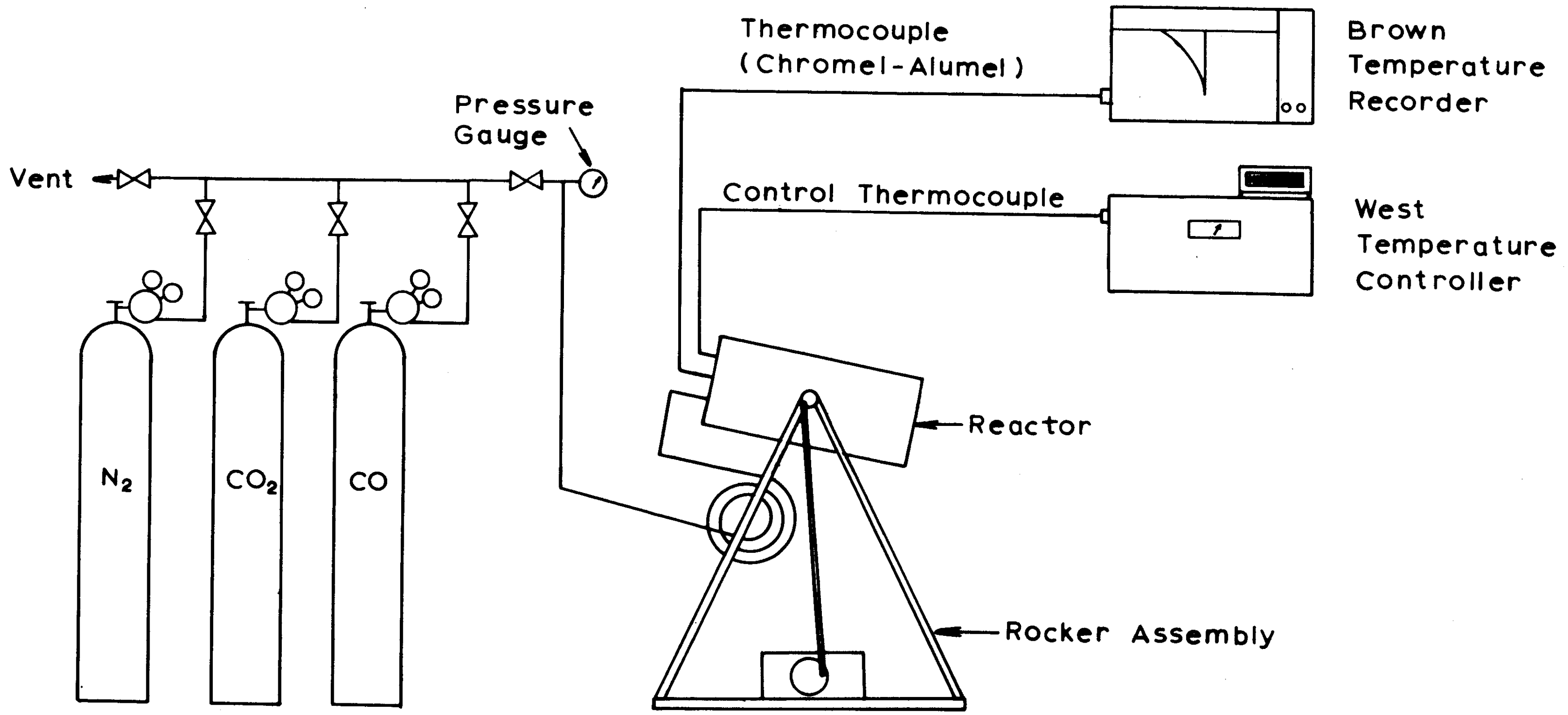


Figure 20 Diagram of Batch Reactor for Coal Liquefaction

The degree of agitation of the coal-water slurry was checked visually in a Lucite model of the reactor mounted in the rocker assembly. Agitation of the slurry in the ranges 30 to 75 RPM was very good.

Valves and fittings used in the setup were of the standard high pressure type; either Swagelok or Autoclave Engineers Ermeto fittings. Tubing was either 1/8 or 1/4 inch O.D.

2. Experimental Procedures for Liquefaction Runs

a. Preliminary

Before each run the reactor was thoroughly cleaned using stainless steel wool pads, a brush and detergent. After several distilled water rinses, the reactor was dried using acetone. The service lines to the reactor were blown clear with nitrogen.

b. Charging the Reactor

Approximately 30.1 grams of previously dried powdered coal, particle size less than 60 mesh, were weighed onto tared glassine paper using a Mettler analytical balance type 115, having an accuracy of ± 0.0002 grams. After transferring the coal powder to the reactor, the glassine paper was reweighed. Catalyst, if used, was added after the coal using the same weighing procedure. All nonpowder catalysts were ground in a mortar and pestle. A spatula was used to blend the coal and catalyst in the reactor. The desired quantity of polycyclic hydrocarbon was then added either by volume or in the case of phenanthrene, by weight. Water was measured by using a graduated cylinder.

c. Reassembly

Before installing the cover on the reactor, a stainless steel 100 mesh screen was fastened with nickel wire to the open end of the gas addition line which protruded through the cover and 1 $^{1}/2$ inches into the reactor. This screen prevented backup of solids from the reactor into the service line and ensured that no solids were lost from the reactor during the run.

The reassembly procedure was as follows:

1. Install gasket and cover.
2. Clean and lubricate cap screws.
3. Insert screws in the body. Finger tighten the cap screws. Tighten the opposed screws to $^{1}/4$ of desired torque. Continue with 1/4 increments of the final torque.

After reassembling, the reactor was inserted into the heating mantle permanently mounted on the cradle of the rocker assembly. The gas service line was then reconnected.

d. Pressure Test and Purging

The unit was then pressure tested at 1500 psi using nitrogen. If no drop in the pressure was observed in 15 minutes, the unit was then purged 5 times via a repeated vent and pressurize procedure using 1500 psi nitrogen. This was done slowly so as not to lose any material from the reactor. After the final purge, about 1 to 2 psig of nitrogen was sealed into the reactor, or if prescribed, the reactor was pressurized with nitrogen or another gas, such as carbon monoxide or carbon dioxide.

e. Heatup

After the purge, the insulation cover was clamped on and additional fiberglass insulation packed around exposed tubing. The two Chromel-Alumel thermocouples were inserted into the thermowells. Rocking was then commenced at the desired RPM, usually 60 RPM. The Variac controlling the heater was switched on and the heatup cycle commenced. When the temperature of the reactor reached about 20°C below the desired reaction temperature, control of the heater was turned over to a West temperature controller which brought the unit to the desired temperature without appreciable overshoot. Normally the heatup time was about 60 to 90 minutes depending on the temperature level desired.

f. Reaction Cycle

With the aid of the temperature controller the reactor was held at the desired temperature within ±2°C for the prescribed time period. During both the heatup and reaction cycles the reactor temperature and pressure were measured and recorded. The time at which the reactor temperature reached the desired temperature was considered to be the start of the reaction cycle.

g. Cooldown

At the end of the reaction cycle, the heater was turned off and the reactor allowed to cool while continuing the rocking. The cooldown to ambient temperature required several hours.

h. Venting and Disassembly

When the reactor was cool, the agitation was stopped and the vent valve very slowly opened to vent the excess pressure. The service line was disconnected; the reactor was removed from the heater and placed in a vise for opening.

i. Product Removal

The reactor contents were carefully transferred to a beaker. Essentially all the solids adhering to the walls and the thermowells, etc. were scraped into this beaker with the aid of spatulas and liberal use of benzene.

j. Solids Separation

After essentially complete transfer of solid residues from the reactor to the beaker, the liquids and solids were separated via a vacuum filtration operation. A 150 mm Pyrex fritted disc funnel, medium porosity was used. The solids, if lumpy, were pulverized on the filter. After three benzene washes, the solids were sucked dry overnight on the filter.

k. Extraction of Benzene Solubles

A Soxhlet extraction apparatus was used to contact hot benzene with the dry carbonaceous residues. The dry coke was transferred from the filter funnel to a previously tared Soxhlet extraction thimble, size 43 x 123 mm. The thimble, normally $^1/2$ to $^2/3$'s full with the solids, was placed in the extraction column and extraction with benzene carried out.

This extraction or leaching was carried out for at least sixteen hours and usually twenty-four hours. All the benzene solubles were leached from the coke during this time. Normally, after four hours of Soxhlet extractions, the benzene extract was almost colorless.

1. Determination of Benzene Solubles

The Soxhlet thimble with contents intact was removed from the Soxhlet apparatus and placed in a ventilated hood for air drying to a constant weight. Normally the drying operation required 24 hours. After drying, the thimble and contents were weighed and the amount of dry solids recovered calculated as the difference between this weight and the tare weight of the empty thimble. Knowing the weight of catalyst used, if any, and the starting weight of the dry coal, the percent conversion of coal to gaseous and liquid products was calculated by the following equation:

$$\%\ \text{Coal Conversion} = 100 \times \frac{\text{Weight of Coal Charge, g. minus Weight of Coke Recovered, g.}}{\text{Weight of Coal Charge, g.}}$$

3. Analytical Methods

a. Elemental Analysis

Elemental analyses were carried out on the starting coal and certain of the cokes by the Physical and Analytical Department of Merck & Co., Inc. Substances assayed for included carbon, hydrogen, nitrogen, sulfur, inorganics (ash) and by difference, oxygen. In addition, an elemental analysis was obtained on the benzene solubles obtained from a water-coal run.

b. Gas Phase Analysis by VPC

A vapor phase chromatographic assay was obtained on the gas phase using the same equipment described in the gasification section of Section III and in Appendix II.

B. PRESENTATION OF EXPERIMENTAL LIQUEFACTION RESULTS

1. Background

The primary objective of the liquefaction experimental program was to determine if water and coal would react at temperatures below 500°C to produce liquid and gaseous products amenable by further processing to desirable hydrocarbons (see Sections II-I, II-M). Since water is extremely nonreactive towards coal or carbon at these temperatures, a catalyst is necessary (see Section II-N). In addition, there are indications that an added liquid phase could facilitate the coal-water reactions (see Section II-N).

a. Description of Coal Used in Liquefaction Studies

The Pittsburgh Seam coal used in the liquefaction work, donated by the Consolidation Coal Company of Library, Pennsylvania, originated from the Ireland Mine in northern West Virginia. Table XII gives the ultimate analysis of this bituminous coal. The ten pound sample of coal supplied, consisting of particles less than sixty mesh, had been thoroughly blended to eliminate inhomogeneities.

b. Catalysts

Various heterogeneous catalysts possessing catalytic functions deemed desirable for promoting the water-coal reactions were tested for effectiveness in the water-coal and the water-coal-polycyclic hydrocarbon systems. These included catalysts possessing one or more of

TABLE XII

ULTIMATE ANALYSIS OF IRELAND MINE COAL[*]

	Weight Percent (Dry Basis)
Carbon	66.05
Hydrogen	4.45
Nitrogen	1.15
Sulfur	4.67
Ash	12.32
Oxygen (by difference)	11.36
Atomic H/C	0.803

[*] Analyses performed by the Physical and Analytical Department of Merck & Co., Inc.

the following functions (see Appendix IV for complete descriptions).

1. Hydrogenation/dehydrogenation
2. Fischer-Tropsch synthesis
3. Methanation
4. Cracking
    (a) Carbon-carbon bond
    (b) Hydrocracking
    (c) Hydrodesulfurization
    (d) Hydrodenitrogenation
5. Hydration/dehydration
6. Carbon oxides interchange

c. Added Liquid Phase

The possible synergistic effects of three polycyclic hydrocarbons on the water-coal system were evaluated. These polycyclic hydrocarbons were:

1. Phenanthrene, an aromatic compound; known to solubilize coal at temperatures in the range 350 to 450°C.
2. Decahydronaphthalene (Decalin), a saturated hydrocarbon; solubilizes coal to a moderate extent by a hydrogen donor type mechanism.
3. Tetrahydronaphthalene (Tetralin), a hydroaromatic compound; an effective agent for coal liquefaction via a hydrogen donor type mechanism.

Physicochemical properties and sources of the polynuclear compounds used in this study are listed in Appendix IV. The Decalin used was a mixture of the _cis_ and _trans_ isomers.

For the reasons listed below, the effects of various solid catalysts on the extent of coal solubilization were studied more extensively in the Decalin-water-coal system than in any of the other systems. The reasons for this emphasis were:

a. Decalin was preferred over Tetralin because the extent of solubilization with Tetralin is so high that effects due to added water would be more difficult to ascertain.

b. Decalin was preferred over phenanthrene for ease of handling, particularly at the end of the reaction. Decalin is a liquid at room temperature, while phenanthrene is a solid. The reactor residues after a phenanthrene run were set solid in the reactor and had to stand with benzene for hours before the residues could be removed.

c. Decalin-water mixtures were preferred over water alone because the former mixture offered the potential for more intimate contact between coal, water and the catalyst.

d. <u>Experimental</u> (For complete description see Section III-A)

All the experiments were carried out in a batch fashion, using a high pressure reactor or autoclave; the autoclave was agitated about its axis by a rocker assembly. Normally, the experiments were carried out for two hours after the reactor had reached temperature; i.e., the two-hour reaction time does not include heatup and cool-down times. Longer reaction times, up to five hours, did not affect the extent of coal conversion significantly; reaction times of about one half hour showed a decrease of 2 to 5 percentage points in coal conversion.

Before the start of the runs air was eliminated from the reactor by a nitrogen pressurization-purge sequence. This procedure was followed as a precautionary measure to ensure that the inherent reactivity of the coal would not be adversely affected by oxidation. Either nitrogen, carbon dioxide, or carbon monoxide was the gas phase present in the reactor at the start of the heatup cycle.

After a run, the solid residues were separated by filtration from the liquids and extracted exhaustively with hot benzene in a Soxhlet extracter. The extracted solid residue was then air dried and weighed. If catalyst was used, the weight of the residue was corrected for the catalyst weight (blank runs without coal were made to determine if the catalyst lost or gained weight under reaction conditions).

The coal conversion has been defined as (see Section III-A):

$$\% \text{ Coal Conversion} = \frac{\text{Coal Charge, g minus Dry Extracted Residue, g}}{\text{Coal Charge, g}} \times 100$$

Coal conversion as defined is thus a measure of the amount of liquid and gaseous products produced during the reaction period. Except for the coal and coal-water runs, the amount of gaseous products produced was almost nil. The recovered residues are not to be considered unreacted coal but a char or coke. In any event, unreacted coal could not be distinguished from reacted coal. These residues have probably all undergone substantial reaction such as cracking followed by polymerization and crosslinking and may even be condensation products of reactive fragments of coal which at some time during the reaction were present in the liquid state.

Soxhlet extraction of "as is" samples of the Ireland Mine coal showed about 0.92% coal conversion.

2. Tabulation of Liquefaction Experiments

The experiments comprising this study of the water-coal system have been grouped into six series; a brief description of each series follows.

The Series I experiments were carried out to determine the action of water on Ireland Mine coal. The effects of the following variables on coal conversion to liquid and gaseous products were explored:

(1) Temperature
(2) Pressure
(3) Reaction time
(4) Water to coal ratio

Heterogeneous catalysts were added to certain of these runs. The earliest Series I experiments served to determine operating characteristics of the equipment and to develop experimental procedures.

The experiments of Series II involved first introducing phenanthrene into the water-coal system and then various heterogeneous catalysts.

The next experimental series, Series III, studied the Decalin-water-coal system with and without various heterogeneous catalysts.

The effect of Tetralin on the water-coal system, again with and without added catalysts, was determined in the Series IV experiments.

The effect of alkali metal compounds on the water-coal system with and without phenanthrene present was studied in the Series V experiments.

The characteristics of the recently reported coal hydrogenation process by the U.S. Bureau of Mines involving carbon monoxide and water were briefly explored in the Series VI runs.

TABLE XIII

TABULATION OF WATER-CATALYST-COAL EXPERIMENTS

		Reactants(1)		Initial Gas & Pressure in Reactor		Reaction Conditions(3)			
			Catalyst(2)						
Series	Run No.	Water Volume (ml)	1. Name 2. Principle Function	Gas	Pressure (psig)	Temp. (°C)	Pressure (psig)	Time (hours)	Coal Conversion (% w/w)
Ia	42	0	None	N_2	1 to 2	400	220	2	11.4
	49	0	None	N_2	1 to 2	420	210	2	6.6
Ib	25	40	None	N_2	1 to 2	382	2000	2	15.4
	26	40	None	N_2	1 to 2	395	2000	2 3/4	17.8
	27	40	None	N_2	1 to 2	418	2800	2	7.8
	39	40	None	N_2	1 to 2	376	2200	2	15.4
	40	40	None	N_2	1 to 2	401	2700	2	15.8
	41	40	None	N_2	1 to 2	356	1900	2	11.3
	43	70	None	N_2	1 to 2	364	2900	2	11.0
	44	70	None	N_2	1 to 2	385	3300	2	16.4
	45	70	None	N_2	1 to 2	407	4000	2	15.9
	50	100	None	N_2	1 to 2	393	4000	2	22.1
	54	100	None	N_2	1 to 2	416	4900	5	23.8
	55	100	None	N_2	1 to 2	417	4900	2	23.9

TABLE XIII (Cont'd)

		Reactants(1)		Initial Gas & Pressure in Reactor		Reaction Conditions(3)			
Series	Run No.	Water Volume (ml)	Catalyst(2) 1. Name 2. Principle Function	Gas	Pressure (psig)	Temp. (°C)	Pressure (psig)	Time (hours)	Coal Conversion (% w/w)
Ib	57	100	None	N_2	1 to 2	404	4750	2	25.9
	58	160	None	N_2	1 to 2	405	7100	2	26.4
	59	160	None	N_2	1 to 2	394	5000	2	20.4
	60	165	None	N_2	1 to 2	414	7150	0.2	23.6
	65	140	None	N_2	1 to 2	396	4500	2	20.2
	75	90	None	N_2	1 to 2	400	4000	2	20.8
	77	90	None	N_2	1 to 2	400	3900	2	18.8
	78	90	None	N_2	1 to 2	400	4100	2	17.8
	79	90	None	N_2	1 to 2	410	4200	2	19.9
	82	90	None	NO	200	403	4500	2	20.1
Ic	129	40	Cobalt Thoria Fischer-Tropsch	CO_2	600	418	5500	2	17.6
	130	40	Chromia Alumina Dehydrogenation	CO_2	600	420	5100	2	16.4
	131	140	Cobalt Molybdate on Alumina Removal of S,N,O	CO_2	600	426	4500	2	16.4

(1) 30 grams coal used in all listed Series I runs.
(2) 20% w/w catalyst (based on coal charge) used in Series Ic runs.
(3) Normal rocker speed was 60 RPM.

TABLE XIV

TABULATION OF PHENANTHRENE-WATER-CATALYST-COAL EXPERIMENTS

Series	Run No.	Phenanthrene Weight (grams)	Water Volume (ml)	Catalyst(4) 1. Name 2. Principle Function	Initial Gas & Pressure in Reactor		Reaction Conditions(6)			Coal Conversion (% w/w)
					Gas	Pressure (psig)	Temp. (°C)	Pressure (psig)	Time (hours)	
IIa(1)	4	10	0	None	N_2	1500	366	N. A.	2	15.0
	5	10	0	None	N_2	1500	390	N. A.	2	25.5
	6	10	0	None	N_2	1500	410	N. A.	1.75	10
	7	10	0	None	CO	1400	363	N. A.	2.5	8.3
	47	30	0	None	N_2	0	375	N. A.	2	17.9
IIb(2)	19	30	15	None	N_2	0	370	N. A.	2	17.5
	20	30	15	None	N_2	0	418	N. A.	2	21.0
	21	30	15	None	N_2	0	400	N. A.	2	15.4
	30	30	40	None	N_2	0	397	N. A.	2.25	22.0
	31	30	40	None	N_2	0	421	N. A.	2	30.7(7)
	32	30	40	None	N_2	0	385	N. A.	2	20.6
	61	30	100	None	N_2	0	405	N. A.	2	24.7

TABLE XIV (Cont'd)

Series	Run No.	Phenanthrene Weight (grams)	Water Volume (ml)	Catalyst[(4)] 1. Name 2. Principle Function	Initial Gas & Pressure in Reactor: Gas	Initial Gas & Pressure in Reactor: Pressure (psig)	Reaction Conditions[(6)]: Temp. (°C)	Reaction Conditions[(6)]: Pressure (psig)	Reaction Conditions[(6)]: Time (hours)	Coal Conversion (% w/w)
IIc(2)	33	30	40	Alumina Dehydration	N_2	0	402	N.A.	0.8	21.0
	34	30	40	"	N_2	0	417	N.A.	2	23.0
	35	30	40	Iron Oxide Dehydrogenation	N_2	0	408	N.A.	2	22.9
	36	30	40	Cobalt Molybdate on Alumina Hydrosulfurization	N_2	0	410	N.A.	2	22.6
	37	30	40	Cr promoted FeO Water Gas Shift	N_2	0	409	N.A.	1.7	24.0
	85	30	50	Cobalt on Kieselguhr Hydrogenation	N_2	0	425	N.A.	2.0	23.2
	93	30	50	Cobalt Molybdate on Alumina Hydrosulfurization	CO_2	1000	405	N.A.	2.25	22.3
IId(3)	23	30	0	None	N_2	0	384	N.A.	2	(5)
	24	30	0	None	N_2	0	415	N.A.	2	(5)

Notes for Table XIV:

(1) 10 grams coal used in Series IIa runs (except Run 47).

(2) 30 grams coal used in Series IIb and IIc runs and Run 47.

(3) No coal used in Series IId runs.

(4) 20% w/w catalyst (based on coal charge) used in Series IIc runs.

(5) No apparent phenanthrene decomposition occurred (no benzene insolubles observed after run; vapor phase chromatogram of phenanthrene before and after run indicated no new peaks).

(6) Normal rocker speed was 60 RPM.

(7) Mechanical Loss of 0.5 - 1 gram residue, true % C ≈ 27%.

TABLE XV

TABULATION OF DECALIN-WATER-CATALYST-COAL EXPERIMENTS

		Reactants(1)			Initial Gas & Pressure in Reactor		Reaction Conditions(5)			
				Catalyst(2)						
Series	Run No.	Decalin Volume (ml)	Water Volume (ml)	1. Name 2. Principle Function	Gas	Pressure (psig)	Temp. (°C)	Pressure (psig)	Time(4) (hours)	Coal Conversion (% w/w)
IIIa	80	60	0	None	N_2	1 to 2	403	1800	2	29.0
IIIb	81	60	60	None	N_2	1 to 2	403	4300	2	26.6
	91	60	62	None	CO_2	1000	394	8000	1.5	21.5
	97	60	50	None	N_2	1150	406	6100	2.25	28.0
	101	60	50	None	N_2	1 to 2	434	5200	1.8	32.4
	124	60	50	None	N_2	1 to 2	464	6000	2	34.0
IIIc	86	60	60	Cobalt on Kieselguhr Hydrogenation	N_2	1 to 2	404	4100	2	25.9
	89	60	50	Cobalt Molybdate on Alumina Removal of S,N,O	CO_2	1000	402	6200	2	32.3
	103	60	50	" "	N_2	1 to 2	425	5200	2	33.0
	112	60	50	" " (H_2S treated before use)	N_2	1 to 2	431	5100	2	33.5
	94	60	50	Cobalt Thoria Fischer-Tropsch	CO_2	1000	408	6200	2	31.4
	95	60	50	" "	N_2	1 to 2	405	6200	2	28.5

TABLE XV (cont'd)

		Reactants(1)			Initial Gas & Pressure in Reactor		Reaction Conditions(5)			
Series	Run No.	Decalin Volume (ml)	Water Volume (ml)	Catalyst(2) 1. Name 2. Principle Function	Gas	Pressure (psig)	Temp. (°C)	Pressure (psig)	Time(4) (hours)	Coal Conversion (% w/w)
IIIc	100	60	50	Cobalt Thoria Fischer-Tropsch	N_2	1 to 2	437	5500	1.8	34.2
	104	60	50	" " (Fired at 500°C before use)	CO_2	800	390	6900	2	17.6
	98	60	50	10% Ruthenium on Carbon Hydrogenation	CO_2	800	406	6300	2	30.2
	110	60	50	Chromia Alumina Dehydrogenation	CO_2	800	405	8100	2	35.4
	113	60	50	" "	N_2	1 to 2	431	5100	2	30.4
	118	60	40	" "	CO_2	700	375	5500	2	14.5
	127	60	50	" "	CO_2	700	389	5800	2	20.1
	99	60	50	Tungsten on Alumina Dehydration	CO_2	800	406	6800	2	26.0
	116	60	50	Phospho Tungsten Dehydrogenation	N_2	1 to 2	431	5200	2	30.5
	120	60	40	Cobalt Molybdate on Alumina Removal of S,N	CO_2	700	420	7500	2	33.1
	122	60	40	Chrome Aluminum Phosphate Dehydrogenation	CO_2	700	420	7700	0.8	29.1
	123	60	50	" "	N_2	1 to 2	424	4800	2	33.8

TABLE XV (cont'd)

		Reactants(1)			Initial Gas & Pressure in Reactor		Reaction Conditions(5)			
Series	Run No.	Decalin Volume (ml)	Water Volume (ml)	Catalyst (2) 1. Name 2. Principle Function	Gas	Pressure (psig)	Temp. (°C)	Pressure (psig)	Time(4) (hours)	Coal Conversion (% w/w)
				Chromium promoted iron oxide.						
IIIc	111(3)	60	50	Cobalt Molybdate on Alumina Molybdic oxide Chromia Alumina	CO_2	900	405	8800	2	30.7
	127	60	50	Chromia Alumina Dehydrogenation	CO_2	710	389	5600	2	20.1
	136	60	40	Nickel Tungsten on Silica-Alumina Hydrocracking and Removal of S & N	N_2	1 to 2	415	3700	2	24.5
	137	60	40	Nickel Tungsten on Alumina Hydrogenation, Removal of S& N	N_2	1 to 2	412	4000	2	32.3
	138	60	40	Nickel Tungsten on Acidified Alumina. Mild cracking and Removal of S & N	N_2	1 to 2	411	3800	2	30.8

TABLE XV (cont'd)

		Reactants(1)			Initial Gas & Pressure in Reactor		Reaction Conditions(5)			
Series	Run No.	Decalin Volume (ml)	Water Volume (ml)	Catalyst(2) 1. Name 2. Principle Function	Gas	Pressure (psig)	Temp. (°C)	Pressure (psig)	(4) Time (hours)	Coal Conversion (% w/w)
IIIc	139	60	40	Nickel Tungsten on Silica Alumina Hydrocracking and Removal of S & N	CO_2	780	416	6700	2	28.1
	140	60	40	Nickel Tungsten on Acidified Alumina Mild Cracking and Removal of S & N	CO_2	750	414	5700	2	28.4
	141	60	40	Chromia Alumina Dehydrogenation	CO_2	600	404	5500	2	26.9
	142	60	40	Silica-Alumina Cracking	N_2	1 to 2	416	3800	2	25.9
	145	60	50	Nickel Tungsten on Alumina. Hydrogenation Removal of S & N	N_2	1 to 2	414	4000	2	27.6

(1) 30 grams coal used in all listed Series III runs.
(2) 20% w/w catalyst (based on coal charge) used in Series IIIc, except Run 111.
(3) Run 111, 6.6% w/w of each of the 4 listed catalysts (based on coal charge).
(4) Reaction time does not include heatup and cooldown times.
(5) Normal rocker speed was 60 RPM.

TABLE XVI

TABULATION OF TETRALIN-WATER-CATALYST-COAL EXPERIMENTS

		Reactants(1)			Initial Gas & Pressure in Reactor		Reaction Conditions(4)			
Series	Run No.	Tetralin Volume (ml)	Water Volume (ml)	Catalyst(2) 1. Name 2. Principle Function	Gas	Pressure (psig)	Temp. (°C)	Pressure (psig)	Time(3) (hours)	Coal Conversion (% w/w)
IVa	105	60	0	None	N_2	1 to 2	412	1000	2	67.2
	115	60	0	None	N_2	1 to 2	419	400	2	65.9
IVb	106	60	50	None	N_2	1 to 2	412	N.A.	2	59.9
	125	60	40	None	N_2	1 to 2	420	3750	2	63.0
	126	60	50	None	N_2	1 to 2	405	3650	2	57.3
	134	60	38	None	N_2	1 to 2	455	4800	2	59.1
	135	60	40	None	N_2	1 to 2	442	4500	2	59.8
IVc	107	60	50	Cobalt Molybdate on Alumina Removal of S,N.O	N_2	1 to 2	407	4600	2	49.1
	109	60	50	G-66^{B} Water-gas shift	N_2	1 to 2	410	4600	2	48.4
	114	60	50	Chromia Alumina Dehydrogenation	N_2	1 to 2	418	5000	2	50.9

(1) 30 grams coal used in all listed Series IV runs.

(2) 20% w/w catalyst (based on coal charge) used in Series IVc runs.

(3) Reaction time does not include heatup and cooldown times.

(4) Normal rocker speed was 60 RPM.

TABLE XVII

TABULATION OF PHENANTHRENE-WATER-ALKALI COMPOUND-COAL EXPERIMENTS

		Reactants(1)			Initial Gas & Pressure in Reactor		Reaction Conditions(2)			
Series	Run No.	Phenanthrene Weight (grams)	Water Volume (ml)	Alkali and Concentration	Gas	Pressure (psig)	Temp. (°C)	Pressure (psig)	Time (hours)	Coal Conversion (% w/w)
V	62	30	100	1.08 m KOH	N_2	1 to 2	415	N.A.	2	36.8
	68	30	100	1.09 m KOH	N_2	1 to 2	397	N.A.	2	35.1
	71	30	100	1.92 m KOH	N_2	1 to 2	395	N.A.	2	43.8
	72	30	85	0.58 m KOH	N_2	1 to 2	396	N.A.	2	32.2
	70	30	100	1.07 m NaOH	N_2	1 to 2	399	N.A.	2	33.6
	63	30	100	0.6 m KOAc	N_2	1 to 2	384	N.A.	2	29.4

(1) 30 grams coal used in all listed Series V runs.

(2) Normal rocker speed was 60 RPM.

TABLE XVIII

TABULATION OF PHENANTHRENE-WATER-CARBON MONOXIDE-CATALYST-COAL EXPERIMENTS

		Reactants(1)				Reaction Conditions(2)			
				Catalyst					
Series	Run No.	Phenanthrene Weight (grams)	Water Volume (ml)	1. Name 2. Principle Function	CO Pressure (psig)	Temp. (°C)	Pressure (psig)	Time (hours)	Coal Conversion (% w/w)
VI	9	10	5	None	1400	395	3200	2	52.9
	10	10	5	None	1600	425	3500	2	56.7
	38	30	40	Chromium promoted iron oxide water-gas shift	1350	407	3550	2	68.1

(1) 30 grams coal used in all listed Series VI runs.

(2) Normal rocker speed was 60 RPM.

3. Presentation of Experimental Liquefaction Results

The significant experimental liquefaction results are presented in the Figures 21 to 28 and Tables XIX and XX. Appendix IV lists the sources of the chemicals used. See Table XII for description of coal used.

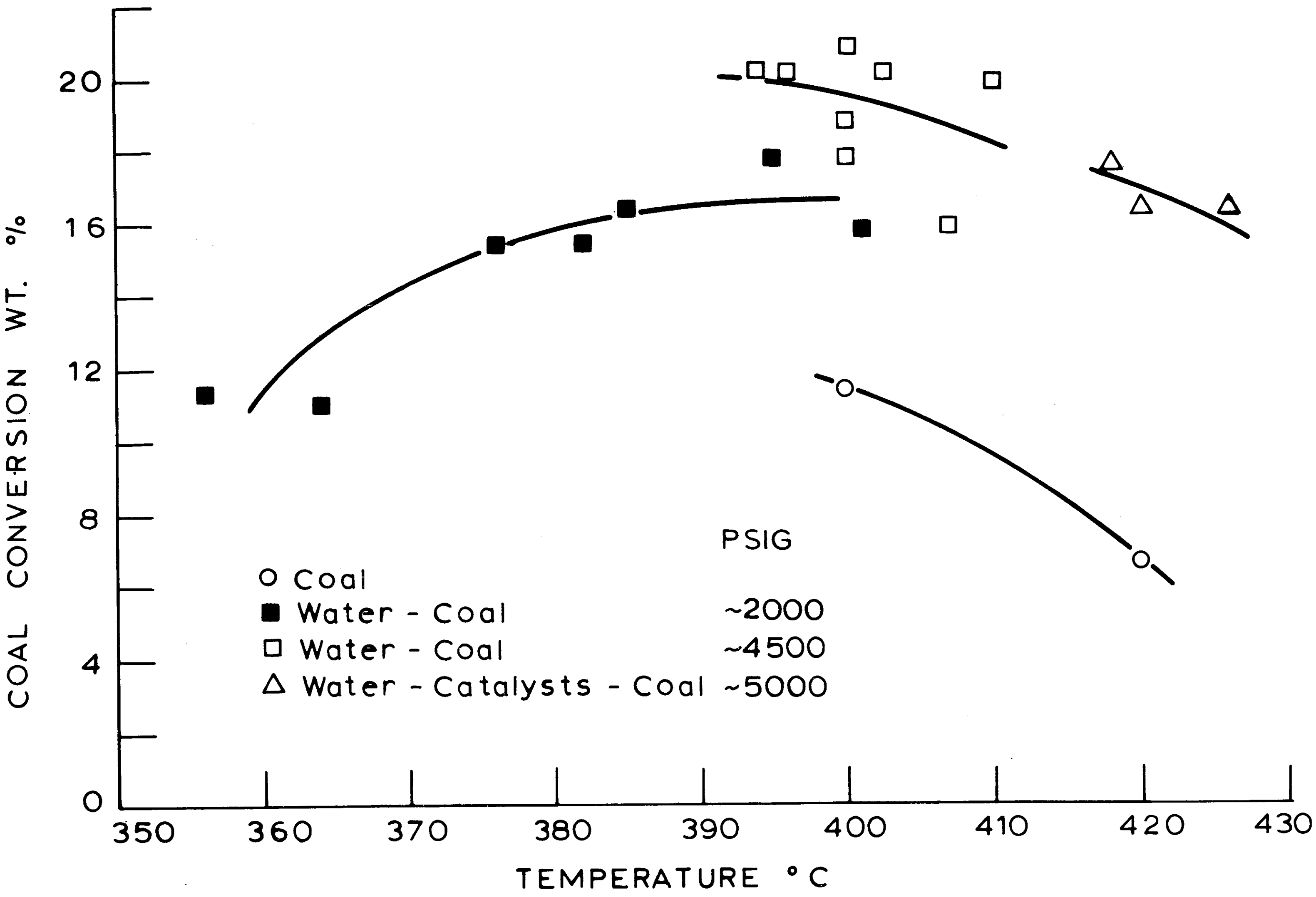


Figure 21 Effect of Temperature on Coal Conversion in Water - Catalyst - Coal Systems

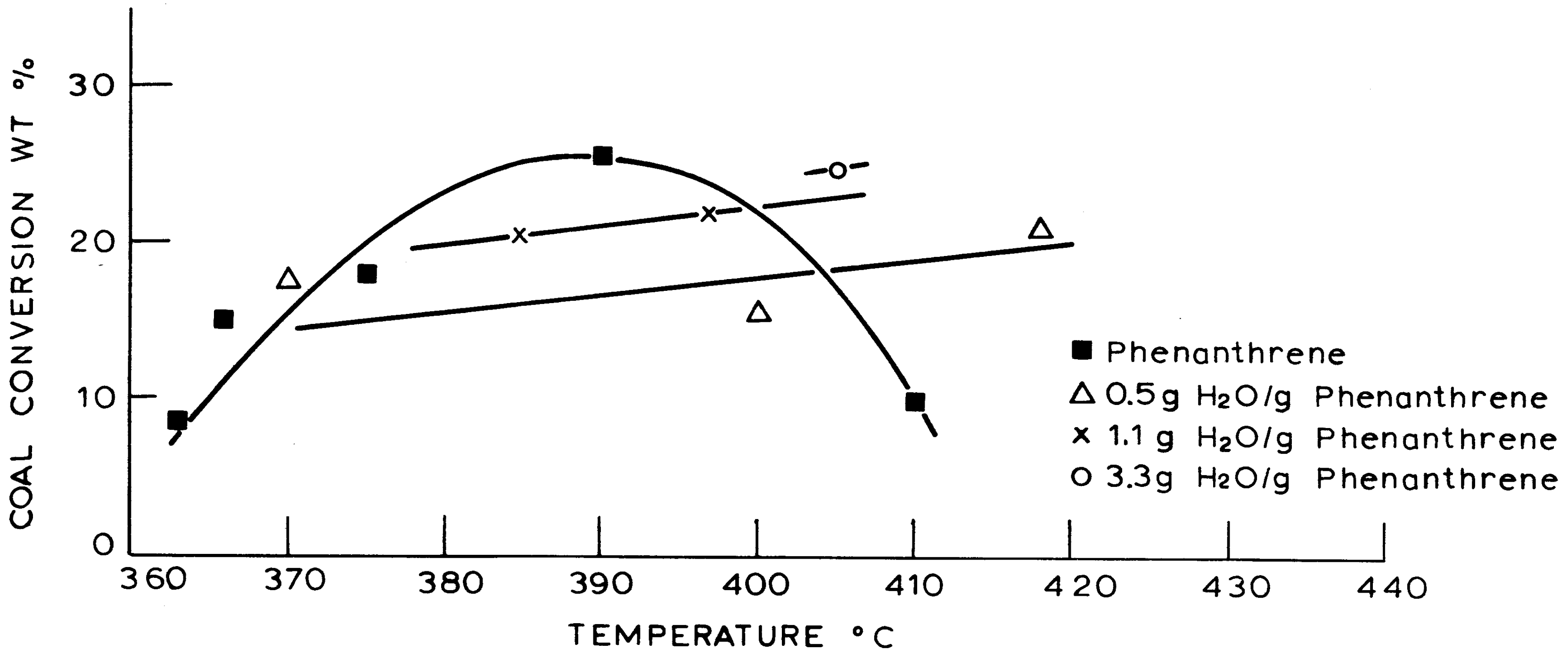


Figure 22 Effect of Temperature on Coal Conversion in Phenanthrene - Water - Coal Systems

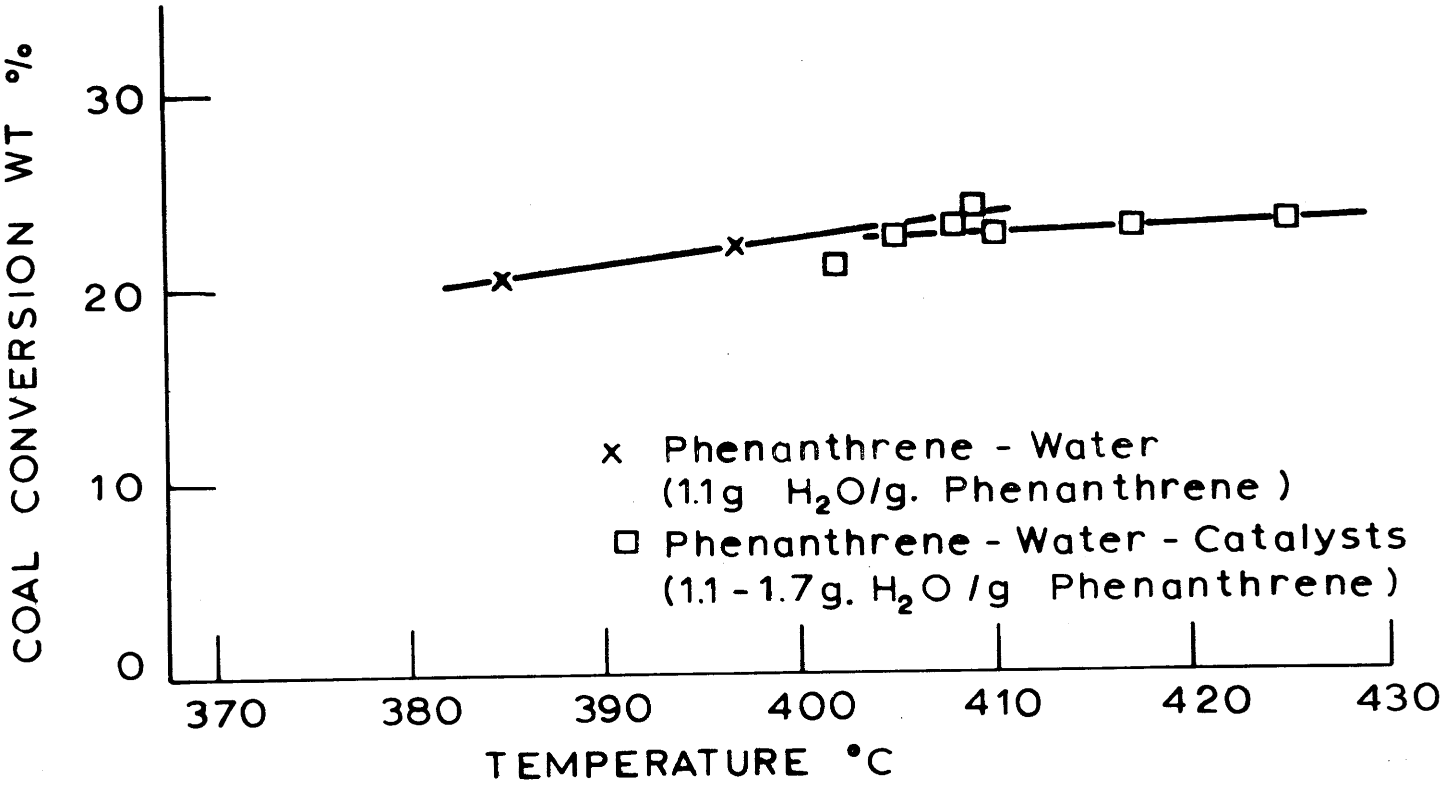


Figure 23 Effect of Temperature on Coal Conversion in Phenanthrene - Water - Catalyst - Coal Systems

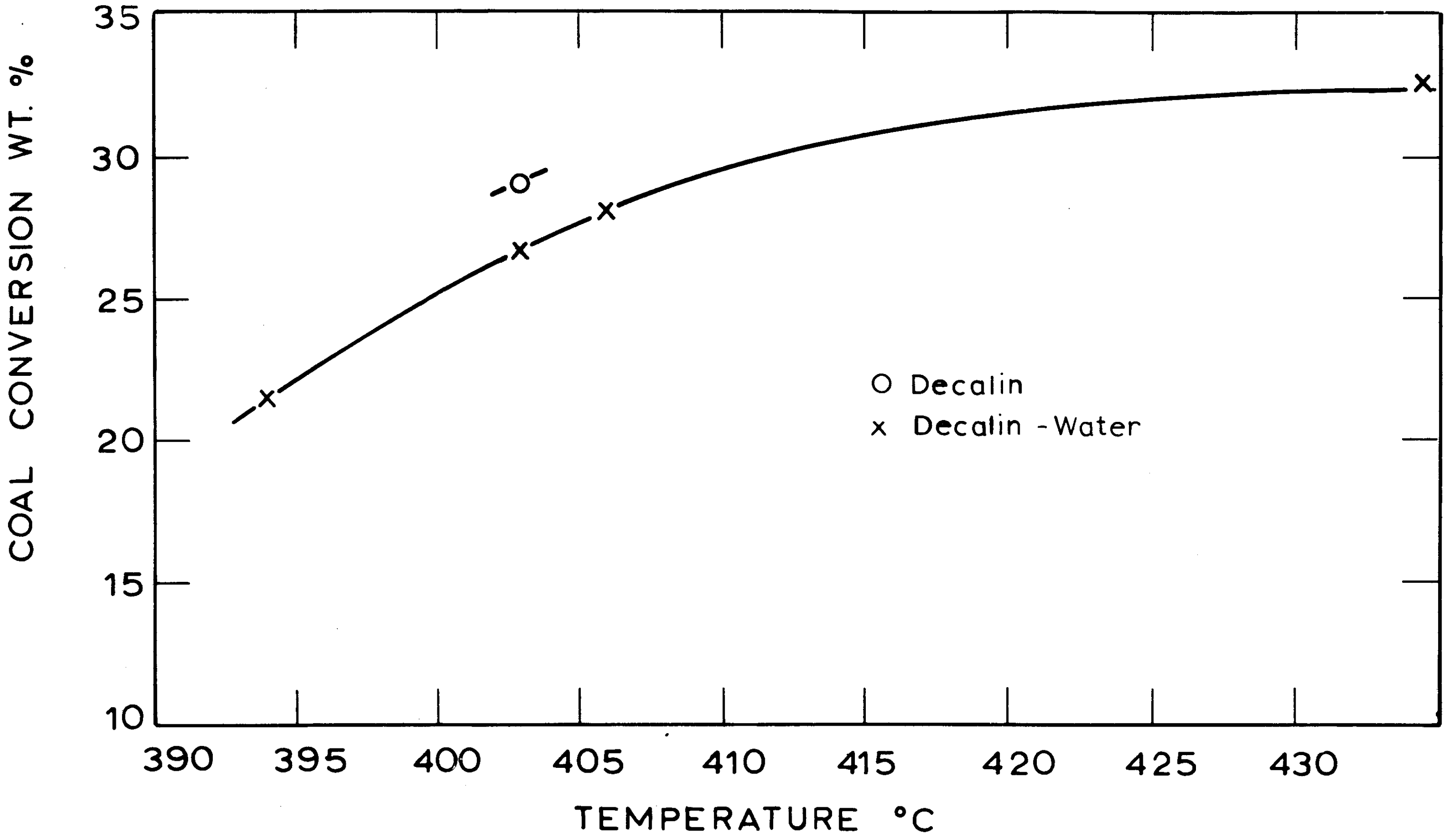


Figure 24 Effect of Temperature on Coal Conversion in Decalin - Water - Coal Systems

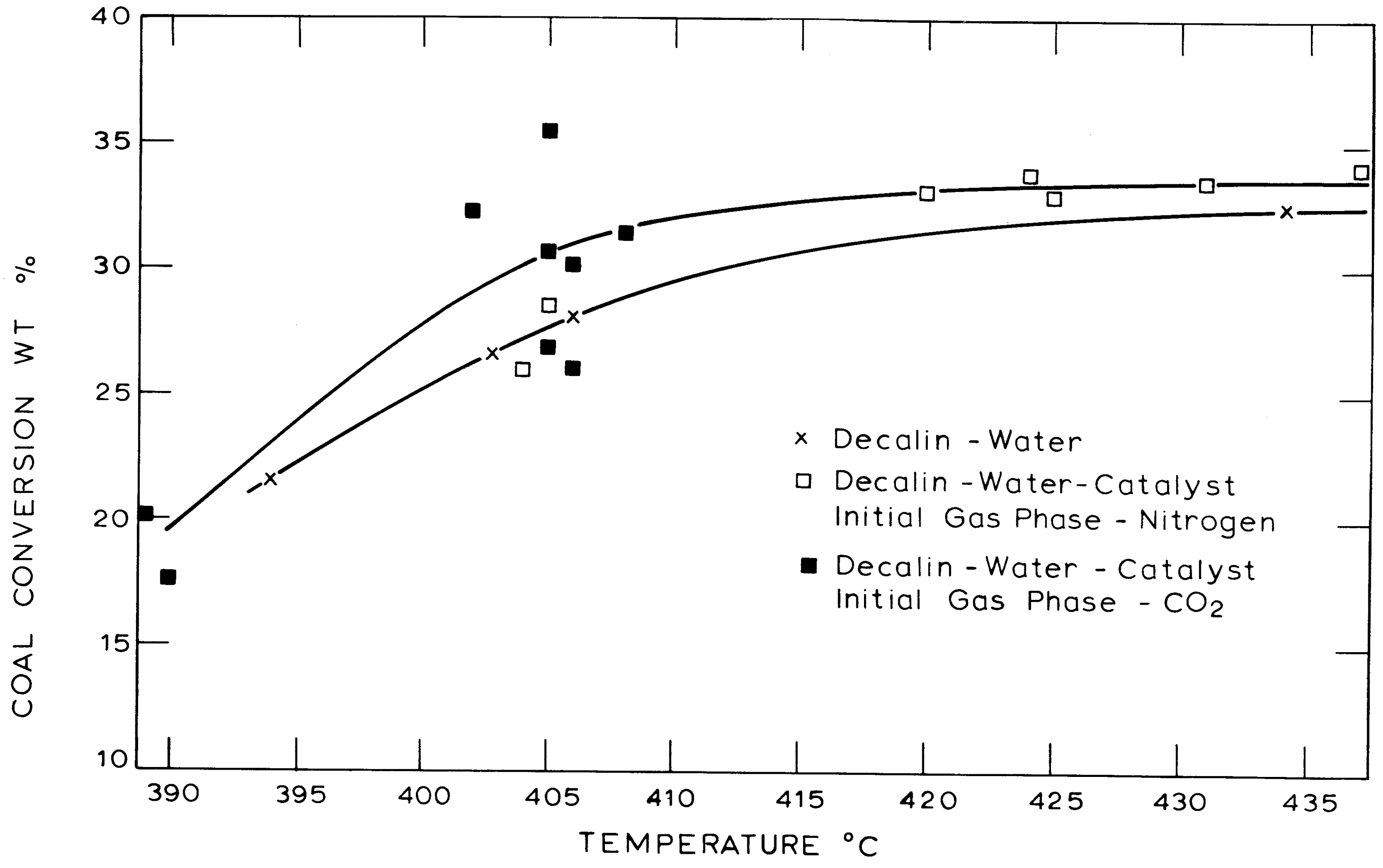


Figure 25 Effect of Temperature on Coal Conversion in Decalin - Water Catalyst - Coal Systems

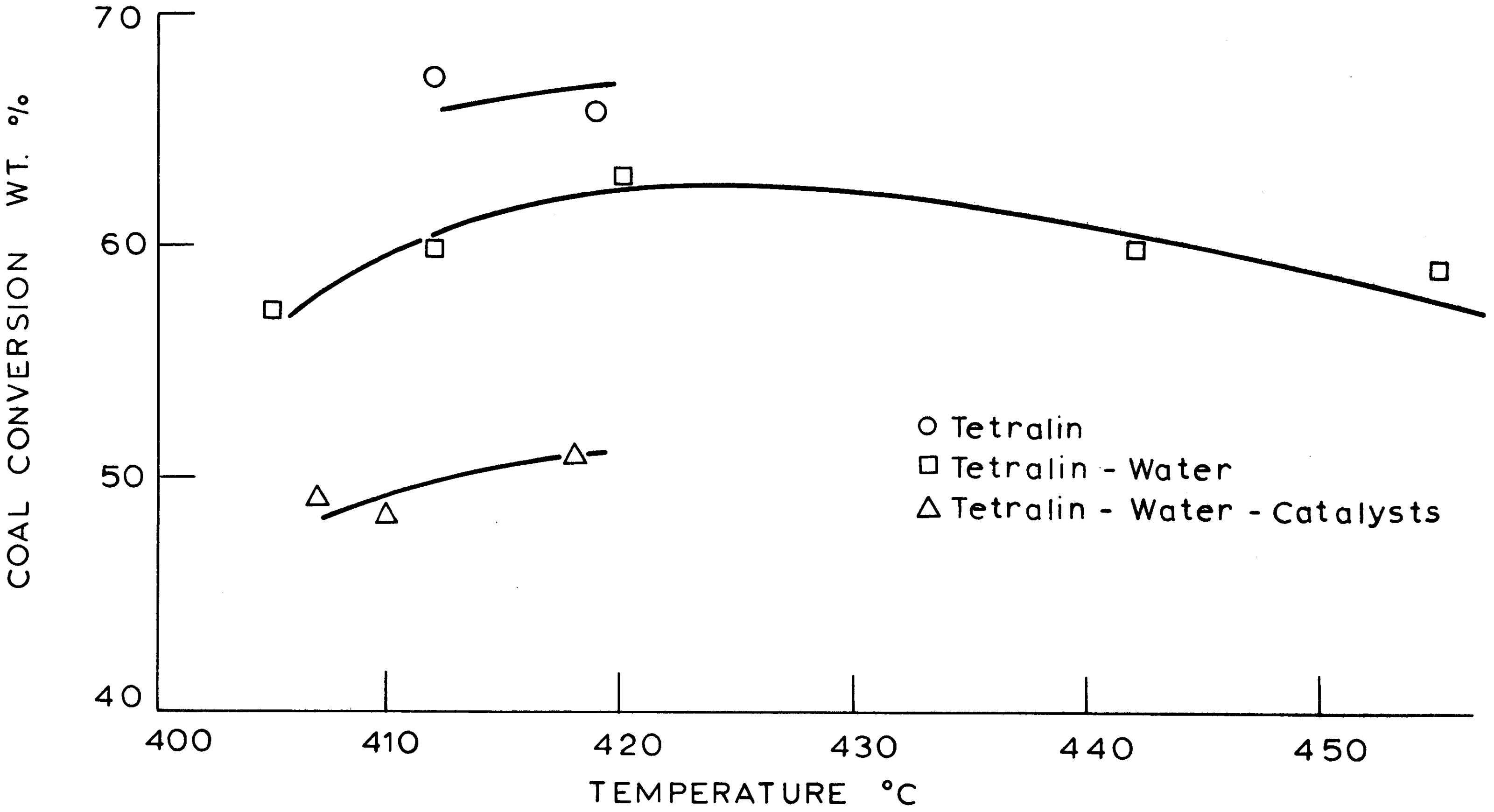


Figure 26 Effect of Temperature on Coal Conversion in Tetralin - Water - Catalyst - Coal Systems

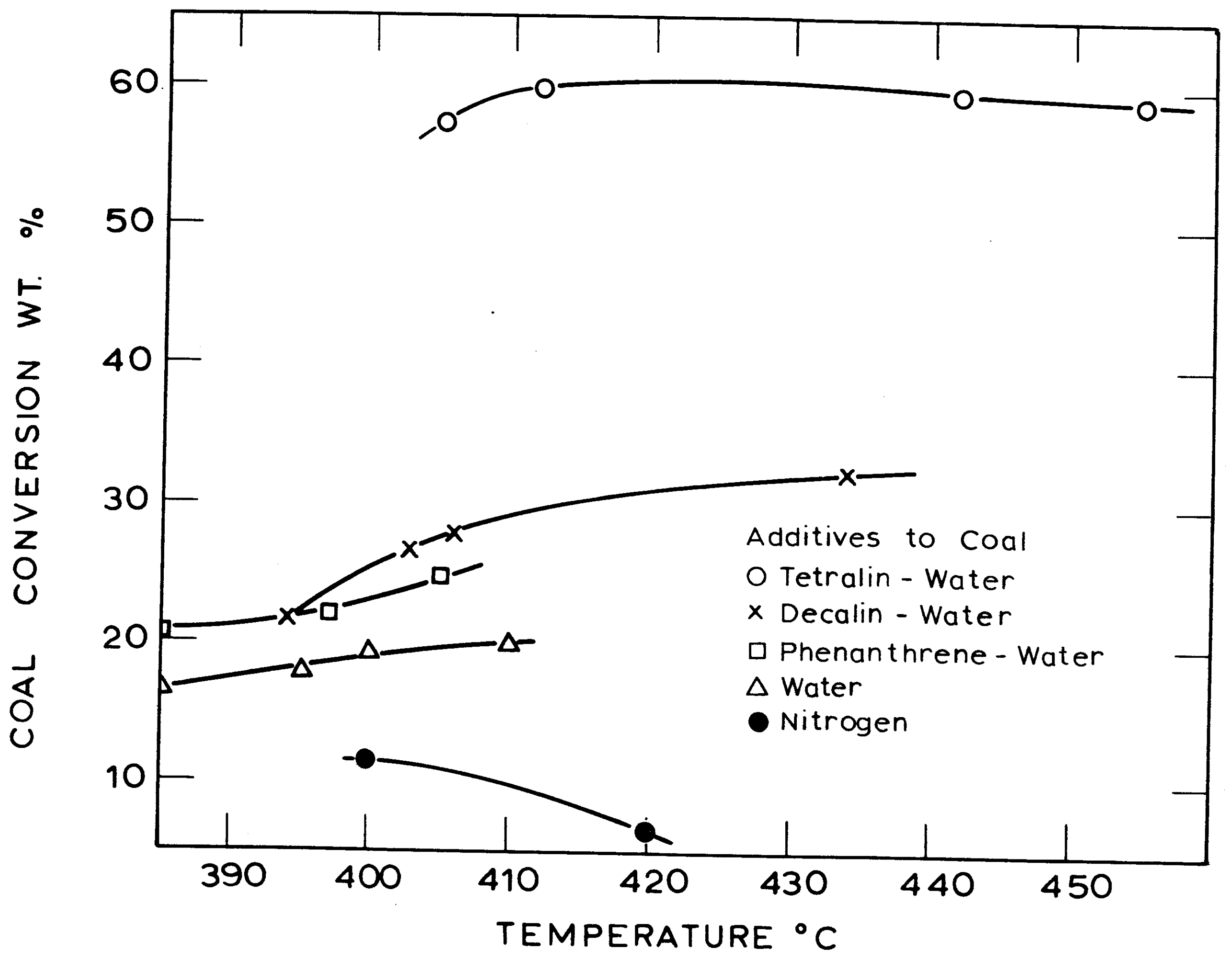


Figure 27 Effect of Water and Polycyclic Hydrocarbons on Coal Conversion

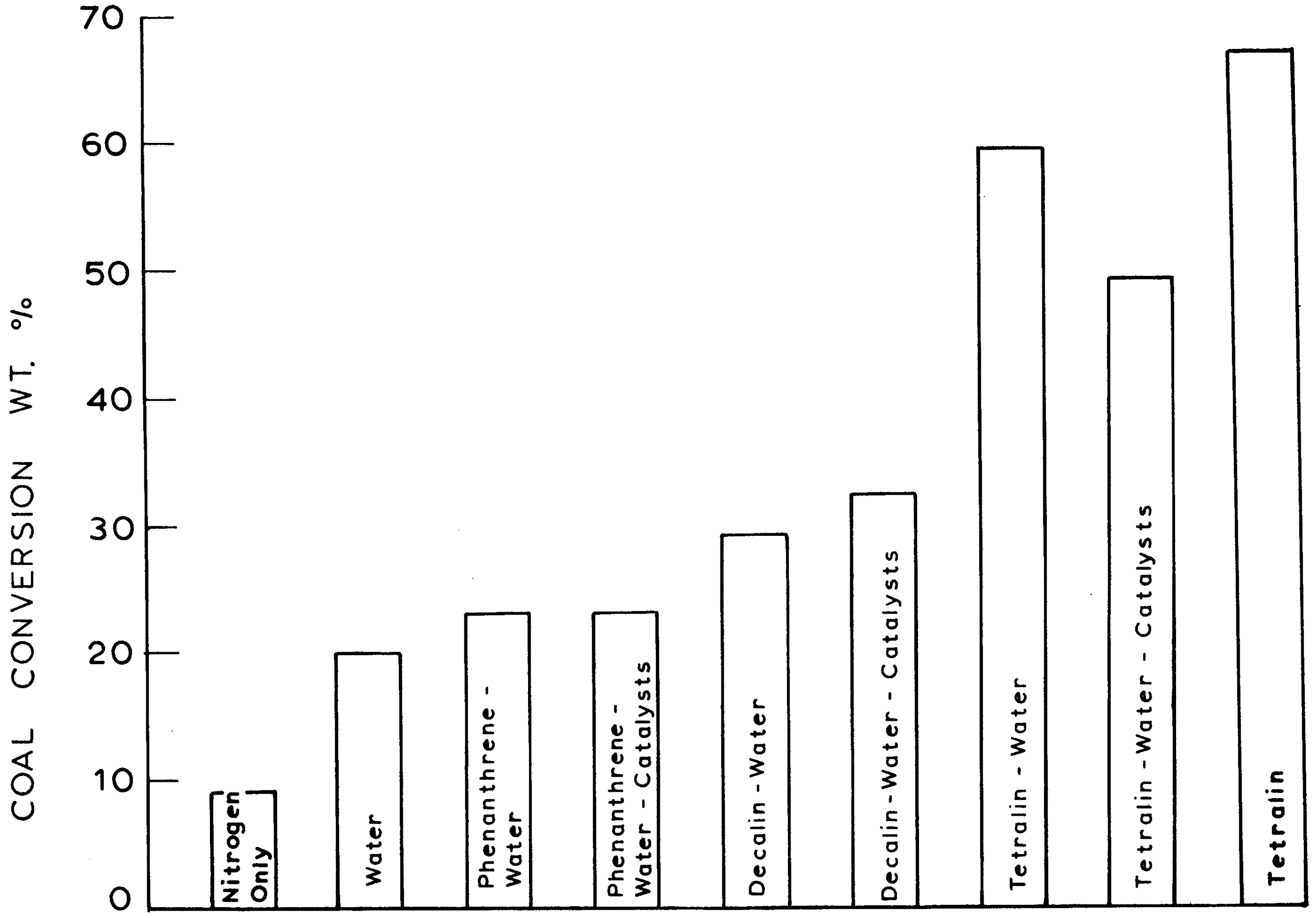


Figure 28 Effect of Water, Polycyclic Hydrocarbons and Heterogeneous Catalysts on Coal Conversion at 410°C

TABLE XIX

ULTIMATE ANALYSES OF TYPICAL COKES ‡

(Wt. %)

	Original Coal	Cokes				
		Water (Run 59)	Phenanthrene-Water (Run 61)	Decalin (Run 80)	Decalin-Water (Run 91)	Tetralin-Water (Run 105)
C	66.05	67.80	69.14	67.39	66.35	48.13
H	4.45	3.66	3.03	3.24	3.16	2.30
N	1.15	0.95	1.17	1.17	1.01	1.02
S	4.67	3.99	3.44	2.52	4.00	6.49
O (by difference)	11.36	9.27	9.74	6.89	9.45	4.50
Ash	12.32	14.33	13.48	18.79	16.03	37.56
Atomic H/C	0.803	0.64	0.52	0.573	0.57	0.57

‡ Analysis performed by the Physical & Analytical Department, Merck & Co., Inc., Rahway, N. J.

TABLE XX

CALCULATED COMPOSITIONS OF COAL-DERIVED OILS [‡]

(Wt. %)

	Oils (Calculated)				
	Water (Run 59)	Phenanthrene-Water (Run 61)	Decalin (Run 80)	Decalin-Water (Run 91)	Tetralin-Water (Run 105)
C	59.2	56.7	62.7	65.0	74.8
H	7.6	8.7	7.5	9.2	5.5
N	1.9	1.1	1.1	1.7	1.2
S	7.3	8.4	10.0	7.1	3.8
O (by difference)	19.6	16.3	22.4	18.4	14.7
Ash	4.4	8.8	-	-	0
Atomic H/C	1.52	1.84	1.42	1.68	0.88

[‡] By material balance using ultimate analysis of coal (Table XII) and coke (Table XIX) with the reported coal conversion (Tables XIII to XVI). This calculation assumes no hydrogen is donated by the added liquids which is known not to be the case with Tetralin and to a lesser extent with Decalin.

4. General Accuracy and Reproducibility

a. Coal

The homogeneity of the coal supplied, often a major source of error, was checked by ashing aliquots from various layers in the drum. The percent ash from four samples agreed with ± 3%.

Other sources of error, besides the coke removal from the reactor, which is discussed below for the individual systems, are the general experimental techniques of weighing, and whether or not the coke was completely extracted or completely dried. Weighings were carried out on a Mettler balance (see Section III-A) to the nearest thousandths although conversions were reported to the nearest tenth. Only transfers to the reactor and from the reactor to the Soxhlet thimble were made. Extractions were carried out for twenty-four to thirty-six hours and the coal was air-dried to constant weight (checked for two or three days). Maximum error in experimental techniques was ± 2%. The combined error for nonhomogeneity of the coal and technique excluding coke removal from the reactor was ± 5%.

b. Water-Coal and Nitrogen-Coal Runs

These runs were subject to more error than the runs with the polynuclear hydrocarbons since more coking on the reactor walls and thermowells occurred. The maximum amount of coke that could have been left in the reactor was about one gram, meaning for a 30 gram charge a loss of 3.3%.

Since the reactor is only seven inches deep, its interior was easily viewed and reached with spatulas. The total error then amounts to approximately ± 5 + ± 3% = ± 8%.

An estimate of the experimental reproducibility can be gleaned from the results for three identical water-coal runs conducted at 400°C.

Run No.	Coal Conversion (% w/w)
75	20.8
77	18.8
78	17.8
average =	19.1
standard deviation =	1.5

c. Phenanthrene-containing Runs

Since phenanthrene freezes at 99°C, removal of the reactor contents was tedious and lengthy. While the reactor walls after finally dissolving the phenanthrene were not coked, because of the additional handling, the error could have been again about 3%.

d. Decalin-and Tetralin-containing Runs

No coking on the walls were observed and the reactor contents were easily removed. Maximum error was 1%. The reproducibility of these polycyclic runs was probably within less than two percentage points of each other.

c. Temperature and Pressure Measurements

Pressure gauges were new high-quality Bourdon-tube type manufactured by Ashcroft and were accurate within 1% of scale. Temperature was controlled within ± 2°C by a West temperature controller. The Chromel-Alumel thermocouples were checked with water in the reactor by comparing the observed temperature and pressure up to the critical point with those in the steam tables and agreed within ± 3°C.

C. DISCUSSION OF LIQUEFACTION RESULTS

1. Qualitative Observations on Liquefaction Results

The general characteristics of the liquefaction results (see Section III-B) will be reviewed before beginning a detailed discussion and interpretation.

a. Water-Catalyst-Coal Systems

(1) Series Ia - Coal System

Two runs were made to determine the effect of temperature on the conversion (see Section III-A or B for definition of coal conversion) of Ireland Mine coal to liquid and gaseous products. These runs were carried out with thirty grams of coal charge and with nitrogen as the initial gas phase in the reactor. At 400°C, the coal conversion was 11.4%; at 420°C, the coal conversion was 6.6% (see Fig. 21).

(2) Series I - Water-Catalyst-Coal Systems

The ranges of reaction variables studied were:

Temperature, °C	350 - 450
Pressure, psig	2000 - 7000
Reaction Time, hrs.	0.2 - 5
Water to Coal Ratio, w/w	1.1 - 5

(Customary Coal Charge, 30 grams)

Several heterogeneous catalysts (see Appendix IV for complete descriptions of catalysts) were introduced into the water-coal system to determine if increased coal conversion would result. These catalysts possessed one or more of the following functions:

1. Hydrodesulfurization/hydrodenitrogenation
2. Hydrogenation/dehydrogenation
3. Fischer-Tropsch synthesis

In Figure 21 is presented a summary of the water-coal and water-catalyst-coal runs. Two curves are shown for the water-coal system. The lower curve represents runs having sufficient water in the reactor to give reaction pressures of about 2000 psig. The upper curve represents runs in which the operating pressure was 4000 to 5000 psig.

The features of Figure 21 are:

1. A small increase in coal conversion occurred when the reaction pressure was increased from approximately 2000 psig to 4000 psig.
2. The maximum coal conversions observed occurred around 390 to 410°C. Below these temperatures coal conversion declined; above 410°C, the data are insufficient to decide whether there was a dropoff in conversion or whether the conversion had reached a plateau.

In the range 390 to 410°C the following results are typical:

Pressures (psig)	Coal Conversion (%, w/w)
2000	16.6
4000	19.1

3. The added catalysts do not appear to have had any effect on coal conversion in the water-coal runs.

b. Series II - Phenanthrene-Water-Catalyst-Coal Systems

The customary reactor charge was equal weights of coal and phenanthrene. Figure 22 portrays the relationship between coal conversion and temperature for the phenanthrene-coal and phenanthrene-water-coal systems. As noted (see Table XIV) the phenanthrene-coal runs were made early in the program at a time when the reactor charge was ten grams of coal rather than thirty grams. Because of the smaller quantity of reactants, twenty versus sixty grams, the phenanthrene-coal results were probably less accurate than the phenanthrene-water-coal results. Figure 22 illustrates the following:

1. A coal conversion maximum with temperature was observed for the phenanthrene-coal system, 25% w/w at 390°C.

2. No maximum in coal conversion occurred in the phenanthrene-water-coal system.
3. The highest conversion for the phenanthrene-water-coal system, 25% w/w, occurred at 405°C.
4. Increased water to phenanthrene ratios enhanced coal conversion both below and above 390°C in the phenanthrene-water-coal system.

Heterogeneous catalysts (20% w/w based on the coal charge) were evaluated in the phenanthrene-water-coal system. These catalysts were each known to possess at least one of the functions listed previously (see Section II-N). The results for the phenanthrene-water-catalyst-coal systems are shown in Figure 23 along with, for comparative purposes, the results for the phenanthrene-water-coal system at corresponding water to phenanthrene ratios. Inspection of Figure 23 shows that the results obtained with catalysts do not differ appreciably from the results obtained without catalysts, at least in the temperature range 400 to 405°C.

Two runs were made with only phenanthrene and water (no coal) to determine if phenanthrene was stable under the reaction conditions. No benzene insolubles were obtained, indicating that the decomposition products of phenanthrene, if any, were substances which would not interfere with the determination of coal conversion by Soxhlet extraction of the reactor products.

c. Series III - Decalin-Water-Catalyst-Coal Systems

In all the Series III runs, two volumes of Decalin were used per part of coal; i.e., 60 milliliters of Decalin per 30 grams of coal.

Figure 24 is a plot of coal conversion as a function of temperature for the Decalin-coal and the Decalin-water-coal systems. Only one run was made without water; this run was made at 403°C. Not shown in Figure 24 is a Decalin-water-coal run (run 124) carried out at 464°C; in this run the coal conversion was 34%.

The characteristics of Figure 24 are:

1. Coal conversion in the Decalin-water-coal system increased with temperature in the range 394 to 435°C.
2. The rate of increase of coal conversion declined markedly above 415°C; this is illustrated by the following corresponding values of temperature and coal conversion:

Temperature (°C)	Coal Conversion (wt.%)
395	22.3
405	27.7
415	30.7
425	32
435	32.3
464	34 (Run 124)

3. The one run without water had a 29% conversion, versus 26.7% conversion for the water-Decalin-coal system. This difference may not be significant; only more runs with the Decalin-coal system would show whether water was adversely affecting the mechanism of coal solvation by Decalin.

The results obtained when various heterogeneous catalysts were introduced into the Decalin-water-coal system are plotted in Figure 25. For comparison, the Decalin-water-coal results included in Figure 24 appear as the lower curve in Figure 25. In about one-half of the catalyzed runs, the reactor was initially pressurized to 700 to 1000 psig with carbon dioxide; the other runs initially had an atmosphere of nitrogen present.

Inspection of Figure 25 reveals the following:

1. Certain catalyzed runs exhibited coal conversions higher than the curve for the uncatalyzed runs.
2. In other cases, the catalyzed runs had lower coal conversions than the uncatalyzed runs.
3. Certain catalysts appeared to have no effect on the extent of coal conversion in the Decalin-water-coal system.

Table XXI lists the specific catalysts that were used along with their function(s), i.e., what reactions these catalysts are known to catalyze; and what effects were noted on coal conversion when these catalysts were added to the Decalin-water-coal system. If the catalyst appeared to have caused an enhancement in coal conversion when compared to the uncatalyzed result at the same temperature, a plus (+) sign appears in the column labelled Catalyst Effect. If the coal conversion for the catalyzed run was less than the uncatalyzed result at the same temperature, a minus (-) sign appears in the Catalyst Effect column. If the catalyst appeared to have neither a beneficial nor an adverse effect on coal conversion, a plus-minus (±) sign appears in the Catalyst Effect column. Each plus (+), minus (-), or plus-minus (±) sign appearing in the Catalyst Effect column represents the result of one run with that particular catalyst. Certain catalysts, always a fresh charge, were used several times, either to ascertain their action at different temperatures or in the presence of a different initial gas phase, nitrogen or carbon dioxide.

The qualitative observations inferred from the above summary of catalyst effects are that certain catalysts, the cobalt and nickel molybdates, and cobalt thoria, consistently gave higher results than were obtained in the uncatalyzed Decalin-water-coal system. Chromia-alumina

TABLE XXI

EFFECTS OF CATALYSTS ON COAL CONVERSION IN THE DECALIN-WATER-COAL SYSTEM

Catalyst[1]	Functions	Catalyst[2] Effect
Cobalt and Nickel Molybdates/Alumina	Hydrosulfurization Hydrodenitrogenation Hydrogenation/ Dehydrogenation	++++
Cobalt-thoria/ Kieselguhr	Fischer-Tropsch a) Hydrogenation of CO b) $CO-CO_2$ interchange	+++ ±
5% Ruthenium/carbon	Hydrogenation/ Dehydrogenation	+
Chromia-Alumina	Dehydrogenation	+ - - ±
Chrome-Aluminum-Phosphate	Dehydrogenation	+
Mixture of MoO_3, G-3A, HDS-6A and Chromia-Alumina	All functions listed in above paragraph	+
Tungsten/Alumina	Dehydration	-
Cobalt Oxide/ Kieselguhr	Hydrogenation	-
Nickel/Tungstate/ Silica-Alumina	Hydrodesulfurization Hydrodenitrogenation Cracking	- -
Nickel-Tungstate/ Alumina (acidified)	Hydrodesulfurization Mild cracking	+ -
Nickel Tungstate/ Alumina	Hydrodesulfurization	±

[1] See Appendix IV for complete descriptions of catalysts.

[2] Denotes whether catalyst improved (+), lowered (-) or had no effect (±) on coal conversion as compared to the uncatalyzed system at the same temperature and pressure (see Figure 25).

catalysts generally gave lower coal conversions than were obtained in the uncatalyzed system. The nickel tungstates gave mixed results depending on the support material. Nickel tungstate on silica-alumina, an acidic support, gave coal conversions less than those obtained in the uncatalyzed system. When supported on a slightly acidic or neutral support, nickel tungstate did not have much effect one way or the other.

The upper curve in Figure 25 was drawn through the data points obtained using the cobalt molybdate and cobalt thoria on kieselguhr. These catalysts appear to be most effective in the temperature range 400 to 415°C where their utilization appears to increase the coal conversion by about 2.5 to 3 percentage points. Above 415°C and below 400°C the conversion curves come closer together.

d. Series IV - Tetralin-Water-Catalyst-Coal Systems

In Figure 26 are shown the extent of coal conversion as a function of temperature for the Tetralin-coal, Tetralin-water-coal and Tetralin-water-coal-catalyst systems. Two volumes of Tetralin were employed per part of coal; i.e., 60 milliliters of Tetralin and 30 grams of coal. For the Tetralin-water-coal runs the customary reactor charge consisted of 60 milliliters of Tetralin, 40 to 50 milliliters of water and 30 grams of coal. The customary catalyst charge was again 20% w/w based on the coal charge.

The salient features of Figure 26 are:

1. Coal conversion was highest for the Tetralin-coal system.
2. Incorporation of water into the Tetralin-coal system lowered coal conversion about 8%.
3. An even greater adverse effect, about 25%, was noted when both water and heterogenous catalysts were introduced into the Tetralin-coal system.
4. Coal conversion in the Tetralin-water-coal system passed through a maximum around 420 to 430°C. The temperature ranges studied in the cases of the other two systems were not broad enough to permit any conclusions about whether maximums will occur.

Generally speaking, the results of Figure 26 can be summarized as follows:

System	Coal Conversion (% w/w)
Tetralin-Coal	67
Tetralin-Water-Coal	62
Tetralin-Water-Catalyst-Coal	51

The heterogeneous catalysts evaluated in the Series IV experiments possessed the following functions:

1. CO-CO_2 transformation (water gas shift)
2. Hydrogenation/dehydrogenation
3. Hydrodesulfurization/hydrodenitrogenation

e. Series V - Alkali-Phenanthrene-Coal System

The Series V experiments (Table XVII) show that coal conversion in the potassium hydroxide-water-phenanthrene-coal system is a function of the alkali molality in the temperature range 395 to 400°C.

Run #	KOH Molality	% Coal Conversion	Temperature °C
72	0.58	32.2	395 - 400
68	1.09	35.1	395 - 400
71	1.92	43.8	395 - 400
62	1.08	36.8	415

One run with 1.07 molal NaOH at 399°C exhibited a coal conversion of 34% essentially equivalent to 35.1% obtained with 1.09 molal KOH. At a lower temperature, 384°C, the use of 0.72 molal potassium acetate resulted in a 29.4% coal conversion.

f. Series VI - Phenanthrene-Water-Carbon Monoxide-Catalyst-Coal System

The recently announced Bureau of Mines process for coal liquefaction with carbon monoxide and water (see Section II-G) was briefly studied in the Series VI runs listed in Table XVIII. Two runs were made in which no catalyst was added and about 55% w/w coal liquefaction occurred. When a known catalyst for the water-gas shift reaction (chromium promoted ion oxide) was added to the system, the extent of coal liquefaction at comparable reaction conditions increased to 68% w/w.

g. Overall Observations

Figures 27 and 28 summarize the principle findings of the coal liquefaction studies. The effect of water and the various polycyclic hydrocarbons on coal conversion in the temperature range of 385 to 440°C (464°C for Decalin and water) is shown in Figure 27. Figure 28 depicts the effect of water, polycyclic hydrocarbons and heterogeneous catalysts on coal conversion at 410°C.

2. Interpretation and Analysis of the Liquefaction Results

a. Water-Catalyst-Coal System

(1) Previous Work

The literature on the reactions of coal and water including the most recent M.I.T. work (Yen, 1960) was reviewed earlier (see Section II-G).

Yen determined coal conversion indirectly by measuring the quantity of benzene solubles obtained and then dividing by the coal charged rather than directly as the difference between the weight of coal charged and the weight of the dried benzene-extracted reactor residues divided by the coal charged (see Sections III-A or III-B for definition of coal conversion). These measurements are comparable provided:

1. The gaseous products were insignificant or accounted for.
2. Negligible low boilers were formed from coal; these would volatilize with the benzene during the determination of the weight of the benzene solubles.

It is believed, within the accuracy of the experimentation, that Yen's results and the present results can be meaningfully compared and contrasted.

Yen's findings were:

1. At 775°F and 4700 psi, a maximum of 18% benzene solubles was obtained.
2. Times above one hour did not increase the amount of benzene solubles.
3. A sharp increase in the amount of benzene solubles was observed between 3000 and 4500 psi.
4. When coal was heated without water with just initial nitrogen pressure in the reactor, the quantity of benzene solubles, c. 6%, was much less than when water was used.

The mechanism postulated by Yen for the formation of benzene solubles involved "mainly the cracking, extracting and distilling out of the volatile matter in the coal, together with the reaction of the cracking volatile matter with the water present." According to Yen, it was the reaction of water and the cracking volatile matter that accounted for the increase in benzene solubles obtained in the water runs as compared to the nitrogen runs.

(2) Present Work

The bituminous coal used by Yen, Wharton coal, contained 0.09% w/w benzene solubles. As noted earlier, the bituminous coal used in the present study, Ireland mine coal, when subjected to Soxhlet extraction with boiling benzene was converted to liquid and gaseous products to the extent of 0.92% w/w.

The effects of the reaction variables, time, temperature and pressure, on the extent of coal conversion (see Table XIII and Figure 21) in the present study are as follows:

1. Time -- No significant differences in coal conversion were noted between one and five hour reaction times; reaction times of about one-half hour showed a decrease of two to five percentage points in coal conversion.
2. Pressure -- There is a moderate increase in coal conversion as the pressure is increased from 2000 to 9000 psig; no sharp changes were noted between 3000 and 4000 psig.
3. Temperature -- While the experimental results are incomplete, a maximum is suggested around 390 to 410°C.

Maximum coal conversions observed were about 18 to 20%.

Yen has presented a thorough and logical discussion of possible mechanisms to explain the experimental findings of the water-coal runs. However, he attributed the increase in coal conversion between runs with and without water to reaction of water with cracking volatile matter. Without water, the cracked volatile matter would polymerize to benzene insolubles.

A very simple mathematical model to explain the observed effect of reaction time on the percent coal conversion can be developed. This model assumes that the liquid and gaseous products produced in the water-coal system arise only from thermal cracking or coking of the coal substance.

Model I

Define:

C = coal amount at any time

C_k = coke amount at any time

L = benzene solubles (oil) and gases at any time

θ = time

$\left.\begin{matrix}\gamma_1\\ \gamma_2\end{matrix}\right\}$ = weight fraction of original coal

$\gamma_1 + \gamma_2 = 1.0$

Consider only the coking of coal; no other reactions consume coal or produce or consume oil (and gases) and coke

$$C \xrightarrow{k_1} \gamma_1 C_k + \gamma_2 L \qquad (5)$$

1. <u>Coal Conversion</u>

$$-\frac{dC}{d\theta} = k_1 C \qquad (6)$$

Boundary Conditions

$\theta = 0, \quad C = C_o$

$\theta = \theta, \quad C = C$

Solution

$$C = C_o\, e^{-k_1\theta} \qquad (7)$$

Equation (7) shows that coal converts via a first order exponential decay if coking (thermal cracking) is the only reaction occurring.

2. <u>Production of Benzene Solubles and Gases</u>

$$-\frac{dC}{d\theta} = \gamma_2 \frac{dL}{d\theta} = k_1 C \qquad (8)$$

substituting for C from equation (7):

$$\gamma_2 \frac{dL}{d\theta} = k_1 C_o\, e^{-k_1\theta} \qquad (9)$$

Boundary Conditions

$\theta = 0, \quad L = 0$

$\theta = 0, \quad L = L$

$$\int_0^L dL = \frac{k_1}{\gamma_2} C_o \int_0^\theta e^{-k_1\theta} \, d\theta \qquad (10)$$

Integrating:

$$L = \frac{k_1}{\gamma_2} C_o \left[-\frac{1}{k_1} e^{-k_1\theta} \right]_0^\theta \qquad (11)$$

The solution is:

$$\frac{L}{C_o} = \frac{1}{\gamma_2} \left[1 - e^{-k_1\theta} \right] \qquad (12)$$

4. Production of Coke

By similar mathematics

$$\frac{C_k}{C_o} = \frac{1}{\gamma_1} \left[1 - e^{-k_1\theta} \right] \qquad (13)$$

This simple coal to coke and benzene solubles (and gases) model predicts that the coal amount decreases via a first-order exponential decay function and that the quantities of benzene solubles (and gases) and coke produced become asymptotic with time. This model is consistent with the present experimental findings and also those of Yen in regards to the relationship between coal conversion and reaction time. It should be pointed out again that it is impossible to distinguish between unreacted coal and coke or char in the reactor product residues.

A more complicated model than the one just presented can be developed which explains:

(1) The substantially higher coal conversions obtained with water and coal vis à vis the coal conversions obtained when coal was heated with only nitrogen present.

(2) The maximum in coal conversion with temperature implied by the present work and obtained by Yen.

This model involves first, thermal cracking of coal to reactive (or active) fragments. Here, it is well to remember that several chemical bonds have to rupture before a fragment of the coal substance can separate from the remainder of the coal mass (see Section II-E). There exists a wide distribution of bond strengths throughout the coal structure. The weakest bonds, the carbon-heteroatom bonds, will crack first; the carbon-carbon type covalent bonds will be much more difficult to thermally crack. The active fragments formed by the thermal cracking of coal thus possess several unshared elections, i.e., these active fragments are multi-centered free radicals. For various reasons, including stereochemical, these unshared points may have different reactivity. The more labile centers will react rapidly either with another radical or perhaps with hydrogen from a donor. The less reactive centers may be quite long-lived. The model being discussed further assumes that the reactive coal fragments, once formed, become stabilized by conversion either to benzene solubles or to coke. Reactive fragments may be converted to more stable fragments and/or molecules which are soluble in benzene by rearrangement-type reactions. Reactive fragments may combine together via condensation or polymerization reactions to give the benzene-insoluble residues which are called polymer or coke.

Model II

Define: All at time, θ

C = coal

F = active fragments (coal-derived multi-centered free radicals)

M = benzene soluble stable molecules

P = polymer or coke

1. Simplest Model Equations

Coal thermal cracking:

$$C + \Delta \xrightarrow{k_1} F \tag{14}$$

Stabilization to benzene solubles:

$$F \xrightarrow{k_2} M \tag{15}$$

Stabilization by coke formation

$$F + F \xrightarrow{k_3} P \tag{16}$$

2. Rate Equations

Production of active fragments

$$\frac{dF}{d\theta} = k_1 C \tag{17}$$

Stabilization by rearrangement (benzene solubles)

$$-\left.\frac{dF}{d\theta}\right)_{\text{solubles}} = k_2\, F \tag{18}$$

Stabilization by polymer formation
(benzene insolubles)

$$-\left.\frac{dF}{d\theta}\right)_{\text{insolubles}} = k_3\, F\left(\frac{F}{V}\right) \tag{19}$$

Note that only equation (19), the rate of polymer formation is concentration dependent.

3. Solving for F

Equating the rate of production of active fragments, equation (17) with the rate of disappearance of active fragments by equations (18) and (19):

$$k_1C = k_2F + k_3\frac{F^2}{V} \qquad (20)$$

or in the familiar quadratic form

$$\frac{k_3}{V}F^2 + k_2F - k_1C = 0 \qquad (21)$$

The solution of which is:

$$F = \frac{-k_2 \pm \sqrt{k_2^2 + 4\frac{k_1k_3C}{V}}}{2\frac{k_3}{V}} \qquad (22)$$

For F to be positive, the positive root has to be taken:

$$F = \frac{-k_2 + \sqrt{k_2^2 + 4\frac{k_1k_3C}{V}}}{2\frac{k_3}{V}} \qquad (23)$$

substituting $a = -k_2$

$b = 2k_3$

$c = 4k_1k_3C$

thus,

$$F = \frac{aV + V\sqrt{a^2 + \frac{c}{V}}}{b} = V\left(\frac{a + \sqrt{a^2 + \frac{c}{V}}}{b}\right) \qquad (24)$$

4. Substituting in rate equations

Substituting equation (24) into equation (18) gives:

$$-\left.\frac{dF}{d\theta}\right)_{\text{solubles}} = k_2V\left(\frac{a + \sqrt{a^2 + \frac{c}{V}}}{b}\right) \qquad (25)$$

Inspection of equation (25) shows that as the volume of reactants increases, the rate of stabilization of reactive fragments to benzene solubles increases.

Substituting equation (24) into equation (19) gives:

$$-\left.\frac{dF}{d\theta}\right)_{\text{insolubles}} = k_3\left(\frac{a + \sqrt{a^2 + \frac{c}{V}}}{b}\right)^2 \qquad (26)$$

Equation (26) predicts that as the volume of reactants increases, the rate of stabilization of reactive fragments to coke decreases.

The above model, which assumes no beneficial effects of water other than simple dilution of the coal, can satisfactorily explain why coal conversions were higher in the water-coal runs than in the nitrogen-coal runs. The effect of water is separation of the reactive coal fragments, which slows the polymerization reactions and allows more time for the desirable rearrangement-type reactions to occur. An additional advantage to water dilution is that the rate of stabilization to benzene solubles increases with dilution. This model is consistent with the observations that higher pressures caused by increased water to coal ratios resulted in higher coal conversions.

Water has been determined to be remarkably soluble in oils at high temperature. For example, at 300°, the approximate solubility of water in oil (gasoline, jet fuel, kerosine and oils) is 50 mol %. Aromatic hydrocarbons and to some extent olefinic hydrocarbons dissolve the most water and paraffinic hydrocarbons dissolve the least (Nelson, 1956). The solubility of oil in water is several times less than the solubility of water in oil at the same temperature and pressure (Griswold and Kasch, 1942).

These observations on the solubility of water in hydrocarbons indicate that water could serve as a diluting medium for the reactive coal fragments as assumed in Model II.

The maximum in coal conversion with temperature suggested by the present data is explainable also by Model II. As the temperature increases, it can be postulated that the reaction rate constant, k_3, of the polymerization reaction increases faster than the reaction rate constant, k_2, of the desirable stabilization reactions. Simply, at higher temperatures, the rate of polymerization of the active fragments increased faster than the benzene solubles formation rate and therefore the coal conversion, as defined, passed through a maximum with temperature.

Model II is also consistent with the experimental observation on the relationship between coal conversion and time. This can be simply arrived at by noting that adding equations (14), (15) and (16) of Model II gives the Model I equation which has already been shown to be consistent with the conversion-time data.

In a complicated system like the water-coal system and also the other systems to be discussed, there are many reaction sequences that can be postulated to be occurring. Undoubtedly, other mathematical models for the water-coal system besides the two already developed could be formulated that would satisfy the experimental observations. However, considering the complexity of the reactions, reaction products, and the lack of rate data, there is probably little to be gained here in pursuing further models.

Other possible reactions that could occur in the water-coal systems besides those already mentioned include reactions of the types discussed earlier (see Section II-K). For example, gasification and gasification-synthesis reactions can occur:

$$C + 2H_2O = CO_2 + 2H_2$$

$$2C + 2H_2O = CH_4 + CO_2$$

Also, reactions between coal or coal-derived active fragments and water:

$$\text{Coal} + x\,H_2O = \text{"oils"} + \left(\frac{x}{2}\,CO_2\right)$$

$$\text{"Active Fragments"} + x\,H_2O = \text{oils} + \left(\frac{x}{2}\,CO_2\right)$$

In addition, hydrogenation of coal by molecular hydrogen produced by cracking reactions (either cracking of coal or active fragments) or by gasification reactions could be occurring. Carbon formation could occur via hydrocarbon cracking reactions.

b. Phenanthrene-Water-Catalyst-Coal Systems

(1) Extraction of Coal with Phenanthrene-Previous Work

Polynuclear aromatic compounds such as phenanthrene have been found to be effective dispersing agents for bituminous coal. For example, at its atmospheric boiling point, 340°C, phenanthrene dispersed 95% of a bituminous coal. The coal dispersion in phenanthrene was examined after cooling to less than 99°C, the freezing point of phenanthrene, and the following observations made:

1. By electron microscopy there was a wide range of particle sizes, with a large proportion in the colloidal range.
2. By cryoscopic determination, using 11.65°/mol/kg for phenanthrene, the average molecular weight of the dispersed material was 657 (Orchin *et al.* 1951).

The same workers also showed that phenanthrene could be recovered in quantitative yield from coal extracts indicating that phenanthrene does not irreversibly interact with the coal substance. The cooled dispersion of coal in phenanthrene was pulverized and leached with benzene (phenanthrene is benzene soluble). It was determined from the amount of benzene insolubles remaining that about 20% of the original MAF coal became benzene soluble as a result of having been dispersed in phenanthrene at 340°C. The benzene solubles had an average molecular weight of 513. Only about 0.3 percent of the original coal evolved as gaseous products during the phenanthrene extractions. These gaseous products included CO, CO_2, H_2 and C_1 to C_4 hydrocarbons.

Orchin et al. suggested a mechanism for coal dispersion by phenanthrene as follows:

1. Phenanthrene dissolves the binding agent for the micellar portion of the coal.
2. This results in complete disintegration of the colloidal coal structure and peptization of the micellar in the solvent.

(2) Phenanthrene-Coal System - Present Work

In the temperature range 365 to 400°C coal conversion ranged from 15 to 21%. These results are similar to the value of 20% benzene solubles at 340°C reported above for a bituminous coal (Orchin et al. 1951).

In Figure 22, a maximum in coal conversion with temperature is indicated for the phenanthrene-coal system. This maximum appears because the run at 410°C showed a conversion of only 10%. This may not be a valid data point since only ten grams of coal and ten grams of phenanthrene were used in these runs (see Table XIV).

Two differences between the water-coal and the phenanthrene-coal systems are to be noted:

1. Appearance of residue after benzene extraction:
    a. Water-coal residue: large lumps of porous coke.
    b. Phenanthrene-coal residue: black, fine powder closely resembling the feed coal powder.
2. Quantity of gaseous products:
    a. Water-coal runs: small but measurable.
    b. Phenanthrene-coal runs: practically none.

Since the extent of coal conversion observed in the phenanthrene-coal system was about the same as observed in the water-coal system, probably the same or similar chemical bonds in the coal substance were being cracked in both systems. This suggests that the models postulated to explain the water-coal results may also be valid for the phenanthrene-coal results. Further, since water was not used in the phenanthrene-coal system, the similar results obtained from the two systems offers indirect evidence that water was not serving as a hydrogen donor to the coal or to the coal-derived active fragments.

In both systems, it appears that the added liquid phase, water or phenanthrene, served only as a diluting medium for the reactive fragments, thus retarding the polymerization reactions which are concentration dependent.

The slight enhancement in the extent of coal conversion in the phenanthrene-coal system over the water-coal system could be related to the higher boiling and critical points of phenanthrene compared to those of water (see Appendix IV). In the phenanthrene-coal system, there probably were larger amounts of liquid phase present during reaction, thus higher dilution of the coal fragments.

As previously pointed out, phenanthrene is an effective coal dispersing agent, chiefly by the mechanism of selective dissolution of binders in the coal matrix. Water probably would not function in this fashion. On cooling a phenanthrene-coal extract the coal particles would be spread throughout the solid matrix of solvent and coal, while on cooling a water-molten coal mixture, fusion of particles could be expected. The latter observation could also explain why phenanthrene produced more benzene solubles from coal than did water.

The smaller quantity of gaseous products in the phenanthrene-coal system is indicative of the occurrence of less cracking and splitting of the coal fragments in this system compared to the water-coal system. This could be a sign of a certain amount of reaction between water and cracked fragments as Yen postulated (Yen, 1960).

(3) Phenanthrene-Water-Coal System

Examination of the results obtained (Figures 22 and 23) indicates that increased amounts of water in the phenanthrene-water-coal system increased the conversion. In addition, no maximum in coal conversion with temperature was observed as was suggested for the water-coal system and possibly the phenanthrene-coal system. There was a slight increase in coal conversion with temperature.

Increased amounts of water means higher pressure in the reactor and additional liquid phase present during the reaction. The higher coal conversion observed with increased amounts of water is consistent with the previously postulated model that dilution of the coal fragments retarded the polymerization reactions and allowed more time for various desirable stabilization reactions to take place.

The fact that the coal conversion did not pass through a maximum with temperature in this system and probably did in the water-coal system is explainable also by noting that in this system, there exists more liquid phase for dilution of the reactive coal fragments than with water alone. The critical temperature of phenanthrene, 611°C, is substantially above that of water (see Appendix IV). Most of the water-coal runs were carried out above the critical temperature of water, thus the diluting effect of water was probably due to solubility in the coal-derived liquids.

While phenanthrene, being an aromatic compound, possesses no hydrogen transfer capability, there does exist the possibility that it could become a hydrogen donor if it becomes partially hydrogenated *in situ* to dihydrophenanthrenes (hydroaromatic compounds) by either hydrogen donated by coal fragments or by water serving as a hydrogen donor. If this occurred, then another desirable stabilization reaction would be operative which could possibly also explain why there was no maximum in coal conversion in the phenanthrene-water-coal system as the reaction temperature was raised.

(4) Phenanthrene-Water-Catalyst-Coal Systems

Various heterogeneous catalysts (see Figure 23) added to the phenanthrene-water-coal system apparently had no effect since the observed coal conversions were no different with or without the catalysts. If phenanthrene was being reduced to hydroaromatic compounds, which then were functioning as hydrogen donor agents, catalysts would not be expected to have any effect. Various workers have fairly well shown that the mechanism of coal liquefaction with liquid-phase hydrogen donor agents is unaffected by solid catalysts (see Section II-F).

c. Decalin-Water-Catalyst-Coal Systems

(1) Liquefaction of Coal with Decalin - Previous Work

Decalin is a saturated polycyclic hydrocarbon which has found applications in coal solubilization when a coal extract closely resembling the original coal in elemental analysis is desired. For example, Decalin extraction of Ireland Mine coal at 650°F resulted in an ash-free coal extract which had essentially the same analyses, on a MAF basis, as the original coal. On a MAF basis, the coal conversion was 23% (Curran, *et al*. 1967)

(2) Decalin-Coal System - Present Work

Only one run was carried out with Decalin and coal. At 403°C, the coal conversion was 29%. The insoluble residue remaining after benzene extraction closely resembled in appearance the original coal just as did the residues from all the phenanthrene-coal systems. The mechanism of coal solubilization, however, with Decalin probably involves a certain amount of hydrogen transfer to active fragments obtained from thermal cracking of coal, since Decalin has this capability and is known to be a hydrogen donor agent (Curran *et al*. 1967).

(3) Decalin-Water-Coal System

The effect of water and Decalin together on coal conversion was studied in the temperature range 394 to 464°C. Coal conversions were substantially greater in this system than in either of the two systems discussed so far, water-coal and phenanthrene-water-coal. Examination of the coal conversion-temperature curve (Figure 24) shows that the rate of increase of conversion decreases markedly as the temperature increases. Coal conversion is 31% at 415°C and, not shown in Figure 24, 34% at 464°C.

The model that can be developed for coal liquefaction in the presence of either Decalin, or Decalin and water, involves thermal cracking of coal to reactive fragments, stabilization of these fragments by, 1) hydrogen donated by Decalin or possible water, or 2) internal rearrangement, and 3) secondary polymerizations of unstabilized fragments (to benzene insolubles). Decalin, like phenanthrene, provides a protective environment for the coal fragments; simple dilution probably reduces the extent of secondary polymerization.

Since the vapor pressure of phenanthrene is lower than the vapor pressures of cis- and trans-Decalin (see Appendix IV), it would be expected, if dilution of the coal-derived active fragments were the most important factor, that phenanthrene would be better than Decalin for coal liquefaction. Since the opposite was observed, the improvement in the extent of coal liquefaction in the Decalin-water-coal system over that of the water-coal and phenanthrene-water-coal systems must be related to the hydrogen donor capabilities of Decalin.

It appears that at the higher temperatures either very little additional cracking is occurring or the rate of thermal cracking is almost offset by the rate of secondary polymerization. The fact that the extent of coal liquefaction became asymptotic with time at the lower temperatures (400 to 425°C) suggests that little additional cracking occurs after a certain number of bonds in the coal structure have ruptured. Thus, at the higher temperatures, the same phenomenon could be occurring and much higher temperatures than used in the present study ($>$464°C) would be necessary before the stronger remaining bonds rupture.

On the other hand, since the critical temperatures of the Decalins and water have been surpassed at the highest temperature (464°C), the beneficial effects of dilution may not be nearly as pronounced as at the lower temperatures. Thus, the additional active fragments produced going to and while at 464°C were stabilized by polymerization reaction and therefore little net gain in coal liquefaction ensued. Also, it has been postulated that the reaction velocity constants for the polymerization reactions may increase at a greater rate with temperature than the rearrangement-type reactions.

(4) Decalin-Water-Catalyst-Coal Systems

Catalysts evaluated were selected from groups of catalysts (see Section II-N) known to catalyze the following:

1. Reactions in which water is either a reactant or product.
    a. Hydration/Dehydration
    b. Water gas shift
    c. Fischer-Tropsch synthesis
2. Reactions believed to occur in coal solubilization.
    a. Cracking
    b. Hydrogenation/Dehydrogenation
    c. Disproportionation
3. Reactions additionally desired in coal solubilization.
    a. Hydrodesulfurization
    b. Hydrodenitrogenation

Information about the individual catalysts used appears in Appendix IV.

Those catalysts possessing hydrodesulfurization and hydrodenitrogenation ability, the cobalt molybdates, appeared to give somewhat higher coal conversions than Decalin-water alone (see Figure 25). Normally these catalysts are used with added hydrogen. It seems reasonable to assume that part of their effectiveness comes from utilization of hydrogen formed in situ by various cracking and disproportionation reactions. In that event both hydogen sulfide and ammonia are possible products. Hydrogen sulfide was detected but not ammonia. This is consistent with the observation that nitrogen appears mainly in the difficult to crack rings rather than in the linking units as does sulfur and oxygen.

Another catalyst enhancing the Decalin-water system was cobalt thoria. This catalyst, a mixture of cobalt oxide and thorium oxide supported on kieselguhr (SiO_2), was an early Fischer-Tropsch catalyst. It was at this point in the study that the use of carbon dioxide in the vapor space of the reactor rather than nitrogen was evaluated. The reason for using carbon dioxide is that one of the products of the Fischer-Tropsch process is carbon dioxide. It was postulated that this gas could have a beneficial role in converting the complex coal liquid products to simpler molecules. However, this proved not the case.

Interesting results were obtained when three nickel tungstates, differing only in the supports used were evaluated.

Catalyst	Results
Nickel-tungstate/silica-alumina	Worse than Decalin-water
Nickel-tungstate/acidified alumina	Same as Decalin-water
Nickel-tungstate/alumina	Same as Decalin-water

Silica-alumina is an acidic support and thus imparts cracking activity to the catalyst. However, in this case this is probably not the cause of the poorer performance. The coal liquids certainly contain basic compounds, e.g., nitrogen bases which could adsorb on the acid sites, polymerize and contribute to the benzene insoluble residues.

Neither hydrogenation nor hydration-type catalysts offered any encouragement. The former observation is an indication that little of the direct gasification-synthesis-type reactions were occurring to form hydrocarbons and hydrogen. The absence of an appreciable gas phase also shows that little direct gasification to produce carbon oxides occurred.

d. Tetralin-Water-Catalyst-Coal Systems

(1) Hydrogen Donor Agents — Review

Free radicals are known to abstract hydrogen atoms from liquid and gaseous hydrocarbons. Using t-butoxy radicals, Williams compared the relative reactivity of various hydrogen atom types and found that the secondary cyclohexyl hydrogen atoms of Tetralin which are activated by the adjacent benzene ring as well as by the alicyclic ring were the most reactive of ten hydrogen atom types evaluated. These cyclohexyl hydrogen atoms, for example, reacted 76 times more rapidly than did the primary unactivated hydrogen atoms of t-butyl benzene (Williams et al., 1956).

Pott and Broche in the commercial process bearing their names, liquefied bituminous and German brown coal using a process-derived stream possessing hydrogen donor properties. This concept recently reappeared as Project Gasoline under development by the Consolidated Coal Company (see Section II-F).

(2) Mechanism of Coal Liquefaction by Tetralin - Previous Work

Tetralin was employed in 1926 for the pressure extraction of coal (Berl, 1926). Subsequently, Pott and Broche achieved 64% liquefaction of bituminous coal using equal parts of phenol and Tetralin. The latter workers attributed the effectiveness of this medium to the following:

1. Hydrogenating effect of the solvent.
    a. Free hydrogen from Tetralin dehydrogenation
    b. "Nascent" hydrogen split from the Tetralin
2. Depolymerization of the coal (Pott and Broche, 1934).

Orchin and Storch (see Section II-F) carried out experiments on the solvation and hydrogenation of coal at 400°C using various aromatic, hydroaromatic and phenolic group-containing hydroaromatic compounds. These workers noted that:

1. Effective coal liquefaction occurred with only a small consumption of hydrogen, c. 1.4% w/w of the MAF coal.
2. The first 20% coal liquefaction occurred with no oxygen elimination from the coal.
3. Above 20% coal liquefaction, a straight line relationship existed between oxygen elimination and coal liquefaction.

Orchin and Storch concluded that coal liquefaction via Tetralin probably involves a mild hydrogenolysis of carbon to oxygen linkages by the hydrogen available from the hydroaromatic diluent.

Rather than hydrogenolysis of carbon-oxygen bonds, Curran suggested that coal first thermally decomposes into free radicals which are stabilized by capture of a hydrogen atom from a donor molecule. This theory was arrived at from these observations:

1. Rate of liquefaction was independent of particle size.
2. Rate of hydrogen transfer for active donors was independent of the chemical structure of the donor; a second order mechanism as postulated by Orchin and Storch would involve very specific stereochemical effects.

3. Their experimental data with Ireland Mine coal and Tetralin did not obey a second-order rate law (Curran et al., 1967).

The mechanism proposed by Curran for coal liquefaction in the presence of a hydrogen donor diluent is analogous to that accepted for the upgrading of petroleum residues by thermal cracking in the presence of Tetralin.

In petroleum refining, mild thermal cracking of crude residues in the presence of hydrogen donor diluents, such as Tetralin and partially hydrogenated process streams containing condensed ring compounds, to more valuable lower boiling products has been described. Thermal cracking of high boiling polycyclic aromatics produces asphaltenes, high molecular weight condensed ring compounds. Asphaltenes are formed presumably by polymerization of the large free radicals which are the primary products of thermal cracking. In the presence of an active hydrogen donor, like Tetralin, polymerization of these large radicals is prevented by hydrogen transfer from the donor molecules (Carlson et al., 1958).

In summary, two models have been proposed for coal liquefaction via treatment with Tetralin under pressure at c. 400°C. These are:

1. Hydrogenolysis of carbon-oxygen bonds.
2. Thermal cracking of covalent bonds to produce free radicals; these free radicals then abstract hydrogen atoms from the Tetralin to become stable molecules.

(3) Tetralin-Coal System - Present Work

The experimental results obtained with Tetralin are consistent with those of previous investigators (Pott and Broche, 1934; Orchin and Storch, 1948; Curran *et al.*, 1967). High coal conversion to liquid products was obtained at 410°C. It was also observed that polymers formed in the reboiler of the Soxhlet apparatus during extraction of the residues from the Tetralin-coal runs, which is indicative of the presence of reactive species in the coal extract. This evidence suggests that coal liquefaction via Tetralin proceeds by thermal cracking of the coal mass to produce large free radicals. Large radicals, for stereochemical reasons, are often long-lived.

(4) Tetralin-Water-Coal System

Introduction of water into the Tetralin-coal system lowered the apparent coal liquefaction by approximately 8%. If the mechanism of coal liquefaction involves hydrogenolysis of the carbon-oxygen bonds by hydrogen arising from the Tetralin, the presence of water presumably should not affect this process, since bond rupture is associated with the presence of hydrogen from the donor molecule. If the primary step in coal liquefaction via Tetralin involves rupture of covalent bonds to form active fragments, i.e., free radicals, then the stabilization of these free radicals is dependent on their accessibility to hydrogen from an active donor. The Tetralin-water-coal runs were made in the 400 to 425°C temperature and 4000 to 5000 psig pressure ranges. Dissolved water molecules could have an adverse effect on the rate of free radical stabilization by hindering contact between Tetralin and the active coal fragments.

In the three systems already discussed, water-coal, phenanthrene-water-coal, and Decalin-water-coal, additional liquid phase was postulated to be beneficial because the active fragments were separated, giving more time for desirable stabilization reactions to occur. This dilution effect is apparently not beneficial in the Tetralin-water-coal system (Figure 26).

A simple mathematical model can be developed which is consistent with these experimental observations. This model assumes that the major reactions occurring in the Tetralin-water-coal system are cracking of coal to active fragments, followed by stabilization of these fragments either to benzene solubles or insolubles. The only reaction considered for active fragments stabilization to benzene solubles is via a homogeneous hydrogenation with Tetralin serving as the hydrogen donor agent. The reaction leading to benzene insolubles (coke) is secondary polymerization or condensation of the active fragments. Stabilization of active fragments by rearrangement-type reactions is not considered in this model, since it was thought that the hydrogen donor stabilization was probably of paramount importance.

Model III

Generalized Reactions

$$\text{Coal} + \Delta \xrightarrow{k_1} \text{Free Radicals} \qquad (27)$$

$$\text{Free Radicals} + \text{Tetralin} \xrightarrow{k_2} \text{Stable Molecules} \qquad (28)$$

$$\text{Free Radicals} + \text{Free Radicals} \xrightarrow{k_3} \text{Polymers (Coke)} \qquad (29)$$

The objective is to see how dilution of the Tetralin with water affects coal liquefaction.

Define

C = Coal amount at any time

F = Active fragments at any time

T = Tetralin amount at any time

θ = Time

V = Volume

1. Simplest Model Equations

Coal Thermal Cracking

$$C + \Delta \xrightarrow{k_1} F \tag{30}$$

Active Fragment Stabilization with Tetralin

$$F + T \xrightarrow{k_2} \text{Stable Molecules (oil)} \tag{31}$$

Active Fragment Stabilization by Coke Formation

$$F + F \xrightarrow{k_3} \text{Polymer} \tag{32}$$

2. Rate Equations

Production of Active Fragments

$$\frac{dF}{d\theta} = k_1 C \tag{33}$$

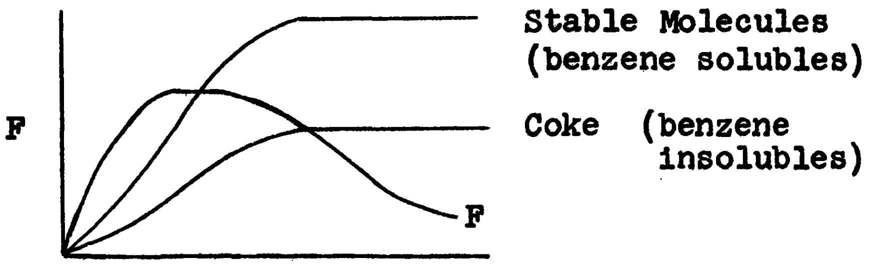
Stabilization with Tetralin (benzene solubles)

$$-\left.\frac{dF}{d\theta}\right)_{\text{molecules}} = k_2 F \frac{T}{V} \tag{34}$$

Stabilization by polymerization (benzene insolubles)

$$-\left.\frac{dF}{d\theta}\right)_{\text{coke}} = k_3 F \left(\frac{F}{V}\right) \tag{35}$$

Graphically



3. <u>Solving for F</u>

Equating the rate of formation of F with the rates of disappearance of F:

$$k_1C = \left(k_2 \frac{T}{V} + k_3 \frac{F}{V}\right) F \qquad (36)$$

in the quadratic form:

$$\frac{k_3}{V} F^2 + k_2 \frac{T}{V} F - k_1C = 0 \qquad (37)$$

the solution is:

$$F = \frac{-k_2 \frac{T}{V} \pm \sqrt{\left(\frac{k_2T}{V}\right)^2 + \frac{4\, k_1k_3C}{V}}}{2\, \frac{k_3}{V}} \qquad (38)$$

rearranging:

$$F = \frac{-k_2\, T \pm \sqrt{\left(k_2T\right)^2 + 4\, k_1k_3C\, V}}{2\, k_3} \qquad (39)$$

Since all terms under square root are positive, for F to be positive, the positive root must be used.

For simplicity, let

$$a = \frac{k_2T}{2k_3} \quad ; \quad b = \left(\frac{k_2T}{2k_3}\right)^2 \quad ; \quad d = \frac{4k_1k_3C}{(2k_3)^2}$$

then,

$$F = -a + \sqrt{b + dV} \tag{40}$$

substituting equation (40) into equations (34) and (35)

$$-\left.\frac{dF}{d\theta}\right)_{\text{molecules}} = k_2\left(-a + \sqrt{b + dV}\right)\frac{T}{V} \tag{41}$$

$$-\left.\frac{dF}{d\theta}\right)_{\text{coke}} = k_3\left(-a + \sqrt{b + dV}\right)^2 \frac{1}{V} \tag{42}$$

It is apparent, from equation (41), that the rate of free radical stabilization will decrease as the dilution of the hydrogen donor agent (Tetralin) increases. Equation (42) shows that dilution increases the rate of coking, contrary to what the simpler model (Model II) predicted. Thus, this assumed model shows that, in a hydrogen donor agent (Tetralin)-nonhydrogen donor agent (water) system, dilution of the hydrogen donor agent decreases the rate of stabilization and also increases the rate of polymerization.

If free hydrogen from Tetralin dehydrogenation were responsible for a portion of the coal fragments stabilization, then this effect would be reduced, since the partial pressure of hydrogen would be much less in the Tetralin-water-coal system than in the Tetralin-coal system. Thus the driving force for hydrogen transfer into the liquid is substantially smaller in the former case and less efficient utilization of the molecular hydrogen would be achieved.

(5) Tetralin-Water-Catalyst-Coal Systems

The model for the Tetralin liquefaction of coal has to satisfactorily explain the 25 to 30% drop in coal conversion to liquid products that occurred when water and various heterogeneous catalysts were introduced simultaneously into the Tetralin-coal system (Figure 26).

In catalytic cracking of crude petroleum, the catalysts used are deactivated by the formation of carbonaceous deposits or coke necessitating their frequent regeneration by controlled combustion. The coke precursors are unsaturated compounds which have been strongly adsorbed on the catalyst surface; these compounds do not desorb but polymerize by various condensation type reactions. These polymers eventually lose hydrogen to form the high carbon containing residues known as coke.

In the discussion of what is currently known about coal structure, it was noted that coal consists of small clusters of aromatic and heterocyclic rings linked by units containing sulfur and oxygen atoms, and by tetrahedral carbon atoms.

The free radicals or active fragments from the thermal cracking of coal contain a high proportion of aromatic rings, and in addition, various heterocyclic rings. Certain of these unsaturated radicals could be absorbed rather strongly on the catalyst surfaces and undergo polymerization reactions. Stabilization of these adsorbed radicals by Tetralin would be much less apt to occur. Stabilized liquid coal molecules might also be apt to adsorb on the catalyst surfaces and undergo condensation reactions. So, regardless of the mechanism of coal liquefaction, less apparent liquefaction could be expected if solid catalysts were present in the reactor and no reactions between water and the Tetralin or the coal fragments were occurring related to the presence of the solid catalyst. The proposed model for this system explaining the 25% drop in apparent coal liquefaction is then:

$$\begin{tikzcd}
\begin{array}{c}\text{Active fragments}\\ \text{or}\\ \text{Coal-derived}\\ \text{molecules}\end{array} \arrow[r, "\text{adsorb on}", "\begin{array}{c}\text{catalyst}\\ \text{surface}\end{array}"'] & \text{Adsorbed species} \arrow[d, "\text{time,heat}"] \\
& \begin{array}{c}\text{Adsorbed polymers}\\ \text{(benzene insoluble)}\end{array}
\end{tikzcd}$$

Since the effect described above apparently did not occur in the phenanthrene-water-catalyst-coal system because there were no differences noted between runs with and without catalysts present there has to exist basic differences between the phenanthrene-water and Tetralin-water coal systems. Two theories can be postulated:

1. Phenanthrene is a better solvent than Tetralin, thus the catalyst surface stays cleaner.
2. The active fragments are different between the two systems.

The active fragments in the Tetralin systems are probably long-lived radicals which have had their more labile centers stabilized by abstraction of hydrogen from a donor molecule shortly after bond rupture. In the phenanthrene containing systems, it has been theorized, the more reactive centers of the radicals become stabilized by condensation and polymerization reactions resulting in structures that could be more cross-linked than the original coal. The fragments separating from the coal masses in the phenanthrene-water-catalyst-coal systems could therefore be almost stable molecules (discussed earlier in the case of vacuum pyrolysis, see Section II-E) and perhaps have less tendency to bond to the catalyst surface.

The model proposed by Curran suggesting that the first step in coal liquefaction in the presence of Tetralin at 400°C under pressure is thermal cracking of covalent bonds in the coal structure appears to be consistent with the results obtained in the present study. The free radicals thus formed are stabilized by transfer of hydrogen atoms from the Tetralin or by condensation and polymerization reactions. The former may be benzene soluble while the latter will not be.

D. CONCLUSIONS FROM THE COAL LIQUEFACTION STUDIES

1. Water does not react with coal or coal-derived liquids to any great extent in the temperature range of 390 to 460°C and pressures up to 8000 psig even in the presence of various heterogeneous catalysts and polynuclear hydrocarbons (hydrogen donor agents and non-hydrogen agents).
2. The higher observed coal conversions in the water-coal system (16 to 20% w/w), as compared to the nitrogen-coal system (11% w/w), at corresponding temperatures were probably due to the dilution of the active free radical fragments produced via the thermal cracking of coal by the water. This dilution retarded the higher than first-order polymerization to benzene insolubles and allowed more time for benzene solubles to form by various rearrangement reactions.
3. The enhancement in coal conversion with phenanthrene-containing systems _vis à vis_ the nitrogen-coal system was probably also related to dilution of the active coal fragments since phenanthrene, an aromatic, possesses no hydrogen donor agent capabilities.
4. The initial mechanism of coal liquefaction in the 400°C temperature region is thermal cracking of coal to reactive fragments. Subsequently, these active fragments are converted to 1) benzene solubles by hydrogen transfer from active hydrogen donor agents

such as Tetralin or by internal rearrangement-type reactions, and 2) benzene insolubles by secondary polymerization reactions.

5. The coal-derived liquids from the Tetralin-coal systems are more reactive than those produced in the Decalin, phenanthrene or water-alone systems. This is evidence for long-lived large radicals which are stable because of stereochemical reasons. Further, this implies that less recombination of radicals occur in the Tetralin system and that the hydrogen donor agent has to be active and present when bond rupture occurs.
6. The implications of the water and catalyst effects in the Tetralin-coal system confirm that solubilization via hydrogen donor agents is a homogeneous liquid-phase process.

E. RECOMMENDATIONS FOR FUTURE WORK

1. This study should be expanded to include lower rank coals and additional heterogeneous catalysts.
2. Homogeneous catalysts which could possibly activate the water molecule should be evaluated.

IV. GASIFICATION SECTION

A. APPARATUS AND PROCEDURE, GASIFICATION RUNS

1. Description of Gasification Equipment

The gasification setup built and operated in this study is shown schematically in Figure 29. Details of construction and drawings of the reactor, water vaporizer and steam condenser are located in Appendix I. All of the equipment and fittings with which the process streams came into contact upstream of the condensate receiver were either stainless steel types 304 or 316, or Pyrex glass. The condensate receiver was copper and the lines connecting it to the chromatograph and wet test meter were Tygon tubing with polyethylene fittings.

Perhaps the most informative way to describe the apparatus is to discuss the principles of its operation.

a. Principles of Operation (Refer to Figure 29)

Under nitrogen pressure (25 psig) from cylinder (1a), distilled water was transferred continuously from the water reservoir (2a), a one-gallon stainless steel tank, through 1/8 inch stainless steel tubing to the water flowmeter (2c), a Brooks rotameter. Needle valves, located upstream and downstream of the rotameter, controlled the water flow. Although the gasification was nominally conducted at atmospheric pressure, there was a back pressure in the system caused by the steam and

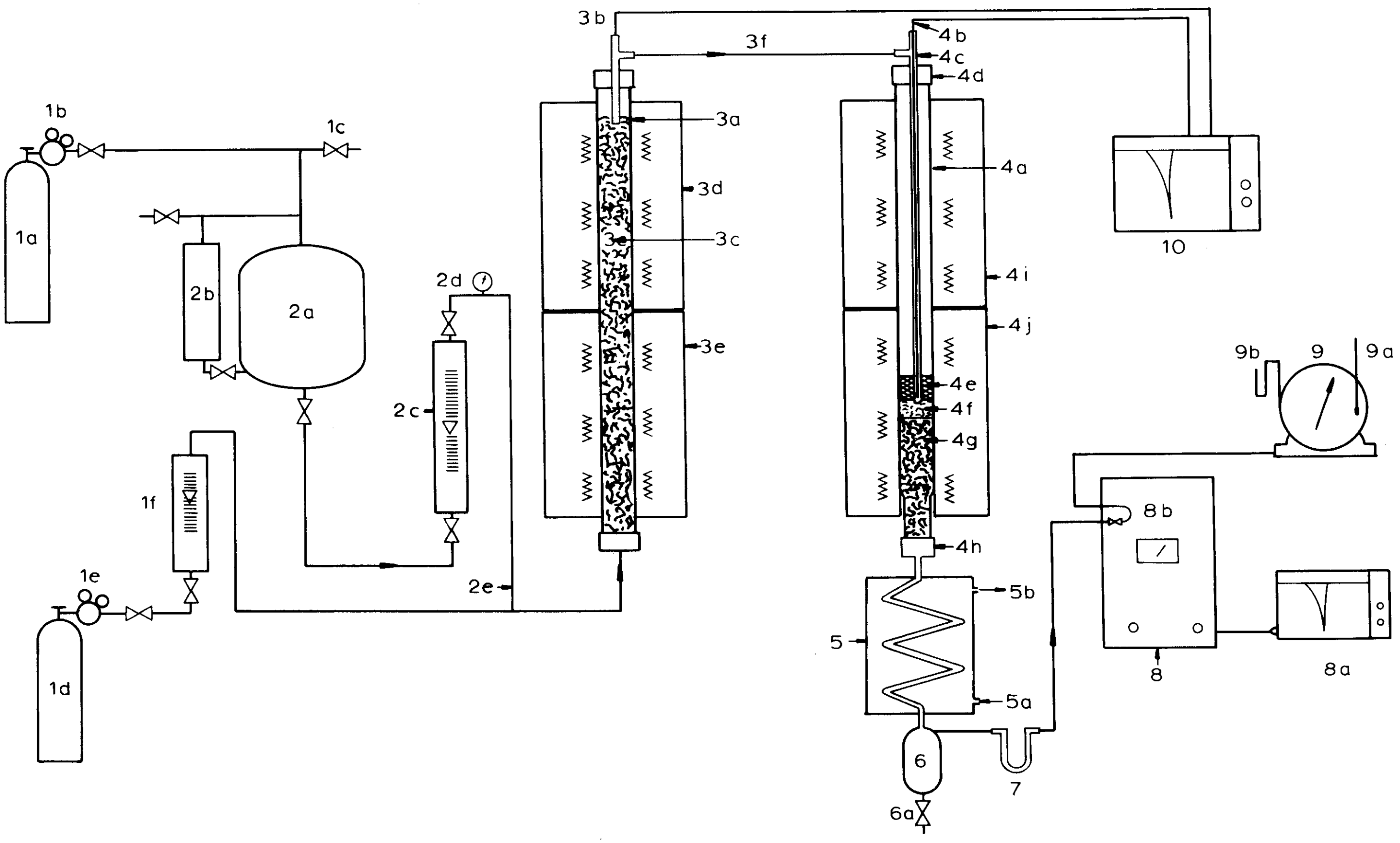


FIGURE 29 DIAGRAM OF FLOW REACTOR FOR GASIFICATION OF CARBON WITH STEAM

Legend to Figure 29

1a	Nitrogen Cylinder
1b	Pressure Reducing Valve
1c	Vent Valve
1d	Nitrogen Cylinder
1e	Pressure Reducing Valve
1f	Nitrogen Flowmeter
2a	Water Reservoir
2b	Water Level Glass
2c	Water Flowmeter
2d	Pressure Gauge
2e	Water Inlet Line
3a	Water Vaporizer
3b	Thermocouple #1
3c	Stainless Steel Wool Packing
3d	Furnace
3e	Furnace
3f	Steam Line to Reactor
4a	Reactor Column
4b	Thermocouple #2 (Sliding)
4c	Thermowell
4d	Top Closure
4e	Coke Bed
4f	Quartz Wool
4g	Stainless Steel Wool
4h	Bottom Closure
4i	Furnace
4j	Furnace
5	Steam Condenser
5a	Cooling Water Inlet
5b	Cooling Water Outlet
6	Condensate Receiver
6a	Condensate Drain Valve
7	Drierite Column
8	Gas Chromatograph
8a	Chromatogram Recorder
8b	Gas Sampling Valve
9	Wet Test Meter
9a	Thermometer
9b	Manometer
10	Temperature Recorder

gases flowing through the reactor and lines, and this was measured by the pressure gauge (2d) located downstream of the water flowmeter. A level glass (2b) on the water reservoir was calibrated with the tank contents to give an approximate number for the water fed during a run.

The water vaporizer (3a) was a vertically mounted 31-inch length of 3/4 inch schedule 40 pipe externally heated along its length by two electric furnaces (3d, 3e) (Hoskins Type FD 303 A, 110V, 5 amps). To facilitate heat transfer from the vaporizer walls to the water, the vaporizer was packed internally with stainless steel wool (3c). Steam, slightly above its saturation temperature, issued from the top of the vaporizer and entered the top of the reactor column. A Chromel-Alumel thermocouple (3b) inserted into a thermowell measured the temperature of the steam leaving the vaporizer. To minimize heat losses, the steam line (3f) between the vaporizer and the reactor was heavily insulated with asbestos tape covered with aluminum foil.

The reactor column (4a), a vertically mounted 30-inch length of schedule 14 tubing (1.084 inches inside diameter) was heated externally by two individually controlled electric furnaces (4i, 4j) of the same type as described for the vaporizer. A 0.25 inch outside diameter thermowell (4c) was positioned in the center of the reactor column and extended from the top to just below the carbon bed. A sliding Chromel-Alumel (4b) thermocouple was used inside this thermowell to monitor the reactor temperature at any point along the length. Positioned 4 inches from the bottom of the lower furnace was the coke-catalyst bed (4e) supported by a plug of quartz wool (4f) on a plug of stainless steel wool (4g).

The temperature of the coke-catalyst bed was maintained at the desired value by individually adjusting the amperage to the two furnaces. The empty reactor volume above the coke bed served as the superheater for the incoming steam and also served to smooth out any flow fluctuations. Superheated steam of the desired temperature flowed through the fixed bed of carbon and catalyst; gasification reactions occurred and the effluent gases, consisting of unreacted steam, carbon dioxide, carbon monoxide, methane and hydrogen exited from the reactor and passed into a water-cooled condenser (5) where the unreacted steam condensed and collected in the condensate receiver (6), a 200 ml copper vessel.

Product gases, saturated with water at about 20°C, passed through a Drierite column (7) where the remainder of the water was absorbed and then through a Carle gas chromatographic sampling valve (8b) and thence to the wet test meter (9), Precision Model 63125, one revolution 0.1 cubic feet capacity, where the amount of dry gases generated was measured. The Carle valve was located inside an in-line process gas chromatograph (8). Periodic samples of the gas stream were taken by activating the Carle valve which injected the gas sample directly into the gas chromatograph for analysis. A manometer (9b) was positioned upstream of the gas meter. The effluent gases were vented to a fume hood.

Temperatures T_1 and T_2 were continuously recorded by a Brown Electronik recorder (10), 0-600°C scale, calibrated by the Instrumentation Laboratory just prior to this application.

b. Charging the Reactor

The procedure for charging the reactor was as follows: Before each run the dismantled reactor was thoroughly cleaned with a brush using soap and water, rinsed with distilled water and dried with acetone. A new stainless steel wool sponge was weighed and forced into the reactor from the bottom filling the reactor from the bottom upward to within 1/8 inch of the thermowell. The bottom closure was then fitted using a high temperature pipe compound on the pipe threads. A rod was used to compress the stainless steel wool so that once it was in place it remained stationary. Quartz wool, also preweighed, was inserted through the top of the reactor and pressed on top of the stainless steel wool to serve as a support plug for the coke bed.

Catalyst and the coke to be gasified were then weighed separately and mixed in a small jar by simulating the motion of a solids blender. About 18.1 grams of coke were used in the charge. After blending, the solids were poured into the reactor using a long stemmed powder funnel. The bed of coke and catalyst, supported by the quartz and steel wool plugs, was about 1 3/4 inches high and occupied about 8.6×10^{-4} cubic feet (24.3 milliliters) of the annulus between the reactor wall and the thermowell. The top closure was then made using again high temperature pipe dope on the threads. It should be noted that the thermowell extended to just the bottom of the coke bed.

After the reactor was inserted into the furnaces, the connections were made between the reactor and vaporizer and between the reactor and the condenser. The final location of the coke-catalyst bed was such that it was positioned in the flat temperature profile zone of the lower furnace; the bottom of the coke bed was 4 inches above the lower end of the furnace. Each furnace had an overall length of 13 inches. Following a leaktest with 25 psig nitrogen for 15 minutes, the lines were insulated with asbestos tape and then covered with aluminum foil. A Chromel-Alumel thermocouple, inserted into the thermowell, was readily movable up and down to monitor the temperature at all points in the coke bed and in the preheating zone of the reactor column.

2. Experimental Procedures for Gasification Runs

a. Devolatilization Procedure

The devolatilization procedure, identical for each run, consisted of heating the reactor at a slow rate to 1150°F, while maintaining a slow purge of nitrogen through the system. The heatup time was between 95 to 100 minutes for all the runs. It was determined in duplicate experiments that about 9.5% of the coke charged evolved as volatile matter during the devolatilization. After 1150°F was reached, the Variacs controlling the amperage to each furnace were lowered to approximate settings for 1000°F reaction temperature. During the cooling step from 1150°F to 1000°F, the nitrogen flow was continued.

b. Gasification Reaction

(1) Preliminary

While the reactor was cooling to 1000°F, (1) the wet test meter was adjusted to zero, (2) a standard gas mixture was injected in duplicate into the gas chromatograph, and (3) the condensate receiver was drained. Also, a measured quantity of distilled water was charged to the water reservoir via residual vacuum; i.e., the water reservoir was isolated by appropriate valving, evacuated, isolated from the vacuum source and a measured amount of distilled water allowed to flow into the tank using the residual vacuum in the tank. Near the end of the cooling period, the water reservoir was pressurized to 25 psig with nitrogen.

(2) Startup and Operation

When the coke bed reached 1000°F, the water flow from the reservoir was started and the rotameter was adjusted to give the desired steam rate. Owing to the overall endothermic characteristic of the steam-carbon reaction, the reaction temperature tended to drop off, but this was quickly compensated for by adjusting the heat input. The coke bed temperatures, top, bottom and middle, were continuously monitored and appropriate Variac adjustments made to keep the average bed temperature at 1000°F.

At least every half hour, the following operations were carried out:

1. Gas sample injected into chromatograph
2. Condensate removed and measured
3. Wet test meter reading recorded
4. Temperature and pressure readings

Actual on-stream times varied between five and thirteen hours.

(3) Shutdown

After the final sequence of data was collected, the inlet water flow and the heating elements were turned off and the reactor allowed to cool overnight.

The next day, the reactor was carefully dismantled; the dry coke bed and the quartz and stainless steel wool plugs removed and weighed. The weight loss between what was charged and what was recovered was the amount of the coke bed which evolved during devolatilization and gasification.

3. Analytical Methods

a. Off-gas Analysis by Vapor Phase Chromatography (VPC)

After removal of the bulk of the unreacted steam in a water-cooled condenser, followed by complete drying via passage through a Drierite column, the gasification reactor effluent gases consisting now wholly of methane, hydrogen and the carbon oxides entered the oven of the gas chromatograph where, by means of an integral gas sampling valve, process gas samples were injected directly into the chromatograph.

Details of the VPC technique, including calibration and sample calculations are located in Appendix II. Briefly, carbon dioxide, methane and carbon monoxide were determined directly from the chromatograms, while hydrogen was determined as the difference between unity and the sum of the mol fractions of the gases analyzed directly. That this method was correct has been shown by a separate determination for hydrogen, using argon as the carrier gas in the chromatograph rather than helium. However, the latter technique was not conveniently carried out since helium is necessary for the accurate analysis of the gases other than hydrogen. No peaks other than nitrogen, oxygen, carbon monoxide, carbon dioxide, methane and hydrogen have been seen on the chromatograms, indicating that no significant gaseous products have been overlooked in the analysis.

b. Ultimate Analysis

Ultimate analyses were carried out on the coke charges, devolatilized cokes and the residues after gasification by the Physical and Analytical Department of Merck & Co., Inc., Rahway, N.J. Elements analyzed for include carbon, hydrogen, nitrogen and sulfur. Ash or residue on ignition assays were also obtained. Oxygen was determined as the difference between one hundred and the sum of the weight percentages of carbon, hydrogen, nitrogen, sulfur and ash. The latter is almost the universal method for oxygen in carbonaceous residues but means that the number for oxygen is the most inaccurate because the errors in all the other determinations appear in the oxygen number.

B. PRESENTATION OF EXPERIMENTAL GASIFICATION RESULTS

1. Background

Carbon sources for the gasification experiments were composites of the residual cokes remaining from water-coal and Decalin-water-coal high pressure liquefaction runs. These cokes are referred to in the following discussions as water coke and Decalin-water coke, respectively. Table XXII gives the details of the water coke and Decalin-water coke composites and their ultimate analyses. None of the residual cokes used in these composites came from liquefaction runs in which heterogeneous catalysts had been used. A mortar and pestle was used to reduce the coke particle size to about forty mesh before the compositing.

All of the gasification runs (see Section IV-A for description of apparatus and procedure) described herein were conducted at essentially atmospheric pressure. An *in situ* devolatilization of the coke charge was carried out prior to admitting steam so as to avoid any uncertainty that might be introduced into the gasification results by the presence of remaining volatile matter in the coke.

Since the comparisons among the various cokes and gasification catalysts are made on the basis of the instantaneous gasification rate, grams of carbon gasifying per minute per gram of carbon present in the bed at that

TABLE XXII

ULTIMATE ANALYSIS(1) OF DECALIN-WATER COKE AND WATER COKE COMPOSITES USED IN GASIFICATION EXPERIMENTS

Component	Decalin-Water(2) Coke	Water Coke(3)
	(Wt.%)	(Wt.%)
C	67.70	69.39
H	3.14	3.62
N	1.15	1.27
S	3.01	3.34
O (by difference)	6.73	7.75
Ash	18.27	14.63
Atomic H/C	0.55	0.62

(1) Analyses carried out by the Physical & Analytical Department of Merck & Co., Inc., Rahway, N.J.

(2) Decalin-Water Coke was a composite of residual cokes from liquefaction run numbers 97, 124 and 101 (see Table XV).

(3) Water Coke was a composite of residual cokes from liquefaction runs 43, 45, 53, 58, 60, 67, 75, 77, 78, 79 (see Table XIII).

time, it was necessary to know the initial weight of carbon present in the bed at the onset of gasification, i.e., after the devolatilization. For this reason, two runs, one with the water coke (Run G-18) and the other with the Decalin-water coke (Run G-19), were carried through the devolatilization step and then terminated without admitting steam. The devolatilized cokes were then removed, weighed and ultimate analyses carried out.

Given in Table XXIII is the ultimate analysis of the devolatilized water coke obtained from Run G-18. Given in Table XXIV is the material balance across the water coke devolatilization. Note that the ash content before and after devolatilization was the same. The recovery of the devolatilized water coke was 90.53% w/w, indicating that 9.47% w/w of the coke evolved during the devolatilization.

The quantity of carbon in the bed after devolatilization, C_o, is obtained by multiplying the amount of water coke charged to the reactor by the weight fraction recovery, 0.9053, then by the weight fraction of carbon in the devolatilized water coke bed, 0.6987. This calculation is valid for all the water coke runs and means that out of the usual 18.1 grams of water coke charge to the gasification reactor, only about 11.4 grams of carbon were present after devolatilization and at the onset of gasification.

TABLE XXIII

ULTIMATE ANALYSIS OF DEVOLATILIZED WATER COKE

RUN G-18

Component	Wt. %
C	69.87
H	2.19
N	1.26
S	2.82
O (by difference)	7.67
Ash	16.19

(1) Ultimate analyses carried out by the Physical and Analytical Department of Merck & Co., Ind., Rahway, N.J.

TABLE XXIV

MATERIAL BALANCE OVER WATER COKE DEVOLATILIZATION

RUN G-18

1. Experimental Data

Water Coke Charged	= 18.3128 grams
Devolatilized Water Coke Recovered	= 16.5788
Volatile Matter Evolved	= 1.7340 grams

2. Material Balance Using Analyses(1) of Water Coke(2) and Devolatilized Water Coke(3)

Element	In Water Coke Charge (grams)	In Devolatilized Water Coke (grams)	In Volatile Matter by Difference (grams)
C	12.710	11.580	1.130
H	.662	.363	.299
N	.232	.208	.024
S	.611	.468	.143
O (by difference)	1.420	1.280	.140
Ash	2.680	2.680	0
	18.315	16.5788	1.736

(1) Ultimate analyses carried out by the Physical & Analytical Department of Merck & Co., Inc., Rahway, N.J.

(2) From Table XXII.

(3) From Table XXIII.

If the assumption is made that all the evolved oxygen appears as carbon dioxide, then the atomic ratio of evolved hydrogen to the remainder of the evolved carbon was about 3.4, *vis à vis* 4 for methane (see Table XXIV).

Carrying out the same analysis on the devolatilized Decalin-water coke resulted in a weight loss of about 9.1% w/w over the devolatilization step with the devolatilized material having a carbon content of 68.3% w/w. Thus, C_o for the Decalin-water coke runs is the product of the coke charged times 0.909 times 0.683 or based on a customary charge of 18.1 grams, 11.2 grams of carbon.

The objectives of this study were:

1. To determine if the carbonaceous residues or chars remaining from the liquefaction experiments were amenable to gasification at 1000°F.
2. To compare cesium compounds with potassium compounds as gasification catalysts.
3. To gain further insight into the mechanism of catalysis of carbon gasification by alkali metal compounds.
4. To check Tung's findings that potassium acetate is superior to potassium carbonate as a carbon gasification catalyst (Tung, 1953).

The first four gasification runs served to check out the equipment, establish the standard devolatilization and operating procedures, and determine approximate gasification rates. After these preliminary runs, the carbon bed in the gasification reactor was repositioned to facilitate the maintenance of an isothermal temperature profile during the operation.

2. Tabulation of Gasification Experiments

In the Tabulation of Experiments that follows, the experimental runs are not listed chronologically, but rather have been arranged into groups dependent on the nature of the coke and the catalyst. The grouping is as follows:

Series I (Runs 5-8) - Decalin-Water Coke Runs with Potassium Acetate and Cesium Hydroxide.

Series II (Runs 10,11,17,15,16) - Water Coke Runs with Potassium Acetate and Potassium Carbonate.

Series III (Runs 9,12,13,14) - Water Coke Runs with Cesium Acetate and Cesium Nitrate.

TABLE XXV

TABULATION OF GASIFICATION EXPERIMENTS

Series	Run No.	Coke		Catalyst				Reaction Conditions(2)		Length of Run (minutes)	Gas Volume Evolved (ft^3)	Carbon in Bed at Start of Gasification (C_o, grams)
		Type(1)	Charge (g)	Name	Charge (g)	g. mols	g. atom cation / g. coke	Temp.(3) (°F)	Steam Rate (g/min)			
I	5	Decalin-water coke	18.9863	KOAc	3.8169	.0389	.00205	1060	1.29	300	.477	11.79
	6	Decalin-water coke	18.0359	KOAc	3.6591	.0373	.00207	975	1.13	300	.139	11.20
	7	Decalin-water coke	18.0811	KOAc	3.6544	.0372	.00206	1000	1.73	450	.233	11.22
	8	Decalin-water coke	18.0353	CsOH	5.5847	.0373	.00207	1000	0.89	444	.230	11.20
II	10	Water coke	18.0911	KOAc	3.6780	.0375	.00207	1000	1.17	550	.586	11.42
	11	Water coke	18.1035	KOAc	3.6815	.0375	.00207	1000	1.16	630	.664	11.43
	17	Water coke	18.1556	KOAc	3.6603	.0373	.00206	1000	1.19	390	.445	11.48
	15	Water coke	18.1029	K_2CO_3	5.5136	.0399	.00441	1000	0.85	630	.768	11.44
	16	Water coke	18.1176	K_2CO_3	2.5884	.0187	.00207	1000	0.70	300	.311	11.46
III	9	Water coke	18.1035	$CsNO_3$	7.2486	.0372	.00205	1000	1.55	720	.901	11.44
	12	Water coke	18.1156	$CsNO_3$	7.2538	.0372	.00205	1000	1.28	480	.554	11.46
	13	Water coke	18.1189	CsOAc	7.1688	.0373	.00206	1000	0.91	540	.965	11.46
	14	Water coke	18.1350	CsOAc	7.1347	.0372	.00205	1000	0.70	660	.895	11.47

(1) See Section IV-B-1 for definitions of Decalin-water coke and water coke.

(2) (a) All runs made at one atmosphere nominal pressure.
(b) All runs used the standard devolatilization procedures (see Section IV-A) except Run G-17, in which the nitrogen flow was omitted.

(3) 1000°F = 538°C.

3. Presentation of Gasification Results

The most significant results of this experimental study of carbon gasification are presented in the following tables and figures. Appendix III contains the sample calculation for Run G-13 which completely illustrates the computational procedures used in evaluating the experiment. Appendix IV lists the sources of the chemicals used.

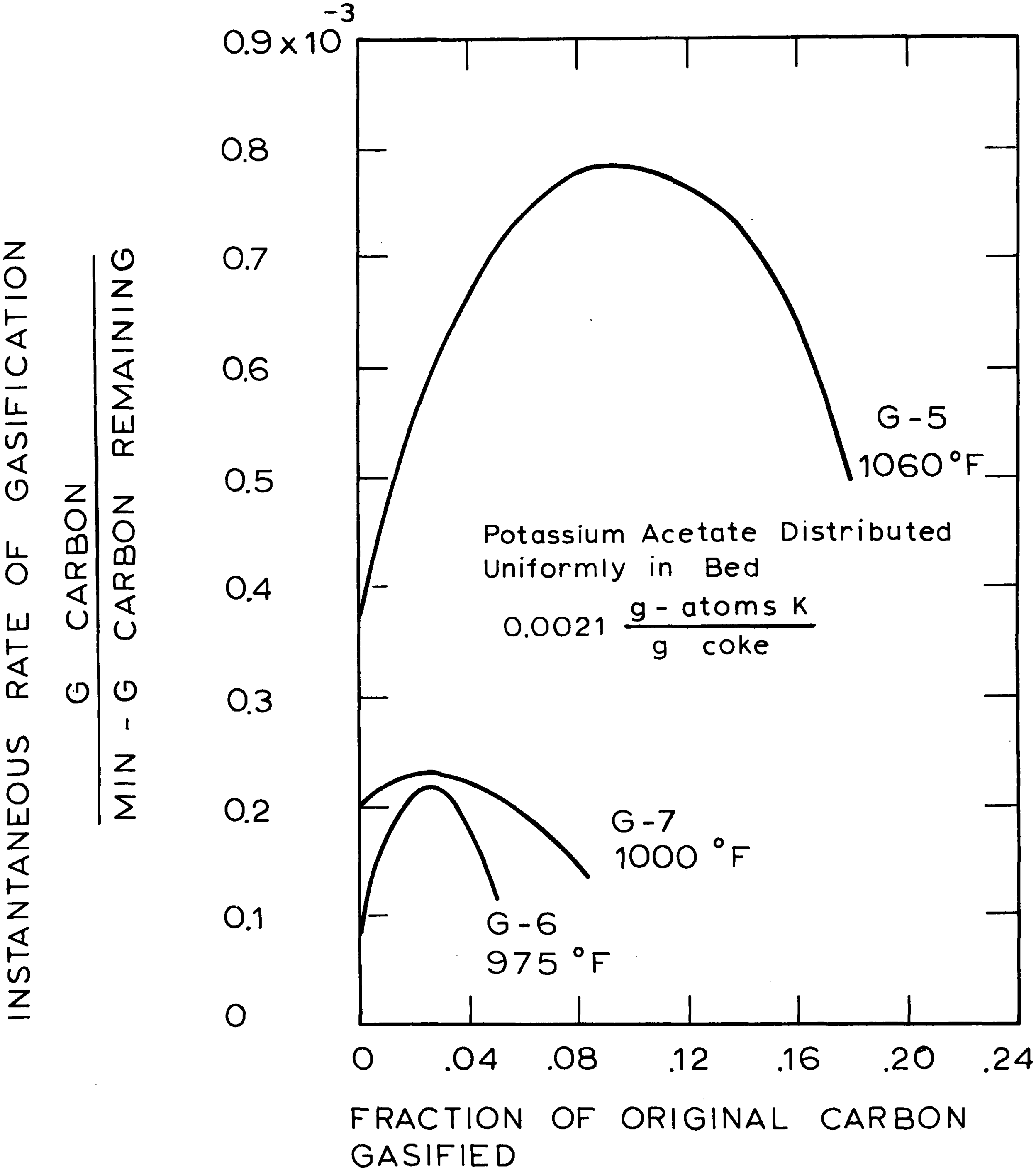


Figure 30 Effect of Temperature on Decalin - Water Coke Gasification

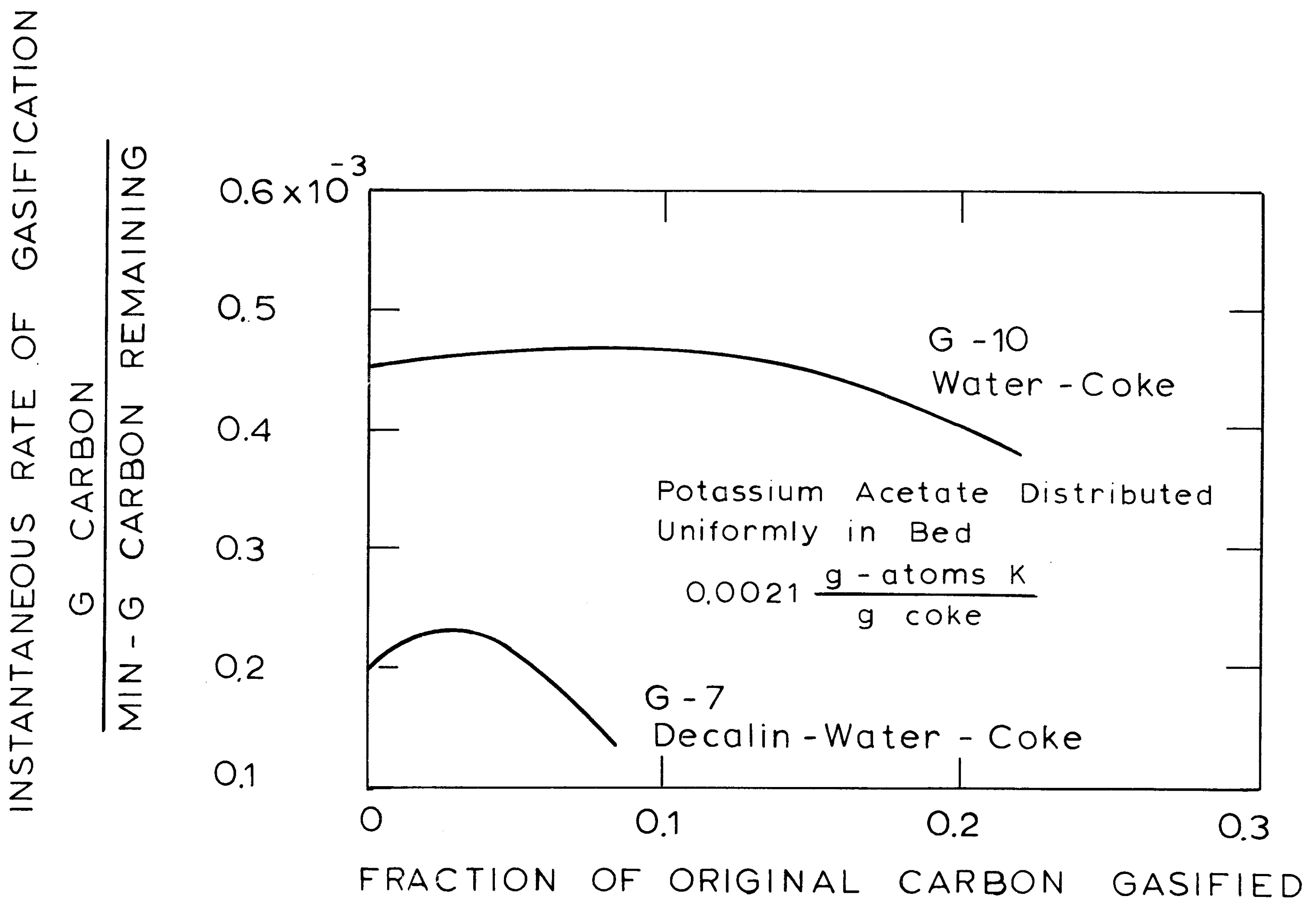


Figure 31 Comparison of Coke Reactivities at 1000 °F

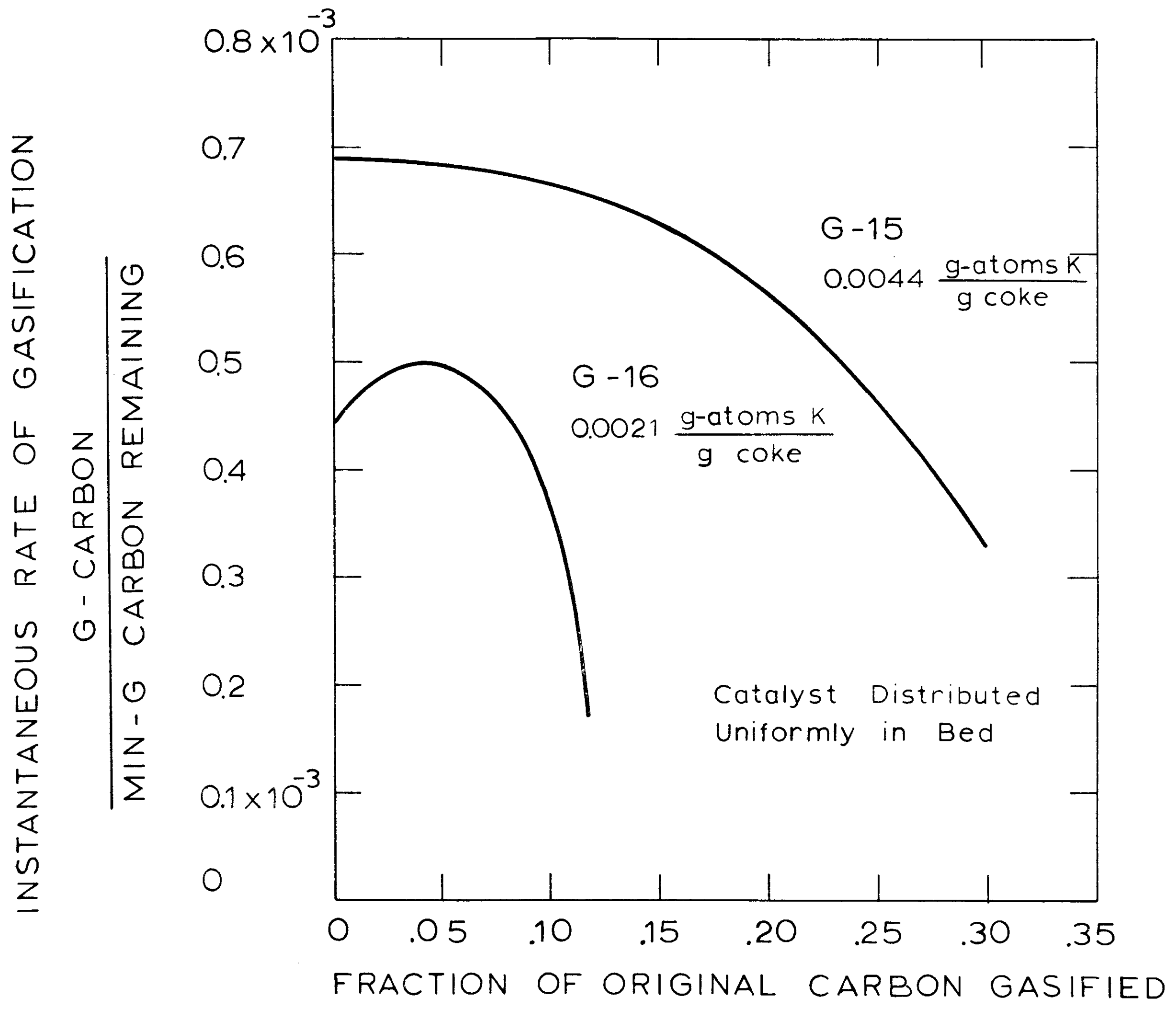


Figure 32 Effect of Potassium Carbonate Conc. on Water Coke Gasification at 1000 °F

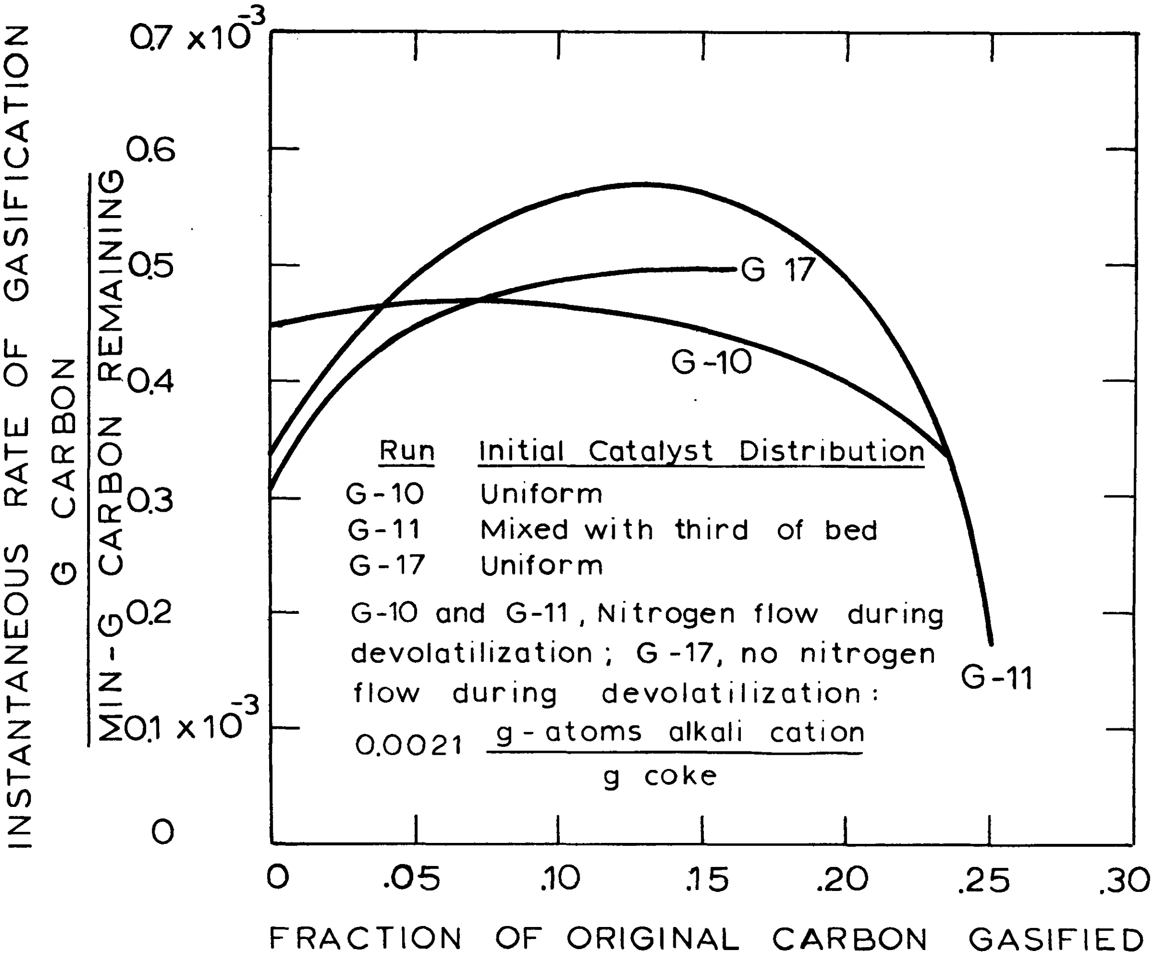


Figure 33 Effect of Initial Potassium Acetate Distribution and Devolatilization Procedure on Water Coke Gasification at 1000 °F

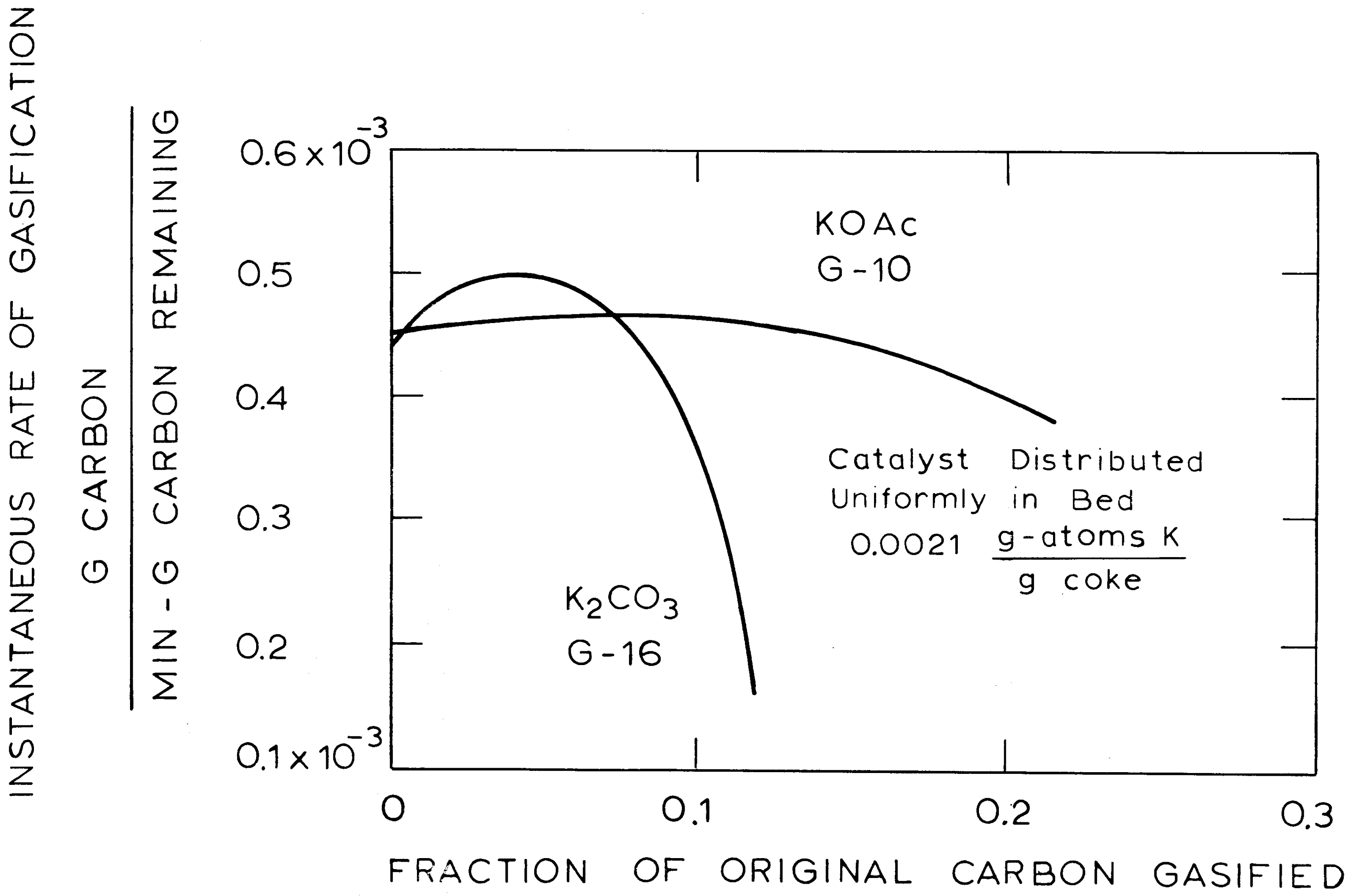


Figure 34 Comparison of KOAc with K_2CO_3 for Water Coke Gasification at 1000 °F

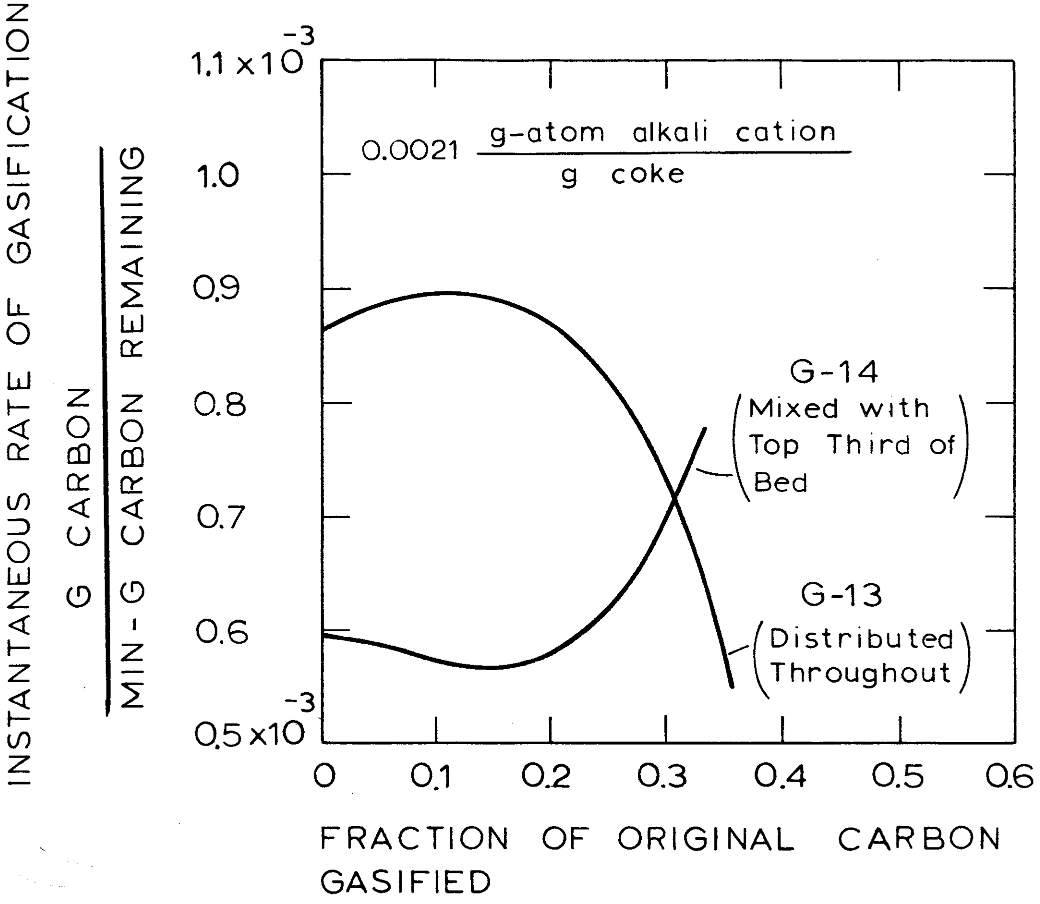


Figure 35 Effect of Initial Cesium Acetate Distribution on Water Coke Gasification at 1000 °F

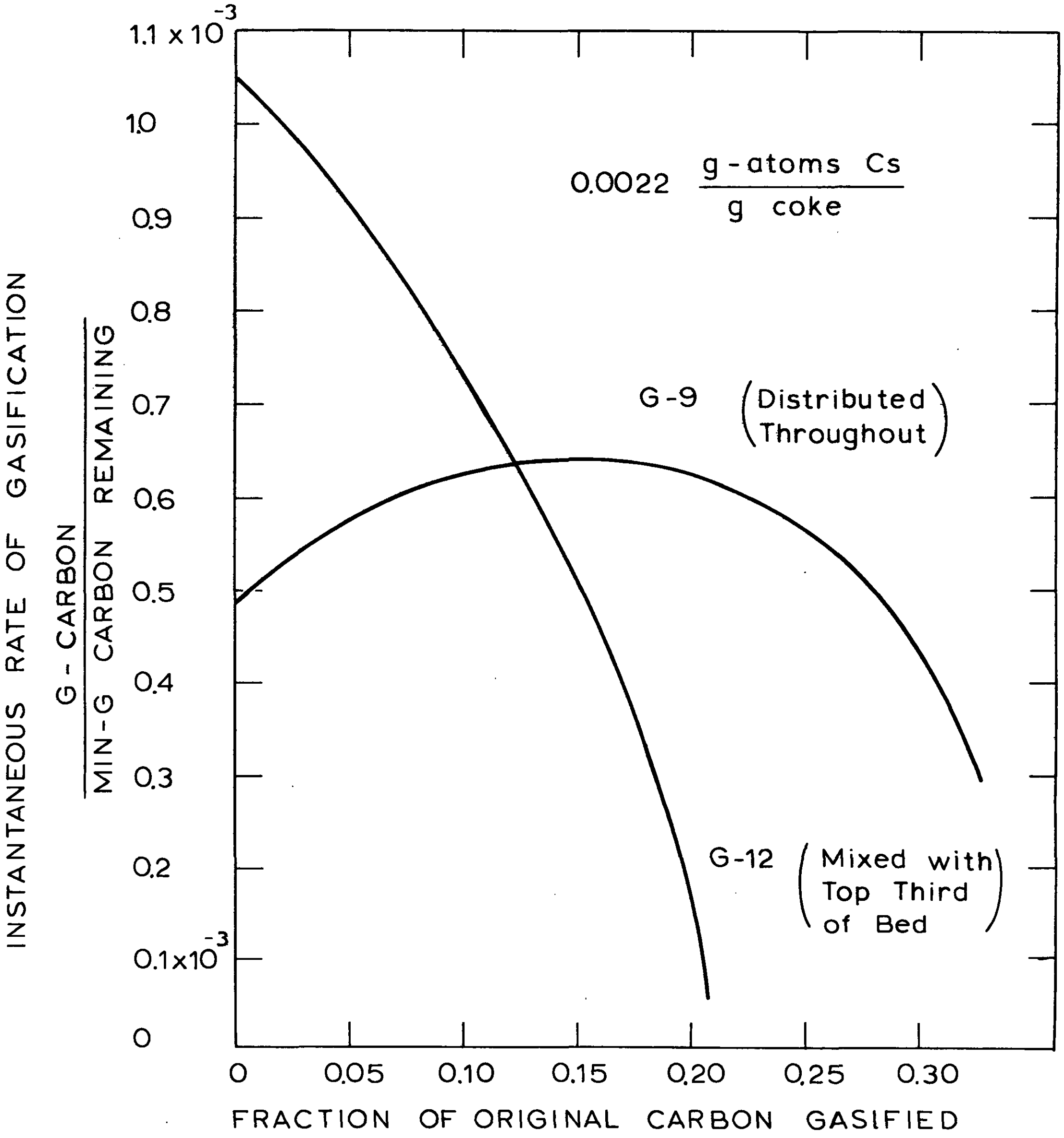


Figure 36 Effect of Initial Cesium Nitrate Distribution on Water Coke Gasification at 1000 °F

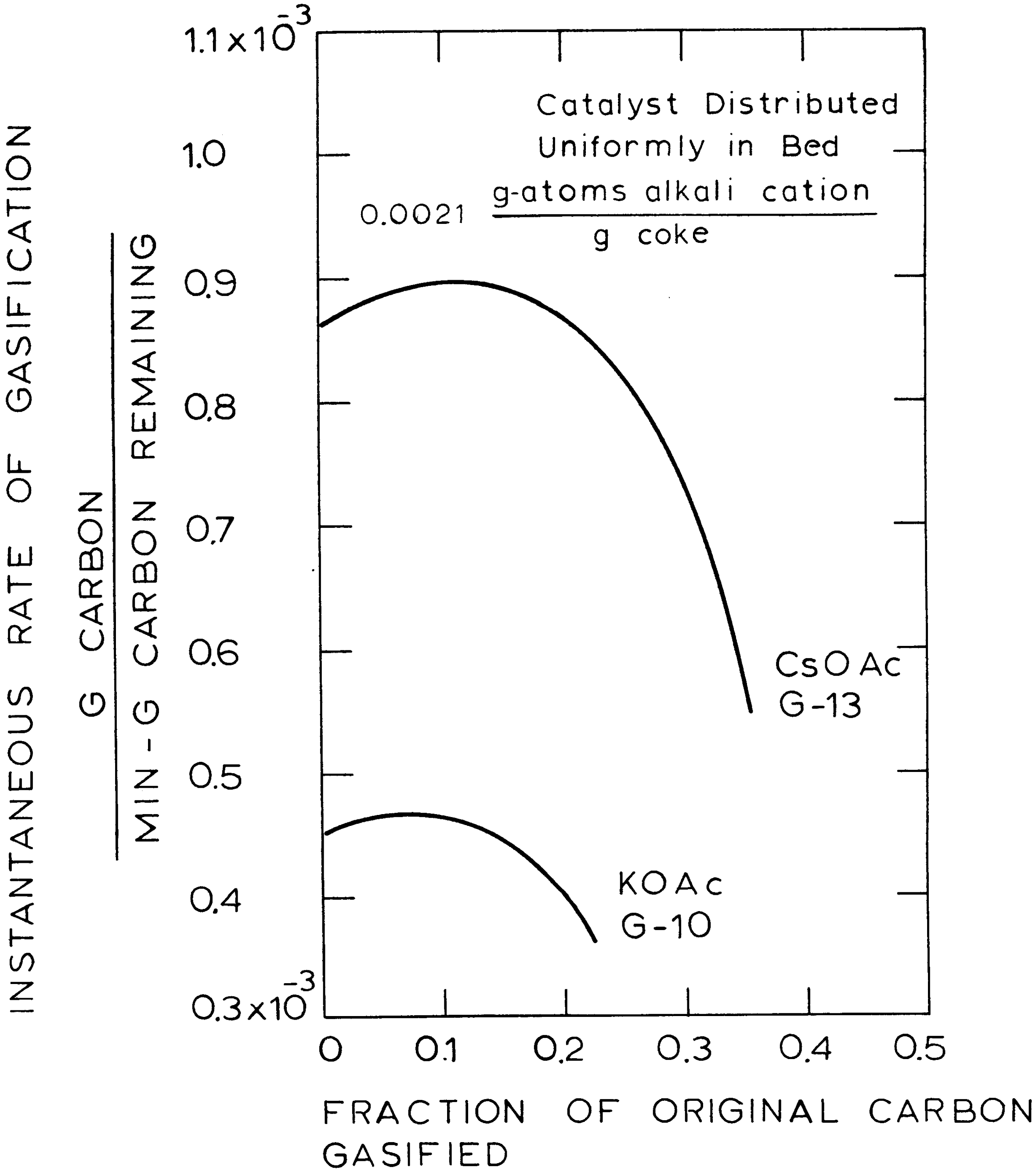


Figure 37 Comparison of Potassium Acetate with Cesium Acetate for Water Coke Gasification at 1000 °F

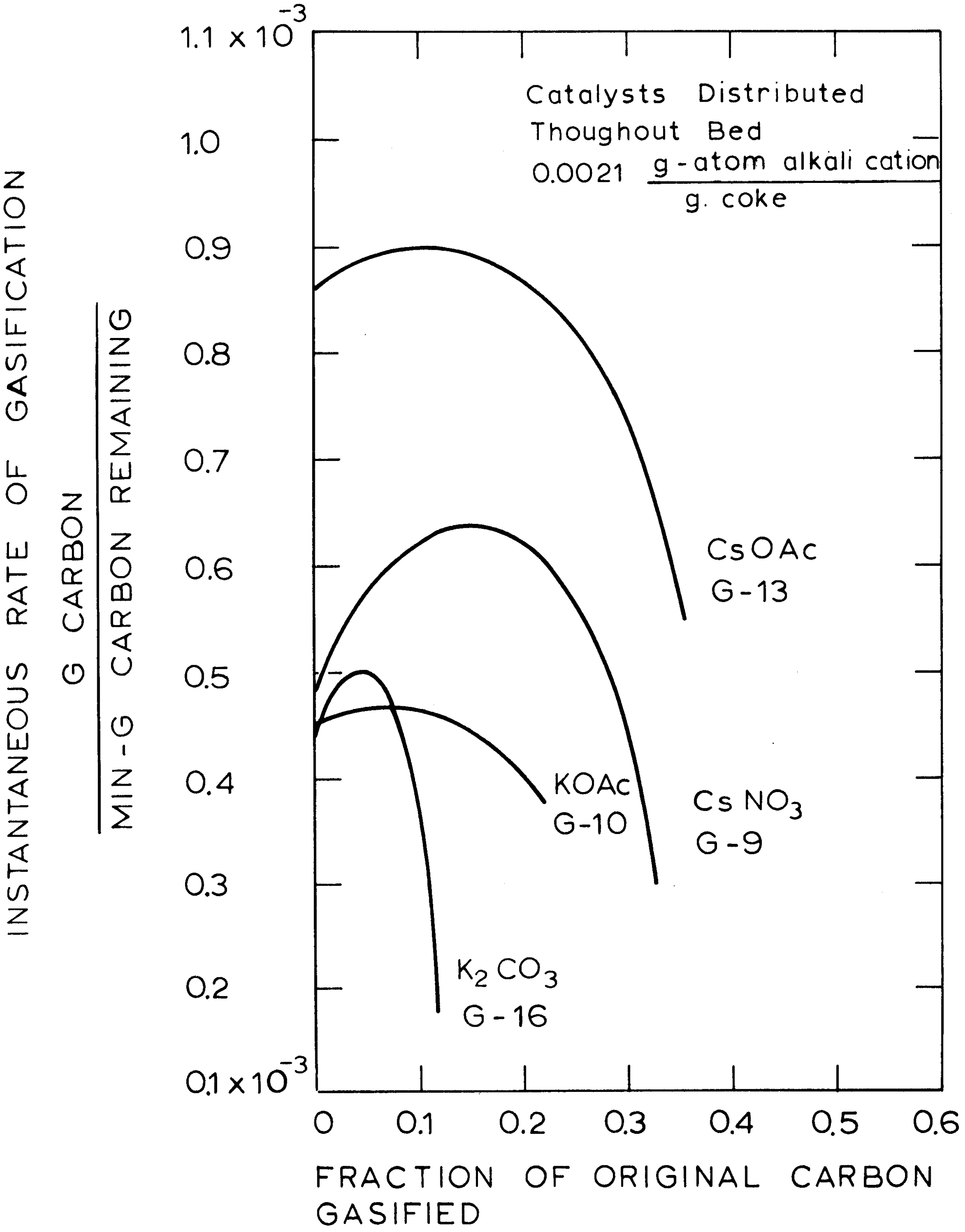


Figure 38 Comparison of Alkali Salts for Water Coke Gasification at 1000 °F

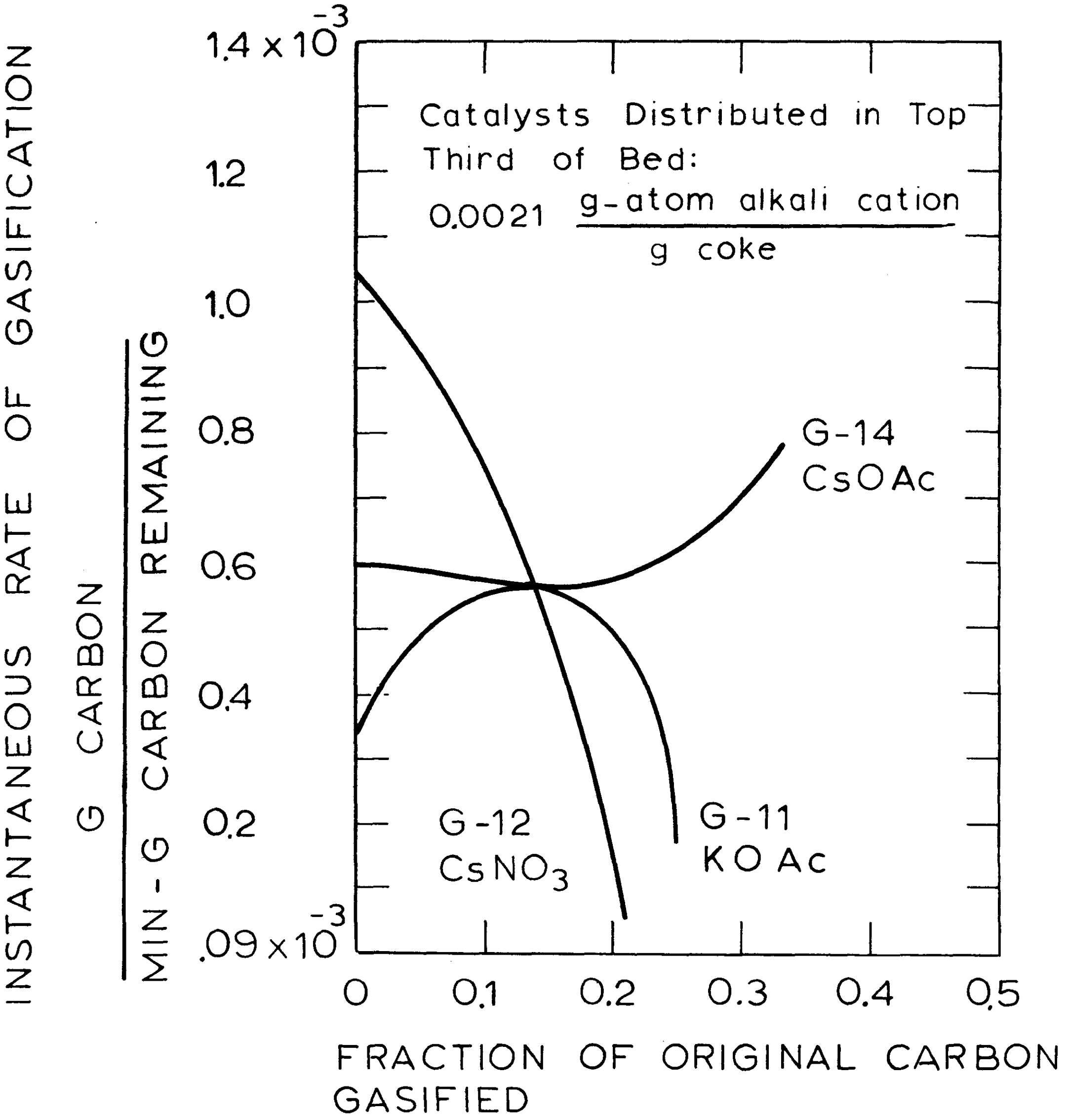


Figure 39 Comparison of Alkali Salts for Water Coke Gasification at 1000°F

TABLE XXVI

CUMULATIVE PRODUCTION OF GASES

	Catalyst				Cumulative Gram-Moles of Gas			
n No.	Name	g. atoms cation / g. coke	Length of Run (min.)	(1) FCG	CO_2	CH_4	CO	H_2
5	KOAc	.00205	300	0.180	0.165	0.00749	0.00429	0.389
6	KOAc	.00207	300	0.0503	0.0420	0.00396	0.000935	0.111
7	KOAc	.00206	450	0.0853	0.0708	0.00660	0.00231	0.196
8	CsOH	.00207	444	0.0878	0.0727	0.00634	0.00282	0.185
9	$CsNO_3$	.00205	720	0.326	0.302	0.00601	0.00239	0.726
10	KOAc	.00207	550	0.217	0.198	0.00577	0.00258	0.480
11	KOAc	.00207	630	0.251	0.226	0.00907	0.00382	0.535
12	$CsNO_3$	.00205	480	0.208	0.191	0.00606	0.00225	0.456
13	CsOAc	.00206	540	0.354	0.327	0.00659	0.00380	0.791
14	CsOAc	.00205	660	0.331	0.306	0.00635	0.00348	0.720
15	K_2CO_3	.00441	630	0.297	0.271	0.00792	0.00407	0.624
16	K_2CO_3	.00207	300	0.118	0.105	0.00537	0.00188	0.256
17	KOAc	.00206	390	0.161	0.143	0.00670	0.00372	0.367

(1) FCG = fraction of original carbon gasified

4. General Accuracy and Reproducibility

a. Coke-Catalyst Mixture

The major source of error was nonhomogeneity of the coke used. The composites were made by combining the cokes from several similar liquefaction runs by crushing the cokes to about 40 mesh particle size, then blending in a wide-mouth jar by simulating the motion of a solids blender. Error is estimated here to be about ± 5%. Mixing the catalysts with the coke was carried out by powdering the catalyst to about 40 mesh and then again blending. No segregation of the coke and catalyst was seen but was possible. Error is estimated to be about ± 5%.

b. Experimental Techniques

Weighings were carried out with a Mettler balance (see Section III-A) to the nearest thousandth. The only transfer was the coke-catalyst mixture into the top of the reactor. Considering the nonhomogeneity and the technique possible error is ± 12% maximum.

Temperature control was manual, and usually within ± 5°C, except at the very beginning, where owing to the endothermic characteristics of the gasification, the temperature fell perhaps 10°C but it was quickly restored. The temperature recorder had been recently calibrated, just prior to this study, by the Instrumentation Laboratory. The Chromel-Alumel thermocouple used agreed with the thermocouples used for the liquefaction studies.

C. DISCUSSION OF GASIFICATION RESULTS

1. Qualitative Observations on Gasification Results

a. Introduction

This section is intended to convey qualitatively significant aspects of the experimental gasification results (see Section IV-B). Detailed and more theoretical discussion of these results appear next in the Interpretation and Analysis Section.

In Section IV-B, the experimental findings of the gasification study are presented graphically as an instantaneous rate of carbon gasification, R_I, grams of carbon gasifying per minute per gram of carbon remaining in the bed at time t, versus, FCG, the fraction of the original carbon gasified by time t. Other workers have used the term "specific integral gasification rate" for R_I (Goring et al., 1952). This parameter FCG is often referred to in the literature as the fractional bed burnoff.

Inspection of Figures 30 to 39 reveals that in general, the instantaneous gasification rate first increases as the FCG increases, then reaches a maximum and subsequently steadily decreases. The exact shape of the R_I versus FCG curves varies depending on the catalyst and its initial distribution in the bed.

b. Discussion of Significant Results

(1) Series I - Decalin-Water Coke Runs with Potassium Acetate and Cesium Hydroxide

The strong influence of temperature on the gasification rate of the Decalin-water coke is shown in Figure 30 for the case where potassium acetate was initially distributed uniformly throughout the coke bed. Run G-5, conducted at 1060°F had a rate approximately four times the rate of Run G-6, carried out at 975°F.

Figure 31 illustrates the difference in reactivity at 1000°F between the water coke, Run G-10, and the Decalin-water coke, Run G-7, with potassium acetate as the catalyst initially distributed uniformly in the bed. Initially, the water coke is approximately twice as reactive as the Decalin-water coke and whereas the maximum gasification rate for the Decalin-water coke occurs around a FCG value of 0.04, the maximum rate for the water coke occurs around a FCG value of 0.075. The rate dropoff is more pronounced for the Decalin-water coke than for the water coke. The maximum rates observed in these cases are 4.6×10^{-4} g.C/(min.)(g.C) for the water coke and 2.3×10^{-4} g.C/(min.)(g.C) for the Decalin-water coke.

(2) Series II - Water Coke Runs with Potassium Acetate and Potassium Carbonate

Figures 32 and 33 present the results of runs with potassium carbonate and potassium acetate, respectively. A direct comparison between gasification catalysis by potassium acetate and potassium carbonate appears in Figure 34.

(a) Potassium Carbonate Catalysis

Figure 32 illustrates, at 1000°F and atmospheric pressure, the effect on the gasification rate of water coke of doubling the amount of potassium carbonate initially distributed uniformly in the coke bed. Run G-15, with an initial catalyst concentration of 0.0044 gram-atom potassium per gram coke, possesses an initial gasification rate of 6.9×10^{-4} g.C/(min.)(g.C), approximately 1.5 times greater than the initial rate of Run G-16 which had an initial catalyst concentration of 0.0021 gram-atom potassium per gram coke. It is also of significance that the rate, at the higher catalyst level, does not fall off nearly as rapidly with increasing carbon burnoff as the rate at the lower catalyst level. For example, at a FCG value of 0.12, the observed rate for Run G-15 is 6.5×10^{-4} g.C/(min.)(g.C), for Run G-16, it is 2.9×10^{-4} g.C/(min.)(g.C), lower by a factor of 2.2; at a FCG value of 0.135, the rate for Run G-16 is 3.6 times lower than the rate for Run G-15.

(b) Potassium Acetate Catalysis

In Figure 33 is depicted the behavior of the potassium acetate catalyzed water coke system at 1000°F, atmospheric pressure and an initial catalyst concentration of 0.0021 gram-atom potassium per gram coke. Runs G-10 and G-11 and Runs G-10 and G-17, respectively, demonstrate the effect of the initial potassium acetate distribution in the bed and variations in the devolatilization procedure on the R_I versus FCG curves.

In Run G-10, the catalyst was admixed with the entire coke charge; while in Run G-11 the catalyst was admixed only with the top third of the bed. Comparing Runs G-10 and G-11:

1. The initial rate for Run G-10, initial uniform catalyst distribution, is about 1.4 times higher than Run G-11, initial catalyst distribution in the top third of the bed.
2. Run G-11, the rate maximum, 5.7×10^{-4} g.C/(min.)(g.C), occurs at a FCG value of 0.13; for Run G-10, the corresponding numbers for the rate and FCG are 4.7×10^{-4} g.C/(min.)(g.C) and 0.07, respectively. Thus, the maximum rate for Run G-11 is about 1.2 times higher.
3. Run G-11 shows a markedly more rapid rate dropoff with increasing burnoff than Run G-10.

In summary, a higher maximum rate was obtained in the case where potassium acetate was distributed initially in the top third of the bed at the expense of a lower initial rate and a sharper dropoff with increased burnoff.

Since the catalyst is present during devolatilization, the devolatilization procedure followed could have an effect on its subsequent catalytic behavior during the gasification phase. Normally, the devolatilization was carried out by heating the bed in situ to 1150°F at 12 to 13°F per minute while maintaining a small flow of nitrogen through the bed. However, in Run G-17, the nitrogen flow was not used; instead the bed was heated to 1150°F in a nitrogen atmosphere. Comparing Runs G-10 and G-17:

1. Omitting the nitrogen flow during devolatilization, Run G-17, results in a 50% lower initial gasification rate than if the nitrogen flow is used, Run G-10.
2. The maximum rate attained in Run G-17, 4.95×10^{-4} g.C/(min.)(g.C), appears to be about 10% higher than the maximum rate attained in Run G-10. The corresponding FCG values are 0.16 and 0.07 to 0.8, respectively.
3. Run G-17 was not carried out for a sufficient length of time to determine its dropoff characteristics.

There is not a major difference between the results obtained from these two variations in devolatilization procedure.

(c) Comparison of Catalysis by Potassium Acetate and Potassium Carbonate

Figure 34 contrasts potassium acetate and potassium carbonate, at the 0.0021 gram-atom potassium per gram coke level, as gasification catalysts at 1000°F and atmospheric pressure.

The salient features of Figure 34 are:

1. At this catalyst level, the initial rates are essentially identical, 4.5×10^{-4} g.C/(min.)(g.C).
2. The maximum rates differ by less than 10%, being slightly higher, 5×10^{-4} g.C/(min.)(g.C), for the potassium carbonate. The corresponding values for the FCG values where the maximum rates occur are 0.04 and 0.07 to 0.08 for potassium carbonate and potassium acetate, respectively.
3. The rate dropoff with potassium acetate is much less than with potassium carbonate at this catalyst level.

If Run G-10, Figure 33 or 34, is compared with Run G-15, Figure 32, it can be seen that if the potassium carbonate level, expressed as gram-atoms of potassium is twice that of potassium acetate on the same basis, the R_I versus FCG curve for potassium carbonate is similar in its dropoff behavior to that of potassium acetate.

At comparable levels in this experimental system, potassium acetate is superior to potassium carbonate because the rate dropoff with burnoff is much less. Both catalysts possess virtually the same initial rates and very similar maximum rates.

(3) Series III - Water Coke Runs with Cesium Compounds

Both cesium acetate and cesium nitrate were evaluated at 1000°F, atmospheric pressure and at the 0.0021 gram-atom cesium per gram coke level as gasification catalysts for the water coke. These results for cesium acetate and nitrate, respectively, are shown in Figures 35 and 36. A comparison between potassium acetate and cesium acetate appears in Figure 37.

(a) Cesium Acetate Catalysis

In Figure 35 are shown the effects on the R_I versus FCG curves when the cesium acetate is either admixed initially with the entire coke bed, Run G-13, or admixed initially with the top third of the coke bed. The highlights of Figure 35 are:

1. The initial rate for the uniformly admixed bed is 8.6×10^{-4} g.C/(min.)(g.C) compared to 5.95×10^{-4} g.C/(min.)(g.C) for the non-uniformly admixed bed, a difference of 45%.
2. The rate increases with increasing burnoff for Run G-14 but decreases with increasing burnoff in Run G-13. The former effect is significant since it means that initial distribution is more important with cesium acetate than with the other catalysts.

(b) Cesium Nitrate Catalysis

The cases of cesium nitrate admixed initially either with the top third of the bed, Run G-12, or with the entire bed, Run G-9, are shown in Figure 36. Comparing Runs G-9 and G-12:

1. There is a striking difference between the R_I versus FCG curves for these two cases of initial catalyst distribution in the bed. The initial rate for Run G-12 is 10.5×10^{-4} g.C/(min.)(g.C) as compared to 4.85×10^{-4} g.C/(min.)(g.C) for Run G-9.
2. The rate dropoff for Run G-12 is dramatic. No rate maximum with FCG is observable. In the case of the initial uniform cesium nitrate distribution, Run G-9, the rate maximizes at a value of 6.4×10^{-4} g.C/(min.)(g.C) and a FCG value of 0.14 to 0.16.

Cesium nitrate, distributed in the top third of the water coke bed, exhibits the highest initial rate observed in this work, about 10.5×10^{-4} g.C/(min.)(g.C).

Figure 37 illustrates clearly that cesium acetate, Run G-13, is considerably more effective as a gasification catalyst than potassium acetate, Run G-10. Their initial gasification rates are 8.6×10^{-4} and 4.5×10^{-4} g.C/(min.)(g.C), respectively, different by a factor of 1.9. The maximum gasification rate observed with cesium acetate, 8.95×10^{-4} g.C/(min.)(g.C) occurs at a FCG value of 0.12, while the corresponding values for the potassium acetate are 4.7×10^{-4} g.C/(min.)(g.C) at 0.07 to 0.08, a difference again of a factor of 1.9. The two alkaline earth acetates exhibit similar rate dropoff behavior with extent of bed burnoff.

(4) Overall Observations

Various potassium and cesium compounds and their initial distributions in the bed have been studied to determine the effects on the gasification rate of the water coke.

Figures 38 and 39 summarize these results. Figure 38 is the comparison between potassium carbonate, potassium acetate, cesium nitrate and cesium acetate — all initially distributed uniformly in the coke bed, at 1000°F, atmospheric pressure and a catalyst concentration of 0.0021 gram-atoms alkali cation per gram coke.

Figure 39 presents the same comparisons for the cases where the catalyst is initially distributed only in the top third of the coke bed. The differences in reactivity of the water coke and the Decalin-water coke are illustrated in Figure 31, previously discussed.

2. Interpretation and Analysis of the Gasification Results

a. Introduction

Many reactions can be written to describe the carbon-steam system (see Section II-J). In Table XXVII are nine reactions selected for examination in the data analysis. These reactions comprise three groups:

(1) primary gasification, reactions G_1, G_2 and GM;
(2) carbon oxides interchange, reactions S_1 and S_2;
(3) methane production, reactions M_1, M_2, M_3 and M_4.

Reaction GM, in addition to being a primary gasification reaction is also a methanation reaction. Similarly, reaction M_1 is also a gasification reaction and reaction M_2 could be considered to be a carbon oxides interchange reaction. It should be noted that the primary gasification reactions, G_1, G_2 and GM, are the only reactions in Table XXVII involving only steam and carbon as reactants. At least one of the products of the primary gasification reactions appear as a reactant in each of the carbon oxides interchange and the other methanation reactions. Reaction S_2 is the well-known water gas shift. Gasification, according to this scheme of nine reactions, is sequenced as:

1. Carbon and steam react producing hydrogen, carbon oxides and methane via certain or all of the primary gasification reactions G_1, G_2 and GM.

TABLE XXVII

POSSIBLE REACTIONS IN GASIFICATION STUDY

Notation		Kp Expression	R (E.O.E.A.) Expression	Value of Kp at 1000 F(atm)
	I. Primary Gasification Reactions			
G_1	$C + H_2O = CO + H_2$	$Kp_{G_1} = \frac{P^{*}_{CO}\ P^{*}_{H_2}}{P^{*}_{H_2O}}$	$R_{G_1} = \frac{P_{CO}\ P_{H_2}}{P_{H_2O}\ Kp_{G_1}}$	0.0653
G_2	$C + 2H_2O = CO_2 + 2H_2$	$Kp_{G_2} = \frac{P^{*}_{CO_2}\ P^{*2}_{H_2}}{P^{*\ 2}_{H_2O}}$	$R_{G_2} = \frac{P_{CO_2}\ P^{2}_{H_2}}{P^{2}_{H_2O}\ Kp_{G_2}}$	0.2768
GM	$2C + 2H_2O = CH_4 + CO_2$	$Kp_{GM} = \frac{P^{*}_{CH_4}\ P^{*}_{CO_2}}{P^{*}_{H_2O}{}^{2}}$	$R_{GM} = \frac{P_{CH_4}\ P_{CO_2}}{P^{2}_{H_2O}\ Kp_{GM}}$	.253
	II. CO-CO_2 Interchange Reactions			
S_1	$C + CO_2 = 2CO$	$Kp_{S_1} = \frac{P^{*\ 2}_{CO}}{P^{*}\ CO_2}$	$R_{S_1} = \frac{P^{2}_{CO}}{P_{CO_2}\ Kp_{S_1}}$	0.0189
S_2	$CO + H_2O = CO_2 + H_2$	$Kp_{S_2} = \frac{P^{*}_{CO_2}\ P^{*}_{H_2}}{P^{*}_{CO}\ P^{*}_{H_2O}}$	$R_{S_2} = \frac{P_{CO_2}\ P_{H_2}}{P_{CO}\ P_{H_2O}\ Kp_{S_2}}$	4.26
	III. Methane Producing Reactions			
M_1	$C + 2H_2 = CH_4$	$Kp_{M_1} = \frac{P^{*}_{CH_4}}{P^{*\ 2}_{H_2}}$	$R_{M_1} = \frac{P_{CH_4}}{P^{2}_{H_2}\ Kp_{M_1}}$	1.187
M_2	$2CO + 2H_2 = CH_4 + CO_2$	$Kp_{M_2} = \frac{P^{*}_{CH_4}\ P^{*}_{CO_2}}{P^{*\ 2}_{CO}\ P^{*\ 2}_{H_2}}$	$R_{M_2} = \frac{P_{CH_4}\ P_{CO_2}}{P^{2}_{CO}\ P^{2}_{H_2} Kp_{M_2}}$	51.2
M_3	$CO + 3H_2 = CH_4 + H_2O$	$Kp_{M_3} = \frac{P^{*}_{CH_4}\ P^{*}_{H_2O}}{P^{*}_{CO}\ P^{*3}_{H_2}}$	$R_{M_3} = \frac{P_{CH_4}\ P_{H_2O}}{P_{CO} P^{3}_{H_2} Kp_{M_3}}$	18.32
M_4	$CO_2 + 4H_2 = CH_4 + 2H_2O$	$Kp_{M_4} = \frac{P^{*}_{CH_4}\ P^{*\ 2}_{H_2O}}{P^{*}_{CO_2}\ P^{*\ 4}_{H_2}}$	$R_{M_4} = \frac{P_{CH_4}\ P^{2}_{H_2O}}{P_{CO_2}\ P^{4}_{H_2}\ Kp_{M_4}}$	4.34

2. These carbon oxides redistribute via reactions S_1 and/or S_2 and/or M_2.
3. Methane forms by the hydrogenation of carbon and/or carbon oxides via combinations of reactions M_1 through M_4 and/or by direct gasification, reaction GM.

Equilibrium and kinetic considerations govern the composition and relative magnitudes of the exit gases from the gasification reactor (see Section II-L for thermodynamic review of the carbon-steam system). It is the purpose of this data analysis to gain insight into the mechanism of gasification, to determine the relative rates of the various reactions, and to compare the present findings with those of earlier workers.

b. Theoretical Background

For the generalized reaction:

$$aA + bB = cC + dD$$

The equilibrium constant is defined in terms of the fugacities of the individual species as:

$$K_f = \frac{f_C^c \, f_D^d}{f_A^a \, f_B^b}$$

In the present study conducted at atmospheric pressure and moderately high temperature, equilibrium partial pressures, denoted by P^*, may be substituted for fugacities to give the following expression:

$$K_P = \frac{P^{*c}_{C}\ P^{*d}_{D}}{P^{*a}_{A}\ P^{*b}_{B}}$$

Under actual operating conditions, equilibrium is often not achieved, not because the above expression is invalid, but because the rates of reactions are not sufficiently rapid enough to attain the equilibrium composition in the allotted reaction time.

It is convenient, at this time, to introduce another quantity, the fractional degree of attainment of equilibrium, which is defined as the ratio of the observed partial pressures of the components to their equilibrium partial pressures. This ratio will often be denoted by R or referred to as the Fractional Extent of Equilibrium Approach (E.O.E.A.). Thus for the generalized reaction:

$$R = \frac{\dfrac{P^{c}_{C}}{P^{*c}_{C}}\ \dfrac{P^{d}_{D}}{P^{*d}_{D}}}{\dfrac{P^{a}_{A}}{P^{*a}_{A}}\ \dfrac{P^{b}_{B}}{P^{*b}_{B}}} = \frac{P^{c}_{C}\ P^{d}_{D}}{P^{a}_{A}\ P^{b}_{B}\ K_P}$$

Included in Table XXVII are the respective expressions for K_P and R for the nine reactions considered along with their K_P values at 1000°F. Figure 6 in Section II shows the dependence of the equilibrium constants for the nine reactions on the reciprocal of the absolute temperature.

Since the gasification experiments in this study were carried out at essentially one atmosphere pressure, the expressions for K_p and R can be further simplified, using Dalton's Law, by substituting mole fractions for partial pressures with P_{Total} equal to one atmosphere.

For the nine reactions listed, the K_p and R expressions are written as if these reactions were proceeding from left to right; i.e., equilibrium is to the right. If a reaction is at equilibrium, its R value is unity. If the R value is less than unity, the reaction is not at equilibrium; but, if it is occurring, equilibrium is being approached from the left hand side of the equation. Similarly, if the R value is greater than unity, the implication is that the reaction is again not at equilibrium; however, in this case, if the reaction is occurring, equilibrium is being approached from the right hand side of the equation; i.e., the reaction is proceeding from right to left.

In addition to the mechanistic insight given by whether a particular R value is less than, equal to, or greater than unity, the relative rates of the various reactions can often be determined by comparison of the magnitudes of the R values. For example, a reaction with a R value close to unity probably has faster kinetics than a reaction with a R value orders of magnitude below unity. A R value orders of magnitude above unity indicates that this reaction is proceeding in the reverse direction, albeit probably very slowly.

Using the above properties of R values as guidelines, effort will now be turned towards elucidating the mechanism of gasification and the relative rates of the various reactions via comparisons of the R values of the primary gasification, carbon oxides interchange, and methanation reactions to see which reaction schemes seem the most plausible. Later the gasification catalysts evaluated will be compared and contrasted as to their effects on the R values of the various reactions. The discussion will be extensively supplemented by graphs of various R values as a function of time and/or fraction carbon gasified. The complete computational procedures used are illustrated in Appendix III, Gasification — Sample Calculations.

c. Comparisons of Actual and Equilibrium Gas Compositions

(1) Primary Gasification Reactions

$$G_1 \quad C + H_2O = CO + H_2$$

$$G_2 \quad C + 2H_2O = CO_2 + 2H_2$$

$$GM \quad 2C + 2H_2O = CH_4 + CO_2$$

The R values (see Table XXVII for definition of R values) for the primary gasification reactions are plotted versus time in Figures 40 to 45. There are a pair of figures for each of the primary gasification reactions; the first figure shows those runs in which the catalyst was initially distributed uniformly in the coke bed, and the second figure shows those runs in which the catalyst was initially distributed only in the top third of the bed.

The common features of Figures 40 to 45 are

1. The primary gasification reactions show very marked deviations from equilibrium; their R values are three to six orders of magnitude below unity.
2. All the reactions show a deviation on the carbon-steam side of equilibrium.
3. The deviation from equilibrium usually becomes more pronounced with time; i.e., as the fraction of the original carbon gasified increases.
4. Catalysts and their initial distribution affect the deviation from equilibrium.
5. Reaction GM is an order of magnitude further from equilibrium than reactions G_1 and G_2.

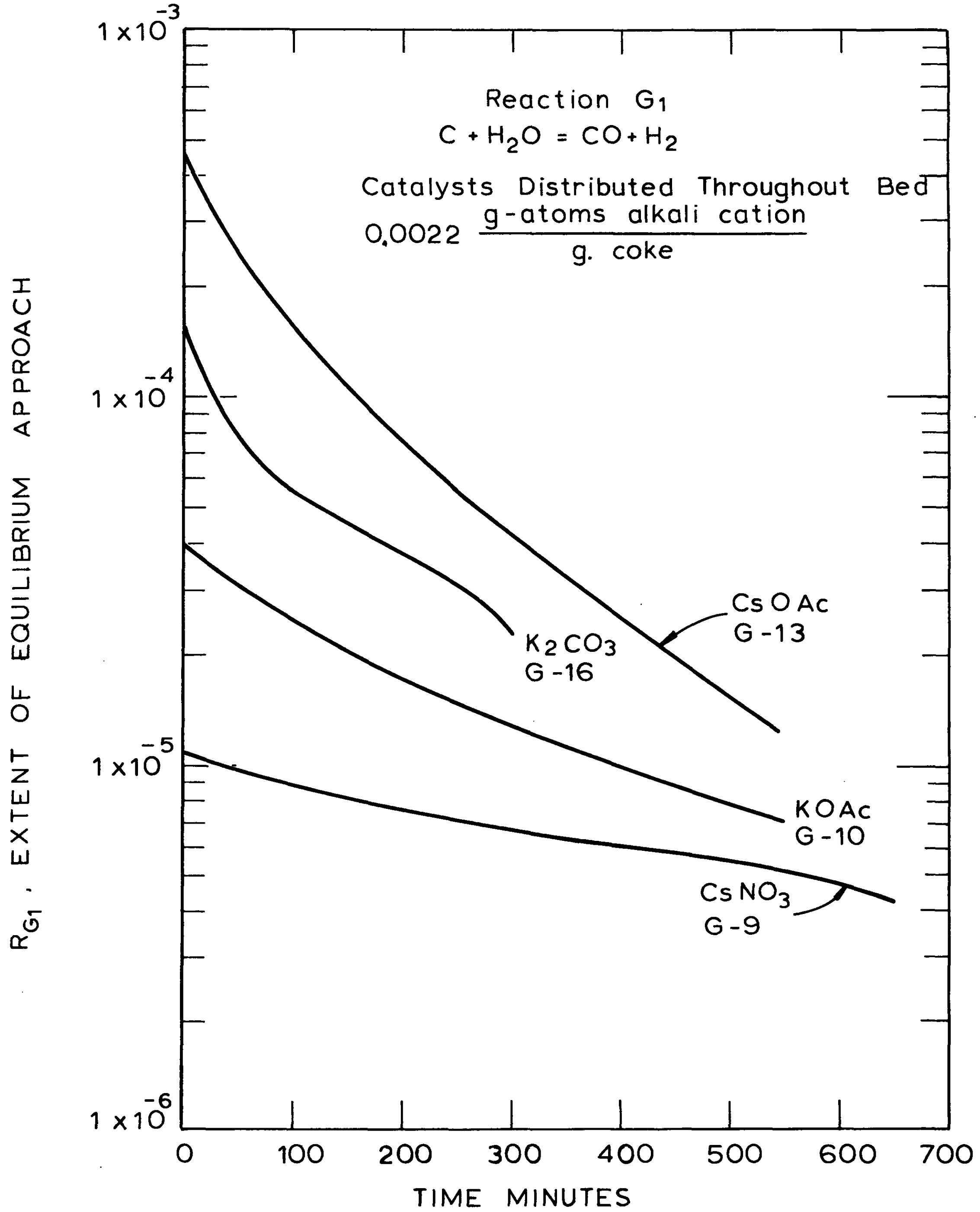


Figure 40 Comparison of Actual and Equilibrium Gas Compositions for Reaction G_1 at 1000 °F, R_{G_1} vs Time

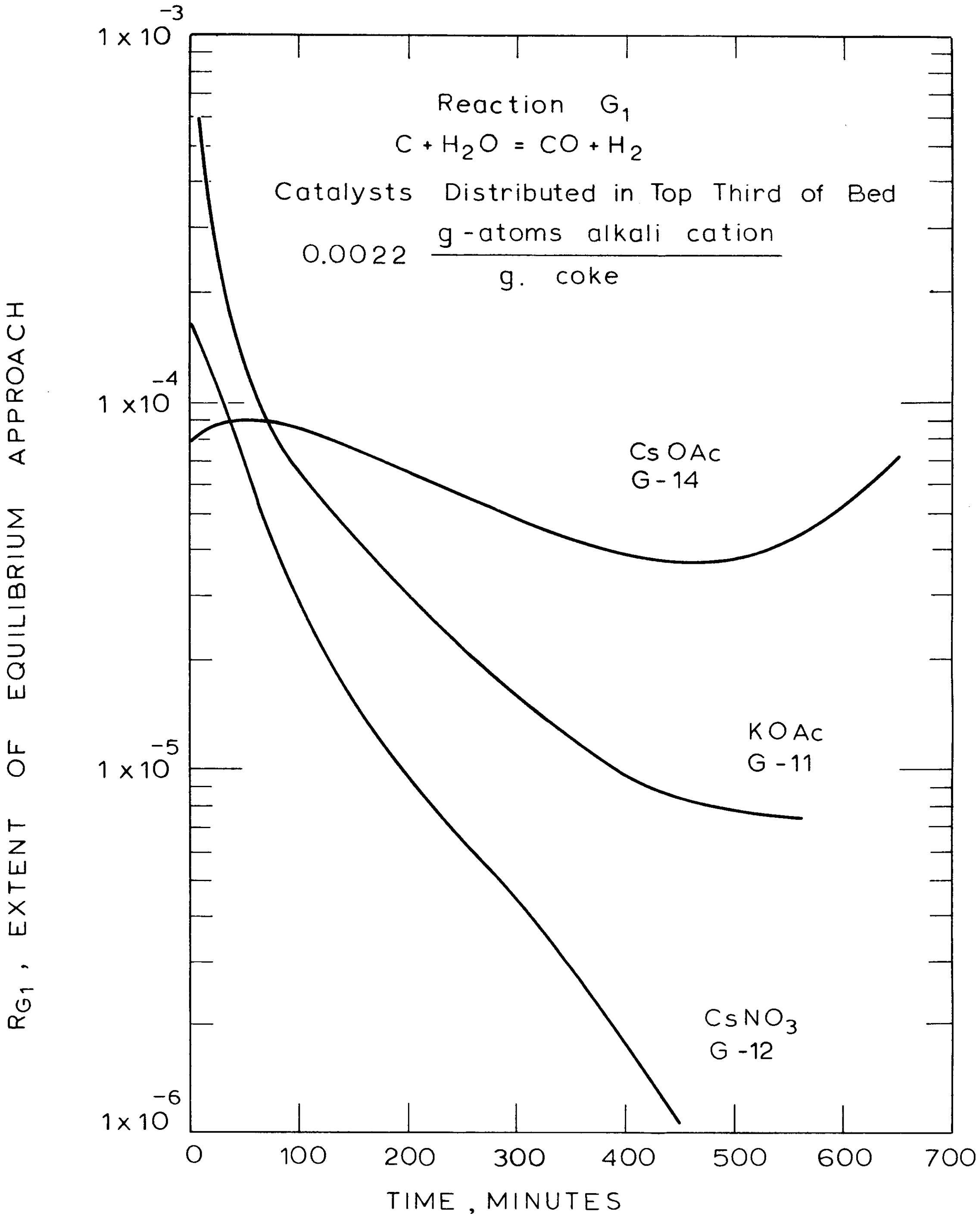


Figure 41 Comparison of Actual and Equilibrium Gas Compositions for Reaction G_1 at 1000 °F, R_{G_1} vs Time

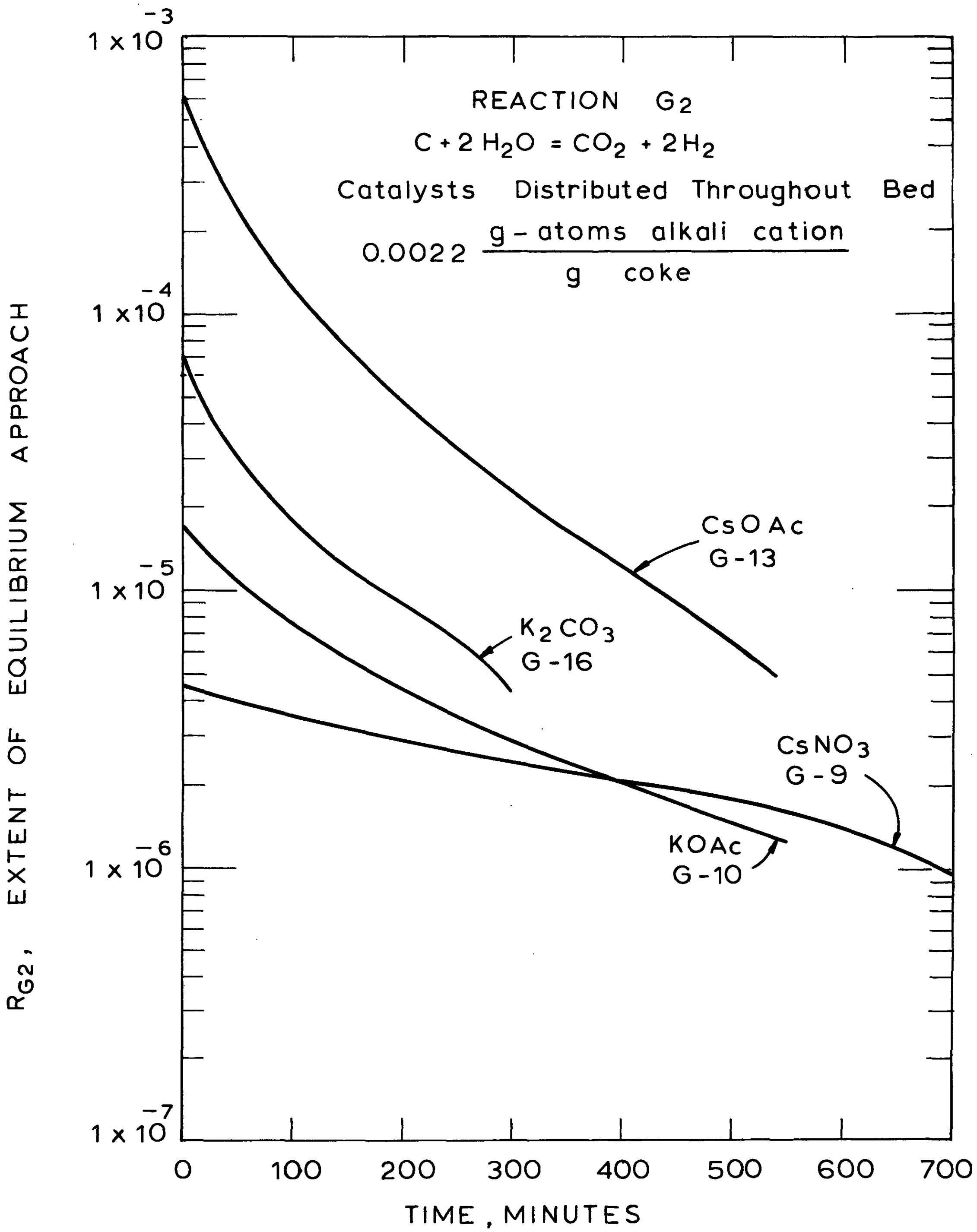


Figure 42 Comparison of Actual and Equilibrium Gas Compositions for Reaction G_2 at 1000 °F, R_{G2} vs Time

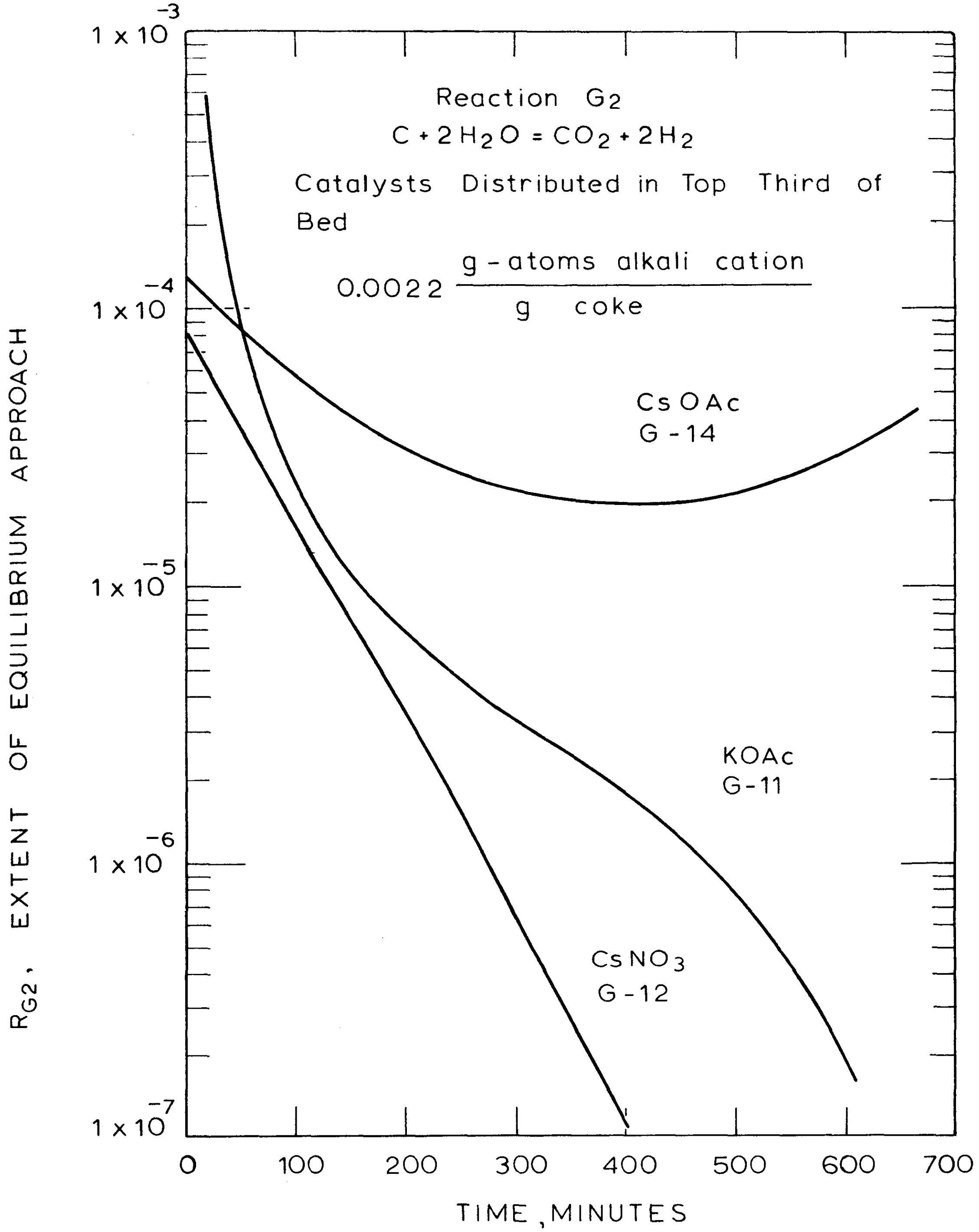


Figure 43 Comparison of Actual and Equilibrium Gas Compositions for Reaction G_2 at 1000 °F, R_{G2} vs Time

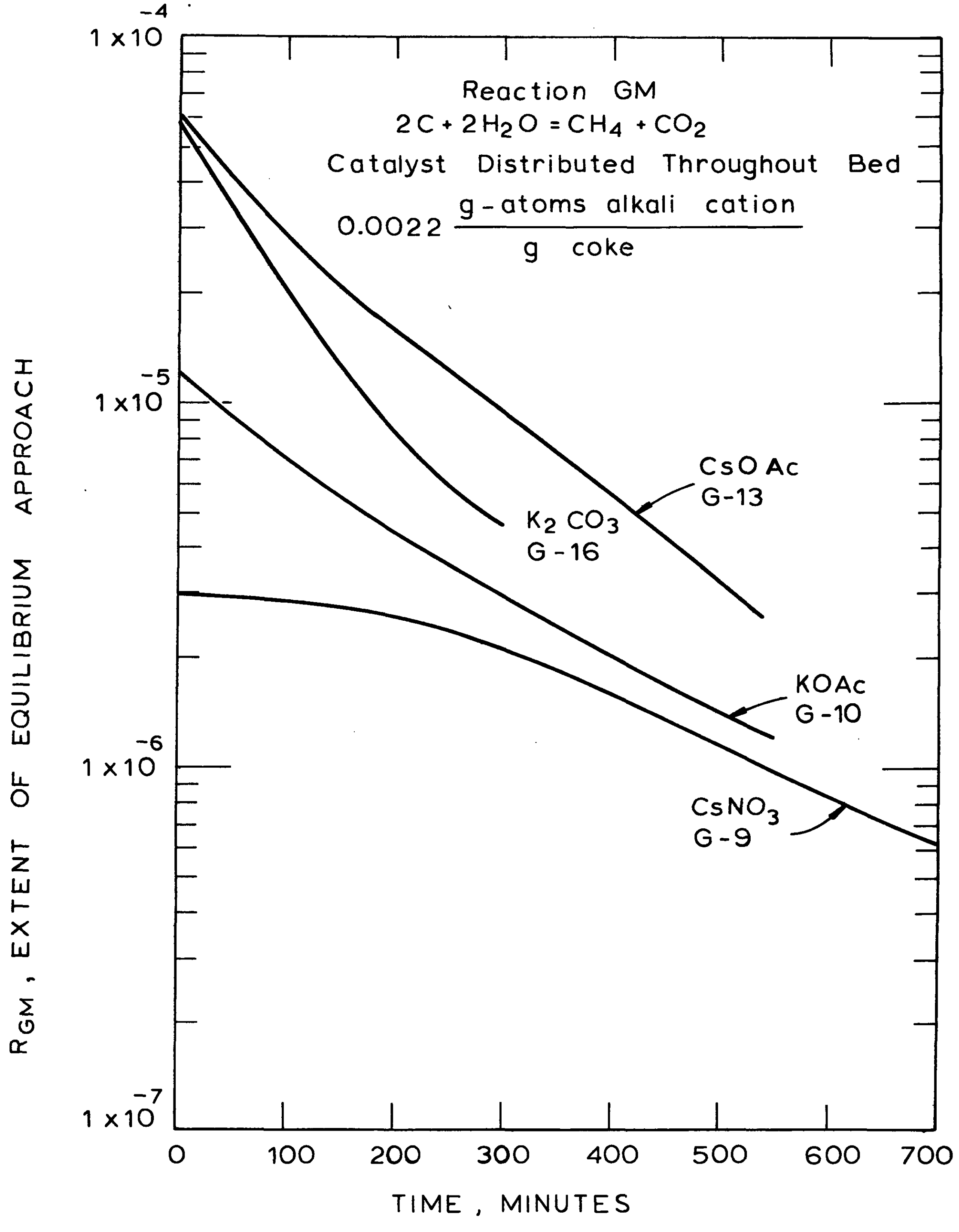


Figure 44 Comparison of Actual and Equilibrium Gas Compositions for Reaction GM at 1000 °F, R_{GM} vs Time

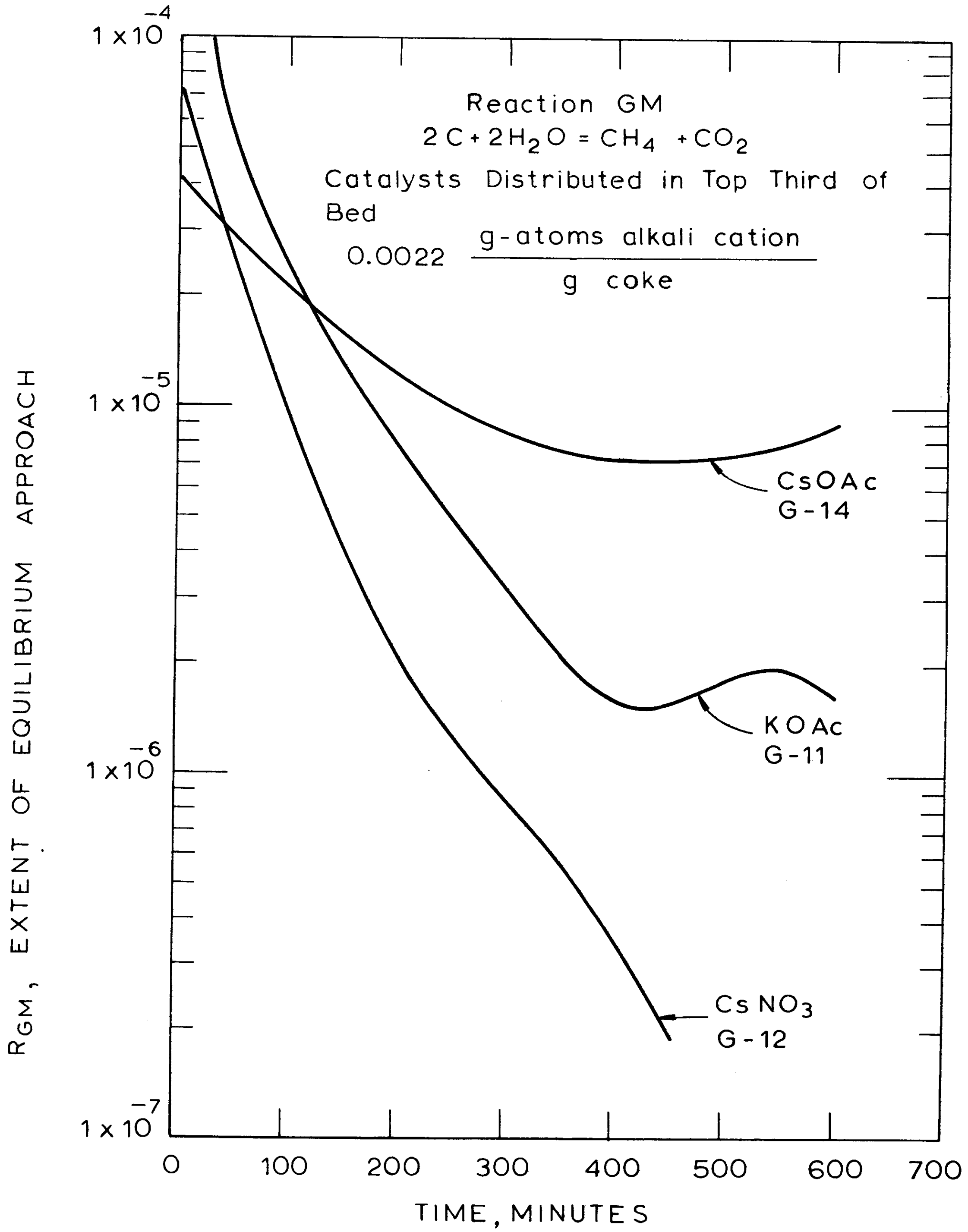


Figure 45 Comparison of Actual and Equilibrium Gas Compositions for Reaction GM at 1000 °F, R_{GM} vs Time

The upswings observed in the R values of Runs G-11 and G-14 are probably related to the catalyst initial distribution and will be discussed later.

The observation that the R values of the primary gasification reactions decrease with increasing fractional carbon gasification is an indication that the reaction rates are a function of the amount of coke present. Other factors that could cause the same phenomenon are a decrease in the inherent activity of the coke or a loss in catalyst or catalytic activity. Later in the discussion, the differences in R values between the various catalyzed runs will be explored more fully.

What has been gleaned thus far from considerations of R_{G_1}, R_{G_2} and R_{GM} is not sufficient to decide whether primary gasification proceeds exclusively through one of the reactions or whether two or all three reactions are occurring simultaneously. The three reactions as written are thermodynamically possible, but if occurring are far from equilibrium.

(2) Carbon Oxides Interchange (CO-CO_2) Reactions

$$S_1 \quad C + CO_2 = 2CO$$

$$S_2 \quad CO + H_2O = CO_2 + H_2$$

An analysis of the approach to equilibrium values (see Table XXVII for definition of R values) of these two gaseous carbon oxides redistribtuion reactions is very informative in discerning the mechanism of gasification. Figures 46 and 47 compare the R_{S_1} values for the various catalyzed runs; Figure 46, those runs in which the catalyst was initially distributed uniformly in the coke bed; Figure 47, those runs in which the catalyst was initially distributed only in the top third of the coke bed. The observations on the R_{S_1} values are quite similar to those already elucidated for the primary gasification reactions. Salient features of Figures 46 and 47 are:

1. Reaction S_1, although thermodynamically possible as written, shows a drastic deviation from equilibrium. R_{S_1} values are typically 10^{-4} to 10^{-5}.
2. This deviation from equilibrium increased as the fraction of the original carbon gasified increased when the catalyst was uniformly distributed initially.
3. When the catalyst was initially distributed in the top third of the bed, R_{S_1} values actually showed an increase with time.

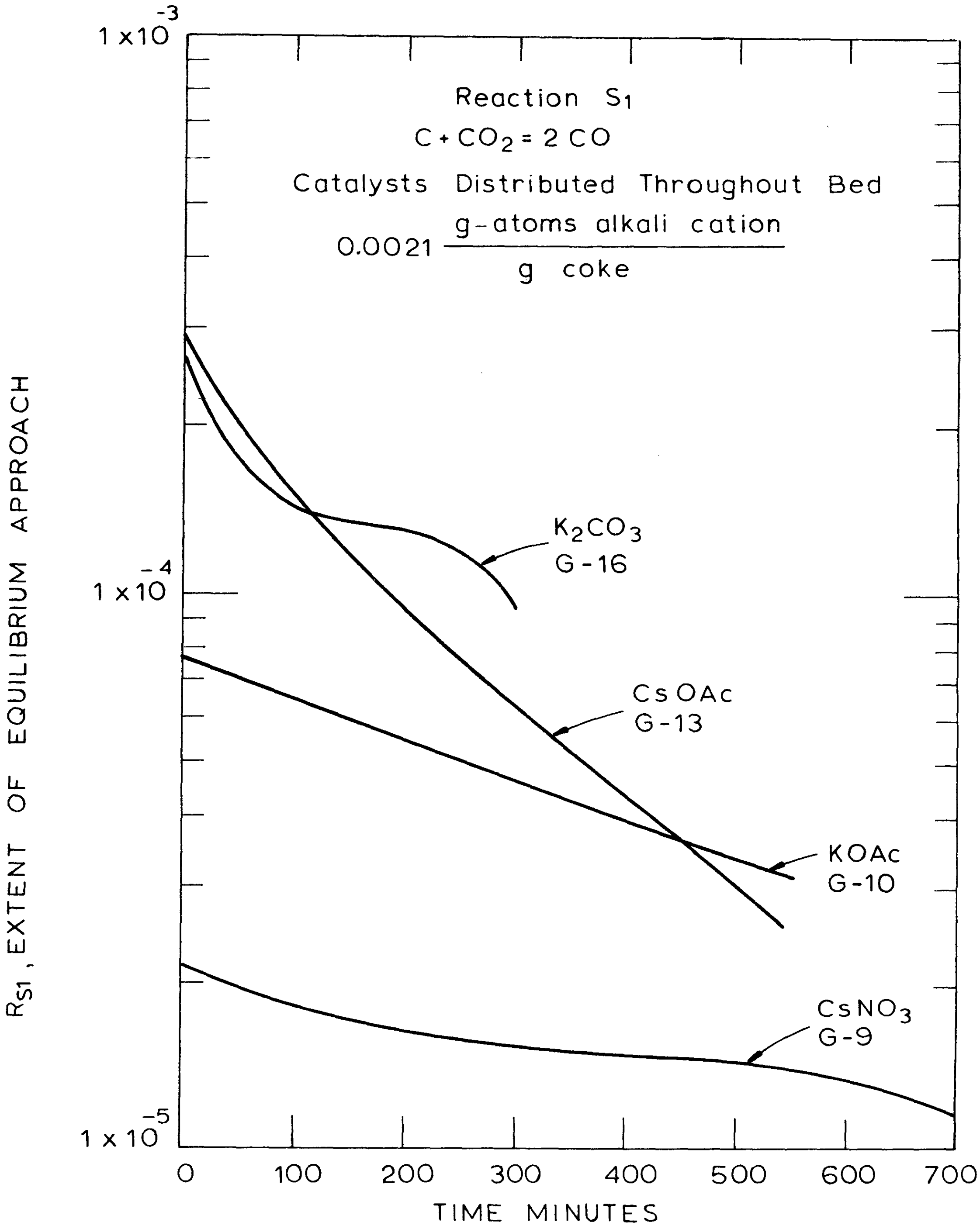


Figure 46 Comparison of Actual and Equilibrium Gas Compositions for Reaction S_1 at 1000 °F, R_{S1} vs Time

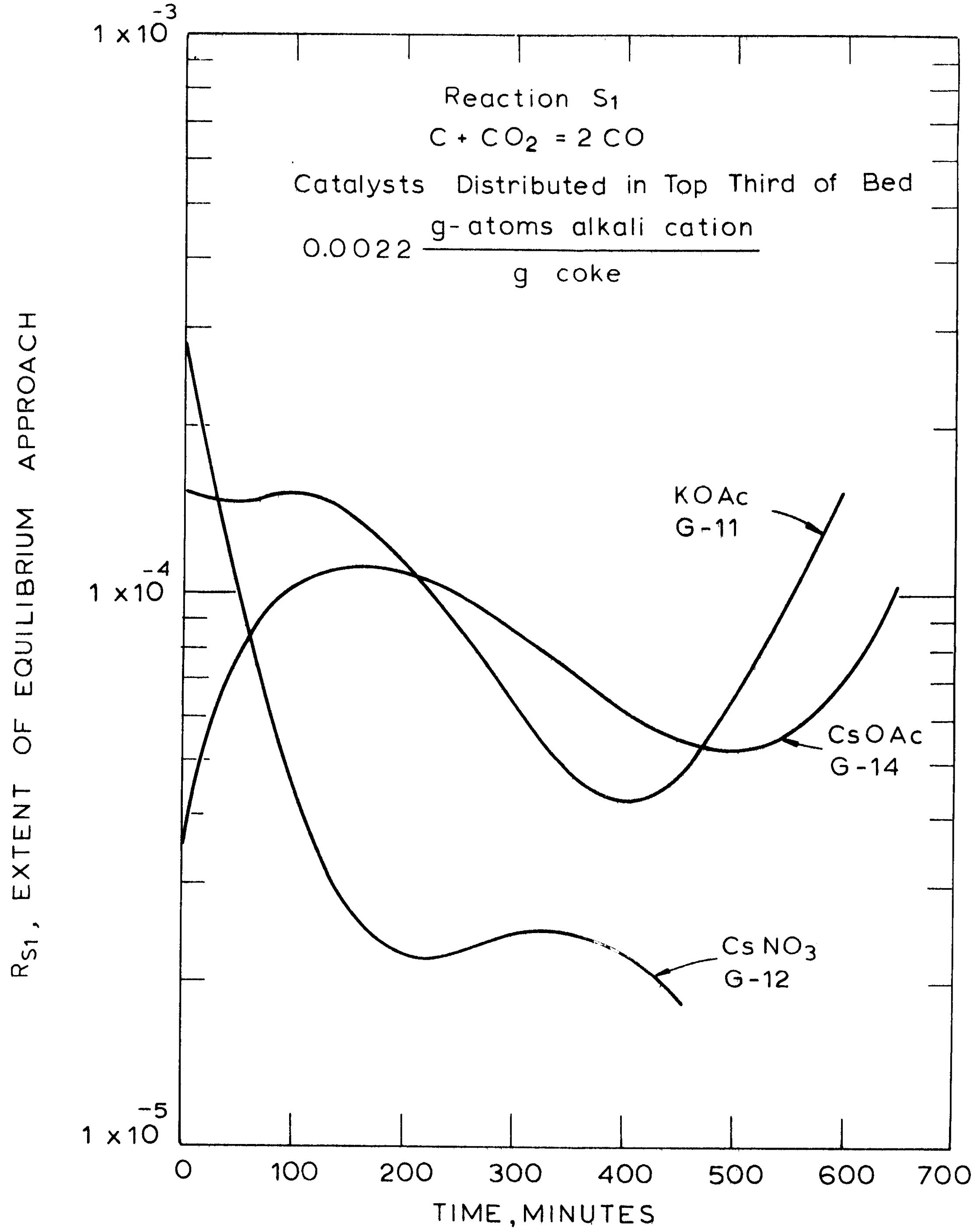


Figure 47 Comparison of Actual and Equilibrium Gas Compositions for Reaction S_1 at 1000 °F, R_{S1} vs Time

Figures 48 and 49 show the deviation of the water gas shift, reaction S_2, from equilibrium versus time for two series of runs; those in which the catalyst was initially distributed uniformly in the coke bed; and those in which the catalyst was initially distributed in the top third of the bed. If, instead of time, the parameters were fraction of original carbon gasified, the curves would have the same appearance (see Figures 69 to 74 in Appendix III).

Features of the R_{S_2} versus time plots are:

1. Reaction S_2 is near to equilibrium.
2. Equilibrium is being approached from the carbon monoxide-water side.
3. The nearness to equilibrium suggests that reaction S_2 is rapid.
4. In all runs (except for Runs G-14 and G-11, discussed later), the deviation from equilibrium increases with increasing time or bed burnoff.
5. Catalysts affect R_{S_2}.
6. Runs having the catalyst initially in the top third of the bed suffer a greater R_{S_2} drop with time, except Run G-14.
7. Cesium acetate is superior to both potassium acetate and potassium carbonate as a water gas shift catalyst.

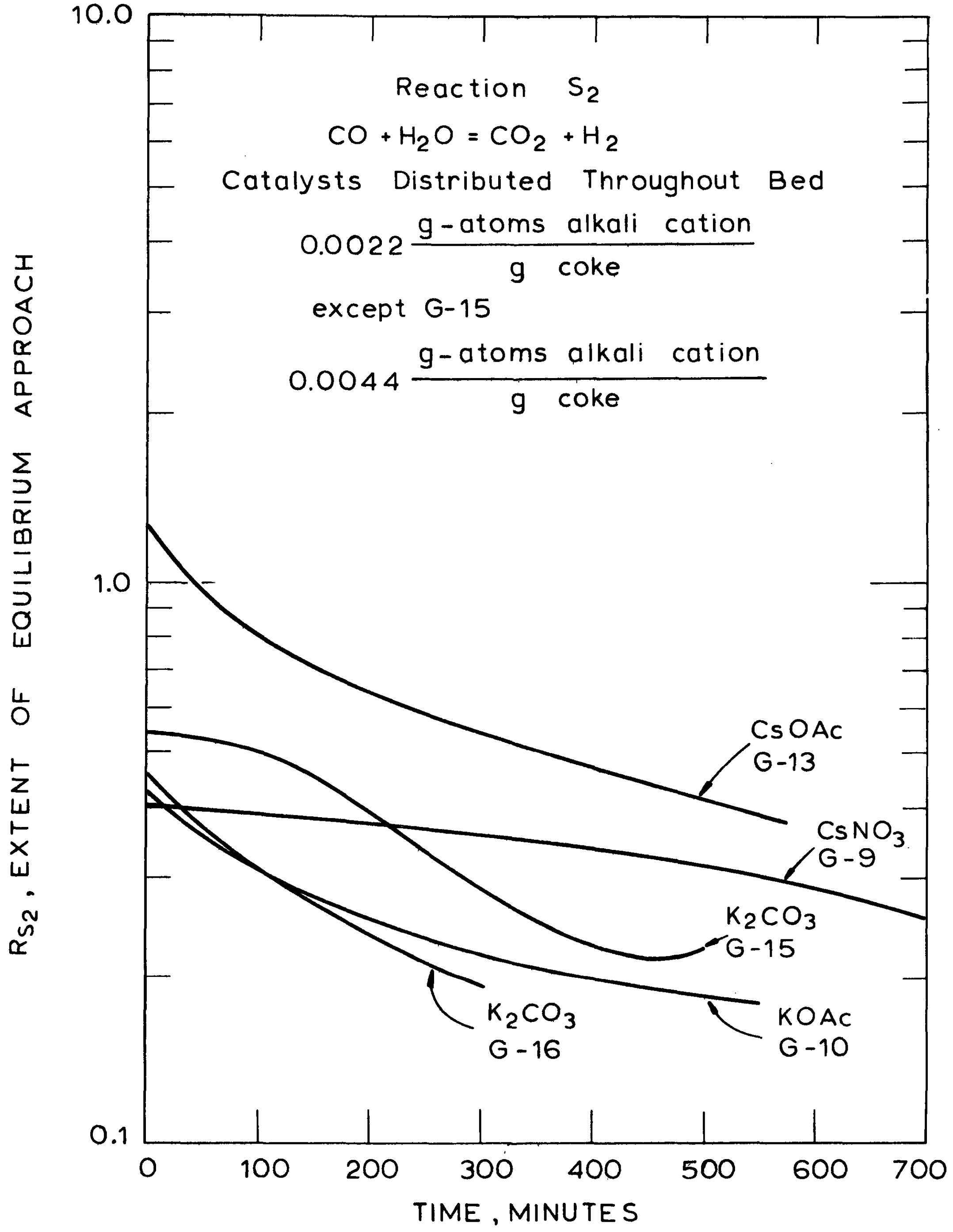


Figure 48 Comparison of Actual and Equilibrium Gas Compositions for Reaction S_2 at 1000°F, R_{S_2} vs Time

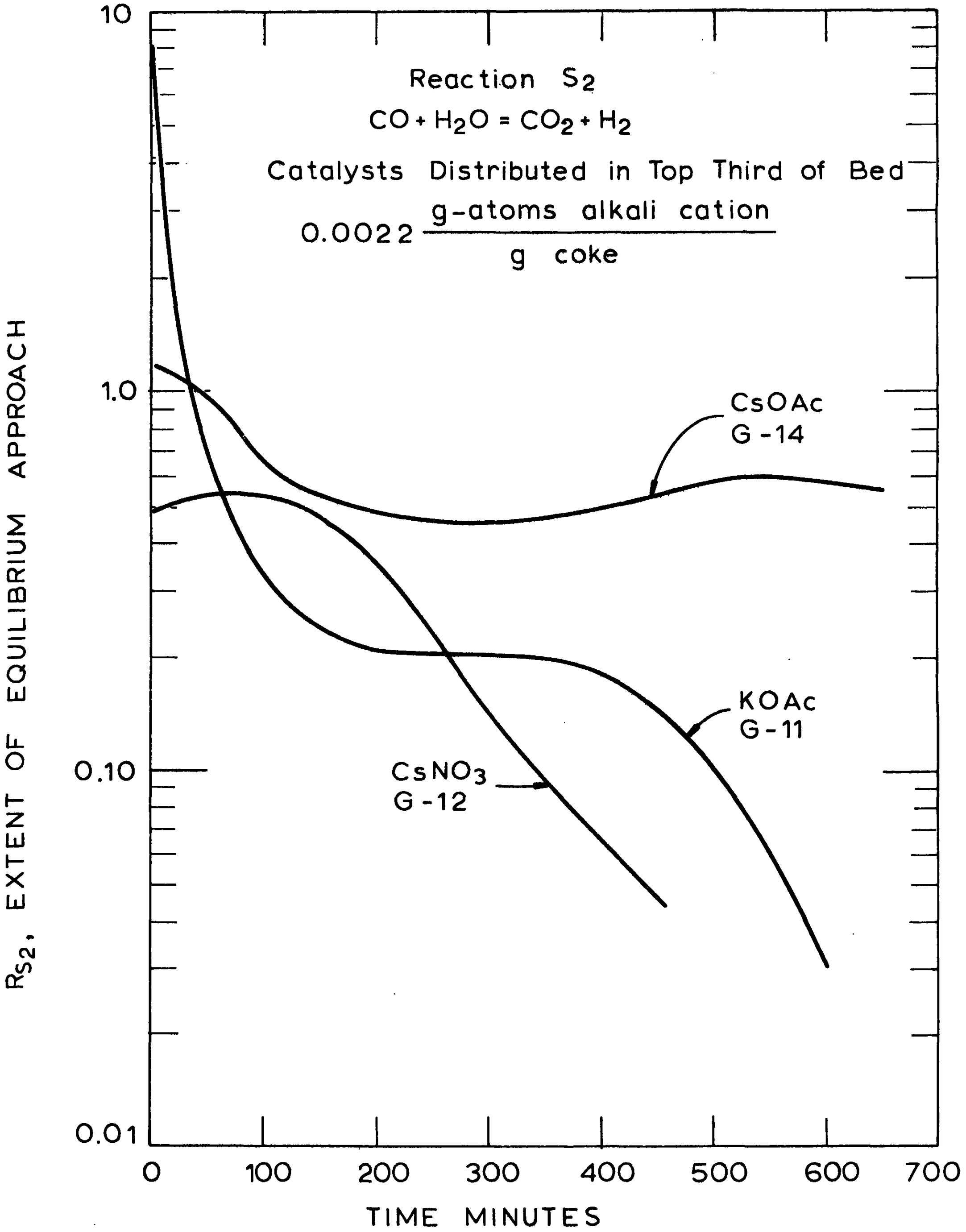


Figure 49 Comparison of Actual and Equilibrium Gas Compositions for Reaction S_2 at 1000°F, R_{S_2} vs Time

8. Potassium acetate and potassium carbonate are nearly identical as catalysts for the water gas shift reaction.
9. Doubling the potassium carbonate level increases R_{S_2} values about 50% (from comparisons of Runs G-15 and G-16).
10. Cesium nitrate is generally intermediate in activity towards reaction S_2, i.e., it lies between cesium acetate and potassium acetate in catalytic activity.

Both R_{S_1} and R_{S_2} are seen to decline with elapsed time of gasification. The reasons presented previously for the decline in primary gasification, namely: (1) rate, a function of carbon remaining; (2) decrease in coke reactivity; or (3) loss in catalysts or catalytic activity are still valid for the case of reaction S_1 which involves a solid-gas reaction. However, reaction S_2, consisting of only gaseous components, is influenced only by the added catalyst and by the <u>in situ</u> catalytic activity of the inorganic components of the coke. Steam excesses, becoming even larger as the gasification proceeds due to the decline in water conversion, would be expected to increase the R_{S_2} values marginally. Thus, the R_{S_2} values prove to be of value in helping to establish the tentative conclusion that the decline in reactivity with time is, at least for reaction S_2, related to the added catalyst.

A qualitative measure of the relative reaction rates of reactions S_1 and S_2 may be obtained from the ratio of the respective values of R which shows that reaction S_2 is probably orders-of-magnitude more rapid than reactions S_1.

(3) Methanation Reactions

$$\begin{array}{llllllll}
M_1 & C & + & 2H_2 & = & CH_4 & & \\
M_2 & 2CO & + & 2H_2 & = & CH_4 & + & CO_2 \\
M_3 & CO & + & 3H_2 & = & CH_4 & + & H_2O \\
M_4 & CO_2 & + & 4H_2 & = & CH_4 & + & 2H_2O \\
GM & 2C & + & 2H_2O & = & CH_4 & + & CO_2
\end{array}$$

Other methane producing, or consuming, reactions include:

$$\begin{array}{llllllll}
M_5 & 4CO & + & 2H_2O & = & CH_4 & + & 3CO_2 \\
GM_1 & 3C & + & 2H_2O & = & CH_4 & + & 2CO
\end{array}$$

These reactions are probably statistically less likely to occur than the others listed above. Reaction M_5 going to the right requires four carbon monoxide molecules to react with two water molecules and going to the left, requires three carbon dioxide molecules to react with one methane molecule. Reaction GM_1 going to the right requires that three carbon atoms react with two water molecules; however, in the reverse direction there is little statistical limitation on reaction GM_1. The probability that all the reactions, including the gas-phase reactions, occur on active surfaces sites will mitigate these statistical limitations but will not eliminate them. On these grounds, reactions M_5 and GM_1 will not be considered as possible methanation reactions although GM_1 could be a methane consuming reaction.

Further examination of the listed methanation reactions highlights the following:

1. Reactions M_2 and M_3, the reaction of carbon monoxide with hydrogen, i.e., the hydrogenation of carbon monoxide, are Fischer-Tropsch reactions.
2. Reaction M_1 going to the left is merely methane cracking or carbon deposition, a familiar reaction.
3. Reactions M_3 and M_4 going to the left are methane hydrolysis reactions.
4. Reactions M_2 and GM going to the left both involve the reaction of methane with carbon dioxide.

The problem now is to differentiate among the various methanation reactions to determine the methane producing mode or modes and conversely, which, if any of the reactions are operative to the left thereby resulting in methane destruction. Any theory on methanation derived from equilibrium and kinetic considerations has to satisfactorily explain the experimental findings that the methane concentration in the gasification reactor exit gases is roughly 0.5 to 1% v/v (on a dry basis).

In Figures 50 and 51 are plotted R_{M1} values (see Table XXVII for R_{M1} definition) versus time for the respective cases where the catalyst was distributed initially: (1) uniformly in the bed, and (2) in the top third of the bed. These figures show:

1. Reaction M_1 is near equilibrium.
2. The deviation from equilibrium is generally on the carbon-hydrogen side; the reaction is proceeding from left to right.
3. With increasing time or bed burnoff, the R_{M1} values for two runs cross over to the methane side of equilibrium.
4. The closeness of this reaction to equilibrium suggests that the reaction may be rapid.

Some investigators have found that the free energy values for carbon are considerably greater than β-graphite by 1500 to 2600 calories per gram atomic weight (see Section II-L) and that the values increase with reaction as suggested by Figures 50 and 51 (Harriott, 1952). It can be determined how much greater the free energy would have to be to bring the high R_{M1} values down to 1.0. For example,

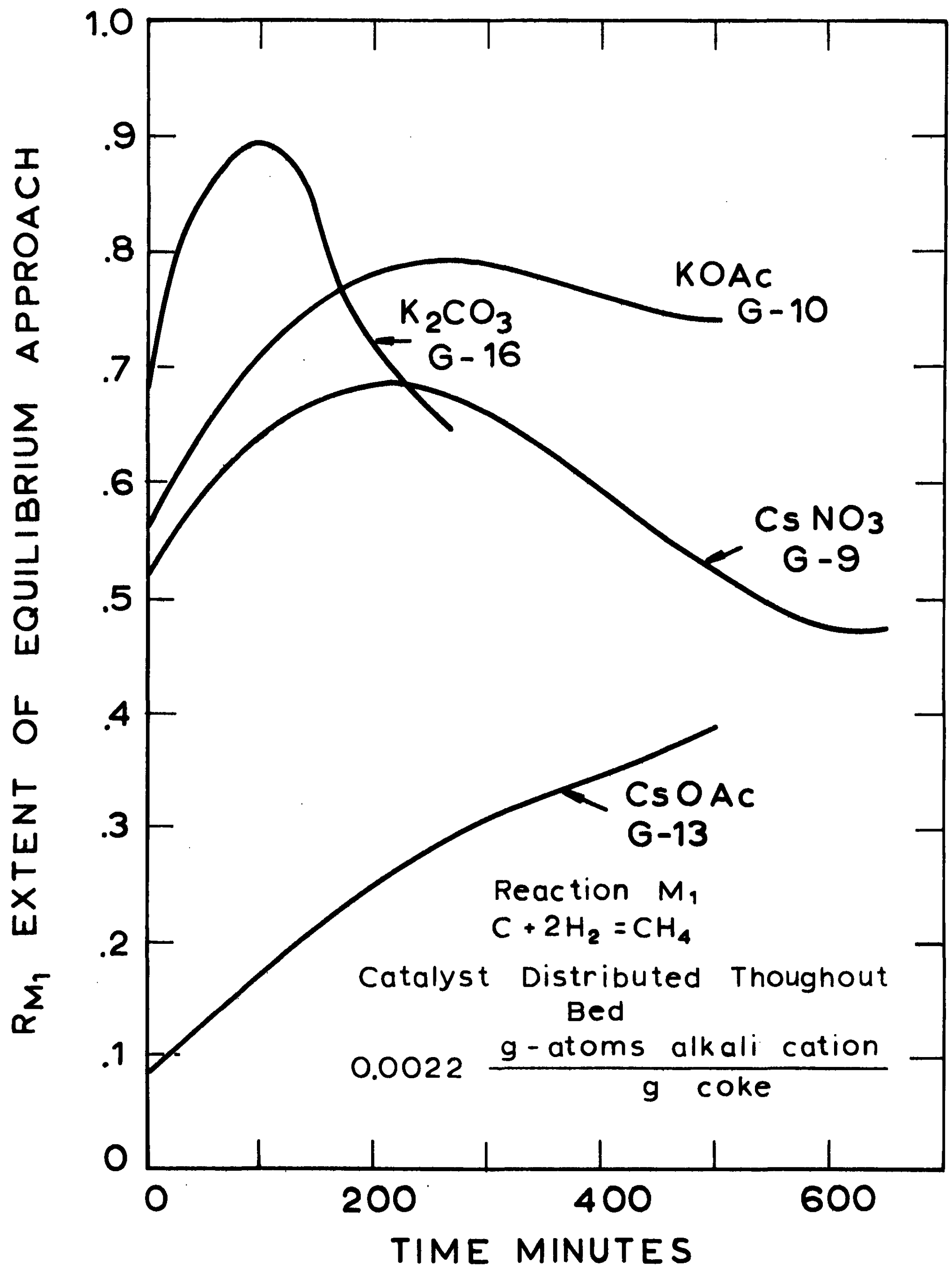


Figure 50 Comparison of Actual and Equilibrium Gas Compositions for Reaction M_1 at 1000 °F, R_{M_1} vs Time

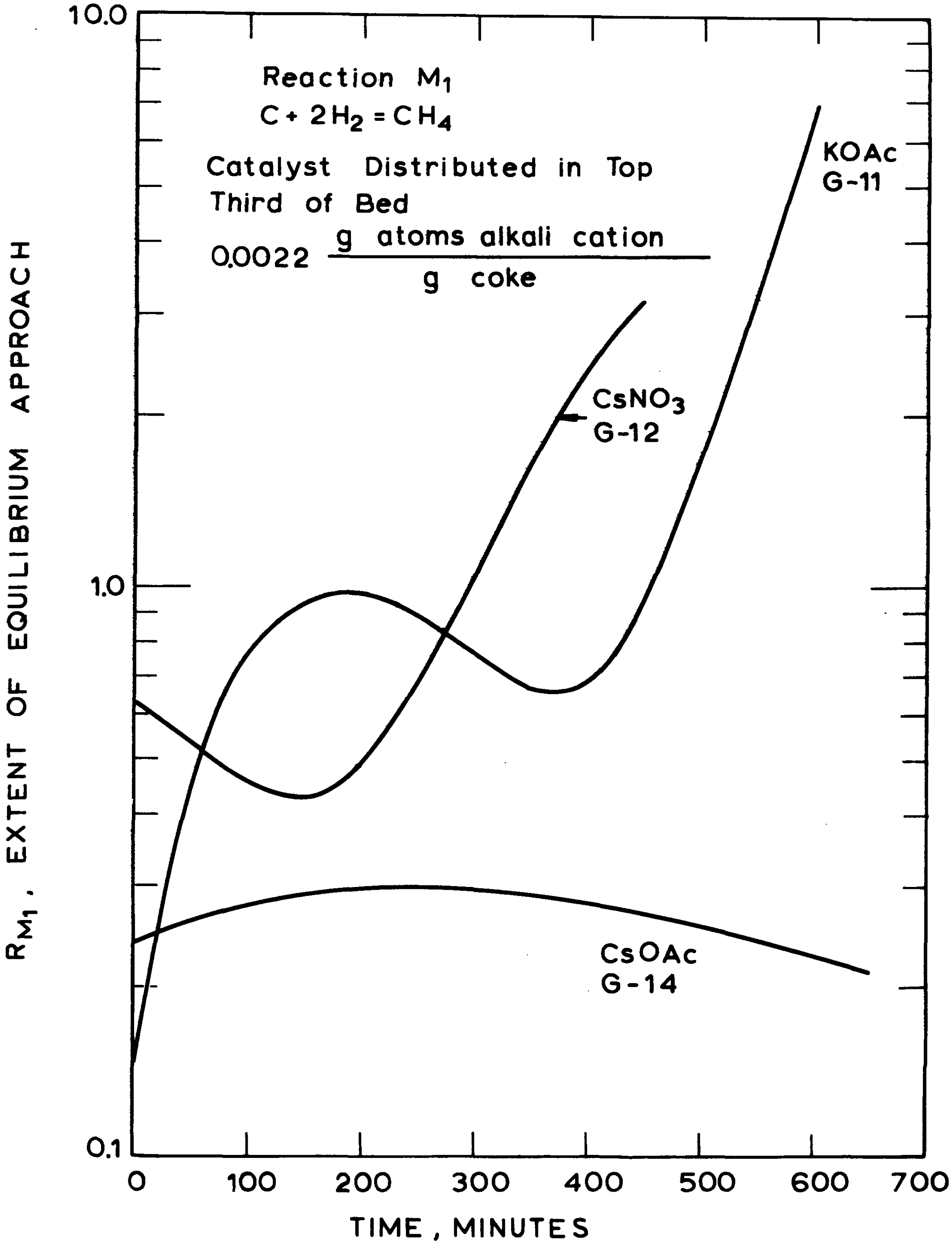


Figure 51 Comparison of Actual and Equilibrium Gas Composition for Reaction M_1 at 1000°F, R_{M_1} vs Time

in Run G-11 at 600 minutes (Figure 51) the value of R_{M_1} is about six. From Table XXVII, the value of $K_{P_{M_1}}$ is 1.187 (based on carbon in the form of β-graphite). If reaction M_1 were actually at equilibrium, then the value of $K_{P_{M_1}}$ would be:

$$\left.K_{P_{M_1}}\right)_{exp} = (1.187)\ (6) = 7.1$$

and the free energy for the coke would be

$$\Delta G° = -RT \ln K_P = -(1.987)(811)(\ln 7.1)$$

$$\Delta G° = 3160 \text{ calories/gram atomic weight}$$

For β-graphite:

$$\Delta G° = (1.987)(811)(\ln 1.187)$$

$$= 280 \text{ calories/gram atomic weight}$$

The free energy of the coke would have to be about 2900 calories per gram mol greater than the free energy of β-graphite to pull this high R value for Run G-11 down to 1.0.

In Appendix III, the R_{M_2}, R_{M_3} and R_{M_4} values for Run G-13 are plotted versus time, Figure 71, and versus the fraction of the original carbon gasified, Figure 74 (again see Table XXVII for definition of R values). These latter plots are typical of all the gasification runs and will be considered together. The properties of these plots are:

1. Reactions M_2, M_3 and M_4 all show drastic deviations from equilibrium; these deviations are on the methane side of equilibrium. Thus, if operative, these reactions proceed from right to left to consume methane. Typically the R values are 10^{-2} to almost 10^{-5}.
2. These deviations from equilibrium increase two orders of magnitude as the fraction of the original carbon gasified increases from zero to 0.35.

With numbers this large, no distinction can be made between the R values of these three reactions.

Aside from considering the respective R values for reactions M_2, M_3 and M_4, it is possible to generalize in a very qualitative way about what one could expect to occur Both reactions M_3 and M_4, having water as a product, could be expected to be greatly hindered by the tremendous excess of steam present in the reactor. Reaction M_3, involving carbon monoxide as a reactant, could also be expected to be hindered because it has to compete with the water gas shift reaction, reaction S_2, for carbon monoxide. It has already been established that reaction S_2 is probably very rapid compared to all the other reactions. Reaction M_2 is similarly affected by reaction S_2.

Two more mechanisms for methane formation should be mentioned for completeness. These are both related to the chemically combined or "fixed" hydrogen in the devolatilized coke charge. It was determined in Run G-18 (see Section IV-B) that the combined hydrogen in the devolatilized water coke amounted to 0.36 grams, far more than the total hydrogen in the methane evolved during gasification. For example, in Run G-13, the total methane evolved during gasification was 0.0068 g-mole (see Fig. 66) which is equivalent to 0.023 grams of hydrogen. Methane containing this combined hydrogen could evolve by two mechanisms during gasification:

1. Thermal coking, i.e., breaking of certain bonds in the cross-linked carbon-hydrogen network giving rise to methane.
2. Hydrogenation of carbon-hydrogen linkages in the coke, unlike reaction M_1 which is the hydrogenation of carbon.

Neither of these two modes of methane formation can be ruled out. The water coke (see Section IV-B for description of the water coke) used in the gasification studies was the dried benzene-extracted carbonaceous residues or coke resulting from certain water-coal high pressure liquefaction runs. As such, the water coke had had a fairly severe time-temperature history, normally two to three hours at 400^{+}°C with water followed by an extended benzene extraction at 80°C. However, during the *in situ* devolatilization (see Section IV-A for devolatilization procedure) considerable methane did evolve as demonstrated in the material balance over the devolatilization procedure (see Table XXIV). If the devolatilization time had been extended, probably more methane would have evolved.

(4) Effect of Catalyst Initial Distribution in the Coke Bed on the Extent of Approach to Equilibrium

When the catalyst was initially distributed uniformly in the bed, the R values for the reactions declined with increasing bed burnoff. However, when the catalysts, potassium and cesium acetates, were mixed only with the top third of the bed, the R values behaved differently. Listed below are the behavior of the R values with time for the runs in which potassium and cesium acetates were mixed with only the top third of the bed.

		Potassium Acetate	Cesium Acetate
R_{G_1}	(Fig. 41)	Declined, then leveled	Fairly level
R_{G_2}	(Fig. 43)	Sharply declined	Declined, leveled, increased
R_{GM}	(Fig. 45)	Sharply declined, then leveled	Declined, leveled
R_{S_1}	(Fig. 47)	Declined, increased	Increased, decreased, increased
R_{S_2}	(Fig. 49)	Declined, leveled, declined	Fairly level
R_{M_1}	(Fig. 51)	Increased and leveled	Increased

These observations show that the R values for the run (G-14) in which cesium acetate was mixed initially with the top third of the bed stayed more constant with time than the R values for the run (G-11) in which potassium acetate was mixed with the top of the bed. These observations suggest that a large part of the decline in the R values for the cases where the catalysts is uniformly admixed with the entire bed is probably due to catalyst loss.

d. Shape of the R_I versus FCG Curves

Other workers have observed that the instantaneous gasification rate, R_I, increases at low values of bed burnoff and then decreases at higher values of bed burnoff or fraction carbon gasified (FCG) (Curran et al., 1967a). These latter workers studied the gasification at 1500°F of lignites having varying sodium contents and found that the gasification rates declined more rapidly when the H_2 to H_2O ratio in the feed gas was increased. A possible explanation for this behavior offered by Curran is that a catalyst present in the char ash (perhaps a sodium compound) volatilized from the char on continued exposure to high H_2 to H_2O ratios.

Examination of Figures 38 and 39 shows that when cesium acetate was admixed only with the top third of the bed (Run G-14), the gasification rate R_I, increased at higher values of fractional bed burnoff rather than decreasing as in the case where the cesium acetate was uniformly admixed (Run G-13). This observation suggests that cesium acetate migrates through the coke bed and further suggests that a large part of the rate drop observed in Run G-13 is probably due to catalyst loss. Higher rates could perhaps be maintained by engineering ingenuity — i.e., reversal of steam flow or in a continuous unit feeding coke countercurrent to the steam flow.

Previously, the observation was made that potassium acetate and potassium carbonate, at comparable levels, exhibited similar initial and maximum rates of gasification, but the rate drop with potassium carbonate was much greater than the rate drop with potassium acetate (see Figure 38). When the concentration of potassium carbonate was doubled the rate drop with time was more like that of potassium acetate even though the latter was only present in half the concentration of the former on a gram atom alkali metal basis (see Figures 32 and 33).

Listed below are the melting points of the catalysts under discussion.

	M.P., °C
Potassium Carbonate	891
Potassium Acetate	292
Cesium Acetate	194

It appears that under the experimental conditions of devolatilization and gasification two of these catalysts are present as liquids while the third, potassium carbonate exists as a solid. The catalyst with the highest activity, cesium acetate, has the lowest melting point and presumably the highest volatility. The catalyst with the highest melting point, potassium carbonate, while initially as effective as potassium acetate which has a much lower melting point, also exhibits the sharpest drop in gasification rate with time.

Comparison of Runs G-10 and G-17 (Figure 33) which differ only in the devolatilization procedure suggests that the higher initial rate observed with Run G-10 may have been due to the nitrogen flow distributing the catalyst. Another reason could be that the nitrogen flow prevented volatile matter from redepositing on the catalyst.

It is possible to visualize another mechanism which would explain the shape of the observed R_I versus FCG curves. As the carbon reacts, it becomes more porous and thus its surface area per unit weight increases with time or FCG. At the same time, the coke reactivity per unit area is decreasing and thus a maximum in the R_I versus FCG curve occurs because of this balance between the change in area per time and the change in reactivity per unit area.

e. Comparison of Observed Gasification Rates with Those of Industrial Gasifiers

A minimum rate for commercial operation is of the order of 50 x 10^{-4} lb. C gasified/(min.)(lb. C inventory) at a steam conversion of 70% (Curran et al., 1967a). The maximum gasification rates observed in the present study with the various catalysts are:

Catalyst	Maximum Observed Gasification Rate $\frac{\text{lb.C gasified}}{(\text{min.})(\text{lb.C})}$	$\frac{\text{Observed Rate}}{(50 \times 10^{-4})}$
Cesium Nitrate	10.5×10^{-4}	0.21
Cesium Acetate	8.95×10^{-4}	0.18
Potassium Acetate	4.7×10^{-4}	0.09
Potassium Carbonate	5×10^{-4}	0.10

Thus, at 1000°F, with cesium and potassium salts catalysis, the gasification rates obtained are 20% and 10%, respectively, of the minimum feasible industrial rate. This latter rate though was determined for the normal gasifier operating at 1500°F and above. It is possible that in new installations, because of the heat economy realized, the minimum feasible gasification rate would be less than the present minimum and the observed rates of gasification of the water coke with potassium or cesium acetates observed here would be practical.

D. CONCLUSIONS FROM THE COAL GASIFICATION STUDIES

1. Gasification Catalysis and Coke Reactivity

a. Cesium acetate is superior to potassium acetate as a gasification catalyst at 1000°F.

b. Potassium acetate is superior to potassium carbonate as a gasification catalyst at 1000°F because at comparable levels the rate drop with time is less. Initial and maximum gasification rates with these catalysts are the same.

c. Alkali salt catalysts, such as cesium and potassium acetates, having lower melting points and hence more volatility and/or mobility (liquid or gas phase) are superior to a catalyst such as potassium carbonate which has a very high melting point and hence little mobility.

d. Observed gasification rate drop with time was probably directly related to catalyst loss in the case of the volatile or mobile catalysts, potassium and cesium acetates, and probably related to very slow migration of the catalyst in the case of the nonvolatile catalyst, potassium carbonate.

e. Maximum observed gasification rates at 1000°F with cesium acetate are about 20% of the minimum feasible industrial gasification rate which is about 50×10^{-4} lb. C/(min.)(lb.C) inventory. Potassium acetate catalyzed gasification rates at 1000°F are about 10% of the feasible industrial gasification rate.

f. The coke from water-coal high pressure runs is more reactive than the coke from the Decalin-water-coal runs.

2. <u>Mechanisms</u>

   a. <u>Primary Gasification and Carbon Oxides Interchange</u>

      (1) With two components, carbon monoxide and carbon dioxide, and four equations, G_1, G_2, S_1 and S_2, the same result can be obtained by a number of different combinations of sequential and parallel reactions.

      (2) All the primary gasification reactions, G_1, G_2 and GM have R values far less than one so apparently all these reactions, if operative, are going to the right.

         1. Carbon dioxide must be produced from reactions G_2 and/or S_2.
         2. Carbon monoxide must be produced from reactions G_1 and/or S_1.
         3. R_{S_2} being close to one suggests that the water-gas shift reaction is rapid relative to the other reactions, but this is not conclusive.

b. Methanation

It has not been possible to decide on the exact mode of methane formation. Several possibilities exist:

(1) Formation via the hydrogenation of carbon, reaction M_1. This reaction is close to equilibrium, R values being near 1.0; this suggests that this reaction may be rapid.

(2) Formation via the primary gasification reaction GM, shown to be thermodynamically possible but far from equilibrium.

(3) Evolution as volatile matter via the mechanism of thermal coking.

(4) Formation via hydrogenation of carbon-hydrogen linkages in the coal structure.

Methane has been shown not to be produced by the hydrogenation of carbon oxides, reactions M_2, M_3 and M_4 (see Table XXVII). These reactions, if operative, proceed from right to left to consume methane.

c. Overall

The overall rate of carbon gasification is the sum of the rates of: the primary gasification reactions G_1, G_2 and GM; the carbon oxides interchange reaction S_1; and the methanation reaction M_1. All these reactions could be operative. In addition, methane can be produced from the coke via coking or hydrogenation. Methane may be consumed by the reverse of reactions M_2, M_3 and M_4.

E. RECOMMENDATIONS FOR FUTURE WORK

Potassium acetate, because of its mobility, is clearly superior to potassium carbonate as a gasification catalyst. The use of cesium acetate may not be practical because of the scarcity of cesium. However, if catalyst losses were very minimal then cesium acetate should be at least considered.

1. Potassium acetate (and cesium acetate) should be evaluated at 1000°F with a more reactive carbon form such as a devolatilized coal like Disco coke.
2. Potassium acetate should be evaluated at 1100 and 1200°F with either the water coke or with a more reactive carbon form. A commercially acceptable rate would probably then be obtained.
3. The higher maximum rates obtained for the acetates could perhaps be maintained by engineering ingenuity – i.e., reversal of steam flow or in a continuous unit feeding coke countercurrent to the steam flow. The simpler unit to initially investigate would be the former. This unit would be a fixed bed reactor with the ability to reverse steam flows periodically. This feature would probably reduce catalyst loss – postulated to be the reason for the rate drop with time.
4. A better picture of the mechanism could be obtained if tests were made with each of the product gases, H_2, CO, CO_2, added individually with the water and the results compared with runs with water alone.

V. APPENDICES

APPENDIX I

A. LIQUEFACTION EQUIPMENT DETAILS

1. Liquefaction Reactors

a. Stainless Steel Reactor

Figure 52 shows the details of the stainless steel reactor including the heater and insulation. The reactor, or autoclave, consisted of the body, cover, gasket and cap screws for effecting the proper seal against the internal pressure. All of the vessel components, including the gasket, were fabricated of type 316 stainless steel. The autoclave was protected against overpressurization by the use of a 3/16 inch frangible disc-safety head assembly, also known as a rupture disc assembly. The capacity of this 1 13/16 inch inside diameter by 7 inch depth vessel was about 280 milliliters.

Openings were provided in the cover for:

1. Two thermowells, 1/8 inch O.D. extending to 1/4 inch off the bottom.
2. Vent and pressure gage connections.
3. Gas pressurization for either purging or reaction purposes.

The openings in the cover were W 125 type thread.

Two of these vessels were available for use in this study. Each reactor underwent a hydrostatic test to 8500 psi prior to the experimentation.

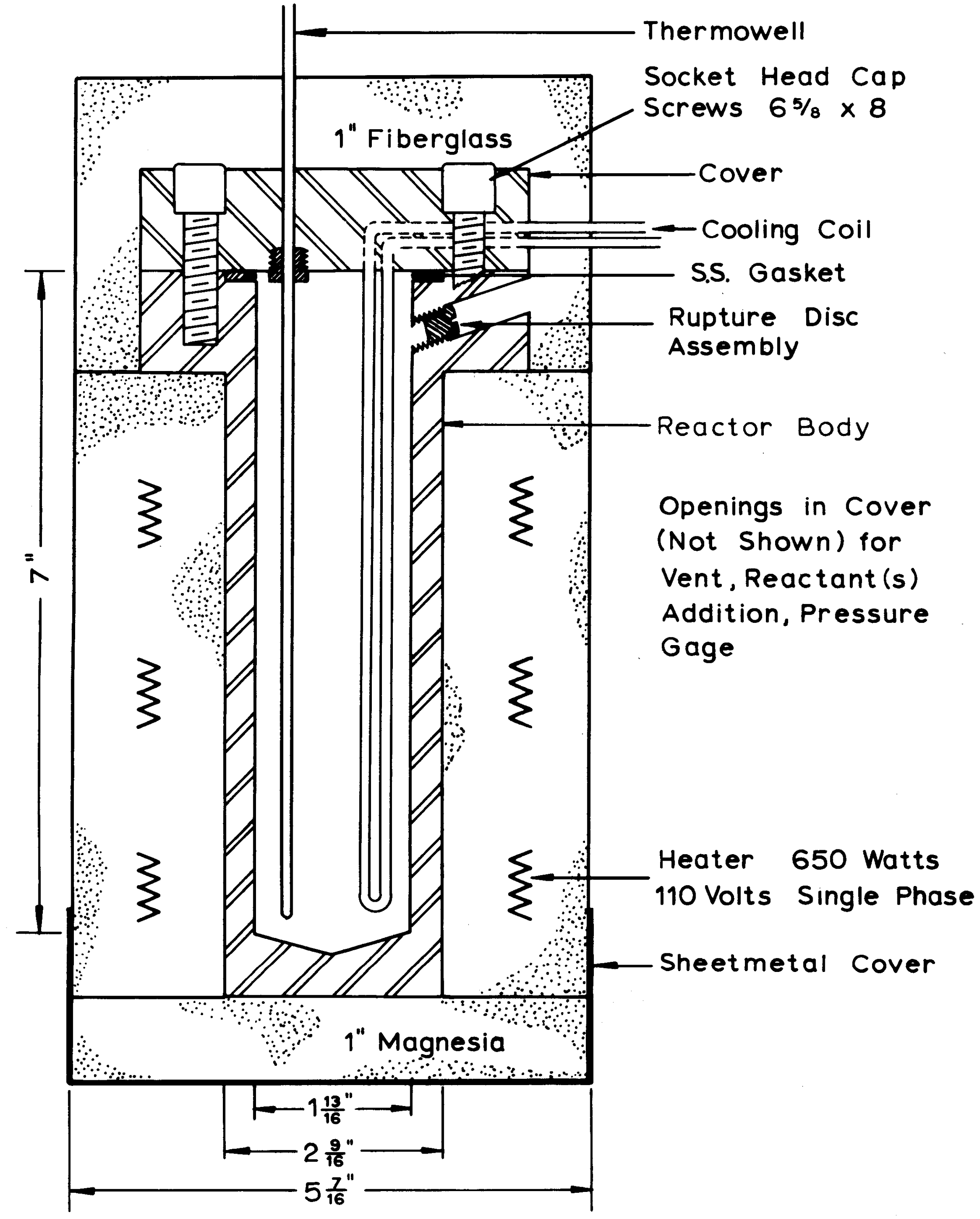


FIGURE 52 DETAILS OF REACTOR

b. Nickel-Lined Reactor

A nickel-lined stainless steel type-316 bodied reactor was designed and fabricated for the experiments involving alkalies. Stainless steels undergo stress cracking in alkaline media at the elevated temperatures required for coal liquefaction.

Details of the nickel-lined reactor are shown in Figures 53 and 54. The nickel-liner, 1/4 inch thick, bored from solid stock, was permanently, hydraulically pressed into the stainless steel body. Weepholes, 1/16 inch diameter, drilled through the stainless steel walls, prevented accumulation of pockets of high pressure gas between the liner and the body which, when the reactor was vented, could cause collapse of the liner. Hydrogen is an example of a gas capable of diffusing through metals. The nickel liner protruded above the stainless steel body to minimize the possibility, in event of leakage at the gasket, of gas leaking between the liner and the body. Structural strength and a high pressure rating were imparted to the reactor by the thick walled stainless steel body. Silver, a soft ductile metal, was used as the gasket material of construction.

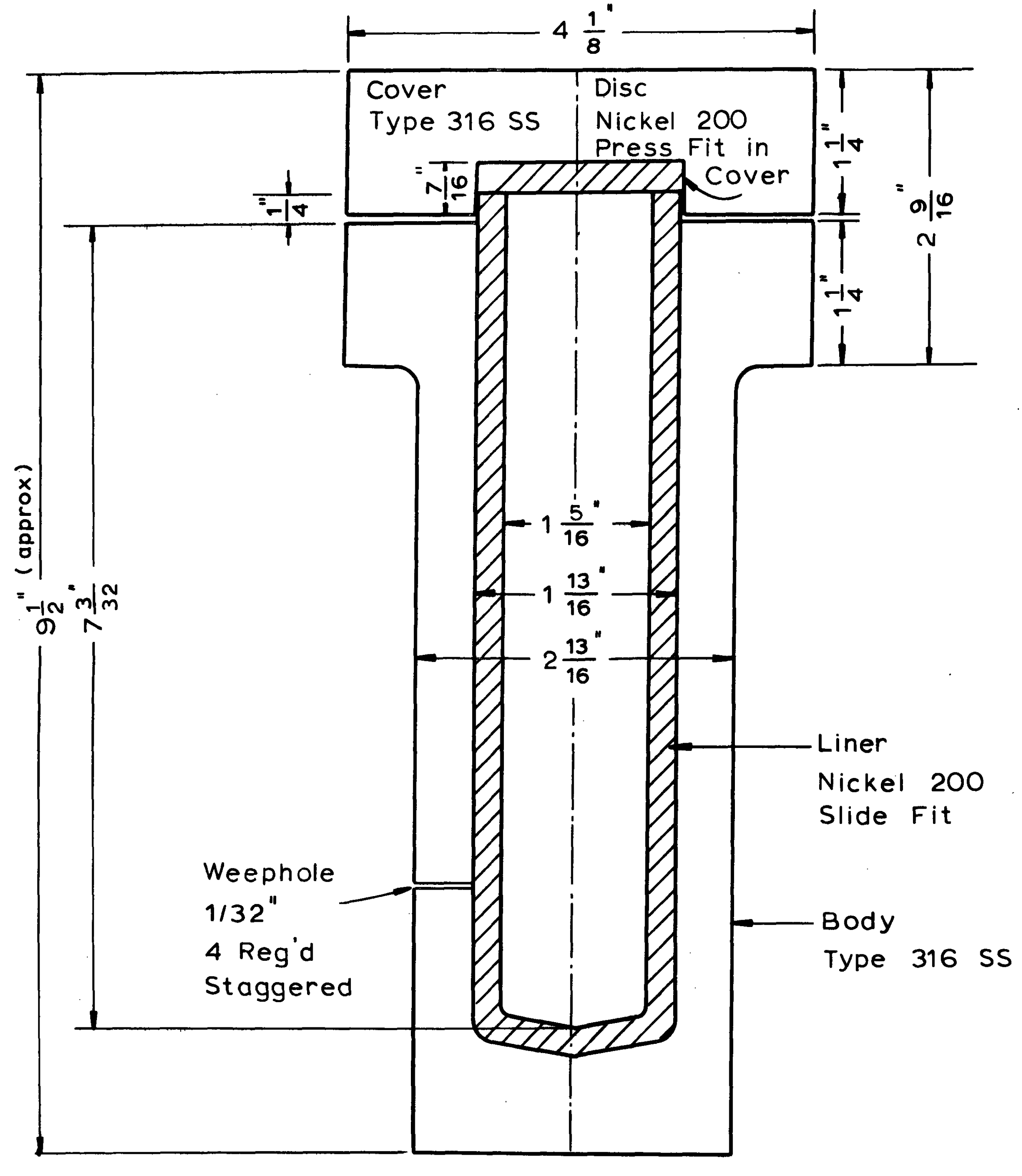


Figure 53 Details of Nickel - Lined Reactor

Cover Details

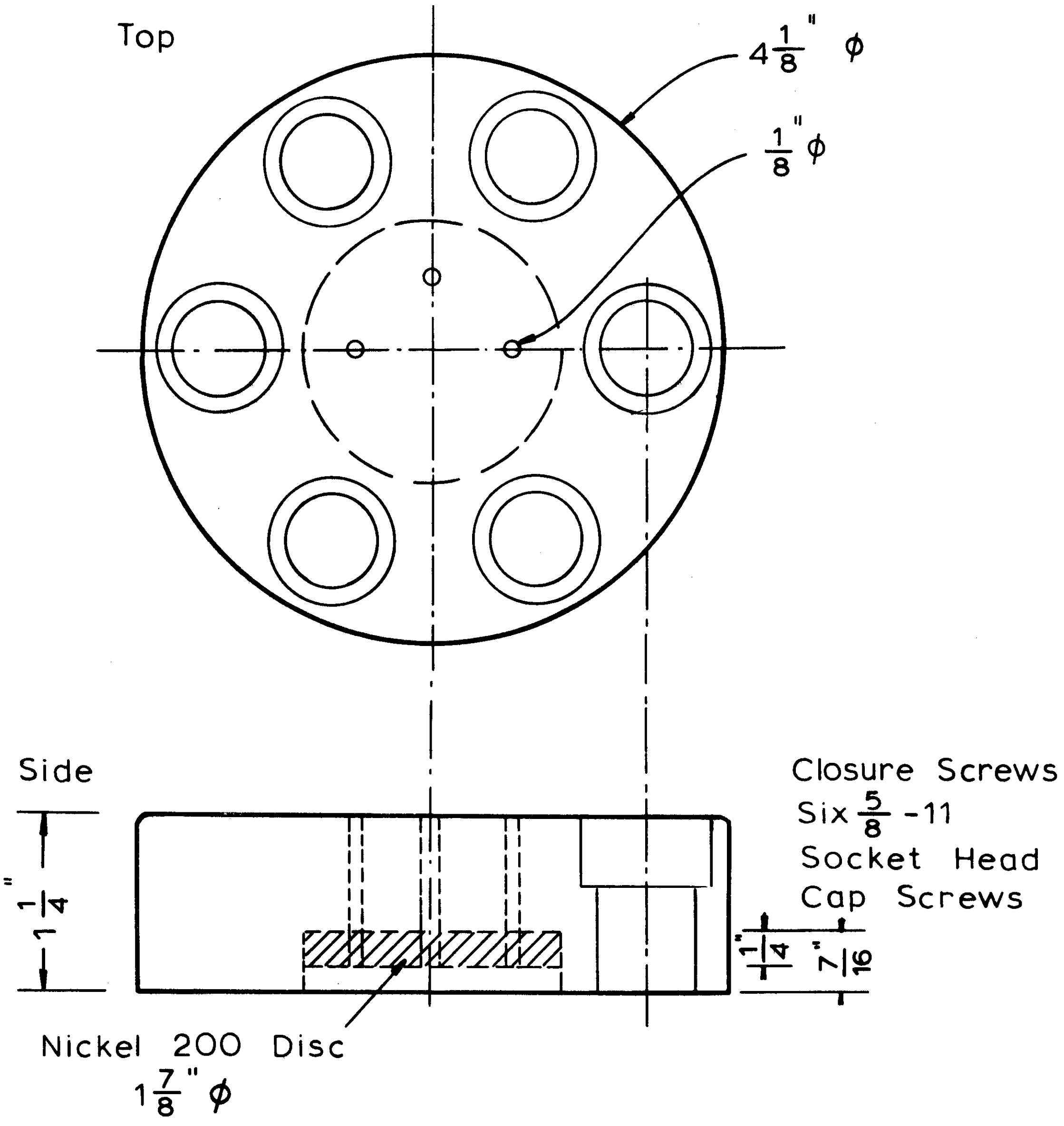


Figure 54 Details of Cover for Nickel - Lined Reactor

2. Rocker Assembly

Details of the rocker assembly are shown in Figure 55. The assembly consisted of the following equipment:

1. Drive: Vickers 3/4 HP variable speed transmission driven by 1/3 HP electric motor
2. Connecting rod
3. Autoclave and heating mantle
4. Cradle and clamp for heating mantle
5. Stand constructed of 1/4 inch angle iron
6. Wood base.

Speed was variable from 0 to 90 RPM and the rocking arc was adjustable by simply relocating the position of the connecting rod on the pinion.

3. Heaters

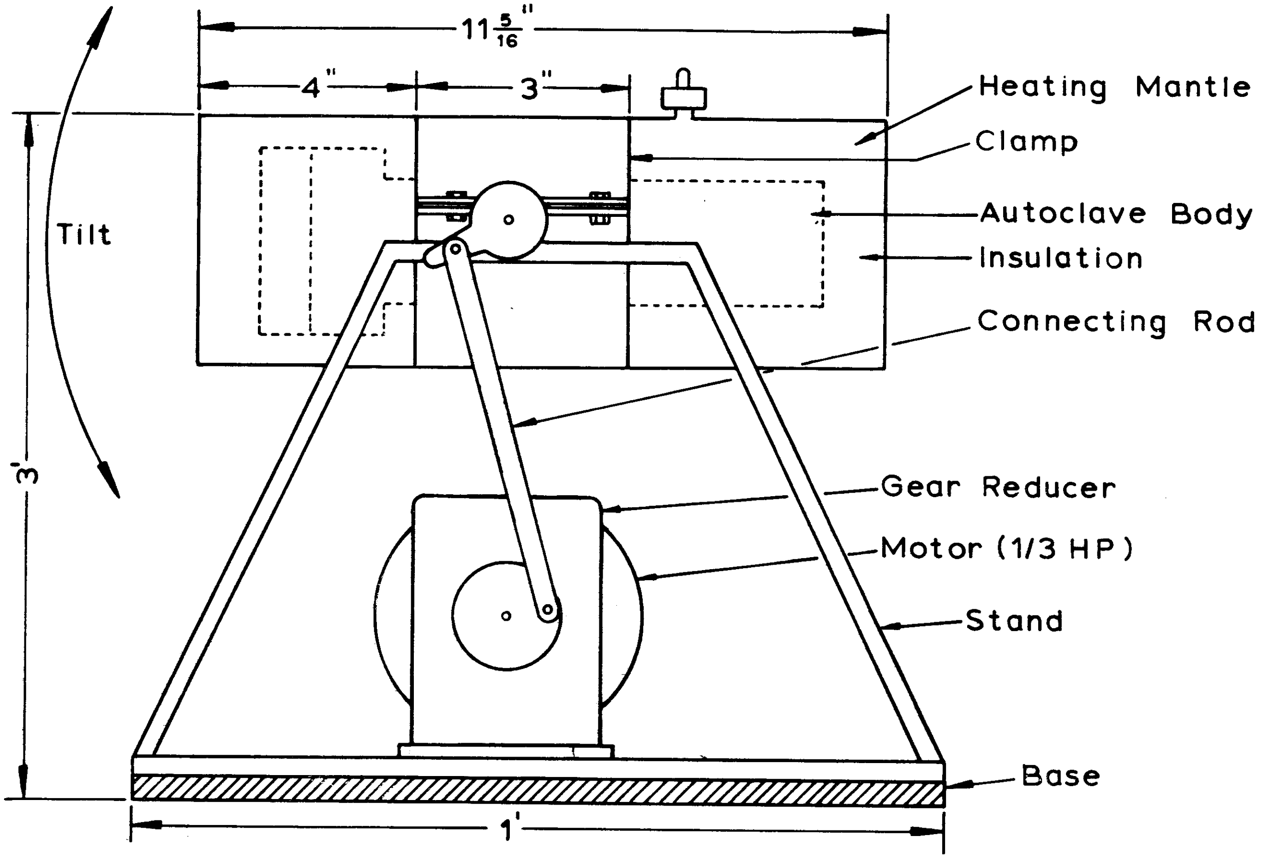
a. Stainless Steel Reactor Heater

A single electric heater, mantle type, 650 watts, wired for 110 volt single phase service was used to heat the stainless steel autoclave. The heater was clamped onto the rocker assembly.

b. Nickel-Lined Reactor Heater

This reactor was heated via electrical windings constructed as follows:

1. A ceramic tube, slightly larger in inside diameter than the reactor body outside diameter, was wound with nichrome wire and then coated with a thin layer of alundum cement.



Tilt From The Horizontal Upward an Angle of Approximately 30 - 40 °, Variable RPM

FIGURE 55 REACTOR AND ROCKER ASSEMBLY

2. The ceramic tube was then insulated with 85% magnesia of one inch thickness.
3. An aluminum jacket fabricated around the insulation completed the furnace.

The resulting furnace was of the same size as the mantles used to heat the stainless steel autoclaves so that it could be mounted in the same clamps used in the rocker assembly to accommodate the mantles. As with the mantles, this furnace was permanently clamped onto the rocking assembly permitting easy assembly and removal of the reactor.

4. Equipment Layout

Safety considerations necessitated locating the two reactor assemblies in a barricaded area, in this case, an area about 5 feet by 5 feet, walled on three sides to a height of 6 feet with cemented concrete blocks The open side, facing an exterior window, functioned as the blowout wall Plywood, attached to wooden 2 x 4's secured to the blocks, served as the ceiling or roof to this cubicle. A 60 cfm blower, exhausting via a 3-inch hose directly outdoors, was installed on one side of the cubicle. A plastic curtain covered the front of the cubicle during runs enabling the blower to be very effective in maintaining the surrounding area fume-free even when a major leak occurred.

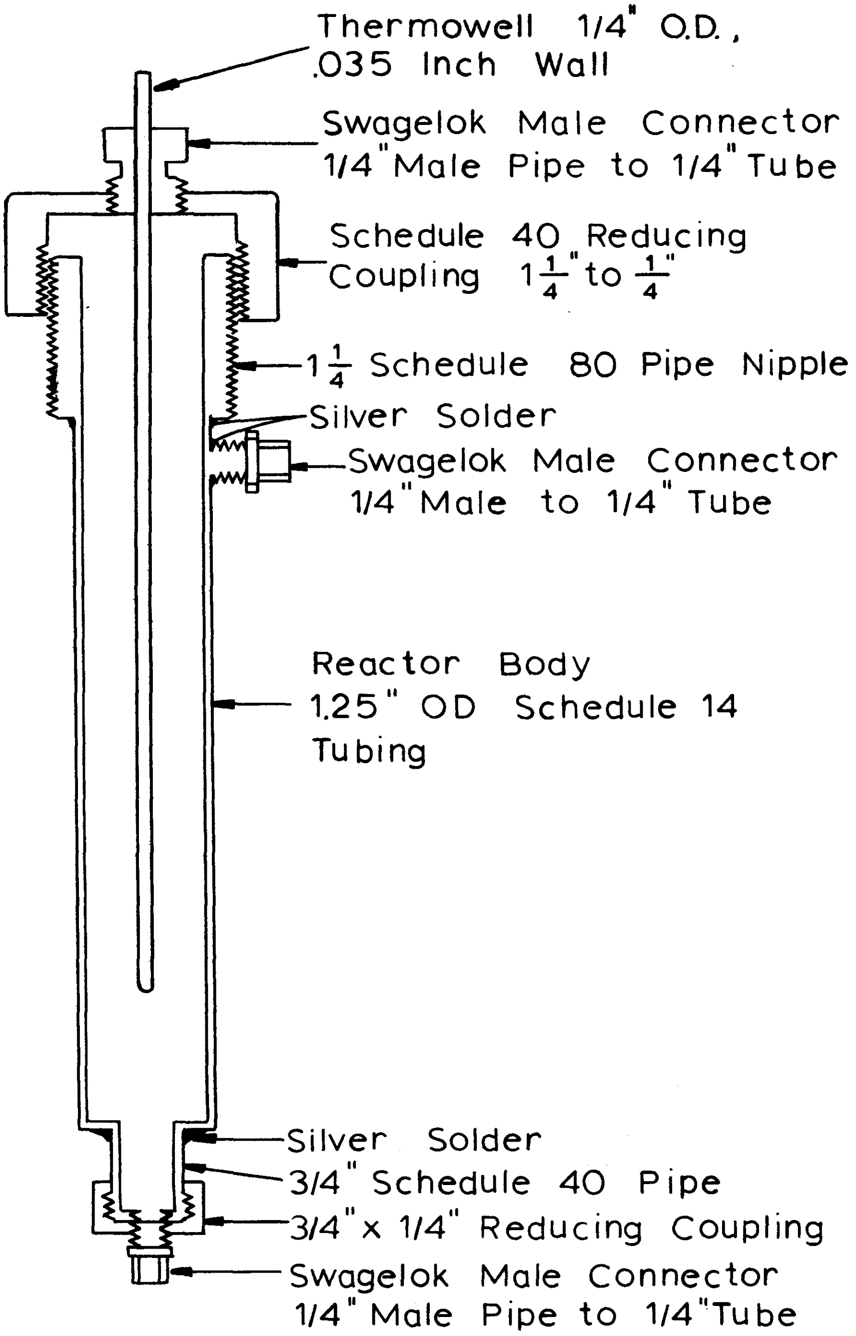
Operation of the equipment was remote. All electrical switches and process valving were accessible without entering the cubicle. Large mirrors, strategically located, permitted visual observation of the two reactor assemblies from a safe vantage point. Entry of the cubicle was allowed only when the units were not under pressure.

B. GASIFICATION EQUIPMENT DETAILS

1. Gasification Reactor

Details of the gasification reactor are shown in Figure 56. All parts were stainless steel type 304. The reactor body consisted of a 30 inch length of 1 1/4 inch O.D. schedule 14 tubing. Since this reactor was mounted vertically, one end can be referred to as the top and the other end the bottom. The top closure will be described first. The reactor body was inserted into a 1 1/4 inch schedule 80 pipe nipple, I.D. = 1.278 inches, to a depth of 1 1/4 inches and a silver solder joint made. Fitted to this nipple was a 1 1/4 to 1/4 inch schedule 40 reducing coupling. Into the top of the reducing coupling was fitted a Swagelok 1/4 inch male pipe to 1/4 inch tube connector. A length of 1/4 inch O.D. tubing, wall thickness 0.035 inches, and 31 1/2 inches length was inserted to serve as the thermowell. About 1 inch below the nipple a hole was drilled into the reactor body to accommodate a Swagelok 1/4 inch male pipe to 1/4 inch tube connector. This connector was silver soldered to the reactor body and served as the steam inlet from the vaporizer.

The bottom closure was made by inserting into the reactor body to a depth of 1/2 inch a 5 inch length of 3/4 inch schedule 40 pipe. A silver solder joint was made between the reactor body and the 3/4 inch pipe. This pipe was threaded at the bottom end and to this threaded end a 3/4 inch by 1/4 inch reducing coupling was fitted.



ALL FITTINGS, TUBING AND PIPE - STAINLESS STEEL, TYPE 304

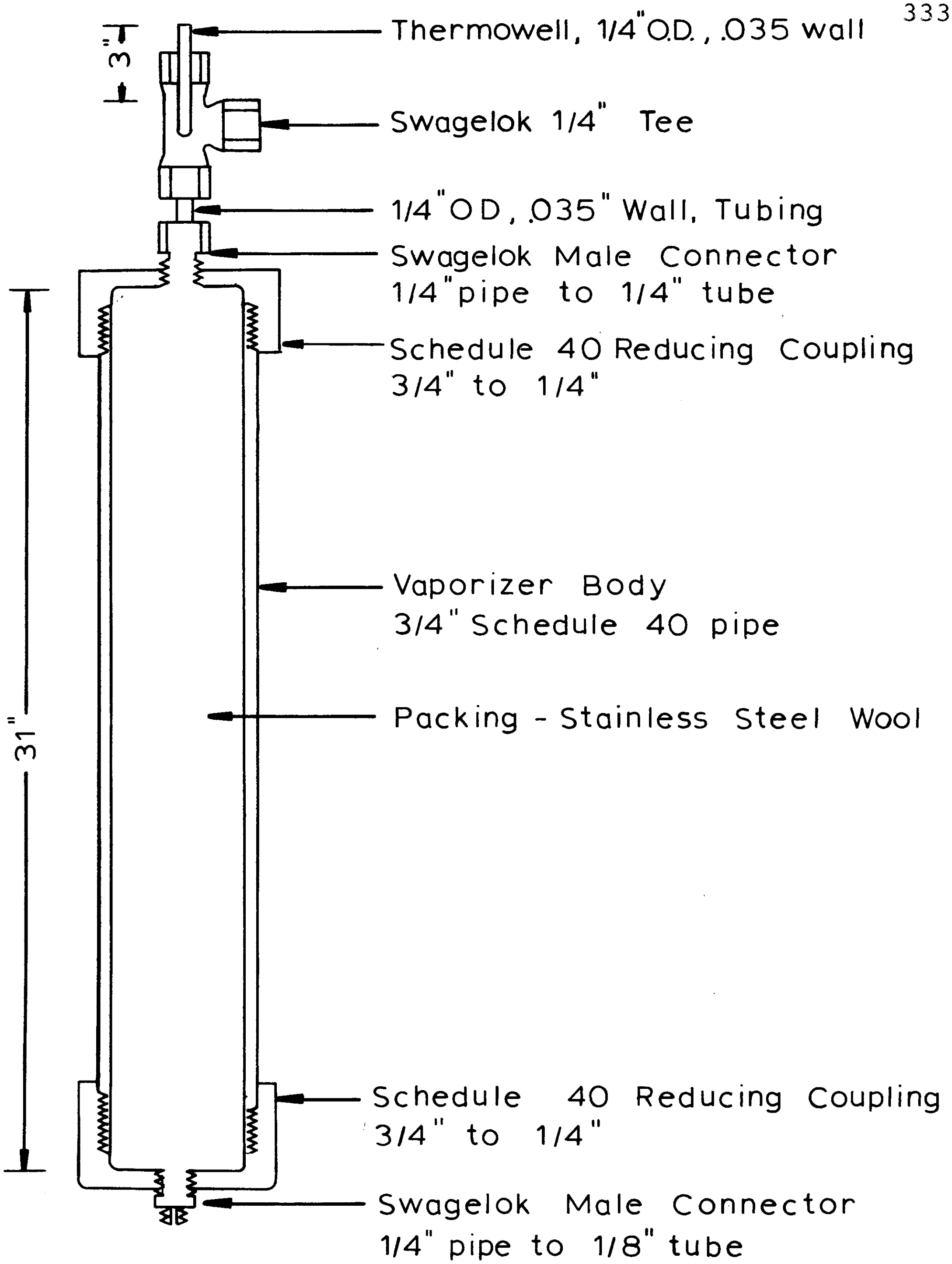
FIGURE 56 GASIFICATION REACTOR DETAILS

To this reducing coupling was fitted a Swagelok 1/4 inch male pipe thread to 1/4 inch tube connector.

2. Water Vaporizer

Details of the water vaporizer are shown in Figure 57. The vaporizer was a 31 inch length of 3/4 inch schedule 40 pipe threaded at both ends. Since the vaporizer was also mounted vertically, it too has a top and bottom. The top closure was made by fitting a 3/4 inch to 1/4 inch reducing coupling onto the pipe. Into the reducing coupling was fitted a Swagelok 1/4 inch male pipe to 1/4 inch tube connector. A 2 inch length of 1/4 inch O.D. tubing led to a Swagelok 1/4 inch tube tee. A thermowell consisting of a short length of 1/4 inch O.D. tubing was inserted into the tube tee permitting a thermocouple to measure the exit steam temperature from the vaporizer. The other side of the tee was connected to the gasification reactor column by a 10 inch length of 1/4 inch O.D. tubing.

The bottom connection of the vaporizer consisted of a 3/4 inch to 1/4 inch schedule 40 reducing coupling. Into this reducing coupling was fitted a Swagelok 1/4 inch male pipe to 1/8 inch tube connector. This fitting was connected to the water flowmeter by a length of 1/8 inch O.D. by 1/16 inch I.D. tubing.



Material of Construction, Type 304 Stainless Steel

FIGURE 57 DETAILS OF WATER VAPORIZER

The vaporizer and all associated fittings were stainless steel type 304. The vaporizer was tightly packed with stainless steel wool (Gottschalk's steel sponge) to provide surface for heat transfer.

3. Steam Condenser

The steam condenser details are shown in Figure 58. It was essentially a shell with a coil inside. The shell was a 12 inch length of 2 $^1/2$ inch O.D. brass tubing sealed at both ends with brass discs which were brazed to the brass tube. The coil was $^1/4$ inch O.D. by 6 feet long stainless steel type 304 tubing. The ends of the coil protruded through the top and bottom discs of the vertically mounted condenser. Reactor off-gases flowed downward through the coil counter current to cooling water entering at the bottom of the shell.

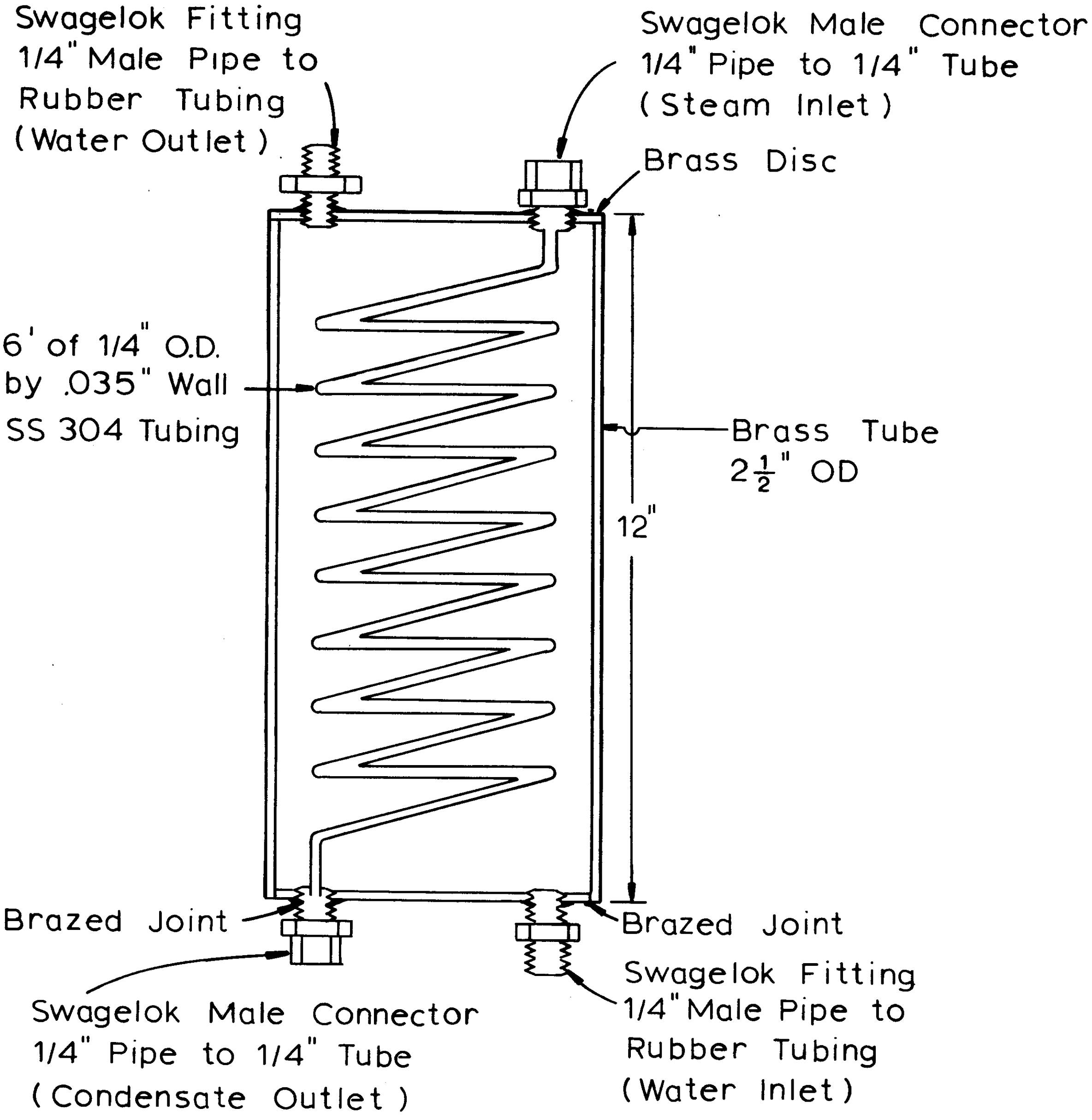


FIGURE 58 DETAILS OF STEAM CONDENSER

APPENDIX II

VAPOR PHASE CHROMATOGRAPHIC ANALYSIS OF GASIFICATION OFF-GASES

1. Technique Details

The gas chromatograph used in this study was a Fisher-Hamilton Model 29 Gas Partitioner specifically designed for the quantitative determination of substances which are gaseous at room temperature. This instrument utilized a dual-column dual-detector chromatographic system to separate and measure the component gases.

a. Principles of the Chromatograph

The sample to be analyzed, in admixture with a carrier gas, usually helium, was swept through, in this case, the two series-connected chromatographic columns each of which was packed with an adsorbent which selectively retarded the passage of the various components of the sample. The components thus separate and were eluted from the system at different times. As each component was eluted, a detector sensed it and produced an electrical signal which was recorded as a measurable peak, or chromatogram. The time elapsed from the injection, or introduction of a particular gas to the appearance of a peak, usually characteristic of a particular gas, can be used to identify it, regardless of the concentration of this component or the presence or absence of other components. The height of a peak is proportional to the concentration of the gas, and after proper calibration is made the percentage of that component in a mixture can be determined.

(1) The Columns

Column No. 1, 6 feet long by 1/4 inch diameter, was packed with Di(2-ethylhexyl) Sebacate (DEHS) on 60-80 mesh Columpak. Column No. 2, 6 1/2 feet long by 3/16 inch diameter, was packed with 42-60 mesh Molecular Sieve.

(2) The Detectors

Only carbon dioxide was detected by the first detector. Carbon dioxide was subsequently permanently adsorbed by the second column. Both detectors were of the thermal conductivity type thus requiring that the gas to be analyzed be free of water vapor.

(3) The Recorder

Used in conjunction with the chromatograph was a Microcord Model 44 recorder, one millivolt range, set at a chart speed of one inch per minute.

b. Analysis Details

The chromatograph thermal conductivity detectors operate on differences between the thermal conductivity of the carrier gas, normally helium, and that of the unknown component. Unfortunately, the thermal conductivity of hydrogen was too close to that of helium for accurate analysis, necessitating that another carrier gas, such as argon, be used when hydrogen was being analyzed. However, argon was not suitable for the accurate determination of the other gases present.

Thus, the chromatograph was first set up with both helium and argon supply cylinders, the intention being that a process gas sample could be taken while helium was being used as the carrier gas and then after this gas sample had passed through the chromatograph and the results recorded, the carrier gas could be changed to argon and another gas sample taken for hydrogen analysis.

However, when this was attempted, it was discovered that the chromatograph required several hours to re-attain equilibrium after a carrier gas switch. For this reason, only helium was used as the carrier gas during the runs and hydrogen analysis was obtained by difference between unity and the sum of the mol fractions of carbon dioxide, methane, nitrogen and carbon monoxide.

2. Calibration of Chromatograph

a. Preparation of Standard Gas Mixtures

A setup consisting of a size 2 Matheson gas cylinder equipped with an accurate combination vacuum-pressure gauge, 0.05 lb. subdivisions, and adequate valving for evacuation and purging operations was used for the preparation of standard gas mixtures for the calibration of the chromatograph. Assuming the gases are ideal in the range 0-50 psia pressure, and knowing the approximate composition of the dry gas generated in the gasification reactor, a mixture was made by evacuating the cylinder and then filling it from various cylinders of pure gases using the incremental pressure changes as a measure of the composition of the standard gas mixture. The mixture prepared for calibration of the chromatograph before and after run G-13 had the following composition:

Component	Mol %
CO_2	33.36
N_2	7.86
CH_4	3.79
CO	2.83
H_2	52.15

The validity of this technique for preparing calibration mixtures was confirmed by analyzing two commercially prepared standard gas mixtures, using the lab-prepared mixture for chromatograph calibration, and obtaining the correct compositions.

b. Carrying Out the Chromatograph Calibration

Before and after each run, the calibration mixture was injected several times into the chromatograph. The resulting peak heights above the baselines for each component were averaged and from the average peak heights, the attenuation factors and the known composition, calibration factors were calculated for the components that could be applied to an unknown chromatogram. A typical chromatogram obtained during calibration is shown in Figure 59.

For example, when the standard gas mixture mentioned in (a) above was chromatographed, the following data were obtained:

Component	Average Peak Height	Attenuation
CO_2	80.4	64
N_2	68.5	16
CH_4	43.4	8
CO	33.1	8
H_2	Not analyzed for directly	

The concentration of an individual component in an unknown sample is given by the equation:

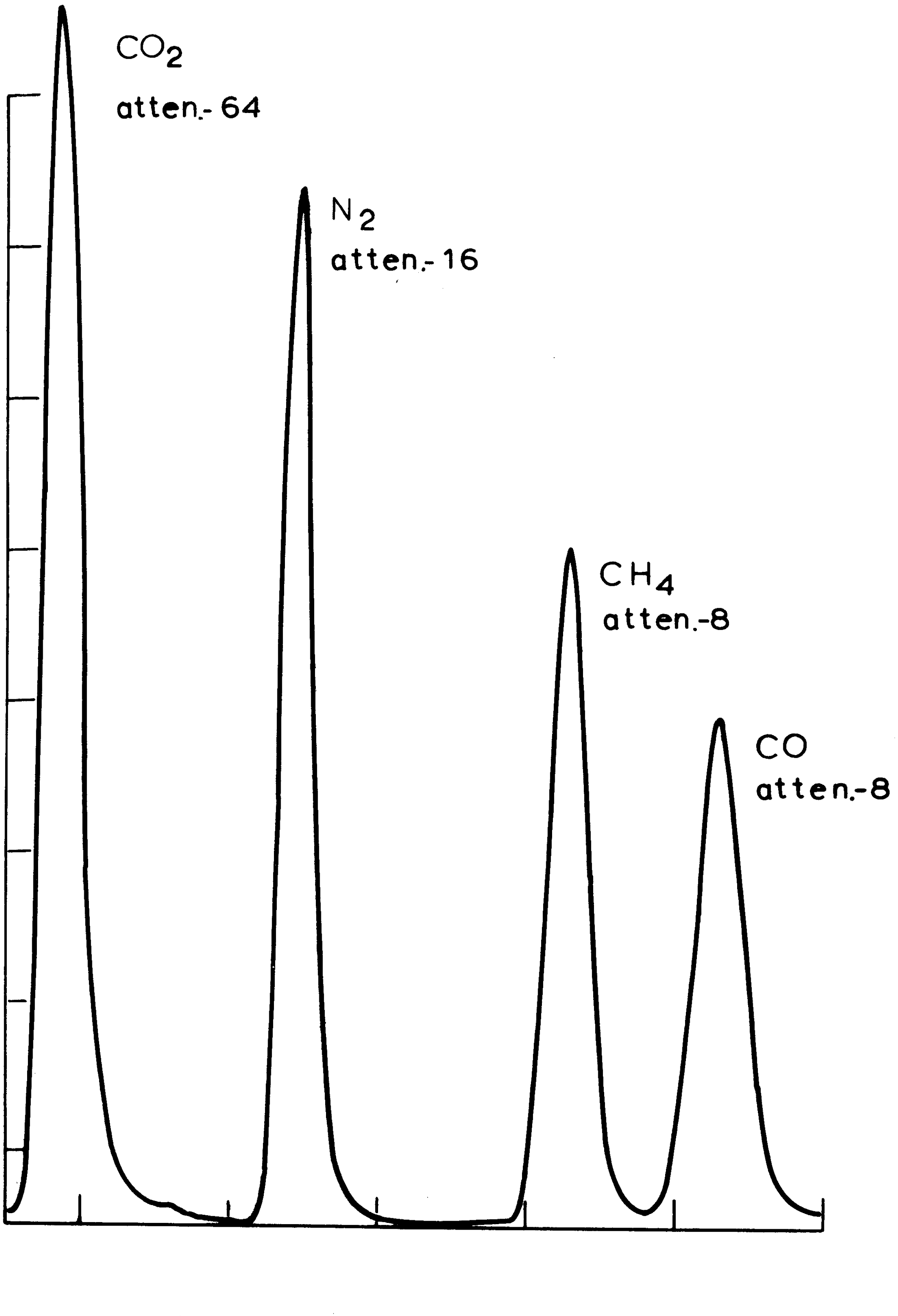


Figure 59 Typical Chromatogram Obtained During Calibration

$$C_S = \frac{H_S}{H_{STD}} (C_{STD})$$

where C_S = concencentration of sample component, mol %

C_{STD} = concentration of component in standard, mol %

H_S = peak height of component in sample, chart units

H_{STD} = peak height of component in standard, chart units

$\frac{C_{STD}}{H_{STD}}$ = calibration factor

H = (Peak Height) (Attenuation Factor)

Using this mixture, the unknown compositions were calculated from peak heights as follows:

<u>Component</u>

CO_2 $$\% \; CO_2 = \frac{H_{CO_2} (33.36)}{(80.4)(64)} = .00648 \; H_{CO_2}$$

N_2 $$\% \; N_2 = \frac{H_{N_2} (7.86)}{(68.5)(16)} = .00717 \; H_{N_2}$$

CH_4 $$\% \; CH_4 = \frac{H_{CH_4} (3.79)}{(43.4)(8)} = .01091 \; H_{CH_4}$$

CO $$\% \; CO = \frac{H_{CO} (2.83)}{(33.1)(8)} = .01069 \; H_{CO}$$

3. Calculation of Dry Gas Composition

A sample chromatogram from Run G-13 is shown in Figure 60. Beside each peak is written the attenuation factor at that time. Simply measuring the peak height above the baseline, multiplying by the attenuation factor and then by the calibration factor gives the mol percentage of that component in the dry gas. Hydrogen was obtained as the difference between 100 and the sum of the mol percentages of carbon dioxide, nitrogen, methane and carbon monoxide.

The complete calculation appears in Table XXVIII and the results are further tabulated in Table XXIX.

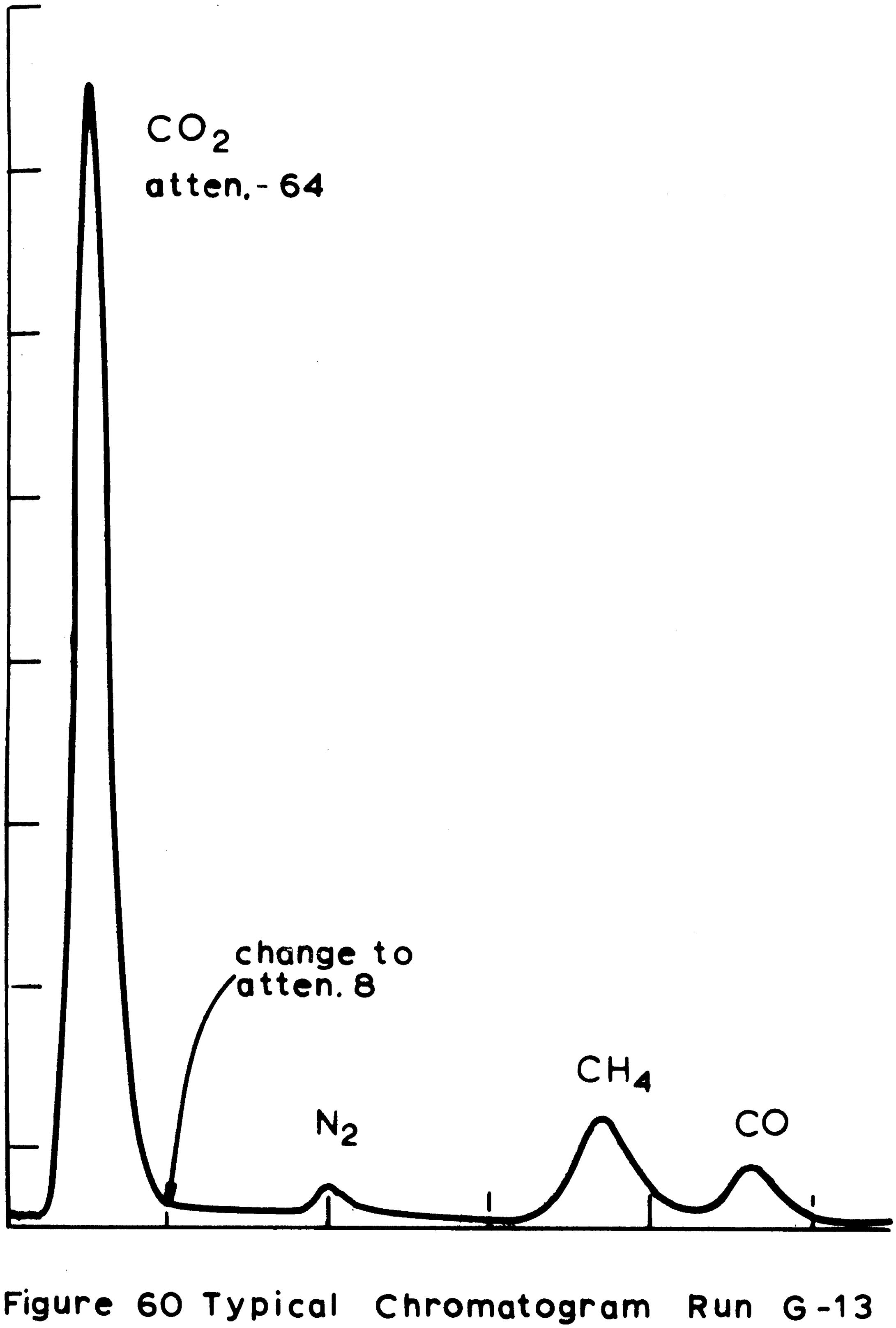


Figure 60 Typical Chromatogram Run G-13 Sample 6

TABLE XXVIII

SAMPLE CALCULATION OF DRY GAS COMPOSITION

Run G-13

Sample 1 - 57 minutes after start of run

Component	Peak Height	Attenuation Factor	Calibration Factor	Mol Percent Component
CO_2	69.8	64	0.00648	28.90
N_2	1.7	16	0.00717	0.195
CH_4	6.3	8	0.01091	0.55
CO	4.5	8	0.01069	0.385
H_2 (by difference)				69.96

Sample 2 - 115 minutes after start of run

Component	Peak Height	Attenuation Factor	Calibration Factor	Mol Percent Component
CO_2	69.6	64	0.00648	28.86
N_2	0.8	8	0.00717	0.046
CH_4	7.0	8	0.01091	0.61
CO	4.2	8	0.01069	0.359
H_2 (by difference)				70.12

Sample 3 - 301 minutes after start of run

Component	Peak Height	Attenuation Factor	Calibration Factor	Mol Percent Component
CO_2	71.0	64	0.00648	29.40
N_2	0.1	64	0.00717	0.046
CH_4	7	8	0.01091	0.61
CO	3.7	8	0.01069	0.316
H_2 (by difference)				69.582

Sample 4 - 379 minutes after start of run

Component	Peak Height	Attenuation Factor	Calibration Factor	Mol Percent Component
CO_2	69.4	64	0.00648	28.78
N_2	5.3	8	0.00717	0.304
CH_4	6.6	8	0.01091	0.576
CO	3.5	8	0.01069	0.30
H_2 (by difference)				70.04

Sample 5 - 442 minutes after start of run

CO_2	69.6	64	0.00648	28.86
N_2	2.4	8	0.00717	0.138
CH_4	5.9	8	0.01091	0.515
CO	3.2	8	0.01069	0.274
H_2 (by difference)				70.21

Sample 6 - 487 minutes after start of run

CO_2	69.6	64	0.00648	28.86
N_2	2.4	8	0.00717	0.138
CH_4	5.9	8	0.01091	0.515
CO	3.2	8	0.01069	0.274
H_2 (by difference)				70.21

TABLE XXIX

GAS COMPOSITION AS A FUNCTION OF TIME FOR RUN G-13

Elapsed Time from Start of Run (min.)	Sample Number	Mol Percent				
		CO_2	N_2	CH_4	CO	H_2
57	1	28.90	0.195	0.55	0.39	69.97
115	2	28.86	0.046	0.61	0.36	70.12
301	3	29.40	0.046	0.61	0.32	69.63
379	4	28.78	0.304	0.58	0.30	70.04
442	5	28.41	0.120	0.57	0.28	70.62
487	6	28.86	0.138	0.52	0.27	70.21

APPENDIX III

GASIFICATION - SAMPLE CALCULATION

The complete computational procedures for the gasification runs are illustrated below using the data of Run G-13. For reference, the original data sheet of Run G-13 has been reproduced and appears at the end of Appendix IV.

Calculations were carried out using the IBM 370 batch processing facility located in the Computation Center. Polynomials were fitted to the experimental data using a General Electric time share computer, known as Mark I; the specific program was Basic-Polfit.** At the end of the calculation, the computer program written for the gasification data analysis appears.

The steps in the calculations are as follows:

1. A third or higher degree polynomial was fitted to the cumulative gas evolved, cubic feet, versus time, minutes, data obtained from the tabulation of times and wet test meter readings contained in the original data sheet. The curve of cumulative gas evolved as a function of time showing the experimental points appears as Figure 61. In the computer program, cumulative gas evolved is designated as GV.

2. A third or higher degree polynomial was fitted to the cumulative water condensed from the exit gases of the gasification reactor, grams, versus time, minutes, data obtained from the tabulation of times and incremental condensate in the original data sheet. This data is shown in Table XXX and in Figure 62. Cumulative water condensed is designated as WW in the computer program.

3. Contained in the original data sheet was the information necessary to convert the measured gas volume, ft^3, to gram moles. This information is:

   Average Temperature at Wet Test Meter = 70°F

   Barometric Pressure = 765 mm Hg

   Pressure at Wet Test Meter = 0.9 inches H_2O

   Thus, the total pressure at the wet test meter was:

$$765 \quad + \quad \frac{(0.9)(25.4 \ ^{mm}/in.)}{13.6} \quad = 766.7 \text{ mm Hg}$$

   Since the vapor pressure of water at 70°F is 18.771 mm Hg, the partial pressure of dry gas at the wet test meter was:

$$766.7 - 18.771 \quad = \quad 747.9 \text{ mm Hg.}$$

$$\frac{\text{g-mols of dry gas}}{\text{ft}^3\text{ of gas measured}} = \frac{28.317\ \dfrac{\text{liters}}{\text{ft}^3}}{\left(22.4\ \dfrac{\text{liters}}{\text{g-mol}}\right)\left(\dfrac{294.7}{273.6}\right)\left(\dfrac{760}{747.9}\right)}$$

$$= 1.155\ \frac{\text{g-mols dry gas}}{\text{ft}^3\text{ wet gas}}$$

In the computer program, this conversion factor is designated as Q; a different Q was required in each run due to temperature and barometric pressure changes.

4. Division of WW by the molecular weight of water, 18.016, converted WW to gram mols of water.

5. Differentiation of the polynomials

   GV = f(time)
   WW = f(time)

   followed by evaluation of the derivatives every ten minutes and application of the appropriate conversion factor gave the dry gas rate, g-mols/min. and the condensate rate, g-mols/min. The sum of these latter quantities is the total outlet gas rate, designated on the computer program as TGO.

On page 1 of the computer printout for Run G-13 was shown:

Time			Check	Gas Rate	Cond.Rate	TGO Rate
(min.)	(ft^3)	(gms)		$\frac{\text{gm-mol}}{\text{min.}}$	$\frac{\text{gm-mol}}{\text{min.}}$	$\frac{\text{gm-mol}}{\text{min.}}$

The column labelled check was a test of internal consistency and will be explained later on.

6. The composition of the exit gas stream, after steam condensation, was then computed for each of the gas samples taken during the run using the chromatogram of the run. This was a hand calculation, and the procedures involved are detailed in Appendix II which deals with the development and the application of vapor phase chromatography to the gas analyses. Gas sample analyses for Run G-13 appear in Tables XXXI and XXXII and in Figure 63. Components of the exit gas stream were carbon dioxide, methane, carbon monoxide and hydrogen. As pointed out in the discussion on the assay development in Appendix II, hydrogen was not directly assayed for but rather determined by difference between unity and the sum of the mol fractions of carbon dioxide, carbon monoxide and methane. The validity of the hydrogen determination was substantiated by a direct measurement using the same chromatograph.

Next, polynomials of third or higher degree were fitted to the gas analyses versus time data contained in Table XXXII. In the computer program these polynomials are designated as: CO2MF, CH4MF, COMF, H2MF. Figure 64 shows the smoothed dry gas composition data, and page 4 of the computer printout for Run G-13 was the complete listing of the gas composition at ten minute intervals during the run.

7. Knowing the mols of dry gas generated per minute, at ten minute intervals, and the corresponding composition, the gram mols per minute of each component was then calculated by multiplication of these two quantities. On page 2 of the computer printout for Run G-13 was listed the outlet rates, gm-mols/min., for carbon dioxide, methane, carbon monoxide and hydrogen. Summation of the rates of the three carbon containing gases gave the total carbon out, expressed as gm-mols/min., CM, and as grams, CG.

   Figure 65 is a graph of the individual component outlet rates.

8. Integration of the individual components outlet rates as functions of time yielded the cumulative production of each component, gm-mols, shown on page 3 of the computer printout and in Figure 66.

9. The column labelled Check on page 1 of the computer printout was the sum of the individual component rates, and was to be compared with the gas rate which was independently determined from the GV. This was an internal check on how well the polynomials fitted the gas analyses data. These two adjacent columns agreed to a remarkable degree.

10. Division of the individual component rates by the total gas out, TGO, gave the wet gas composition, i.e., the composition of the gas exiting from the gasification reactor. Wet gas compositions and mol fractions were shown on page 5 of the computer printout for Run G-13.

11. Approximately 18.1 grams of water coke was changed to the gasification reactor. After the standard devolatilization procedure about 90.53% w/w of the original charge remained; having a carbon analysis of 69.87% w/w. At the onset of gasification, the carbon actually present in the bed for Run G-13 was

$$(18.12)(.9053)(.6987) = 11.48 \text{ grams}$$

In the computer program, the latter quantity is termed CZRO.

On page 6 of the computer printout for Run G-13 was tabulated the cumulative carbon gasified, grams, designated as CGC which was merely the C column from page 3 converted to grams.

12. The difference between CGC and CZRO is the carbon present in the bed at any time; this quantity was termed CR, or carbon remaining, and appeared also on page 6.

13. The instantaneous rate of carbon gasification is the ratio of the grams per minute out, CG on page 2, to the carbon present at that time, CR. The instantaneous rate of gasification was called in the program. RI is plotted versus time in Figure 67.

14. The last column on page 6 was FCG, the fraction of the original carbon present at the onset of gasification already gasified at the time listed. FCG was computed as the ratio of CGC to CZRO or as the ratio of CZRO CR to CZRO. RI versus FCG appears as Figure 68.

15. Values of the equilibrium constant expressions for the nine reactions considered in the data analysis were computed using the wet gas compositions, in mol fractions (not mol percentages). The extent of equilibrium approach was then computed for these nine reactions by dividing the values of the equilibrium constant expressions

by the respective equilibrium constants at 1000°F. The K values at 1000°F for the nine reactions are listed in Table XXVII of the Discussion. On page 7 of the computer printout for Run G-13 were listed these R values:

R_{G_1}, R_{G_2}, R_{S_1}, R_{S_2}, R_{M_1}, R_{M_2}, R_{M_3}, R_{M_4} and R_{GM}. Figures 69, 70, and 71 are plots of these R values versus time and Figures 72, 73, and 74 are plots of these R values versus FCG. Both types of graphs are included to show that R versus time and R versus FCG plots closely resemble one another.

16. The water conversion was calculated by dividing the outlet rate of oxygen in the oxygen containing gases by the sum of the condensate rate and the outlet rate of the oxygen in the oxygen containing gases. This calculation assumed that all the oxygen in the outlet gases arose from the water converted and not from the combined oxygen in the coke.

Thus, % Water Conversion

$$= 100 \quad x \quad \frac{2\,x \text{ mols } CO_2/\text{min} + \text{mols } CO/\text{min}}{\text{Condensate/min} + \text{numerator}}$$

or as written on program

$$\text{PCT H2O CON} = \text{WCON} = 100\ \frac{2(\text{CO2M}) + \text{COM}}{\text{WMP} + 2(\text{CO2M}) + \text{COM}}$$

PCT H2O CON appeared on page 8 of the printout.

17. The atomic ratio of hydrogen to carbon in the outlet gases also appeared on page 8 of the computer printout and was calculated as follows, again using as in PCT H2O CON the individual component outlet rates:

$$H/C = HC = \frac{2 \times \text{mols } H_2 + 4 \times \text{mols } CH_4)/\text{min}}{(\text{mols } CO_2 + \text{mols } CO + \text{mols } CH_4)/\text{min}}$$

18. The atomic ratio of hydrogen to oxygen was computed as a function of time and appeared on page 8 of the computer printout.

$$H/O = HO = \frac{(2 \text{ mols } H_2 + 4 \text{ mols } CH_4)/\text{min}}{(2 \text{ mols } CO_2 + \text{ mols } CO)/\text{min}}$$

19. Lastly, the molar ratio of hydrogen to carbon dioxide was calculated from the ratio of their outlet rates.

$$H_2/CO_2 = \text{H2CO2} = \frac{\text{Mols } H_2/\text{min}}{\text{Mols } CO_2/\text{min}}$$

TABLE XXX

STEAM CONDENSATE VOLUME AS A FUNCTION OF ELAPSED TIME FROM THE START OF RUN G-13

Elapsed Time (Minutes)	Condensate Volume (Milliliters)	Cumulative Condensate Volume (Milliliters)
0	0	0
66	37	37
127	46	83
300	156	239
403	110	349
489	93	442
537	43	485

TABLE XXXI

EXIT GAS COMPOSITION (DRY BASIS)

RUN G-13

Elapsed Time from Start of Run (min.)	Sample Number	Mol Percent				
		CO_2	N_2	CH_4	CO	H_2
57	1	28.90	0.195	0.55	0.39	69.97
115	2	28.86	0.046	0.61	0.36	70.12
301	3	29.40	0.046	0.61	0.32	69.63
379	4	28.78	0.304	0.58	0.30	70.04
442	5	28.41	0.120	0.57	0.28	70.62
487	6	28.86	0.138	0.52	0.27	70.21

TABLE XXXII

EXIT GAS COMPOSITION (DRY NITROGEN-FREE BASIS)

RUN G-13

Elapsed Time from Start of Run (min.)	Sample Number	Mol Percent				
		CO_2	N_2	CH_4	CO	H_2
57	1	28.96	-	0.55	0.39	70.11
115	2	28.87	-	0.61	0.36	70.15
301	3	29.41	-	0.61	0.32	69.66
379	4	28.87	-	0.58	0.30	70.75
442	5	28.41	-	0.57	0.28	70.70
487	6	28.90	-	0.52	0.27	70.31

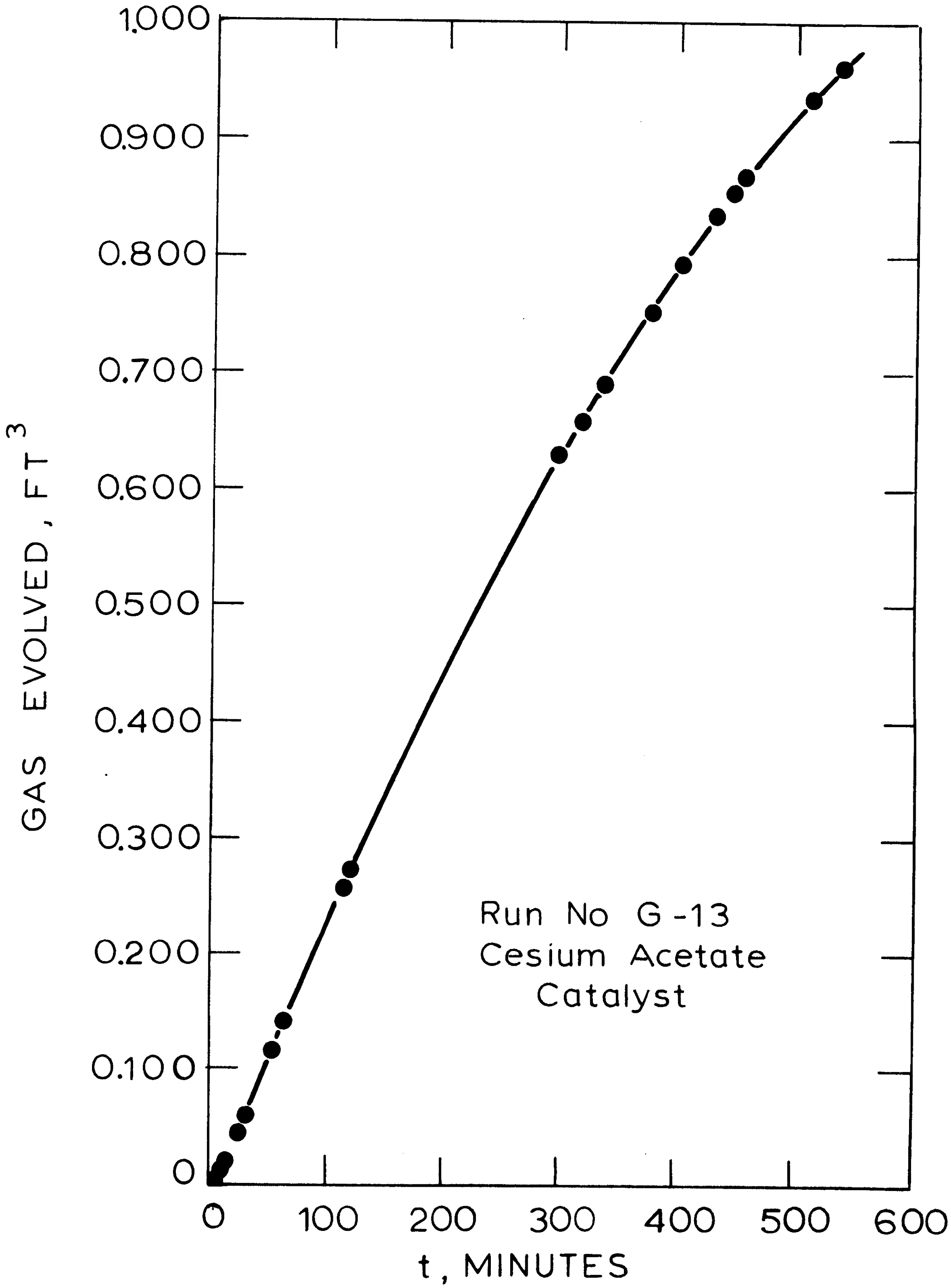


Figure 61 Cumulative Dry Gas Evolution vs Elapsed Time

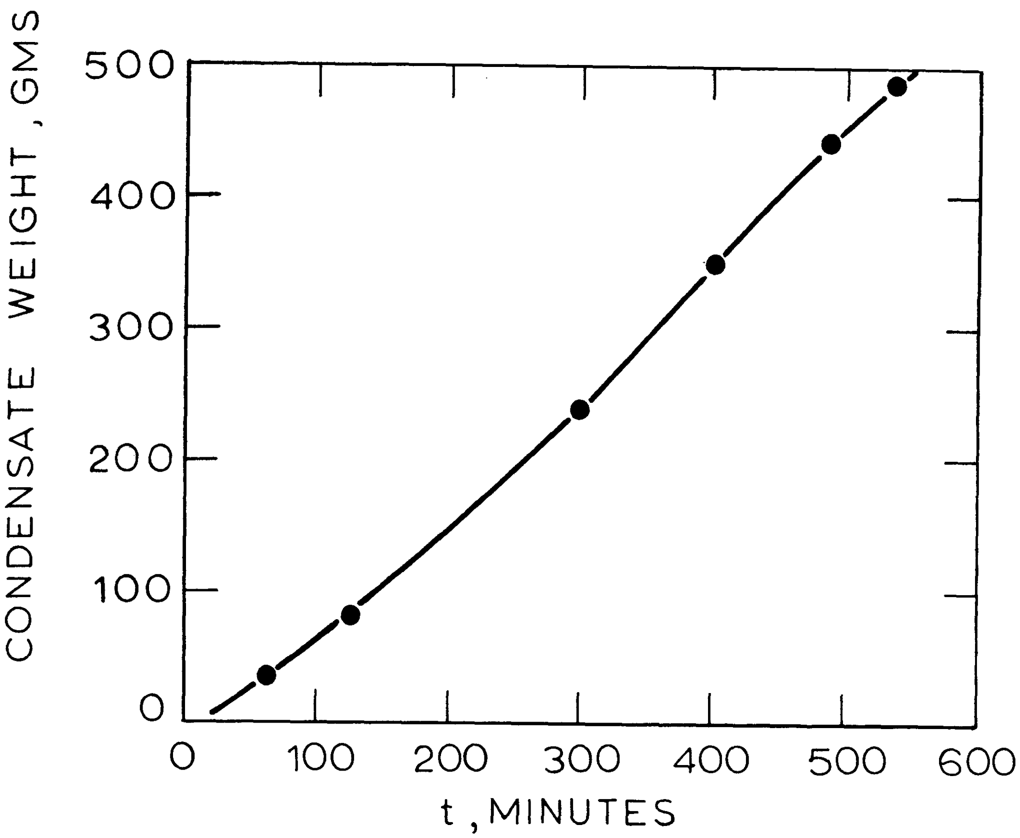


Figure 62 Condensate Weight vs Elapsed Time Run G-13

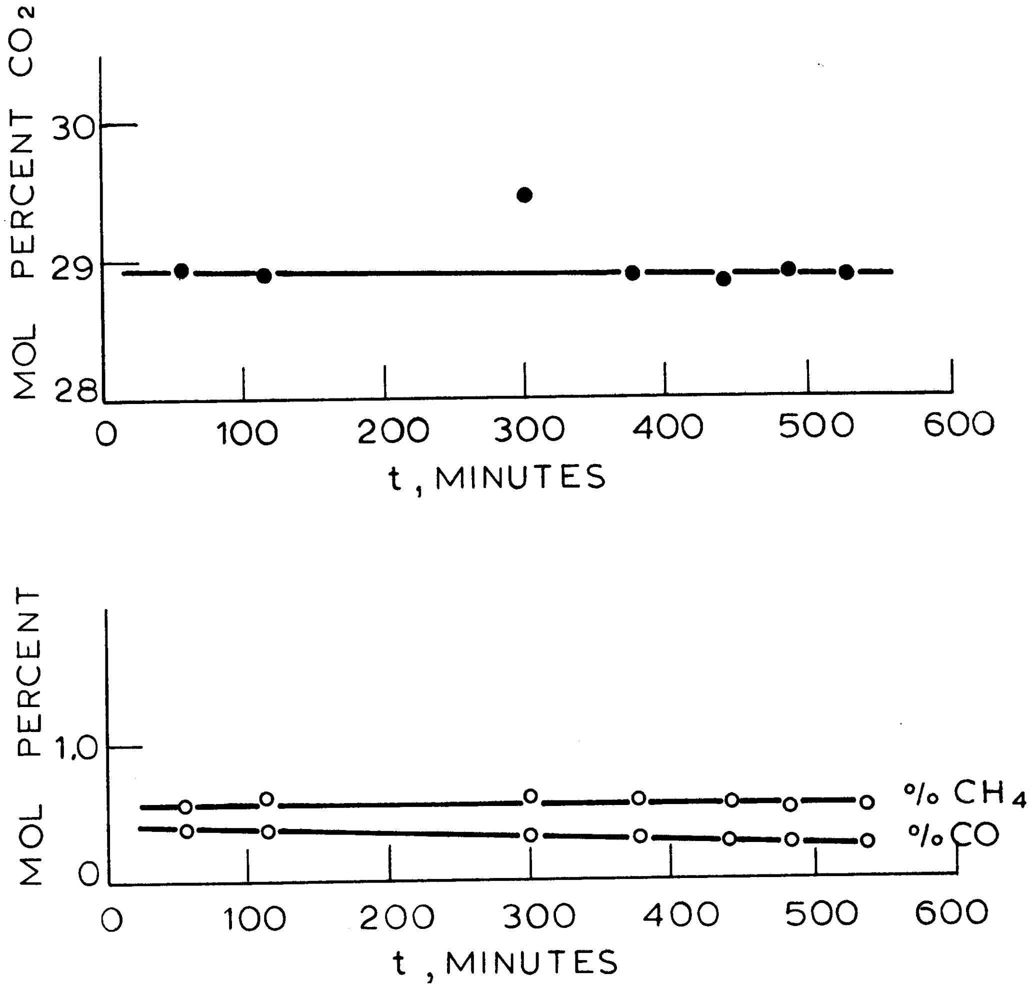


Figure **63** Gas Analysis vs Time for Run G-13

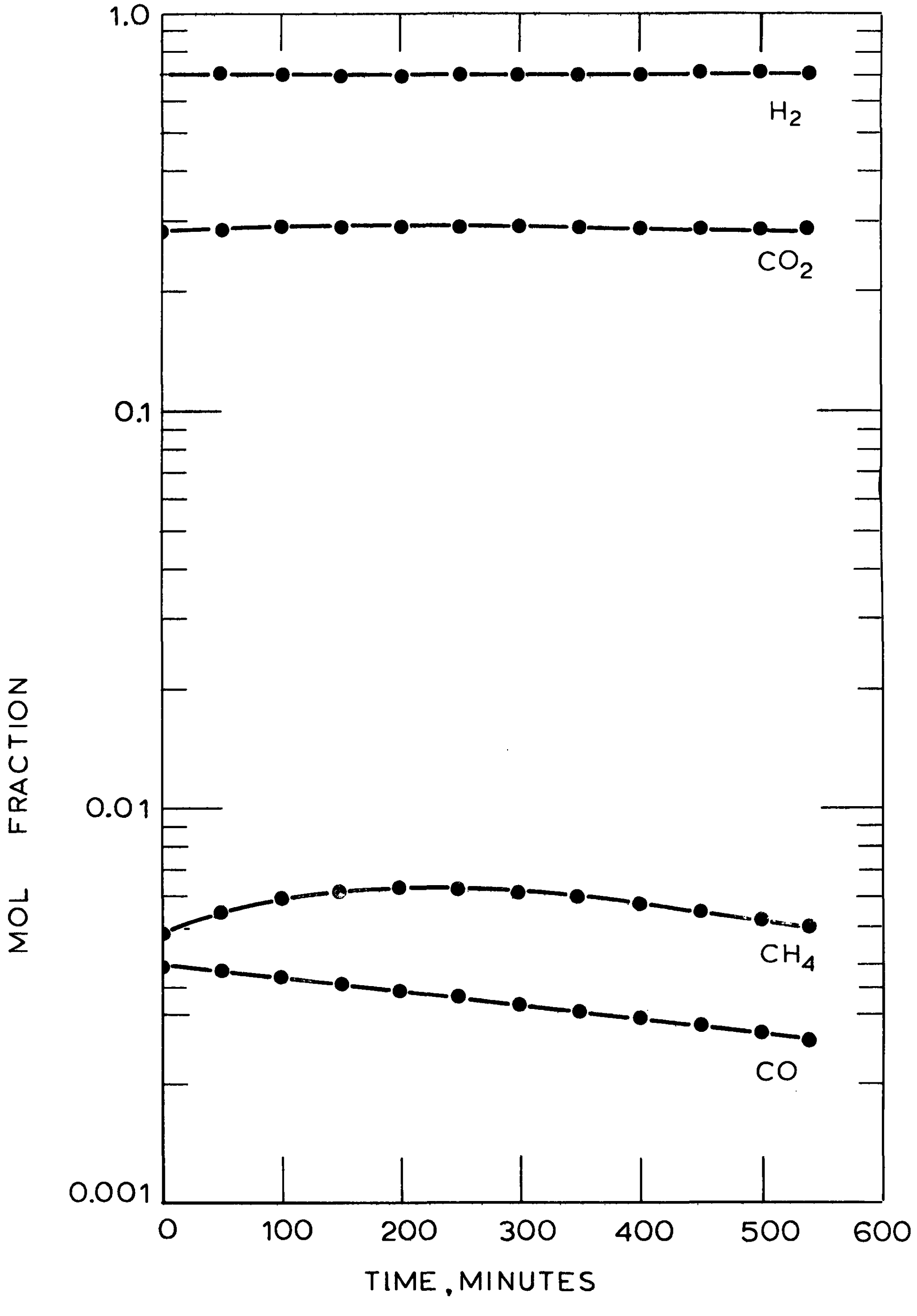


Figure 64 Dry Gas Composition Run G - 13

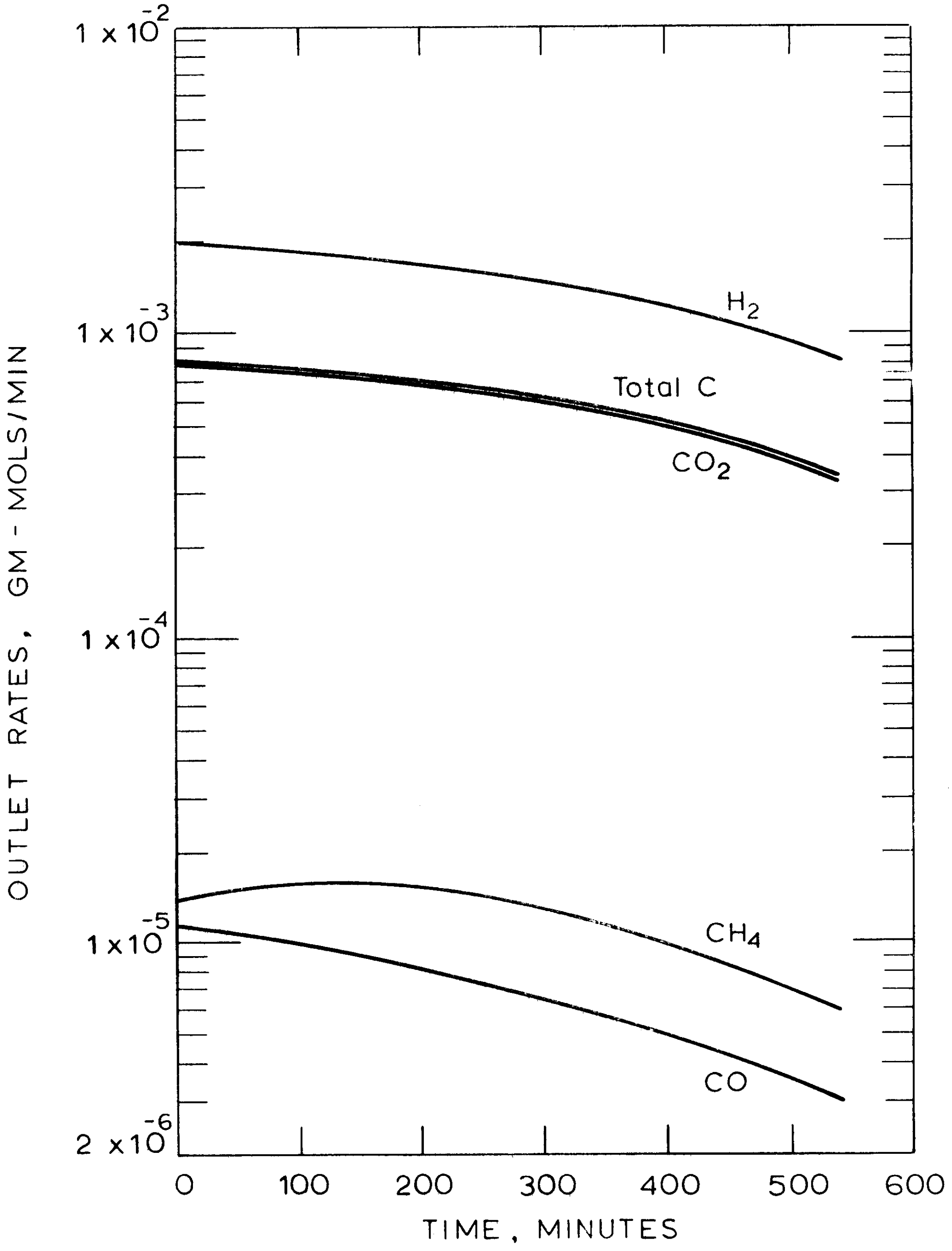


Figure 65 Component Outlet Rates Run G-13

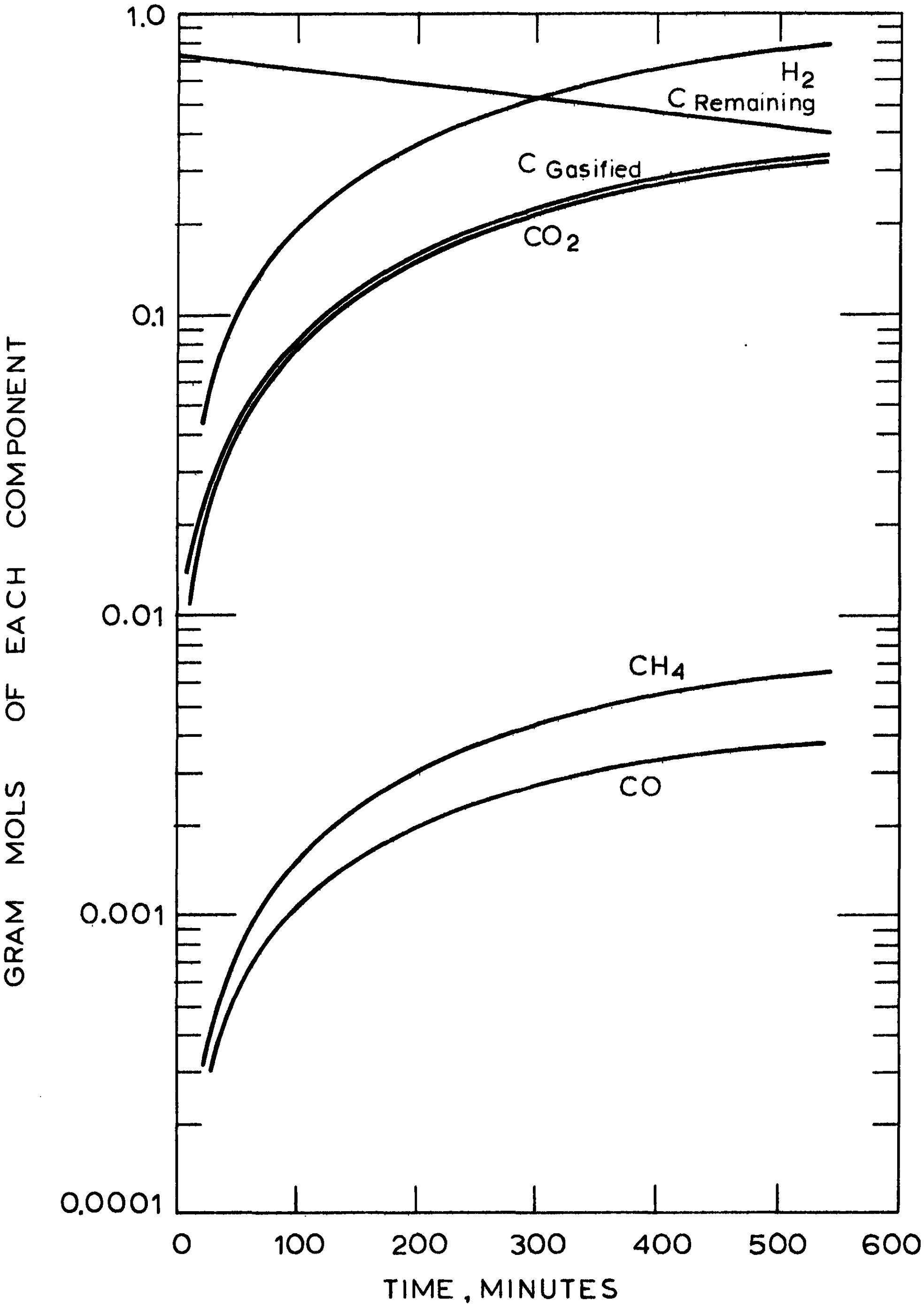


Figure 66 Cumulative Production of Each Component, Carbon Gasified and Carbon Remaining as a Function of Time Run G-13

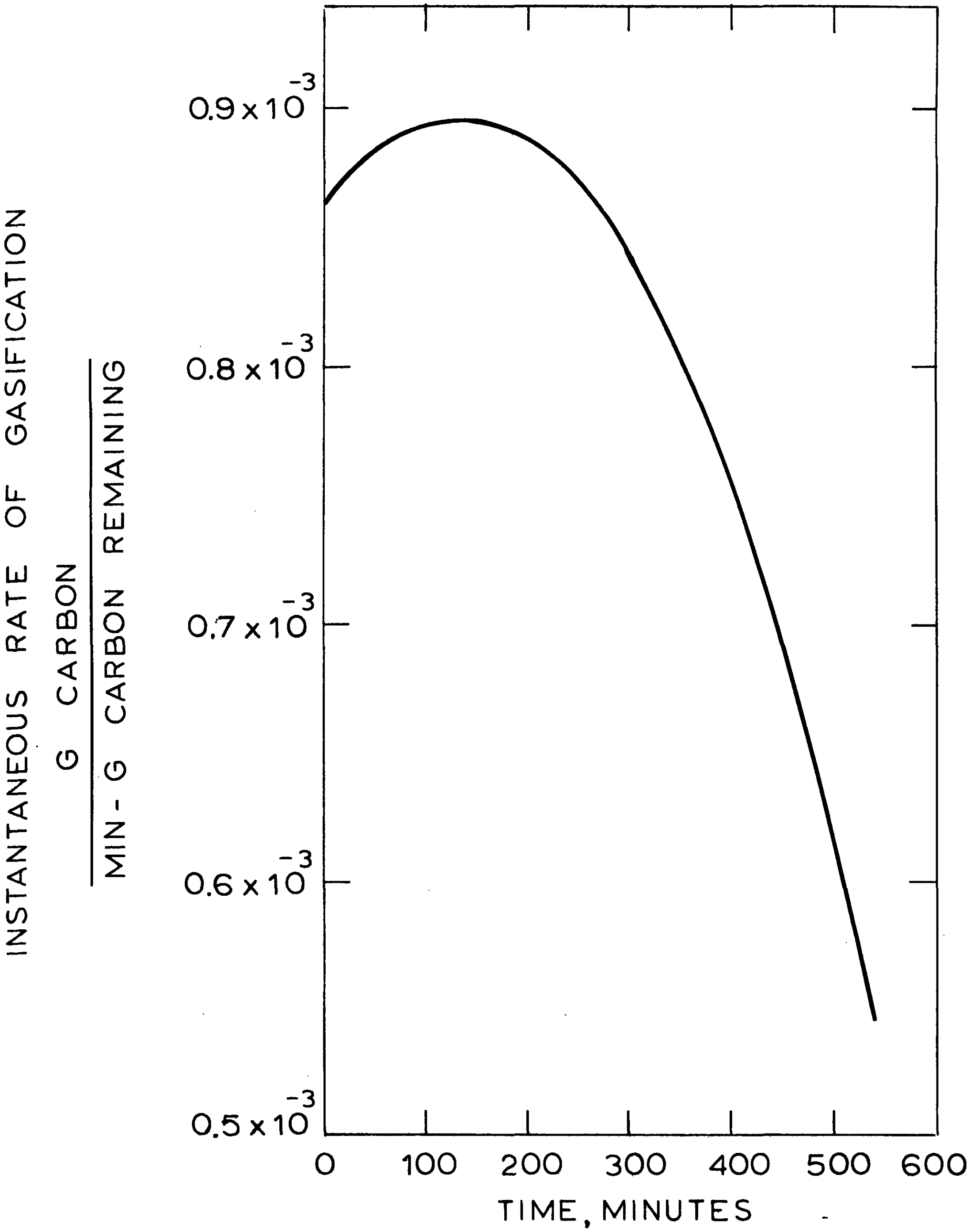


Figure 67 Instantaneos Carbon Gasification Rate vs Time Run G-13

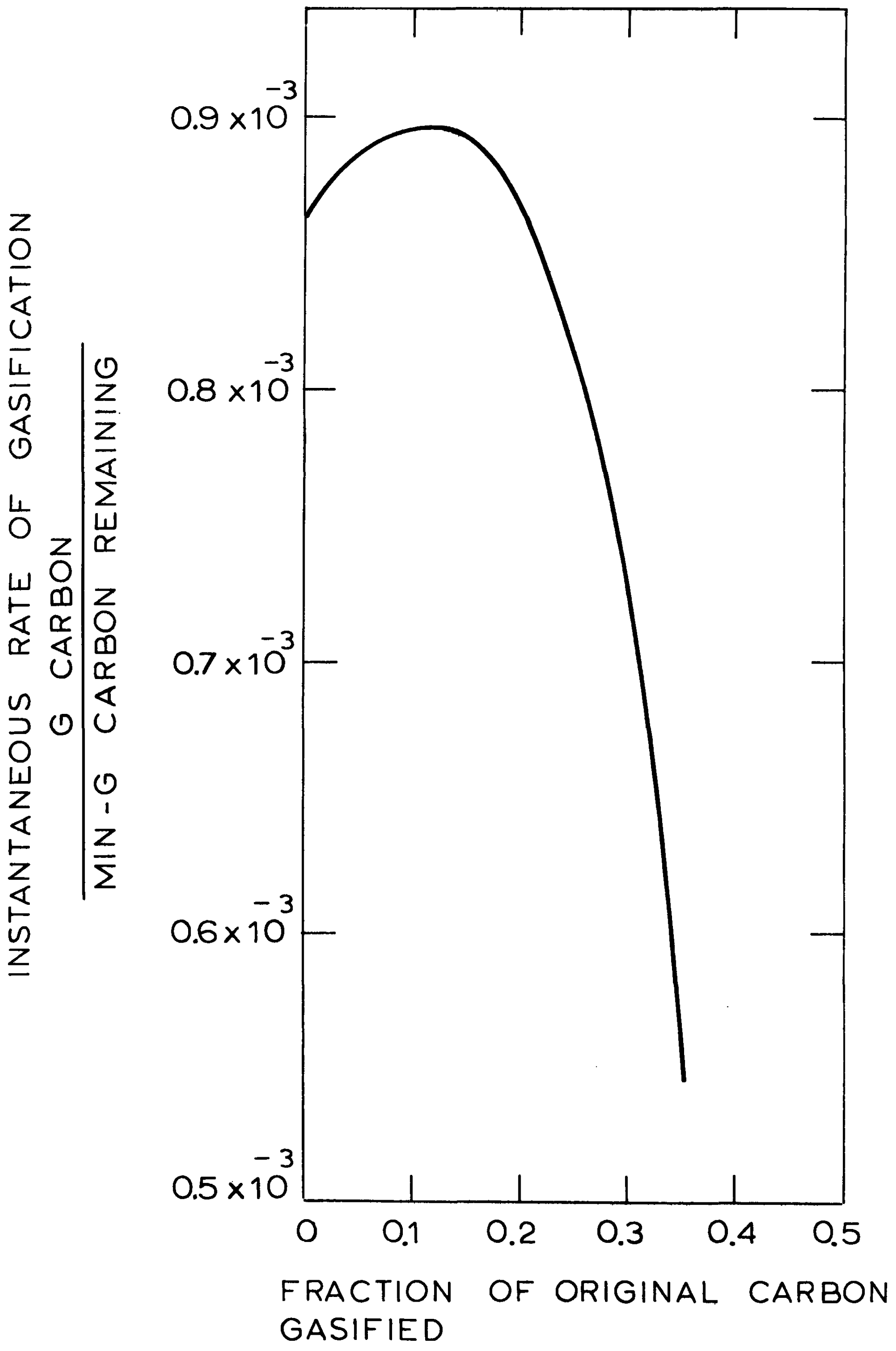


Figure 68 Instantaneous Carbon Gasification Rate vs Fraction of Original Carbon Gasified Run G-13

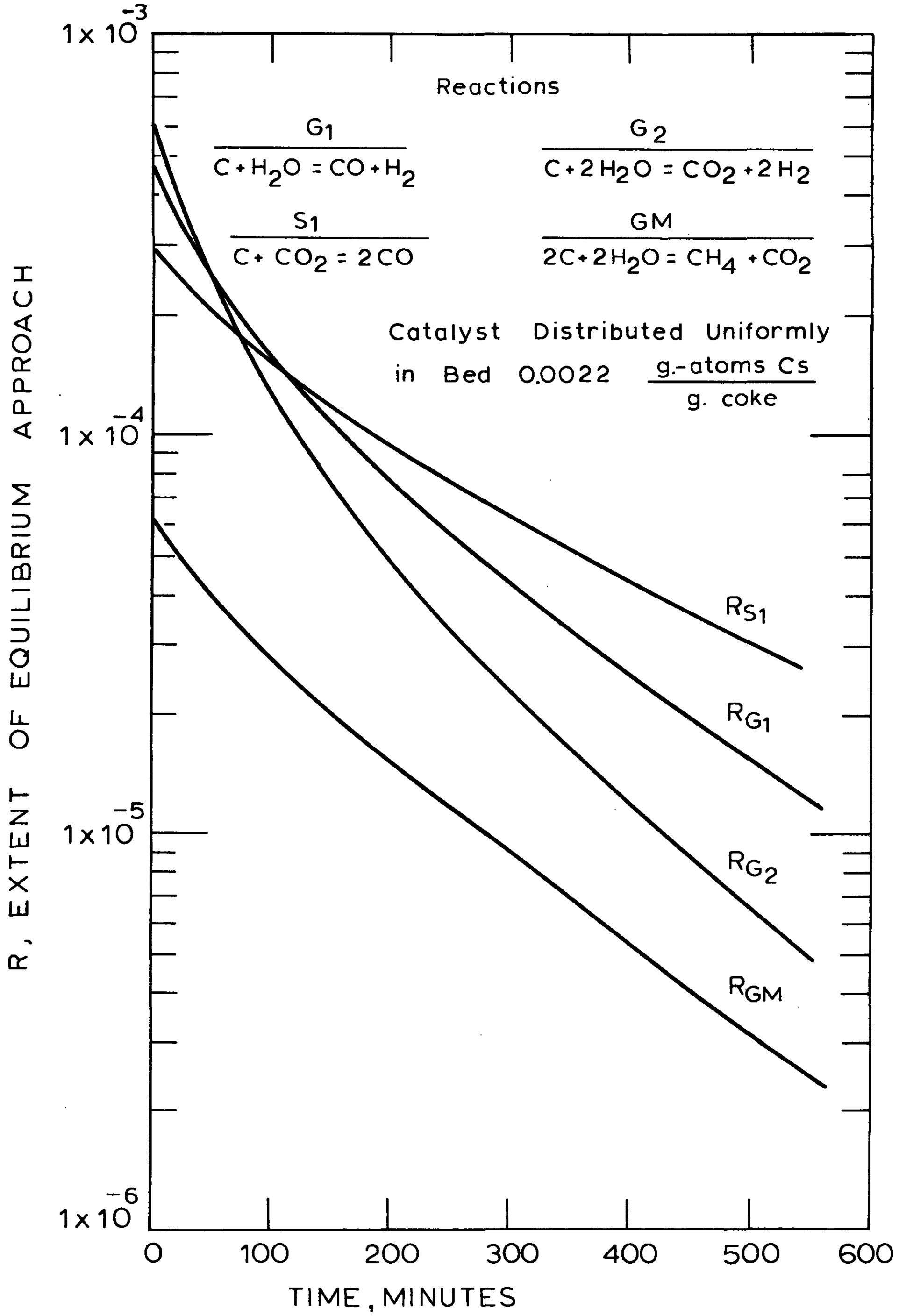


Figure 69 Comparison of Actual and Equilibrium Gas Compositions for Reactions G_1, G_2, S_1 and GM at 1000 °F with Cesium Acetate Catalyst Run G-13

R_{G1}, R_{G2}, R_{S1}, R_{GM} vs Time

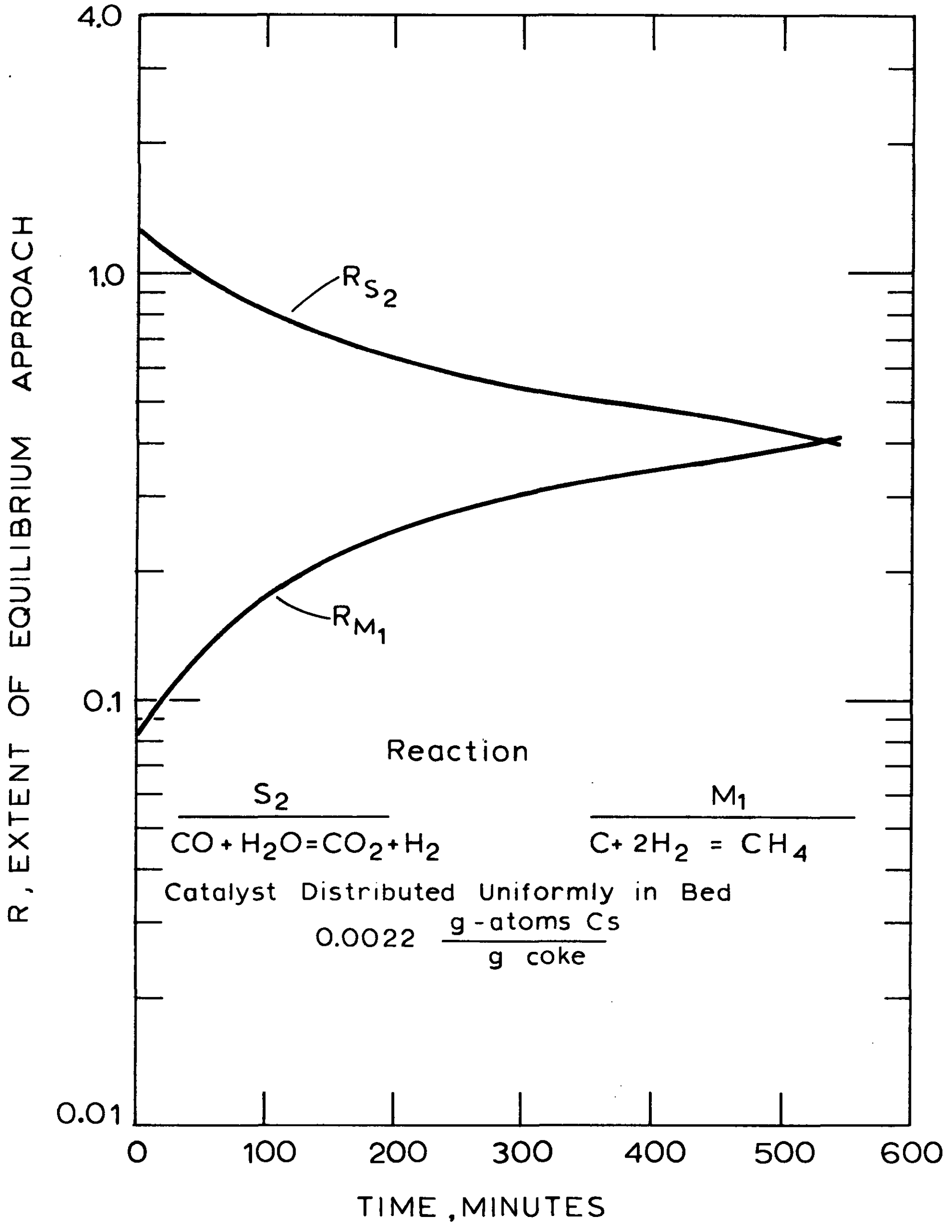


Figure 70 Comparison of Actual and Equilibrium Gas Compositions for Reactions S_2 and M_1 at 1000 °F with Cesium Acetate Catalyst Run G-13 R_{S2} vs Time & R_{M1} vs Time

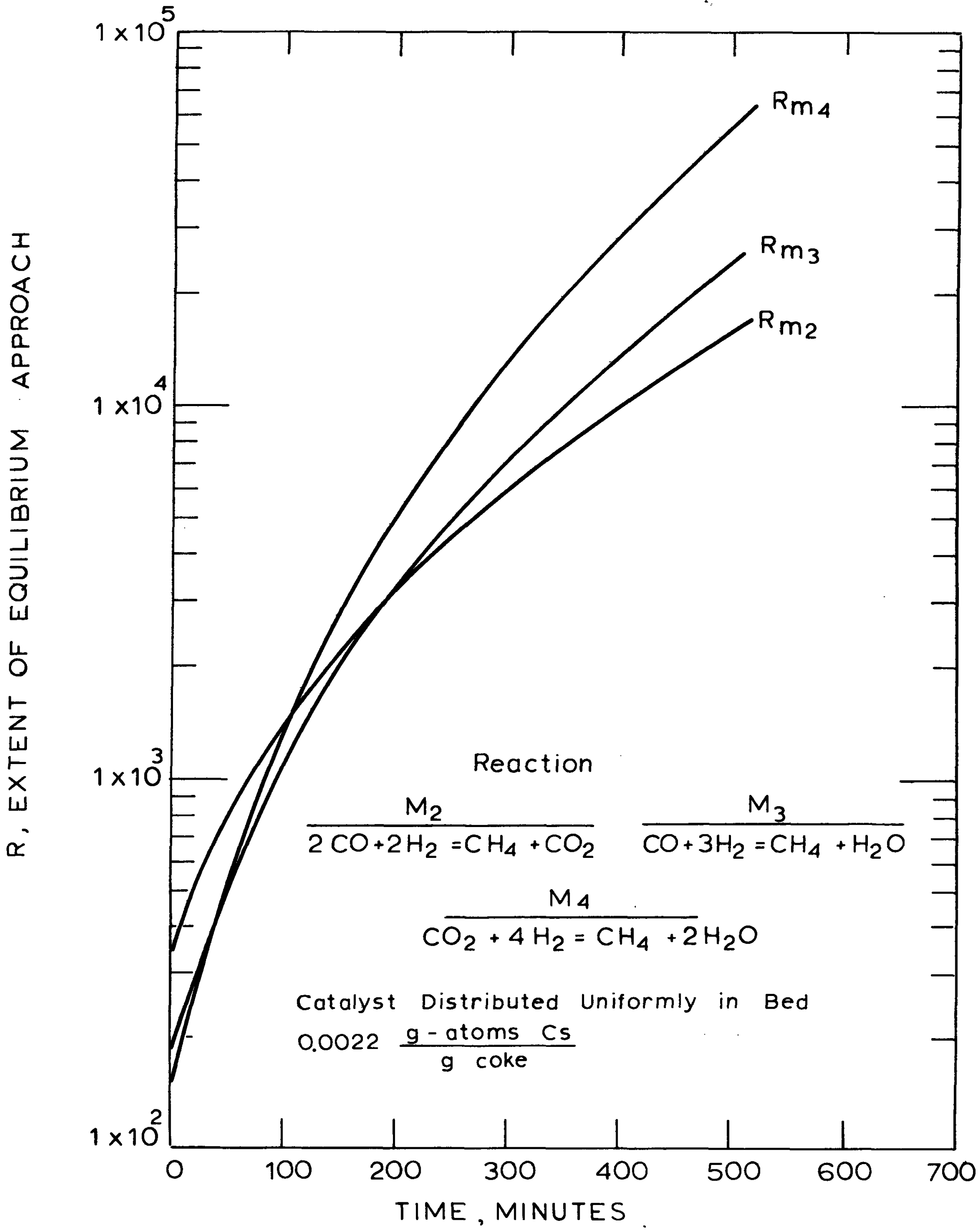


Figure 71 Comparison of Actual and Equilibrium Compositions for Reactions M_2, M_3 and M_4 at 1000 °F with Cesium Acetate Run G-13. R_{M2}, R_{M3}, R_{M4} vs Time

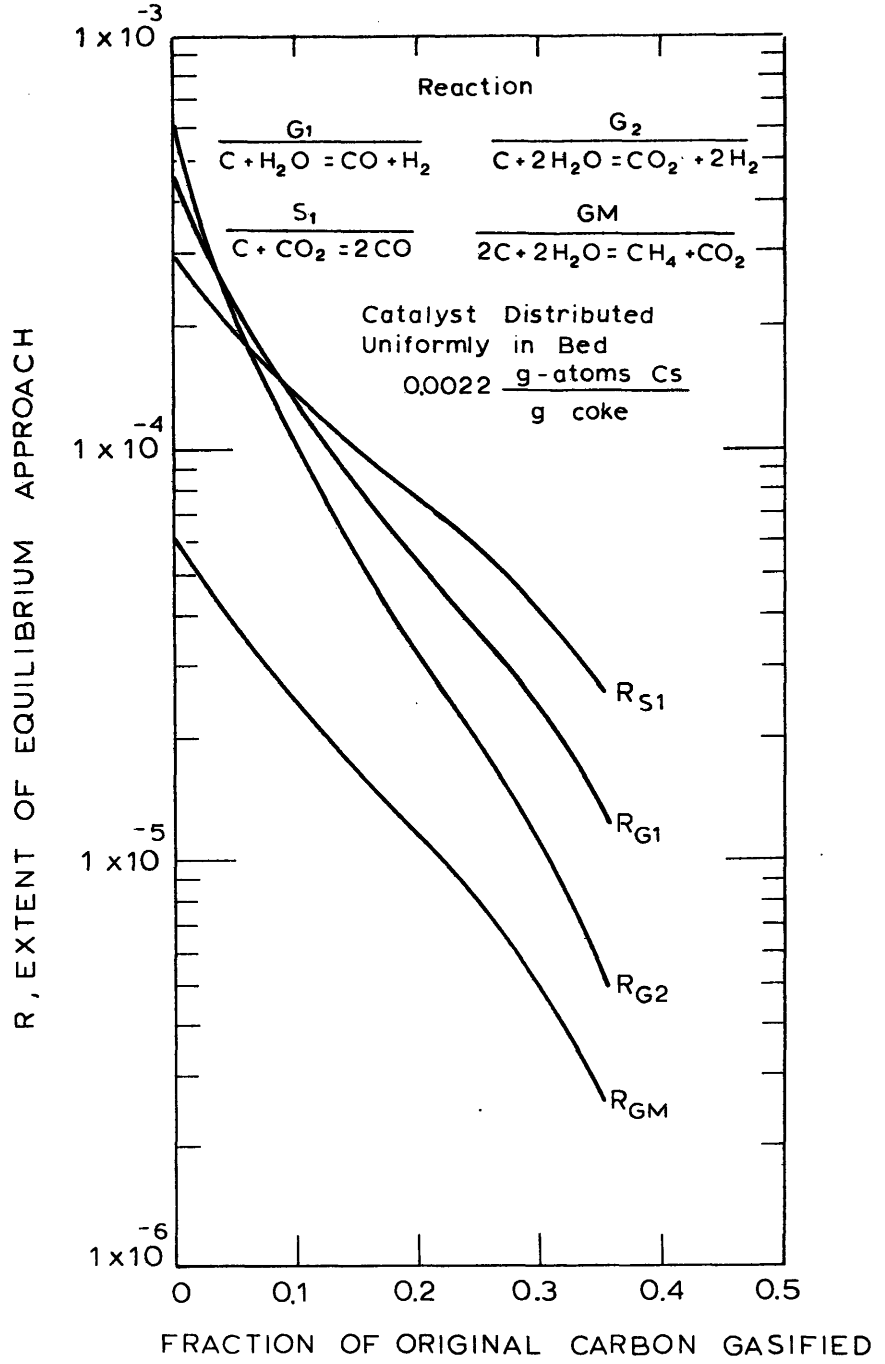


Figure 72 Comparison of Actual and Equilibrium Composition for Reactions G_1, G_2, S_1 and GM at 1000 °F with Cesium Acetate Run G-13 R_{G1}, R_{G2}, R_{S1}, R_{GM} vs FCG

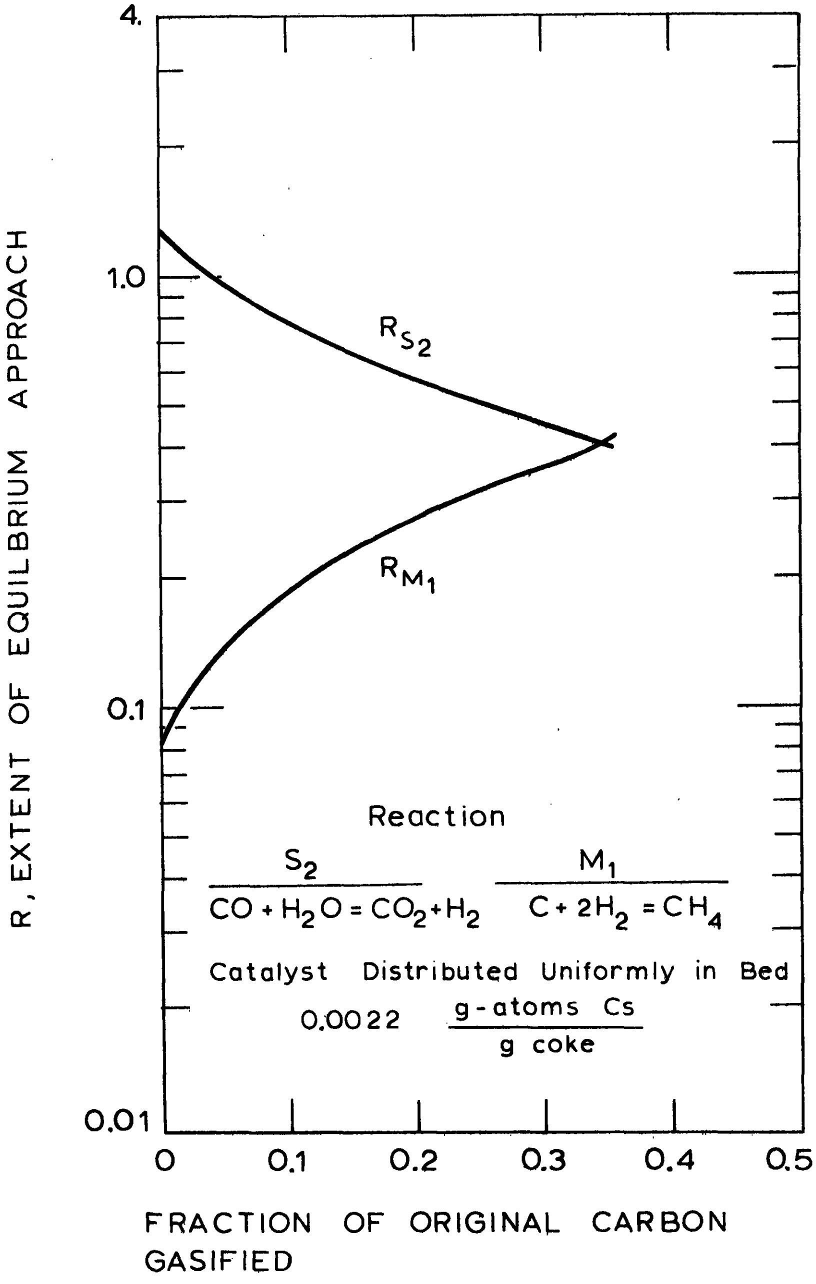


Figure 73 Comparison of Actual and Equilibrium Gas Compositions for Reactions S_2 and M_1 at 1000 °F with Cesium Acetate R_{S_2} vs FCG & R_{M_1} vs FCG

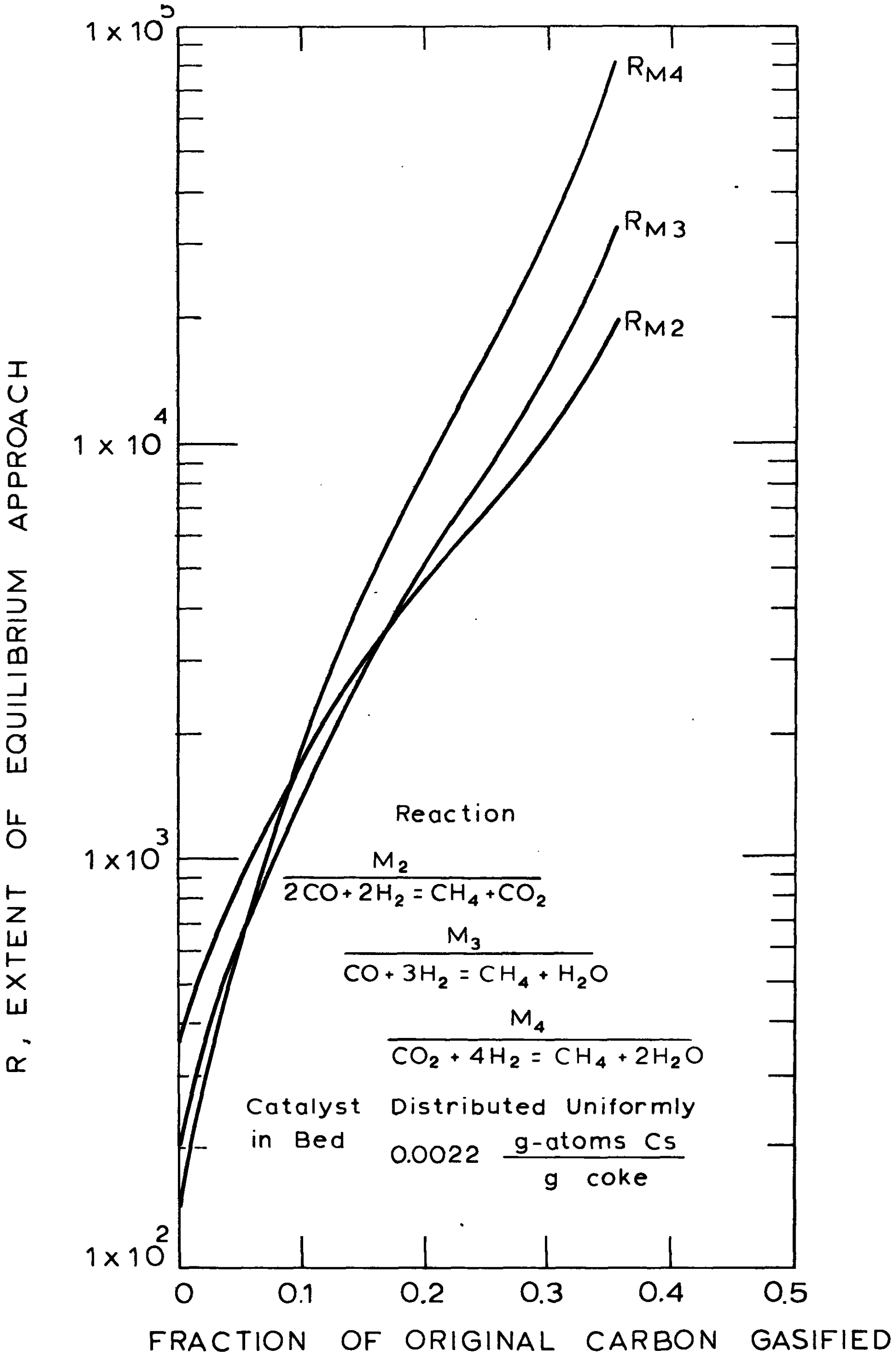


Figure 74 Comparison of Actual and Equilibrium Gas Compositions for Reactions M_2, M_3 and M_4 at 1000 °F with Cesium Acetate Run G-13. R_{M2}, R_{M3}, R_{M4} vs FCG

COMPUTER PROGRAM FOR GASIFICATION DATA ANALYSIS

```
      DIMENSION RICH4(100)
      DIMENSION GV(100),WW(100),GMP(100),WMP(100),
          CO2MF(100),CH4MF(100)
      DIMENSION COMF(100),H2MF(100),CO2M(100),
          CH4M(100),COM(1000)
      DIMENSION CM(100),CG(100),CHECK(100),TGO(100)
          CO2(100),CH4(100)
      DIMENSION H2(100),H2)(100),HC(100),HO(100)
          WCON(100),RG1(100)
      DIMENSION RS1(100),RS2(100),RM1(100),RM2(100),
          RM3(100),RM4(100)
      DIMENSION CH4C(100),COC(100),H2C(100),CHC(100),
          CR(100),RI(100)
      DIMENSION NTIM(100)
      DIMENSION H2M(100),CO(100),RG2(100),CO2C(100),
          FCG(100)
      DIMENSION CGC(100)
      DIMENSION RM5(100),H2CO2(100)
      DO 30 K=1,12
      READ(5,99) NRUN
 99   FORMAT(1X,I2)
      READ(5,100) NT
  100 FORMAT(1X,I3)
      READ(5,200) Q,CZRO
  200 FORMAT(1X,E13.3,E13.3)
      READ(5,300) G1,G2,G3,G4
  300 FORMAT(1X,4E13.3)
      READ(5,300) W1,W2,W3,W4
      READ(5,300) CO2MF1,CO2MF2,CO2MF3,CO2MF4
      READ(5,300) CH4MF1,CH4MF2,CH4MF3,CH4MF4
      READ(5,300) COMF1,COMF2,COMF3,COMF4
      READ(5,300) H2MF1,H2MF2,H2MF3,H2MF4
      DT=10
      NI=(NT/10)+1
      T =-10
      CO 10 I=1,NI
      T = T+DT
      GV(I)=G1+G2*T+G3*T*T+G4*T*T*T
      WW(I)=W1+W2*T+W3*T*T+W4*T*T*T
      GMP(I)=(G2+2.*G3*T+3.*G4*T*T)*Q
      WMP(I)=(W2+2.*W3*T+3.*W4*T*T)/18.016
      NTIM(I)=T
```

```
      CO2MF(I)=CO2MF1+CO2MF2*T+CO2NF3xTxT+CO2NH4*T*T*T
      CH NF(I)=CH4MF1+CH4MF2*T+CH4MF3*TxT+CH4MF4*T*T*T
      COMF(I)=COMF1+COMF2*T+COMF3*T*T+COMF4*T*T*T
      H2MF(I)=H MF1+H2MF2xT+ H2MF 3*T*T+H2MF4*TxT*T
      CO2M(I)=CO2MF(I)*GMP(I)
      CH4M(I)=CH4MF(I)*GMP(I)
      COM(I)=COMF(I)*GMP(I)
      H2M(I)=H2MF(I)*GMP(I)
      CM(I)=CO2M(I)+CH4M(I)+COM(I)
      CG(I)=CM(I)*12.01
      CHECK(I)=CM(I)+H2M(I)
      TGO(I)=GMP(I)+WMP(I)
      CO2(I)=CO2M(I)/TGO(I)
      CH4(I)=CH4M(I)/TGO(I)
      CO(I)=COM(I)/TGO(I)
      H2(I)=H2M(I)/TGO(I)
      H2O(I)=WMP(I)/TGO(I)
      HC(I)=(2.*H2(I)+4.*CH4(I))/(CO2(I)+CO(I)+CH4(I)
      HO(I)=(2.*H2(I)+4.*CH (I))/(2.*CO2(I)+CO(I)
      WCON(I)=100.*((2.xCO2M(I)+COM(I))/
                (WMP(I)+2.xCO2M(I)+COM(I)))
      H2CO2(I)=H2(I)/CO2(I)
      RG1(I)=(CO(I)xH2(I))/(H2O(I)*.0653)
      RG2(I)=(CO2(I)*(H2(I)**2.))/((H2O(I)**2.)*.2768)
      RS1(I)=(CO(I)**2.)/(CO2(I) * .0189)
      RS2(I)=(CO2(I)*H2(I))/(CO(I)*H2O(I) 4.26)
      RM1(I)=CH4(I)/(H2(I)**2.)1.187)
      RM2(I)=(CH4(I)*CO2(I))/(((CO(I)*H2(I))**2.)*51.2)
      RM3(I)=(CH4(I)*H2O(I))/(CO(I)*(H2(I)**3.)*18.32)
      RM4(I)=(CH4(I)*(H2O(I)**2.))/(CO2(I)*(H2(I)**4.)
                x4.34)
      RM5(I)=(CH4(I)*CO2(I))/((H2O(I)xx2.)x0.253)
   10 CONTINUE
      CALL QSR(DT,CO2M,CO2C,NI)
      CALL QSR(DT,CH4M,CH4C,NI)
      CALL QSR(DT,COM,COC,NI)
      CALL QSR(DT,H2M,H2C,NI)
      CALL QSF(DT,CM,CMC,NI)
      T=-10.
      DO 20 I=1,NI
      T=T+DT
      CGC(I)=CMC(I) 12.01
      CR(I)=CZRO-CMC(I)x12.01
```

```
       RI(I)=CG(I)/CR(I)
       FCG(I)=CMC(I)*12.01/CZRO
       RICH4(I)=CH4M(I)*12.01/CR(I)
 20    CONTINUE
 550   WRITE(6,550) NRUN
 550   FORMAT(1X,'RUN NUMBER 'I2///)
       WRITE(6,2)
 2     FORMAT('0'//'OTIME     RICH4'///)
       WRITE(6,1) (NHIM(I),RICH4(I), I=1,NI)
 1     FORMAT(1X,I3,2X,E13.3)
       WRITE(6,851)
 851   FORMAT('1')
 30    CONTINUE
       CALL EXIT
       END
       SUBROUTINE QSF(H,Y,Z,NDIM)
       DIMENSION Y(100),Z(100)
       HT=.3333333*H
       IF(NDIM-5) 7,8,1
 1     SUM1=Y(2)+Y(2)
       SUM1=SUM1+SUM1
       SUM1=HT*(Y(1)+SUM1+Y(3)
       AUX1=Y(4)+Y(4)
       AUX1=AUX1+AUX1
       AUX1=SUM1+HT (Y(3)+AUX1+Y(5)
       AUX2=HT*(Y(1)+3.875*(Y(2)+Y(5))+2.625*
                (Y(3)+Y(4))+Y(6)
       SUM2=Y(5)+Y(5)
       SUM2=SUM2+SUM2
       SUM2=AUX2-HT*(Y(4)+SUM2+Y(6))
       Z(1)=0.0
       AUX=Y(3)+Y(3)
       AUX=AUX+AUX
       Z(2)=SUM2-HT*(Y(2)+AUX+Y(4))
       Z(3)=SUM1
       Z(4)=SUM2
       IF(NDIM-6) 5,5,2
 2     DO 4 I=7,NDIM,2
       SUM1=AUX1
       SUM2=AUX2
       AUX1=Y(I-1)+Y(I-1)
       AUX1=AUX1+AUX1
       AUX1=SUM1+HT*(Y(I-2)+AUX1+Y(I))
       Z(I-2)=SUM1
```

```
      IF(I-NDIM)  3,6,6
    3 AUX2=Y(I)+Y(I)
      AUX2=AUX2+AUX2
      AUX2=SUM2+HT*(Y(I-1)+AUX2+Y(I+1))
    4 Z(I-1)=SUM2
    5 Z(NDIM-1)=AUX1
      Z(NDIM)=AUX2
      RETURN
    6 Z(NDIM-1)=SUM2
      Z(NDIM)=AUX1
      RETURN
    7 IF(NDIM-3) 12,11,8
    8 SUM2=1.125*HT*(Y(1)+3.*Y(2)+3.*Y(3)+Y(4))
      SUM1=Y(2)+Y(2)
      SUM1=SUM1+SUM1
      SUM1=HT*(Y(1)+SUM1+Y(3))
      Z(1)=0.
      AUX1=Y(3)+Y(3)
      AUX1=AUX1+AUX1
      Z(2)=SUM2-HT*(Y(2)+AUX1+Y(4))
      IF(NDIM-5) 10,9,9
    9 AUX1=Y(4)+Y(4)
      AUX1=AUX1+AUX1
      Z(5)=SUM1+HT*(Y(3)+AUX1+Y(5))
   10 Z(3)=SUM1
      Z(4)=SUM2
      RETURN
   11 SUM1=HT*(1.25*Y(1)+Y(2)+Y( )2-.25*Y(3))
      SUM2=Y(2)+Y(2)
      SUM2=SUM2+SUM2
      Z(3)=HT*(Y(1)+SUM2+Y(3))
      Z(1)=0.
      Z(2)=SUM1
   12 RETURN
      END
```

APPENDIX IV

PHYSICAL PROPERTIES AND SOURCES OF CHEMICALS USED

A. CHEMICALS USED IN COAL LIQUEFACTION EXPERIMENTS

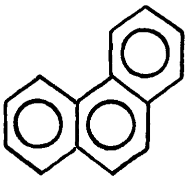
1. Physico-Chemical Constants(1)

Compound & Formula		Molecular Weight	Melting Point	Boiling Point	Critical Temperature
			(°C)	(°C)	(°C)
Water	H_2O	18.01	0	100	374
Phenanthrene	$C_{14}H_{10}$	178.23	100.5	340	611(2)
cis-Decalin	$C_{10}H_{18}$	138.25	-43	195.7	429
trans-Decalin	$C_{10}H_{18}$	138.25	-30	187.3	414
Tetralin	$C_{10}H_{12}$	132.21	-35.8	207	442(2)

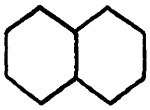
(1) See Fig. 75 for vapor pressure vs. temperature plots.

(2) Calculated by Modified Guldberg Rule, Lydersen's Method.

2. Structural Formulas

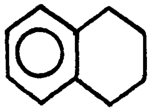


Phenanthrene



Decahydronaphthalene

"Decalin"



Tetrahydronaphthalene

"Tetralin"

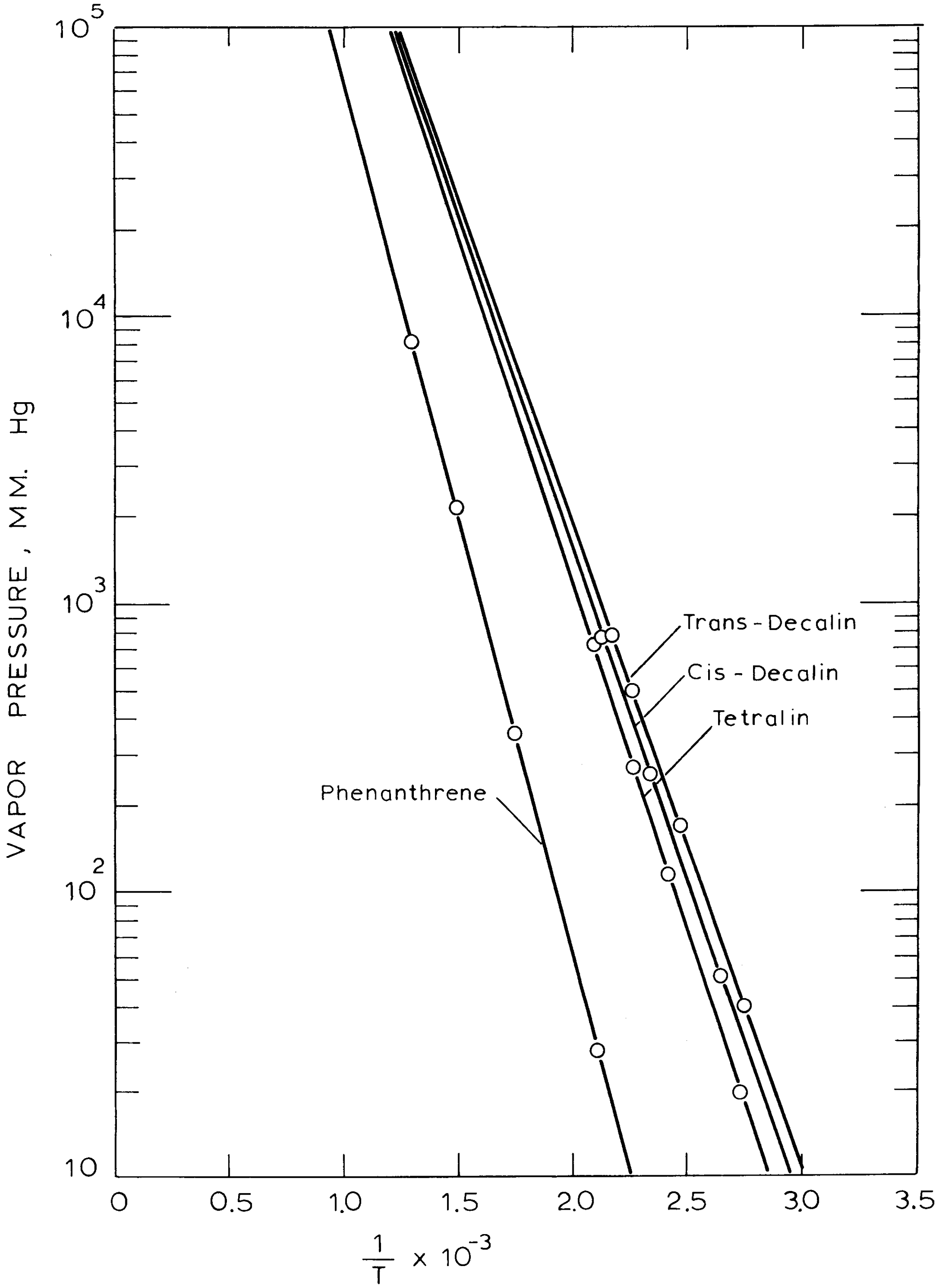


Figure 75 Vapor Pressures of Phenanthrene, Cis- and Trans Decalin, and Tetralin

3. Description of Chemicals Used In Liquefaction Studies

Compound or Substance	Description
Phenanthrene	Technical grade, T599 Eastman Organic Chemicals Distillation Products Industries Rochester, New York
Decalin	$n_D^{20} = 1.4756$, D25 Aldrich Chemical Co., Inc. Milwaukee, Wisconsin
Tetralin	Practical grade, P550 Eastman Organic Chemicals Distillation Products Industries Rochester, New York
Coal	See Section III-B for description and source of coal used.
Water	Deionized
Benzene	Reagent grade, b.p. 80.1°C

The catalysts used in the liquefaction studies are listed in Table XXXIII.

TABLE XXXIII

CATALYSTS USED IN LIQUEFACTION STUDIES

Name Used in Text	Function(s)	Description
Cobalt Thoria on Kieselguhr	Fischer-Tropsch Synthesis	32% Cobalt present as cobalt oxide and 6% thorium oxide on kieselguhr Surface area = 21 m^2/q Pore volume = 0.36 cc/g Harshaw CO-0202 T 1/8"
Chromia-Alumina	Dehydrogenation	5% Cr_2O_3 on activated alumina Surface area = 160 m^2/g Pore volume = 0.36 cc/g Harshaw Cr-0104 T 1/8"
Alumina	Hydration Dehydration	Alcoa F-110
Iron Oxide	Dehydrogenation	Girdler G-64
Chromium-promoted iron oxide	Water-Gas Shift Reaction	Girdler G-3A
Cobalt on Kieselguhr	Hydrogenation	Girdler G-61RS
Nickel Tungsten on Silica-Alumina	Hydrocracking Hydrogenation Removal of S, N	6% Nickel and 19% tungsten on silica alumina Surface area = 152 m^2/g Pore volume = 0.37 cc/g Harshaw Ni-4301
Nickel Tungsten on Alumina	Hydrogenation Removal of S, N	6% Nickel and 19% tungsten on alumina Surface area = 152 m^2/g Pore volume = 0.54 cc/g Harshaw Ni-4303
Nickel Tungsten on Acidified Alumina	Hydrogenation Removal of S, N Mild Cracking	4.5% Nickel and 9.5% tungsten on alumina Surface area = 184 m^2/g Pore volume = 0.53 cc/g Harshaw Ni-4309 (4305)

TABLE XXXIII (Cont'd)

Name Used in Text	Function(s)	Description
Chromia-Alumina	Dehydrogenation	Davison SMR-55-10222
Cobalt Molybdate on Alumina	Removal of S,N,O Dehydrogenation under hydrogen pressure	American Cyanamid HDS-6A
Silica-Alumina	Cracking	92% Alumina 6% Silica Surface area = 210-240 m ^{2}/g Harshaw Al-1605P
Chrome-Aluminum-Phosphate	Dehydrogenation	Girdler T-1122
G-66B	Water-Gas Shift (low temperature)	Girdler G-66B
Tungsten on Alumina	Dehydration	10% Tungsten oxide on high activity alumina Surface area = 145 m ^{2}/g Pore volume = 0.36 cc/g

B. CHEMICALS USED IN GASIFICATION STUDIES

Compound	Description	Source
Potassium Acetate	A.C.S. Reagent Grade	Merck & Co., Inc. Rahway, N.J.
Potassium Carbonate	A.C.S. Reagent Grade	Merck & Co., Inc. Rahway, N.J.
Cesium Hydroxide	--	Penn Rare Metals, Inc. Revere, Pa.
Cesium Acetate	Lot #02079	Alfa Inorganics, Inc. Beverly, Mass.
Cesium Nitrate	Lot #02207	Alfa Inorganics, Inc. Beverly, Mass.

LOCATION OF ORIGINAL DATA

The original data and computer printouts are in the possession of the author at Merck & Co., Inc., Rahway, New Jersey 07065.

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Sklarz, W. A. and Wildman, G. T., "Elimination of H_2S and Metallic Sludge Problems by Replacing Reductive Desulfurization with Selective Oxidation", Environmental Symposium, 75th National Meeting, AIChE, Detroit, Michigan, June 1973.