Coal Devolatilization and Hydrogasification

The fundamental understanding of coal and its behavior under gasification conditions is far from complete, but significant insights into the complex chemical and physical phenomena have been achieved. This review of available fundamental information focuses on thermal decomposition of coal in inert gas and in hydrogen, with emphasis on the effects on yield of products exerted by time, temperature, heating rate, pressure, hydrogen partial pressure, and particle size, and on the development of chemical and transport models of engineering importance.

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SCOPE

Coal has emerged as the principal potential source of the synthetic pipeline gas and fuel gases that may be needed to supplant our rapidly dwindling natural gas reserves and to provide fuel alternatives for electrical utilities and other industries. At least four coal gasification processes are commercially available for certain operating conditions and are being used in some countries, but the United States is still without a large-scale commercial system. In an effort to improve the economic viability of coal gasification and to broaden the range of operating conditions, over thirty new processes are now in various stages of development in the United States, six of which have reached pilot plant scale. Efficient progress toward the identification and optimization of the best processes will require a basic understanding of the controlling physical and chemical phenomena. Coal research pertinent to gasification is not new, and considerable experimental data are dispersed throughout the scientific and technical literature. Unfortunately, the phenomena are so complex that no unifying theory has evolved. The type of coal, the nature of the experiment, and the apparatus each profoundly influence the results; hence, only restricted interpretations have been possible. Several authors at different times have reviewed many of the diverse findings, each time identifying new aspects of the problem and new directions for research. The recent acceleration of coal research has generated much new information which must be reconciled and reviewed. The objective of this review is to assess the available fundamental information on devolatilization and hydrogasification with emphasis on the development of chemical and transport models suitable for chemical engineers.

CONCLUSIONS AND SIGNIFICANCE

The mechanisms involved in the rapid thermal decomposition and hydrogasification of coal are exceedingly complex, and the influence of many experimental variables is not well understood. Coal is an intermediate product of the very slow decomposition of organic matter deposited in prehistoric times. The final product would be pure carbon. This natural carbonization can be artificially accelerated by elevating the temperature. Although most of the carbon remains in the solid when a relatively massive sample of coal is heated, it is often possible to volatilize 50% or more of the initial carbon by rapidly heating a finely ground and well-dispersed sample and by rapidly quenching the products. Furthermore, if this rapid heating takes place under sufficient hydrogen pressure, nearly all of the carbon in the coal can be converted to methane in fractions of a second.

Much evidence supports the hypothesis that the devolatilization of coal is a chemical decomposition reaction. Measurable devolatilization does not start until temperatures of 350° to 400°C are reached, and thereafter its extent is a strong function of temperature. Coal is a complex organic polymer consisting of aromatic clusters of several fused rings strung together by assorted hydrocarbon and heteroatom (O, N, S) linkages. Heating causes the structure to decompose, the weaker bonds rupturing at lower temperatures and the stronger ones at higher temperatures, and the fragments that are volatile attempt to escape from the particle. Some of the fragments are highly reactive free radicals subject to a variety of secondary reactions such as cracking and repolymerization. Generally, such secondary reactions are undesirable in practice, since they deposit a portion of the volatile matter as a solid or char and diminish gas and liquid yields. The extent of secondary reactions can be reduced by enhancing the transport of volatile fragments away from the reactive enverironment, such as by operating at reduced pressures with smaller and more widely dispersed particles.

The complexity of these phenomena has handicapped the development of models suitable for design and scale-up. A powerful but convenient technique available for modeling the numerous chemical reactions involved in the decomposition process is the use of a statistical distribution of activation energies. Such a model simulates the decomposition behavior over an extraordinarily broad range of conditions without creating a large number of adjustable constants. Secondary reactions are more difficult to model because they occur in competition with the transport and escape of volatiles, the quantitative description of which remains in question. Many United States bituminous coals melt or become plastic in certain temperature ranges, casting considerable doubt on simple porous-solid diffusion models. Simplistic models that correlate the data reasonably well have been advanced, but refinements allowing for the coal plasticity seem more likely to be useful in the long run.

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Hydrogen will react with devolatilizing coal several orders of magnitude faster than with the residual char. The short-lived period of high reactivity lasts only a few seconds or less at temperatures of interest in gasification. The so-called rapid-rate carbon species is not clearly identified, though convincing evidence suggests that hydrogen interferes with the char forming secondary reactions presumably by hydrogenating reactive fragments sufficiently to stabilize them during their escape.

The rate of total product generation appears to be controlled by thermal decomposition of the coal. Competition between mass transfer, secondary reactions, and rapid hydrogenation affects only the relative proportions of volatile and solid product formed.

Several empirical kinetic models advanced to explain hydrogasification behavior have been successful in correlating data under limited conditions. However, models which recognize thermal decomposition as rate controlling appear more realistic and should prove more fruitful in exploring wider ranges of conditions. The transport of volatiles out of the coal particle coupled with the countercurrent diffusion of hydrogen is poorly understood, but modification of available devolatilization models to include hydrogenation effects offers a limited correlative technique.

Evolution of an improved picture of rapid coal devolatilization and hydrogasification has stimulated recent developments toward commercial application. The COED and Garrett processes are designed to minimize the extent of secondary reactions in the absence of high pressure hydrogen. Relatively low operating temperatures maximize the yield of liquid products. Hygas and Hydrane, on the other hand, are operated at hydrogen pressures in excess of 70 atm. Substantial hydrogasification takes place at high temperatures with methane the principal product. Coalcon's hydrocarbonization at fairly low temperatures and modest hydrogen pressures appears to involve very little rapid-rate carbon.

1. INTRODUCTION

1.1. Background

Coal represents approximately 70% of the recoverable fossil fuel resources in the United States (Averitt, 1975) and may eventually become our principal source of hydrocarbon fuels and feedstocks. National recognition of the enormous immediate and long-range potential of coal has resulted in substantial efforts toward the development of economically and environmentally viable coal utilization technologies. Coal conversion to clean gaseous and liquid products is especially attractive with respect to minimal impact on existing consumption patterns. The approaches now under extensive development in the United States include gasification, liquefaction, and hybrid schemes. Despite a myriad of proposed processes at various stages of development, no full-scale commercial coal conversion plant is under construction in the United States.

Interest in clean gaseous fuels from coal has been stimulated by the introduction of enviromental constraints and the significant decline of proven and recoverable U.S. natural gas reserves. While improvements in the gas pricing structure will undoubtedly stimulate gas exploration, the estimated U.S. recoverable gas resources yet to be found is so low (Miller et al., 1975) that the development of alternatives is imperative.

Present coal gasification efforts are directed toward low Btu, intermediate Btu, and high Btu (pipeline quality, essentially methane) gas. The higher the gas heating value, the more expensive is the conversion. Choice among these options and other possible fuels from coal will be decided locally and will be strongly influenced by required fuel characteristics and distribution considerations. However, a relatively secure market for pipeline quality gas will exist for many years since most residential, many commercial, and some industrial users of natural gas can not easily adapt to different qualities of gas or to other fuels, and large capital is already invested in gas transmission and distribution facilities. Therefore considerable attention has been focused on coal conversion to methane.

The atomic hydrogen to carbon ratio of coals of potential commercial interest for conversion processes is typically 0.6 to 1.0, which is substantially less than the value for liquid and gaseous fuels commonly used (Table 1). Therefore, the primary requirement of any coal conversion scheme is either to increase the hydrogen content or to

Table 1. Hydrogen to Carbon Ratio and Calorific Value of Selected Fossil and Process-Derived Fuels (cokes-Spiers, 1962; Coals-Given, 1975; Shale Oil, Kerogen, and Bitumen-Cameron Engineers, 1975; Others-Perry et al., 1963; Linden, 1965)

Fuel type	*H/C*, atomic*	Gross heating value, kcal/g†
Gaseous		
High-B.t.u.: methane	4.0	13.3
natural gas	3.5-4.0	11.7-11.9
Intermediate-B.t.u.:		
hydrogen	∞	33.9
coke oven gas	4.9	9.6
water gas (H_2 — CO)	2.0	4.3
Low-B.t.u.:		
Producer gas (N_2-diluted; from bituminous coal)	1.2	1.2
Liquid		
Methanol	4.0	5.3
Gasoline	2.0-2.2	11.2-11.4
No. 2 fuel oil	1.7-1.9	10.7-11.0
No. 6 fuel oil	1.3-1.6	10.0-10.5
Crude shale oil	1.6	10.3-10.4
Bitumen (Athabasca tar sands)	1.4-1.5	9.8-10
Solid		
Kerogen (Green River oil shale)	1.5	10
Lignite	0.8	3.9-5.4
Subbituminous coal	0.8	5.5
Bituminous coal	0.5-0.9	6.7-8.8
Anthracite	0.3	8.4
Low-temperature coke	0.4	8.2
High-temperature coke	0.06	8.0

* Mineral-matter-free C and total organic H (that is, including H bound with O, S, and N).

† Coals-moist, mineral-matter-free; cokes-dry, ash-free; 1 kcal/g = 1 800 Btu/lb.

reject carbon, thereby upgrading the hydrocarbon fraction. The latter effect can be accomplished directly by coal pyrolysis* which yields a hydrogen rich volatile fraction and a carbon rich solid residue (char or coke). The residue will react with hydrogen,† quite rapidly during or just after volatile release. This direct conversion contrasts markedly the more established technology of complete gasification of the coal with steam and oxygen to produce primarily hydrogen and carbon monoxide at high temperatures. Methane, methanol, and other hydrocarbons can be catalytically synthesized from these gases after purification downstream of the gasifier. Process analyses indicate that catalytic methane formation is less efficient and more costly than methane formation by devolatilization and hydrogasification (Wen et al., 1972; Henry and Louks, 1971).

The extent of direct methane formation in the various processes now under development varies from negligible contributions to 95% of the final product gas (Hottel and Howard, 1971). The chronological record of developments reflects a strong emphasis on the enhancement of direct conversion. In support of development and demonstration activities, accurate kinetic and yield data are required for design and scale-up, and a mechanistic understanding of the controlling phenomena is essential for efficient progress toward full realization of the potential advantages.

1.2. Previous Reviews

Considerable research on coal devolatilization and hydrogasification has been conducted over the years, but the reported results are widely dispersed in the scientific and technical literature. For example, early pyrolysis work is found predominantly in combustion and carbonization literature, while research on coal-hydrogen reactions is discussed in gasification and liquefaction literature. Very little crossfertilization has occurred.

Several past reviews are available. The best single source is probably Lowry's (1963) compilation of review articles. In that work, H. C. Howard (1963) reviewed coal pyrolysis reactions (mostly information obtained by slow heating techniques), and C. G. Von Fredersdorff and M. A. Elliott (1963) reviewed the state-of-the-art in coal gasification technology. Devolatilization research at low heating rates was critically evaluated by Yellow (1965), and work at high heating rates was summarized by Badzioch (1967). Jones (1964) similarly reviewed a number of pyrolysis studies, most of which were done at low heating rates. Essenhigh and Howard (1971) reviewed the devolatilization literature in a monograph on combustion and explosion phenomena in coal dusts. The Institute of Gas Technology recently published an in-depth review (Pyrcioch et al., 1972) of its extensive coal gasification research including a brief recapitulation of some of the most important hydrogasification studies. The remaining critical assessments are contained in research papers referenced below.

Finally, it is important to mention that, in almost every case, the two phenomena of devolatilization and hydrogasification are afforded separate treatment with their interrelationship, although acknowledged, remaining unexplored. This area of omission has now become an important focal point of many gasification efforts.

1.3. Scope of Present Review

With the rapidly accelerating pace in coal research, the tolerable time lag between critical reviews has shortened appreciably. The primary intent of this paper is to provide a current review of coal devolatilization and hydrogasification, with particular emphasis on the interrelationship of these phenomena and on the rapid reactions anticipated to be of most interest commercially. Beginning with a review of experimental techniques, typical data are described with attention to the method of acquisition and to possible influences of technique on interpretation. Specific results, correlations, and postulated mechanisms of coal devolatilization are then analyzed. Since thermal decomposition is common to all coal conversion schemes, devolatilization is first treated independent of gasification discussions. Then, in the section on hydrogasification, the apparently important effect of devolatilization on coal reactivity to hydrogen is pursued.

Despite the authors' concern over a basic understanding of the phenomena involved, there are no apologies for a heavy reliance on empiricism and semiempiricism. A brief review of fundamental work on coal chemistry offers opportunity for reflection upon the incipient efforts to establish truly theoretical models for reactions involving coal. However, the prevailing intense debate questioning the value of fundamental studies with small-scale equipment to pilot and demonstration plant studies must be recognized. The primary objective of all these efforts is to assemble a datum base suitable for design and scale-up of commercial coal conversion plants. A genuine understanding of basic devolatilization and hydrogasification phenomena will ease the difficult selection between alternatives and decrease the risk associated with building large-scale plants.

2. EXPERIMENTAL METHODS

2.1. Data Requirements

It is, of course, important that the range of experimental conditions in the laboratory be comparable to those expected in full-scale operation. From a review of proposed coal gasification processes (Hottel and Howard, 1971), the expected commercial conditions include coal types from lignite and subbituminous to caking and noncaking bituminous, temperatures of 500° to 1 000°C, heating rates up to 10^4°C/s, particle sizes from several millimeters to 50μm of less, and pressures up to 100 atm. [On the latter point, Wen *et al.* (1972) conclude that 69 atm is most likely optimum for pipeline gas production, since this pressure is employed in distribution systems.] The necessary laboratory techniques include methods for time resolved collection, separation, and analysis of the solid residue, liquid products, and assorted gaseous components including hydrocarbons, carbon oxides, and hydrogen, and species containing sulfur and nitrogen.

Such experimental conditions with the attendant sampling and analysis requirements are difficult to achieve in small scale. The phenomena are so complex that the equipment itself often significantly influences the results. Precise definition of apparatus, procedure, and conditions is tantamount to meaningful comparison or application of the published results. Thus, the following portion of the review is devoted specifically to a critical assessment of the experimental features of past work.

2.2. Experimental Equipment

The types of apparatus are grouped into two general areas: captive sample techniques where the coal sample is stationary or fixed during the run, that is, a batch experiment with respect to the solid phase, and continuous coal flow schemes where the coal is continuously fed and withdrawn from the apparatus. The techniques and conditions achieved in many of the recent investigations are consolidated in Table 2. Numerous other studies have been carried out at extremely low heating rates, and it remains to be established whether such data are applicable to the high heating rates anticipated in coal gasification operations. Also, several studies based on the heating of coal particles using shock tubes (Woodburn et al., 1974), plasma jets (Anderson et al., 1968; Bond et al., 1963; Graves et al., 1966), xenon flash tubes (Sharkey et al., 1964; Rau and Seglin, 1964; Granger and Ladner, 1970), and lasers (Sharkey et al., 1964; Schultz and

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* Variously termed thermal decomposition, carbonization, devolatilization.

† Referred to as hydrogasification, hydrocarbonization, hydrogenation, hydrogenolysis, noncatalytic methanation.

TABLE 2. EXPERIMENTAL TECHNIQUES AND CONDITIONS

Investigator	Technique	Residence time, *s*	Temp., °C	Heating rate, °C/s
Captive sample techniques				
Standard proximate analysis (ASTM, 1974)	Crucible	420	950	15-20
Wiser et al. (1967)	Crucible	300-72 000	400-500	15-20
Portal and Tan (1974)	Crucible and basket	15-1 200	550-1 150	0.5-250
Gray et al. (1974)	Crucible	420	950-1 200	0.3-20
Hiteshue et al. (1962*a, b*; 1964)	Hot rod	20-900	480-1 200	10
Feldkirchner and Linden (1963); Feldkirchner and Huebler (1965)	Semiflow	10-480	704-927	100-300 (seems high)
Moseley and Paterson (1965*a*)	Railway heater	15-165	815-950	25
Feldkirchner and Johnson (1968); Johnson (1971)	Thermo-balance	Several to 7 200	≤925	≤100
Gardner et al. (1974)	Thermo-balance	25-3 000	850-950	—
Loison and Chauvin (1964)	Elect. grid	0.7	≤1 050	1 500
Rau and Robertson (1966)	Elect. grid	1-1.5	900-1 200	600
Jüntgen and Van Heek (1968)	Elect. grid	0.7	≤1 000	1 500
Koch et al. (1969)	Elect. grid	7	≤1 500	167
Mentser et al. (1970, 1974)	Elect. grid	0.05-0.15	400-1 200	8 250
Cheong et al. (1975)	Elect. grid	<1-1 800	300-1 000	≤1 000
Anthony et al. (1974, 1975, 1976)	Elect. grid	0.1-20	400-1 100	100-12 000
Graff et al. (1975); Squires et al. (1975)	Ring of coal	1-6 (gas), 10-30 (solid)	600-1 000	650
Coal-flow techniques				
Stone et al. (1954)	Fluidized bed	10-2 500	400-700	—
Peters et al. (1960, 1965)	Fluidized bed	1-15	600-1 100	300
Pitt (1962)	Fluidized bed	10-6 000	400-700	—
Jones et al. (1964)	Fluidized bed	~2 400	427-1 093	1 000+
Friedman (1975)	Fluidized bed	1 800-3 600	300-650	—
Zielke and Gorin (1955)	Fluidized bed	—	816-927	—
Birch et al. (1960, 1969)	Fluidized bed	500-9 500	500-950	—
Eddinger et al. (1966)	Entrained flow	0.008-0.04	625-1 000	2 500+
Howard and Essenhigh (1967)	Entrained flow	0-0.8	200-1 550	22 000
Badzioch et al. (1967, 1970)	Entrained flow	0.03-0.11	400-1 000	25 000-50 000
Kimber and Gray (1967*a, b*)	Entrained flow	0.012-0.34	780-2 000	150 000-400 000
Belt et al. (1971, 1972)	Entrained flow	≤1	816-1 038	—
Sass (1972)	Entrained flow	A few	538-650	10 000
Coates et al. (1974)	Entrained flow	0.012-0.34	650-1 370	—
Moseley and Paterson (1965*b*)	Entrained flow	0.17-2.5	790-1 000	1 000+
Glenn et al. (1967)	Entrained flow	2.4-10.4	921-971	—
Johnson (1975)	Entrained flow	5-14	482-843	28 (or very fast)
Shapatina et al. (1960)	Free fall	0.45-14 400	≤550	—
Moseley and Paterson (1967)	Free fall	A few	840-1 000	—
Feldmann et al. (1970)	Free fall	A few	650-900	—

Sharkey, 1967; Joy et al., 1970; Vastola and Pirone, 1966) were conducted at such high heating rates as virtually to defy acquisition of kinetic data. Such work has typically been of an exploratory nature and confined to incomplete analysis of final decomposition products for varying exposures times and intensities.

2.2.1. Captive Sample Techniques

The best known example of the captive sample technique is the standard proximate analysis for volatile content (ASTM, 1974). A weighed sample of ground coal in a crucible is suspended for a designated time in a vertical furnace at a specified temperature. The measured weight loss in excess of moisture is attributed to volatile release. The major disadvantage of such an apparatus for kinetic studies is the slow heating [rate estimated by Zielinski (1967) and recently confirmed by Gray et al. (1974) and Portal and Tan (1974) to be approximately 15° to 20°C/s], during which most of the devolatilization occurs. Wiser et al. (1967) employed a variation of this technique in studying coal pyrolysis rates. The initial reading was taken after 300 s when, for example, at a final temperature of 500°C, over 60% of the final weight loss had already occurred. The problem is magnified at higher temperatures since the rate of pyrolysis increases approximately exponentially with temperature.

A semicontinuous technique called the hot rod reactor was employed for hydrogenation studies by the Bureau of Mines (Hiteshue et al., 1962*a*, *b*; 1964). Several grams of coal particles were placed in an electrically heated vertical tube, and hydrogen was passed through the bed. The coal was heated to the final temperature in about 20s, and the resulting products were analyzed. Workers at I.G.T. in the early early 1960's also used a semiflow reactor, where a few grams of coal char were charged batchwise into a vertical reactor and suspended on a screen above a bed of preheated alumina (Feldkirchner and Linden, 1963; Feldkirchner and Huebler, 1965). Various gas mixtures, primarily hydrogen and steam, were passed through the static charge, and the effluent was analyzed. The char heat-

Press., atm	Ambient gas	Particle size, μm
1.0	Air (lid on)	≤250
1.0	N_2	246-417
1.0	N_2	≤45-88
1.0	N_2	≤200
18-400	H_2	250-600
34-168	H_2, H_2O	841-1 000
18-95	H_2	150-300
≤100	H_2, N_2, H_2O, etc.	425-850
35-69	H_2	500-1 000
Vacuum	—	50-80
1.0	—	250-425
Vacuum	—	50-60
Vacuum	—	75-630
Vacuum	—	44-53
Vacuum-3.4	—	90-355
0.001-100	H_2, He N_2	53-1 000
69	H_2	≤44
1.0	N_2	200-600
1.0	N_2	1 000-3 000
1.0	—	200-600
1.0	N_2, H_2O	≤1 000
1.0	H_2O	250-710
1-30	H_2, H_2O, etc.	150-212
21-42	H_2, etc.	150-710
1.0	He	6 150
1.0	Air	80% ≤ 74
1.0	N_2	20
1.0	Ar	22-50
1-28.2	H_2, N_2	70% ≤ 74
1.0	—	25-80
1.0	H_2, H_2O, etc.	≤74
50-520	H_2	100-150
70-84	H_2, CO, etc.	≤44
18-52	H_2, He	75-90
45-490	N_2	150-200
45-490	H_2	100-150
35-205	H_2	150-300

ing rates were allegedly several hundred degrees centigrade per second, and the initial gas sample was taken after 20 s. It is interesting to note that one of the stated reasons for developing these techniques was an apparent need for rapid heating and the capability to analyze data for short residence times at high temperatures. Moseley and Paterson (1965*a*) used a novel variation on this theme: coal and char powders were spread along a tubular reactor mounted horizontally above a railway along which a series of burners were propelled followed by jets for cooling. Heating and cooling rates of 25°C/s were achieved with a minimum of 15 s at temperature.

A thermobalance system has been used by Johnson in recent studies at I.G.T. (Feldkirchner and Johnson, 1968; Johnson, 1971). About 0.5 g of coal enclosed in a cylindrical wire mesh basket is lowered into a preheated reaction zone, and the sample weight is continuously recorded. The maximum heating rate attainable is probably no more than a few hundred degrees per second, based on the work of Portal and Tan (1974) which included use of a similar wire mesh basket and bed temperature measurement with a thermocouple and fast-speed recorder While the mesh basket is a substantial improvement over the crucible, the above-mentioned problem of slow heat up (and also cooling) still requires attention. A delay of 15 s or more before the first data are taken prevents resolution of a regime of considerable reaction as noted by both Moseley and Paterson and the Bureau of Mines workers. The observed initial rate is necessarily an average over this minimum residence time and the associated temperature-time history. Continuous weighing (for example, Johnson) circumvents the difficulty of a minimum residence time, but the fact that nearly all the pyrolysis and a substantial portion of the reaction with hydrogen occurs while the temperature is rising complicates the kinetic analysis. The thermobalance is suited primarily for studies of slower char gasification reactions (time scale of minutes) and has been so employed successfully at I.G.T. and at Case-Western Reserve (Gardner et al., 1974).

Several studies have involved devolatilization of approximately monolayer samples of coal particles on an electrically heated screen. Loison and Chauvin (1964) achieved rapid heating to about 1 050°C with this technique, measured yields of gas, liquid and char, but did not obtain rate date. Jüntgen and Van Heek (1968) investigated the kinetics of evolution of several gaseous species with a similar technique combined with mass spectometry. Apparently no attempt was made to weigh or analyze the solid residue. Rau and Robertson (1966), on the other hand, heated their grid more slowly but held the sample at the final temperature for several seconds. They measured sample weight loss but did not analyze the volatile products.

Mentser et al. (1970) pyrolyzed in vacuo 250μg coal samples in microcylinders formed with 400 mesh stainless steel screen and determined total weight loss by microbalance weighings of the screen and sample. The screens were heated at a constant predetermined rate of 8 250°C/s for different times, thereby generating data on the effect of final temperature on weight loss. The gases were analyzed by mass spectrometry in many of the tests. The data exhibited an unusual negative rate of weight loss for several coals over the temperature range 700° to 1 000°C. One plausible explanation is that certain volatile species expelled from the coal at temperatures below 700°C cracked on the screen at higher temperatures and redeposited significant quantities of carbon. This effect might have been avoided by sweeping the products away with continuous pumping or by dilution with inert gases.

Anthony et al. (1974, 1975, 1976) used approximately 10 mg samples and a dual heating circuit that permitted control of heating rate, from 100 to 12 000°C/s, and maintenance of a preselected final temperature. Weight loss was measured by weighing sample plus screen before and after the run, and the temperature-time history of the sample was obtained with a fast-response thermocouple and recorder. A weight loss vs. time curve for a given set of conditions was obtained from a series of runs of different time duration. Time resolution of the weight-loss data was about 20 ms, adequate for kinetics studies even for the most rapid heating rates. The heating element was enclosed in a high-pressure vessel, permitting hydrogenation as well as pyrolysis studies. The initial coal/gas ratio was small enough to ensure large dilution of the volatiles in order to retard cracking and carbon deposition on the screens. The apparatus was recently modified to permit volatile product collection and analysis. A complementary study by Cheong et al. (1975) is also underway.

A disadvantage of the grid heating technique is the necessity for heavy electrical leads which preclude continuous monitoring of conversion. Also, caution should be exercised in the use of such apparatus in the study of volatiles composition, which may be appreciably altered by catalytic cracking on the hot screens. Under certain conditions, carbonaceous deposits have been observed, indicating major changes in volatile species (Anthony et al., 1975, 1976).

Use of a technique in which about 10 mg of coal particles are deposited in a thin ring on the inside surface of a stainless steel pipe through which hydrogen is passed was recently reported (Squires et al., 1975; Graff et al., 1975). The pipe is electrically heated, and the volatiles are swept away for analysis. The amount of carbon contained in the char, and presumably also in any material deposited in the hot system, is determined by measurement of carbon dioxide produced in a subsequent burnout cycle with oxygen. Preliminary results indicate some difficulties with carbon balances, since up to 20% of the carbon is unaccounted for at lower temperatures. The extent of cracking in the tube is unknown, although it appears to be significant based on the carbon balances and previous measurements (Gentry, 1928*b*; Brooks, 1966; Slotboom and Penninger, 1974). Finally, the acquisition of kinetic data would appear to be difficult. Attempts to obtain such information from product gases would require accurate, knowledge of residence time distributions and species production and loss in wall catalyzed reactions. The latter knowledge is, of course, also needed to infer what the volatile product distribution and yield would be in the absence of the hot tube wall. In addition, since the solid phase cannot be monitored continuously, some means of rapidly heating and cooling the sample for run times of varying duration would be needed. Given the relatively large thermal inertia of the pipe, whose weight is over 2 000 times that of the coal, rapid quenching of the sample would be difficult.

2.2.2. Coal Flow Techniques

Fluidized Bed. Stone et al. (1954) and Pitt (1962) injected coal particles into preheated fluidized beds of sand at 400° to 700°C. The technique provided rapid heat transfer to the particles, and sampling times were about 10 to 15 s. However, nearly all of the devolatilization occurred prior to the first datum point. Based on total volatiles released, Pitt's coal at the first datum point was 62% devolatilized at 450°C and 89% at 650°C. Peters et al. (1960, 1965) studied much larger particles (1 to 1.15 mm) at higher temperatures (600° to 1 100°C) and used improved sampling procedures that permitted data acquisition to start at a residence time of 1 s, essential for a process that was complete in 3 to 4 s. Knowledge of particle temperature was imprecise, since the response of the center of a 1 mm coal particle will lag that of the surface by nearly 3 s. Jones et al. (1964) report fluidized-bed results that serve as a harbinger of the COED process, discussed later.

There are several instances of fluidized beds being employed to study the hydrogenation of coal or coal chars (Birch et al., 1960, 1969; Zielke and Gorin, 1955). One of the key problems with fluidized-bed studies is the agglomerating tendency of fresh bituminous coal. The above studies were confined to partially devolatilized chars (for example, Zielke and Gorin with Disco char) or nonagglomerating coals (for example, Birch et al. with Yalbourn brown coal). Residence time definition and control are also exceptionally difficult in work with fluid beds.

Entrained Flow. Eddinger et al. (1966) published results obtained by passing a gas entrained stream of coal particles through a heated tube. The principal objective of this work was to achieve rapid heating conditions and simultaneously to obtain sufficient quantities of products for analysis and characterization. Howard and Essenhigh (1967) reported data on rapid pyrolysis of coal particles as a part of a broader study on pulverized coal combustion. Samples were simultaneously collected and quenched with a water cooled probe at points along the flow path through the pyrolysis zone of a vertical one-dimensional or plug flow flame of pulverized coal and air. Time resolved records of total weight loss and weight loss by devolatilization were estimated from volatile and ash analyses of the collected particles and knowledge of the flow velocity. Particle temperature in this system typically rose from 200° to about 1 550°C, with a heating rate of approximately 22 000°C/s.

Badzioch et al. (1967, 1970) entrained very fine coal particles ($\sim$20 μm) in a preheated laminar gas stream and then collected the reacted particles in a water cooled probe at designated distances downstream of the feed point. Heating rates of 25 000 to 50 000°C/s were reportedly attained for transit times of 30 to 110 ms and temperatures of 400° to 1 000°C. The higher temperature results are reported by Kimber and Gray (1967*a*, *b*). Direct weight loss measurements were not possible, since the apparatus did not permit quantitative recovery of freshly devolatilized particles stuck to the inside walls of the collector tube. However, estimated weight losses were obtained from proximate analysis of the collected char for volatile matter and ash. No analysis of product gases was attempted. Laminar flow reactors of the Badzioch type are now in use at M.I.T. and Pennsylvania State University, and both groups are building high-pressure versions of the reactor.

Moseley and Paterson (1965*b*) introduced a high-pressure apparatus in which finely divided particles of coal chars (100 to 150 μm) entrained in hydrogen were passed through a preheated reaction zone. Heating rates well over 1 000°C/s and residence times as short as 0.17 s were possible. The unit could handle coal chars and dry lignite but failed to operate with fresh caking coal owing to agglomeration. Glenn et al. (1967) used an electrically heated, vertical, continuous flow reactor into which coal particles (250 μm), slurried in water, were fed with various mixtures of synthesis gas. They reported that the addition of very fine silica particles ($\sim$3 μm) and a reduction in coal concentration in the slurry remedied the agglomeration problem. Johnson (1975) recently described a coiled tubular reactor, used for the study of lignite hydrogasification, that can be heated in stages so as to attain different heating rates.

Free Fall Reactor. Coal particles are introduced and dispersed at the top of a large diameter reactor and allowed to fall at terminal velocity through a preheated reaction zone. For example, Shapatina et al. (1960), as reported by Badzioch (1961), studied rapid devolatilization of coal by dropping particles (150 to 200 μm) through a vertical furnace. The emphasis of their work was on composition of volatile products instead of kinetics, and most of their data were obtained at temperatures below 550°C. Feldmann et al. (1970), using a scheme suggested by Hiteshue et al. (1964), employed coal particles in the size range 150 to 300 μm and estimated a residence time of 0.33 s in a reaction zone of length 91 cm. Moseley and Paterson (1967) studied 100 to 150 μm particles and estimated a residence time exceeding 0.5 s for a 137 cm fall. An important feature of the free fall technique is the ability to gasify coal particles under rapid heating conditions without agglomeration. The difficult estimation of residence time for a particle undergoing significant density changes due to swelling and gasification is one of the most serious drawbacks to the use of this method in kinetics studied.

Consolidation of the results from different equipment requires a good understanding or model of the controlling phenomena. Even to scale-up geometrically similar reactors without a clear appreciation of the relative influences of heat and mass transfer and chemical kinetics is risky. This rationale is the basis for the following expiscation for models.

3. DEVOLATILIZATION

3.1. General Observations

Coal is the product of very slow decomposition of organic matter deposited in prehistoric times. The age of coal is indicated by its carbon content or rank, for example, lignite, bituminous, anthracite, and the nature of the original organic matter is reflected by the maceral composition of the coal. The decomposition can be accelerated artificially by elevating the temperature. Upon being heated at a more or less conventional rate, coal begins to decompose at 350° to 400°C into a carbon rich residue and a hydrogen rich volatile fraction as mentioned earlier. The decomposition continues until a temperature typically around 950°C is reached which, if maintained for an extended time, results in a residue of nearly pure carbon possessing a structure approaching that of graphite. The accumulated volatiles are comprised of various gases and liquids, the relative proportions of which depend on the coal type and the manner of heating.

In the early 1960's investigators in Germany (Peters et al., 1960, 1965), France (Loison and Chauvin, 1964), England (Badzioch, 1961), and the United States (Jones et al., 1964) found that rapid heating techniques for coal permit substantially more volatiles than traditional slow heating methods. Furthermore, the liquid or tar fraction seemed most strongly influenced, resulting in considerable excitement over the prospects of renovating the obsolete coal carbonization industry. Much work has since focused on the kinetics, mechanism, and product distribution in order to provide a basis for choosing and optimizing a commercial scheme.

3.2. Kinetics and Mechanism

3.2.1. *Simple Reaction Models*

The complex decomposition and transport phenomena involved in coal devolatilization are not yet amenable to exact description. Many authors have approximated the overall process as a first-order decomposition occurring uniformly throughout the particle. Thus, the rate of devolatilization is expressed as

$$dV/dt = k(V^* - V) \tag{1}$$

where $V \rightarrow V^*$ as $t \rightarrow \infty$. The unknown parameters k and V^* have usually been the focus of kinetic studies.

V^* represents the effective volatile content of the coal. Badzioch and Hawksley (1970) emphasize that V^* is to be carefully distinguished from volatile matter VM, determined by proximate analysis, which is a convenient standard but a deceptive reference when the conditions of interest differ significantly from those of the proximate test. For example, it is incorrect to associate VM with the potential yield of volatiles from pulverized coal particles widely dispersed in a gas. The volatiles escaping from particles in the packed bed employed in proximate analysis apparently undergo degradation, since a thin film of carbon is readily observable on the upper surfaces of the crucible, but the extent of such cracking within the bed is unknown.

Workers at the British Coal Utilization Research Association (BCURA) studied the relationship (or lack thereof) between actual volatile yield and proximate volatile content of coal and char under a wide range of conditions. Gregory and Littlejohn (1965) analyzed extensive literature data on retort carbonization of coals and found the yields to be less than *VM*. Badzioch and Hawksley (1970) observed that the yield of volatiles from pulverized coal particles entrained and rapidly heated in preheated inert gas exceeds the loss of proximate volatile matter found from the difference between the proximate volatile matter of coal and that of char. The results for eleven different coals were correlated by the empirical relation

$$V^* = Q(1 - VM_c)VM \tag{2}$$

Experimental values of Q varied from 1.3 to 1.8, depending on coal type, which led to values of V^*/VM greater than 1.

The observation of volatile yields exceeding proximate volatile matter is consistent with the results of other investigators who rapidly heated pulverized coal particles dispersed in gas or held in monolayers or thin beds (Loison and Chauvin, 1964; Jones et al., 1964; Eddinger et al., 1966; Rau and Robertson, 1966; Mentser et al., 1970, Anthony et al., 1975). The ratio V^*/VM varies from 0.75 to 1.36 for several American, British, and French coals (Table 3). In a similar manner, both Peters (1960) and Sass (1972) found flow schemes with rapid heating of coal particles suspended in gas to give significantly higher yields than the standard Fischer retort method.[*]

The data in Table 3 indicate that changes in heating rate in the range 600° to 50 000°C/s produce very little effect on volatiles yield as substantiated by Anthony et al. (1976) using a bituminous coal and a lignite. Yield increases sometimes attributed to heating rate probably result primarily from the conditions employed to achieve faster heating, such as small particles well dispersed or thinly spread, which avoid some of the cracking reactions and carbon deposition associated with packed beds. Another important observation is that not all coals give yields exceeding the proximate volatile content. Although the BCURA workers correctly note that some of their yields exceed by 80% [value of Q in Equation (2)] the loss of proximate volatile matter, none of the yields exceed the total proximate volatile matter by more than 36%. Residence times much longer than those (several seconds) associated with the data in Table 3 would be required to complete the devolatilization of char, which is known to be very slow and to account for about 5 to 8% of the original moisture free, ash free coal (Shapatina et al., 1960; Howard, 1965; Badzioch, 1967; Anthony, 1974). Therefore, the experimental yields shown in Table 3 are not truly V^* ($t = \infty$) as indicated, but only a close approximation.

The rate constant in Equation (1) is typically correlated with temperature by an Arrhenius expression

$$k = k_0 e^{-E/RT} \tag{3}$$

A collection of experimental k values is illustrated in Figure 1, and the associated rate parameters and coal prop-

TABLE 3. COMPARISON OF EXPERIMENTAL YIELDS WITH PROXIMATE VOLATILE MATTER

Investigators, coals, and conditions		Prox. *VM*	Expt'l[a] V^*	V^*/VM
Loison and Chauvin (1964)				
Maigre Oignies		8.4	8.4	1.00
Bergmannsgluck	(MF[d] basis;	18.1	23.6	1.30
Emma	heated to	20.4	24.5	1.25
Lens-Lieven	1 000°C at	24.4	26.7	1.09
Flenus de Bruay	1 500°C/s)	31.0	39.6	1.18
Wendell III		33.9	34.5	1.02
Faulquemont		36.4	36.7	1.01
Rau and Robertson (1966)				
Colver (MVB[b])		25.3	19	0.75
Kopperston #2 (HVAB[c])	(MF[d] basis;	31.6	36	1.14
Federal (Pitts. HVAB[c])	heated to	37.7	49	1.30
Elkol (Wyo. Subbit.)	950°C at	40.7	48	1.17
Orient #3 (HVB[b])	600°C/s)	44.0	41	0.93
Mentser et al. (1974)				
Pocohontas #3	(MF[d] basis;	16.8	18.5	1.10
Lower Kittanning	heated to	25.3	30.8	1.22
Pittsburgh	1 200°C at	35.1	47.9	1.36
Rock Springs	8 000°C/s)	37.7	42.4	1.12
Colchester		48.0	55.8	1.16
Badzioch and Hawksley (1970)				
NCB 203 (K)		17.7	17.7	1.00
NCB 301a (J)		22.7	20.6	0.91
NCB 301b (H)	(MAF[e] basis;	25.2	26.0	1.03
NCB 602 (E)	heated to	34.3	44.2	1.29
NCB 401 (G)	950°C at	34.4	35.1	1.02
NCB 601 (F)	25 000-	35.3	45.1	1.28
NCB 802 (D)	50 000°C/s)	36.1	47.0	1.30
NCB 902 (B)		36.4	40.0	1.10
NCB 802 (C)		37.8	42.8	1.13
NCB 902 (A)		37.9	42.9	1.13
Anthony et al. (1975)				
Pittsburgh (Bit.)				
650°C/s	(MAF[e] basis;	46.2	53.7	1.16
10 000°C/s	heated to	46.2	56.2	1.22
Montana Lignite	1 000°C at			
650-10 000°C/s	rates shown)	46.2	41.1	0.89

[a] Peak weight loss corresponding to V^* was achieved at the final (highest) temperature in all cases except Mentser et al., where the peak occurs at intermediate temperatures.

[b] Medium volatile bituminous.

[c] High volatile A bituminous.

[d] Moisture free.

[e] Moisture and ash free.

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[*] The Fischer retort procedure involves slowly heating 20 to 100 g of coal to a designated temperature (400 to 600°C) and holding it there until evolution of volatiles ceases. The coal is heated in a special aluminum retort with an outlet tube leading to a condenser where liquid products are collected (Fischer, 1925).

erties are summarized in Table 4. There is little agreement on the observed rate constants, with several orders of magnitude discrepancy at a given temperature. Apparent activation energies range from 2 to over 50 kcal/mole. Some, but by no means all, of the disagreement is probably attributable to coal type even though the data shown are limited to high volatile coals. Differences in equipment and experimental procedures are undoubtedly also important.

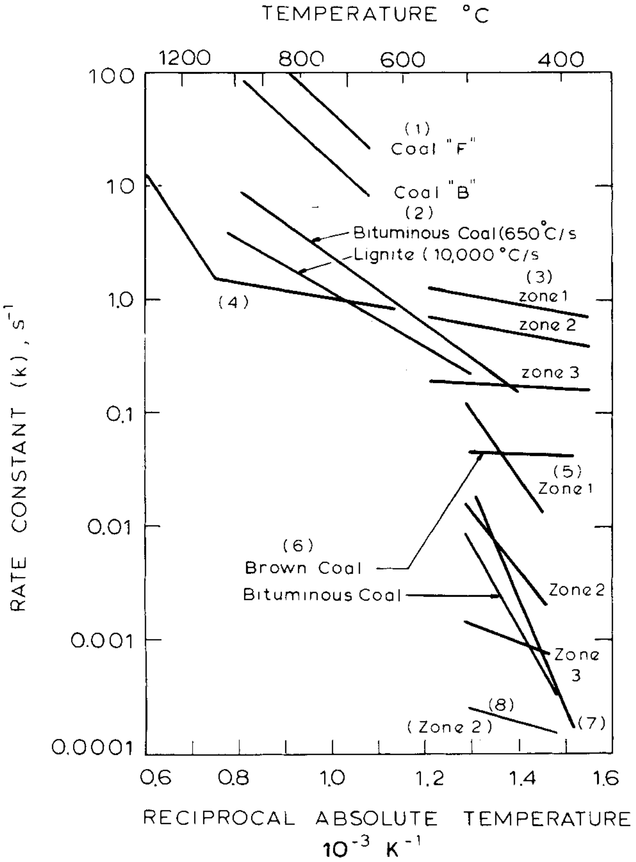

Fig. 1. Comparison of simple first-order coal devolatilization rate constants from different investigators [(1) Badzioch and Hawksley (1970), (2) Anthony et al. (1975), (3) Shapatina et al. (1960), (4) Howard and Essenhigh (1967), (5) Stone et al. (1954), (6) Van Krevelen et al. (1951), (7) Boyer (1952), (8) Wiser et al. (1967)].

Many authors have contended that a simple, first-order model is inadequate. One attempt to improve the utility of Equation (1) has been to describe devolatilization as a series of several first-order processes occurring in different time intervals. Thus, Shapatina et al. (1960) depict three stages (0 to 0.06, 0.06 to 0.1 and 0.1 to 180 s), and Stone et al. (1954) use time intervals typically much longer than the Soviet work and dependent on coal type and temperature. Another approach has been to use an n^th^ order rate expression

$$dV/dt = k'(V^* - V)^n \qquad (4)$$

Thus, Wiser et al. (1967) found that $n = 2$ gave the best fit to their data over the first 3 600 s of weight loss, while $n = 1$ was preferred for longer times (zone 2 of Figure 1). Skylar et al. (1969) found that values of n from 2 to 8 were required to fit nonisothermal devolatilization data for different coals, which casts much doubt on the validity of Equation (4). Pitt (1962) successfully correlated his devolatilization data with the empirical relation

$$(V^* - V)/V^* = A - B \log(t) \qquad (5)$$

where A and B are constants.

The most serious shortcoming of Equations (1), (2), (4), and (5) is that the apparently asymptotic yield observed after some time at the final temperature, that is, the apparent value of V^*, is a function of final temperature, a fact that is neither mechanistically consistent with nor mathematically amenable to these equations. Figure 2 illustrates how pyrolysis yields depend on temperature. The data of each investigator have been normalized to 100% yield at 1 000°C, an observation consistent with all the previous work save that of Kimber and Gray (1967*b*). The various curves on the plot require some explanation. Dryden's (1957) correlation is based on the slow carbonization of a large number of American and British coals here representing a coal having about 35 to 40% volatile matter (moisture and ash free). The curve is general in the sense that it will accommodate any coal by simply sliding the abscissa to the right or left (~ 50°C to the left

TABLE 4. COAL PROPERTIES AND DEVOLATILIZATION RATE PARAMETERS IN FIGURE 1

Investigators	Coal	*VM* (MF)*	*VM* (MAF)†	*E*, kcal/mole	k_0, s^{-1}	Comments
Badzioch and Hawksley (1970)	B NCB 902	35.2	36.4	17.8	1.14×10^5	
	F NCB 601	34.9	35.3	17.8	3.12×10^5	
Boyer (1952)	St. Fontaine bituminous	—	36.0	45	1.00×10^{11}	Reported by Yellow (1963)
Howard and Essenhigh (1967)	Pittsburgh Seam bituminous	35.9	37.4	27.7	4.92×10^4	$T > 1\,060°$C
				3.4	5.37	$T < 1\,060°$C
Shapatina et al. (1960)	Moscow district brown coal	34.5	50.2	3.6	11.0	Zone 1 (0 — 0.06 s)
				3.8	6.63	Zone 2 (0.06 — 0.1 s)
				1.0	0.37	Zone 3 (0.1 — 180 s)
Stone et al. (1954)	Pittsburgh Seam bituminous	40.7	42.2	27.3	5.41×10^6	Zone 1
				24.4	1.10×10^5	Zone 2
				7.0	0.131	Zone 3
Van Krevelen et al. (1951)	Brown coal	—	51.0	0.7	0.07	Values corrected
	Low-rank bituminous	—	39.5	32.5	1×10^7	by Jüntgen and Van Heek (1970)
Wiser et al. (1967)	Utah bituminous	47.5	—	15.0	47.5	Zone 2 (> 3 600 s)
Anthony et al. (1975)	Pittsburgh Seam bituminous	40.5	46.2	13.3	1.80×10^3	
	Montana lignite	40.3	46.2	20.0	2.90×10^5	Excluding cooling
				11.1	2.83×10^2	Including cooling

* Moisture free.
† Moisture and ash free.

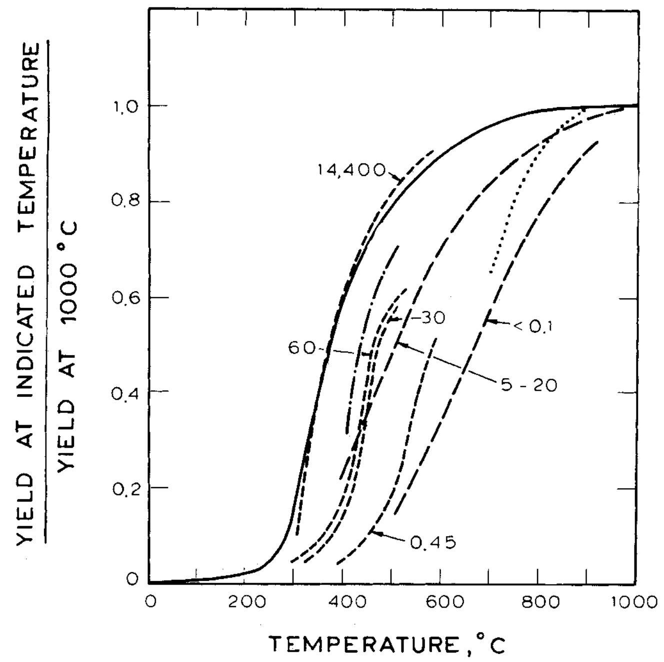

Fig. 2. Effect of temperature on coal devolatilization yields achieved up to different residence times [numbers on curves: residence time (where available), s. curves: solid, Dryden (1957); dots, Kimber and Gray (1967*b*); short dashes, Shapatina et al. (1960); long dashes, Anthony et al. (1975); alternating long and short dashes, Wiser et al. (1967)].

per 10% increase in *VM*) Shapatina et al. (1960) dropped coal particles through a heated chamber (minimum residence time 0.45 s) and then caught and soaked them in a heated trap for the duration of the run. Particles soaked for 14 400 s show a weight loss trend consistent with Dryden's correlation. The yields are less for shorter residence times, for example, 30 to 60 s, and they are diminished further if only the heat up period of 0.45 s is considered. The fact that the additional weight loss observed between 0.45 and 30 s is roughly equivalent to the amount lost between 30 and 14 000 s supports the existence of rapid initial decomposition followed by very slow degasification of char. The results of Kimber and Gray, also for times much less than 1 s, are significantly displaced from Dryden's correlation. Wiser et al. (1967) determined values of V^* by including the contributions of a final devolatilization stage identified as a constant rate period. The yields obtained by Anthony et al. (1975) using bituminous coal at residence times of 5 to 20 s are in good agreement with those of Shapatina et al. at 30 to 60 s. The conversions obtained by Anthony et al. with very rapid heating (10 000°C/s, conversion during heat up only) establish a trend similar to the Soviet yields at 0.45 s.

Since all data in Figure 2 are normalized by using the yields observed at 1 000°C, the curves do not reflect the above-mentioned occurrence of yields in excess of proximate volatile content. Dryden and Wiser used experimental conditions comparable to those of proximate analysis and would not be expected to see changes in total yield at high temperatures. The Soviet workers calculated weight loss as the difference between the measured proximate volatile content of the fresh coal and that of the recovered char. This technique obviously cannot detect yields greater than proximate volatile matter which very likely occurred in the dispersed phase system employed. The measurements of Kimber and Gray were extended to temperatures between 1 000° and 2 000°C where an increase in weight loss and a corresponding decrease in residual volatile matter were observed. Unfortunately, their weight loss determinations were based on the use of the coal ash as a tracer, a questionable procedure in view of changes in ash weight resulting from inorganic reactions at the higher temperatures and loss of ash particles in the collection procedure employed. An experimental check of the Kimber and Gray results at temperatures up to 1 800°C is now underway at M.I.T. (Kobayashi, 1976).

Much of the foregoing discussion has proceeded on the assumption that the rate controlling steps in coal devolatilization are the decomposition reactions. In contrast to this picture, Berkowitz (1960) concluded from his investigation of the pyrolysis of Alberta subbituminous coals at 250° to 524°C that the rate was limited by mass transfer. After studies at higher temperatures, this conclusion was modified by postulating that movement of carbon lamellae is the rate determining process (Berkowitz and Den Hertog, 1962). These conclusions were strongly influenced by low activation energies obtained from the use of Equation (1). Also, Zielinski (1967) collated devolatilization data from several different authors and concluded that heating rate is the controlling factor. In both cases, these mechanisms were predicated on observations better explained by alternative theories. Furthermore, simple heat and mass transfer models are woefully inadequate for dealing with the complexities of coal devolatilization.

3.2.2 *Complex Reaction Schemes*

Quantitative methods for modeling the temperature dependent behavior of coal devolatilization are clearly not well established. Wiser et al. (1967) treated their data isothermally, integrating first- and second-order versions of Equation (4) and then inserting an appropriate value of V^* depending on temperature. Similarly, Badzioch and Hawksley (1967) correlated data with an expression derived by isothermal integration of Equation (1) and substitution of a temperature dependent function for V^*. Thus neither of these two groups of investigators considered the difficult integration involved in nonisothermal cases where a finite heating period exists. Badzioch and Hawksley claimed that little decomposition occurred during their extremely rapid heat up, and Wiser et al. neglected the weight loss occurring before their sample reached the desired temperature (~300 s to reach temperature). The problem of how to include in kinetic studies the weight loss occurring during heat up has confounded nearly all investigators attempting to evaluate coal decomposition on an isothermal basis.

Pitt's (1962) recognition of this problem led him to adapt, as described below, Vand's (1943) treatment of a large number of independent, parallel rate processes. If the thermal decomposition of a coal molecule is assumed to consist of a large number of independent chemical reactions, differences in the strengths of chemical bonds throughout the molecule will cause marked differences in the temperatures at which the various bonds rupture. Since the thermal decomposition of a single organic species is typically described as an irreversible reaction first order in the amount of unreacted material remaining, the rate of volatiles production by a particular reaction within the coal structure can be described in a manner similar to Equation (1) with a subscript i used to denote one particular reaction:

$$dV_i/dt = k_i(V_i^* - V_i) \qquad (6)$$

If k_i is of the Arrhenius form [Equation (3)], integration of Equation (6) for isothermal conditions to find the amount of volatiles yet to be released gives

$$V_i^* - V_i = V_i^* \exp[-k_o t \exp(-E/RT)]_i \qquad (7)$$

Values of $k_{o,i}$, E_i, and V_i^* cannot be predicted a priori

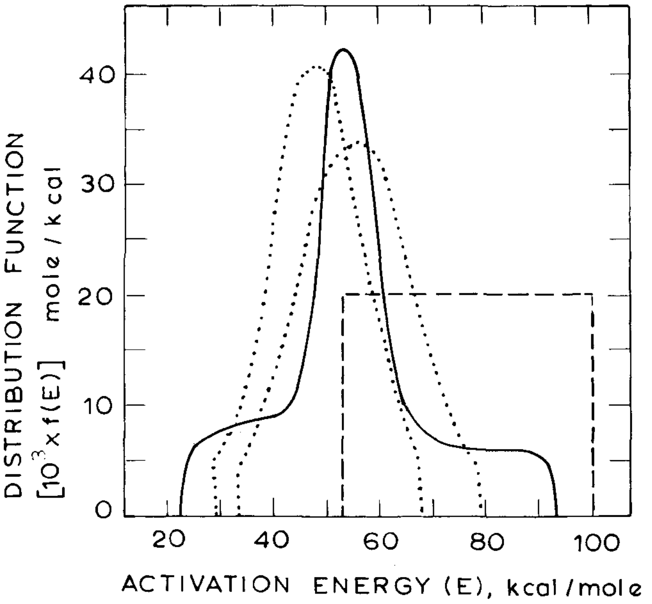

Fig. 3. Comparison of activation energy distributions for coal pyrolysis [curves: solid, Pitt (1962); dashed, Anthony et al. (1975), left-k_0 = $1.07 \times 10^{10} s^{-1}$, right-$k_0$ = $1.67 \times 10^{13} s^{-1}$; dashed, Chermin and Van Krevelen (1957)].

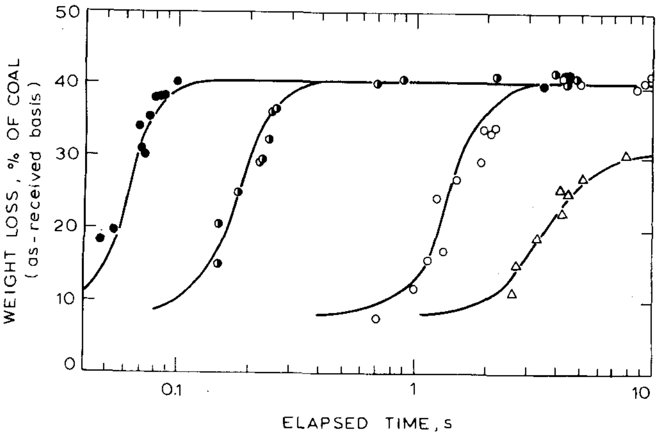

Fig. 4. Effect of time on devolatilization weight loss from Montana lignite at different heating rates and final temperatures [Anthony et al. (1975); Savage Mine lignite; t = 0 at initiation of heating; pressure, 1.0 atm helium; mean particle diameter, 70 μm; final temperature (if attained)—1,000°C (●, ○, ○), 700°C (△); nominal heating rate (°C/s)—10 000 (●), 3 000 (○), 650 (○), 180 (△); curves—Equations (10a) and (11) with V^* = 40.6% by wt. of original coal, E_0 = 48.72 kcal/mole, k_0 = $1.07 \times 10^{10} s^{-1}$, and σ = 9.38 kcal/mole].

and must be estimated from experimental data, a problem multiplied by the number of reactions postulated. The problem is simplified if it is assumed that the k_i's differ only in activation energy (that is, $k_{0i} = k_0$ for all i) and that the number of reactions is large enough to permit E to be expressed as a continuous distribution function $f(E)$, with $f(E)dE$ representing the fraction of the potential volatile loss V^* which has an activation energy between E and $E + dE$. Then V_i^* becomes a differential part of the total V^* and may be written

$$dV^* = V^* f(E) dE \tag{8}$$

with

$$\int_0^\infty f(E) dE = 1 \tag{9}$$

The total amount of volatile material yet unreleased is obtained by summing the contribution from each reaction or by integrating Equation (7) over all values of E using Equation (8). Thus

$$\frac{V^* - V}{V^*} = \int_0^\infty \exp[-k_0 t \exp(-E/RT)] f(E) dE \tag{10}$$

By approximating the term $\exp[-k_0 t \exp(-E/RT)]$ as a step function equal to zero for $E < E_t$ and unity for $E \geqq E_t$, where $E_t = RT \ln(k_0 t)$ and $k_0 = 1.67 \times 10^{13} s^{-1}$, Pitt constructed an $f(E)$ curve to best fit his weight loss data. The resulting activation energy distribution is shown in Figure 3 (other curves discussed later).

Pitt's results are not considered reliable in the initial stages of decomposition because he did not obtain data at solids residence times less than 10 to 15 s. Before the first sample was taken, *devolatilization of the coal was over* 60% complete at 450°C and almost 90% complete at 650°C. Furthermore, Pitt's determination of weight loss as the difference between the proximate volatile content of the coal and that of the char precluded the observation of yields larger than the standard volatile matter content.

Anthony et al. (1975) generalized Equations (7) and (10) as follows to allow for nonisothermal processes:

$$V_i^* - V_i = V_i^* \exp\left(-\int_0^t k_i dt\right) \tag{7a}$$

$$\frac{V^* - V}{V^*} = \int_0^\infty \exp\left(-\int_0^t k dt\right) f(E) dE \tag{10a}$$

In addition, $f(E)$ was assumed to be a Gaussian distribution with mean activation energy E_0 and standard deviation σ. Thus

$$f(E) = [\sigma(2\pi)^{1/2}]^{-1} \exp[-(E - E_0)^2/2\sigma^2] \tag{11}$$

Equations (10*a*) and (11) permit correlation of coal decomposition data by using four parameters (V^*, E_0, σ, k_0) which is only one more than is required in the simple single-step model represented by Equations (1) and (3) (V^*, E, k_0). This replacement of E with E_0 and σ and the associated use of the somewhat more complicated equations eliminates the temperature dependence of V^* and allows data on a given coal under different sets of experimental conditions to be correlated with one set of parameter values, whereas the simple model requires a different set of parameter values for each set of experimental conditions (Anthony, 1974; Anthony et al., 1975). The curves fitted in Figure 4 to data (points) on volatile yields from Montana lignite at different heating rates and final temperatures illustrate the good correlations obtained with the improved model. Although the model can also accommodate a statistical distribution of k_0, the associated introduction of an additional adjustable parameter (that is, the single k_0 is replaced by a mean and standard deviation) is unnecessary in the correlation of total weight loss data in view of the good fits already obtained.

The activation energy distribution found by Anthony et al. (1975) for Montana lignite is compared in Figure 3 with Pitt's results. Both the lignite and Pitt's Binley coal contained 46.2% (MAF) volatile matter. Pitt used a fixed value of k_0 ($1.67 \times 10^{13} s^{-1}$), while the value reported by Anthony et al. ($1.07 \times 10^{10} s^{-1}$) was estimated directly from the lignite data. The higher value of k_0 tends to shift the distribution to higher activation energies. Thus, refitting the lignite data with the statistical model with k_0 fixed at $1.67 \times 10^{13} s^{-1}$ shifted E_0 from the previous value of 48.7 to 56.3 kcal/mole, while the width of the distribution remained almost unchanged (σ = 10.91 vs. 9.38 kcal/mole, previously). Use of the higher value of k_0 is justified, at least to some extent, on theoretical grounds.

From transition state theory, the frequency factor is calculated to have a value around $10^{13}\,s^{-1}$. This is roughly equivalent to the preexponential factor (k_o) in the Arrhenius expression if the entropy of activation is close to zero (Benson, 1968). However, the entropy of activation of reactions in the coal phase is yet to be established. Anthony et al. (1976) recently found $E_o = 54.8$ kcal/mole and $\sigma = 17.2$ kcal/mole with k_o fixed at $1.67 \times 10^{13}\,s^{-1}$ for a strongly caking Pittsburgh Seam coal also of 46.2% (MAF) volatile content.

An interesting characteristic of the statistical distribution model is that it offers a plausible explanation for the low activation energies found with the single-step, first-order model [Equation (1)]. The observed values are typically less than 20 kcal/mole and have led some authors (for example, Berkowitz, 1960) to reject chemical kinetics in favor of mass transfer as the rate controlling process. However, data of Anthony et al. (1975) from experiments in which heat and mass transfer effects were virtually eliminated by design of the technique give activation energies around 10 kcal/mole in the single-step correlation and around 50 kcal/mole in the multiple-step model as noted above. In a similar vein, Jüntgen and Van Heek (1970) demonstrated theoretically that a set of overlapping, independent, parallel first-order reactions can be approximated by a single first-order expression having both lower activation energy and preexponential factor than any of the reactions in the set. In order to illustrate this phenomenon, weight loss vs. time curves for four hypothetical independent first-order reactions having $k_o = 2 \times 10^{10}\,s^{-1}$, and activation energies of 47, 50, 53, and 56 kcal/mole were added together and approximated successfully by a single first-order expression with $k_o = 1.6 \times 10^{6}\,s^{-1}$ and $E = 30.3$ kcal/mole. This finding is clearly in accord with the experimental results of Anthony et al.

The foregoing analysis was limited to correlating coal weight loss or volatile evolution. Acquisition of other types of evidence during the devolatilization process has led to various alternative theories. Based on the melting or plastic behavior of some coals during heating, Van Krevelen et al. (1956, 1961) have pictured coal decomposition as a series of consecutive reactions [coal → metaplast (an intermediate product) → semicoke → coke] with primary volatiles formed in the resolidification of the metaplast and secondary gas evolved during the final coking stage. Recognizing the inadequacy of this simple sequence for explaining temperature-dependent yields, Chermin and Van Krevelen (1957) theorized that secondary gas evolution from semicoke becomes progressively more difficult as the reaction proceeds. This behavior was represented by the conversion-dependent activation energy in the following rate equation:

$$dV/dt = k_o(V^* - V)\exp\{-[E_{\max} - a(V^* - V)]/RT\} \tag{12}$$

It can be shown that Equation (12) is simply a special case of Equation (10), where $f(E)$ is a uniform distribution. Integration of Equation (8)

$$\int_0^V dV^* = V^* f(E) \int_{E_{\min}}^{E} dE \tag{13}$$

with $f(E) = (E_{\max} - E_{\min})^{-1}$ and $a = (E_{\max} - E_{\min})/V^*$ gives

$$E = E_{\max} - a(V^* - V) \tag{14}$$

Chermin and Van Krevelen estimated values for the uniform distribution using data on the residual volatile content of chars. Their results are included in Figure 3.

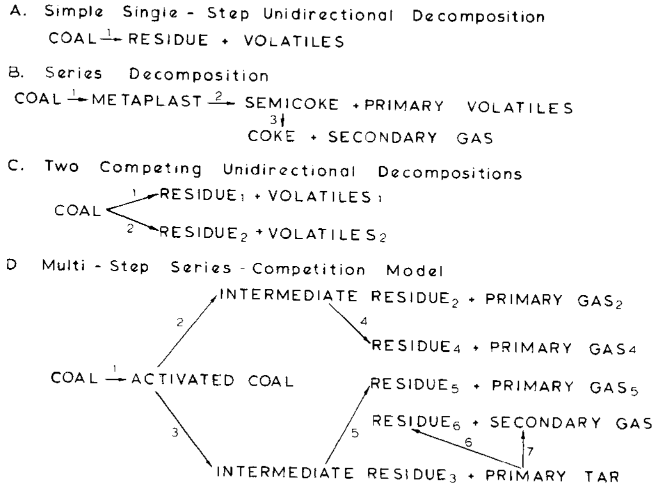

Fig. 5. Coal pyrolysis models [A. Equation (1); B. Van Krevelen (1961); C. Kobayashi (1972); D. Reidelbach and Summerfield (1975)].

The shape of the assumed uniform distribution is, of course, very different from the ones found by Pitt and Anthony et al. Furthermore, estimation of the distribution from data on residual volatile matter neglects yields in excess of proximate volatile matter, and predicted rates based on the results disagree badly with high temperature data.

Jüntgen and Van Heek (1968) proposed that modeling attempts should focus on the individual volatile species and subsequently correlated their results with a nonisothermal variation of Equation (1). By replacing k with an Arrhenius expression and substituting a constant heating rate, that is, $dT/dt = m$, they obtained

$$dV_j/dT = (k_{o,j}/m)(V_j^* - V_j)\exp(-E_j/RT) \tag{15}$$

The parameters are determined for each evolved species j. Therefore, direct comparison of this information with total weight loss data of the type discussed above is difficult. Most of their experimental work focused on the kinetics of evolution of particular volatile species ($C_1's - C_4's$). The implication was that each volatile species would represent a specific fundamental reaction within the coal structure. However, the evidence showed that the formation of the major volatile species involved complex sets of reactions, thus forcing a definition of activation energy distributions for each species (Hanbaba et al., 1968; Jüntgen and Van Heek, 1969, 1970). This approach seems reasonable in principle, but calculation of total weight loss from such a large set of equations will remain impossible until all evolving species have been measured.

An alternative approach to modeling coal decomposition has been to assume the existence of competitive reactions by which the decomposing material may follow any of a number of reaction paths depending on the temperature-time pattern. This concept is attractive since it offers an explanation of the effects on yield of both temperature and heating rate. Shapatina et al. (1960) attribute to Chuckhanov a model in which coal is assumed to decompose through a combination of parallel and consecutive reactions, each of different kinetic characteristics, but we have no details of this model. Kobayashi (1972) used a model comprised of two competing first-order reactions to correlate devolatilization data published by Kimber and Gray (1967*a*) and Badzioch and Hawksley (1970). Recently, Reidelbach and Summerfield (1975) proposed a ten-step coal pyrolysis model and used a simplified five-step version of it to correlate data of Badzioch and Hawksley (1970) and Peters and Jüntgen (Hanbaba et al., 1968; Koch et al., 1969). The models of Kobayashi and Reidelbach and Summerfield are illustrated in Figure 5, where the reaction

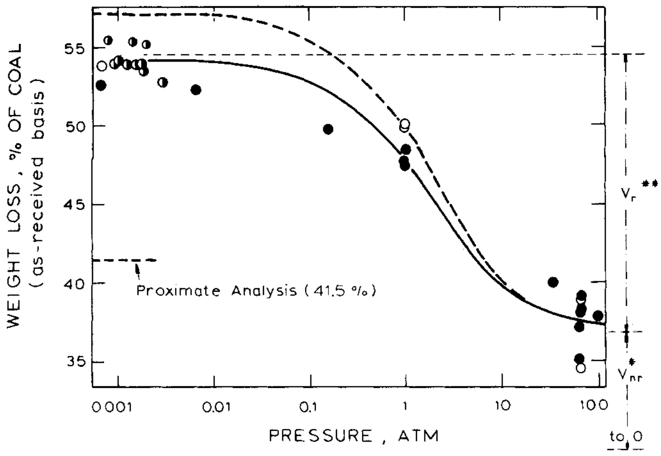

Fig. 6. Secondary reaction model fitted to data on devolatilization weight loss from Pittsburgh Seam bituminous coal at different pressures [Anthony et al. (1975); Ireland Mine coal; final (holding) temperature, 1 000°C; experimental time, 5 to 20 s; mean particle diameter, 70 μm; atm = helium; nominal heating rate (°C/s)—10 000 (○) 3 000 (○), 650 to 750 (●); curves (solid-uncorrected for cracking deposition on sample holder; dashed-corrected for said cracking deposition)—Equation (16) with V_r^{**} (% of original coal) = 17.0 (solid), 20.0 (dashed), V_{nr}^{*} = 37.2% of original coal, and $k_1/k_c = 0.56$ atm^{-1}].

paths proposed by Van Krevelen et al. (see above) are included for comparison. According to the Reidelbach-Summerfield model, coal becomes thermally activated and then decomposes either to tar and char or to primary gas and char. The residual char in each step further decomposes to produce additional gas. The two sets of data noted above were successfully fitted by adjusting fifteen rate and stoichiometric parameters, but such agreement is not unlikely, given the number of adjustable parameters. In comparison with the foregoing, one of the main advantages of Equation (10*a*) is the use of fewer parameters.

Furthermore, Equation (10*a*) is fundamentally a more realistic description of the coal devolatilization process. Coal heated at low temperatures even for extended times will always devolatilize further when the temperautre is raised. The competitive schemes in Figure 5 are inconsistent with this observation when fitted to high-temperature data, since they then predict that pyrolysis may be driven to completion even at low temperatures in times available in the laboratory. By contrast, Equation (10*a*) predicts that the time required to achieve a certain degree of completion of the decomposition decreases strongly with increasing temperature and is so large at low temperatures as to be unattainable in practice. This effect can give the impression of an asymptote having been reached by a low-temperature decomposition when it is compared with one at high temperature (Anthony et al., 1975), thereby explaining why the residual char from low-temperature experiments yields additional volatiles upon being heated to a higher temperature. Such additional volatiles are apparently formed by reactions having activation energies so large as to be immeasurably slow at the lower temperature. The introduction of the concept of a distribution of activation energies is thus seen to allow realistic description of multiple decomposition reactions without the need for a large number of parameters.

It would be premature to reject the schemes of Figure 5 altogether, since product distributions may be significantly influenced by competitive reaction paths. However, each of these schemes will undoubtedly have to be modified by incorporating a distribution of activation energies in some manner. Furthermore, the most important competitive path with regard to effects on product distribution is probably secondary reactions of volatiles during their escape from the particle and passage out of the reactor. For a designer seeking a correlation of devolatilization yields, Equation (10*a*) combined with a description of secondary reactions (see below) is presently the best recommendation.

2.3.3. *Effect of Secondary Reactions*

Mazumdar and Chatterjee (1973) found the dimensions of the coke charge to be quite significant in determining volatile yields, while heating rate was of secondary importance. Similar findings were reported by Gray et al. (1974) and Anthony et al. (1975). In the last paper, sample dimensions as small as single particles 50 μm in diameter were studied. The effect of sample size is sometimes misconstrued as a heating rate effect, since the time required to attain the final temperature usually increases with increasing sample size.

It is generally agreed that secondary reactions are responsible for these variations in yield, though Yellow (1965) and Van Krevelen et al. (1956) have suggested the possibility of fragments of a pyrolysis intermediate (metaplast in Figure 5) being physically carried away by rapidly escaping gases. There is also broad support for the contention that these reactions are primarily concerned with the tar fraction of the volatiles. The increasing tar-gas ratio with increasing yields coupled with the known instability of the tarry species compared to the gaseous volatiles gives considerable weight to this position. There is still disagreement over whether the primary volatiles are relatively small free radical ring structures or large condensed ring structures (essentially identical to the tar ultimately evolved). ESR spectra by Bond (1968) with Den Hertog and Berkowitz's (1960) devolatilization work in the presence of a known free radical scavenger, nitric oxide, support the existence of free radical processes, but the size of the species remains undetermined. In a hydrogen deficient environment, the small species would polymerize to coke unless they could escape as tar at some intermediate stage of polymerization. The escaping tar might also undergo cracking reactions producing coke and gas. Mazumdar and Chatterjee (1973) have discounted the latter reaction since they observed no increase in gas yield as tar was lost in larger beds. However, data of Peters (1960) definitely show an increase in gas yield under retort conditions. Presumably, both cracking and polymerization are involved, but their relative extents are unestablished.

Regardless of the exact nature of the secondary reactions, their extent is strongly influenced by the residence time and concentration of reactive species in contact with hot surfaces. Large packed beds and the accompanying slow rate of heating virtually insure a minimum yield of volatiles by providing sufficient surface area and residence time for the secondary reactions. Similarly, devolatilization at elevated pressures retards the escape of these reactive species, thereby increasing internal concentrations and thus the rate of secondary reactions. Belt et al. (1971) discovered that highest yields of char were obtained from their entrained flow carbonizer at highest inert gas pressures. A similar pressure effect on yield from Pittsburgh Seam bituminous coal was reported by Anthony et al. (1975). Coal type is also important. Thus, Anthony et al. found yields from the Pittsburgh Seam bituminous coal to increase with decreasing particle size and decreasing pressure, while yields from Montana lignite were independent of both pressure and particle size.

In order to develop an approximate model for the effect of secondary reactions on yields of volatiles, Anthony et al. (1975) derived a selectivity expression describing assumed

TABLE 5. DISTRIBUTION OF VOLATILE PRODUCTS OF COAL PYROLYSIS

		Coal		Volatile products, wt.% of coal				$V^*/$
Investigators	Method	Type	VM†	Tar	Gas	Water**	V^*	VM
Sass (1972)	Fischer assay, 500°C	W. Kentucky	41.0	16.3	5.0	9.4	30.7	0.75
	Flow tube, 530-650°C	HVB bit.	41.0	33.0	6.6	1.7	41.3	1.01
Peters (1960)	Fischer assay, 600°C	Furst Leopold	31.0	11.2	10.0	8.1	29.3	0.95
	Fluidized bed, 600°C		31.0	18.7	7.0	7.5	33.2	1.07
Shapatina	Slow heating, 0.08°C/s	Moscow brown	34.5	4.6	11.9	6.0	22.5	0.65
et al. (1960)	Rapid heating to 500°C	coal	34.5	4.0	8.1	9.6	21.7	0.63
Loison and	Thin layer of particles		31.0	25.2	9.6	4.4	39.2	1.18
Chauvin (1964)	heated to 1 050°C at		33.9	22.5	7.9	4.1	34.5	1.02
	1 500°C/s		36.4	18.9	12.6	5.2	36.7	1.01

† Proximate volatile matter, % by weight, moisture free basis.
** Chemically produced, that is, not from coal moisture.

competition between diffusional escape and secondary reaction of reactive volatile species (principally tarry compounds). Thus

$$V^* = V_{nr}^* + V_r^{**}/(1 + k_1P/k_c) \qquad (16)$$

where k_c/P is the overall mass transfer coefficient. This equation was fitted to data accumulated over a pressure range of 10^{-3} to 10^2 atm with values of $V_{nr}^* = 0.37$, $V_r^{**} = 0.17$, and $k_1/k_c = 0.56$. A good correlation is obtained, as shown in Figure 6, with experimental weight loss asymptotes exhibited as expected at high and low pressure extremes. A correction for carbon deposition from volatiles cracking on the sample holding screens is included.

The simplicity of the the above model is misleading. The escape of volatiles is not simply diffusion but a complex process involving a time-dependent pore structure and hydrodynamic flow during the rapid stages of devolatilization. In order to account for this behavior in the study of secondary reactions, Lewellen (1975) recently developed a considerably improved model of volatiles transport in caking coals, based on the concept that the transport occurs primarily through growth and escape of volatile filled bubbles. The model successfully predicts the above-described variations with pressure and particle size of the effects of secondary reactions on volatiles yield and offers a valuable new approach for detailed study of these reactions.

3.3. Composition of Volatile Products

Product distributions from coal devolatilization have been reported in several studies. Some of this information is summarized in Table 5, which should not be construed as comprehensive or even representative. Yields of tar (all liquids except water), gas, and chemically produced water, and the sum of these (V^*), are listed for several different coals and devolatilization methods. The total yield of volatiles is compared with the proximate volatile content of the coal by the ratio V^*/VM, which exceeds unity in several cases. Sass, Peters et al., and Loison and Chauvin all found large tar fractions comprising from 38 to 80% of the volatiles. Rapid heating appears to increase the tar fraction, and Sass as well as Peters et al. note that higher temperatures decrease the tar-to-gas ratio. The Russian work with brown coal produced substantially less tar (around 20% of the volatiles), and rapid decomposition neither enhanced the volatile yield nor increased the tar fraction.

Gas compositions associated with the data in Table 5 are given in Table 6. Methane is a major constituent in all cases, while carbon oxides and hydrogen account for most of the rest. Shapatina et al. (1960) also reported some gas compositions, but interpretation is difficult since their various experiments were not conducted at comparable time intervals. At 541°C with rapid decomposition, the gas analysis was 58.5% carbon dioxide (plus hydrogen sulfide), 22.9% carbon monoxide, 2.4% hydrogen, 10.3% saturates, and 6.9% unsaturates. At higher temperatures, the concentration of carbon dioxide decreased, and that of carbon monoxide and hydrogen increased. Hydrocarbons reached a maximum concentration at 500° to 700°C. It should be emphasized that coal type is likely a major factor in determining the composition of devolatilization products.

The order of appearance of the volatile species when coal is heated at a constant rate is discussed by Howard (1963). After drying, the sequence is chemical water, carbon dioxide, carbon monoxide, higher hydrocarbons (tars, etc.), ethane, methane, and finally hydrogen. The order is not precise, and substantial overlapping occurs. However, a much improved picture emerges when such evidence is linked with information on the chemical structure of coal.

TABLE 6. COMPOSITION OF GASEOUS PRODUCTS OF COAL PYROLYSIS

	Coal	Gas composition, vol. %				
Investigators and conditions	VM††	CO_2	CO	H_2	CH_4	Other
Sass (1972):						7.6†
Flow tube, 530°-650°C	41	10.6	4.9	25	42.3	5.6 C_2H_6
						4.0 C_3H_8
Loison and Chauvin (1964):	31	4.1	15.8	16.9	54.3	8.9†
Thin layer of particles	33.9	2.4	10.0	21.8	52.8	13.0†
heated to 1 050°C at 1 500°C/s	36.4	6.1	20.6	13.1	50.3	9.9†
Peters (1960); Peters et al. (1965):						
600°C fluidized bed	31	12.0	12.3	14.7	50.5	10.5†
600°C Fischer assay	31	10.3	8.7	22.4	54.2	3.7†

†† Proximate volatile matter, % by weight, moisture free basis.
† By difference, composition unknown.

3.4. Physical Factors

3.4.1. *Plastic Behavior*

A coal is characterized as plastic or nonplastic, depending on whether it exhibits thermoplastic behavior, that is, softening and becoming deformable followed by resolidification to form a char, upon being heated either through a certain temperature range or to a temperature above the softening point and there maintained for a certain period of time. Plastic coals are also referred to as caking coals because coal particles in the plastic state are viscous liquid masses capable of coalescence and, upon resolidification, formation of a cake.

The organic matter of a given coal is a heterogeneous mixture of petrographic constituents called macerals which differ in chemical composition and physical behavior. Neavel (1975) states that plasticity is only exhibited by the macerals exinite (a minor constituent of typical coals) and vitrinite, of which only vitrinite has plastic capability in bituminous coals except for a few very unusual coals. A plastic coal ground fine enough to effect substantial liberation of macerals may exhibit under a given set of heating conditions a wide range of individual particle behavior including no softening or swelling, moderate swelling with formation of approximately uniformly distributed macroscopic pores, and extreme cenosphere formation. In the present discussion, the behavior attributed to a given plastic coal represents that of the dominant maceral, vitrinite.

The occurrence of the plastic state is associated with and kinetically similar in many ways to pyrolysis. The temperature limits and time duration of plasticity depend on heating rate and other conditions. At a constant heating rate of about 0.05 °C/s, the plastic region is typically 420° to 500°C (Van Krevelen et al., 1956) with some variation among different coals. At heating rates characteristic of those attained in pulverized coal flames (up to 10^4°C/s), the plastic region extends to 2 000°C or higher (Littlejohn, 1967).

3.4.2. *Internal Structure*

The internal structure of pyrolyzing coal and that of the char product are important in the analysis of mass transfer associated with devolatilization and gasification reactions. The porosity of the fine (molecular sieve) structure of the char from virtually any coal increases steadily as the temperature of its formation is increased, but the accessibility of these pores to penetrant molecules only increases below 500° to 600°C and then decreases dramatically in the range 600° to 1 000°C (Franklin, 1949*a*, *b*; Bond and Spencer, 1958; Van Krevelen, 1961; Evans, 1970). Accessible surface area follows a similar trend for noncaking coals but is radically different for caking coals, showing a sharp minimum extending over the plastic region of the coal (Cannon, et al., 1944).

The most striking macroscopic change occurring during pyrolysis of plastic coals is the formation and motion of gas bubbles within the liquid mass. Under a hot stage microscope, the particles may be seen to soften, become rounded, and swell, while large bubbles of gas repeatedly break through the particle surface as pyrolysis continues (Ergun et al., 1959; Woods et al., 1967; Spackman and Berry, 1968; Schapiro, 1975). The resulting char has a high large-scale porosity, presumably formed by entrapped gas bubbles (Woods et al., 1967; Feldmann et al., 1971).

The development of large-scale porosity is carried to an extreme in the formation of swollen, essentially hollow, char particles called cenospheres from plastic coal particles heated at moderate to rapid rates in the absence of air (Newall and Sinnatt, 1924, 1926, 1927; Sinnatt et al., 1927; Sinnatt, 1928, 1929; Mason and Schora, 1967; Lightman and Street, 1968; Street et al., 1969). Cenosphere structure varies considerably but is characterized by the presence of one to a few large cavities in a generally contiguous spherical shell and by a large degree of swelling, frequently as much as a fortyfold increase in volume over that of the original coal (Sinnatt, 1928, 1929). Street et al. (1969) noted an apparent absence of pores in the surfaces of cenospheres, suggesting that any large pores in the original coal do not survive passage through the plastic region.

3.4.3. *Transport Processes*

The growth and escape of gas filled bubbles constitutes an important mode of volatiles transport in plastic coals. Thus, when hydrodynamic and diffusional flows become greatly impeded by the essentially impenetrable pore structure developed during the period of plasticity, regions of high-pressure gas form within the particle and expand against the viscous and other forces to produce growing gas bubbles that may eventually burst through the particle surface as small jets. The above-noted decrease in the accessibility of the fine structure porosity of nonplastic coals also presumably leads to development of high-pressure regions, but these coals cannot flow and allow the incipient bubble to expand. Hence, the pressure is expected to rise until the rate of hydrodynamic flow matches the rate of volatiles generation or the particle decrepitates. The latter phenomenon is, in fact, observed for nonplastic coals, particularly the sparking lignites.

As mentioned above, Lewellen (1975) has developed a bubble transport model for volatiles flow in plastic coals. The model describes the nucleation, growth, coalescence, and escape of volatiles filled bubbles under the influence of viscous forces, pressure, and surface tension, among which the last is relatively unimportant, with mass addition to and loss from the bubbles by volatiles formation and mass deposition accompanying secondary reactions at the bubble surfaces, respectively. A key feature of the model is the assumption, prompted by Fitzgerald's concept of fluid coal (Bronowski et al., 1953; Fitzgerald, 1956*a*, *b*), that viscosity of the decomposing mass is inversely proportional to the concentration therein of a plasticizing material formed by pyrolysis and released into the volatile (bubble) phase at a mass transfer controlled rate. Thus, fluidity is a transient property tuned to pyrolysis rate [Equation (10*a*)] in a manner that accounts for experimentally observed characteristics of the softening and resolidification phenomena and permits realistic description of instantaneous bubble inventory and particle volume, periodic volatiles release from the particle, and other properties of the particle behavior. The model has been critically tested by comparing with experimental observations the predicted effects of particle size, pressure, and heating rate on volatiles yield and particle swelling. Although some questions remain, the predicted trends are in excellent agreement with experiment.

Lewellen's interest in secondary reactions required a more sophisticated volatiles transport model than had been used previously when the main focus was on the relative importance of chemical kinetics and heat and mass transfer in the control of devolatilization rate. The previous workers usually resorted to highly simplified or even only implied concepts of particle structure and transport mechanism. Nevertheless, the resulting empirical information, summarized below, is of much practical interest.

If devolatilization of a coal particle were chemically controlled, the rate would be independent of particle size or structure. Badzioch and Hawksley (1970) observed the same devolatilization rate for 20 and 60 μm particles, and Howard and Essenhigh (1967) found no particle size influence using conventional pulverized coal (50 wt.% $<$ 35 μm; 80 wt.% $<$ 74 μm). Also, weight loss curves prepared by Wiser et al. (1967) were unaltered for samples of 60 to 74 μm vs. 246 to 417 μm. Nevertheless, under a given set of conditions, heat and/or mass transfer will become limiting at some critical particle size, the identification of which requires information on the pertinent heat and mass transfer mechanisms. Three limiting cases are discussed below with the net heat of the pyrolysis reactions being neglected because it appears (Davis and Place, 1924*a*, *b*; Davis, 1924; Gentry, 1928*a*) to be small enough to impose only second-order effects on heating under most conditions.

(i) External heat transfer. If the dominant heat transfer resistance lies between the coal particle and its surroundings, the temperature of the particle is uniform during heat up, and the rate of temperature rise decreases with increasing particle size. Pyrolysis rate during heat up under these conditions increases with decreasing particle size, but the amount of reaction occurring during heat up becomes negligible as heating rate is increased beyond some value. Therefore, for particles smaller than a certain size, pyrolysis rate is essentially chemically controlled and depends on the final temperature attained, not heating rate or particle size. Calculations by Badzioch (1967) indicate that the transition occurs at a particle diameter of approximately 100 μm, but the answer clearly depends on the assumed pyrolysis kinetics, the mode of heat transfer to the particle, and the final temperature of the particle.

(ii) Internal heat transfer. The external heat transfer coefficient can be high enough in some systems such as fluidized beds or intensely mixed entrained flow reactors to produce significant temperature gradients within the particle. In the extreme case where heat transfer rate is completely controlled within the particle, the transition between chemical and heat transfer control of pyrolysis rate occurs at a particle size below which the center temperature closely approaches the surface value before significant reaction can occur. Peters (1960) provided the following empirical equation to explain the apparently zero-order reaction observed for particles of 250 to 2 000 μm diameter:

$$dV/dt = 0.03(T_a - 330)/d^{0.26} \qquad (17)$$

This result was interpreted as representing the propagation of an evaporation front ($T \sim 330°C$) through the particle, with the rate of volatiles release being controlled by the overall temperature gradient. Koch et al. (1969) used this result to predict as a function of heating rate (presumably representing surface temperature under these conditions) the particle size at which devolatilization rate shifts from being controlled by a first-order reaction [Equation (15)] occurring uniformly throughout the particle to being heat transfer controlled [Equation (17)]. The following selected values are representative of their predictions

Heating rate,	°C/s	100	1 000	10 000
Critical diameter,	μm	2 000	500	200

Unpublished M.I.T. data indicate that the transition occurs at d = 100 to 1 000 μm for a heating rate of 600°C/s.

(iii) Mass transfer. Approaching the problem from a different point of view, Essenhigh (1963) modeled the devolatilization of larger coal particles (295 to 4 760 μm) in terms of a shrinking spherical liquid core in a porous char matrix. Postulating the rate to be controlled by volatiles transport from the liquid surface through the char shell, he predicted the time required for devolatilization to be

$$t_v = K_v d^2 \qquad (18)$$

where K_v is a constant inversely proportional to the char permeability and directly proportional to the volatile matter content of the coal. Essenhigh's single-particle data on ten British coals in the stated size range confirmed this square-law behavior, and the mean value of K_v was found to be 0.9 s/mm². These findings are apparently contrary to the data of Peter's discussed above, wherein devolatilization time reportedly increases with particle diameter to the 0.26 power. However, direct comparison is difficult because Essenhigh did not specify the temperature functionality of K_v which Peters found to be linear.

Experimental verification of Equation (18) does not directly distinguish between heat and mass transfer control. Since transient transport is usually described in terms of the Fourier group $\alpha t/d^2$, where α is mass or thermal diffusivity, the expected time for either heat or mass transport is proportional to diameter squared.

Howard and Essenhigh (1967) show that extrapolation of Equation (18) to particle diameters less than about 150 μm seriously underestimates pyrolysis times, implying that transport processes are not rate controlling. However, the absence of such control in small particles does not mean that mass transfer is unimportant with regard to the yield and composition of volatiles. As discussed above, Anthony et al. (1975) support the concept that chemical decomposition is rate controlling for fine particles, but that yield is dependent on the outcome of competition between mass transfer and secondary reactions.

4. HYDROGASIFICATION

4.1. Existence of Rapid-Rate Carbon

The residual fixed carbon in char reacts with hydrogen to produce methane, but the reported rates for this reac-

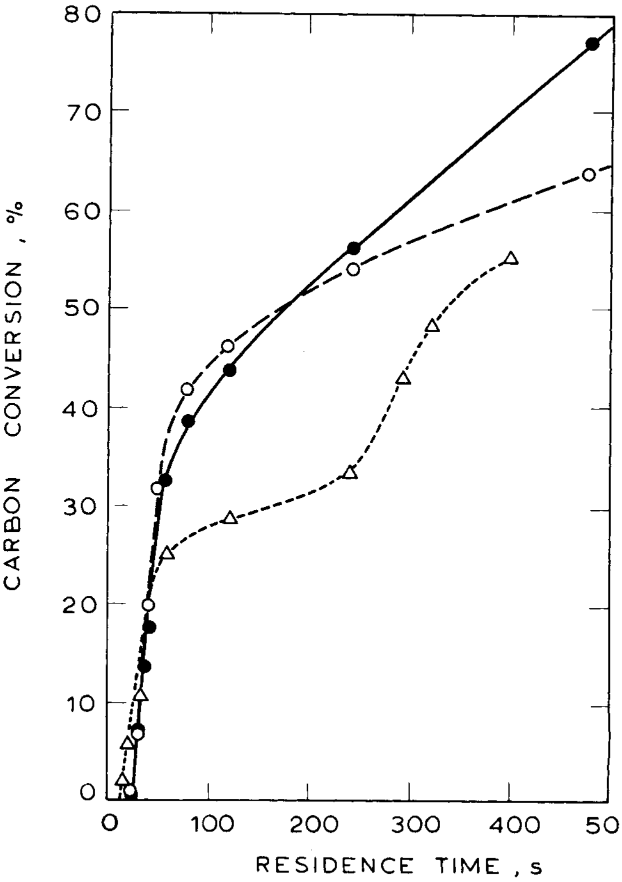

Fig. 7. Effect of time on carbon conversion in the hydrogasification of coal and char [Feldkirchner and Linden (1963); final (holding) temperature, 927°C; hydrogen pressure, 100 atm; particle diameter, 841-1 190 μm. (●) Pittsburgh Seam bituminous coal, VM = 35.5% by wt. (as received); (○) N. Dakota lignite, VM = 41.2% by wt. (as received); (△) bituminous coal char, VM = 17.3% by wt. (as received)].

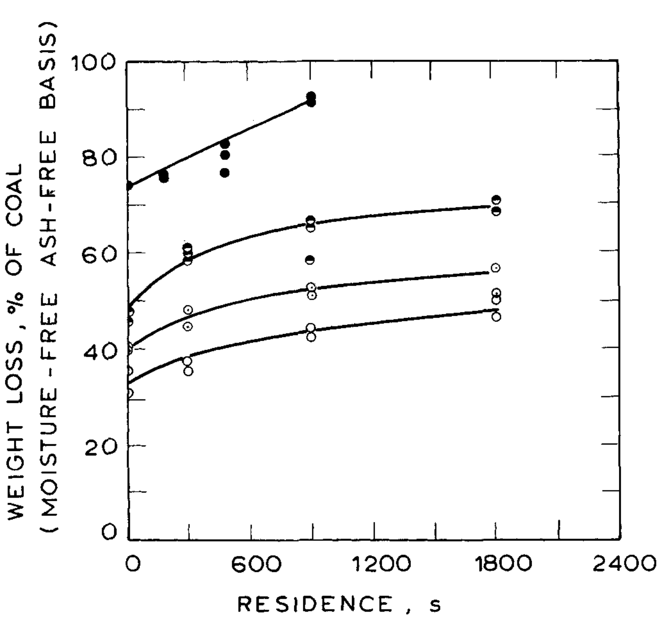

Fig. 8. Effect of time on weight loss in the hydrogasification of Pittsburgh Seam bituminous coal [Hiteshue et al. (1962*b*, 1964); *VM* = 37.5% by wt. (dry, ash free); final (holding) temperature, 800°C. Hydrogen pressure, atm: 18 (○), 35 (⊙), 69 (◑), 409 (●). No catalyst added: (○), (⊙), (◑). 1% Mo Catalyst (●)].

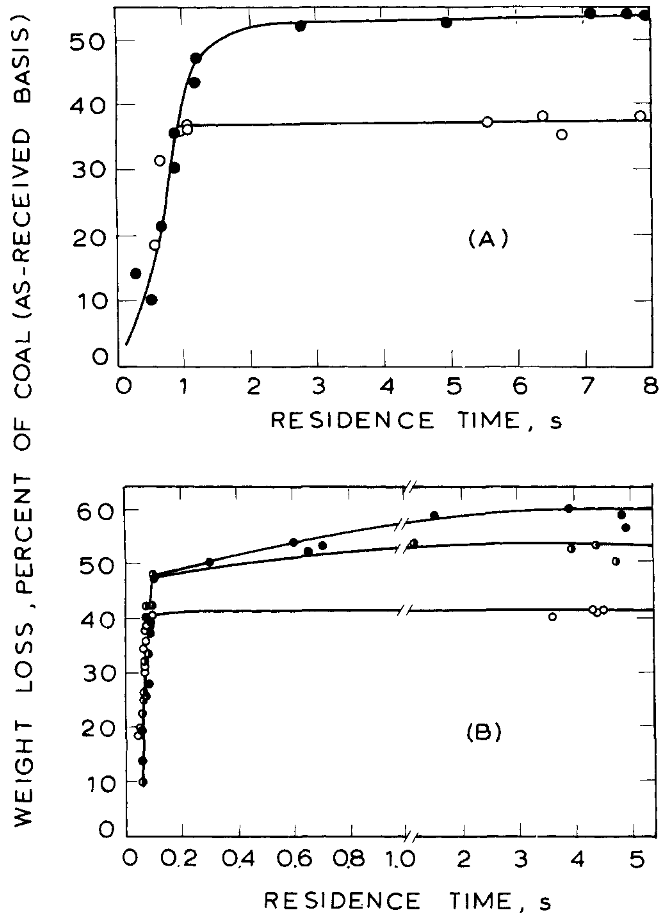

Fig. 10. Effect of time on weight loss from coal heated in helium and hydrogen atmospheres [Anthony (1974); mean particle diameter, 70 μm. (A) Pittsburgh Seam bituminous coal (Ireland Mine); final (holding) temperature, 900°C; nominal heating rate, 750°C/s; pressure, 69 atm; (○) helium; (●) hydrogen. (B) Montana lignite (Savage Mine); final (holding) temperature, 1 000°C; nominal heating rate, 10 000°C/s; (○) helium, 69 atm; (○) hydrogen, 69 atm; (●) hydrogen, 103 atm].

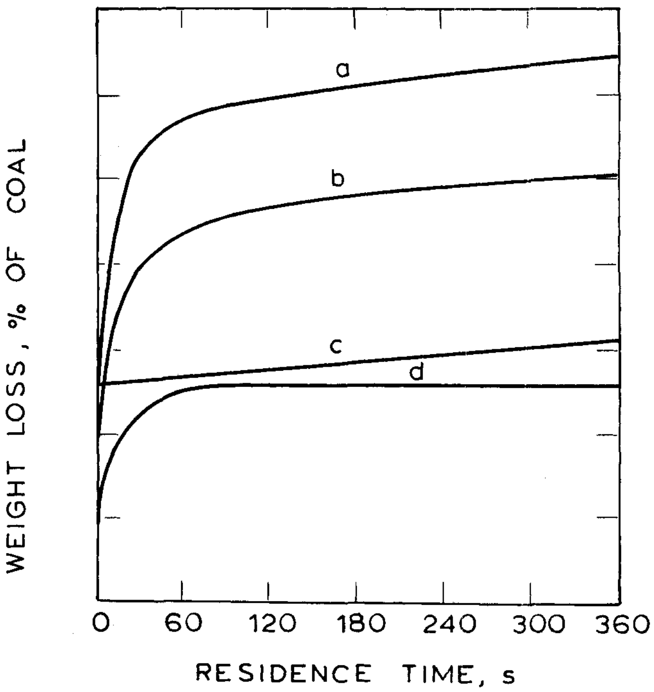

Fig. 9. Effect of time on weight loss in the devolatilization and hydrogasification of Pittsburgh Seam bituminous coal and char [Johnson (1971); Ireland Mine coal; final (holding) temperature, 927°C. (a) coal, 69 atm H_2; (b) coal, 35 atm H_2; (c) N_2-pretreated char, 35 atm H_2; (d) coal, 35 atm N_2].

tion are relatively slow, ranging from 0.167 to 0.833% of carbon/ks atm hydrogen at 927°C (Feldkirchner and Linden, 1963). Early work by Dent (1944) showed that a substantial portion of the carbon in raw coal can be coverted to methane more rapidly than can the carbon in char. Birch et al. (1960, 1969) identified two distinct stages in their fluid-bed hydrogasification of raw brown coal, the second of which was comparable in rate to the hydrogenation of char. In the initial stage, described as a rapid hydrogenation of volatiles, the gas yield for residence times exceeding 360 s depended on temperature and hydrogen pressure but not on residence time.

Feldkirchner and Linden (1963) studied hydrogasification of two coals and a char by dropping a few grams of sample onto a preheated alumina bed through which gas mixtures containing hydrogen were passed. Their data, shown in Figure 7, also exhibit two distinct rate periods, with the first and more rapid stage occurring during heat up. Linear extrapolation from the slow rate period to zero time indicates conversions roughly equivalent to proximate volatile contents, which supports the argument that the short-lived period of high reactivity is simply hydrogenation of volatile constituents.

Schroeder (1962) and later Hiteshue et al. (1962*a*, 1962*b*, 1964) were the first workers to report rapid-rate hydrogenation yields exceeding proximate volatile content. They passed hydrogen through a heated bed of raw coal and measured weight loss from the coal as a function of time as illustrated by the data in Figure 8. Certain amounts of time were required for heating the bed to temperature and for cooling at the end of the run. Zero residence time on the graph corresponds to a run in which the sample was quenched immediately after heat up (total time of 40 s spent at temperatures above 300°C). The substantial initial conversions indicate that the early reactions are indeed rapid, and that a significant portion of the coal's proximate fixed carbon participates in the rapid-rate period.

Corroborative evidence was forthcoming in subsequent studies. Using a free-fall reactor at 900° to 925°C, Moseley and Paterson (1967) obtained nearly complete conversion of raw coal to methane at 500 atm of hydrogen in a residence time of only a few seconds (data shown later in Figures 11 and 15). They also found that pretreating the coal by devolatilization at 680°C in inert gas before contact with hydrogen substantially reduced reactivity to hydrogen, whereas pretreatment at 450°C had no effect on reactivity. In a similar manner, the thermobalance data of Johnson (1971) presented in Figure 9 show that the conversions obtained by gasification of raw coal at 927°C in 35 atm of hydrogen are much larger than those obtained when the coal is first devolatilized in nitrogen at the same temperature and pressure and then subjected to the hydrogen treatment. Johnson's data also exhibit the early period of high reactivity of raw coal to hydrogen (top two curves), where the yield is much larger than that obtained by pyrolysis alone (N_2 curve), and show that the rate of char gasification with hydrogen in the slower second stage is approximately the same whether the coal was first heated in nitrogen or hydrogen. Data of Anthony et al. (1976) illustrated in Figure 10 provide improved time resolution of the rapid first stage and show that a substantial part of the increase in yield observed in hydrogen as compared to the pyrolysis yield observed in helium occurs on a time scale comparable to that of pyrolysis, indicating that the rapid hydrogenation may be coupled with thermal decomposition. By heating coal rapidly to 1 000°C in 69 atm of hydrogen, yields 50% larger than the proximate volatile content were achieved in only 2 s with both a bituminous coal and a lignite. High resolution of the early stage indicates that a substantial part of the contribution of hydrogen occurs in only 0.1 s. With limited information available, it appears that workers at the University of Utah have also achieved high yields (to 85 wt%) with a free-fall reactor (<½ s residence time, Wiser et al., 1971). These yields were reportedly attained at substantially less severe temperatures (about 500°C) with the aid of a catalyst.

Several of the studies discussed above have in common the heating of Pittsburgh Seam coal in hydrogen to temperatures in the range 800° to 927°C, thereby permitting intercomparison of different sets of time-resolved hydrogasification conversion data which together cover residence times from about 0.4 to 1 800 s. Smooth curves that were drawn through the original data are collected in Figure 11, where hydrogen pressure in atmospheres is indicated on the curves, and cross references, in parentheses, refer to coal properties given in Table 7. Conversion is defined as weight loss excluding moisture, expressed as percentage of the original coal on a dry ash free basis, except for the data of Feldkirchner and Linden (1963) which are percentages carbon conversion. In the present coordinate system, comprised of conversion on a rectilinear ordinate and residence time on a logrithmic abscissa, a first-order rate in the amount of material yet to be converted will appear as a steep s shaped curve. For example, the data represented by curves (1) were correlated by a nonisothermal model involving first-order kinetics (Figure 10), and the upper portion of curve (4) also appears to be first order. Furthermore, it should be noted that similarly appearing slopes at widely different times actually reflect very different rates. Thus, the upper portions of curves (2) and (3) indicate very slow rates and would appear as asymptotes on a rectilinear time abscissa. All the curves tend toward complete conversion, since carbon reacts with hydrogen, although very slowly.

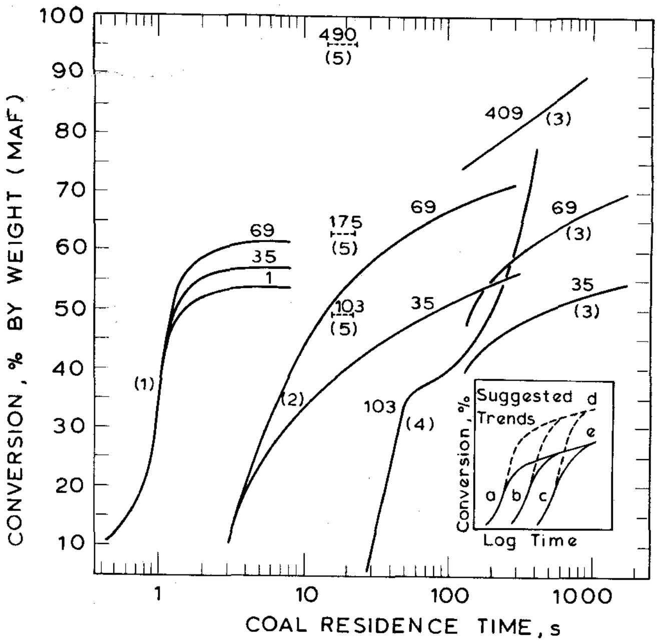

Fig. 11. Effect of heating rate, hydrogen pressure, and time on coal conversion to gases in hydrogasification [numbers in parentheses: (1) Anthony et al. (1976); (2) Johnson (1971); (3) Hiteshue et al. (1962*b*) 409 atm with 1% Mo catalyst, (1964) 35 and 69 atm; (4) Feldkirchner and Linden (1963); (5) Moseley and Paterson (1967). Hydrogen pressure, atm: numbers on curves. Final (holding) temperature: (1) 900°C; (2) 927°C; (3) 800°C; (4) 927°C; (5) 850°-950°C. Coal type (Table 7): Curves—Pittsburgh Seam bituminous; dashed lines—Warwickshire bituminous. Insert: Idealized suggested trends].

TABLE 7. PROPERTIES OF COALS REPRESENTED IN FIGURE 11

Property	% by weight of Coal* (1)	(2)†	(3)	(4)	(5)
Ultimate analysis (MAF)					
Carbon	77.0	79.8	82.8	83.0	78.4
Hydrogen	5.7	4.8	5.7	5.5	4.8
Oxygen	10.2	9.9	7.7	—	—
Nitrogen	1.2	1.5	1.7	—	—
Sulfur	5.9	4.0	2.1	1.6	—
Proximate analysis					
Volatile matter	39.8	28.4	33.9	33.5	34.5
Fixed carbon	46.3	60.7	56.5	56.9	54.0
Moisture	1.7	0	1.9	1.1	6.7
Ash	12.2	10.9	7.7	8.5	4.8

* (1) and (2) Pittsburgh Seam No. 8, Ireland Mine; (3) Pittsburgh Seam; (4) Pittsburgh Seam, Montour No. 4 Mine; (5) Warwickshire Seam, English National Coal Board No. 902.
† Air pretreated char.

The lower portions of all the curves in Figure 11 were obtained under the nonisothermal conditions of heat up. The lateral displacements between curves are attributed almost entirely to different heating rates; that is, the apparent conversion rate at a given hydrogen pressure is dominated by the rate of temperature rise. For example, 50% conversion at 69 atm of hydrogen can be obtained in 1.2, 15, or 150 s (curves 1, 2, or 3), depending on heating rate. Furthermore, it appears that the conversions achieved in short times can be very large indeed if hydrogen pressure is sufficiently high. In order to emphasize the latter point, the data of Moseley and Paterson (1967) are included in the figure (dashed lines), even though these workers did not use Pittsburgh Seam coal. The range of residence times shown for their data are our estimations based on calculated terminal velocities for the reported experimental conditions. Their coal, a non-caking high-volatile bituminous, appears to be less reactive than Pittsburgh Seam coal since, for example, the

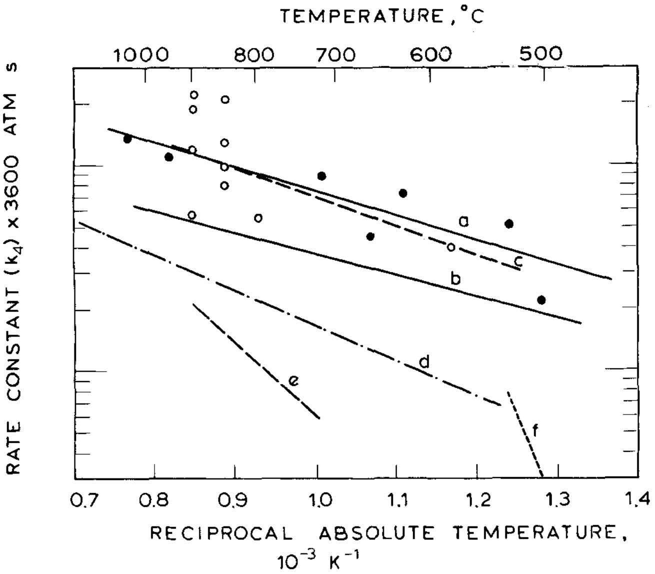

Fig. 12. Comparison of hydrogasification rate constants from different investigators [Anthony (1974), 69 atm H_2: (a) and (●) Pittsburgh Seam bituminous coal; (b) Montana lignite. (c) and (○) Feldmann et al. (1972), Pittsburgh Seam bituminous coal 69 atm H_2. (d) Jüntgen et al. (1973), 69 atm H_2, CH_4 production only. (e) Feldman et al. (1970), 205 atm H_2. (f) Wiser et al. (1971), 137 atm H_2].

conversion at 15 to 22 s under 175 atm only slightly exceeds that of Anthony et al. for 69 atm and much smaller times. Nevertheless, the effect of increasing hydrogen pressure as indicated by the data of Moseley and Paterson is qualitatively similar to that observed by Anthony et al., and the former workers achieved over 90% conversion in 15 to 22 s at 490 atm of hydrogen.

Although some of the behavior shown in Figure 11 undoubtedly reflects effects of particle size, method of heating, and contacting the coal with hydrogen, and other experimental conditions that vary between the different sets of data, the dominant effects are attributed to heating rate and hydrogen pressure. Our conception of the trends is illustrated in the insert, where conversions achieved at different heating rates ($a > b > c$) under a given hydrogen pressure (d or e, $d > e$) eventually converge. This idealized view implies that heating rate does not significantly alter the path of secondary reactions or the reactivity of the residual char. Evidence supporting this hypothesis is limited, since heating rate is usually not varied without also changing apparatus, final temperature, or other conditions. The data of Anthony et al. (1975, 1976) are consistent with this view, but the picture is not complete. The correct answer will have considerable bearing on the design philosophy guiding future hydrogasification developments.

4.2. Kinetics and Mechanisms

Practical interest in the foregoing hydrogasification rate phenomena and the associated need for quantitative understanding of the underlying kinetics and mechanisms has led to the development of purely empirical correlations of the data as well as more sophisticated models based on proposed mechanisms with kinetics parameters evaluated from the data. The various approaches found in the literature and some additional data are discussed below.

4.2.1. *Empirical Correlations*

The principal correlative tool in this category is the simple model in which rate of gasification of rapid-rate carbon is proportional to hydrogen partial pressure and amount of rapid-rate carbon material remaining. Thus

$$dX/dt = k_4 P_{H_2}(X^* - X) \qquad (19)$$

where k_4 is the rate constant, usually of the Arrhenius form. Equation (19) was used by Wen and Huebler (1965), Feldmann et al. (1970), Wiser et al. (1971), Jüntgen et al. (1973), and Anthony (1974), although Wen and Huebler replaced P_{H_2} with the difference between the actual hydrogen partial pressure and the value at equilibrium on the grounds that the rate must be zero at equilibrium.

The present definition of X represents a necessarily broad standardization of four different nomenclatures used previously:

Moseley and Paterson[†] (1965*a*)
Zahradnik and Glenn (1971)
Jüntgen et al. (1973)

$$X = \frac{\text{grams of carbon as methane}}{\text{grams of original carbon}}$$

Wen and Huebler (1965)
Feldmann et al. (1970)

$$X = \frac{\text{grams of carbon gasified}}{\text{grams of original carbon}}$$

Wiser et al. (1971)
Anthony (1974)

$$X = \frac{\text{grams of coal gasified}}{\text{grams of original coal}}$$

Johnson (1974)

$$X = \frac{\text{grams of fixed carbon gasified}}{\text{grams of original fixed carbon}}$$

Such fine distinctions are not used here, since it remains unestablished which definition provides the best measure of conversion. Cross correlations between weight, carbon content, and methane formation are provided later.

Values for k_4 as a function of temperature are shown in Figure 12 for the various studies. Data points for Pittsburgh Seam bituminous coal at 69 atm hydrogen from Feldmann et al. and Anthony are plotted for comparison. Activation energies are low, 5 to 6 kcal/mole for bituminous coal. Anthony's data for lignite, the results of Jüntgen et al. for methane evolution (major hydrogenation product), and the data of Feldmann et al. at 205 atm exhibit lower rate constants. At low temperatures, Wiser et al. (1971) report catalytic hydrogenation results with much higher activation energies. Data of Feldmann et al. at temperatures below 575°C are omitted here because of mass deposition in the reactor at lower temperatures (Feldmann, 1976).

The principal point from Figure 12 is not that hydrogenation of coal has been successfully modeled, but rather that data obtained by widely varying experimental techniques are comparable in magnitude. In fact, the curves of Jüntgen et al. and Wiser et al. may not be entirely applicable in the discussion of rapid-rate conversion, since they were obtained at very low heating rates and involve a minimum time scale of 600 s or more where slow gasification of relatively old char is likely to be important. In any case, the value of the rate constant is poorly defined by this figure, partly because Equation (19) does not account for devolatilization yields, thereby causing an apparent pressure effect on the rate constant which is particularly noticeable in the results of Feldmann et al. at 69 and 207 atm. These workers attempted to correct for devolatilization at the higher pressure by use

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[†] Moseley and Paterson also reported total carbon conversion and weight loss.

of an integration constant in Equation (19), representing the instantaneous volatiles yield or conversion that appeared at $t = 0$. The question of how to treat devolatilization yields in the analysis of hydrogasification kinetics will be discussed further.

The major shortcoming of Equation (19) is the necessity to know the amount of potential rapid-rate carbon (X^*) as a function of the pertinent parameters. Although the integrated form of the equation for constant temperature and hydrogen pressure is sometimes assumed to be

$$X = X^*[1 - \exp(-k_4 P_{H_2} t)] \qquad (20)$$

Wen and Hueber and Wiser et al. agree that X^* is a function of temperature, Feldmann et al. contend that X^* is dependent on hydrogen pressure and temperature, and Anthony found it to vary also with particle size.

4.2.2. *Active Species Model*

In order to explain the rapid decay of the initial reactivity of coal to hydrogen and the effects of temperature and pressure on hydrogasification yields, Moseley and Paterson (1965*a*) proposed that thermal decomposition of coal produces, in addition to volatiles, active sites that then form either methane by hydrogenation or relatively unreactive char by cross linking. The resulting char was assumed to react very slowly with hydrogen to produce methane, while the primary methanation reaction was assumed to be rapid, to result in no net consumption of active sites, and to be expressed as

$$dX/dt = k_4 P_{H_2} C^* \qquad (21)$$

By assuming the rate of disappearance of active sites is controlled by a first-order thermal decomposition

$$C^* = C_o^* \exp(-k_5 t) \qquad (22)$$

Equation (21) becomes

$$dX/dt = k_4 P_{H_2} C_o^* \exp(-k_5 t) \qquad (23)$$

Defining $X = 0$ at $t = 0$ and $k_3 = k_4 C_o^*/k_5$, integration of Equation (23) gives

$$X = (k_3 P_{H_2})[1 - \exp(-k_5 t)] \qquad (24)$$

The destruction of active sites was assumed to be so fast that the exponential term in Equation (24) becomes negligible within fractions of a second. Thus, the predicted rapid-rate yield was proportional to hydrogen pressure:

$$X = k_3 P_{H_2} \qquad (25)$$

Zahradnik and Glenn (1971) used a somewhat similar model based on active species rather than sites. Equation (22) was modified to include disappearance of active species by methanation as well as cross linking. Thus

$$C^* = C_o^* \exp[-(k_4 P_{H_2} + k_5)t] \qquad (26)$$

and Equation (24) becomes

$$X = [k_3 P_{H_2}/(1 + k_4 P_{H_2}/k_5)][1 - \exp\{-(k_4 P_{H_2} + k_5)t\}] \qquad (27)$$

Again, neglecting the exponential term after some minimum residence time, we get

$$X = (k_3 P_{H_2})/(1 + k_4 P_{H_2}/k_5) \qquad (28)$$

Johnson (1974), on the other hand, viewed the active sites as catalyzing the reaction between fixed carbon and hydrogen and altered the form of Equation (21) as follows:

$$dX/dt = k_4 P_{H_2} (1 - X)^{2/3} \exp(-a' x^2) C^* \qquad (29)$$

Based on experimental data, Johnson found $a' = 0.97$ and concluded that

$$\int_o^X dx/(1 - X)^{2/3} \exp(-a' X^2) \simeq -\ln(1 - X) \qquad (30)$$

Therefore, Equation (29) is approximately

$$dX/dt = k_4 P_{H_2} (1 - X) C^* \qquad (31)$$

Again, using C^* as given by Equation (22) and the approximation $\exp(-k_3 t) << 1$, integration of Equation (31) gives

$$-\ln(1 - X) = k_3 P_{H_2} \qquad (32)$$

Equation (32) was found to be inadequate at temperatures below 816°C (1 500°F), and a temperature-dependent relationship for C_o^* was proposed by Johnson (Pyrcioch et al., 1972):

$$C_o^*(T) = C_o^*(T_o) \left[1 - \int_o^\infty f_s(E_s) \exp\left(- \int_o^t k_s dt \right) dE_s \right] \qquad (33)$$

or, assuming the ratio k_4/k_3 to be temperature independent

$$-\ln(1 - X) = (k_4/k_5) C_o^*(T_o) P_{H_2} \left[1 - \int_o^\infty f_s(E_s) \exp\left(- \int_o^t k_s dt \right) dE_s \right] \qquad (34)$$

where $f_s(E_s)$ is an assumed distribution of activation energies such that $\int_o^\infty f_s(E_s) dE_s = 1$, and k_s is a rate constant of the Arrhenius form. The derivation of Equation (33) was based on the hypothesis that the active sites are formed by a very large (mathematically infinite) set of parallel reactions of differing activation energies described by $f_s(E_s)$. Furthermore, the rate of active sites formation was assumed to be much slower than their subsequent decomposition ($k_s << k_5$) in constrast to the models of Moseley and Paterson and Zahradnik and Glenn, where the formation of active sites or species is essentially instantaneous relative to their disappearance.

Johnson (1975) recently published data on methane and ethane yields from lignite and employed a kinetic model similar to that of Zahradnik and Glenn; that is, Equation (21) was substituted for Equation (31). Johnson assumed that the intermediate solid active species is destroyed in the methanation and ethanation step and hence arrived at a yield correlation identical in form to Equation (28). The temperature dependence of X, though, in contrast to the model of Zahradnik and Glenn, was assumed to arise from C_o^* rather than k_4/k_5, and Equation (33) was used to incorporate this phenomenon. Johnson drew heavily on detailed stoichiometric relationships.

Moseley and Paterson (1965*a*) have also introduced evidence, although unaccounted for in their model, that the concentration of active sites is dependent on temperature but not pressure. Their data on the decay of methanation rate at different temperatures and hydrogen pressures are shown in Figure 13. A step change in temperature from 815° to 915°C at 96 atm hydrogen resulted in a surge and subsequent rapid decay in rate (Figure 13*a*), whereas a step change in hydrogen pressure from 42 to 96 atm at 860°C produced only a small increase in rate (Figure 13*b*). This behavior is consistent with the picture that active species were produced by raising the tem-

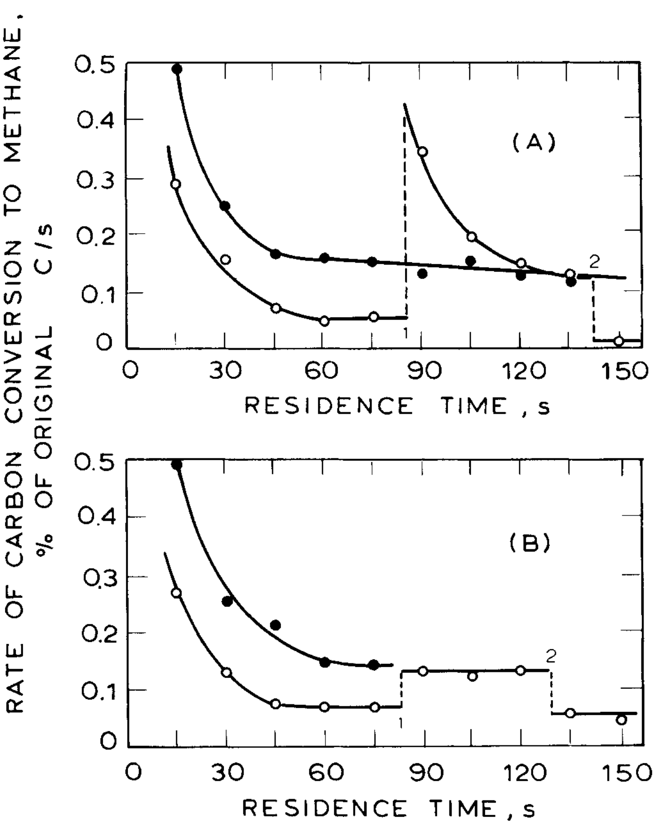

Fig. 13. Effect of temperature and pressure on hydrogasification rate [Moseley and Paterson (1965*a*), Kingsbury char prepared at 700°C. (A) 96 atm H_2: (●) 950°C; (○) 815°C stepped to 915°C at (1) and back to 815°C at (2). (B): (●) 865°C, 96 atm H_2; (○) 860°C, 42 atm H_2 stepped to 96 atm H_2 at (1) and back to 42 atm H_2 at (2)].

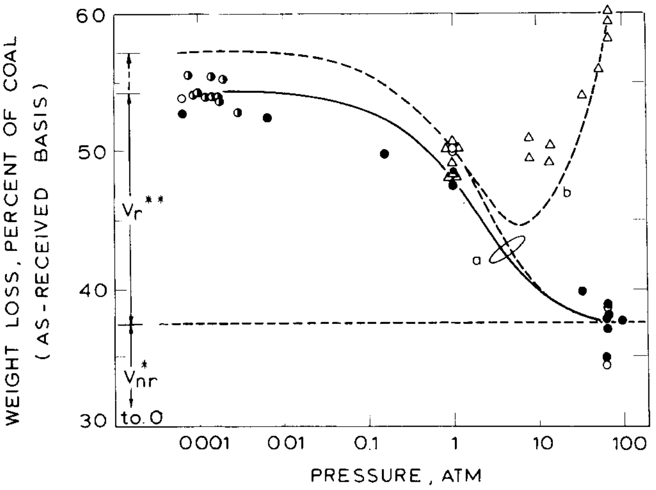

Fig. 14. Effect of pressure on weight loss from Pittsburgh Seam bituminous coal heated in hydrogen and helium atmospheres [Anthony et al. (1976), Ireland Mine coal, final (holding) temperature, 1 000°C; residence time, 5 to 20 s; mean particle diameter, 70 μm; (○) helium, nominal heating rate = 10 000°C/s; (◑) helium, nominal heating rate = 3 000°C/s; (●) helium, nominal heating rate = 650° to 750°C/s; (△) hydrogen, nominal heating rate = 750°C/s. Curves: (a) Equation 16; (b) Equation (37); (solid) V_r^{**} = 17.0% of original coal; (dashed) V_r^{**} = 20.0% of original coal, corrected for cracking deposition on sample holder; V_{nr}^{*} = 37.2% of original coal].

perature while increasing the pressure only increased the rate of char gasification.

Zahradnik and Glenn (1971) argue that the methane formation step is favored at high temperatures and support this position by showing a plot of ln $(k_4C_o^*/k_5)$ vs. $1/T$ to be a straight line with negative slope. The negative slope was taken as proof that the methane formation step is more highly activated than the thermal destruction of active sites. However, the implied assumption that C_o^* is independent of temperature is inconsistent with the results of Johnson discussed above [Equation (33)]. Furthermore, values of C_o^* calculated from the constants reported by Zahradnik and Glenn correspond to an amount of carbon which, when added to that released in devolatilization, exceeds the total carbon in the coal. In revised versions of the model, the fractional available carbon is defined as unity (Zahradnik and Grace, 1972, 1974). Thus, the issue again arises as to the proper method for treating the carbon evolved by thermal decomposition.

4.2.3. *Contribution of Volatiles*

Moseley and Paterson (1967) did not distinguish between volatiles formed by pyrolysis and products of hydrogenation based on the assumption that carbon in the volatiles is readily hydrogenated in the presence of hydrogen, and they suggested their model [Equation (25)] would be inaccurate at hydrogen pressures below 100 atm. As mentioned above, Feldmann et al. (1970) introduced a constant in Equation (19) representing volatiles from pyrolysis. They reported the initial fractional conversions to be 0.22 at 725°C and 0.14 at 900°C which seem inordinately low compared to the proximate volatile content of the coal (40.9% MAF). Furthermore, a decreasing volatile yield with increasing temperature is the reverse of pyrolysis behavior. Zahradnik and Glenn (1971) assumed that devolatilization finishes before rapid hydrogasification begins and added a constant in Equation (28) to account for the contribution of pyrolysis products to yield. However, the values they obtained for this constant by fitting the modified Equation (28) to their hydrogasification data are small and essentially independent of temperature, unlike volatile yields. Zahradnik and Glenn based their assumption of extremely fast devolatilization on the results of Badzioch (1967). Surprisingly, this constitutes one of the few references in the literature on rapid hydrogasification to the extensive literature on thermal release of volatile matter from coal.

Recent research at M.I.T. (Anthony, 1974; Anthony et al., 1976) has focused on the interaction of rapid hydrogasification and devolatilization for a bituminous coal and a lignite at pressures, temperatures, and heating rates up to 100 atm, 1 100°C and 12 000°C/s. Volatiles yields (weight loss) from Pittsburgh Seam coal attained in 5 to 20 s at 1 000°C and different pressures of hydrogen are shown as data points in Figure 14 along with similar data for runs in helium discussed above (Figure 6). Weight loss in hydrogen exhibits a peculiar minimum (48 to 50%; dotted curve discussed later) in the pressure range 1 to 20 atm and then rises with increasing pressure to about 60% of the original coal at 69 atm. As discussed above, weight loss in helium decreases with increasing pressure and is only 37.2% of the original coal at 69 atm, apparently reflecting increased char formation by secondary reactions of volatiles. These and other data were shown to be consistent with the picture that the rapid hydrogenation proceeds in two stages (Anthony et al., 1976). First, hydrogen can react with some of the volatiles to form light hydrocarbons sufficiently stable to avoid the secondary char forming reactions. Thus, volatiles yield is increased during pyrolysis without affecting the rate of the primary decomposition. Secondly, hydrogen reacts with the fresh solid residue, as proposed by Moseley and Paterson (1965*a*), with a rate faster than hydrogasification of older char but slower than devolatilization.

Volatile yields were correlated as a function of total pressure and hydrogen partial pressure by modifying Equation (16) to account for hydrogenation as well as secondary reactions (Anthony et al., 1976). The volatiles formed within a coal particle were assumed to include unreactive species that escape directly from the particle and reactive species that may polymerize and/or crack and deposit carbon on hot coal surfaces, or escape either directly if mass transfer is much faster than secondary reactions or through the formation of stable species by reaction with hydrogen. A material balance on the reactive volatile species present in a coal particle may be written as

$$dV'_r/dt - K_c(C - C_\infty) - k_1C - k_2CP_{H_2} = dC/dt \tag{35}$$

where dV'_r/dt is the rate of the irreversible decomposition reaction.

In Equation (35), a coal particle is viewed as possessing a fixed internal void space of uniform composition and temperature. Reactive species enter this volume by thermal decomposition of the coal and leave by mass transfer into the ambient gas or by solid deposition, or they become hydrogenated and unreactive. With assumptions of pseudo steady state ($dC/dt = 0$) and excess ambient gas ($C_\infty = 0$), the net yield of escaped reactive or previously reactive volatiles up to $t = \infty$ was shown to be

$$V_r^* = V_r^{**}(K_c + k_2P_{H_2})/(K_c + k_1 + k_2P_{H_2}) \tag{36}$$

where V_r^{**} is the amount of reactive volatiles formed up to $t = \infty$, that is, the total potential yield. K_c was assumed to be proportional to the diffusion coefficient of the volatiles and hence inversely proportional to total pressure ($K_c = k_c/P$). The resulting correlation for total yield including unreactive volatiles (V_{nr}^{**}) and the contribution of heterogeneous hydrogenation [Equation (25)] was

$$V^* = V_{nr}^{**} + V_r^{**}[1 + k_1/(k_c/P + k_2P_{H_2})]^{-1} + k_3P_{H_2} \tag{37}$$

The curves in Figure 14 were obtained with Equation (37) by using $V_r^{**} = 20\%$, $V_{nr}^{**} = 37.2\%$, $k_1/k_c = 0.56$ atm^{-1}, $k_2/k_c = 0.02$ atm^{-2}, and $k_3 = 0.1\%$ atm^{-1}. Although there are noticeable discrepancies, the model does predict the observed minimum yield in pure hydrogen. According to the model, the minimum arises because both volatiles deposition and hydrogenation, which exert opposite effects on yield, are enhanced by increasing hydrogen pressure. An overly simplistic view of particle structure and mass transfer phenomena is believed to be the principal source of error. Furthermore, this approximate treatment of the heterogeneous reaction precludes application of Equation (37) for hydrogen pressures above those of the data on which k_3 is based.

The different yield correlations discussed above are illustrated in Figure 15 along with representative data of Moseley and Paterson (1967) and Hiteshue et al. (1964). The model of Feldmann et al. (1970) [Equation (20)] is not presented here because it was intended for use only in the short period of rapid-rate behavior. The models presented apply to extended residence times for which their predicted conversions become approximately independent of time, as discussed above. If Equation (20) were used under these conditions, the predicted conversion would be complete at all hydrogen pressures. The straight line predicted by Equation (32) (Johnson, 1974) has an intercept at zero hydrogen pressure which is fixed at a weight loss equal to the proximate volatile content in agreement with $X = 0$ in Johnson's nomenclature (see above). The model of Anthony et al. (1976) is not extrapolated beyond the maximum hydrogen pressures

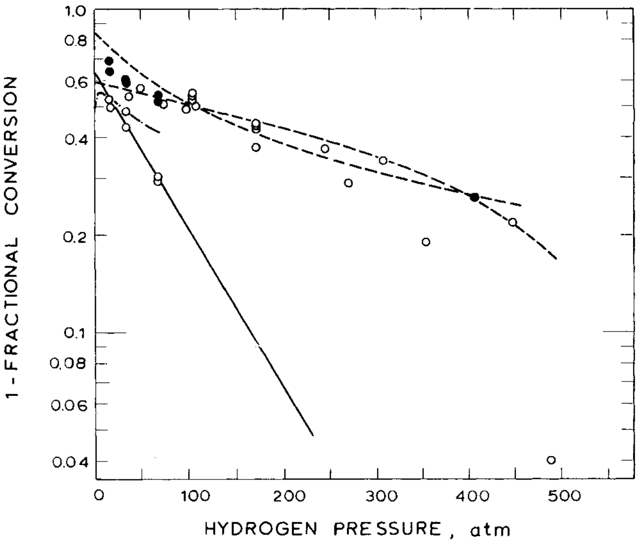

Fig. 15. Comparison of effects of pressure on coal conversion in hydrogasification from different investigators [Temperature, 800°-1000°C. Data points: (●) and (⊙) Hiteshue et al (1964), residence time 3-4 s (●), 1 800 s (⊙); (○) Moseley and Paterson (1967), several s residence time. Curves: long dashes, Moseley and Paterson (1967); short dashes, Zahradnik and Glenn (1971); alternating long and short dashes, Anthony et al. (1976), data points in Figure 14; solid, Johnson (1974)].

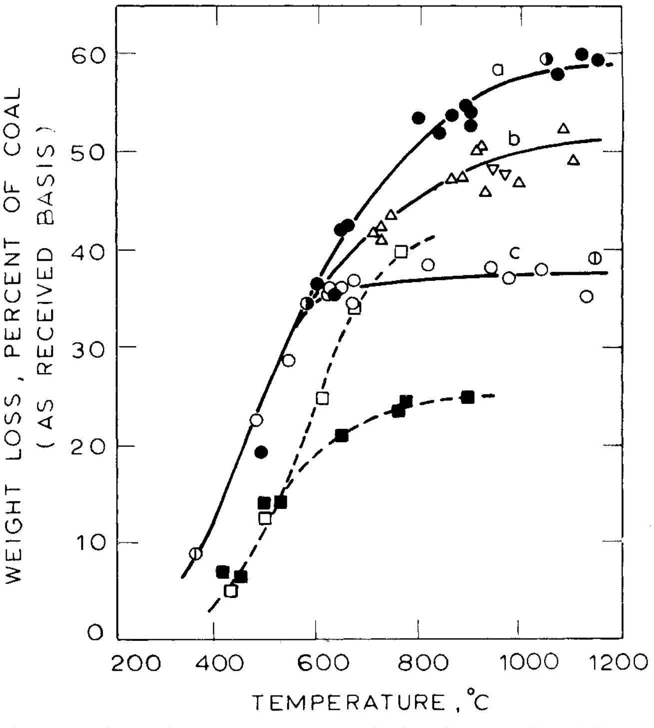

Fig. 16. Effect of temperature on weight loss from Pittsburgh No. 8 Seam (Ireland Mine) bituminous coal and char heated in hydrogen and inert atmospheres at different pressures [Square points: Pyrcioch et al. (1972); char (VM = 28.4%, moisture = 0); 35 atm. (□) hydrogen; residence time, 180 s. (■) nitrogen; residence time, 3600 s. Circles and triangles: Anthony et al. (1976); coal (VM = 39.8%, moisture = 1.6%); nominal heating rates, 65° to 750°C/s; mean particle diameter, 70 μm; residence times, 5 to 20 s. (●) hydrogen, 69 atm; (▽) helium and (△) nitrogen, 1 atm; (○) helium, 69 atm; (○) two-step heating, helium, 69 atm; (◑) two-step heating, hydrogen, 69 atm. Solid curves Equation (38) with parameter values given in text and (a) $P = P_{H_2} = 69$ atm; (b) P = 1 atm, $P_{H_2} = 0$; (c) $P = 69$ atm, $P_{H_2} = 0$].

covered in Figure 14 (69 atm). It is interesting to note, however, that such an extrapolated curve would be shaped like the curve of Moseley and Paterson, reflecting use in Equation (37) of their heterogeneous reaction term which becomes very significant at the higher pressures, and it would be roughly midway between the Moseley and Paterson curve and that of Johnson. The disagreement between the correlations can probably be attributed to differences in the coals and experimental conditions.

4.2.4. *Effect of Temperature*

Increasing temperature increases not only the rate of coal conversion to gases in rapid-rate hydrogasification as shown in Figures 12 and 13*a* but also the extent of conversion achieved before the rate decays to that of very slow hydrogasification of residual char. Figure 16 illustrates the effect of temperature on weight losses attained in 5 to 20 s in hydrogen at 69 atm (Anthony et al., 1976) and in 180 and 3 600 s in hydrogen at 35 atm (Pyrcioch et al., 1972). The latter data for bituminous coal char were said to exhibit an effect of hydrogen at all temperatures, whereas Anthony et al. found no effect of hydrogen for bituminous coal at temperatures below about 600°C, and Moseley and Paterson, as noted above, observed no loss of reactivity to hydrogen in chars prepared at 450°C but definitely a reactivity loss for chars prepared at 680°C and higher. This apparent difference seems to be explained by the fact that Pyrcioch et al. developed their temperature dependency correlation from run times of 3 600 s. In Figure 16, the original data at residence times of 180 s are replotted, and these show much better agreement with the temperature dependency of rapid-rate yields found by Anthony et al. (1976).

In order to compare the effect of temperature on hydrogasification yields with that on pyrolysis yields, other data of Anthony et al. on weight losses attained also in 5 to 20 s but in an inert gas at 1 and 69 atm are included in Figure 16. Inspection of the complete set of data from Anthony et al. shows that yields increase equally under the different conditions up to about 600°C, above which (1) yields at 69 atm become much greater in hydrogen than in inert gas, (2) yields in inert gas become greater at 1 atm than at 69 atm, and (3) yields at 69 atm in inert gas are almost independent of temperature. Furthermore, with respect to (1), a substantial part of the increase in yield achieved with hydrogen occurs at a rate comparable to that of rapid devolatilization (Figure 10), the magnitude of which is difficult to explain in terms of heterogeneous reaction. These data were shown to agree with the picture that the rate of total product generation under all these conditions is controlled by pyrolysis, while competition between mass transfer, secondary reactions, and hydrogenation affects only the relative proportions of gaseous and solid products formed. Thus, in terms of above discussions, it appears that (1) and (2) reflect the roles of hydrogenation of reactive volatiles and increased rates of mass transfer, respectively, in the reduction of solid deposition by secondary reactions. In view of (3), it appears that no additional unreactive volatiles are formed by raising the soaking temperature above about 600°C. Conversely, reactive volatiles appear to be formed only at temperatures above 600°C, since no augmentation of yield by increased mass transfer rate or by hydrogenation is observed at lower temperatures. Since large reactive fragments (free radicals) are certainly produced at temperatures below 600°C, the foregoing approximate generalization implies that such species require further decomposition of higher activation energy in order to leave the particles.

Accordingly, the decomposition reactions forming reactive volatiles appear to have activation energies generally higher than those of reactions that form only nonreactive volatiles. Some nonreactive species such as methane and hydrogen may be released at the higher temperatures as secondary decomposition products of reactive species, but according to (3) the associated contribution to volatiles yield is small. Using the simplifying approximation that all the decomposition reactions forming reactive volatiles have activation energies exceeding E_1 and all those forming nonreactive volatiles have values less than E_1, Anthony et al. (1976) showed that Equation (10*a*) and the transient form of Equation (37) lead to the following expression for volatiles yield as a function of time including the effects of hydrogenation and secondary reactions:

$$V = V_{nr}^{**}\left[1 - \int_o^{E_1} \exp\left(-\int_o^t k_o e^{-E/RT} dt\right) f(E)\,dE\right]$$
$$+ [V_r^{**}\{1 + k_1/(k_c/P + k_2 P_{\mathrm{H_2}})\}^{-1} + k_3 P_{\mathrm{H_2}}]$$
$$\times \left[1 - \int_{E_1}^{\infty} \exp\left(-\int_o^t k_o e^{-E/RT} dt\right) f(E)\,dE\right] \quad (38)$$

Unlike Equation (37) and its limitation to the condition $t = \infty$, which is satisfied in only a few seconds at 1 000°C, Equation (38) is applicable not only at such high temperature but also at lower temperatures where the assumption $t = \infty$ is often not satisfied in available data owing to the associated slower reaction rates.

Equation (38) was fitted to all the data of Anthony et al. in Figure 16 by using the experimental temperature-time histories, the above-stated values of k_1/k_c, k_2/k_c, k_3, V_{nr}^{*} $(= V_{nr}^{**})$ and V_r^{**}, and $k_o = 1.67 \times 10^{13}$ s^{-1}. The distribution $f(E)$ was again assumed to be Gaussian [Equation (11)]. The curves shown in Figure 16 were obtained with mean activation energy $E_o = 54.8$ kcal/mole, standard deviation $\sigma = 17.2$ kcal/mole, and $E_1 = 61.4$ kcal/mole. In addition to correlating the hydrogasification data, these parameters constitute a reassessment of the pyrolysis kinetics in the light of the observed behavior in hydrogen.

The foregoing success of Equation (38) in correlating data obtained under a range of heating rates, final temperatures, inert gas pressures, and hydrogen pressures supports the underlying hypothesis that the rate limiting step of both devolatilization and rapid-rate hydrogasification is thermal decomposition of the coal, while subsequent steps of mass transfer, secondary reaction, and hydrogenation affect the relative proportions of volatile and solid products formed. This picture seems to be consistent with the role of pyrolysis in coal liquefaction described by Wiser (1968) and Neavel (1975). Similar behavior has been described by Virk et al. (1974) for simple aromatic hydrocarbons which decompose with the same rate in hydrogen as in inert atmospheres, although the product in hydrogen is predominately methane while substantial carbon is formed in inert atmospheres under otherwise similar conditions. The overall activation energies of these reactions were found to correlate with the calculated aromatic delocalization energies, and rate control was therefore attributed to destabilization of the aromatic structure. The possible application of this or other mechanisms to coal reactions is an important area for further study.

According to the above picture, the primary effect of temperature on rapid-rate hydrogasification is on pyrolysis. In contrast, as noted above, several authors have postulated a competition between gasification and decay of active sites or species as an explanation of temperature effects. However, the data of Anthony et al. (1976) as well as the collection of data in Figure 11 show little influence of heating rate on yield. Furthermore, Anthony et al. reheated two samples of char from low-temperature runs at 69 atm to high temperatures at 69 atm and found that the cumulative weight loss in each case was essentially identical to that for raw coal heated directly to the same high temperature (Figure 16). If, in fact, only a fixed concentration (C_0^*) of active sites were originally available as assumed in Equations (21) to (32), the extent of deactivation observed at a given temperature would increase with increasing residence time up to that temperature. Such behavior is not in line with the above data.

As noted above, Moseley and Paterson recognized that C_0^* would have to be a function of temperature, and Johnson replaced C_0^* in Equation (32) with an expression involving statistically distributed activation energies [Equation (33)]. To the extent that Anthony et al. used a statistical distribution of activation energies for pyrolysis and explained the temperature effects in terms of competitive reactions involving reactive volatiles, which could be called active (gas phase) species, their approach has an important similarity to that of Johnson, although it is fundamentally different. Rate of conversion in both models depends on the formation rate of reactive species, which are volatiles according to Anthony et al. Thus, the change in conversion rate caused by a step change in temperature would occur instantaneously according to these models. The rate changes shown in Figure 13*a* caused by a step increase from 815° to 915°C and a subsequent step back to 815°C appear to support this picture, but the time resolution of the data is not good enough to exclude a slower change. Furthermore, Blackwood and McCarthy (1966) have shown that cycling the temperature of a devolatilized char produces repeated peaks in rate of methane formation from hydrogen. This phenomenon should be considered along with hydrogenation associated with the further devolatilization in Figure 13*a*, but its contribution indicated by the data of Blackwood and McCarthy is relatively small. It should be noted, however, that both of the rate changes shown in Figure 13*a* correspond to an apparent activation energy of 53 to 61 kcal/mole which is consistent with the above stated mean value of 54.8 kcal/mole found by Anthony et al. In a recent correlation of lignite data, Johnson (1975) assumed a uniform distribution of activation energies which was found to extend from 79.5 to 118.1 kcal/mole with a preexponential factor of 7 × 10^{20} s^{-1}. The use of k_0 values much larger than 10^{13} s^{-1} would imply that extremely large entropies of activation are associated with the solid phase reactions.

4.2.5. *Effect of Particle Size*

Very little experimental evidence has been accumulated on the effect of particle size on hydrogasification behavior. Although the available hydrogasification data were obtained by using a wide range of particle sizes (Table 8), the effect of particle size was usually not an object of study. Moseley and Paterson (1967) reported a definite tendency for conversion to rise with smaller particles, but their experimental technique was unsuited for extensive studies of particle size. A particle size effect on conversion rate has been built into several models but without direct experimental verification. Johnson [Equation (29)] found rate to be proportional to $(1 - X)^{2/3}$, implying a shrinking core behavior. Pyrcioch et al. (1972) rationalize this result by assuming that a coal or char particle consists of a large number of internally dispersed subelements that individually gasify with a shrinking core mechanism. Zahradnik and Glenn originally derived their model by assuming the methanation step [Equation (21)] to be described as

$$dX/dt = k_3 P_{H_2} C^{*2/3} \qquad (39)$$

also a shrinking core postulation. In both cases, the expression for yield was independent of particle size.

TABLE 8. PRIMARY PARTICLE SIZE RANGE USED IN PREVIOUS INVESTIGATIONS

Investigators	Particle diameter, μm
Glenn, Donath, and Grace (1967)	< 44
Belt and Roder (1972)	70% < 74
Anthony et al. (1975, 1976)*	53-88
Moseley and Paterson (1967)	100-150
Feldmann et al. (1970)	150-300
Wiser et al. (1967)	246-417
Hiteshue et al. (1964)	250-600
Johnson (1974)	420-841

* Some runs performed with particles up to 1000 μm diameter in study of size effects.

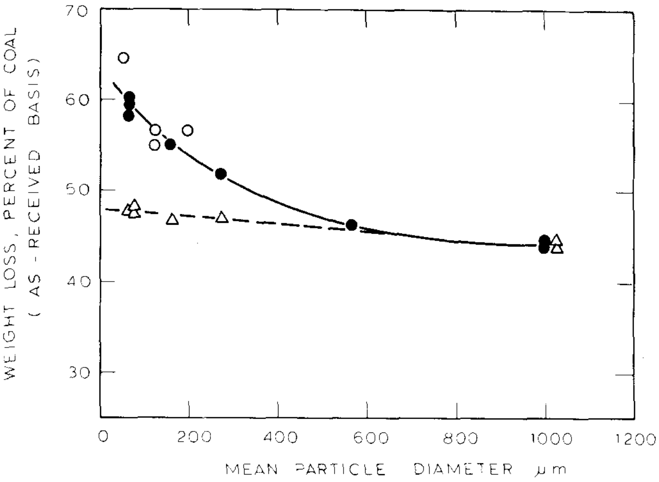

Fig. 17. Effect of particle size on weight loss from bituminous coal heated in hydrogen and helium [(○) Moseley and Paterson (1967), Warwickshire coal, 175 atm H_2, 920°C final (holding) temperature, several s residence time. (●) and (△) Anthony et al. (1976), Pittsburgh Seam coal, 1 000°C final (holding) temperature, 5-20 s residence time, 650-750°C/s nominal heating rate, 69 atm H_2 (●), 1 atm He (△)].

Anthony et al. (1976) systematically varied particle size over the range 53 to 1 000 μm in both hydrogasification and pyrolysis experiments. The effect of particle size on yield was found to be substantial for Pittsburgh Seam bituminous coal in hydrogen atmosphere but, as noted above, small for helium (Figure 17). At 69 atm hydrogen and 1 000°C, reduction of particle diameter from 1 000 to 70 μm increased the weight loss attained in 5 to 20 s from 44 to 59% of the original coal. The observed trend indicates that still larger increases in yield would result from further reduction of particle size. In the case of Montana lignite, no significant effect of particle size was observed in either hydrogen or helium.

Since the yield from Pittsburgh Seam coal rises with increasing hydrogen pressure above about 10 atm (Figure 14), the data in Figure 17 can be interpreted as meaning that mass transfer of hydrogen to the interstices of the particle is constrained. Such behavior would be expected in view of the particle structure (see above) prevailing during pyrolysis when hydrogenation competes with solid deposition reactions. Anthony (1974) cross plotted the data from Figures 14 and 17 to determine the effective

TABLE 9. RAPID HYDROGASIFICATION PRODUCT DISTRIBUTIONS

Investigators and residence time information	Temp., °C	H_2 press., atm	Weight, % of original coal CH_4	C_2H_6 $+C_3H_8$	CO	CO_2	H_2O	Oil & tar	Char
Birch et al. (1960)	754	42	22.3	—	[15.7]		22.3	4.8	43.1
(includes slow	850	42	45.0	—	[11.9]		29.3	0.9	29.8
gasification)	855	20	25.8	—	[18.6]		28.9	0.9	41.8
	951	42	61.1	—	[14.2]		28.4	0.4	16.4
Hiteshue et al.	800	35	8.2	1.8	—	—	—	10.0	59.6
(1964) (120 s)		69	10.9	2.6	—	—	—	15.2	54.5
	1 200	35	46.7	2.5	—	—	—	1.7	43.0
Moseley and Paterson (1967) (several s)	900	106	35.7	—	6.8	—	—	—	50.0
Feldmann et al. (1974)	850	69	14.5	0.9	1.5	1.0	4.1	3.0	64.6
(several s)	900	35	22.8	0.0	3.7	0.0	3.6	1.7	61.8
	900	76	27.2	0.3	3.5	0.4	3.2	0.5	66.3
Squires et al. (1975)	750	100	11.8	10.2	—	—	—	7.5	56.0
(vapor $\sim$ 0.6 s; solid $\sim$ 10 s)	1 000	100	34.5	0.0	—	—	—	2.3	52.0
Steinberg and Fallon (1975) (16-22 s)	700	102	18-27	9-13	[6]		—	18-23	44-33

hydrogen partial pressure as a function of particle size. According to this concept, the effective hydrogen partial pressure at 1 000 atm and 1 000°C was about 34% larger for a 70 μm particle than for a 1 000 μm particle. Much more sophisticated mass transfer studies and experimental measurements on very fine particles are clearly needed.

4.3. Yield and Composition of Products

Typical product distributions from rapid hydrogasification (Table 9) exhibit the following trends. High temperatures and high hydrogen pressures give the highest yields (gases plus liquids), with methane the predominant fluid product. The production of heavier hydrocarbons is higher at lower temperatures even though the total yield is less. The yields at lower hydrogen pressures are lower in quality, that is, hydrogen content, as well as quantity. Coal type (not shown) is of major importance, probably accounting for much of the variation between the different sets of data, although differences in equipment and technique are also important. The present ability to predict product distributions is poor, and extrapolations to equipment of larger scale than that used to collect the data are risky.

Although it is impossible to anticipate the final destination of the many simultaneous and sequential reactions taking place, a potentially fruitful approach is becoming available. Gray et al. (1975) recently presented correlations of coal carbon conversion with weight loss and coal hydrogen, nitrogen, and sulfur conversions. In many cases, these correlations were independent of apparatus and conditions. Similarly Johnson, as mentioned above, was able to infer complex stoichiometric relationships from correlations between methane and ethane yields and coal hydrogen. While such correlations stop short of offering a full understanding of the detailed chemistry, they may approximate actual phenomena closely enough to be satisfactory for design purposes.

Concern was previously expressed over the varied definitions of conversion used in previous modeling attempts, but the distinctions were subsequently ignored for simplicity. Objections to that simplification are partially mollified by the correlations of literature data in Figures 18 and 19. A high degree of correlation between carbon conversion and weight loss is apparent in Figure 18, while a somewhat poorer but nevertheless useful correlation between methane yield and carbon conversion is presented in Figure 19. There is need for further work along these lines, especially on the development of stoichiometric relations initiated by Johnson.

5. SIGNIFICANCE OF COAL COMPOSITION

5.1. Coal Petrography

It was mentioned above that the organic material in coal is a heterogeneous mixture of organic minerals known as macerals. Coal petrographers have identified fourteen different types of maceral groups by microscopic analysis with reflected and transmitted light (Spackman, 1975). The precise chemical nature of the macerals is not yet known, but their botanical origins seem to be rather well understood (Van Krevelen, 1961).

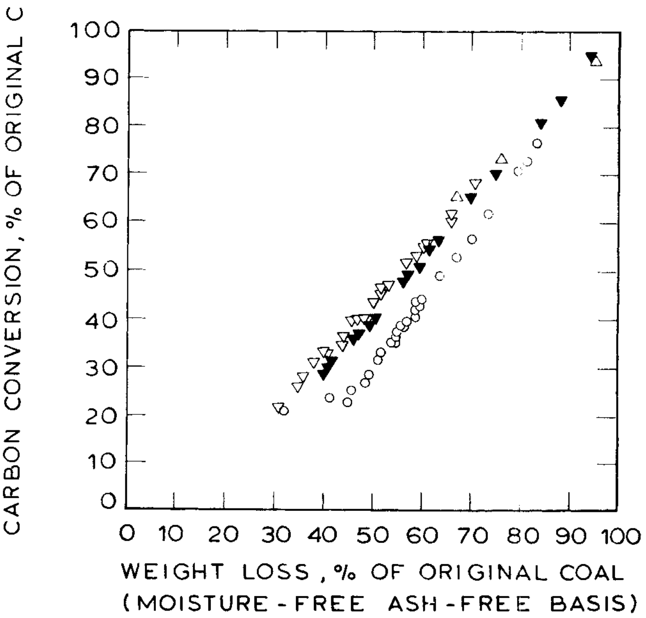

Fig. 18. Relationship between weight loss and carbon conversion in coal hydrogasification data of different investigators [(○) Birch et al. (1960); (△) Moseley and Paterson (1967); (▽) 800°C and (▼) 1 200°C, Hiteshue et al. (1964)].

Table 10. Composition of Some American Coals (Gan et al., 1971)

Coal No.[a]	Location (state)	ASTM rank[b]	Ultimate analysis, % by wt. (MAF)[c]					Vitrinite content, % by vol.[e]
			C	H	N	S	O[d]	
85	Penna.	Anthracite	91.2	3.8	0.60	1.1	3.1	97.5
80	Penna.	Anthracite	90.8	2.6	0.75	0.64	5.1	96.3
130	W. Va.	L. V. Bit.	90.5	4.3	1.1	0.55	3.4	72.7
127	Penna.	L. V. Bit.	89.5	5.0	1.0	0.83	3.6	77.7
135	Alabama	M. V. Bit.	88.3	4.9	0.25	0.65	5.7	83.1
142	Oklahoma	M. V. Bit.	88.2	4.5	0.20	1.0	6.4	—
4	Kentucky	H. V. A. Bit.	83.8	5.7	1.5	0.88	7.9	67.3
95	Washington	H. V. A. Bit.	81.6	6.0	1.0	1.7	9.4	89.6
105A	Indiana	H. V. B. Bit.	81.3	5.7	1.0	1.8	9.9	62.5
24	Illinois	H. V. C. Bit.	80.0	5.5	1.0	4.5	8.8	88.1
213	Kentucky	H. V. C. Bit.	78.8	5.6	1.7	4.2	9.4	73.4
22	Illinois	H. V. C. Bit.	78.7	5.8	1.5	2.8	11.0	88.3
26	Illinois	H. V. C. Bit.	77.2	5.6	1.1	7.4	8.3	88.5
197	Penna.	H. V. B. Bit.	76.5	5.6	1.2	4.5	12.2	85.3
164	Missouri	H. V. B. Bit.	76.4	4.2	1.2	7.3	11.4	—
190	Illinois	H. V. C. Bit.	75.5	5.3	1.0	3.3	14.6	88.9
97	Wyoming	Subbit.	75.0	5.5	0.58	1.3	17.5	86.7
138	Texas	Lignite	74.3	4.9	0.37	0.75	19.6	75.1
100	Wyoming	Subbit.	72.0	5.2	0.81	0.55	21.2	86.0
141	Texas	Lignite	71.7	5.2	1.3	0.90	20.8	75.3
90	Montana	Lignite	71.5	4.8	0.83	0.50	22.2	60.9
89	N. Dakota	Lignite	63.3	4.6	0.47	1.5	29.9	70.3

[a] PSOC numbers employed in Pennsylvania State University—Office of Coal Research (now ERDA) coal characterization study.
[b] L, M and H refer to low, medium, and high; V to volatile; and A, B, and C to bituminous classes.
[c] Moisture free, ash free basis.
[d] Oxygen determined by difference.
[e] Mineral matter containing basis.

For ease of discussion, the various types of maceral groups are often combined into the following three principal groups called microlithotypes: vitrinite, exinite, and inertinite. With regard to physical and chemical properties, exinite is characterized by the highest hydrogen content, volatile matter content, and heating value, while inertinite has the least. Inertinite has the highest density and the greatest degree of aromaticity, while exinite is the lowest in both these properties. Thus vitrinite, by far the most abundant of the three microlithotypes as can be seen in Table 10, usually exhibits chemical and physical properties between those of the other two (Drvden, 1963).

The different microlithotypes exhibit markedly different behaviors under pyrolysis, and presumably also hydrogasification, conditions (Howard, 1963). As might be expected from the above-stated order in volatile matter content, the total yield of volatiles is usually in the order exinite > vitrinite > inertinite. There are also compositional differences among the products. For example, liquids from exinite have been characterized as primarily neutral oils, while those from vitrinite tend to be lighter and more phenolic in nature.

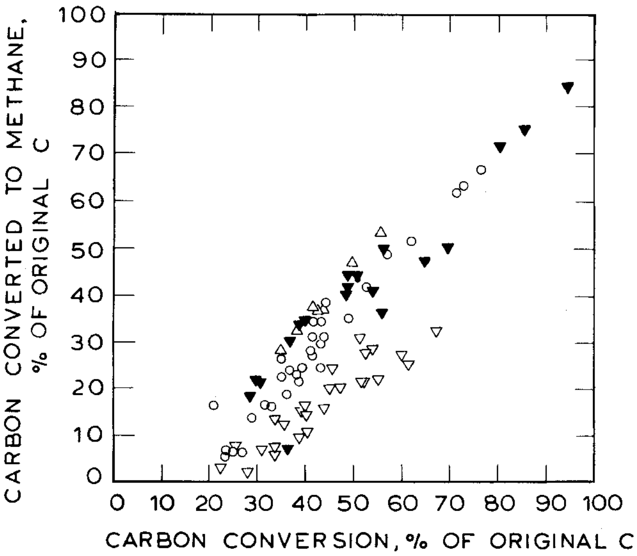

Fig. 19. Relationship between methane yield and carbon conversion in coal hydrogasification data of different investigators [(○) Birch et al. (1960); (△) Moseley and Paterson (1967); (▽) 800°C and (▼) 1 200°C, Hiteshue et al. (1964)].

This brief discussion of petrographic constituents points up the approximate character of the available pyrolysis and hydrogasification models which treat coal as a single material. If extensive rate and yield data on the different microlithotypes eventually become available, the behavior of different coal types might be described in terms of petrographic compositions and kinetic parameters evaluated for each microlithotype.

5.2. Coal Chemistry

The organic matter in coal consists primarily of carbon, hydrogen, oxygen, nitrogen, and sulfur, although trace quantities of other elements are also found. Typical elemental or so-called ultimate analyses of American coals are given in Table 10, where organic and inorganic sulfur contents are lumped together in accordance with ASTM standards. In proximate analysis, discussed above, the total coal is divided into moisture, volatile matter, fixed carbon, and ash. Either volatile matter or fixed carbon on a moisture free, ash free (MAF) basis and the MAF calorific value of the coal permit classification of coals in the ASTM system (Standard 388-38) in decreasing rank as anthracitic, bituminous, lignitic, or brown. The rank of a coal is directly related to its carbon content, with a highly graphitic material representing the ultimate product of the coalification process. Unfortunately, this information provides very little direct insight into chemical structure or petrographic composition.

There have been substantial efforts to elucidate the molecular structure of coal, but the task is exceedingly difficult because of the variety of coal types, the hetero-

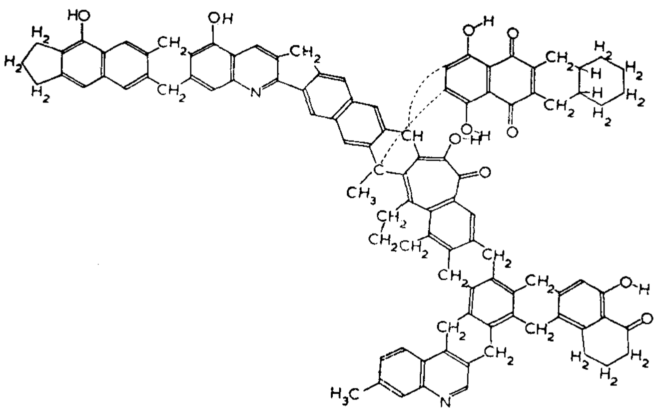

Fig. 20. Given model for molecular structure of coal [Given (1960); a vitrinite of 82% C (dry, mineral-matter-free basis); $C_{102}H_{78}O_{10}N_2$].

geneous nature of a single coal, and the complexity of individual coal constituents. The results of numerous diverse measurements have been synthesized in attempts to develop a consistent picture (for example, Van Krevelen, 1961; Dryden, 1963) but much work remains to be done. Given (1960) presented the hypothetical structure shown in Figure 20 for bituminous coal vitrinite processing 82% carbon as one possible arrangement of the atoms consistent with most of the facts available at that time. Although other structures have been proposed, some less complicated than Given's and clearly not in accord with recent findings (Fuchs and Sandhoff, 1942) and others including a larger variety of possible arrangements (Hill and Lyon, 1962), the Given model is generally accepted as a reasonable working hypothesis certainly suitable for discussion purposes.

Immediately evident in the structure is the high degree of aromaticity involving about two-thirds of the carbon and about 20% of the hydrogen. Condensed aromatic clusters each comprised of 1 to 3 rings are in line with Hirsch's (1958) x-ray scattering studies which also showed that the number of rings per cluster increases with increasing rank of the coal, ultimately approaching a fully condensed graphitic structure. The linkages between clusters is an area of considerable debate. The Given model is built around a 9, 10-dihydroanthracene module. Dryden (1963) recommended a dihydrophenanthrene module as being more compatible with the absence of methylene bridges which was reported by Brown et al. (1960) based on NMR work. In addition, other types of linkages such as short-chain aliphatics several carbons in length, ethers, sulfides, and disulfides are certainly possible. Much of the linkage structure, though, is hydroaromatic according to the results of Reggel et al. (1968, 1970, 1973). Aliphatic side chains such as the methyl groups in the Given model are also distributed throughout the coal matrix. Oxygen appears predominately in hydroxyl and carbonyl groups in all types of coal (Blom, 1960). Carboxylic acid groups and ether linkages are common to lower rank coals only. The nitrogen in coal is shown in the Given model as ring substituted azine structure. Organic sulfur, although not shown, will also appear in heterocyclic aromatic rings as well as sulfide functional groups.

Blayden et al. (1945) found that interatomic distances in coal are approximately two to three times greater in one dimension than in the other two. This result indicates a highly planar polymeric molecule in a layered structure with considerable internal pore volume and surface area. In fact, this layering phenomenon persists even in the intertwined and highly cross linked structures of the less ordered lower rank coals (Hirsch, 1954). Internal surface areas of up to several hundred square meters per gram are typically found in all ranks of coal (Dryden, (1963). The porosity of various coals is reported by Sevenster (1954) as ranging from 8 to 20%. Extensive data on the pore structure of numerous American coals are being generated at Pennsylvania State University (Gan et al., 1971; Given, 1975).

5.3. Relationship to Conversion Reactions

Given (1960) speculated that the course of pyrolysis anticipated from his model would consist of four steps: a low temperature (400° to 500°C) loss of hydroxyl groups, dehydrogenation of some of the hydroaromatic structures, scission of the molecule at the methylene bridges, and rupture of the alicyclic rings. Wiser et al. (1967) postulated a sequence of events initiated by the formation of two free radical species from a thermal cracking of the linkages forming the aromatic clusters. These free radical species would then stabilize either through a rearrangement of atoms within a fragment or by collision with another species. The resultant stabilized structure, depending on its vapor pressure, would either evolve as volatile material or remain as part of the residual char.

The amount of hydrogen in coal if allocated appropriately to the carbon would be sufficient to permit nearly complete devolatilization at least for medium and low rank coals. Unfortunately, the structure of coal preferentially evolves hydrogen as chemical water (possibly from the hydroxyl groups) and light highly stable aliphatics (such as methane and ethane), depleting the remaining carbon of much needed hydrogen. This inefficient use of intrinsic hydrogen is the reason why it is impossible, even under the most favorable conditions, to avoid formation of heavy tarry compounds and residual char. In the absence of external hydrogen, the aromatic clusters appear immune to internal rupture. In fact, prolonged heating at the highest temperatures usually employed results in only a slow dehydrogenation and further condensation of the clusters.

From a reaction rate viewpoint, the free radical secondary reactions pictured by Wiser et al. will be extremely fast compared to the thermally invoked bond ruptures as radical formation steps. Given has already indicated the presence of a hierarchy of bond susceptibilities to scission within the starting molecule. Intermediate char structures formed by free radical recombinations similarly will be subject to thermal bond rupture at high temperatures, thus assuring a virtual continuum of rate determining bond energies. This structural observation established the basis for the distributed activation energy model introduced previously. Increased interest in coal research and the accessibility of powerful computer systems has prompted reexamination of more fundamental reaction mechanisms. In the past, however, a manageable set of fundamental reactions usually proved inadequate to describe experimental results, and a larger, more complete set resulted in too many degrees of freedom for useful modeling since it was impossible to specify a priori coal reaction rates or to determine them independently.

Cheong et al. (1975) have recently proposed a set of fourteen reactions to describe coal pyrolysis. The Given model was simplified to a carbon-hydrogen structure of naphthalene clusters and an equal number of methylene and ethylene bridges. Rate constants selected from gas-phase reactions believed to be similar to those occurring in pyrolysis and appropriate initial conditions were employed to predict weight loss as a function of time and temperature. The results are preliminary but nevertheless interesting.

Table 11. Selected Potential Commercial Coal Conversion Processes Based on Pyrolysis and/or Reaction in Hydrogen Rich Gas

Process name	Developer	Stage of development (kg coal/s)*	Reactor type	Temperature, °C	Coal resid. time, s	Atmosphere and pressure	Particle size, μm	Typical products, % by wt.	
Pyrolysis									
COED (Jones, 1975)	FMC (OCR Contract)	Pilot plant (0.38)	4 stage fluidized beds	1. 316 2. 454 3. 538 4. 816	(?)	Hot combustion gases and/or volatile products; 1.3-1.7 atm	≤3 180	Char gas oil & tar liquor	60 15 19 6
Garrett flash pyrolysis (Green, 1975)	Garrett Research and Development	Pilot plant (0.042)	Entrained flow	600-850	>0.1	Combustion gases; 1.0 atm	≤150	Char gas oil & tar water	57 6 35 2
Hydrocarbonization									
Coalcon (Martin, 1975; Morgan, 1975)	Union Carbide et al.	Pilot plant (0.21)	Fluidized bed	470-560	440-2 650	Hydrogen rich; 20-70 atm	≤750; mainly 75-500	Char gas oil & tar water	42 22 31 5
Hydrogasification									
Hygas (Anastasia and Bair, 1975)	IGT (AGA-ERDA Contract)	Pilot plant (0.76)	2 stage, fluidized beds	1. 700-800 2. 900-1 000	(?)	Hydrogen rich; 70-100 atm	≤1 500	Primarily CH_4, 65-70% made in gasifier	
Hydrane (Gray and Yarvorsky, 1975)	ERDA (Pittsburgh Energy Research Center)	Bench scale (0.0006-0.002)	1. Dilute phase free fall	600-800	1/4-3/4	H_2-CH_4 mixture; 76 atm	150-300	Primarily CH_4, 95% made in gasifier	
			2. F. bed	900	(?)	H_2, 76 atm			

* 1 kg/s ≃ 95 short tons/day.

6. COMMERCIAL INTEREST

There is considerable commercial interest in the behavior of coal in hydrogen and inert atmospheres under the relatively rapid heating conditions afforded by fluidized beds and entrained or suspended flow reactors. Several of the new processes under development are reviewed and compared by Hottel and Howard (1971), and less detailed but more extensive reviews are given by Bodle and Vyas (1975) and Howard-Smith and Werner (1975). An abbreviated list of emerging processes representing the wide range of emphasis on hydrogenation and including some of the available operating characteristics is given in Table 11. Details, although incomplete in some cases, are given in the references cited in the table. The processes are divided into three classes: pyrolysis, no hydrogen or steam fed; hydrocarbonization, hydrogen rich atmosphere, relatively low temperatures, and long residence times; and hydrogasification, hydrogen rich atmosphere, relatively high temperatures, and short residence times. The focus here on processes relying primarily on devolatilization and/or reaction with hydrogen rich gas excludes numerous other systems in which pyrolysis occurs, such as those involving oxidizing environments (for example, coal combustors), direct coal feed and high temperature steam gasification (where volatiles are broken down to hydrogen and carbon monoxide), and slurry contacting (for example, solvent extraction and liquefaction).

6.1. Pyrolysis Processes

The COED (Char Oil Energy Development) and Garrett processes are hybrid systems to the extent that they produce gaseous and liquid products. The economic viability of both processes clearly depends on utilization of the by-product char. The Garrett organization promotes use of the char as boiler fuel (Sass et al., 1973; Sass, 1974), while a private consortium (Seglin et al., 1974) is developing a process for the production of pipeline quality gas from COED char. Since pyrolysis in both systems is conducted at or near atmospheric pressure, the need for expensive high-pressure equipment is eliminated, as is also the ability to incorporate outside hydrogen directly into the products. This trade off is a major consideration in the design of coal gasification schemes, and its clarification will require a good understanding of pyrolysis, secondary reactions, reactions involving hydrogen, and associated interactions.

It is evident from Table 11 that COED and Garrett Flash Pyrolysis represent divergent reactor designs. The former is based on a series of temperature staged fluidized beds in which the coal residence time is undoubtedly several minutes, while the Garrett process uses a single pass entrained flow reactor with a coal residence time of fractions of a second. FMC researchers at an early stage also employed a short residence time entrained flow reactor (Eddinger et al., 1966; Friedman et al., 1968). Each process capitalizes on a unique aspect of the devolatilization process.

A series of temperature staged fluidized beds is practical acknowledgment of the state function relationship between pyrolysis yield and temperature; that is, extended solids residence times at low temperatures do not significantly alter the higher temperature yields. Furthermore, this concept allows for relatively short product vapor residence times (several seconds) and a gentle treatment of low temperature products. Products formed and removed at low temperatures are not exposed to higher reaction temperatures and the associated higher rates of secondary reactions. Thus, this procedure does have advantages over the use of a single fluidized bed operating at an intermediate or high temperature, but these advantages must be balanced against the cost of installing and operating a number of reactors, each with a fairly substantial coal holdup.

The entrained flow reactor permits even further reduction of the extent of secondary reactions, with a total yield of volatiles exceeding the standard volatile content of the coal, whereas the COED yield approximately matches the standard value. The entrained flow characteristics underlying the larger volatiles yield would appear to be smaller particles, better particle dispersion, and shorter residence time, all of which reduce volatiles contact with hot coal surfaces. Rapid heating is a necessary feature of short residence time, but, according to the pyrolysis literature, there is little if any effect of heating rate per se on volatiles yield.

6.2. Hydrocarbonization and Hydrogasification Processes

The last three processes in Table 11 involve hydrogen treatment. A Coalcon demonstration plant (27.5 kg coal/s or 2 614 short tons/day) is forthcoming, based on a hydrocarbonization pilot plant study completed in the early 1960's. Of the hydrogasification processes, Hygas is currently in pilot plant operation, while Hydrane has been studied only at bench scale. Fluidized beds are employed in all three processes, but not for the initial coal contacting in the case of Hydrane. Here the coal is fed into an upper dilute phase, free fall section, where caking coal is sufficiently reacted to become nonagglomerating before falling into the fluidized bed. The off gases from the bed, which are rich in hydrogen and methane, serve as transport gas and flow downward in the free fall section. An oxidation pretreatment requiring another vessel and entailing the loss of some initial reactivity is being studied in the Hygas project as a means for handling caking coal.

At the relatively low temperatures of the hydrocarbonization process, little rapid-rate carbon would be available for hydrogasification according to the above discussions (Figure 16). IGT studies of bituminous coal char indicate that 15 to 25% weight loss in addition to the standard volatile matter content would be obtained by the slower hydrocarbonization in 1 500 to 1 800 s at 35 atm hydrogen (Pyrcioch et al., 1972). Both Hygas and Hydrane are highly touted for the high percentage of the final methane product that is made in the gasifier (Table 11), compared with the performance of other processes for pipeline gas production from coal. This characteristic, which is especially good in the case of Hydrane, reflects achievement of considerable rapid-rate hydrogasification and prevention of excessive cracking of methane formed by devolatilization. Methane is also a significant product of hydrocarbonization, but the low temperatures of this process are selected to favor oil and tar production.

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NOTATION

a = constant, kcal/mole
a' = dimensionless constant
A = dimensionless constant
B = dimensionless constant
C = vapor phase concentration of reactive volatiles within the coal particle, fraction of original coal mass
C_∞ = vapor phase concentration of reactive volatiles in the ambient gas, fraction of original coal mass
C^* = dimensionless concentration of active sites
C_o^* = value of C^* at $t = o$
d = particle diameter, mm
E = activation energy for pyrolysis, kcal/mole
E_o = mean of activation energy distribution, kcal/mole
E_t = $RT \ln(k_o t)$
E_1 = maximum activation energy of reactions forming nonreactive volatiles and minimum activation energy of reactions forming reactive volatiles, kcal/mole
E_s = activation energy for active site formation, kcal/mole
$f(E)$ = activation energy distribution function for pyrolysis, mole/kcal
$f_s(E_s)$ = activation energy distribution function for active site formation, mole/kcal
k = first-order rate constant for pyrolysis, s^{-1}
k' = n_{th} order rate constant for devolatilization, g^{1-n}/s
k_o = apparent frequency factor, s^{-1}
k_1 = overall rate constant for deposition reaction, s^{-1}
k_2 = overall rate constant for hydrogenation of reactive volatiles, s^{-1} atm^{-1}
k_3 = $k_4 C_o^* / k_5$
k_5 = rate constant for decay of active sites, s^{-1}
k_c = pressure-independent overall mass transfer coefficient, atm/s
k_s = first-order rate constant for active site formation, s^{-1}
K_c = overall mass transfer coefficient ($K_c = k_c/P$), s^{-1}
K_v = constant, s/m^2
m = constant heating rate, K/s
n = reaction order
P = pressure, atm
P_{H_2} = hydrogen pressure, atm
Q = ratio of total weight loss to loss of proximate volatile matter
R = ideal gas constant, kcal/mole K
t = time, s
t_v = time required for devolatilization, s
T = absolute temperature, K
T_a = ambient temperature, °C
T_o = base temperature, K
V = volatiles lost from particle up to time t, fraction of the original coal weight
V^* = volatiles lost from particle up to $t = \infty$ (ultimate yield), approximated by measurements at long reaction times, fraction of the original coal weight
V_r' = reactive volatiles formed up to time t, fraction of the original coal weight
V_r^{**} = reactive volatiles formed up to $t = \infty$ (potential ultimate yield of reactive volatiles), fraction of the original coal weight
V_{nr}^* = nonreactive volatiles lost from particle up to $t = \infty$ (ultimate yield of nonreactive volatiles), fraction of the original coal weight (Note: $V_{nr}^* = V_{nr}^{**}$)
V_{nr}^{**} = nonreactive volatiles formed up to $t = \infty$ (potential ultimate yield of nonreactive volatiles),

fraction of the original coal weight (Note: $V_{nr}^{**} = V_{nr}^{*}$)

VM = volatile content as measured by proximate analysis, fraction of original coal weight

VM_c = proximate volatile matter in char at $t = \infty$, fraction of initial proximate volatile matter

X = conversion up to time t of original carbon material (carbon, coal, or fixed carbon) to products in rapid-rate hydrogasification, fraction of the original weight of carbon material

X^* = total rapid-rate carbon material initially in coal, fraction of original weight of carbon material

α = mass or thermal diffusivity, m^2/s

σ = standard deviation of activation energy distribution, kcal/mole

Additional Subscripts

i = one member of a large group of independent parallel pyrolysis reactions

j = a single volatile species

max = maximum value

min = minimum value

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The Role of *n*-Butane in Hydrate Formation

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The role of *n*-butane in the formation of hydrates has been a matter of some uncertainty. The experimental measurements resulting from this work have shown conclusively that *n*-butane does enter the hydrate lattice when hydrates are formed in the presence of methane at pressures from about 1 000 to 10 000 kPa over a temperature range from 0° to about 13°C. At higher pressures and temperatures, *n*-butane ceases to enter the crystal and behaves like a nonhydrate former.

SCOPE

The formation of hydrates from pure *n*-butane with water has never been confirmed, and the literature contains conflicting opinions on the role of *n*-butane in hydrate formation from mixtures. The object of the work undertaken in this study was to obtain new experimental

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