only close to its roof, while the wedging effect produces horizontal tensile stress over the entire intrusive body (Figs. 2 and 3).

An important feature of the stress distribution (Fig. 2) is that the maximum stress concentration is highest immediately above the top of the intrusive body, but the contour of stress concentration has two peaks in the higher part over the intrusive body. Another important point is that the direction of maximum compression (minimum tensile stress), indicated by short lines in Fig. 2, is nearly vertical over the intrusive body but becomes progressively more horizontal away from the axis of the body. Such stress distribution due to wedging of a magmatic body at depth would produce horizontal extension above the igneous mass and horizontal compression outward and at the side perpendicular to the direction of elongation of the intrusive body (Fig. 3). Such horizontal compressions have been measured outside the rift valley in Iceland by Hast (*27*). In many areas dikes occur perpendicular to the trend of the central rift valley or inclined in a conjugate system. These dike swarms also suggest horizontal compression perpendicular to the trend of the rift valley (Fig. 3). Roberts (*28*) estimated maximum excess magma pressure on the order of – 1 kbar at a depth of 10 to 30 km, if basaltic magma is in equilibrium with lithostatic stress at a depth of about 60 km. Convection of heated water in the crust can raise pore pressure over the intrusion and helps brittle fracturing. If the aspect ratio of the basaltic intrusive body is more than 1 : 10, our analyses show that fractures can develop extensively when the top of the intrusive body is at a depth of 10 to 30 km (that is, at – 1 kbar excess magma pressure) because stress becomes effectively tensile or near tensile in a wide area around its apex (Eq. 1). This depth for the top of intrusion is consistent with the general width of rift valleys of 20 to 60 km (*2*).

Calderas have characteristics similar to rift valleys except for the difference in horizontal dimension. We indicated earlier (*21*) that calderas may have formed over the intrusion of prolate magma bodies whose plan view is circular instead of elliptical. Stress concentrations around such prolate intrusions are found to be of much lower magnitude than around oblate intrusions, and generally produce radial, radial-concentric, and concentric fracturing around the prolate protrusions with increase in aspect ratio and stress.

This analysis suggests that excess magma pressure in vertical dike-like intrusions pushes lithospheric plates apart almost horizontally. Graben subsidence occurs inside the funnel-shaped normal faults above the intrusion. Horizontal transverse compression produces domal uplift on the flanks of a rift valley, and secondary dike intrusions or rift valleys can also develop perpendicular to the main rift valley. Rift valleys can also branch into a set of conjugate strike-slip faults at the ends, producing triple junction fracture geometry (*29*). Such rift valley branching is observed in the Carlsberge, Mid-Atlantic Ridge, East Pacific Rise, Rhine graben, and Red Sea regions.

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Flash Hydrogenation of a Bituminous Coal

Abstract. *Flash heating of Illinois coal (to 700°C in 1 second) in flowing hydrogen at 100 atmospheres, limiting the vapor residence time at 700°C to 3 seconds, converts 14 percent of the coal's carbon to methane, 7 percent to ethane, and 10 percent to benzene, toluene, and xylenes. The remainder is coke; the carbon balance shows that heavy tar, if any exists, is less than 3 percent.*

We believe that economics will soon cause a turning away from the practice of burning chemically bound hydrogen for the large-scale production of electricity. Bound hydrogen in coal will be viewed as too valuable to burn and send as water vapor to a stack. This hydrogen can become part of some clean fuel, more convenient and more valuable than coal. The hydrogen-rich fuel would be "creamed off," leaving a residue that would be burned to generate electricity.

This idea is, of course, not original with us. The by-product coke oven is 100 years old, and many teams have attempted to displace it with improved coking procedures. The first step in such procedures is crucial in determining what products will be obtained and how difficult subsequent processing will be. A step with a minimum yield of heavy tar will be preferred, since tar is difficult to upgrade by hydrogenation and has little value.

In our search for a likely first step, we were struck by U.S. Bureau of Mines data from rapid noncatalytic hydrogenation of bituminous (*1*) and subbituminous (*2*) coals at 69 and 400 atm, respectively, and 800°C. An earlier experiment (*3*) was modified so that vapor products were swept from the reaction zone into a cooler region in a few seconds.

Rapid heating of coal avoids polymerization reactions that produce a solid of high molecular weight before much evolution of light species has occurred (*4*). The presence of hydrogen directs free radicals evolving from rapidly heated coal into reaction paths that lead to light stable species.

What was new in the Bureau's rapid hydrogenation (*5*) was the short gas residence time at the reaction temperature. Following Dent's lead of just 40 years ago (*6*) and with methane as the objective, researchers have treated coal with hydrogen at pressure in experiments with slow heating (*7*), with rapid heating (approximately 1 to 2

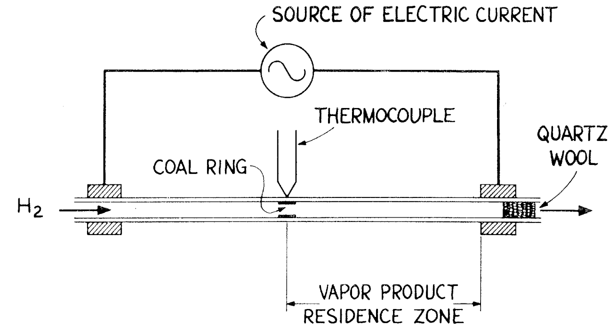

Fig. 1. Schematic diagram of the reactor. The location of the coal deposit in the tube and the hydrogen flow rate are selected to give the desired vapor product residence time.

minutes to reach the reaction temperature) (*1–3, 5, 6, 8*), and with flash heating (about 1 second or less) (*9–12*). Except in the processes described in (*1, 2, 5, 9, 11*), gas residence time in the reaction zone was long, generally running to minutes. At long gas residence times, with either rapid or flash heating, the usual products are methane, ethane, and a little heavy tar [for example, see (*12*)].

What caught our attention about the Bureau's experiments with the rapid heating of coal and short gas residence time was the extraordinary yield structure (*13*): liquid yields often approached the yield of gas. We wondered what liquid would result from flash heating combined with a short gas residence time (*9*). We have modified the Bureau's experiment (*3*) to provide flash heating as well as close control of the times that both solid and gas spend at the reaction temperature. Our reactor (Fig. 1) is a tube of 316 stainless steel, 6.35 mm in outside diameter, 5.1 mm in inside diameter, and 300 mm long. Our usual practice is to use a reactor tube only once. A weighed sample of coal (about 10 mg) ground to a fineness smaller than 325 mesh (about 44 μm) is deposited in a thin cohesive ring at a selected position on the interior tube surface. The reactor is clamped between electrical leads and connected to a source of hydrogen on the left and to evacuated collection tanks on the right. A thermocouple is spot-welded to the tube exterior at the coal's position.

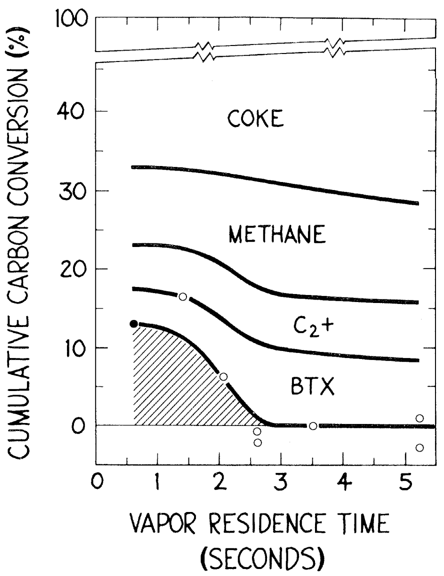

Fig. 2. Yield structure from the flash hydrogenation of Illinois No. 6 coal at 100 atm and about 700°C as a function of the vapor product residence time; C_{2+}, yield of ethane and propane (with a trace of butane). The shaded area in the lower left is carbon unaccounted for by the carbon balance. A plotted point is the carbon not found in the vapor products of hydrogenation or carbon oxides from a subsequent combustion; a point falling on the abscissa represents a perfect carbon balance.

The flow of hydrogen is established at 100 atm while the reactor is at room temperature. At time zero, power is supplied at 12 kw, resistively heating the reactor tube. When a preset temperature is reached, an automatic control circuit switches over to a lower power level to maintain that temperature for 10 seconds. The current is shut off, and the reactor quickly cools. Total products of the reaction generated while the sample is at high temperature are collected in one of the evacuated tanks. Hydrogen in the reactor is replaced by oxygen at 4 atm, the residual char burned, and combustion products collected separately. Products are analyzed by gas chromatography.

The vapor residence time is that required for the evolved products to be carried by flowing hydrogen to the right-hand electrical lead. Because of its large mass, the lead stays at its initial temperature and serves to quench the products (*14*).

Figures 2 and 3 give a yield structure based on 29 runs (23 with carbon balances) made with a mine-mouth sample of Illinois No. 6 coal (*15*) at a heating rate of approximately 650°C per second (*16*). Over the range 600° to 1000°C, the only light products observed in more than trace amounts (above 1 percent) are methane, ethane, propane, and BTX (benzene, toluene, and xylenes). Direct tests show that xylene and lighter species introduced ahead of the reactor are transmitted quantitatively to our collection reservoir. Carbon balances suggest that little if any material heavier than xylene appears in products from runs beyond about 3 seconds in Fig. 2 and beyond about 850°C in Fig. 3. The precision of the carbon balance for these runs (95 percent confidence level) is ± 3 percent, placing an upper limit to heavy tar, if any is present.

We believe that carbon unaccounted for in runs below about 3 seconds in Fig. 2 and below about 850°C in Fig. 3 reflects the presence of species heavier than xylene. The data of Fig. 2 tend to confirm the suggestion of Friedman *et al.* (*2*) that there is an optimum vapor residence time for the yield of light aromatic liquids, because initially evolved species are relatively heavy. Comparison of Fig. 2 with Bureau data for catalyzed coal hydrogenation at short gas residence times (*13*) suggests that lighter species are evolved from coal heated at 650°C/per second than at about 7°C per second.

Noncatalyzed flash hydrogenation of coal could supply the needs of the pipeline gas, petrochemical, liquid fuel, and electric power industries. Our data, like the bureau's (*1, 2*), are for a supply of hydrogen far too large relative to the coal sample to be economic (that is, far too low a degree of hydrogen conversion). Data for the reaction path at a realistic supply of hydrogen are needed before flash hydrogenation can be evaluated economically. That such data are worth getting is illustrated by our yields from Fig. 2 at 3 seconds: a plant consuming 36.4 × 10^6 tons (1 short ton = 0.907 metric ton) of Illinois No. 6 coal (*15*) could supply 0.22 × 10^{12} standard cubic feet of methane [1 standard cubic foot at 60°F (15.6°C) is 0.0268 normal cubic meter

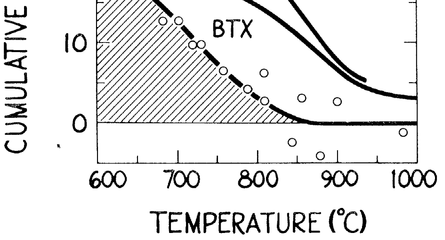

Fig. 3. Yield structure at a product residence time nominally 0.6 second as a function of temperature. (For an explanation of the symbols, shaded area, and plotted points, see the legend for Fig. 2). The propane yield falls linearly from 2 percent at 620°C to nearly zero at 780°C. The ratio of benzene to total BTX rises nearly linearly from 0.41 at 620°C to substantially unity beyond 790°C.

at 0°C]; about 1.4 × 10^6 tons of ethylene (obtained by cracking the ethane product); and 2.7 × 10^6 tons of benzene. These are, respectively, 1, 13, and 50 percent of the 1973 U.S. consumption.

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13. In most of the Bureau's experiments at short gas residence times, coal catalyzed with 1 percent molybdenum was treated at 400 atm at 800°C. Hiteshue *et al.* (*5*) reported a 26 percent yield (by weight of coal) at 6 seconds and a 4.5 percent yield of a lighter liquid at 30 seconds. Friedman *et al.* (*2*) reported liquid yields of 35, 41, 31, 23, and 10 percent at 2.3, 5, 6.7, 10, and 25 seconds, respectively. The yield of single-ring aromatics at 5, 6.7, and 25 seconds was 3.4, 4.1, and 3.5 percent, respectively. The yield of asphaltenes at 6.7 seconds was 3.7 percent, and the liquid produced at 2.3 seconds was heavier than that at 5 seconds. These liquids from rapid heating were far heavier than the liquids from flash heating reported here.
14. R. A. Graff, S. Dobner, and A. M. Squires (in preparation) give further experimental details and results of an exploration of coal heating rate, time of the coal sample at the reaction temperature, gas environment, and vapor residence time.
15. The Illinois State Geological Survey supplied the coal sample and its ultimate analysis (percent by weight, moisture-free basis) was as follows: hydrogen, 5.11; carbon, 68.18; nitrogen, 1.06; oxygen, 9.38; sulfur, 4.16; and ash, 12.11.
16. S. Dobner, R. A. Graff, and A. M. Squires (in preparation) give detailed results on which Figs. 2 and 3 are based.
17. The work is supported by grant AER-72-03426 A No. 4 (formerly GI-34286) from the RANN Program (Research Applied to National Needs) of the National Science Foundation. Under this grant, we are also studying high-velocity fluidized beds suitable for flash-hydrogenating coal. We thank A. Chiaravalotti, who performed most of the experiments; E. Gilbert, who assisted in developing the experiment; and R. D. Harvey and his colleagues at the Illinois State Geological Survey for their cooperation.

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Scanning Proton-Induced X-ray Microspectrometry in an Atmospheric Environment

Abstract. *Collimated million-electron-volt proton beams, brought out into air, can be used as a scanning microprobe to examine specimens with a spatial resolution of the order of 1 micrometer. Trace elements at concentrations as low as 1 part per million can be detected. Some preliminary results based on the use of this simple method are presented.*

X-ray emission spectroscopy, induced either by incident x-rays of higher energy (fluorescence) or by bombardment with charged particles, has been used as a tool for the detection of extremely small quantities (as little as 10^{-12} g) of particular chemical elements (*1–3*). Protons of energies ≈ 2 to 4 Mev are particularly effective, combining large x-ray production cross sections with small x-ray backgrounds [the dominant x-ray background coming from proton bremsstrahlung and secondary-electron bremsstrahlung (*4*)]; indeed, the method is so sensitive to trace concentrations that the difficulty of preparing sufficiently pure substrate materials often poses a practical limitation (*2*). Roughly speaking, concentrations of the order of 1 part in 10^6 or 10^7 are detectable in reasonably short times, as compared with limiting concentrations of 1 part in 10^2 for (continuum) x-ray–induced fluorescence and 1 part in 10^3 for the electron microprobe (*4, 5*).

Unlike neutron activation, x-ray emission is immediate, and so it is possible to use a scanning point source to produce x-ray emission pictures or micrographs. This has been done with electrons [the "scanning electron microprobe" (*6*)], with x-rays [both conventional x-ray sources (*7*) and collimated synchrotron radiation (*8*) have

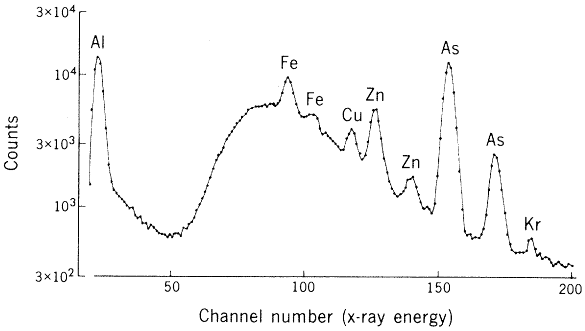

Fig. 1. X-ray energy spectrum from a silicon wafer doped with 60 ppm of arsenic. The aluminum x-rays are produced by fluorescence from silicon x-rays in an aluminum foil covering the detector; atmospheric krypton, as well as metallic impurities, are also clearly visible.

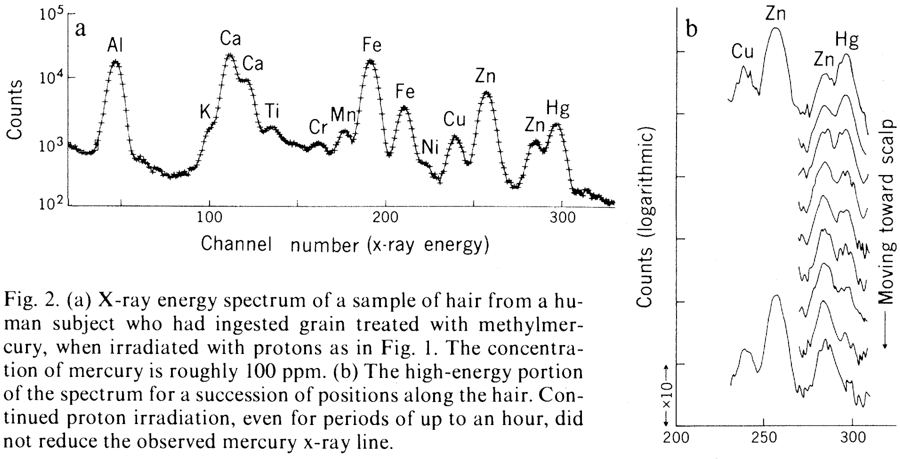

Fig. 2. (a) X-ray energy spectrum of a sample of hair from a human subject who had ingested grain treated with methylmercury, when irradiated with protons as in Fig. 1. The concentration of mercury is roughly 100 ppm. (b) The high-energy portion of the spectrum for a succession of positions along the hair. Continued proton irradiation, even for periods of up to an hour, did not reduce the observed mercury x-ray line.