

AN ABSTRACT OF THE THESIS OF

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OF COOS BAY COAL

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With the object of supplementing and eventually replacing the decreasing fuel reserves in the form of petroleum and natural gas, the liquefaction of coal, the reserves of which are relatively inexhaustible, by the addition of hydrogen has been a subject of renewed interest in recent years. Commercial plants at the present time accomplish the direct hydrogenation of coal at hydrogen pressures of 200-700 atmospheres and at temperatures of 400-500°C. However, it is well established that in the hydrogenation of certain materials, including carbonaceous materials, nascent hydrogen has a significantly greater reactivity than does the molecular form. The fact that one of the most reactive forms of nascent hydrogen is that obtained from the electrolysis of water, together with the simplicity and convenience of this source of the material, leads to speculation as to whether coal may be liquefied by the electrolytic hydrogenation of an aqueous suspension at relatively low pressure and temperature.

Experimental work was undertaken by the author in order to ascertain the possibilities of accomplishing this reaction. Preliminary familiarization with techniques was accomplished by the open-cell electrolytic hydrogenation of an aqueous solution of phenol to cyclohexanol in a manner reported in the literature. Following this, coal-solubility and water-miscibility tests at one atmosphere pressure and below 100°C. were performed on twelve liquids whose chemical structures indicated potential solvent effect on coal. Coos Bay coal, being of subbituminous rank and available locally, was used. None of the solvents tested proved to be suitable under these conditions.

The third phase of experimentation consisted of hydrogenation of a suspension of finely-ground Coos Bay coal in 0.5N. NaOH in the open-cell apparatus previously used in the hydrogenation of phenol. The progress of these coal-hydrogenations was indicated qualitatively by color-comparisons of successive samples of the cathode solutions during the progress of the runs. It appeared that, under the conditions tested, the rate

of the net reaction occurring in the cathode solution was unaltered either by changing from a platinum cathode to a nickel cathode, or by doubling the cathode current density, but was doubled by doubling the original concentration ratio of coal to electrolyte, and was multiplied six-fold by increasing the cell temperature from 20°C. to approximately 60°C.

The final portion of experimental work consisted of the hydrogenation of suspensions of coal in 0.5N. H_2SO_4 in a closed-cell apparatus designed and assembled for the purpose. The progress of these reactions was indicated quantitatively by constant-pressure measurement of the volumetric deficiency of hydrogen leaving the cell. A considerable amount of time was consumed in modifying and revising the original equipment. Results indicated an average consumption within the cell of 1.13% and 1.46% of the first 100 and of the first 200 ml., respectively, of hydrogen generated. However, the results were not sufficiently consistent to allow conclusions regarding the relative effects of the operating variables involved.

ELECTROLYTIC HYDROGENATION
OF COOS BAY COAL

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ELECTROLYTIC HYDROGENATION
OF COOS BAY COAL
OBJECTIVES

By increasing the H:C ratio above that found in the ultimate analysis of raw coal, liquid and gaseous hydrocarbons of higher heat value can be synthesized. These hydrogenation products can then be used to supplement and eventually to replace the rapidly decreasing reserves of petroleum and natural gas. The present proven fuel reserves of the United States, solid, liquid, and gaseous, have been calculated to amount to the energy equivalent of 2.6 trillion tons of bituminous coal having a heat value of 13,000 BTU/lb. Of this reserve, coal and lignite comprise 98%. It has been estimated that this huge reserve is adequate to supply, through full development of the hydrogenation and carbonization processes on coal, the total fuel needs of the nation for well over one thousand, probably for two thousand, years in the future. (1,2)

The present commercial catalytic processes for this hydrogenation operate in the range of 230-700 atmospheres

1. Lewis, W. K., Replaceability of natural gas. Gas Age 98:29-30, Sept., 1946.
2. Fieldner, Arno C., The national fuel reserves: relation to the future supply of liquid fuels. Mechanical Engineering 69:221-6, 1947.

pressure and 350-500° C. (3). It is believed that the development of an electrolytic process would enable a substantial reduction of these operating conditions. In addition, such a process could conceivably be of particular interest in the Pacific Northwest, inasmuch as supplies of both subbituminous coal and hydroelectric power are available, whereas supplies of petroleum and of natural gas are negligible in this region. The Coos Bay area alone was proven by the U. S. Bureau of Mines in 1946 (4) to be underlain with approximately 10,800,000 tons of coal, largely subbituminous, of which 8,600,000 tons are considered recoverable, in addition to an indicated and inferred reserve of 6,193,000 tons, of which 4,955,000 tons are considered recoverable.

3. Holroyd, R., Report on the investigation by fuels and lubricants teams at the I. G. Farbenindustrie A. G. Leuna works, Merseburg, Germany. U. S. Bureau of Mines Information Circular I. C. 7370:18, 19, July, 1946.
4. Fieldner, A. C., and Ambrose, P. M., Annual Report of Research and Technologic Work on Coal, Fiscal Year 1946. U. S. Bureau of Mines Information Circular I. C. 7417:34, July, 1947.

INTRODUCTION

Summary of development of present commercial processes for coal hydrogenation:

The first known hydrogenation of coal was performed by Berthelot in 1869 when he heated finely powdered coal with a saturated hydriodic acid solution at 270° C. for several hours. Tropsch, in 1917, improved this reaction by the addition of red phosphorous and found that, in general, the younger coals were quite susceptible to hydrogenation (5).

In 1914, Fischer and Keller began experiments with destructive distillation of coal, finding that yields of both oil and volatile products increased with increased hydrogen pressure (6).

Credit for the first direct addition of hydrogen to coal is claimed by Dr. Fredrich Bergius (7) for his experiments in Hanover in 1913, when he used one hundred atmospheres hydrogen pressure at 350-450° C. to convert as much as 85% of his coal, dispersed in liquid hydrocarbons, to liquid and gaseous hydrocarbons. A large-scale operation of the Bergius process was begun at Rheinau in 1926, using 150-

5. Beuschlein, W. L., Christensen, Bert E., and Wright, C. Studies in hydrogenation of certain American coals. University of Washington Engineering Bulletin 69:6, 1933.
6. Ellis, Carleton, Hydrogenation of organic substances, 3rd ed. New York, D. Van Nostrand Company, Inc., 1930, p. 505.
7. Bergius, F., British Patent 18,232.

atmospheres pressure and 450-490° C. on a paste of finely pulverized coal mixed with about 40% of its weight of oil from a previous cycle. The I. G. Farbenindustrie acquired the Bergius patents, added improved catalysts, and constructed in 1927 a plant in Leuna with a capacity of 70,000 tons of products per year from brown coal and tar (8). By 1937, Bergius system plants were reported in England, France, Russia, and Japan (9).

At the Leuna plant, continued development had led to a reported yearly capacity in 1944 of 600,000 tons of products, consisting of 40% aviation-base gasoline, 20% motor gasoline, and 40% Diesel oil. Pulverized clean brown coal containing, on ash-and-moisture-free basis, 71% C, 5% H, 5-6% S, 17-18% O, and 1% N, was mixed with recycle oil from the process to form a paste containing 49% solids. This paste was reacted with hydrogen at 230 atmospheres and 430-490° C. over an aluminum oxide catalyst (10). A similar plant at Blechhammer operated on a three-stage process: 700-atmosphere liquid-phase hydrogenation of coal to yield heavy oil, middle oil, and gasoline; liquid-phase hydrogenation of

8. Fieldner, Arno C., Hydrogenation and liquefaction of coal. U. S. Bureau of Mines, Minerals Yearbook, 1933, p. 433.

9. Ibid.: 1934, p. 627; 1936, p. 642; 1937, p. 950.

10. Holroyd, op. cit., p. 122.

heavy oil distillate to yield middle oil and gasoline; and vapor-phase hydrogenation of middle oils to gasoline (11).

In 1920, Fischer and Schröder (12) exposed coal to nascent hydrogen generated under pressure from sodium formate within the reaction vessel and obtained an ether-soluble fraction twenty times that obtained when molecular hydrogen was used. They discovered also that a similar increase in yield was obtained when carbon monoxide and steam were reacted within the vessel to produce nascent hydrogen.

Further work by Fischer and Tropsch on the catalytic reduction of carbon monoxide (13) led eventually to the present indirect hydrogenation process bearing their names. In the Fischer-Tropsch process, coal or lignite (or other carbonaceous material) is converted to water gas, a mixture of carbon monoxide and hydrogen, which mixture is then converted catalytically under pressure to gasoline, Diesel oil, liquefiable gases, and paraffin wax. With the adaptation of the fluid-catalyst technique, this process is being utilized in the United States at the present time.

11. Holroyd, op. cit., p. 122.

12. Ellis, op. cit., pp. 500, 502.

13. Golumbic, Norma R., Review of Fischer-Tropsch and related processes for synthetic liquid fuel production. U. S. Bureau of Mines Information Circular I. C. 7366:2, Aug., 1946.

COLOR SPRINGS ROAD

The importance of direct hydrogenation of coal and coal tar in Germany is apparent from design capacity data as of April 1944, given as tons of total petroleum products per year (14):

Hydrogenation (18 plants)	3,918,000 tons/yr.
German petroleum	1,920,000
Fischer-Tropsch (9 plants)	591,000
Brown coal distillation	50,000
Bituminous coal carbonization	36,000

Hydrogen was supplied from an external source in each of these hydrogenation plants, the most modern method being the Winkler process of gasifying a fluidized solid bed of coal particles with oxygen and steam and separating hydrogen from the resulting mixture of carbon dioxide and hydrogen.

14. Holroyd, op. cit., pp. 2-4, 128-132.

Chemical structure of coal:

Scores of investigations have been made on the chemical structure of coal. It has long been recognized that coal consists of a heterogeneous mixture of hydrocarbons and that the progression of coal ranks from lowest to highest can be attributed to a progression in the relative amounts of characteristic constituents. With the exception of ultimate analysis, direct chemical analyses have been impossible because of the large number of complex structures present.

It has been determined (15) that up to 85% of the carbon in all coals is present in complex condensed ring structures, largely saturated, and probably to a large extent six-membered, with average "molecular weights" in the range of 200 to 300. These molecules, some of which contain carboxyl and hydroxyl groups as well as aliphatic chains of varying lengths, are linked both by saturated and unsaturated primary bonds and by secondary hydrogen-bridging associations such as those that occur in oxygen-and-nitrogen-containing compounds in which the $R-OH:\overset{H}{O}-R$ oxygen atom functions as an electron donor and the hydrogen as an electron acceptor to form a coordinate valence bond (16).

15. Lowry, H. H. (editor), Chemistry of coal utilization. New York, John Wiley and Sons, 2 vols., 1945. Chapter 8, Weiler, J. F., pp. 341-345.
16. Fieldner and Ambrose, op. cit., p. 130.

Largely as a result of the investigation of oxidations of various coals, it has been concluded (17) that coal ranks vary progressively from a vegetable debris of mixed aliphatics, heterocyclics, and carbocyclics, at the lower end, to graphite, the completely condensed carbocyclic structure, at the highest. Upon oxidation, the larger proportion of linear structures and of oxygen-containing rings in the lower-rank materials are found to give, as would be expected, greater yields of the simple aliphatic acids, whereas the large proportion of condensed carbocyclic structures in the higher-rank materials are found to furnish higher yields of acids of the benzenecarboxylic series. In fact, macrocrystalline graphite, the ultimate in completely condensed carbocyclic structure, yields, upon oxidation, only mellitic acid (hexacarboxylic acid) and carbonic acid. The four principal divisions of coal ranks are designated by limits of fixed carbon or BTU heating value, on ash-and-moisture-free basis, as follows (18):

1. Anthracitic..... Dry fixed carbon not less than 86%.
2. Bituminous..... Dry fixed carbon less than 86%, and moist BTU not less than 11,000.
3. Subbituminous... Moist BTU 8,300-11,000.
4. Lignitic..... Moist BTU less than 8300.

In addition, these classifications involve certain specifications as to degree of physical agglomeration.

17. Lowry, op. cit., Chapter 9, Howard, H. C., p. 376.

18. Fieldner, A. C., Rice, W. E., and Moran, H. E., Typical analyses of coals of the United States. U. S. Bureau of Mines Bulletin 446:13, 1942.

The following comparison shows that the only essential difference between the ultimate analyses by weight of a Bruceton bituminous coal and of a Texas crude oil is in the proportions of hydrogen present (19):

	Crude condition		After removal of oxygen as water	
	Coal	Oil	Coal	Oil
Carbon	83.8%	84.6%	91.8%	86.44%
Hydrogen	5.5	10.9	4.9	10.9
Oxygen	7.6	2.0	----	----
Sulfur	1.6	1.6	1.7	1.64
Nitrogen	1.5	0.9	1.6	0.92

It is apparent that addition to the above coal of 6% hydrogen after elimination of the oxygen would result in an ultimate analysis nearly identical to that of the oil. A similar calculation on the ash-and-moisture-free analysis of the Coos Bay coal given on page 55 yields a final composition of 91.1% C, 4.2% H, 2.5% S, 2.2% N.

Factors of suitability of various coals for hydrogenation are expressed negatively in that high carbon content gives asphalt-like materials which are difficult to remove from large-scale equipment and that high ash gives undesirable catalytic activity, largely condensing reactions. The Bureau of Mines' general conclusion is that the best coals for hydrogenation in the United States

19. Pelipetz, M., Kuhn, E. M., Friedman, S., and Storch, H. H., Effect of catalysts on the hydrogenolysis of coal. *Industrial and Engineering Chemistry* 40:1259, July, 1948.

today are subbituminous coals containing low ash and low opaque matter, and some low-ash lignites (20). The Coos Bay coals of Oregon are, by these criteria, suitable for hydrogenation.

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20. Storch, H. H., Kiebler, M. W., Howard, H. C., Lowry, H. H., Theissen, G., and Charnbury, H. B., Hydrogenation of coal. *Industrial Engineering Chemistry* 36:298, April, 1944.

Mechanism of reactions involved in coal hydrogenation:

The primary step in any coal hydrogenation is depolymerization and solvation of the solid coal molecules by solvent, aided to some extent by heat, if present. The theory is advanced (21) that this results from the rupture of the associated hydrogen bonds and is followed immediately by saturation of the dissociated fragments by hydrogen. In addition, saturation of the olefinic bonds takes place. Comparison of the results of subjecting coal to nitrogen pressure and to hydrogen pressure under conditions otherwise identical (22) shows clearly the necessity of hydrogen in liquefaction:

Products of direct pyrolysis of a bituminous coal for one hour at 450° C. in the presence of 1% tin and 0.5% ammonium chloride:

	2500 psi N ₂ pressure	1000 psi H ₂ pressure
Gaseous hydrocarbons	5.9%	11.35%
H ₂ S	0.11%	0.19%
NH ₃	0.79%	0.06%
Benzene-soluble material	1.20%	69.70%
Water of reaction	----	6.20%
Benzene-insoluble	----	1.20%

21. Fieldner and Ambrose, op. cit., pp. 130-133.

22. Pelipetz, et al, loc. cit.

Although all recent reported experimental work on coal hydrogenation involves externally-supplied hydrogen in conjunction with a catalyst, the theory does not preclude the substitution of nascent hydrogen. It is believed (23) that the function of high temperature (370-440° C.), when used, is cracking of the molecules by rupture of primary C-C and/or C-O bonds, followed by further solvation and hydrogen addition, though above 440° C. repolymerizations occur unless prevented by high hydrogen pressure and catalyst.

23. Storch, et al, loc. cit.

Particular advantages of electrolytic hydrogenation:

Providing that a successful electrolytic hydrogenation of coal were developed, its most certain favorable characteristic would be its independence from an external source of hydrogen, which would eliminate the necessity of such a process either being restricted in location to the vicinity of an existing source of the gas or operating its own separate hydrogen plant. Of further advantage in this respect would be its available by-product oxygen.

Another advantage of such a process, if it is to be practical, would be a considerable reduction in operating pressure and temperature from those presently used in the previously cited German catalytic processes. On the basis of the disclosed data on nascent hydrogen processes discussed in the following three paragraphs, it is hoped that the active condition of the cathode and of the nascent hydrogen in the proposed process will be such that the reaction will proceed under relatively mild conditions.

By definition, hydrogen from any source whatsoever is, at the instant of its formation, in the nascent state. In this condition it is known to be much more reactive than is molecular hydrogen. Furthermore, it is claimed that the most active form is that released from water, either by dissociation of water vapor, wherein its reactivity is

believed to be due to the presence of the hydroxyl radical (24), or by electrolytic release from liquid water at a platinum or palladium cathode. It is believed (25) that cathodic H ions from water successively become H atoms, excited H₂ molecules, and finally normal H₂ molecules, with progressively decreasing chemical activity, and that from cathodes with greater overvoltages the more active forms can be desorbed and thus utilized advantageously.

With regard to the present problem, certain relevant cases have been reported in the literature. Specifically, electrolytic atomic hydrogen liberated from water has been used to reduce various salts, oxides, and hydroxides, (26, 27, 28) and to synthesize ammonia (29). Patents

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24. Ellis, op. cit., p. 866.
25. Kobozer, N. I., Monblanova, V. V., and Kirillova, S. V. The excited state of cathodic hydrogen. *Journal of Physical Chemistry (U.S.S.R.)* 20:653-66, 1946. *Chemical Abstracts* 41:342, 1947.
26. Jolibois, Pierre, and Nicool, Albert. Reducing power of electrolytic hydrogen. *Comptes rendus hebdomadaires des séances de l'académie des sciences*, 223:225-6, 1946. *Chemical Abstracts* 40:7006, 1946.
27. Kobozer, et al, loc. cit.
28. Jolibois, Pierre. Reductions with nascent hydrogen. *Comptes rendus hebdomadaires des séances de l'académie des sciences*, 212:981-4, 1941. *Chemical Abstracts* 38:1957, 1944.
29. Lawaczeck, Frank. Process and means for producing ammonia. U. S. Alien Property Custodian Patent 1,815,410. July 21, 1931.

have been granted for hydrogenation of aqueous slurries or suspensions of carbonaceous materials by electric-arc dissociation of the water, (at temperatures short of decomposition) (30, 31, 32, 33). In addition, patents have been obtained for hydrogenation of carbonaceous materials with nascent hydrogen produced by the reactions of metallic zinc powder and water (450° C., 250 atmospheres) (34), spongy iron and water (400-500° C., 100-500 atmospheres) (35), and iron filings plus copper or brass shavings and water (200-1000° C., 5 atmospheres to super-pressures) (36).

30. Uhlmann, A., British Patent 283,177, Production of hydrocarbons from coal and water. Jan. 5, 1928. British Chemical Abstracts B:232, 1929.
31. Johnson, J. Y. (to I. G. Farbenindustrie), British Patent 286,825, Production of (unsaturated) hydrocarbons from coal, tars, minerals, etc. Jan. 3, 1927. British Chemical Abstracts B:356, 1928.
32. Hansen, British Patent 284,655, Feb. 2, 1927. Ellis, op. cit., p. 561.
33. Hansen, J. M., British Patent 284,224, Production of liquid hydrocarbons. Jan. 24, 1928. British Chemical Abstracts B:507, 1929.
34. Pfirrmann, Theodor Wilhelm, Process of hydrogenating carbonaceous materials. U. S. Alien Property Custodian Patent 2,012,318, Aug. 27, 1935.
35. Pfirrmann, Theodor Wilhelm, Hydrogenation of carbonaceous materials. U. S. Alien Property Custodian Patent 2,041,858, May 26, 1936.
36. Fohlen, British Patent 313,963, June 20, 1928. Ellis, op. cit., p. 559.

A different method of attack consists of dissociation in the hydrogenation vessel of externally generated molecular hydrogen. The dissociation may be accomplished by passing the molecular hydrogen over glowing tungsten wire and removing by means of two charged plates the H ions formed, or by dissociation by irradiation with ultraviolet light of wave length above 2300 \AA from a mercury arc in the reaction vessel. Both methods have been employed in polymerization and hydrogenation of hydrocarbons (37). The Wood-Bonhoefer method consists of passing molecular hydrogen or deuterium through a high-voltage discharge tube, and the resulting atomic hydrogen has been utilized in hydrogenating various hydrocarbons (38, 39, 40).

37. Houtman, J. P. W., van der Berg, K., and Heertjes, P. M. Polymerization with atomic hydrogen. *Recueil des travaux chimiques des Pays-Bas*, 62:672-80, 1943. *Chemical Abstracts* 38:5118, 1944.
38. Ellis, *op. cit.* p. 866.
39. White, Harold W., Winkler, C. A., and Kenalty, B. J. The reaction of H atoms with isobutane. *Canadian Journal of Research* 20-B:255-64, 1942.
40. Rabinovich, B. S., Davis, S. G., and Winkler, C. A. The reaction of H atoms with propylene. *Canadian Journal of Research* 21-B:251-7, 1943.

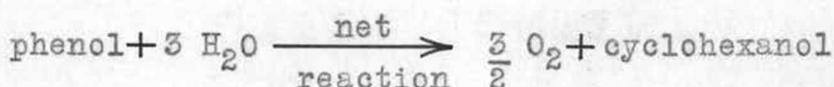
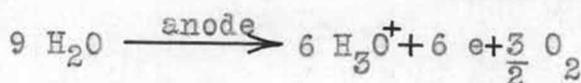
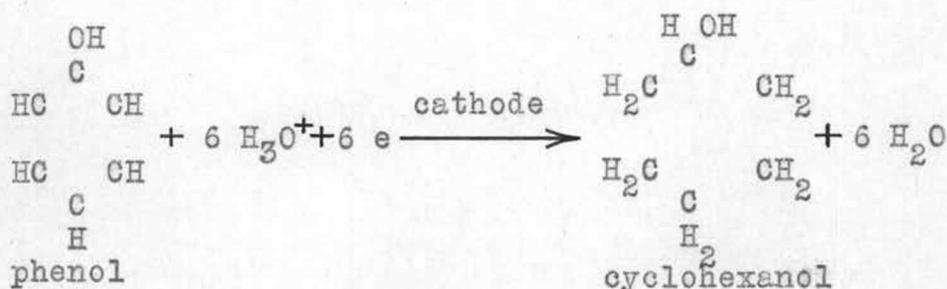
PRELIMINARY EXPERIMENTS

Prior to attempting the electrolytic hydrogenation of coal, preliminary work was done by the author in order to study the techniques involved and to provide information on the relative suitabilities of various solvents. Electrolytic hydrogenation of phenol:

On the basis of its chemical similarity to some of the known compounds contained in coal structure, phenol was chosen as the compound to be hydrogenated, the desired product being cyclohexanol. The catalytic hydrogenation of phenol is now carried out in both vapor and liquid phase under mild conditions, averaging 150-250°C. and 5-25 atmospheres pressure (41). On the other hand, Fichter (42), in 1914, obtained cyclohexanol by electrolyzing a sulfuric acid solution of phenol under the following conditions: 5 grams phenol in 350 ml. 2N. H_2SO_4 , platinized platinum cathode, current density 5.58 amp./in.², anode space separated by a porous cup. Following, in general, this method, an electrolytic cell was assembled and operated, with qualitative evidence of conversion of aqueous phenol to cyclohexanol. The reaction may be represented as follows:

41. Ellis, *op. cit.*, pp. 213, 231.

42. Fichter and Stocker, *Berichte der deutschen chemischen gesellschaft*, 47:2015, 1914.



The electrolytic cell consisted of an open beaker in which were suspended electrodes, one of which was surrounded by a porous cup (alundum thimble). Direct current was furnished by either an Edison cell or a motor-generator set. A motor-driven stirrer was used. The electrodes were varied with succeeding runs.

Approximately 300 ml. of the electrolyzing solution was poured into the beaker, the submergence of the electrodes and of the cup was adjusted, the stirrer was turned on, and the D. C. power switch was closed. After several hours of operation, the current was turned off and the solution within the porous cup was separated from the remaining solution.

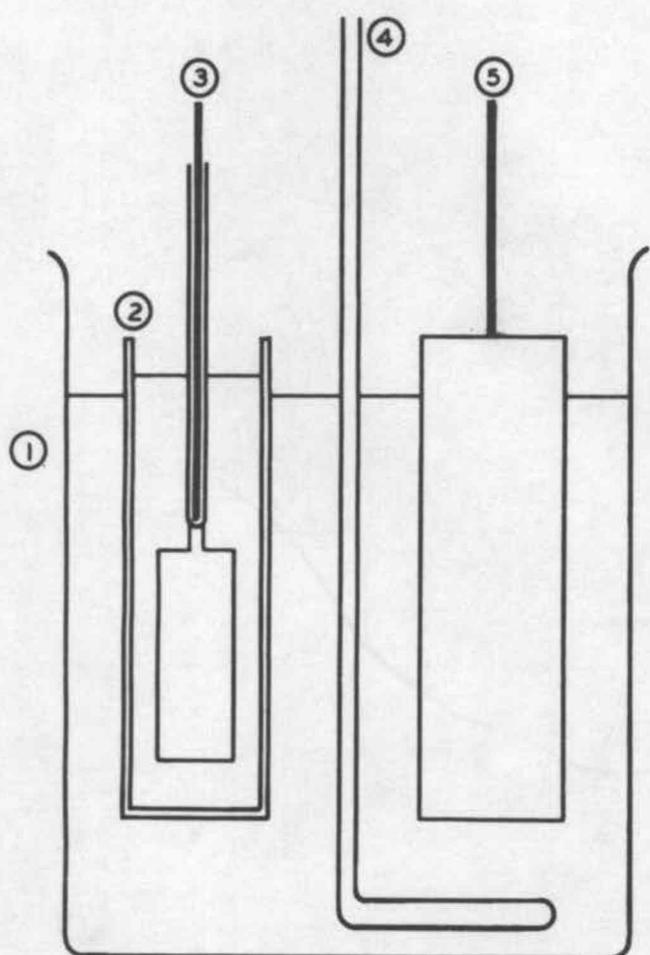
Six separate reagents which were found to give distinctive tests on phenol or on alcohols were used to indicate the presence or absence of these materials from the original and the final cell solutions:

1. Ceric nitrate in alkaline or acid solution gives chocolate-brown precipitate for phenol.
2. Iodine crystal in alkaline solution gives cloudy grey for alcohols.
3. Potassium permanganate in alkaline solution gives green for alcohols.
4. Potassium dichromate in acid solution gives dark brown precipitate for phenol.
5. Millon's reagent in acid or alkaline solution gives light red for phenol.
6. Sodium hypobromite in acid solution gives pale blue for phenol.

The presence of phenol does not interfere with the above alcohol tests, and vice versa.

For data on runs, see Appendix, page 55.

Application of these tests to the products from runs #3 and #4 indicated the presence of both phenol and alcohol in both the anode solution and the cathode solution.



- | | |
|---------------|------------|
| 1. BEAKER | 3. ANODE |
| 2. POROUS CUP | 4. STIRRER |
| | 5. CATHODE |

DIAGRAM OF OPEN CELL

Figure 1

Testing of coal solvents:

Any solvents to be used in the proposed process not only must dissolve coal to some extent, but also must be partially miscible with or must form a good emulsion with water in order to allow intimate contact between the coal constituents and the liberated H atoms.

As a result of the experimental work leading to the hydrogen-bond theory of association in coal discussed on page 7, the U. S. Bureau of Mines has reported that the following substances possess relatively good solvent action on coal: tetralin, cresol, o-and-p-cyclohexanol, and 5 hydroxyl-1-2-3-4-tetrahydronaphthalene. On the basis of chemical structural similarities to these compounds and on the basis of availability, twelve solvents were selected by the author for testing. Due, apparently, to insufficient drying of the residues prior to weighing, the calculated solubilities on the first three runs disagreed widely. An attempt in runs 6, 7, and 8 to assist the drying process by first washing the high-boiling solvents from the filter residues with petroleum ether resulted in limited success. However, at temperatures below 90° C., none of the solvents tested produced significantly higher coal losses than did water under the same conditions. Tests on coal alone showed that

approximately 11% loss in weight was due to its original moisture content and that at least 1% additional loss was due to the carrying of fines through the filter paper by wash water. Considering these facts, it was apparent that none of the solvents tested actually dissolved any appreciable portion of the coal.

Because of the uncertain flammabilities of these solvents at elevated temperatures, together with the fact that the proposed hydrogenation experiments were to be carried out at temperatures well below 100° C., this investigation was carried no further. Instead, it was reasoned that either sodium hydroxide, because of its hydroxyl group as a potential solvent, or sulfuric acid, because of the belief of some investigators (44) that neutralization of the basic constituents of the mineral matter in coal is a necessary pretreatment for hydrogenation, might be found useful in the process. A further reason for using either of these materials would be to supply the required ions for conductivity in the cell mixture. Though not measured quantitatively, it was found that dilute sodium hydroxide does either suspend very well or dissolve a portion of the coal, whereas sulfuric acid does neither.

44. Lowry, op. cit., Chapter 38, Storch, H. H., p. 1759.

A sample of Coos Bay coal was obtained and reduced by means of a jaw crusher and a rotary pulverizer to four grades, from plus 16 mesh to minus 24 mesh. By the use of a motor-driven mortar and pestle, the smaller size was further reduced to 65-100, 100-150, 150-200, and minus 200 mesh. Some typical analyses of coal from the Coos Bay field, as reported by the U. S. Bureau of Mines (45), are given in the appendix, page 55.

In the coal-solubility tests, 65-100 mesh coal was used, since it appeared to be completely retained by Whatman #42 paper in a 4.25 cm. Buchner suction funnel, whereas 150-200 mesh coal was not completely retained. Using an analytical balance, portions of approximately 2.0000 grams of coal were weighed on filter papers, then poured from the papers into test tubes, and the papers were carefully set aside. Next, 4.0 ml. samples of the solvents were pipetted into the tubes, which then were corked, shaken for sixty seconds, and placed in a water-bath at 65-80° C., with occasional additional sixty-second shakings. After three hours, the tube-contents were filtered through the previously saved papers, care being taken to wash down each tube with either 2-4 ml. of

45. Toenges, Dowd, Turnbull, Schopf, Cooper, Abernethy, Yancey, and Geer, U. S. Bureau of Mines Technical Paper 707:50, 1948.

its own solvent, or, in runs 6, 7, and 8, 6-8 ml. of petroleum ether. The papers and residues were carefully removed and dried at 80-90°C. in an oven for periods of 5, 12, 18½, or 21½ hours, cooled in the open for 1 or 16 hours, and weighed. Petroleum ether, because of its high volatility, instead of being placed in the hot water bath, was set aside at room temperature for three hours, then filtered and oven-dried in exactly the same manner as were the other solvents. Drying runs 8x1, 8x11, and 8x111 were made on the products of run 8x and on two fresh samples of coal, heating in an oven at 105°C. and cooling in a dessicator.

For data, see Appendix, pages 56-58.

Water-miscibility tests:

Since the proposed process is to be carried out in the presence of water, experiments were undertaken simultaneously with the previously described solubility tests, in order to determine the relative miscibilities and the relative stabilities of the solvents with water.

To 5.0 ml. pipetted samples of the solvents in test tubes were added a trace of minus 24 mesh coal and a 5.0 ml. pipetted portion of water, and each tube was shaken vigorously. Observations were made of the approximate number of seconds required for each mixture to separate to the same extent and of the relative degrees of

separation after $5\frac{1}{2}$ days. Following this, each mixture was forced twice through a Cenco emulsifier and observed 24 hours later. Run #2 was made on identical mixtures, but with the addition of one gram of 150-200 mesh coal and one drop of Aerosol 10% wetting agent. Each of these mixtures also was forced twice through the emulsifier and observed 24 hours later.

For data, see Appendix, page 56.

It was found that, of the solvents tested, none was sufficiently miscible with water in a 1:1 volume ratio to approach homogeneity, but that the emulsions produced were fairly durable, the durability generally being increased by the addition of Aerosol.

COAL HYDROGENATION

Having determined that the solvents tested were not suitable for use in the proposed process, a series of electrolytic hydrogenation experiments was performed on suspensions of minus 200 mesh Coos Bay coal in 0.5N. NaOH in open cells of the same type previously used in the hydrogenation of phenol. Following this a new series of experiments was performed in closed cells with both 0.5N. NaOH and 0.5N. H₂SO₄.

Open cell:

The apparatus used was that previously described on pages 18-20, but was assembled in duplicate, allowing the operation of two runs simultaneously. The procedure remained nearly the same, but included frequent checking and adjustment of the current, periodic withdrawal of samples of the cathode solution, and operation at both room temperature and in the range of 60° C. Twenty grams of minus 200 mesh coal was stirred vigorously with either 250 or 500 ml. of 0.5N. NaOH containing two or four drops of Aerosol, and this mixture was poured into the beaker, after which the anode cup was filled with 0.5N. NaOH. Periodically, during the six-to-twelve hour operation of the runs, ten-ml. samples of the cathode solution were withdrawn by pipette, centrifuged at 1000 r.p.m. for

twenty minutes, and set aside for color comparison in a Klett-Summerson colorimeter. The anode solutions remained colorless. Elevated temperature was accomplished by means of a hot-water bath. An asbestos thimble which was tried in place of the alundum thimble was found to tear easily from the agitation produced by the stirrer. The generator-supplied current was varied from approximately 0.00330 to 0.00771 amperes per square inch of cathode surface.

For data, see Appendix, pages 59-60.

A preliminary spectrophotometric investigation of sample #57 by the chemistry department showed a definite single maximum absorption band at 380 to 440 millimicrons wave length. Therefore, a filter transmitting 400-465 millimicrons wave length was used in the Klett-Summerson colorimeter. Because these cathode-solution samples contained unknown mixtures of materials which together produced the colors observed, plots of relative concentration of coloring matter vs. ampere hours can not be calibrated by means of known concentrations contained in the unknown solutions. However, they should indicate the relative extents of the net reactions which had occurred.

The colorimeter curves are shown in Figures 2, 3, 4, and 5. It is evident that the slopes of these plots should be direct indications of the rates of the net reactions occurring. The fact that the colors remained

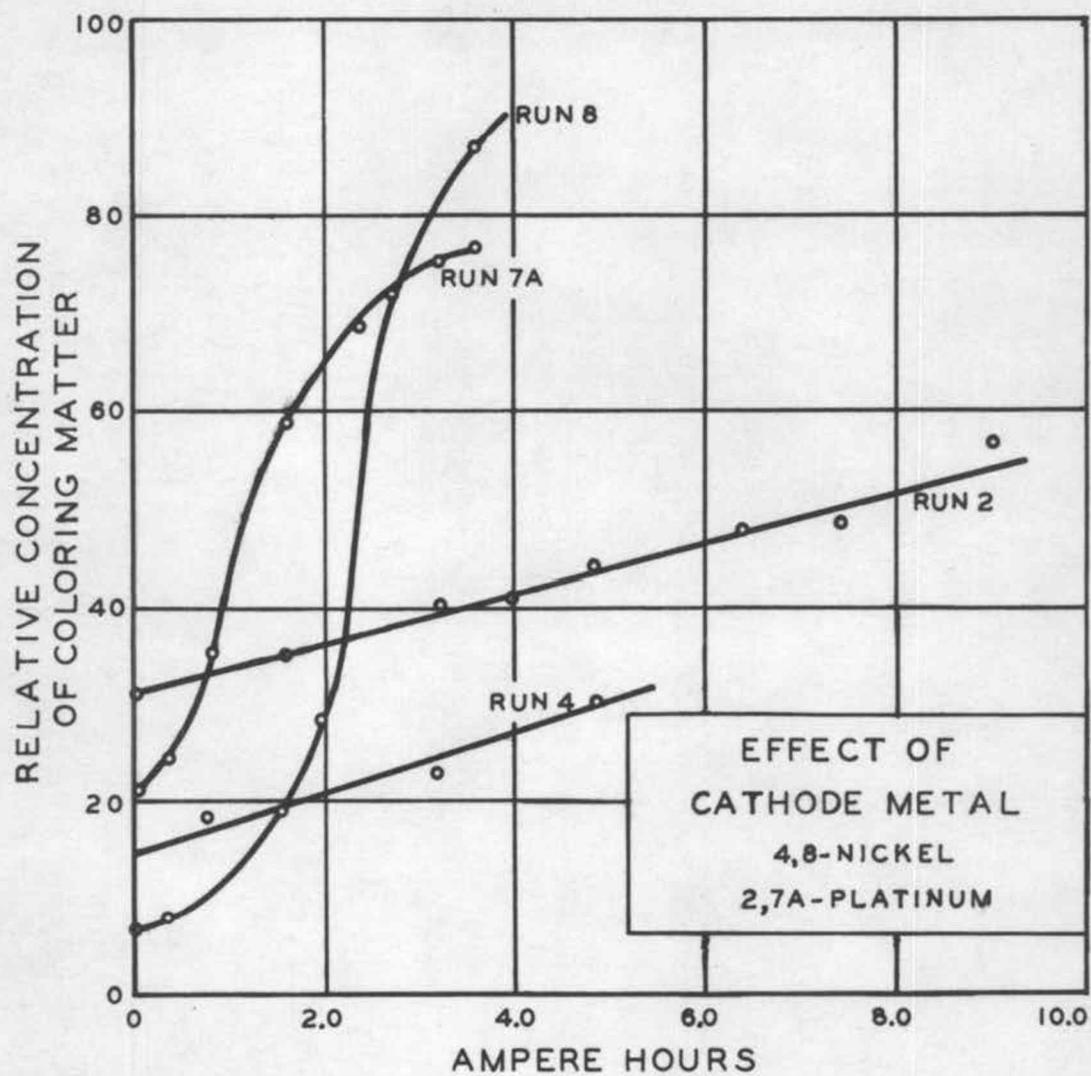


Figure 2

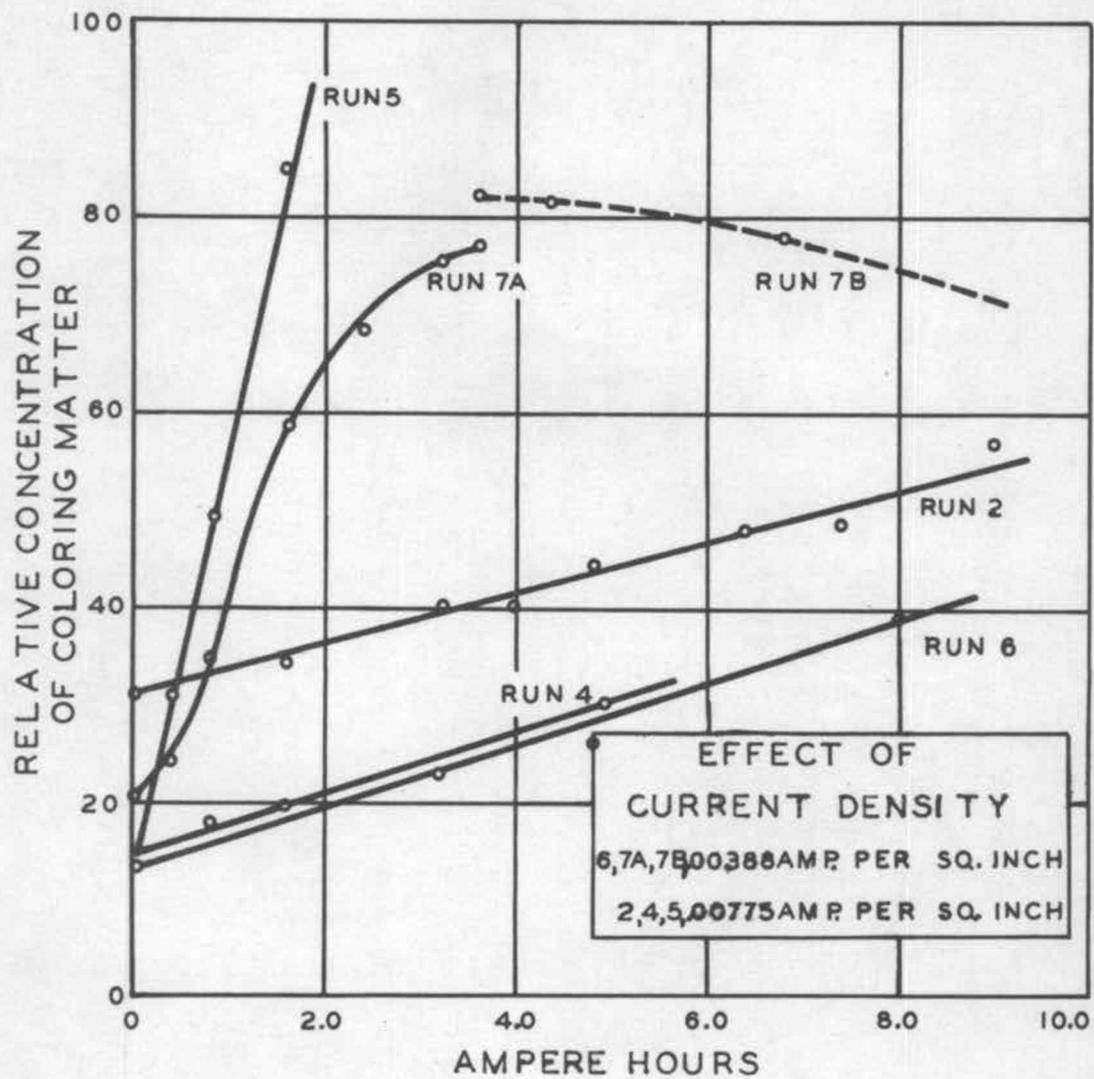


Figure 3

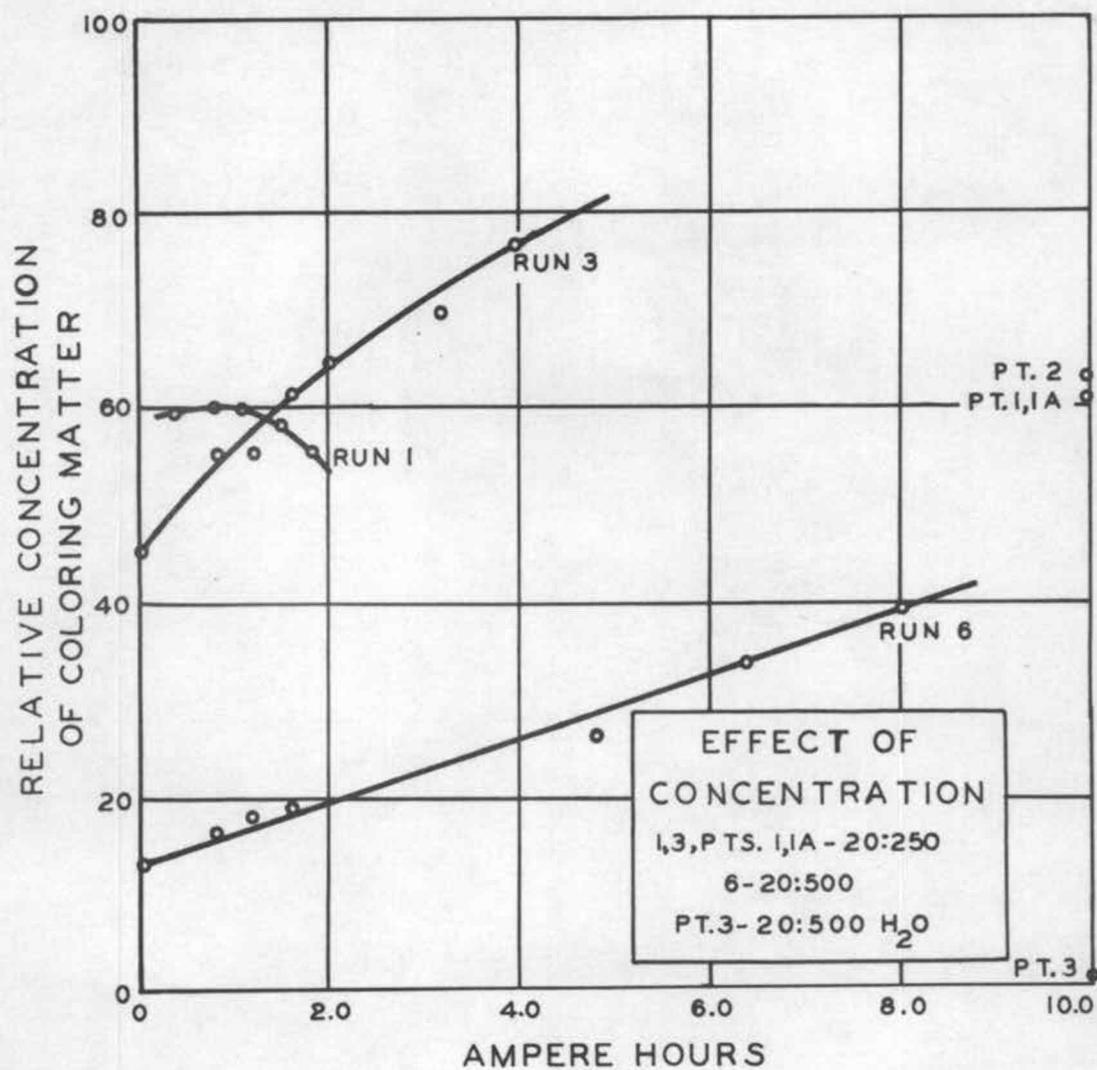


Figure 4

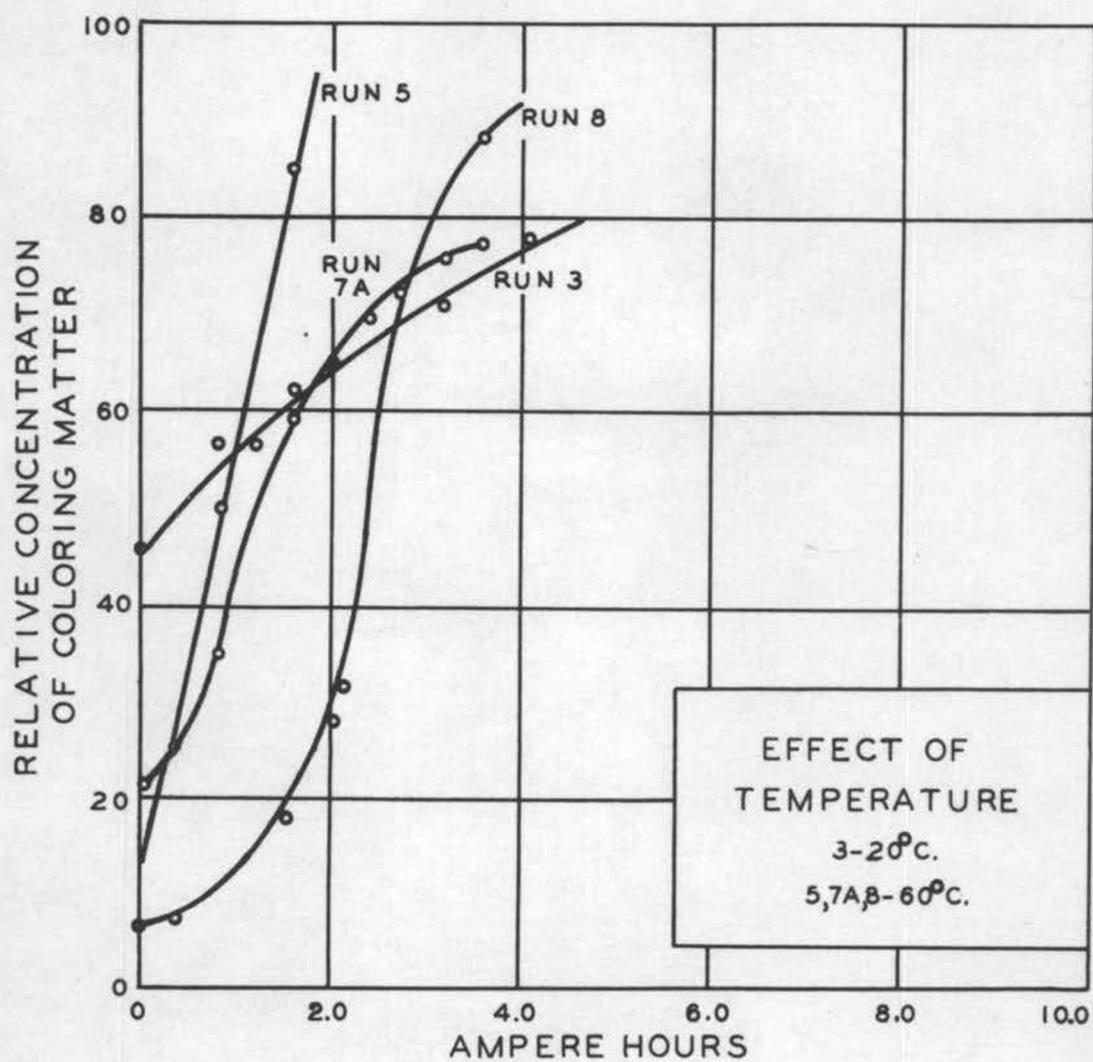


Figure 5

fixed and distinct even though each sample was set aside until the entire collection could be put through the colorimeter in one day, an elapse of time ranging from forty-four to seventeen days, shows definitely that the changes were due in part to time of exposure to the cell reaction rather than due to time of exposure to electrolyte alone. On the other hand, comparison of points 1, 1A, and 2 with point 3 indicates that a long period of contact with 0.5N. NaOH alone does result in solution of a part of the coal. A study of the factors contributing to increases in the slopes should yield information on the effects of variables on the efficiency of the cell reaction. Positive slopes are exhibited by each run except #7b and the last half of #1. A possible explanation for the slope reversal in run #1 may be leakage from the asbestos cup before its replacement by the alundum thimble. Since run #7b was made on the products from run #7a after their standing undisturbed overnight, it is quite possible that interdiffusion of the anode and cathode solutions may account also for the negative slope of this run. Of the remaining curves, the slope of run #3 is twice that of numbers 2, 4, and 6, whereas runs 5, 7a, and 8 have average slopes approximately seven times that of #3. According to the initial equality of concentrations, the intercepts of curves 2, 4, and 6

should be equal, and those of curves 1, 3, 5, 7a, and 8 should be equal. It is believed that the observed inequalities are due either to incomplete mixing of the dry pulverized coal or to insufficient stirring of the cell mixture.

Examination of the data and of the curves enables independent conclusions regarding the effects of changes in each of three operating variables and an inferred conclusion regarding a fourth variable:

1. Platinum and nickel cathodes have equal effects. This is shown by comparison of curve #4 with #2, and #7a with #8.
2. Cathode current densities of 0.00388 amp./in.² and 0.00775 amp./in.² have equal effects. This is shown by comparison of #5 with #7a and #4 with #6, and is supported by comparison of #2 and #6, provided the first conclusion is true.
3. Concentration ratio (grams of coal to milliliters of electrolyte) of 20:250 results in 100% increase in slope over that of ratio 20:500, as shown by comparing #3 with #6, providing the first conclusion is true.

4. Increasing the cell temperature from 20° C. to approximately 60° C. increases the slope by 600 %, comparing #7a with #3. Comparison of #8 with #3 verifies this conclusion, providing the first conclusion is valid, and comparing #5 with #3 lends further substantiation, providing the second conclusion is true.

It is believed by the author that this simple and inexpensive procedure can be of considerable value in enabling the fairly rapid qualitative estimation of the effects of operating variables on the electrolytic hydrogenation of coal. The apparatus and the method could give much information if applied to an enlarged systematic study of the variables involved.

Closed cell:

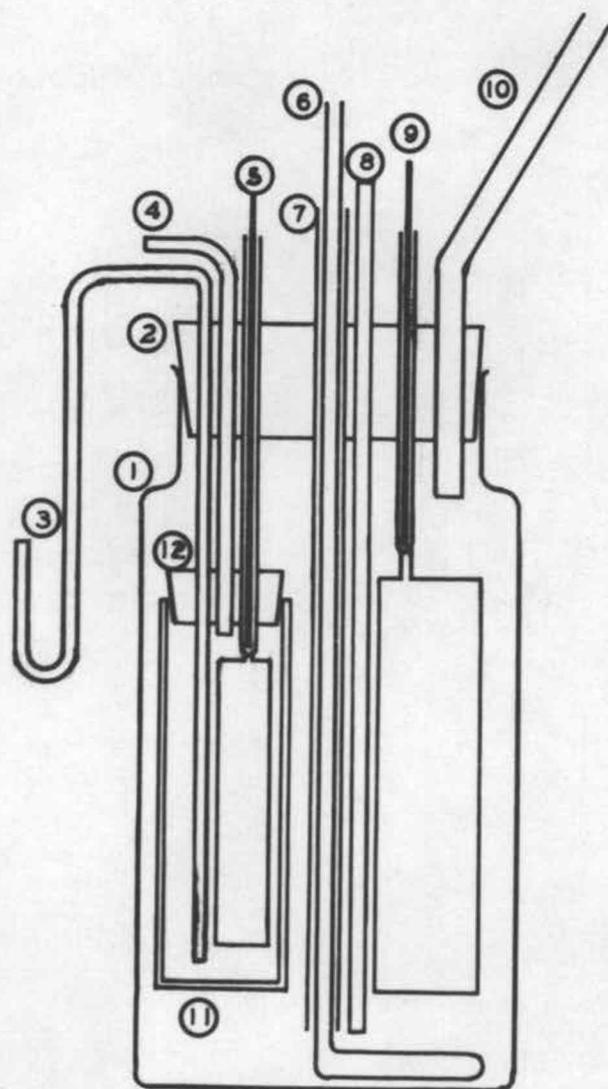
Having developed and proved to be practicable the preceding method for qualitative study of the electrolytic coal hydrogenation, the author deemed advisable the development of a method for quantitative study of the reaction. It is well known that the progress of high-pressure reactions may be conveniently followed by observation of the rate of fall of hydrogen pressure in a batch process within a constant-volume bomb. The generally high cost of such equipment not only makes its procurement somewhat difficult but also renders undesirable the alteration of borrowed standard apparatus in order to accommodate fittings for electrodes and sampling tubes. Equally useable, but less obvious, is the scheme of measuring the decreasing gas volume in a constant-pressure apparatus. Furthermore, considering the study of the reaction at atmospheric pressure, an apparatus utilizing this scheme is fundamentally simple. The requirements are: 1., a closed vessel with two separated compartments, each containing an electrode, a liquid inlet and/or outlet, and a gas outlet; 2., a means of agitating the cell contents; and 3., a constant-pressure volume-measuring device for the gases from each compartment. A successful apparatus involving these components was gradually developed and eventually

utilized to obtain quantitative evidence that electrolytic hydrogen reacts with coal. Though not used, provision also was made for separate storage of the gases from the two compartments, thus enabling their analysis.

Initially, the cell consisted of the original open-beaker cell previously used, with the addition of a Tygon-painted plywood cover through which holes were drilled to accommodate the necessary glass tubes, connections, and the stirrer. The alundum thimble was fitted with a rubber stopper which contained the holes necessary to accommodate its fittings. The stirrer was surrounded by a rubber-mounted glass tube projecting nearly to the bottom of the beaker in order to prevent gas leakage and to allow for shocks due to imperfect alignment of the stirrer. The cover was held tightly against a gasket of sponge rubber by means of clamps bolted to an iron ring which fit under the lip of the beaker. Leakage of hydrogen through the gasket finally was stopped by rubber cement with the entire joint sealed over with Plicene cement, similar to sealing-wax. Even upon removal of the clamps, this joint would hold gas under the pressure of several inches of water, but the necessity of breaking and remaking the hard-wax joint between runs was undesirable.

Subsequently, it was discovered that a wide-mouthed bottle could be fitted with a readily-removable rubber stopper containing all the attachments formerly contained by the plywood cover on the beaker. Two cells of this type, illustrated in Figure 6, were constructed and used alternately in the experimental runs. A V-tube attached to the anode liquid inlet was used to indicate and to adjust the liquid level inside the anode compartment. Early fouling of the cathodes by copper from the wax-and-Tygon-coated copper electrical connections led to soldering the electrodes to narrow strips of platinum which were sealed into glass tubes containing mercury-contact joints into which wires were inserted. The solder joints, as well as all inner rubber surfaces and the joint around the top of the anode compartment, were protected by Tygon paint, peeled off and repainted each time the cell was opened.

It was discovered that generation of hydrogen within the closed cells containing coal suspended in 0.5N. NaOH resulted in a relatively stable foam which soon was forced into the cathode-gas line and subsequently carried up the vertical delivery line to the burettes, causing not only fouling of the line but also a very appreciable varying pressure-head against the cathode compartment. It was evident that such action would render impossible the



- | | |
|-----------------------|-------------------------|
| 1. BOTTLE | 7. LIQUID SEAL |
| 2. RUBBER STOPPER | 8. CATHODE LIQUID INLET |
| 3. ANODE LIQUID INLET | 9. CATHODE CONNECTION |
| 4. ANODE GAS OUTLET | 10. CATHODE GAS OUTLET |
| 5. ANODE CONNECTION | 11. POROUS CUP |
| 6. STIRRER | 12. RUBBER STOPPER |

DIAGRAM OF CLOSED CELL

Figure 6

accurate measurement of the gas. Instead of elimination of the runs with sodium hydroxide, two alternate means could be used to eliminate the foam: either a defoaming chemical or a mechanical foam-breaker. The former was decided against because it would be expected to have some effect on the net reaction occurring, thus increasing the difficulty of studying the reaction of the coal alone. The latter scheme was eventually put into practice by means of a reflux tube of diameter larger than the normal delivery line, inclined at approximately sixty degrees from horizontal and wrapped with a chromel-wire heating unit connected to an A. C. Powerstat. This reflux tube was topped with a water-cooled spiral, the entire combination being made of glass. Application of elevated temperature to the reflux tube effected an expansion of the gas rapid enough to rupture the majority of the bubbles. The bubble-type condenser served to break the remaining foam and to cool the gas, and the spiral served as the final cooler. The shearing action of the liquid reflux assisted materially in breaking the foam. Simple traps, each consisting of a test tube containing inlet and outlet lines and a thermometer, were installed immediately following the spiral cooler and at the beginning of the anode-gas line. These traps served the

double functions of preventing liquid from being carried into the remaining part of the delivery lines, and checking of the temperatures of the two gases.

The combination pressure-regulating and volume-measuring device consisted simply of graduated water-filled burettes with levelling flasks, each burette being connected at the top to a three-way cock in such a manner as to allow its alternate filling with gas from the cell compartment and emptying of the gas into either the air or bottle-storage over water. One pair of burettes was required for each of the two gases (the anode gas and the cathode gas), in order to accommodate continuous flow of the gases from the cell. Provision of another cock in each gas line allowed direct purging into the air when desired. Figure 7 illustrates the assembly of this apparatus.

Before the first run and at any later time between runs when its necessity was indicated, the cells and gas lines were conveniently leak-tested under the pressure of approximately eighteen inches of water in the burettes by immersing them in a pail of water. Pressure could be applied to either compartment or to both while the burette-levels were carefully watched for movement indicating leakage, which leaks usually were immediately located

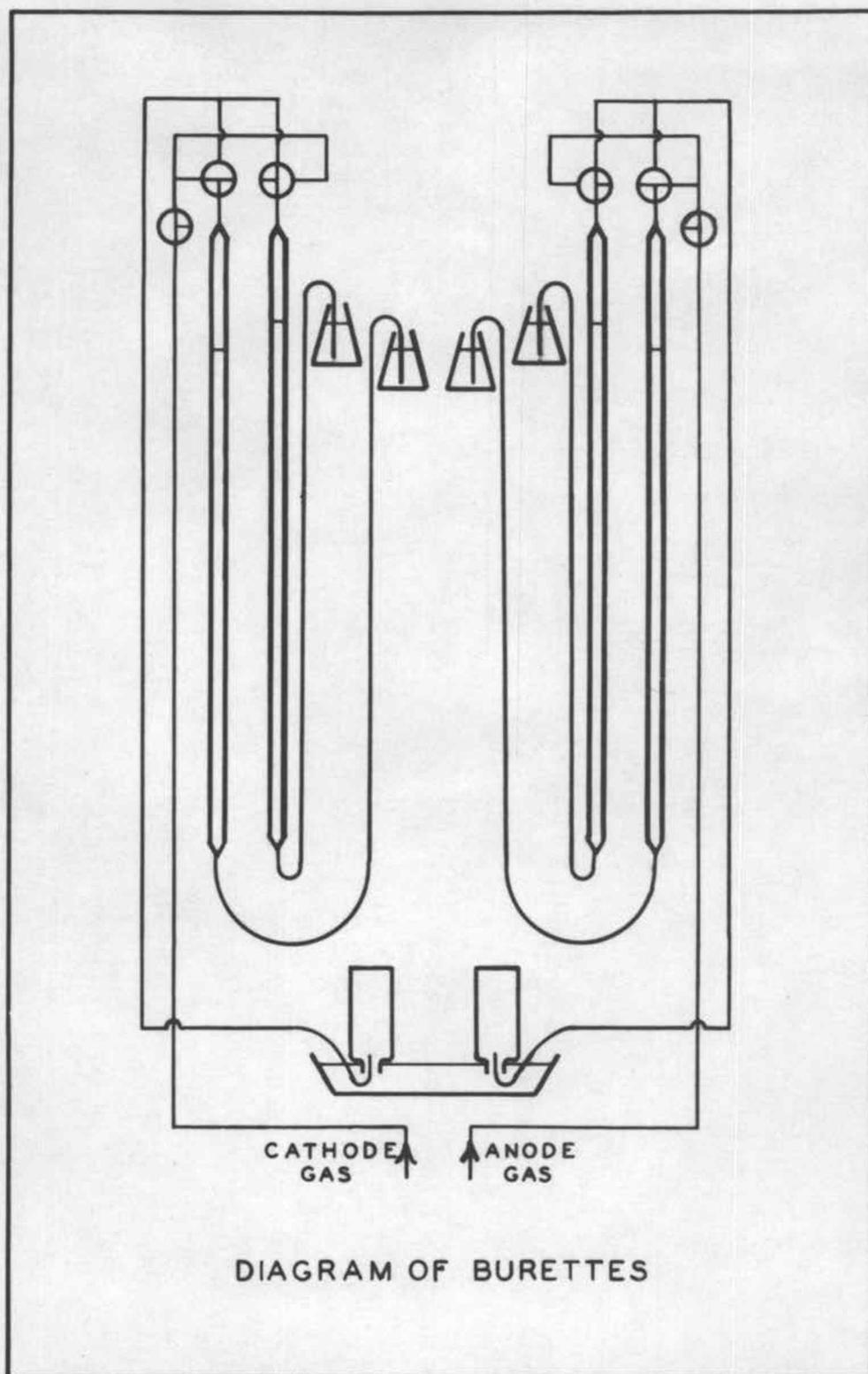


Figure 7

by a stream of bubbles within the pail. Such leaks occurred frequently in the first stages of familiarization with the apparatus, but gradually were minimized by improvements in connections and assembly.

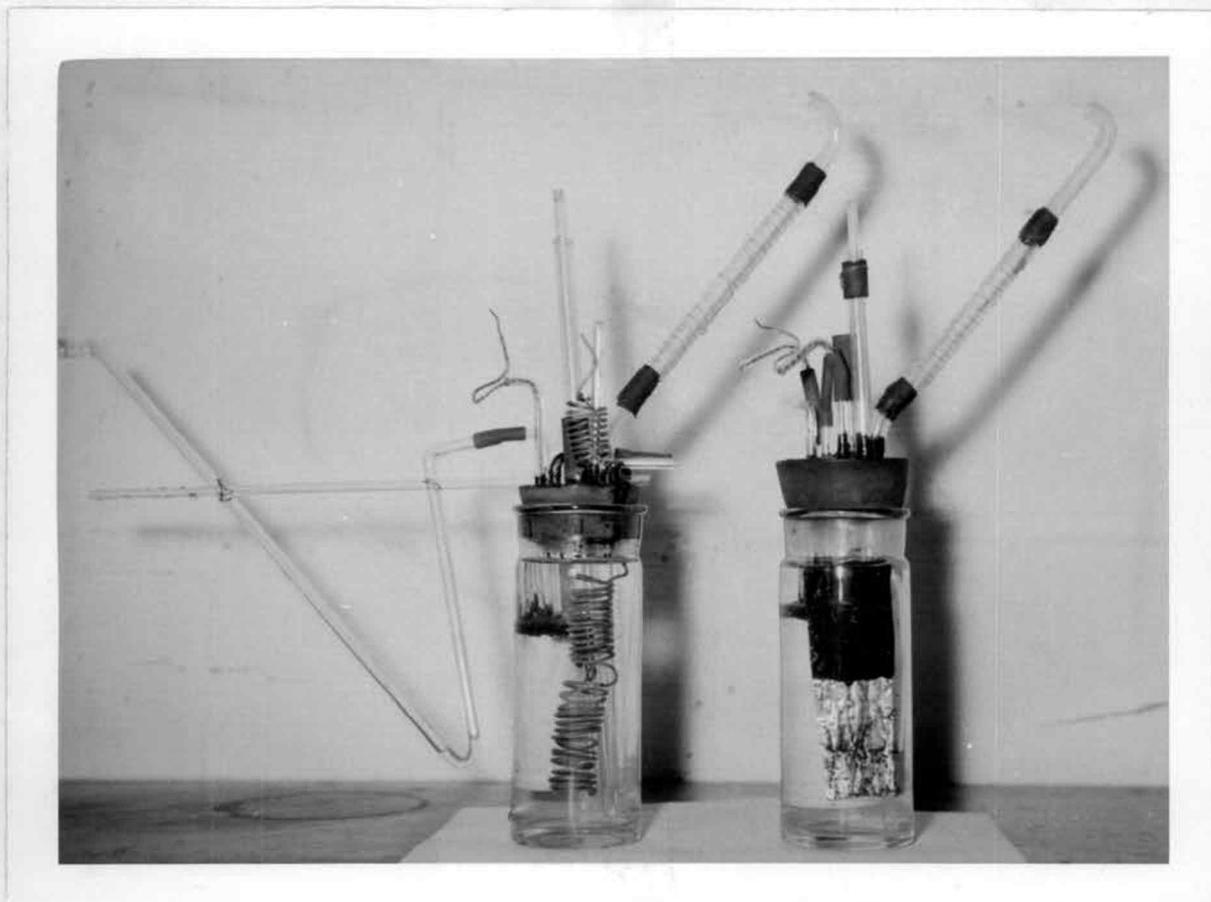
Operation of the apparatus consisted of the following consecutive steps: 1., filling the anode compartment full and the cathode compartment to within $3/4$ inch from the top; 2., opening purge cocks to purge position; 3., adjusting the burette levels to zero at upper ends and setting the three-way cocks so that one burette of each pair will receive gas; 4., simultaneous starting of a stopwatch and the current; 5., adjustment of the current to the desired value; 6., simultaneous stopping of the stopwatch, closing of one of the purge cocks, and starting of a second stopwatch, followed immediately by simultaneous closing of the other purge cock and starting of a third stopwatch; 7., recording and resetting of the first stopwatch (purge time), followed by frequent levelling of the corresponding burettes and levelling-flasks and periodic adjusting and recording of the current, voltage, and temperatures; 8., at the instant of a levelled-burette's reaching a predetermined value (usually 25 ml. on the anode gas and 50 ml. on the cathode gas), simultaneous stopping of the corresponding stopwatch and starting of another. Whenever one of the

burettes became completely filled with gas, to this eighth step was added the simultaneous closing of its inlet and opening of the inlet of the second burette in the pair. At the earliest opportunity, each stopped stopwatch was recorded and reset, and any filled burettes were emptied into the air or storage and reset to zero level. Mounting of four stopwatches compactly on a board containing paper for their recording enabled simultaneous pressing of any two of them and also enabled the distinct association of one watch with each burette.

The principle of the use of this apparatus to determine the amount of hydrogen reacted with the coal is embodied in the known fact that electrolysis of one mole of water by means of passage of current between two inert electrodes results initially in exactly one mole of atomic oxygen and two moles of atomic hydrogen. Provided that these two kinds of atoms are kept separated by a diaphragm and provided that they do not react with any other material, each two atoms combines to form a molecule of gas. Thus, for each mole of water dissociated, exactly one mole of oxygen and exactly two moles of hydrogen are formed. At approximately atmospheric pressure, the two moles of hydrogen will occupy exactly twice the volume of one mole of oxygen under the same condition of temperature and pressure. Therefore, the volume of hydrogen collected

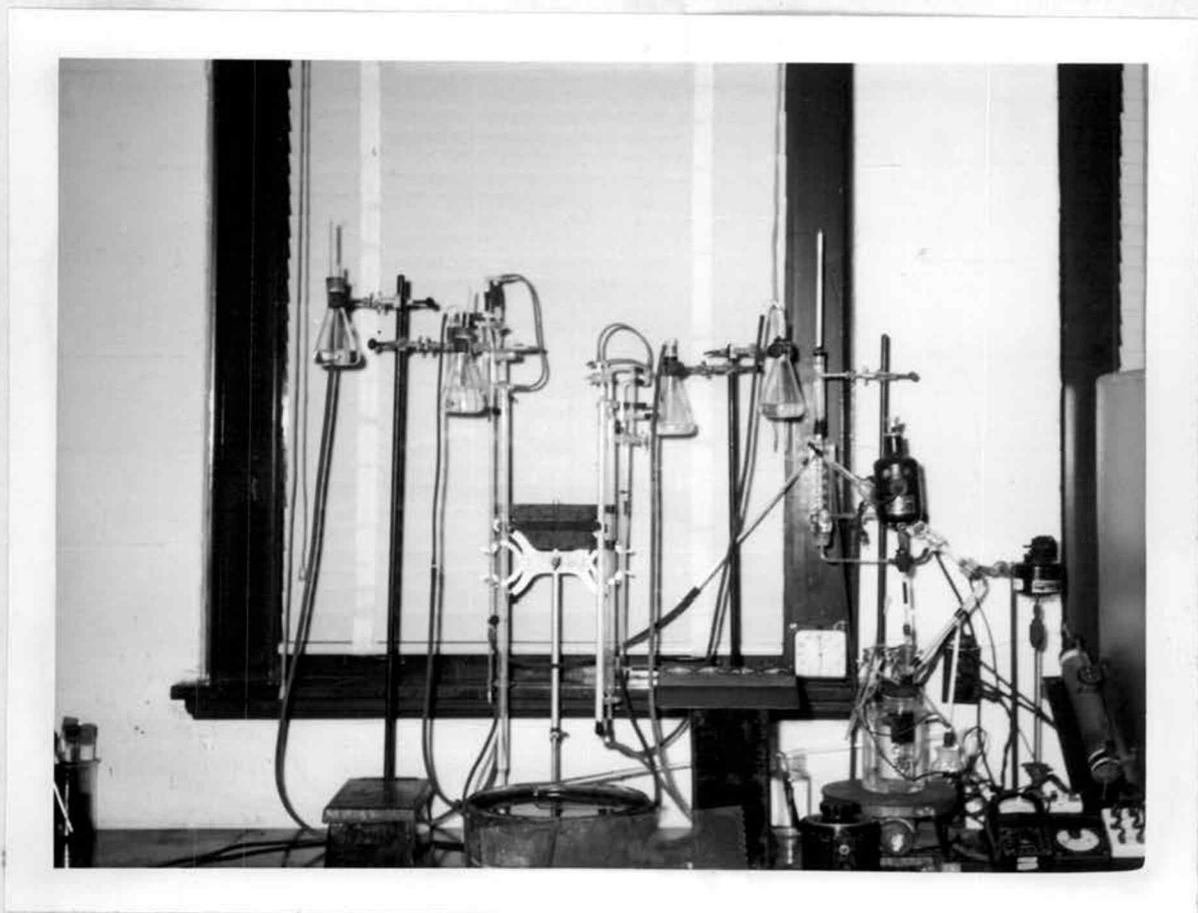
over any given interval of time should be exactly twice the volume of oxygen collected from the same cell over the same period of time, and any deviations from this relation will indicate a deficiency of one or the other of the gases, due to the occurrence of either a leak or a reaction.

The author estimates that by means of the levelling-flasks, variations of pressures on each gas were kept not only within a maximum of three inches of water during the experimental runs, but within one fourth of an inch of water at the instants of recording the times elapsed. These deviations are negligible in comparison with one atmosphere, approximately thirty-four feet of water. As will be observed in the data, the maximum rate of hydrogen-evolution was approximately twenty-six milliliters per minute, although the figure seldom exceeded seventeen. Considering the large surface areas contained by the burrettes and the lines, it is reasonable to assume that the two gases were at exactly the same temperature when measured from a room-temperature run not involving the use of the foam-breaker and cooler. It is believed also that the temperatures of the measured gases were substantially equal when generated from a cell operating at approximately 80°C. A slight doubt arises, however, as to their equality when the cathode gas is passed through the



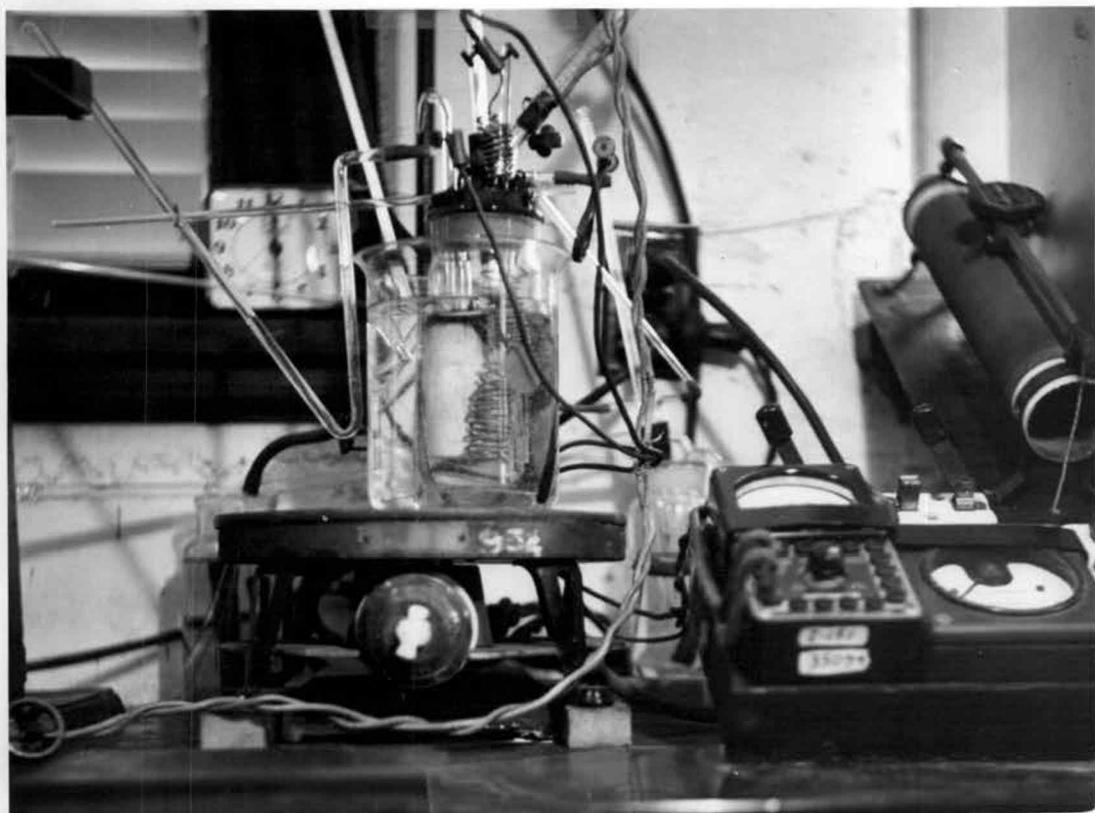
PHOTOGRAPH OF CLOSED CELL

Figure 8



PHOTOGRAPH OF APPARATUS

Figure 9



PHOTOGRAPH OF APPARATUS

Figure 10

operating foam-breaker and the anode gas is not. The flow of cooling water following the heating section could be increased or decreased at will in order to equalize the readings of the thermometers in each line, but it was observed that these thermometers were very slow to react to changes in conditions. However, the thermometers were kept within 4°C. , and it is believed that the gas temperatures were equalized in the burettes.

For data, see Appendix, pages 61-63.

Including numerous blank runs for the purpose of checking the equipment, a total of ninety runs were made with this apparatus by the author. From the latter one-third, ten coal-hydrogenations were selected for study because of their individual reliabilities' being indicated by correct test runs immediately preceding or following. Plots of the data obtained are shown in Figures 11 and 12. All runs were made with a concentration ratio of ten grams coal to 300 ml. 0.5N. H_2SO_4 , except number two, the ratio of which was 20:300. A study of these curves shows definite inconsistencies, rendering impossible any rational conclusions regarding the relative effects of the variables involved. However, of utmost importance is the fact that each run shows, over at least one range, a definite deficiency in the amount of hydrogen collected outside the cell. On the supposition that this deficiency

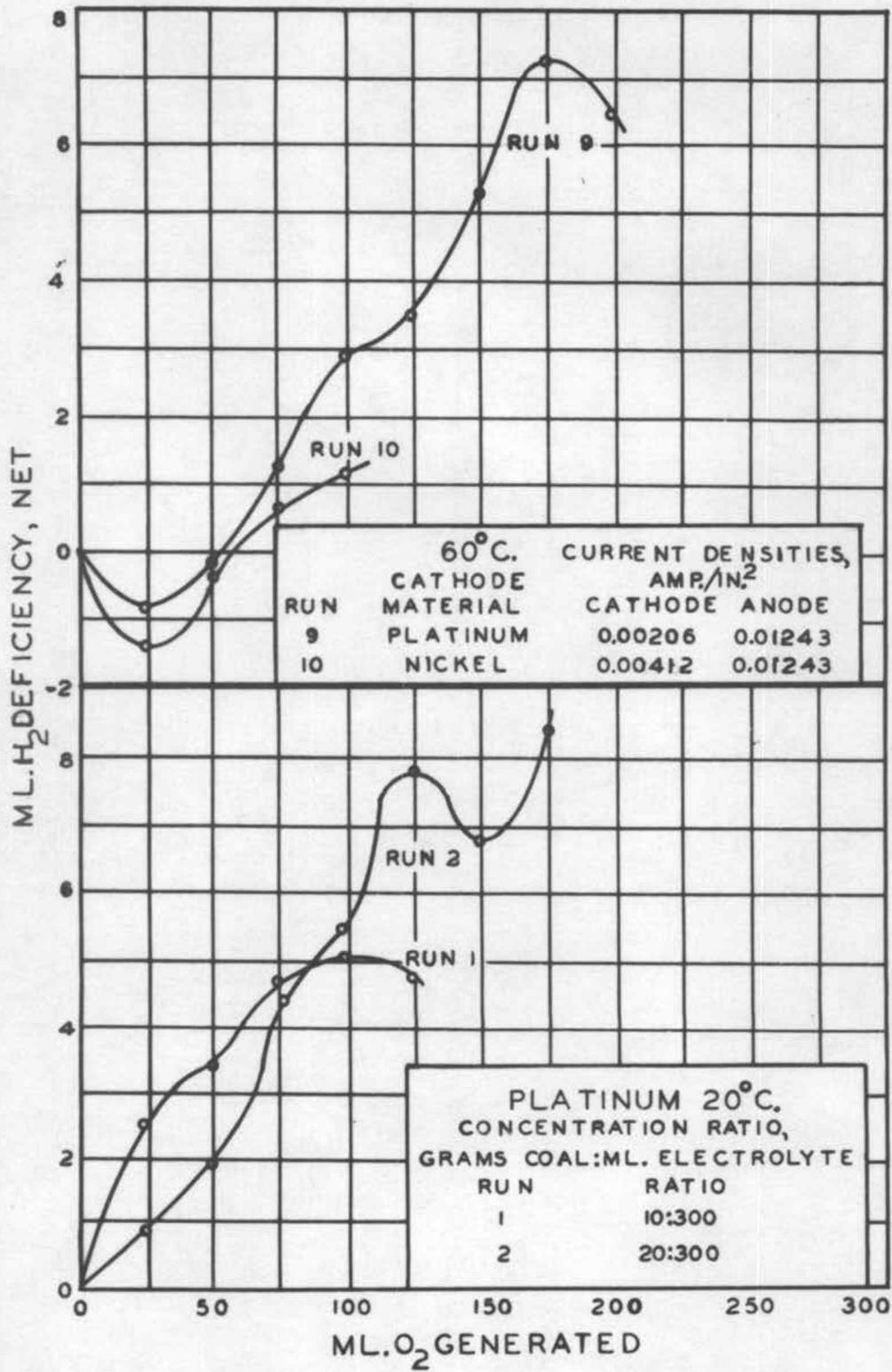


Figure 11

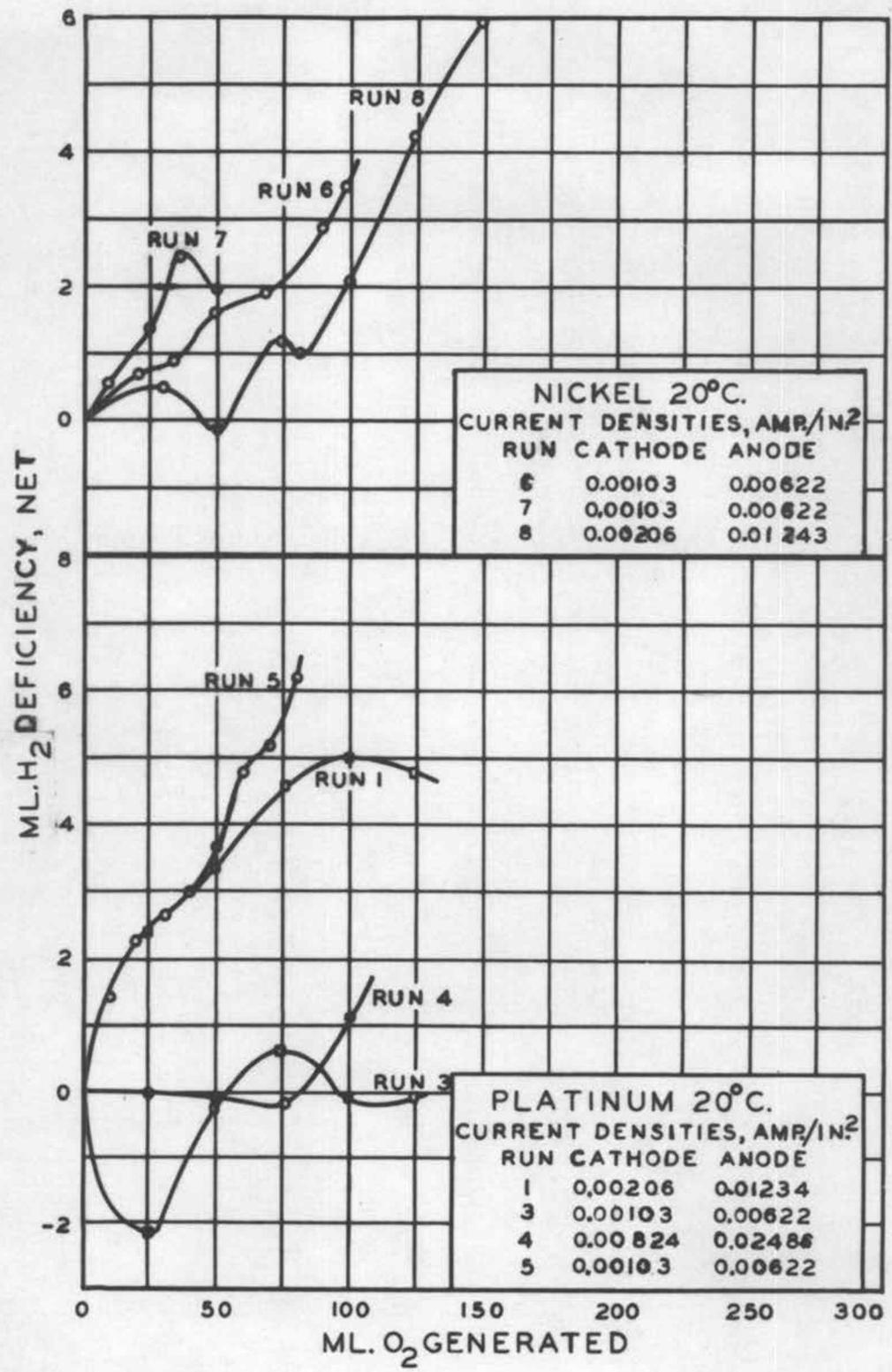


Figure 12

represents hydrogen reacting with the coal constituents, it may be stated that during the generation of the first 50 ml. of oxygen, an average of 1.13 ml. of hydrogen was consumed. Likewise, with the first 100 ml. of oxygen, an average of 2.92 ml. of hydrogen was consumed. Converting these figures to percentage hydrogen consumed gives averages of 1.13% and 1.46%, respectively. The corresponding maximums are 3.70% and 2.78%. Oxygen volumes of 50 and 100 ml. at 21°C. and one atmosphere pressure represent, respectively, 0.083 and 0.166 moles of hydrogen generated.

The basis of all calculations made on these runs is that the oxygen volume collected is exactly equal to the oxygen volume generated; therefore the hydrogen volume generated is presumed to be exactly twice the measured oxygen volume. Thus, for 50 ml. oxygen collected, it is presumed that 100 ml. hydrogen has been generated, and if only 98 ml. hydrogen were collected, then the deficiency is 2%. However, if, for the 50 ml. oxygen collected, 51 ml. were actually generated, then 102 ml. hydrogen has been generated, and the deficiency is 4%. Thus, the calculated deficiencies are conservative, and the dips appearing in some of the curves may be due to loss of oxygen, either by its solution in the cell mixture or by reaction.

The reaction of a portion of the oxygen to ozone definitely occurred in many unreported runs during the latter part of the work. Not only did this result in a volume decrease, but the corrosive action on rubber-tube connections resulted in leaks which made impossible further volume measurement. Of interest is the fact that ozone formation did not occur while the cells were operated at less than 7.5 volts and 1.032 amp./in.² anode current density, but definitely occurred at 11 volts and 1.032 amp./in.². Furthermore, a cell which had been forming ozone would again do this at low voltage unless allowed to stand idle for at least an hour or unless thoroughly washed. The most probable explanation for the phenomenon is that the particular combination of the anode metal, the anode cup, and the anode solution resulted in a decidedly favorable catalytic effect on this reaction. The same phenomenon took place when a lead anode was substituted for the platinum anode.

The author believes that the experimental error occurring with the present construction and technique would be decreased sufficiently by eliminating all rubber-tube connections and assembling a pair of all-glass cells to enable accurate quantitative comparison of the effects of the variables involved in the electrolytic hydrogenation process for coal and for any other material. The presence

of two operators would enable uninterrupted operation because the alternate cells could be prepared in advance for each forthcoming run, and would also enable the analysis of the collected gases and of the liquid products.

GENERAL CONCLUSION

For the conclusions regarding each of the four phases of experimental work performed, reference is made to the respective sections.

Considering both the open-cell and the closed-cell experiments, it appears that, by means of platinum or nickel electrodes separated by a porous cup, a portion of the constituents of minus 200 mesh Coos Bay coal suspended in either 0.5N. NaOH or 0.5N. H₂SO₄ may be to some extent hydrogenated electrolytically.

APPENDIX

Electrolytic hydrogenation of aqueous phenol:

Run #3

Solution: 300 ml. of wt. analysis 1.5 phenol:100
 $H_2O:20 H_2SO_4$.
 Cathode: 0.40 in.² platinum sheet, electrically connected by apraffin-coated copper wire.
 Anode: Platinized platinum closed cylinder, 0.59 in. diam. x 3.54 in. long, 1/3 submerged, inside cup.
 Current: 0.4 amp. Current density 0.00438 amp./in.² on anode and 0.0239 amp./in.² on cathode.
 Duration: Eight hours.

Run #4

Solution: 270 ml. of wt. analysis 4.5 phenol:265.5
 H_2O .
 Cathode: Same as Run #3, but connected by glass-sealed mercury contact.
 Anode: Same as Run #3, 1/2 submerged.
 Current: 0.33 amp. Current density 0.00242 amp./in.² on anode and 0.0197 amp./in.² on cathode.
 Duration: Six hours.

Typical analyses of Beaver Hill coal, Coos Bay field:(45)

Proximate analyses, % by wt.

Condition	moisture	volatile matter	fixed carbon	ash
1	14.2	35.1	37.4	13.3
2	40.9	43.6	15.5
3	48.4	51.6

Ultimate analyses, % by wt.

Ash	S	H	C	N	O	BTU/lb.
13.3	1.5	5.6	53.8	1.3	24.5	9,500
15.5	1.7	4.6	62.8	1.5	13.9	11,070
....	2.0	5.5	74.2	1.8	16.5	13,100

Conditions 1, 2, and 3 refer to "as received", "dried at 105°C.", and "ash-and-moisture-free", respectively.

Tests on solvents:

- Solvents are designated as follows:
- I. methyl naphthalene (distilled)
 - II. methyl cyclohexane
 - III. decahydronaphthalene
 - IV. cresol
 - V. methyl naphthalene (practical)
 - VI. benzene
 - VII. monoamyl naphthalene
 - VIII. tetralin
 - IX. petroleum ether
 - X. cyclohexanol
 - XI. water
 - XII. acetone

A. Water-miscibility tests on solvents:

- line a: solvent used
 b: seconds to clear
 c: seconds to semi-clear
 d: miscibility, 5½ days
 e: miscibility 24 hours after emulsifier

Run #1

	II	III	IV	I,V	VI	VII	VIII	X
b	2	25			3			60
c			35	180		120	50	
d	no	fair	fair	good	no	good	good	fair
e	no	fair	no	good	fair	good	fair	no

Run #2

e	no	fair	fair	best	good	good	good	fair
---	----	------	------	------	------	------	------	------

B. Coal-dissolving tests on solvents:

Explanation of columns appearing on the two following pages:

- Runs 3,4,5..Oven 21½ hours, cool 1 hour
 Runs 6,7,8..Oven 12 hours, cool 1 hour
 Run 6x.....Oven 5 more hours, cool 1 hour
 Run 8x.....Oven 18½ more hours, cool 1 hour
 Run 7x.....Oven 5 more hours, cool 14 ¾ hr.
 Run 6xy.....Cool 16 more hours
 Run 8x1.....105°C. 3 hours, dessicator 1 hour
 Run 8x11....105°C. 1½ more hours, dessic. 1 hr.
 Run 8x111...105°C. 3 more hours, dessic. 1 hr.
 Data; net loss of coal from original, weight %

Coal-dissolving tests on solvents, continued

<u>Solvent</u>	<u>3,4,5</u>	<u>6,7,8</u>	<u>6x,7x</u>	<u>8x</u>	<u>6xy</u>
I,V	7.37%	9.59%	10.70%	9.21%
I,V	6.21	9.20	8.40
I,V	8.50	9.51
II	9.89
II	14.70
III	12.08	12.53	11.97
III	11.30	10.32	9.39
III	9.20	11.63	14.27
IV	6.99	7.67	8.90	5.83
IV	4.36	5.52	5.22
IV	2.86	6.60	8.32
VI	12.60
VII	10.66
VII	9.04	9.25	8.58
VII	9.83	10.78
VIII	7.69	11.28	11.93	10.53
VIII	7.32	7.15	8.73
VIII	10.00	10.90	11.37
IX
IX	12.90	12.33
IX	12.41	13.64
X	10.10	7.05	8.56	6.52
X	7.12	6.90	6.65
X	7.88
XI	14.70	13.46	13.61	12.27
XI	10.50	11.40	12.41
XI	12.00

Coal-dissolving tests on solvents, continued:

Solvent	Run 8	Run 8x	Run 8x1	Run 8x11	Run 8x111
III	11.63	14.27	15.78	16.20	16.58
IV	6.60	8.32	10.40	11.44	11.97
VII	9.83	10.78	13.40	13.97	14.32
VIII	10.90	11.37	13.90	14.45	14.97
IX	12.41	13.63	17.32	17.47	17.66
XI	11.40	12.41	15.07	15.66	16.03
None	10.16	10.37	10.62
None	10.35	10.53	10.70

Remained

Coal hydrogenation data, open cell:

Column headings:

- a. NaOH concentration, normality
 b. concentration ratio, grams coal/ml. electrolyte
 c. time-weighted average current, amperes
 d. cathode material
 p, platinum cylinder
 pp, platinized platinum cylinder
 n, nickel wire
 e. cathode current density, amp./in.², average
 f. anode current density, amp./in.², average
 g. time-weighted average temperature, deg. C.
 h. cathode sample numbers
 i. time fractions represented by the cathode samples, hours elapsed/hours total run
 j. relative absorption of light at dilution ratio of 1 ml. unknown to 10 ml. distilled water
 k. ampere hours, cumulative

a	b	c	d	e	f	g	h	i	j	k
0.5 <u>20</u> Run #1	250	0.18	pp	0.00174	0.00357	20	1,6	2/10	597	0.46
							9,12	4/10	605	0.80
							18,19	6/10	610	1.12
							16,28	8/10	592	1.47
							14,15	10/10	567	1.80
0.5 <u>500</u> Run #2	500	0.75	pp	0.00725	0.00744	20	3	0/12	316	0.0
							29	2/12	345	1.6
							31	4/12	403	3.2
							32	5/12	410	4.0
							35	6/12	445	4.8
							37	8/12	480	6.4
							39	10/12	490	7.4
41	12/12	570	9.0							
0.5 <u>250</u> Run #3	250	0.34	pp	0.00327	0.00667	20	10	0/12	455	0.0
							30	2/12	560	0.8
							32	4/12	560	1.2
							34	5/12	590	1.6
							36	6/12	650	2.0
							38	8/12	650	2.6
							40	10/12	700	3.2
42	12/12	770	4.0							
0.5 <u>500</u> Run #4	500	0.80	n	0.00775	0.00775	20	43	1/6	183	0.8
							45	2/6	198	1.6
							47	4/6	280	5.2
							49	6/6	315	4.8

Coal hydrogenation data, open cell, continued:

a	b	c	d	e	f	g	h	i	j	k
0.5	$\frac{20}{500}$	0.40	p	0.00776	0.00776	61	44	1/6	310	0.4
Run #5							46	2/6	495	0.8
							48	4/6	850	1.6
							50	6/6	900	2.4
0.5	$\frac{20}{500}$	0.80	n	0.00388	0.00776	20	51	0/10	139	0.0
Run #6							53	1/10	174	0.8
							55	2/10	187	1.6
							57	4/10	270	3.2
							59	6/10	266	4.8
							61	8/10	335	6.4
							63	10/10	395	8.0
0.5	$\frac{20}{500}$	0.36	p	0.00405	0.00701	68	52	0/10	212	0.0
Run #7a							54	1/10	246	0.4
							56	2/10	345	0.8
							58	4/10	620	1.6
							60	6/10	686	2.4
							62	8/10	756	3.2
							64	10/10	770	3.6
1.25	$\frac{20}{300}$	0.80	p	0.00388	0.00776	20	65	0/9	826	3.6
Run #7b							67	1/9	826	4.4
							69	3/9	782	6.8
							71	5/9	776	10.8
							73	7/9	722	16.4
							75	9/9	680	23.6
0.5	$\frac{20}{250}$	0.40	n	0.00388	0.00776	57	66	0/9	67	0.0
Run #8							68	1/9	83	0.4
							70	3/9	188	1.2
							72	5/9	284	2.0
							74	7/9	720	2.8
							76	9/9	870	3.6
0.0	$\frac{15}{187.5}$	0.4	49	B2	2/8	900	...
							B3	4/8	900	...
							B4	6/8	900	...
							B5	8/8	900	...
0.5	0.4/10		Blank			20	1	Inf.	610	...
0.5	0.4/10		runs,			20	1A	Inf.	610	...
0.5	0.8/10		no			20	2	Inf.	634	...
0.0	0.4/10		current.			20	3	Inf.	9	...

Coal hydrogenation data, closed cell:

Column headings

- a. concentration ratio, grams coal/ml. electrolyte
 b. voltage
 c. cathode material
 p, platinum sheet
 n, nickel wire
 d. cathode current density, amp./in.²
 e. anode current density, amp./in.
 f. average temperature of cell, deg. C.
 g. ml. hydrogen collected/time, minutes and seconds
 h. ml. oxygen collected/time, minutes and seconds

All runs were made with 0.5N. H₂SO₄ and a platinum anode

a	b	c	d	e	f	g	h
<u>10</u>	4.0	p	0.00206	0.01243	23	<u>50.0</u>	<u>25.0</u>
<u>300</u>						6:39.6	6:19.6
Run #1						<u>50.0</u>	<u>25.0</u>
						6:22.9	6:16.6
						<u>50.0</u>	<u>25.0</u>
						6:32.1	6:23.8
						<u>50.0</u>	<u>25.0</u>
						6:29.9	6:27.1
						<u>50.0</u>	<u>25.0</u>
						6:28.7	6:30.3
<u>20</u>	4.0	p	0.00206	0.01243	23	<u>50.0</u>	<u>25.0</u>
<u>300</u>						6:20.7	6:14.1
Run #2						<u>50.0</u>	<u>25.0</u>
						6:12.9	6:04.8
						<u>50.0</u>	<u>25.0</u>
						6:19.2	6:10.9
						<u>50.0</u>	<u>25.0</u>
						6:23.1	6:10.9
						<u>50.0</u>	<u>25.0</u>
						6:42.8	6:24.6
						<u>50.0</u>	<u>25.0</u>
						6:23.7	6:31.3
						<u>50.0</u>	<u>25.0</u>
						6:30.0	6:17.6
<u>10</u>	4.3	p	0.00103	0.00622	23	<u>50.0</u>	<u>25.0</u>
<u>300</u>						6:08.9	6:24.7
Run #3						<u>50.0</u>	<u>25.0</u>
						6:29.1	6:15.0
						<u>50.0</u>	<u>25.0</u>
						6:07.0	6:00.9
						<u>50.0</u>	<u>25.0</u>
						6:13.9	6:08.9

a	b	c	d	e	f	g	h
<u>10</u>	7.5	p	0.00824	0.02486	25	50.0	25.0
<u>300</u>						2:57.3	2:57.8
Run #4						50.0	25.0
						2:51.5	2:52.2
						50.0	25.0
						2:54.4	2:54.0
						50.0	25.0
						3:02.7	2:57.6
<u>10</u>	2.7	p	0.00103	0.00622	23	20.0	10.0
<u>300</u>						4:56.8	4:34.5
Run #5						20.0	10.0
						5:15.0	5:27.9
						20.0	10.0
						5:01.2	4:56.5
						20.0	10.0
						4:57.8	4:47.4
						20.0	10.0
						5:08.3	4:49.3
						20.0	10.0
						5:24.1	5:18.0
						20.0	10.0
						5:21.6	5:04.7
<u>10</u>	2.7	p	0.00103	0.00622	23	20.0	10.0
<u>300</u>						4:56.8	4:34.5
Run #6						30.0	15.0
						3:50.3	3:49.3
						30.0	15.0
						3:40.6	3:34.7
						40.0	20.0
						4:59.1	4:56.0
						40.0	20.0
						5:10.3	5:03.7
						20.0	10.0
						2:34.8	2:30.8
<u>10</u>	3.0	n	0.00103	0.00622	23	20.0	10.0
<u>300</u>						5:53.3	5:53.5
Run #7						30.0	15.0
						7:51.2	7:40.1
						24.0	12.0
						5:58.0	5:41.5
						26.0	13.0
						6:20.7	6:27.3

a	b	c	d	e	f	g	h
<u>10</u>	3.2	n	0.00206	0.01243	23	60.0	30.0
300						7:00.7	7:04.7
Run #8						40.0	20.0
						4:47.5	4:51.9
						50.0	25.0
						6:08.6	5:58.7
						15.5	6.6
						1:34.9	1:33.9
						16.5	18.4
						4:47.5	4:41.9
						50.0	25.0
						6:34.4	6:17.8
						50.0	25.0
						6:38.4	6:24.6

<u>10</u>	3.0	n	0.00206	0.01243	65	50.0	25.0
300						6:33.0	6:39.9
Run #9						50.0	25.0
						6:37.7	6:32.2
						50.0	25.0
						6:25.5	6:14.5
						50.0	25.0
						6:35.9	6:22.8
						50.0	25.0
						6:48.5	6:33.9
						50.0	25.0
						6:51.3	6:34.9
						50.0	25.0
						6:16.2	6:23.0

<u>10</u>	3.3	n	0.00412	0.01243	62	50.0	25.0
300						6:14.0	6:24.2
Run #10						50.0	25.0
						6:21.5	6:13.6
						50.0	25.0
						6:28.0	6:20.7
						50.0	25.0
						6:22.9	6:18.8