BITUMINOUS COAL RESEARCH, INC.
SPONSORED RESEARCH PROGRAM

GAS GENERATOR RESEARCH AND DEVELOPMENT
FLUIDIZED-BED GASIFICATION

Progress Report No. 9-A
May 1972
(BCR Report L-471)

I. INTRODUCTION

This report summarizes progress achieved during the month on the program "Fluidized-bed Gasification" which is a part of the general program, "Gas Generator Research and Development," being conducted by Bituminous Coal Research, Inc., for the Office of Coal Research. This represents the ninth report of progress under Contract No. 14-32-0001-1207.

During the period covered by this report, work continued on char reactivity, using the small batch fluidized-bed reactor.

Evaluation of design engineering proposals for the revised fluidized-bed PEDU is proceeding.

Appendix A of this report constitutes a summary of the char reactivity study that has been conducted to date. The summary describes the use of thermo-gravimetric techniques to develop rate equations for the gasification reactions of various chars with steam and carbon dioxide as oxidizers.

A. Fluidized-bed PEDU

The fluidized-bed gasification PEDU was originally designed for experimental work on the gasification of coal chars. The chars to be studied were those produced as by-products from certain coal conversion processes. Design engineering, specifications, and erected-cost estimates for a single-bed unit were completed and were submitted to OCR for review.

Discussions with OCR resulted in the conclusion that the single-bed unit, designed to study char gasification only, would limit the usefulness of the PEDU in the broad support program being conducted. Consequently, OCR requested that a new look be taken at a PEDU concept which would have flexibility to handle coal or char, or a mixture of both, with a variety of oxidants and moderators.

In addition, proposals for design engineering services were invited from several engineering companies, since it was desirable to develop some new engineering input for the revised PEDU concept.

By May 24, proposals were received from Koppers Company, Inc., Blaw-Knox Chemical Plants, Inc., and Matrix Engineering. A fourth company, Foster Wheeler Corp., requested the opportunity to bid the job. We were advised by

OCR that we could permit Foster Wheeler to submit a proposal as long as it did not cause undue delay in our selection of a successful bid. It was agreed, therefore, to honor the proposal if it were submitted by May 31, 1972.

Recommendations will be submitted to OCR shortly following receipt of the fourth proposal.

B. Laboratory Investigations

The laboratory work this month centered on tests made in the fluidized-bed batch reactor. FMC char was gasified with a mixture of oxygen and carbon dioxide at a temperature of approximately 1120 C.

1. Char Reactivity Studies: A summary of the char reactivity work to date is given in Appendix A. The study of the reaction of HYGAS char with steam is nearing completion and should be reported next month.

2. Fluidized-bed Gasification Batch Reactor: The fluidized-bed batch reactor, which was described in Progress Report No. 6, has been used successfully to demonstrate the significance of the TGA-derived rate equations in the design of a fluidized-bed reactor. The reactor is now being used to study the combined effect of oxygen-carbon dioxide gasification.

Using a 20 gram charge of char, oxygen was fed to the reactor at the rate of 400 scc/min and carbon dioxide at 1000 scc/min. Because of delays in obtaining chromatographic gas analyses, no material balances are yet available. Tentative kinetic data have been collected and are shown in Figure 1 as a plot of weight-loss versus time. This gives a gasification rate of 0.6 gram carbon/min which is independent of the carbon inventory in the reactor. These data will be examined more completely during the next report period.

Mechanical failures were encountered early in the month when the distribution plates, which were made of 304 stainless steel, would burn out after less than a half hour of operation. These were replaced with plates of 316 stainless steel, and they show no signs of failure after five hours of operation.

C. Future Work

Reactivity studies will continue.

Following receipt of all proposals for the fluidized-bed PEDU design engineering, they will be evaluated and our recommendations will be submitted to OCR for approval.

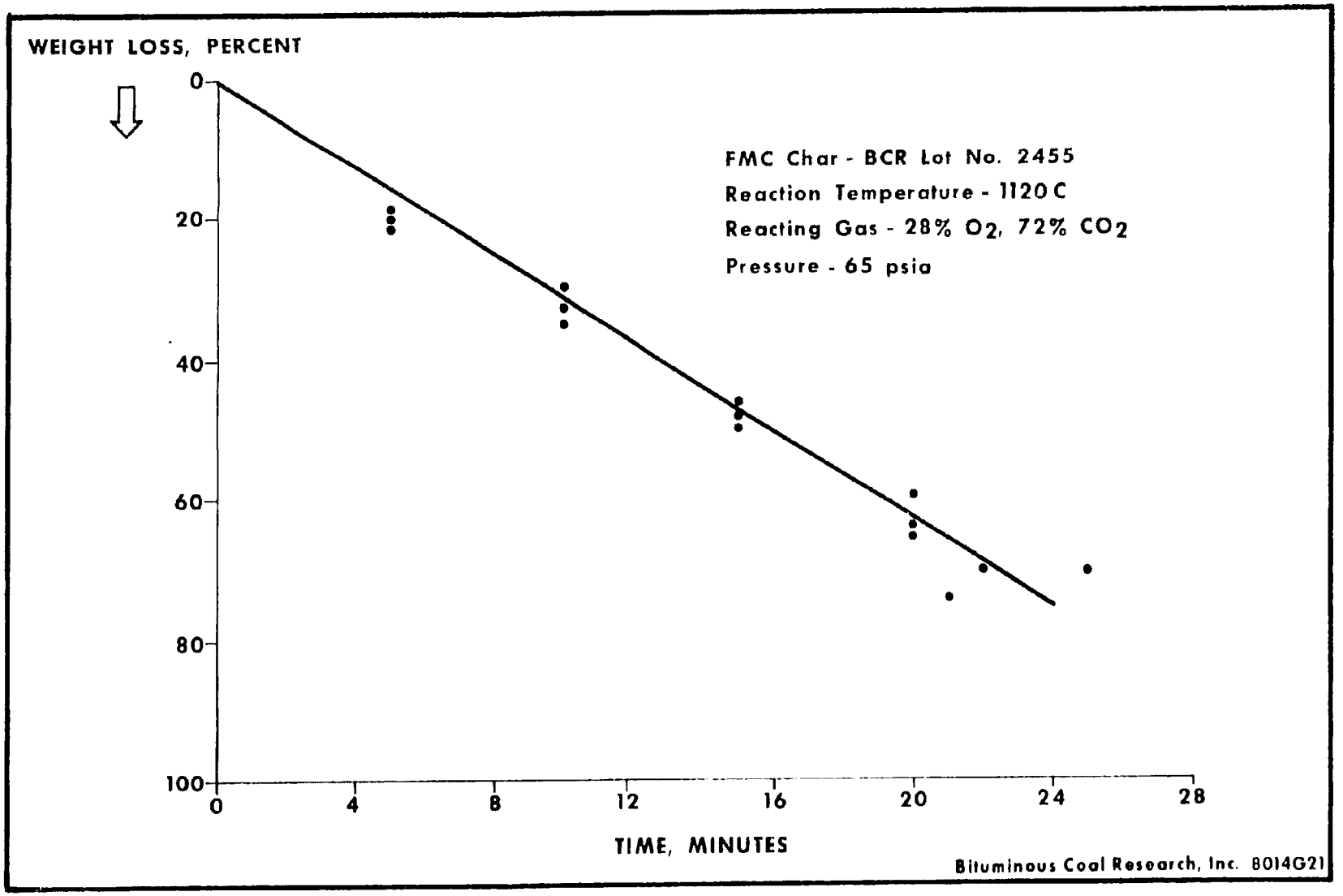

Figure 1. Rate Data Obtained from the Gasification of FMC Char with Oxygen and Carbon Dioxide in a Fluidized-bed Batch Reactor

APPENDIX A

CHAR REACTIVITY STUDY

I. SUMMARY

Rate equations for five different chars have been determined for the char/steam reaction as well as for two chars for the char/carbon dioxide reaction using thermo-gravimetric techniques. The effects of particle size, temperature, and reacting gas concentration are reported.

The reaction was found to proceed uniformly throughout the particle. This is demonstrated by photomicrograph and screen analysis evidence indicating that the particles do not shrink during reaction; i.e., the particle diameter remains constant and the density decreases in proportion to carbon burn-off. In addition, the experimental kinetic data show the reaction rate to be independent of particle diameter.

The complete rate equation is of the form:

$$(1-x) = Ash + (1 - Ash)\, e^{-k\,(C)^n t}$$

and

$$k = a\, e^{-E/RT}$$

where

x = fraction of char reacted

T = temperature in ° Kelvin

C = concentration of reacting gas

t = time in minutes

k = apparent reactivity $\left(\frac{\text{lb C reacted}}{\text{lb C inventory min}}\right)$

Ash = weight percent of ash in unreacted char

E = activation energy, cal/mole

R = gas constant = 1.98 cak/mole/°K

n = order of reaction with respect to gas concentration

Reported activation energies are of the order of 40 kcal/mole. Both the char/steam and char/carbon dioxide reactions are found to be approximately half-order with respect to reacting gas concentration.

II. INTRODUCTION

The fluidized-bed studies for producing industrial gases were initiated in anticipation of the need for a method of utilizing char that might be available as a by-product from coal conversion systems producing liquid fuels or pipeline

gas as primary products. Because of some of the basic characteristics of fluidized-bed reactors, among which are extended solids residence time, intimate gas-solids contact, and uniformity of temperature, fluidized-bed gasification of the above chars can help bring about complete utilization of the carbon in the process feed coals.

The first priority of the fluidized-bed gasification program was subsequently changed, with the goal being the development of a multiple bed system that could start with coal and produce fuel gas. The need for char reactivity studies remained the same, however, in order to understand the kinetic behavior of the devolatilized coal, or "char," following the first step in a multiple bed gasification scheme.

End use of the gasification product dictates the operating conditions as well as the gasifying medium. Thus, gasification with air and steam will yield a low-Btu fuel gas; gasification with oxygen and steam can yield a higher-Btu gas containing a greater ratio of combustible components; and gasification with carbon dioxide can yield a carbon monoxide-rich gas that could conceivably serve as a fuel for power generation by MHD.

The overall objective of this study is to develop sufficient data to permit the design of a process equipment development unit, PEDU, which will ultimately lead to the design, erection, and operation of a pilot fluidized-bed gasifier. Rate equations for the various char gasification reactions are among the first bits of information needed for the PEDU design.

The literature abounds with information regarding carbon/steam and carbon/carbon dioxide reactions, but there is little agreement among the results of different investigators. For example, reported activation energies for the carbon/carbon dioxide reaction range from 25 to 90 kcal/mole. This wide variance may be attributed to the different types and ranks of carbon used, the different temperature and pressure ranges investigated, the different particle size distributions, and the various simplifications and interpretations of the observed data. Many investigators allowed the reaction to proceed to only 25 or 30 percent carbon burn-off. In this short time period they found the reaction rate to be approximately constant with time, thus making the simplification that the reaction rate was independent of the mass of carbon left unreacted. It is assumed, however, that most investigators interpreted their data correctly, and that the different results are indicative of the different reaction mechanisms and rate controlling steps that occur under different experimental conditions.

No correlations were found in the literature that could adequately describe the kinetics of the gasification reactions of FMC type char at approximately 1000 C, thus it was necessary to develop rate equations from actual laboratory data.

At the outset of the program, it was decided that thermogravimetric techniques would be used to study char reactivity. Therefore, the experimental program was developed around the use of an American Instrument Company "Thermograv" available for the study.

III. EXPERIMENTAL EQUIPMENT AND PROCEDURE

A. Equipment: Thermogravimetric Balance. A schematic view of the TGA is shown in Figure 2.

B. Operation: Samples are placed in the sample holder, a crucible or flat pan, which is connected to and suspended beneath the transducer coil and a precision spring. This entire assembly is mounted inside a quartz and Pyrex housing. During operation, the sample is located inside the well of the furnace where temperatures are continuously monitored by a chromel-alumel thermocouple.

As the test progresses, changes in sample weight cause an extension or contraction of the spring which changes the positional relationship of the armature and transducer coil. A resulting electrical signal proportional to the change in sample weight is developed, amplified, and fed to the vertical (Y) axis of the recorder. The input to the horizontal (X) axis of the recorder is proportional to time or temperature.

C. Experimental Procedure: A 0.1000 gram sample of char is placed in a flat, shallow crucible and mechanically vibrated to form an evenly distributed thin layer. The crucible is placed in the quartz reaction tube and brought to the chosen reaction temperature in an inert atmosphere. The inert gas stream is turned off and simultaneously the reaction gas stream is turned on. Sample weight loss is then recorded as a function of time. Data precision is checked and maintained within $\pm$0.1 percent weight loss/unit time by duplicating all experimental runs.

IV. MATHEMATICAL MODEL AND REGRESSION ANALYSIS

The purpose of this study is to establish the rate controlling step and thus rate equations for the char/steam and char/carbon dioxide reactions. The effects of temperature, reacting gas concentration, and particle size are to be determined. Mass transfer between the bulk gas phase and the exterior of the char particles is not being investigated; therefore, it was experimentally determined that the reactant gas flow rate is maintained well in the region where overall reaction rate is independent of gas velocity.

The conversion of solids in a heterogeneous gas-solids reaction can follow one of two extremes. At one extreme the diffusion of gaseous reactant into the particle is rapid enough, compared to the chemical reaction rate, that the reaction takes place at the same time and at the same rate everywhere. This is called the continuous reaction model. If diffusion into the particle is slow, the reaction is restricted to a thin shell which moves from the outside of the particle inward. This is the unreacted core model.

The appropriate model may be chosen by determining the time needed for complete conversion of solids of different sizes, as summarized below:

Define t_c as the time needed for complete conversion.

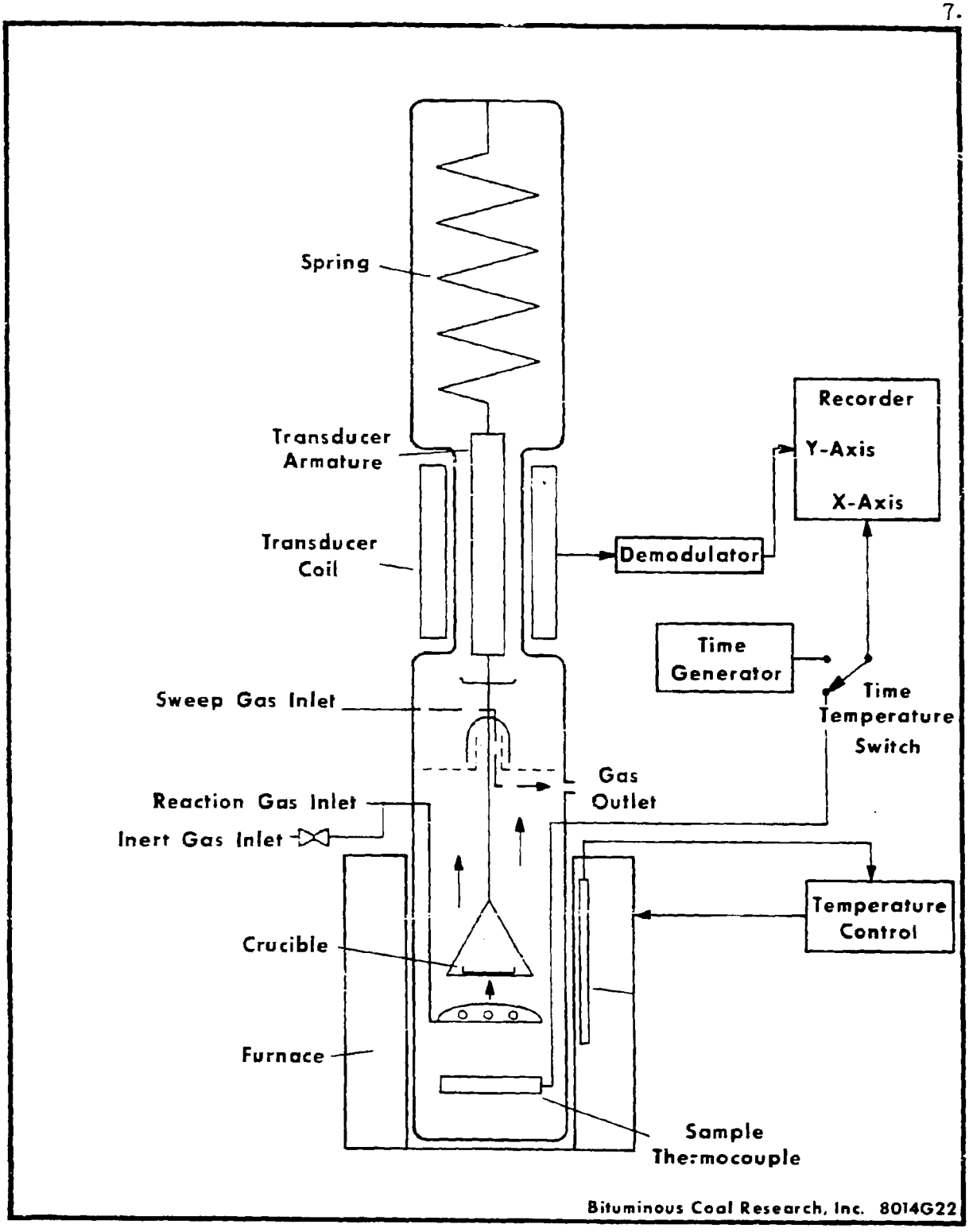

Figure 2. Schematic View of Thermogravimetric Analysis Equipment

This time, t_c is:

1. Independent of particle diameter for the continuous reaction model.

2. Directly proportional to particle diameter for the unreacted core model with chemical reaction at the reaction front as the rate controlling step.

3. Directly proportional to the square of the particle diameter for the unreacted core model with diffusion through the ash layer as the rate controlling step.

Experiments were carried out with particles ranging in size from 70 mesh (210μ) to minus 325 mesh, (44μ). Within the temperature ranges investigated, the reaction rate was independent of particle diameter. Therefore, the continuous reaction model was chosen to develop a rate equation, as follows:

(rate of consumption of carbon) is proportional to (concentration of reacting gas around particles) (amount of carbon left unreacted)

In terms of the fraction of carbon reacted, X, this becomes

$$\frac{dX}{dt} = k\, C^n\, (1 - X) \tag{1}$$

where C^n is the concentration of reacting gas to some power, n.

Rearranging equation (1) gives:

$$\frac{dX}{(1 - X)} = k\, C^n\, dt \tag{2}$$

Integrating equation (2) yields:

$$\ln (1 - X) = -k\, C^n t \quad \text{or} \quad (1 - X) = e^{-k\, C^n t} \tag{3}$$

The proportionality or rate constant, k, may be assumed to vary with temperature in an Arrhenian fashion:

$$k = a\, e^{-\frac{E}{RT}} \tag{4}$$

Combining equations (3) and (4) gives:

$$(1 - X) = e^{-\left(a\, e^{-\frac{E}{RT}}\right) C^n t}$$

Letting X now represent the amount of char reacted, the complete rate equation becomes:

$$(1 - X) = Ash + (1 - Ash)\, e^{-\left(a\, e^{-\frac{E}{RT}}\right) C^n t} \tag{5}$$

where X = fraction of char reacted

T = temperature in °K

C = concentration of reacting gas

t = time in minutes

k = apparent reactivity, $\frac{\text{lb C reacted}}{\text{lb C inventory min}}$

Ash = weight percent of ash in unreacted char

E = activation energy, $\frac{\text{cal}}{\text{mole}}$

R = the gas constant = 1.987 $\frac{\text{cal}}{\text{mole °K}}$

n = the order of reaction with respect to reacting gas

a = the Arrhenius' constant (frequency factor), min^{-1}

The experimental data are in the form of a plot of $(1 - X)$ as a function of t. The constants a, E, and n may then be found from equation (5) when $(1 - X)$, Ash, T, C, and t are known variables. The regression analysis proceeds in two steps. For each value of Ash, C, and T, $(1 - X)$ versus t is solved for the constant M as follows.

$$\text{Let} \qquad M = a\, e^{-\frac{E}{RT}} C^n$$

then $$(1 - X) = Ash + (1 - Ash)\, e^{Mt}$$

and $$\ln \frac{(1 - X - Ash)}{(1 - Ash)} = Mt$$

The square of the error in this equality is:

$$\epsilon = \Sigma \left[\ln \left(\frac{1-X_i-Ash}{1 - Ash}\right) - Mt_i^2\right]^2$$

where ϵ is the error and the subscript i denotes individual data points ϵ is minimized by differentiating and setting it equal to zero

$$\frac{d\epsilon}{dM} = 0 = -2 \Sigma \left[t_i \ln \left(\frac{1-X_i-Ash}{1 - Ash}\right) - Mt_i^2\right]$$

$$0 = \Sigma \left[t_i \ln \left(\frac{1-X_i-Ash}{1 - Ash}\right) - Mt_i^2\right]$$

$$M = \frac{\Sigma\, t_i \ln \left(\frac{1-X_i-Ash}{1 - Ash}\right)}{\Sigma\, t_i^2}$$

$$M = \frac{\Sigma\, t_i \ln (1-X-Ash) - \ln (1 - Ash)\, \Sigma t_i}{\Sigma\, t_i^2}$$

Once M is found from the above equation for each C and T, a multiple linear regression approach may be used to find the constants -E/R, a, and n by solving

$$M = ae^{-E/RT} C^n$$

or

$$\ln M = \ln a - E/RT - n \ln C$$

Again, the partial derivatives of the error function with respect to M, T, and C are set equal to zero and the three resulting equations are solved simultaneously for a, -E/R, and n.

V. EXPERIMENTAL RESULTS

To date, rate equations have been established for two chars, an FMC char and a Consol char, for both the char/steam and the char/carbon dioxide reaction. Table 1 presents the proximate and ultimate analyses for the FMC char, and Table 2 contains the analyses for the Consol char.

A full 6 x 5 x 3 factorial design study was performed for the FMC char/carbon dioxide reaction. A reduced number of tests was performed with the Consol char. The particle diameters ranged in size from 60 x 100 mesh to minus 325 mesh in six increments. Reaction temperatures were 1,000, 1,080, and 1,115 C. Carbon dioxide was diluted with nitrogen to concentrations of 15, 25, 50, 75 and 100 percent carbon dioxide (volume basis).

A series of photomicrographs gave the first physical clues leading to the selection of a reaction model. Figures 3 through 6 show unreacted char, 50 percent reacted char, 80 percent reacted char, and ash. It is immediately apparent that the average particle diameter does not change with increasing carbon burn-off. The particles become increasingly porous, but even the ash residue retains a skeletal structure similar in overall dimension to the unreacted char.

Particle size distribution as a function of attrition in a fluidized-bed as well as a function of carbon burn-off was also investigated. An as-received sample of char was used· the average particle diameter was 210μ, determined by screen analysis. This sample was then reacted to 16 percent carbon burn-off and 40 percent carbon burn-off. Screen analysis after each reaction gave an average particle diameter of 210μ.

The 40 percent reacted char particles were fluidized with air in a 1-inch I.D. glass tube at a superficial velocity of approximately 0.2 feet per sec. Screen analysis after four hours of fluidization showed that the average particle diameter was still 210μ. This is further evidence that the continuous reaction kinetic model is consistent with experimental observations.

Along with these physical observations, the experimental data showed that the time needed for complete reaction was independent of particle diameter. Thus, the continuous reaction model as described in Section IV was chosen to develop the rate equation.

TABLE 1. FMC CHAR USED IN LABORATORY TESTS

Identification: Utah Char; PLU-167 CRD-9746
BCR Lot No. 2455

Chemical Analyses, Percent

Proximate	
Moisture	0.60
Volatile Matter	2.85
Fixed Carbon	88.90
Ash	7.65
Total	100.00
Ultimate, dry basis	
Carbon	88.7
Hydrogen	0.8
Nitrogen	1.3
Oxygen	0.9
Sulfur	0.6
Ash	7.7
Total	100.0

TABLE 2. CONSOL CHAR USED IN LABORATORY TESTS

Identification: Char received from Consolidation Coal Company's Project Gasoline Pilot Plant BCR Lot No. 2469

Chemical Analyses, Percent

Proximate

Moisture	0.38
Volatile Matter	11.55
Fixed Carbon	58.20
Ash	29.87
Total	100.00

Ultimate, dry basis

Carbon	56.10
Hydrogen	1.92
Nitrogen	1.16
Oxygen	1.43
Sulfur	9.39
Ash	30.00
Total	100.00

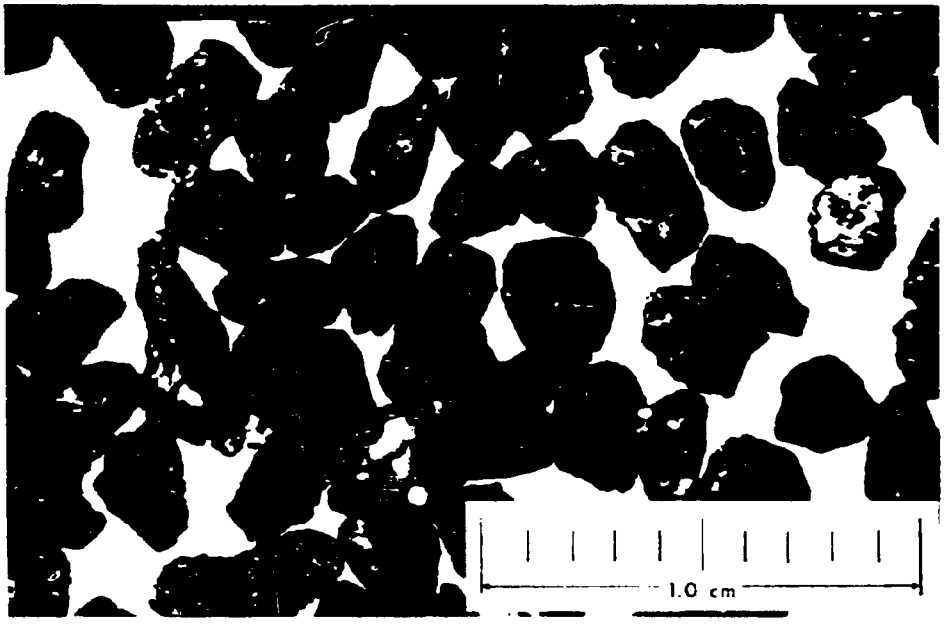

Figure 3. Photomicrograph of Unreacted Char

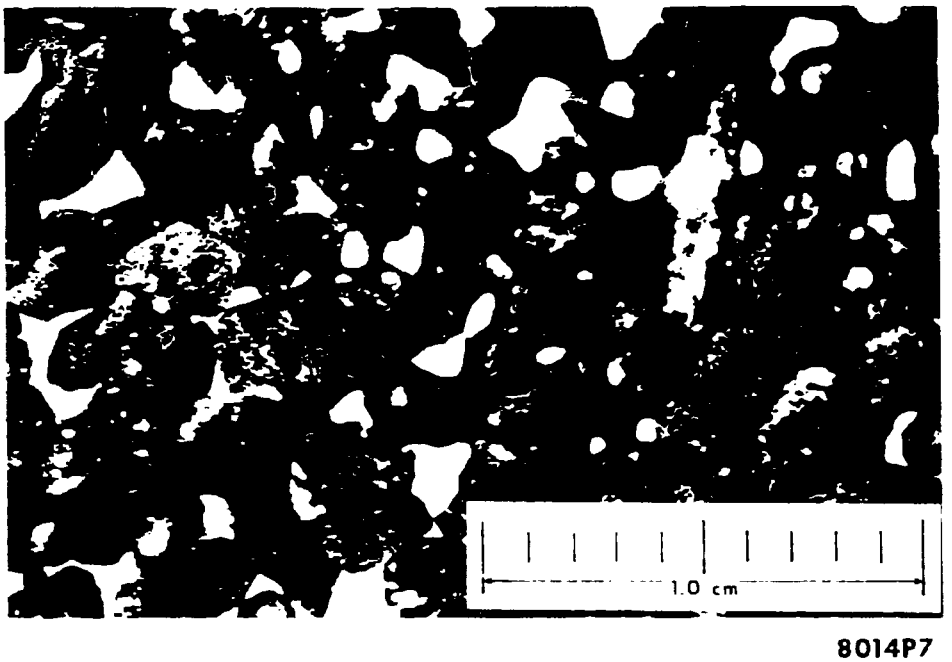

Figure 4. Photomicrograph of Char after 50% Carbon Burn-off

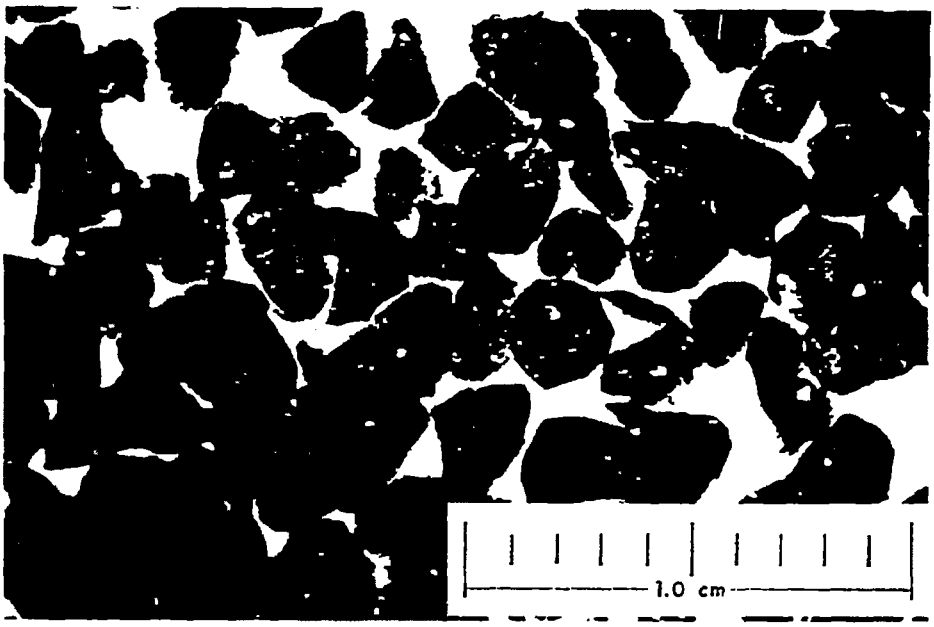

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Figure 5. Photomicrograph of Char after 80% Carbon Burn-off

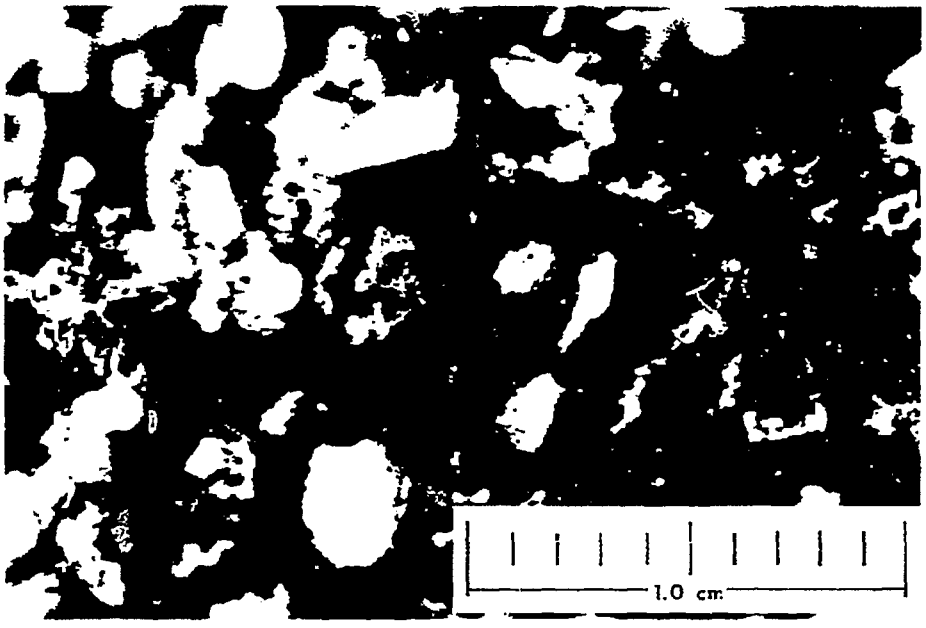

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Figure 6. Photomicrograph of Char Ash after 100% Carbon Burn-off

It has already been stated that convective external mass transfer was not the rate controlling step because the reaction rate was independent of gas velocity surrounding the char particles. However, if diffusion to the top layer of char particles controls, the rate could also be independent of particle diameter. To show that this was not the case, a series of tests was made in which the only variable was sample weight. That is, in each case the amount of "top layer" surface area was different. This was found to have no effect on the rate of reaction.

The experimental data were found to fit the following rate equations:

Char No. 2455:

A. Reacted with steam

$$(1-X) = \text{Ash} + (1-\text{Ash})e^{-k\,(C_{H_2O})^{0.58}t}$$

$$k = 9.5 \times 10^{5}\, e^{-1.7 \times 10^{4}/T}$$

B. Reacted with CO_2

$$(1-X) = \text{Ash} + (1-\text{Ash})e^{-k\,(C_{CO_2})^{0.52}t}$$

$$k = 3.96 \times 10^{5}\, e^{-2.36 \times 10^{4}/T}$$

Char No. 2469:

C. Reacted with steam

$$(1-X) = \text{Ash} + (1-\text{Ash})e^{-k\,(C_{H_2O})^{0.58}t}$$

$$k = 8.64 \times 10^{5}\, e^{-1.93 \times 10^{4}/T}$$

D. Reacted with CO_2

$$(1-X) = \text{Ash} + (1-\text{Ash})\, e^{-k\,(C_{CO_2})^{0.55}}$$

$$k = 3.97 \times 10^{5}\, e^{-2.01 \times 10^{4}/T}$$

The significance of these rate equations is demonstrated in Figures 7 through 10 which are plots of the proposed rate equations versus the experimental data. Table 3 and Table 4, and Figures 11 and 12, give the apparent reactivity, k value, as a function of temperature. From these equations an activation energy of 34 kcal/mole and a pre-exponential factor (Arrhenius' constant) of 9.5×10^{5} min^{-1} for the reaction of char No. 2455 with steam were obtained. This compares with 38 kcal/mole and 8.64×10^{5} min^{-1} for char No. 2469. Both char reactions are fractional order, 0.58, with respect to the steam concentration.

It has been mentioned that there is a wide variance in the reported kinetic parameters for the carbon/steam and carbon/carbon dioxide reaction. A recent

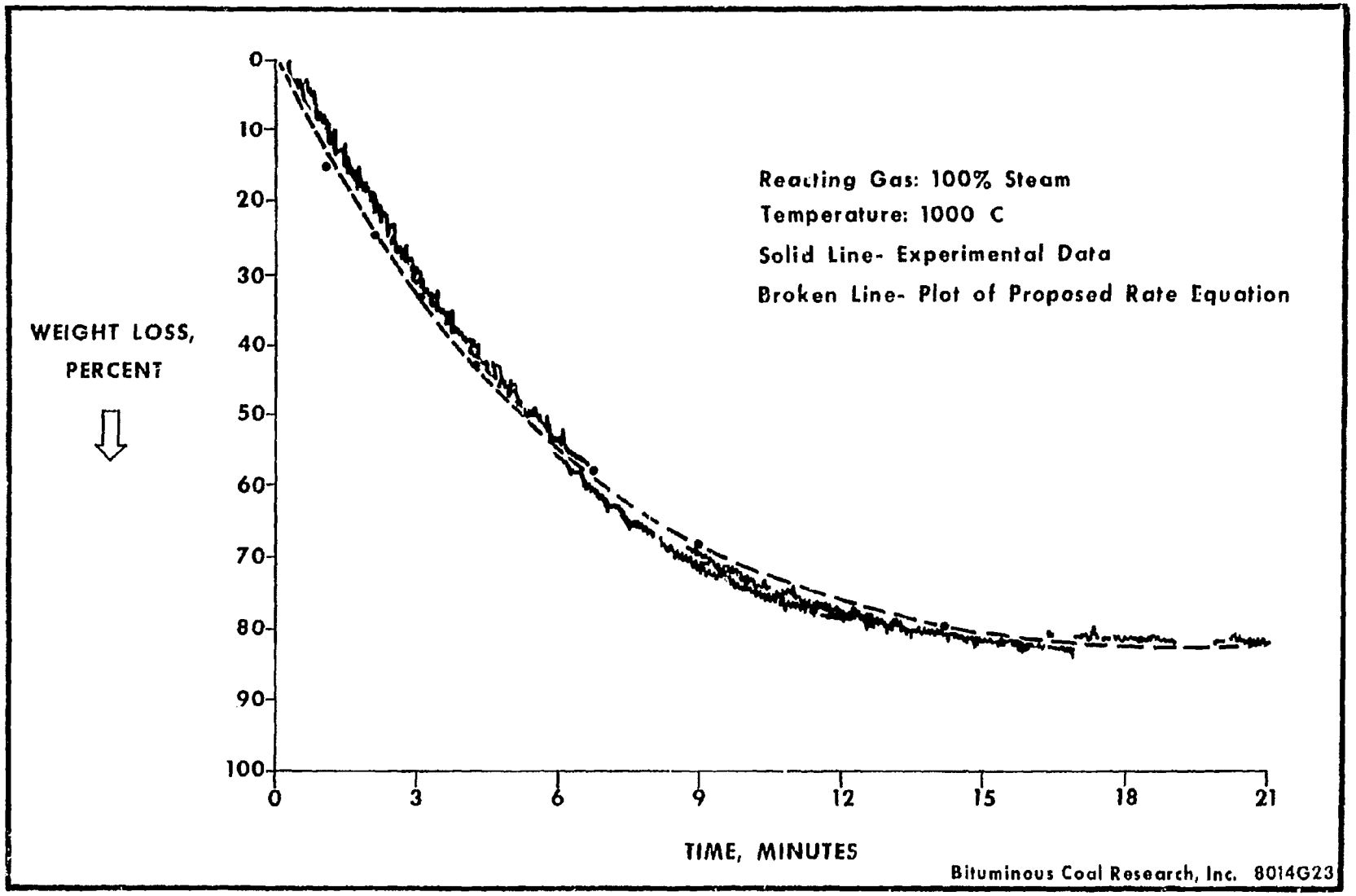

Figure 7. Correlation of FMC Char Reactivity Data

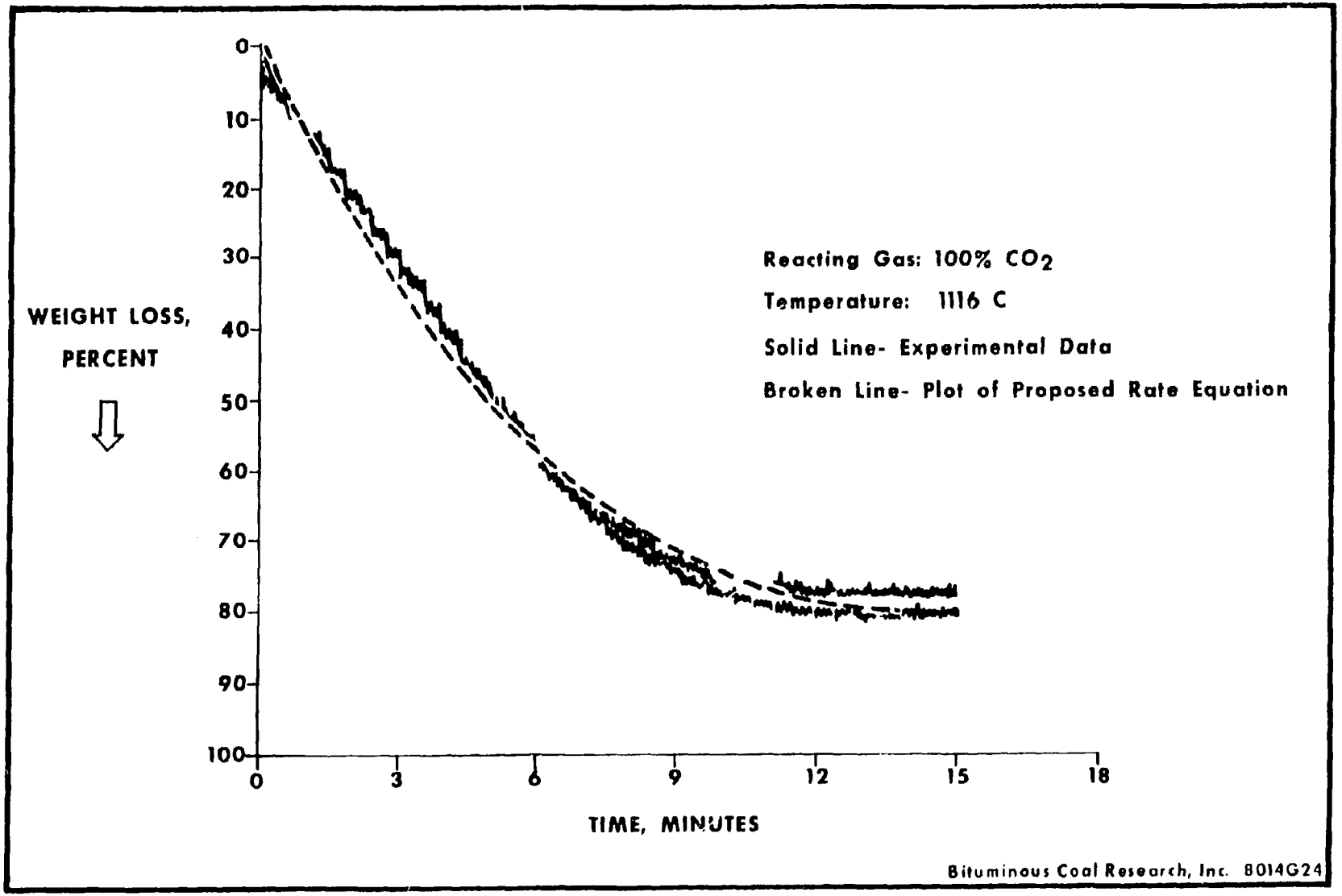

Figure 8. Correlation of FMC Char Reactivity Data

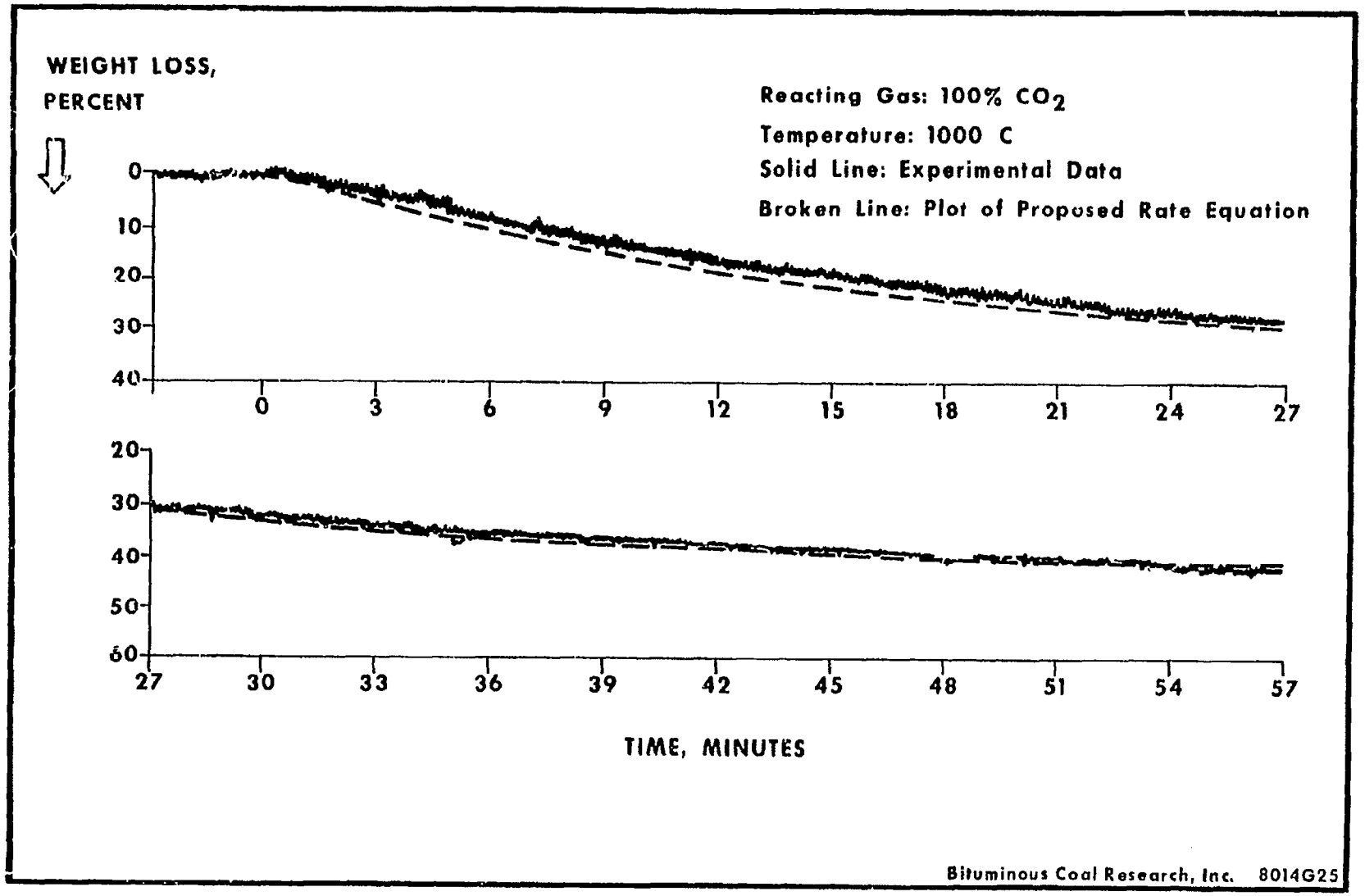

Figure 9. Correlation of Consol Char Reactivity Data

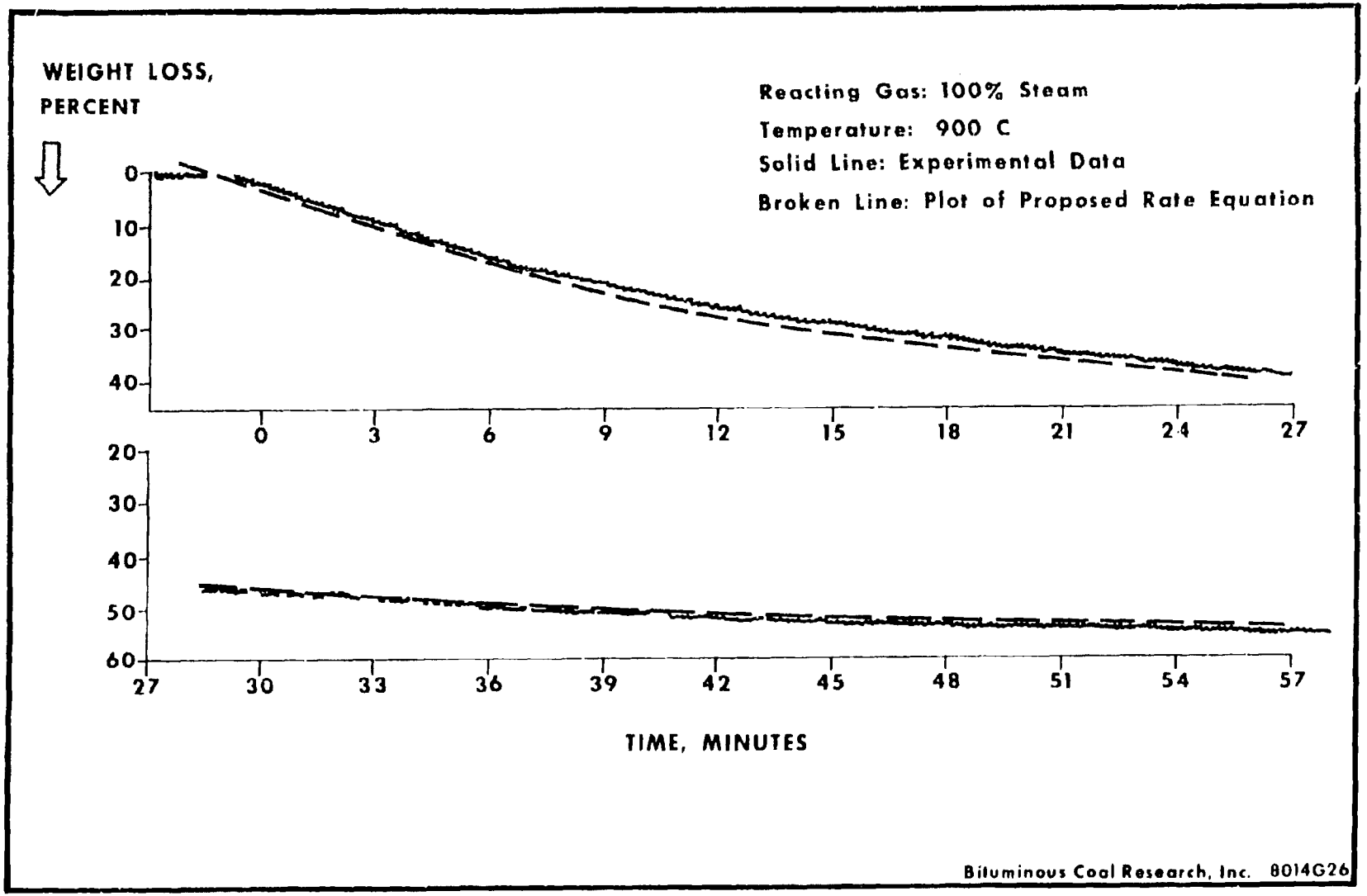

Figure 10. Correlation of Consol Char Reactivity Data

TABLE 3. APPARENT REACTIVITY VALUES FOR FMC AND CONSOL CHAR SAMPLES CHAR + STEAM REACTION

Sample	Equation	Temperature, C			
		900	1000	1100	1200
FMC Char (BCR Lot No. 2455)	$k = \frac{\text{lb C reacted}}{\text{lb C inventory - min}}$	.0483	.1507	.3985	.9236
Consol Char (BCR Lot No. 2469)	$k = \frac{\text{lb C reacted}}{\text{lb C inventory - min}}$	.0618	.2250	.6788	1.7626

TABLE 4. APPARENT REACTIVITY VALUES FOR FMC AND CONSOL CHAR SAMPLES CHAR + STEAM REACTION

Sample	Equation	Temperature, C			
		900	1000	1100	1200
FMC Char (BCR Lot No. 2455)	$k = \frac{\text{lb C reacted}}{\text{lb C inventory - min}}$	.0072	.0352	.1358	.4361
Consol Char (BCR Lot No. 2469)	$k = \frac{\text{lb C reacted}}{\text{lb C inventory - min}}$	.0136	.0476	.1479	.3821

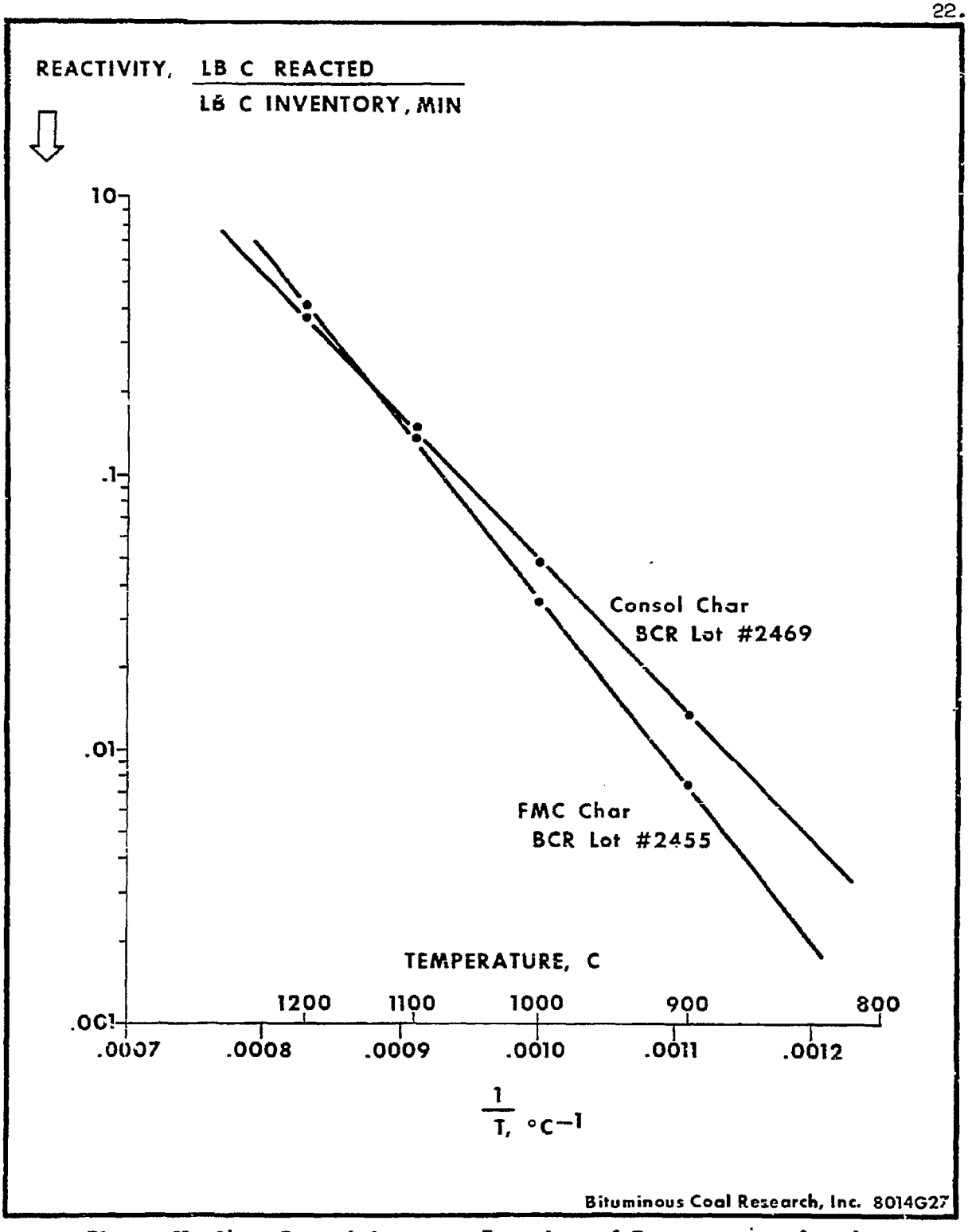

Figure 11. Char Reactivity as a Function of Temperature for the Char + Carbon Dioxide Reaction

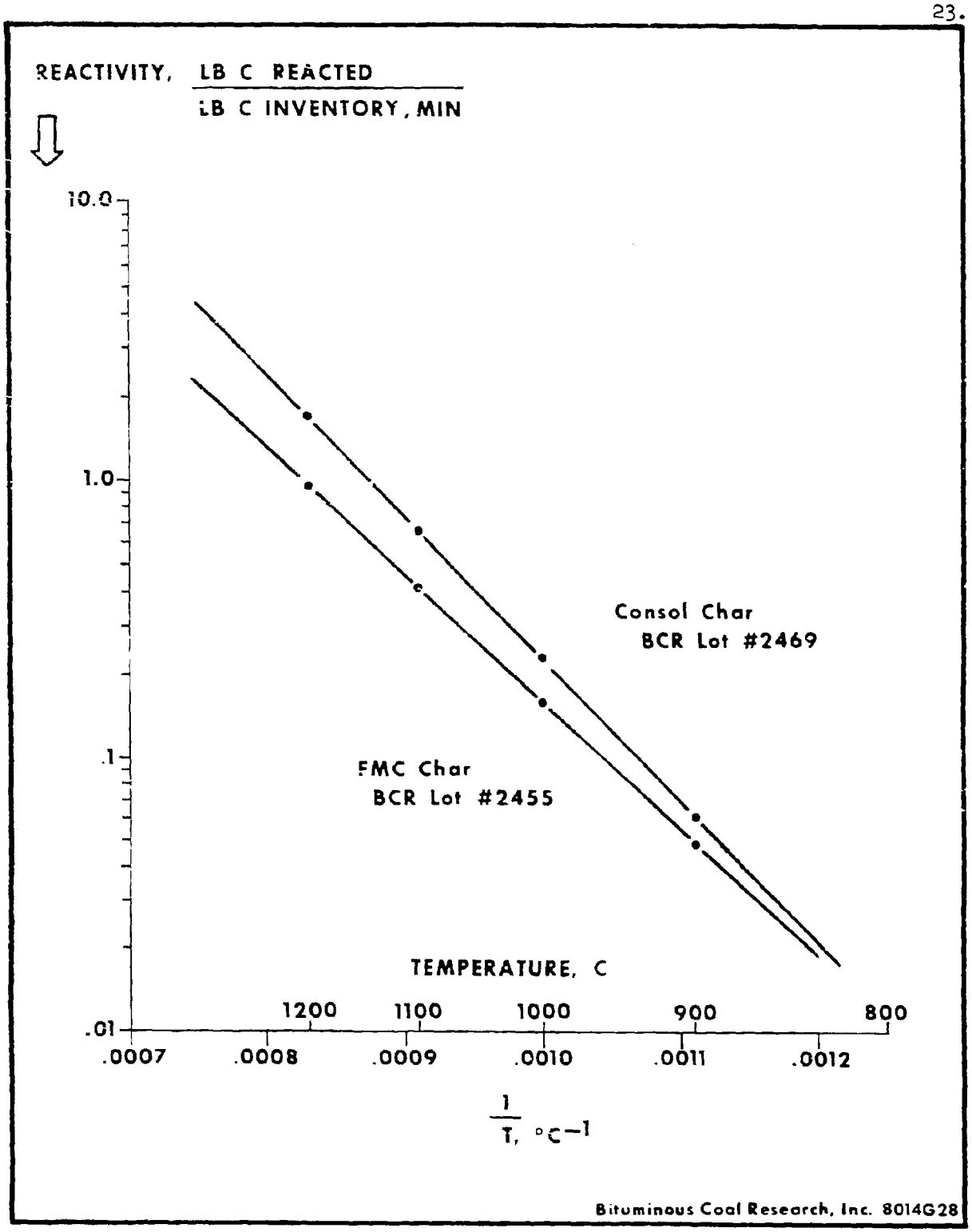

Figure 12. Char Reactivity as a Function of Temperature for the Char Plus Steam Reaction

paper entitled "Fundamental Studies on Coal Gasification with Regard to the Utilization of Thermal Energy from Nuclear High Temperature Reactors" by K. H. Van Heek, contained apparent kinetic parameters for coal/steam and char/steam reactions that were in close agreement with those obtained in this study. Van Heek reported activation energies for the coal/steam reaction ranging from 31.8 to 38.9 kcal/mole, and pre-exponential factors ranging from 5×10^4 min^{-1} to 2×10^6 min^{-1}. Van Heek had not yet investigated the effect of steam concentration, but the similarity of the results so far, despite the fact that the experimental apparatus and procedure are quite different, suggests that both investigators are exploring the same reaction mechanism.

VI. CONCLUSIONS

Within the temperature and concentration ranges investigated, the char/steam and char/carbon dioxide reactions may be described by the continuous reaction kinetic model with a rate equation of the form:

$$(1-X) = Ash + (1-Ash)e^{-k (C)^n t}$$

and

$$k = a\, e^{-E/RT}$$

Diffusion of reactants into and products out of these small, porous chars is so fast compared to the chemical reaction, that the reaction may take place everywhere throughout the particle at the same time. That is, the particles do not shrink as the reaction proceeds.

Measured activation energies of about 40 kcal/mole are consistent with a chemical reaction controlling rate equation.

Both the char/steam and char/carbon dioxide reactions are approximately half order with respect to reacting gas concentration.

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