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HIGH PRESSURE

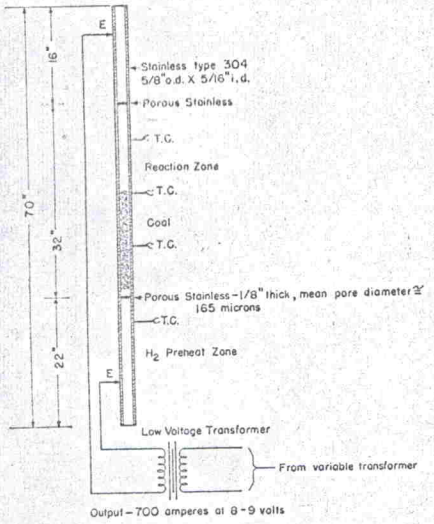
R. W. HITESHUE, R. B. ANDERSON, and M. D. SCHLESINGER
Bureau of Mines, U. S. Department of the Interior, Pittsburgh, Pa.

Hydrogenating Coal at 800° C.

With this new technique, 69% yields of gaseous hydrocarbons can be obtained from coal

HYDROGENATING COAL for producing liquid hydrocarbons is normally done at 450° to 480° C. and 3000 to 8000 pounds per square inch gage. Under these conditions, about 60% of the coal can be converted to oils, 20% to gaseous hydrocarbons, and the balance to water, carbon dioxide, ammonia, and hydrogen sulfide.

Recently the Bureau of Mines, U. S. Department of the Interior, began a study of this reaction at high temperatures to determine if appreciable quantities of gaseous hydrocarbons and low-boiling aromatics could be produced from coal. The first phase of the program was designed to elucidate the effect of short residence time at 800° C. and 6000 pounds per square inch on hydrogenation of a bituminous C coal from Wyoming, using ammonium molybdate plus sulfuric acid as a catalyst. These experiments extend the studies of Dent (*4*), Channabasappa (*2*), and the Bureau of Mines (*3*) on the hydrogenation of coal under severe conditions.



This is the reactor devised to evaluate short residence time

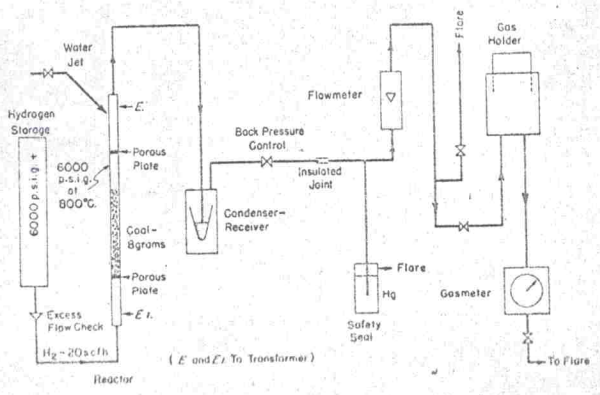
Since hydrogenation of coal begins around 400° C., the effect of short residence time could not be determined at very high temperatures in conventional autoclaves because of the long heating and cooling cycles (3 to 4 hours), required for such devices. Consequently, a reaction vessel was developed for rapid heating and cooling of the reactants. An expendable vessel was necessary because the time to rupture under these conditions would be less than 1 hour for most alloys. A tubular reactor using direct resistance heating seemed most desirable from the standpoint of cost and availability. With this design it was possible to attain a temperature of 800° C. in about 2 minutes and to cool to room temperature in about 10 seconds. Rapid cooling was accomplished by spraying the entire assembly with cold water.

Experimental Procedure

The reactor was simply a 6-foot length of stainless steel, Type 304, tubing having an outside and inside diameter of $^5/_8$ and $^5/_{16}$ inch, respectively. The coal was supported and retained within the reaction zone by two porous plates forced into the bore of the tube. The electrodes, placed at the ends of the tube, reduced heat losses and provided a preheat zone for the hydrogen.

Current was supplied by a transformer capable of delivering up to 700 amperes at 9 volts, and its output was controlled by varying the input voltage with a variable transformer. In initial hydrogenation experiments, temperatures were measured with bare internal as well as conventional external thermocouples. After it became evident that the differential between these two temperature zones was small, only external thermocouples were used. The reactor was completely covered with $^1/_2$-inch pipe insulation, and the water jet was placed at the top of the assembly between the insulation and the reactor.

Adequate stress-to-rupture data for stainless steel under these conditions were not available; therefore, operational limits of the reactor had to be determined by destructive tests. These were conducted at 600° to 1000° C. and 1000 to 8000 pounds per square inch, with $^5/_8$ by $^5/_{16}$ inch Type 304 stainless steel tubing. All tests were performed with hydrogen to include possible effects of embrittlement (Figure 1). Exact dimensions of the test specimens are shown in Figure 1 to enable designers to calculate these results on a



The semicontinuous unit was arranged in this manner

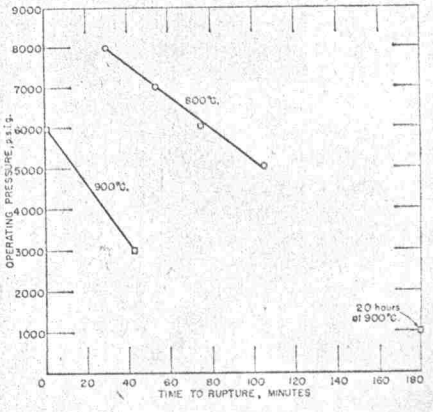


Figure 1. Time to rupture vs. operating pressure, stainless steel, Type 304, tube having outside and inside diameters of 0.628 and 0.317 inch, respectively

basis of stress. Rupture time was increased little or not at all by using a higher grade alloy such as 19-9 DL.

Hydrogen flowed from a storage vessel into the bottom of the reactor, through a preheat zone, and into the static bed of coal. After a constant flow of hydrogen was established, the charge was heated to 800° C. in about 2 minutes by passing a current of 700 amperes through the tube. Hydrocarbon vapors and gases and excess hydrogen passed at pressure into a small condenser-receiver where the low-boiling liquid hydrocarbons (overhead oils) and water were collected in a small glass vial. Noncondensable gases were reduced to atmospheric pressure, passed into a small gasholder, and after an appropriate storage period, were sampled, metered, and finally vented. Carbon dioxide, hydrogen sulfide, and ammonia were not separated from the effluent gas stream. At the end of the experiments, the reactor and its charge were cooled to room temperature by spraying with cold water.

After the bulk of unreacted solids was removed, the reactor was washed with benzene to remove the remainder of the solids and high molecular weight oils. The unreacted solids and the benzene washings were filtered, and the solids were extracted with benzene in a Soxhlet apparatus. The insolubles remaining were thus composed of organic benzene insolubles plus inorganic material from the coal and added catalyst. The filtrate and extract contained *n*-hexane-soluble oils, asphaltenes, and other benzene-soluble solids. These soluble fractions were not analyzed. The percentage of coal reacted was calculated by subtracting weight per cent of the unreacted organic solids (organic benzene insolubles) from 100.

The low-boiling liquid hydrocarbons and water were collected in the condenser-receiver. The oils were analyzed by a mass spectrometer for single-ring aromatics (C_6 to C_{10}), naphthalene, tetralin, and methylindane. These analyses were based on molecular ion peaks. The mass spectrometer was also used for analyzing the effluent gas stream for C_1 to C_3 hydrocarbons.

Yields of oils and hydrocarbon gases were expressed as weight percentages based on moisture- and ash-free coal. The total yields of all products on this basis would thus be larger than 100 by an amount equal to the percentage of hydrogen absorbed based on moisture- and ash-free coal.

A high-volatile, bituminous C coal from Rock Springs, Wyo., was selected for this study becasue it is of the type of coal that would probably be used for future coal-to-oil or coal-to-gas processes. It is noncoking, low in ash, and exists in formations amenable to inexpensive mining techniques. This particular run-of-mine coal was coal furnished by the Union Pacific Coal Co. from the D. O. Clark mine. The bulk came from seams 7 and 7½ and a minor portion from seam 15. The ultimate analyses of the coal on an as-received and on a moisture- and ash-free basis are shown in Table I, and petrographic analyses are shown in Table II. The latter analyses were made with reflective light on a briquet of granular coal and with transmitted

Table I. Analyses of Rock Springs, Wyo., Coal

	%	
	Moisture- and ash-free basis	As-received basis
Carbon	77.6	75.0
Hydrogen	5.6	5.4
Nitrogen	1.7	1.7
Sulfur	0.8	0.8
Oxygen (by difference)	14.3	13.6
Ash	...	2.0
Moisture	...	1.5

Table II. Petrographic Analyses of Rock Springs, Wyo., Coal

% Compn. by			
Reflected light, ash-free basis		Transmitted light	
Vitrinite + exinite	96.3	Anthraxylon + translucent attritus	90
Micrinite	1.4	Opaque attritus	8
Fusinite	2.3	Fusain	2

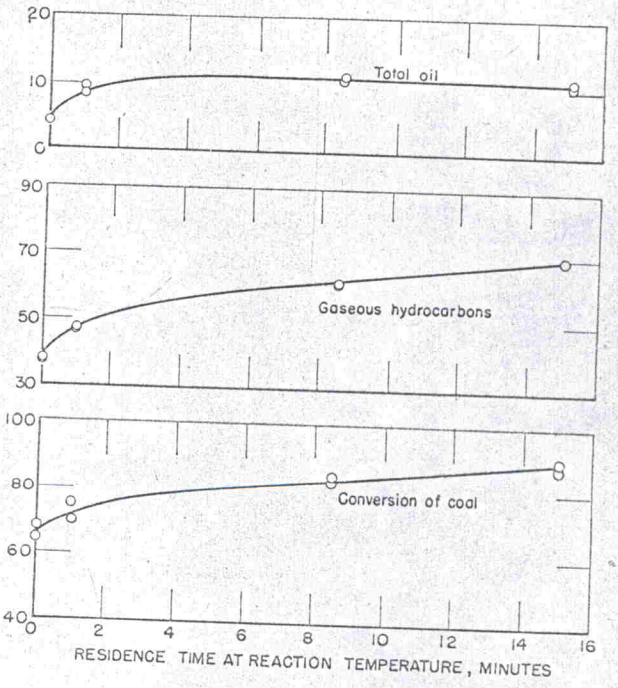


Figure 2. Residence time *vs.* coal conversion showing liquid and gaseous hydrocarbon yields

Rock Springs, Wyo., coal, 6000 pounds per square inch at 800° C., catalyzed with 1% molybdenum as ammonium molybdate

Table III. Effect of Residence Time on Product Distribution

(Rock Springs, Wyo., coal; 1% Mo on coal as ammonium molybdate; 6000 lb./sq. in. gage; 800° C.)

		Yields, % Based on M.A.F. Coal							
Expt. No.	Residence Time at Temp., Min.	Conversion to liquids and gases	Total liquid hydrocarbons	Overhead liquid hydrocarbons	High mol. wt. liquid hydrocarbons	Total hydrocarbon gases	Methane	Ethane	Propane
1	0	65.0	4.8	0.6	4.2	38.1	29.8	7.8	0.5
2	0	68.0	4.4	0.0	4.4	37.0	29.7	7.3	...
3	1	69.9	9.5	6.5	3.0	48.6	41.1	7.0	0.5
4	1	75.6	8.3	5.3	3.0	47.9	40.8	6.6	0.5
5	8½	84.2	11.1	9.2	1.9	62.7	51.4	10.1	1.2
6	8½	83.8	11.9	9.7	2.2	62.8	54.1	8.2	0.5
7	15	88.1	10.7	8.8	1.9	...	...	...	...
8	15	90.3	11.4	8.5	2.9	69.3	59.5	9.3	0.5

Here Are the Results

Zero residence time, 6000 pounds and 800° C.—65 to 68% of coal converted to liquids and gases. After 15 minutes, 90% conversion. Zero residence—38% of the coal converted to gaseous hydrocarbons. After 15 minutes, yield goes to 69%, with 90 volume % methane and about 10% ethane. Yield of oil based on coal rose rapidly from 5% at zero residence to 9% at 1 minute. At lower temperatures (400° to 480° C.), mechanism (6) of coal hydrogenation reaction differs. Active catalyst can prevent polymerization of primary products to char. Stabilization results in high yields (60%) oil and low yields (20%) hydrocarbon gases.

Eighty weight per cent of total oil yielded was overhead product. Balance stayed with char, and was high in asphaltenes. Overhead oils analysis: 32% naphthalene (volume %), 36% benzene, 3% xylenes, 19% unknowns. C_9 and C_{10} single-ring aromatics. Tetralin and methylindane were present in quantities of less than 1%. C_6 to C_{10} single-ring aromatics and yield of naphthalene each amounted to 3 to 4% based on moisture and ash-free coal.

light using a thin section of coal. Anderson and others (7) have shown the pore volume of a similar sample to be 0.115 ml. per gram, the porosity, 0.133 ml. per milliliter, and the surface area in nitrogen, 3 square meters per gram. The density in helium was 1.338 grams per milliliter.

The coal was washed in a heavy-density medium, pulverized, and dried simultaneously in a ball mill with inert gas at 80° C. Ammonium molybdate (1% molybdenum) and 0.8% acid (on moisture- and ash-free coal) were added (5) to a weight of water 1.3 times the weight of coal. After standing for 5 minutes, the solution was added to the dry coal and the slurry was concentrated by evaporating on a hot plate with constant stirring at about 100° C. The mixture was finally dried on a tray in air at 70° C. for 20 hours.

Experiments were conducted with 8 grams of coal at 6000 pounds per square inch gage, 800° C., and residence times of zero to 15 minutes. Zero residence time is that where the coal attains reaction temperature. The hydrogen rate for all experiments was 20 standard cubic feet per hour corresponding to 2.5 cubic feet (5.9 grams) of hydrogen per hour per gram of coal and to a nominal lineal velocity of 6 feet per minute at 6000 pounds per square inch gage and 800° C. For the size of the coal particles used, this velocity was below that required for fluidization.

Acknowledgment

The authors acknowledge the assistance of H. Greenfield and S. Friedman for suggestions and advice in planning the experiments; R. A. Friedel, A. G. Sharkey, Jr., and staff for mass spectrometer analyses; A. P. Pipilen, H. Ginsberg, and R. W. Fridy for design, construction, and operation of the unit.

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(3) Clark, E. L., Pelipetz, M. G., Storch, H. H., Weller, S., Schreiber, S., *Ibid.*, 42, 861–5 (1950).
(4) Dent, F. J., "Production of Gaseous Hydrocarbons by the Hydrogenation of Coal," Gas Research Board, Communication GRB 13, London, England.
(5) Weller, S., Pelipetz, M. G., IND. ENG. CHEM. 43, 1243 (1951).
(6) *Ibid.*, 42, 334 (1950).

RECEIVED for review April 8, 1957
ACCEPTED October 9, 1957

Division of Industrial and Engineering Chemistry, High Pressure Symposium, 131st Meeting, ACS, Miami, Fla., April 1957.

Corrections

Vapor-Liquid Equilibrium

In the article on "Vapor-Liquid Equilibrium" [IND. ENG. CHEM. 49, 411 (1957)] several discrepancies in Table I were caused by using the wrong thermometer constants in calculating temperature from the resistance of a platinum resistance thermometer. The corrected data are as follows:

T, ° C.	Mole % Acetone		Activity Coefficient	
	Liquid	Vapor	Acetone	Methanol
62.40	5.84	11.75	1.615	1.021
61.93	7.56	15.32	1.653	1.019
60.54	13.60	25.15	1.584	1.023
59.88	16.72	29.50	1.546	1.027
59.25	20.09	35.31	1.575	1.010
58.81	22.87	38.10	1.519	1.019
57.12	36.29	50.09	1.336	1.071
56.78	39.77	52.60	1.295	1.092
55.61	58.38	65.31	1.143	1.217
55.45	61.13	66.62	1.120	1.264
55.10	74.63	75.93	1.060	1.418
55.40	91.66	90.75	1.020	1.635
55.42	92.11	91.34	1.022	1.618

The Van Laar equation derived previously fits these data equally well and would indicate our original conclusion is still valid. The new apparatus and method for determining vapor-liquid equilibrium compositions are capable of giving reliable data.

B. G. HARPER
J. C. MOORE

Alumina

In the article on "Alumina" by Kenneth M. Reese and W. H. Cundiff [IND. ENG. CHEM. 47, 1675 (1955)], the footnote of Table III should read:

Amounts of bauxite, steam, and evaporation are given in pounds per pound of Al_2O_3 recovered.

Butadiene Rubbers

In the article on "Butadiene-2-methyl-5-vinylpyridine Rubbers for General Purpose Use" [H. E. Railsback and C. C. Biard, IND. ENG. CHEM. 49, 1043 (1957)], the following change should be made:

On page 1047, Table IV, footnote ° should read *N*-Oxydiethylene-2-benzothiazolesulfenamide (American Cyanamid Co.)

System Equilibria

In the article on "Equilibria for the System Ethanolamines–Hydrogen Sulfide–Water" [K. Atwood, M. R. Arnold, and R. C. Kindrick, IND. ENG. CHEM. 49, 1439 (1957)] the heading of the last column in Tables I and II should read: $\gamma\pm$, Fig. 3.