Award Lecture

A NEW LOOK AT AN OLD FOSSIL:
KINETICS OF COAL PROCESSING

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The 1979 ASEE ChE Division Lecturer was Dr. Daniel Perlmutter of the University of Pennsylvania. The 3M Company supports this annual award.

Dan Perlmutter earned his Bachelor's Degree (Magna Cum Laude) from New York Univ. and his Doctorate in ChE from Yale Univ. From 1955 to 1958 he worked for the Exxon (then Esso) Standard Oil Company. His academic career began in 1958 at the U. of Illinois, Urbana, and moved to the U. of Pennsylvania in 1964. Following a reorganization of the College of Engineering and Applied Science, he became the first Chairman of the department of Chemical and Biochemical Engineering, a position he held from 1972 to 1977. He has been a visiting Professor at Harvard U., the U. of Manchester, the U. of Zagreb, and the Hebrew U. of Jerusalem, in the capacity of a Fulbright Professor in England and Yugoslavia and as a Guggenheim Fellow in Cambridge.

He has developed new course materials in chemical reactor control, optimization, and stability problems. His textbook, Introduction to Chemical Process Control, *was one of the first available in its field, and was widely adopted in the U.S. and abroad. His monograph on* Stability of Chemical Reactors *provided a unified view of a wide range of questions by combining some original work with an integrated survey of material only available in scattered journal articles. His most recent research has been on the kinetics of gas-solid reactions, prompted especially by their connections with energy-related problems in coal drying, oxidation, and gasification, as well as reversible storage in the form of heat of reaction.*

THE WIDELY PROCLAIMED energy crisis that so profoundly affects world affairs should be understood to be caused not by a lack of fossil fuel resources, as much as by a shortage of fuel in the highly desirable gaseous and liquid forms. It is accepted in all quarters that proved coal reserves are ample to supply anticipated world energy needs for at least several hundred years and further that no geographic monopoly is possible, since the deposits are very widely distributed over virtually every continent. It is evident in this context that the technology of the so-called gasification and liquefaction processes are central to handling the crisis: techniques for coal conversion are being sought that will supply transportation, space heating, chemical feedstocks, and industrial needs at prices comparable to petroleum sources. The objective moves closer as OPEC prices continue to rise.

It is convenient to think of gasification as composed of three steps: (i) coal pretreatment, (ii) pyrolysis, and (iii) char reaction, even though a particular process may circumvent one or more of these, or may be designed to accomplish several objectives in a single reactor. The step-wise view-

point leads most smoothly into an examination of the appropriate chemical and physical properties of coal, and of the changes that need to be sought and monitored.

PRETREATMENT

THE PRIMARY MOTIVATION for a study of coal pretreatment is a practical processing difficulty. When common bituminous coals are subjected to high temperature gasification conditions they tend to soften and swell, and can plug reactors and transport lines before ultimately resolidifying as a porous char or coke. This process is commonly referred to as caking; it must be controlled if the solid fuel is to be successfully gasified. A mild oxidative pretreatment is commonly used to reduce or eliminate this coal caking propensity, providing two steps in one: drying to re-
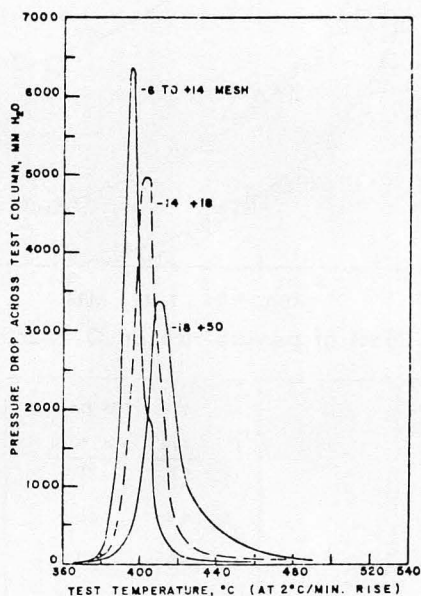

FIGURE 1. Caking test results for feed coal samples.

move naturally occuring water on the coal surfaces, and the chemical oxidation.

Many laboratory test methods have been used to study the plastic properties of coals, all empirical in nature and devised to characterize the plastic behavior of coal by means of numerical indices. Comprehensive summaries and reviews of the methods have been given by Brewer (1945) and Loison et al. (1963). One common test is the Gas Flow test (Foxwell, 1924; Coffman and Layng, 1927, 1928), chosen for its simplicity in apparatus design and operation and for its close resemblance to the caking of coal in a packed bed

reactor. In this test, a sample of the coal is heated at a constant rate of temperature rise (2°C/min) inside a tube with a constant flow of nitrogen through the coal sample. The differential pressure drop across the sample is monitored, as the sample goes through its plastic range. Pressure drop vs. temperature readings are taken as data, as shown in Figure 1. After the oxidizing pretreatment the same test shows a sharp reduction in pressure drop as in Figure 2, reflecting a lesser degree of softening, swelling, and "caking."

Changes recorded as mechanical properties need to be matched to chemical effects, if one is to understand the details of the preoxidation. For this purpose, a HVA bituminous coal was oxidized in a packed-bed reactor with a once-through mixture of N_2 and O_2, monitored by analyzing the composition of the feed and product gases with a dual-column Gas Chromatograph.

Typical results on overall reaction rates are shown in Figures 3 to 7, emphasizing the effects of flow rate, particle size, oxygen concentration, pressure, and temperature, respectively. In addition, the chromatographic analysis run on each sample of reactor effluent provided a record of carbon dioxide and carbon monoxide production to match
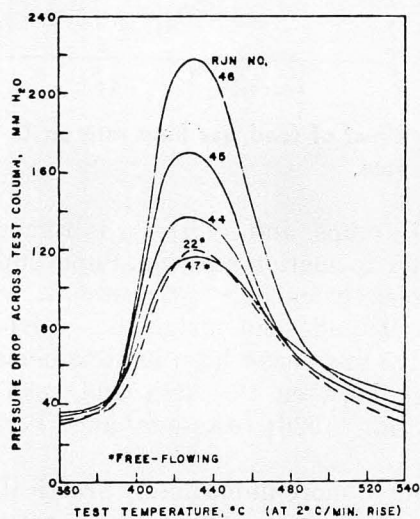

FIGURE 2. Caking test results for −18 to +50 mesh oxidized coal samples.

the rates of oxidation. Cross plots are presented as Figures 8 and 9 to illustrate the linearity and to demonstrate that the correlations for the various coals do indeed persist as flow rate, particle size, and conversion vary. Evidently, the two carbonic gases are formed in a constant ratio, presumably by the same mechanism.

Correlation of all these findings by means of a comprehensive argument requires formulation of a model that includes several steps. The two carbonic gases appear to form together by a direct burnoff reaction. Simultaneously, oxygen is adsorbed by the coal to form any of a series of oxy-
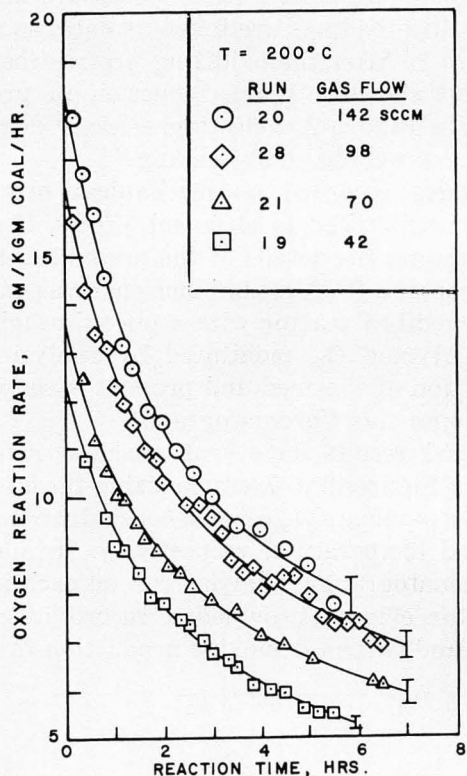

FIGURE 3. Effect of feed gas flow rate on O_2 reaction rate.

functional groups, and hydrogen is removed in a direct water formation reaction. Superimposed on this complex chemistry are possible transport limitations outside and inside the coal particles. Quantitative tests have been used to demonstrate consistency between the data and such models (Kam *et al.*, 1976; Karsner and Perlmutter, 1980).

Turning to more immediately practical results, it is of interest to relate oxidation rates to the geologic history of various coals. In Figure 10 comparable rates are presented as a function of
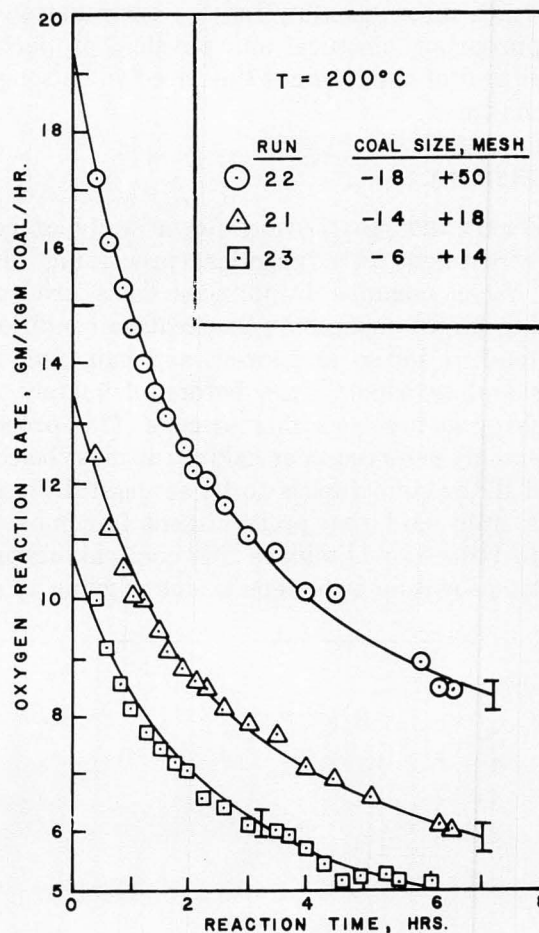

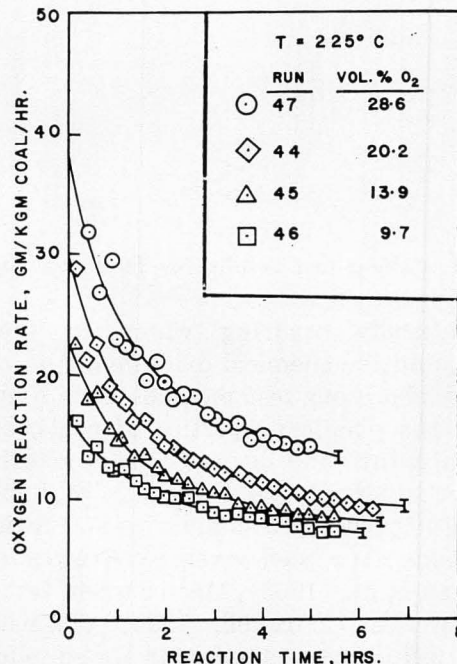
FIGURE 4. Effect of particle size on O_2 reaction rate.

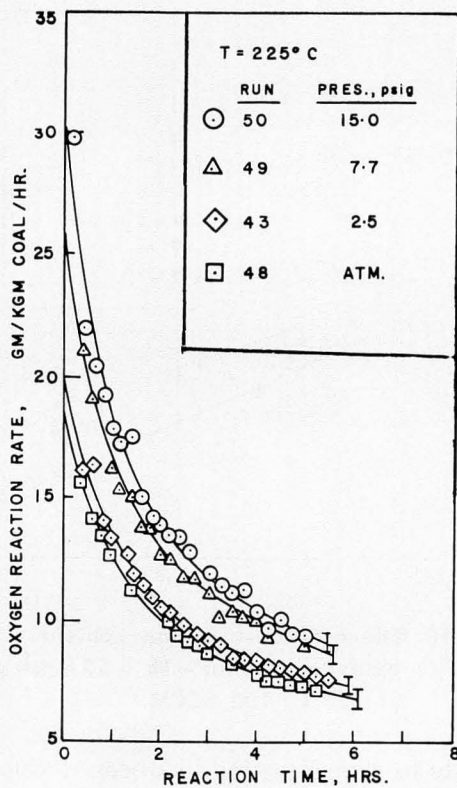FIGURE 5. Effect of feed O_2 concentration on oxygen reaction rate.

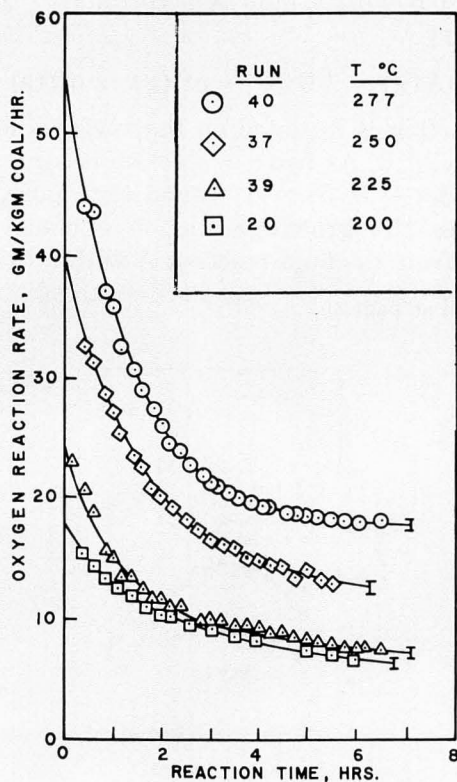**FIGURE 6. Effect of pressure on oxgen reaction rate.**

FIGURE 7. Effect of temperature on oxygen reaction rate.

carbon content, a commonly used index of a coal's rank. As shown, by the duplicate runs, the cross-hatched band is primarily a reflection of variability among coals and only in minor part caused by experimental scatter. A balanced evaluation of pretreatment must also consider the economic losses that accompany any reduction in heating values. The data show a strong correlation with the carbon content of a sample. Regardless of particle size, the heating value of a material changed upon oxidation primarily as the carbon changed for a wide range of coals of different types. There is also a suggestion in the data that

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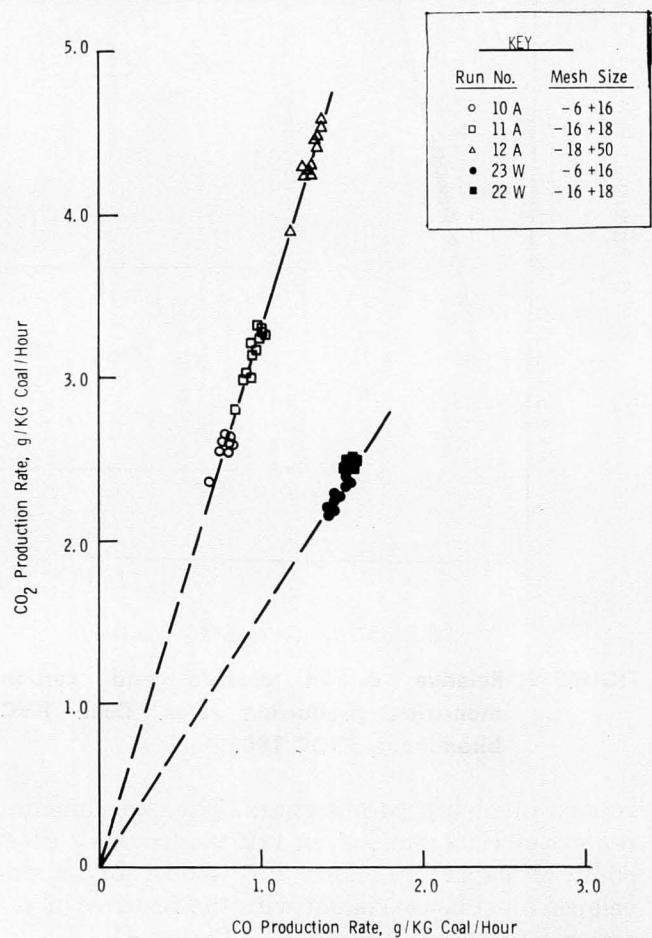

FIGURE 8. Relative carbon dioxide and carbon monoxide production rates. Coal: MV bituminous, PSOC 135.

generalizations regarding the fixation of oxygen that occurred for all the various bituminous coals do not apply to the lignite (PSOC 87) and the anthracite (PSOC 80) coals.

CHAR REACTION

TURNING ATTENTION TO the downstream side of a coal gasification process, models are needed to describe kinetics of the several gas-solid re-
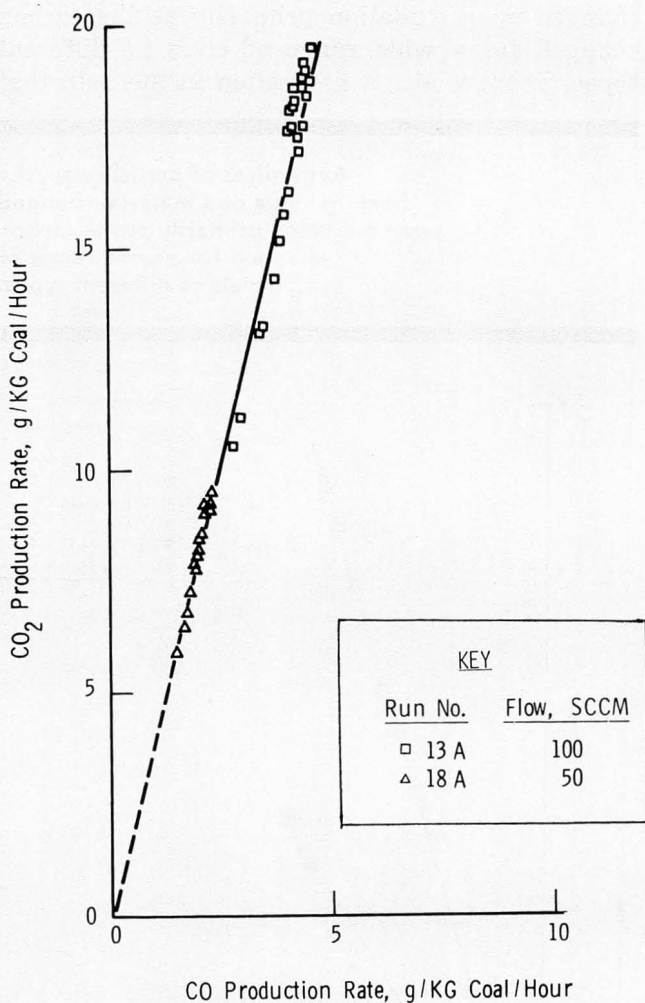
FIGURE 9. Relative carbon dioxide and carbon monoxide production rates. Coal: HVC bituminous, PSOC 190.

actions involving porous chars. The experimental reports of Hashimoto et al. (1979) provide a good point of departure, since any model to be developed must be consistent with the features of reaction such as are presented in Figure 11.

Above all a viable model must permit the development of a maximum in rate (or reactive surface) as a function of conversion. A promising
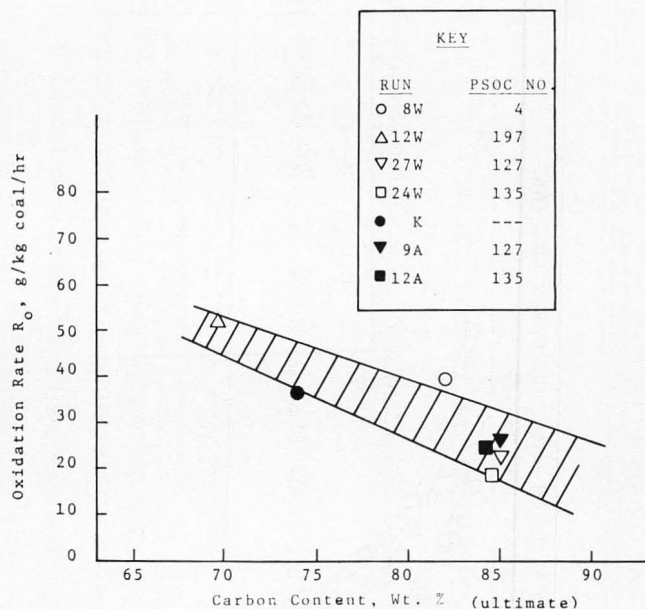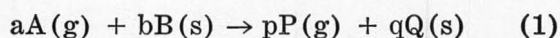
FIGURE 10. Effect of coal carbon content on initial oxidation rate for −18 +50 mesh particles at 225°C, 100 SCCM.

candidate in this direction has been developed by Bhatia and Perlmutter (1980), who considered the isothermal chemical reaction of particles of the solid B with a fluid A according to the stoichiometry

$$aA(g) + bB(s) \rightarrow pP(g) + qQ(s) \qquad (1)$$

The reaction is initiated on the surfaces of pores in the solid B. As further reaction occurs, a layer of product Q is formed around each pore, which separates the growing reaction surface of the solid B from the fluid reactant A within the pores.
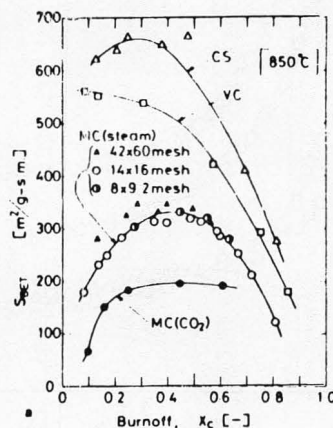
FIGURE 11. Effect of char conversion on surface area, after Hashimoto et al. (1979).

the Canadian methanol consumer while benefitting neither the American methanol producer nor American consumers.

A word of caution is necessary to warn the reader that the actual price will probably not be equal to the one calculated above. Obviously the two competitor model is much too simple to be applicable in the commercial world. The extension of the technique to a multi-competitor one is straightforward in principle and a natural application for a computer simulation. However, even the more complicated model would probably not arrive at a realistic price because of the unavailability of accurate input data. The model would be useful in the commercial world in the hands of someone familiar with the industry. The technique has proven to be a very useful tool in showing students how the technical, economic and regulatory factors influence the potential markets for a chemical commodity. □

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AWARD LECTURE

Kinetics of Coal Processing

Reactant A diffuses through the product layer to the reaction surface where chemical change occurs. As reaction progresses, each pore of the particle has associated with it a growing reaction surface which initially corresponds to the inner surface of the pore. As the various reaction surfaces in the particle grow, it is inevitable that neighboring surfaces will intersect one another as the solid B separating them is consumed and replaced by the product Q.

The growth of the total reaction surface may be followed in terms of the radial growth of a given set of overlapping cylinders, as shown in Figure 12. If the rate of reaction on the actual surface is proportional to the total surface area
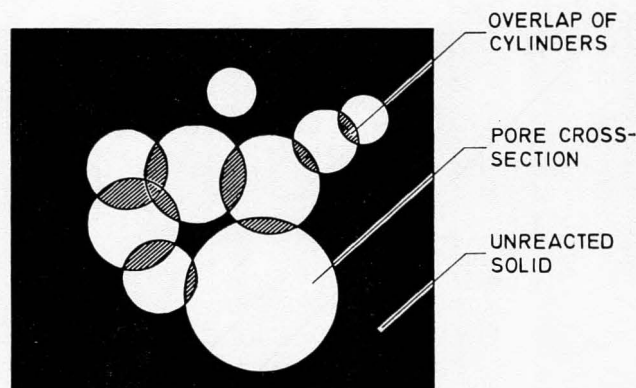
$$\frac{S}{S_o} = \frac{1-X}{\left(1-\frac{\tau}{\sigma}\right)^3} \sqrt{1 - \Psi ln \left[\frac{1-X}{\left(1-\frac{\tau}{\sigma}\right)^3}\right]} \quad (2)$$

and the conversion is

$$X = 1 - (1 - \frac{\tau}{\sigma})^3 \exp\left[-\tau(1 + \frac{\Psi\tau}{4})\right] \quad (3)$$

The surface development predicted by Equation (2) is shown in Figure 13, exhibiting the anticipated maximum, but only for pore structures that


FIGURE 12. Overlapping of cylindrical surfaces. The hatched area shows the overlapped portion. The blackened area represents unreacted solid B. The reaction surface is the interface between the nonoverlapped portion of the cylindrical surface and the unreacted solid. The product layer that is deposited as the reaction surface moves is not shown in this figure. (After Avrami).

provide $\Psi \geq 2$. In this regard the model is more flexible than those based on an order of reaction or a grain model. The Petersen model (1957) can also describe either kind of behavior; but it makes no provision for further pore wall intersections and neglects the distribution of pore sizes. As an example of the use of the above technique, it is worthwhile to return to the data of Hashimoto et al. (1979) on the surface areas produced by steam activation of chars. As $\sigma \to \infty$, Equation (2) predicts a linear semilog relationship between the group $[S/(1-X)]^2$ and $(1-X)$. This expectation is supported by the data within the limits of experimental error, as shown in Figure 14.

That the subject of coal processing is a complex matter with multiple branches is a commonplace. The emphasis of this paper has been to demonstrate that the newer techniques of experimentation and modeling can shed new light on the old fossil, if the broad problems of practice are disected into manageable parts, each to be digested in its turn. □
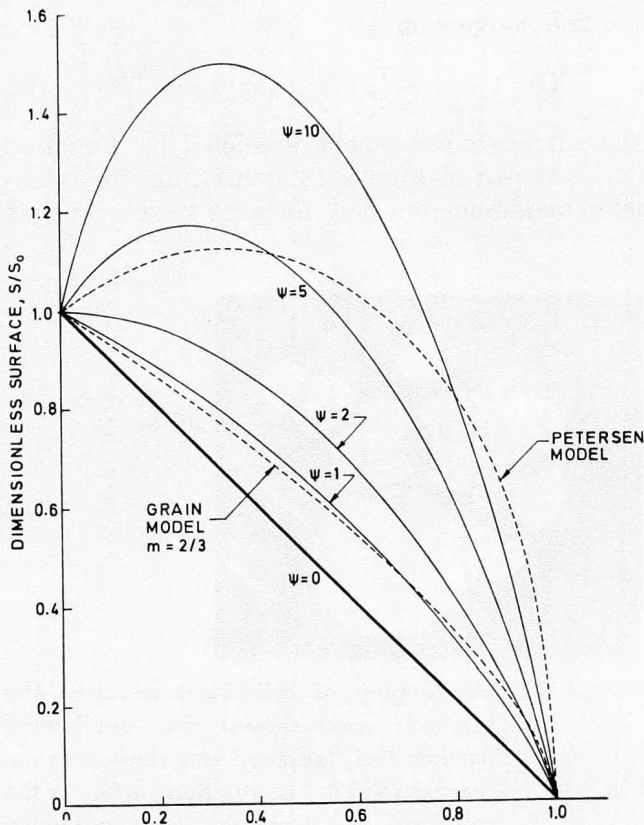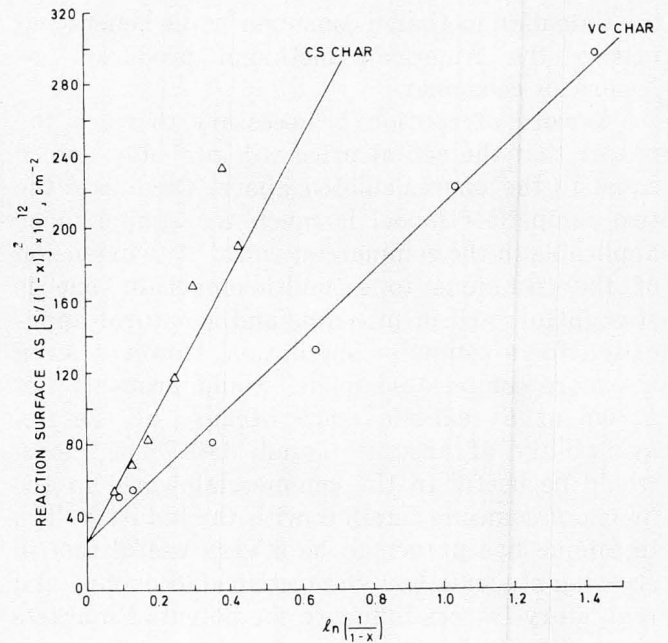
FIGURE 13. Development of the reaction surface with conversion according to the random pore model, compared with grain model for m = 2/3 and Petersen model for ϵ_0 = 0.26, L_0 = 3.14 x 10^6 cm/cm³, S_0 = 2,425 cm²/cm³.

FIGURE 14. Correlation of the data of Hashimoto et al. (1979) with random pore model.

NOTATION

a, b	=	stoichiometric coefficients
C	=	concentration of gaseous reactant A
k_s	=	rate constant for surface reaction
L	=	length of overlapped system
n	=	reaction order with respect to gas A
p, q	=	stoichiometric coefficients
R_o	=	initial particle radius
S	=	reaction surface area per unit volume
S_0	=	S at t = 0
t	=	time
X	=	conversion

GREEK LETTERS

ϵ	=	porosity
ϵ_0	=	initial value of ϵ
Ψ	=	$4\pi L_0 (1 - \epsilon_0)/S_0^2$, structural parameter
σ	=	$R_o S_0/(1-\epsilon_0)$, particle size parameter
τ	=	$k_s C^n S_0 t/(1 - \epsilon_0)$, dimensionless time

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