

CHEMISTRY OF COAL HYDROGENATION^{1,2}

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A review is presented of the important variables in the hydrogenation of coal. Catalysts, contact time, temperature, and pressure are the chief topics of the discussion. Volatile halogen compounds and a few amphoteric sulfides—namely, molybdenum and tungsten disulfides and stannous sulfide—are the most active of the coal-hydrogenation catalysts. The halogens and stannous sulfide are reported to be particularly effective in primary liquid-phase hydrogenation; molybdenum and tungsten disulfides are preferred for vapor-phase hydrogenation of tars or of liquid primary coal-hydrogenation products.

The probable mechanism of the coal-hydrogenation reactions is discussed on the basis of results of a study of the temperature coefficients of the rates of consumption of hydrogen, removal of oxygen, and liquefaction of coal. Data are given on the effects of temperature in the range 420–460°C., of contact times from 1.5 to 4 hr., and of pressures from 200 to 300 atmospheres on the yield of oil from coal by hydrogenation.

I. INTRODUCTION

The essential chemical difference between bituminous coal and petroleum is that the carbon-to-hydrogen atomic ratio is about 1.2 for the former and about 0.6 for the latter. In 1913 Dr. F. Bergius discovered that it is possible to add hydrogen to coal at a pressure of about 200 atmospheres and a temperature of about 450°C. Under these conditions most of the oxygen in the coal was hydrogenated to form water, some of the nitrogen to form ammonia, and most of the sulfur to form hydrogen sulfide; enough additional hydrogen atoms were chemically combined with the coal substance to produce a liquid similar to petroleum. Subsequently, the I. G. Farbenindustrie A.-G. discovered contact catalysts that increased the speed

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of the addition of hydrogen to the coal. Gasoline is now being produced on a large scale from coal by hydrogenation in Germany and in Great Britain. In 1939 Germany, with its huge plants at Leuna, Stettin, Gelsenkirchen, Bolen, and Magdeburg, was producing about 1,000,000 tons of such gasoline a year. Great Britain has a large plant at Billingham, erected by the Imperial Chemical Industries, which produces about 150,000 tons of gasoline a year by this method. Similar, though smaller, plants are in operation in Japan, France, and the United States.

II. AGITATION AND VEHICLE

One should expect that, in a heterogeneous reaction such as that between a suspension of coal in oil and hydrogen, agitation would be of paramount importance. Unfortunately, the evidence on this point is both meager and confusing. In experiments at the Bureau of Mines coal-hydrogenation plant (17) and in those at the British Fuel Research Laboratory (3), variations in rate of hydrogen flow by a factor of about 10 produced no appreciable variation in yield of oil. In the systems as set up for these tests the only source of agitation was that produced by hydrogen-gas bubbles rising through a vertical column of coal-oil suspension. However, the results obtained by Morgan and Veryard (31) for hydrogenation of coal and tar under conditions of turbulent flow of the reactants show that the rate of reaction is markedly increased by turbulence. This conclusion should be entertained with the reservation that, as Morgan and Veryard did not use any catalyst, the effect of turbulence may have been largely one of providing a catalyst: namely, the converter walls, by rupture of the adhering oil film on the metal surface.

Recent work by Storch and his coworkers (36) indicates that the rate of consumption of hydrogen is limited by a diffusion process, presumably diffusion of one of the reactants to the contact catalyst surfaces. This work was done in 1.2-liter rotating autoclaves, involving no agitation by gas bubbles; hence it is perhaps illogical to compare this system with that in the continuous experimental plant (17). If, however, one assumes that neither the mechanical agitation in the rotating autoclave nor the agitation by gas bubbling in the continuous plant is capable of disturbing the liquid film on the catalyst surfaces, then relatively large changes in the amount of such agitation would not affect the rate of the contact catalytic hydrogenation reaction, provided no turbulence were produced.

The effects produced in coal hydrogenation by adding a vehicle (liquid suspension medium) and catalysts to the coal were studied by Horton, King, and Williams (19) and by Warren, Bowles, and Gilmore (41). The data show that the separate effects of catalyst and vehicle are not additive. With small amounts of catalyst the addition of a vehicle results in an ap-

preciably enhanced yield; however, with large amounts of catalyst (that is, greater than about 0.5 per cent), the effect of the addition of vehicle is small and may even become negative. The two variables,—amounts of catalyst and of vehicle,—are therefore not independent of each other. This is probably due to the primary liquid product serving as vehicle for the remainder of the coal substance. Hence if a large proportion of catalyst is present, the production of vehicle is rapid enough to result in a yield of oil that equals or is even greater than that obtained in the presence, at the start, of both vehicle and catalyst. The vehicle produced from the coal itself is probably a more efficient solvent than any of the other vehicles employed by the experimenters listed above (19, 41).

TABLE 1

Experiments on wall catalysis with 2-liter converter

Beamshaw coal, low-temperature tar vehicle; contact time, 2 hr.; temperature, 450°C.; initial pressure, 100 atmospheres of hydrogen

EXPERIMENT NO.	LINER FITTED	CATALYST	INSOLUBLE RESIDUE (PER CENT OF DRY ASH-FREE COAL)
1	No	None	12.0
2	Yes	None	45.0
3	No	0.1 per cent Sn(OH) ₂	9.8
4	Yes	0.1 per cent Sn(OH) ₂	14.5
5	No	50 per cent Pyrex glass	15.3

III. CATALYSTS

The catalytic behavior of the converter walls has been investigated by the British Fuel Research Laboratory (6) and found to have considerable importance. These experiments were conducted in a 2-liter autoclave, using a Pyrex-glass "liner." The results are given in table 1.

Experiment 5 shows that Pyrex glass has very little effect; hence, conclusions concerning the catalytic effects of the converter walls and of the stannous hydroxide are sound. In present industrial coal-hydrogenation practice the converters are about 1 meter in diameter; hence catalysis by the converter walls may have less importance than is indicated in table 1. It should, however, be remembered that in engineering development, work such as was done by Vallette (39) in France and recently by Morgan and Veryard (31) in Great Britain, where very much narrower tubes were used than those in the experiments of table 1, the catalytic effect of the converter walls has considerable importance. One might suppose that the activity of the converter walls would be rapidly decreased by poisoning. Such is not the case, as was shown by experiments in the British Fuel Research Laboratory (4). The only way in which converter-wall activity

could be avoided was by the use of a glass liner. Indeed, one patent (10) specifies periodic activation of the converter walls by the action of small amounts of iodine in the hydrogenation of pitch and coal. No addition of iodine or its compounds is made to the reaction mixture. Additional data indicating the importance of the catalytic activity of the converter walls are reported in connection with some laboratory experiments on tar hydrogenation (27). These results also indicate that the walls of the autoclave have considerable influence on the hydrogenation process.

The results of Warren, Bowles, and Gilmore (41), who used stannous oxide in the absence of a vehicle, showed that the yield of volatile products is an approximately linear function of the logarithm of the per cent of catalyst used. This relationship holds until about 1 per cent of stannous oxide is present; for larger percentages the increase in yield due to additional catalyst is smaller than would be expected. In the presence of a vehicle the relationship between yield and amount of catalyst is such that the yield increases much more slowly than the logarithm of the per cent of catalyst used.

The nature of the catalysts employed in coal hydrogenation has been the subject of numerous patents. The presence of appreciable quantities of sulfur compounds and organic substances of high boiling points makes impractical the use of the well-known active hydrogenation catalysts, such as reduced nickel. Moreover, the latter frequently show a negative temperature coefficient⁴ at temperatures of 400° to 500°C. in hydrogenation reactions where sulfur and high-boiling organic substances are absent; because of this, they are not as active as other catalysts that are inferior to them at lower temperatures (1).

The catalysts mentioned in numerous recent patents concerning the destructive hydrogenation of coal and other carbonaceous materials may, for convenience, be classified in four groups as follows: (1) Volatile halides or compounds that will yield volatile halides upon decomposition at process temperatures (42); (2) promoted heavy-metal sulfide and oxide catalysts (43); (3) finely divided metals (44); (4) alkali and alkaline-earth metals and their compounds, plus finely divided metals (45).

The recent patent literature shows the outstanding importance of volatile halogens as catalysts in the primary liquefaction of coal by hydrogenation. This fact may be correlated with the ability of halogens, alkyl halides, and

⁴ The term "negative temperature coefficient" is used to indicate a decreasing rate of reaction with increasing temperature; or, as used in that section of this paper on the solubility of hydrogen, it indicates a decreasing concentration of hydrogen with increasing temperature. These "negative" coefficients as nominally measured are, of course, ratios the value of which is less than unity, as compared with the "positive" coefficients which are greater than unity.

halogen acids to function as catalysts in the thermal decomposition of such oxygenated organic compounds as ethers and aldehydes (11, 16).

A few amphoteric sulfides—namely, molybdenum and tungsten disulfides and stannous sulfide—are the most active of the metal sulfide catalysts. Stannous sulfide is reported to be particularly effective in the primary liquid-phase hydrogenation, whereas molybdenum and tungsten disulfides are preferred for vapor-phase hydrogenation of tars or liquid primary coal-hydrogenation products. The metal sulfides are, in general, more active than the oxides, and it is desirable to maintain a minimum partial pressure of about 1 atmosphere of hydrogen sulfide to avoid conversion of metal sulfides to oxides or to metals. The metalloids phosphorus, arsenic, selenium, and tellurium, or their compounds, are reported to be desirable additions to liquid-phase coal-hydrogenation catalysts (22).

The results obtained from experiments with various catalysts for the liquid-phase hydrogenation of tar are in general very similar to those for the liquid-phase hydrogenation of coal. An extensive survey (8) was made in the British Fuel Research Laboratories, using for each experiment 250 g. of topped low-temperature tar, a 2-liter rotating autoclave, an initial (cold) hydrogen pressure of 100 atmospheres, a temperature of 450°C., a reaction time of 2 hr., and 5 per cent of powdered catalyst. The halogens were found to have outstandingly high catalytic activity, iodine being more active than bromine or chlorine. The hydrogen halides and volatile organic halides gave results similar to those of the halogens. Stannic oxide was a good catalyst, but stannous chloride was much superior. The power possessed by sulfur of activating other substances, or perhaps acting catalytically in the presence of other substances, was found to be most marked with molybdic acid. Thus, while 2.5 per cent of molybdic acid gave a tarry product containing 23.4 per cent of pitch, a mixture of 2.5 per cent each of sulfur and molybdic acid yielded a light amber-colored oil that was completely soluble in petroleum ether and contained only traces of tar acids and bases. The effect of sulfur was also very marked when it was used with tungstic oxide. The latter is, *per se*, inactive, but a mixture of equal parts of tungstic oxide and sulfur was an active catalyst. Iron, nickel, cobalt, and chromium oxides, which were only slightly active, showed some improvement when mixed with sulfur, whereas the cadmium, tin, and vanadium oxides (which are mildly active catalysts) showed no improvement.

Most of the published information on catalysts for vapor-phase hydrogenation concerns low-temperature tar rather than oils obtained from coal by hydrogenation. A considerable amount of experimental work published in England (8, 24) and Japan (2) on the hydrogenation of low-temperature tar shows that molybdenum oxide supported on alumina gel is a satisfactory

vapor-phase catalyst when used at 480–500°C. and a pressure of 200 to 300 atmospheres of hydrogen. It deteriorates at a relatively slow rate and can be reactivated by oxidation with air. However, for partly hydrogenated middle oils that are free from asphaltic and bitumen-like materials, much more active catalysts, such as pelleted molybdenum and tungsten disulfides, may be used. These catalysts may be prepared by precipitation of the sulfide by acidification of an ammonium thiomolybdate (or thio-tungstate) solution, followed by washing, drying, and pelleting of the powdered trisulfide and subsequent reduction to the disulfide. They are extraordinarily active for vapor-phase hydrogenation, some hydrogenation being effected by them at as low a temperature as 250°C., although 380–400°C. is the practical operating temperature (24). In addition to these catalysts being much more active than molybdenum oxide supported on alumina gel, the composition of the gasoline products obtained by the hydrogenation of middle oils (from coal hydrogenation) with pelleted

TABLE 2
Gasolines produced from middle oils by different vapor-phase catalysts

PER CENT BY WEIGHT	ALUMINA-GEL-SUPPORTED CATALYST	PELLETED CATALYST
Aromatic hydrocarbons.....	27	2
Naphthenic hydrocarbons.....	66	50
Paraffinic hydrocarbons.....	7	48

molybdenum disulfide is characteristically different (7, 15), as shown in table 2.

The enormous differences in the results obtained with these catalysts cannot be due entirely to the fact that one is initially molybdic oxide and the other the disulfide, for it is probable that the oxide catalyst is at least partly converted to sulfide during operation. An x-ray study of these two catalysts would probably be profitable.

It appears desirable to maintain a minimum partial pressure of about 1 atmosphere of hydrogen sulfide to avoid conversion of metal sulfides to oxides or metals (20, 21). The work of Varga and Makray (40) shows that hydrogen sulfide, when used along with a molybdenum catalyst, promotes the hydrogenation of naphthalene, *m*-cresol, and tar oils in general. Hydrogen selenide has a selective effect when used with a molybdenum catalyst, in that it promotes the hydrogenation of naphthalene more energetically than does hydrogen sulfide, and retards the hydrogenation of *m*-cresol and tar acids in general.

The experiments of Hollings, Bruce, and Griffith (18) on the influence of silica as a promoter for molybdic acid in the hydrogenation of tars showed

that, when the yield under a given set of conditions was plotted against the atom percentage of silicon, a curve was obtained containing two maxima at 3.0 and 5.5 per cent and a minimum at 4.5 per cent. These authors also studied the adsorption, at temperatures up to 450°C., of hydrogen, benzene, hexane, and cyclohexane by molybdic acid containing varying amounts of silica. An inspection of the data given for the rate of activated adsorption of hydrogen shows that large decreases in the energy of activation occur between 0.0 and 3.0 atom per cent silicon and between 4.4 and 5.5 per cent, whereas this energy is virtually constant between 3.0 and 4.4 per cent. If one assumes a steadily increasing retardation by coal tar or its hydrogenation products with increasing atom percentage of silicon, it is reasonable to predict on the basis of the changes in energy of activated adsorption of hydrogen precisely the form of curve actually obtained; that is, two maxima, one somewhere between 0.0 and 3.0 per cent silicon and the other between 4.4 and 5.5 per cent.

The efficiency of various promoters in increasing the catalytic activity of molybdenum oxide in the catalytic hydrogenation of phenol to benzene was studied by Kingman and Rideal (25, 5). It was found that a very effective method of introducing the promoter was to prepare the catalyst from the appropriate heteropoly acid, with the promoter as the central atom in the complex. The ammonium salts of the acids were used, and the catalysts were treated with hydrogen for 6 hr. at 480°C. before testing. Of the four catalysts prepared from $(\text{NH}_4)_n[\text{X}(\text{Mo}_2\text{O}_7)_6]$, where X = phosphorus, silicon, tin, or thorium, those containing phosphorus and silicon were much more active than molybdenum oxide, whereas those containing tin and thorium were appreciably less active than molybdenum oxide. The three catalysts prepared from $(\text{NH}_4)_n[\text{M}(\text{MoO}_4)_6]$, containing nickel, chromium, and copper, were much more active than molybdenum oxide. X-ray analysis of the first group of catalysts showed an extremely small particle size for the phosphorus- and silicon-promoted catalysts, the structure of the phosphorus catalysts being entirely different from that of pure molybdenum dioxide. The thorium-promoted catalyst is more crystalline than that promoted with phosphorus, and both the thorium- and the tin-promoted catalysts have structures similar to that of pure molybdenum dioxide. The efficiency of a promoter in the first group of catalysts may therefore depend on prevention of the sintering of nearly amorphous catalysts. X-ray analysis of the second group shows a fairly well developed crystalline structure similar to that of pure molybdenum dioxide; hence, the high activity of these catalysts may be due to an effect different from that for the phosphorus- and silicon-promoted catalysts of the first group. This effect may be distortion of the space lattice caused by introduction of the promoter. The relative surface areas of some of the catalysts were

measured, and it was found that, while the more active catalysts presented larger areas, the variations in surface areas were not directly proportional to the measured differences in catalytic activity. However, inasmuch as it is known that in heat sintering the activity of some catalysts decreases manifold faster than the surface area, this lack of proportionality is not necessarily indicative of a new or qualitatively different phenomenon.

A detailed study of promoters for the dehydrogenation of hexane and the hydrogenation of phenol was published recently by Griffith (12, 13). The optimum promoter concentration for the decomposition of hexane at 500°C., using a molybdenum oxide catalyst, is found to be 4.3 atom per cent for sodium, chromium, cerium, aluminum, barium, boron, and thorium, and 2.2 atom per cent for iron, copper, and lead. The metal oxides of the first group are not reducible under the operating conditions, whereas iron, copper, and lead oxides are reduced to the respective metals. For the hydrogenation of phenol at 400°C., the optimum promoter concentrations for a molybdenum oxide catalyst were 16 atom per cent for cerium, 16.5 for aluminum, and 15.0 for silicon. No adsorption measurements for phenol or hydrogen are reported, and until further data are available it will be difficult to determine the significance of these optimum promoter concentrations.

The same author also presents a series of determinations of dehydrogenation rate for decahydronaphthalene, decane, hexane, and cyclohexane, using chromic oxide gel plus various amounts of magnesia (13, 14). For decahydronaphthalene the activity is constant from 0.0 to 90.0 per cent magnesia and then drops off linearly with increasing content of magnesia. For decane the constant activity range is 0.0 to 50.0 per cent and for hexane 0.0 to 20.0 per cent; for cyclohexane the activity drops continuously with increasing content of magnesia. Griffith explains these data by assuming that the larger hydrocarbon molecules cover many active centers upon adsorption, and hence the dilution effect due to the inert carrier magnesia is not apparent until the active centers are farther apart than the distance necessary for activation and reaction. Similar experiments with a chromic oxide-silica catalyst and addition of various amounts of magnesia show an immediate dilution effect with all hydrocarbons. Griffith concludes from this that chromic oxide promoted with silica presents a surface that differs qualitatively from unpromoted chromic oxide and is not merely one with a larger number of active centers.

Unquestionably this research will be of importance in developing the chemistry of vapor-phase hydrogenation. It would, however, be desirable to have catalytic rate studies on the destructive hydrogenation of larger molecules. There is also a dearth of rate measurements on destructive hydrogenation in the liquid phase of pure compounds of high molecular

weight. Where relatively large molecules are involved, it seems probable that adsorption of such molecules will, beyond a certain limit, retard destructive hydrogenation reactions. Especially in liquid-phase hydrogenation of large molecules, one would expect the rate to be determined largely by that of the activated adsorption of hydrogen on a surface which is almost completely covered by the other reactant. It would, perhaps, be more logical to search for hydrogenation catalysts that do not strongly adsorb the organic molecule to be hydrogenated destructively, or for hydrogenation catalysts that are soluble in the liquids to be hydrogenated, thus avoiding the necessity of a contact catalytic reaction. Tetrahydronaphthalene probably functions in part as a liquid-phase catalyst for coal hydrogenation, and it is likely that the desirability of compounds such as methylnaphthalene, phenols, quinoline, etc., in liquid-phase coal-hydrogenation systems may also be a matter of labile hydrogen atoms in these molecules, in addition to their well-known solvent action on coal. Observations have been reported which indicate that aromatic amines may be regarded as catalysts for the dehydrogenation of glyceraldehyde (37).

IV. TEMPERATURE AND PRESSURE

It is commonly supposed that one of the important reasons for the necessity of a temperature above 400°C. for the liquid-phase hydrogenation of coal is the fact that active pyrolysis of coal does not occur until such temperatures are employed. This explanation probably is too simple, for other factors are involved, such as the positive temperature coefficient of the solubility of hydrogen in most liquids, the decrease in retardation of the reaction rate at high temperatures, owing to decreased absorption of bituminous materials on the contact catalyst, and the effect of temperature and particle size on the rate of depolymerization and solution of the coal substances.

Maxted and Moon (32) showed that the temperature coefficient of the molar solubility of hydrogen in all the liquids tested by them is positive. With a given gas-liquid interfacial area (which is largely determined by the rate and manner of recirculation of hydrogen) both the rate and the total equilibrium amount of hydrogen dissolved by a given weight of liquid will increase with the temperature.

Körösy (26) plotted the critical temperature of gases against the logarithm of the molar solubility. He obtained a straight line for all solvents, but found that hydrogen exhibits anomalous behavior in that its solubility is much higher than would be predicted from its critical temperature. Gases with critical temperatures above 180°A. (-93°C.) have negative temperature coefficients of solubility in liquids, and those with

lower critical temperatures (such as hydrogen, helium, neon, nitrogen, carbon monoxide, argon, oxygen, and nitric oxide) have positive temperature coefficients in most solvents except water, which, at about room temperature, shows a negative coefficient for all gases. This is due to the fact that most solvents have appreciable expansion coefficients at room temperature, whereas that for water is very low. The temperature coefficient of solubility at constant volume of solution is negative for all gases and all solvents. Experiments made in the British Fuel Research Laboratories (9) also showed that hydrogen has a positive temperature coefficient of solubility in hydrocarbon solvents and yielded the results given in table 3 for the solubility of hydrogen and a mixture of hydrocarbons (mainly methane plus ethane) in several oils.

TABLE 3

Solubility of hydrogen and gaseous hydrocarbons in products of tar hydrogenation

SOLVENT	SOLUBILITY AT 20°C., IN VOLUMES OF GAS PER UNIT VOLUME OF SOLVENT PER 1 ATMOSPHERE PARTIAL PRESSURE	
	Hydrogen	Hydrocarbons
Product of hydrogenation of low-temperature tar..	0.065	0.7
Fraction of product boiling to 200°C.....	0.090	0.9
Fraction of product boiling from 200° to 300°C.....	0.050	0.6

TABLE 4

Temperature coefficient of solubility of hydrogen in a middle oil at 200 atmospheres pressure

Temperature, °C.....	25	100	200	300	350
Hydrogen per kilogram of oil, liters....	13	18	28	37	39

The temperature coefficient of the solubility of hydrogen in a middle oil is indicated by the data (34) of table 4. The heat of solution of the hydrogen calculated from these data ranges from about 9500 calories for the 25–100°C. interval to 16,000 calories for the 200–300°C. interval. The variation may be due to failure to reach equilibrium.

Some data on the kinetics of the primary liquefaction of coal by hydrogenation have recently been obtained by H. H. Storch and his coworkers (36). This work was done in a rotating 1200-cc. bomb, using equal weights (100 g. of each) of tetralin and coal plus 1 per cent of tin sulfide and an initial (cold) pressure of 1000 pounds of hydrogen per square inch. The results of this work indicate the following mechanism for the primary liquefaction of bituminous coal by hydrogenation:

(1) The curves of hydrogen consumption vs. time in the temperature

range 370–430°C. are virtually straight lines the slope of which shows a temperature coefficient of 1.20 per 10°C. The low temperature coefficient indicates that the slow step is probably a diffusion process, such as the transport of hydrogen through a liquid film covering the catalyst surfaces. The rates of all of the reactions mentioned in paragraphs 3, 4, and 5 below are independent of the rate of hydrogen consumption.

(2) Below 370°C. the extent of coal liquefaction (as measured by solubility in acetone and benzol) depends on depolymerization by the solvent. The activation energy of this reaction is about 7 kg.-cal., as calculated in the usual way from the temperature coefficient.

(3) Above 400°C. a fast reaction with an activation energy of about 65 kg.-cal. occurs; this reaction is probably the thermal decomposition of the coal substance. It is accompanied by rapid elimination of about 60 per cent of the oxygen of the coal and by absorption of only a negligible quantity of hydrogen.

(4) A second reaction can be clearly differentiated at temperatures above 370°C.; it proceeds at a measurable rate at 400°C., with an activation energy of about 40 kg.-cal. This reaction is slower than that described in paragraph 3 and is apparently also thermal in nature, since the rate is not changed when a glass liner and no catalyst are used. A large consumption of hydrogen occurs concomitant with this reaction, but the slowest or rate-determining step does not involve hydrogen. This step may be the reaction between the products of the thermal dissociation of coal and tetrahydronaphthalene.

(5) At all temperatures above 370°C. there is a condensation of free radicals or unsaturated compounds (generated by the thermal decomposition of the coal substance) into materials more stable than the original coal substance. This new polymer dehydrogenates at temperatures above about 450°C. at a rapid enough rate so that, despite the presence of hydrogen under pressure and of hydrogenation catalysts, some coke is formed. This condensation reaction obscures the kinetics of the reactions mentioned in paragraphs 3 and 4 and results in apparent negative temperature coefficients for the liquefaction and oxygen-removal reactions at temperatures above 400°C.

The above outline of the probable mechanism of coal hydrogenation indicates that the chief function of catalytic hydrogenation is to saturate the free radicals or unsaturated compounds provided by the thermal decomposition of the coal and to hydrogenate carbon to oxygen and double bonds in the later stages of the liquefaction. The kinetics of these hydrogenation reactions is largely obscured by the variety of other reactions proceeding at the same time. Additional experiments similar to those by Storch and his coworkers (36) have been done with a glass liner and in the

absence of catalysts (unpublished work by Storch and others). The results of such work show that, while the rate of hydrogen consumption is markedly increased by the presence of catalysts, the rates of liquefaction and oxygen elimination are not greatly affected by catalysts.

Morikawa (29, 30) and his associates have studied the effect of water vapor and of stannous chloride on the hydrogenation of coal in a 1-liter rotating autoclave. Their results indicate that the primary step of coal liquefaction occurs at about 300°C. and higher. This step is the production of bitumen upon fusion of the coal substance at about 340°C. It is accelerated by the presence of 5 to 20 per cent of water, and is profoundly affected by prolonged heating at low temperatures. The rate of production of normally gaseous hydrocarbons is but slightly affected by the presence of a catalyst such as stannous chloride; Morikawa and his associates state that the primary coal-liquefaction reaction may be the change occurring inside the polymer molecules of the coal substance and may have little to do with the side chains, which yield gaseous hydrocarbons upon hydrogenation. These authors believe that the primary reaction of coal liquefaction is depolymerization of the coal substance, involving some hydrogenation and deoxygenation but with little cracking (rupture of normal carbon-to-carbon valence bonds).

Tests on the effect of pressure, temperature, and contact time were made at the British Fuel Research Laboratory (3) in a small-scale liquid-phase continuous plant having a capacity of about 35 pounds of coal per day. Pressure variations were from 180 to 250 atmospheres; the effect was very small in this pressure range. The effect of increasing the paste input was to increase the heavy-oil product (boiling point, above 310°C.) from zero at 1.2 pounds per hour to 22.9 per cent at 2.2 pounds per hour. The temperature range studied was 420° to 460°C. The yield of insoluble residues was almost constant throughout, in contrast to the results of Hirst and his coworkers (17), given in table 5. The yield of heavy oil decreased with temperature until it vanished at 460°C. Although some increase in gasoline (boiling point, below 200°C.) and middle oil (boiling point, 200–310°C.) accompanied this, there was also a large increase in the formation of gas.

The effect of temperature in the liquid-phase continuous hydrogenation of Pittsburgh-bed coal, calculated from the results obtained by Hirst and his coworkers (17), is shown in table 5.

The fraction of unreacted ash-free coal decreases markedly with the temperature between 420° and 460°C., but the increased liquefaction does not result in an increased yield of oil; the latter decreases, in fact, owing to a rapid increase in the amount of normally gaseous hydrocarbons produced. The effect of varying the contact time, as calculated from Hirst's

data (17), is shown in table 6. The increase in carbonaceous insoluble residue and decrease in yield of gaseous hydrocarbons, with decreasing contact time, is accompanied by a slow increase in yield of oil. The latter, however, reaches a maximum for contact times of about 1.6 hr. and then decreases for shorter times. This maximum is due to the fact that, for any given type of molecule, solubility in benzene is determined largely by molecular weight. When the contact time is too brief to reduce the molec-

TABLE 5

Effect of temperature on hydrogenation of Pittsburgh-bed coal

Contact time, 2 hr.; catalyst, 0.5 per cent SnS + 0.5 per cent MoO₃; pressure, 200 atmospheres; all figures in per cent of moisture- and ash-free coal

TEMPERATURE	ASH-FREE BENZENE-INSOLUBLE RESIDUE	BENZENE-SOLUBLE OILS	NORMALLY GASEOUS HYDROCARBONS	HYDROGEN ABSORBED
°C.				
420	16.3	73.0	10.4	5.8
433	11.3	71.0	20.7	6.1
447	7.2	67.0	35.2	7.7
459	6.3	57.0	39.8	7.8

TABLE 6

Effect of contact time on hydrogenation of Pittsburgh-bed coal

Temperature, 440°C.; pressure 200 atmospheres; catalyst, 0.5 per cent SnS + 0.5 per cent MoO₃; all figures in per cent of moisture- and ash-free coal

CONTACT TIME*	ASH-FREE BENZENE-INSOLUBLE RESIDUE	BENZENE-SOLUBLE OILS	NORMALLY GASEOUS HYDROCARBONS	HYDROGEN ABSORBED
hours				
4.0	0.0	72.0	33.8	12.5
2.0	3.0	74.0	21.8	6.9
1.80	6.8	77.0	18.0	7.4
1.64	7.9	77.5	16.0	5.7
1.50	13.4	68.5	14.6	6.2

* This time is the number of hours required to pump one converter volume of paste. The heavy-oil slurry containing the unreacted coal was at the reaction temperature for about 1.5 times the indicated contact time, owing to the continuous evaporation and removal of low-boiling products in the stream of hydrogen passing through the converter.

ular weight below a certain limit, the yield of oil, as measured by solubility in benzene, must decrease. This explanation also accounts for the somewhat abrupt increase in benzene insolubles for a contact time of less than about 1.6 hr.

Pressures of at least 200 atmospheres of hydrogen are found to be desirable in liquid-phase hydrogenation of coal at temperatures of about 450°C. At appreciably lower pressures repolymerization occurs and coke

is formed. The work of Pott and Broche (35) showed that 80 to 90 per cent of the carbonaceous material in bituminous and sub-bituminous coals is rapidly dissolved by tetralin-phenol mixtures at 390-410° C. under the pressure created by the reaction mixture, i.e., with no added hydrogen. The equilibrium partial pressure of hydrogen for the tetrahydronaphthalene-naphthalene equilibrium at 450°C. is reported to be about 10 atmospheres (28). Hence it is probable that hydrogen pressures greater than 10 atmospheres are not thermodynamically necessary for the primary liquefaction of coal. Two other possible functions of high-pressure hydrogen are (1) to increase the amount of dissolved hydrogen, and (2) to accelerate the regeneration of hydroaromatic compounds, such as tetrahydronaphthalene, which serve as hydrogen carriers. It is probable that in the liquid-phase hydrogenation of coal the saturation of the unsaturated molecules produced by the thermal decomposition of the coal is accomplished mainly by reaction with hydroaromatic compounds, and to only a very minor extent by reaction with dissolved or catalytically adsorbed

TABLE 7
Effect of pressure in liquid-phase hydrogenation of coal

PRESSURE		PRODUCTS		
Initial	Maximum	Solids	Water	Oil
<i>atmospheres</i>	<i>atmospheres</i>			
80	203	41.2		37.2
100	245	26.1	6.1	50.2
120	283	21.6	6.4	56.7

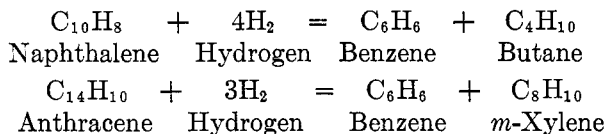
hydrogen. Hence the chief function of high hydrogen pressures and of catalysts is probably the rapid regeneration of hydroaromatics. The slow step in such regeneration may be the diffusion of one or both reactants to the catalyst surfaces.

As an example of the practical importance of high pressures in liquid-phase coal hydrogenation, Pier (33) cites the following: ". . . the conversion of old coals or of asphalts of high molecular weight which goes but slowly at 200 to 300 atmospheres, but proceeds without difficulty and at a satisfactory rate for large scale production at considerably higher pressures, e.g. 700 atmospheres or more."

The results of experiments by King (23), given in table 7, show the effect of pressure on the hydrogenation of Beamshaw coal in small autoclaves at 445°C. in the absence of a catalyst.

In the vapor-phase hydrogenation of oils obtained from the hydrogenation of coal or coal tar in the liquid phase, hydrogen at high pressure is essential in order to avoid condensation reactions leading to the formation

of coke. It is, however, not known whether the necessity for high pressures of hydrogen is of thermodynamic or kinetic origin. Destructive hydrogenation reactions may be written and their equilibrium relationships calculated from specific-heat data, which indicate that hydrogen pressures above 10 to 50 atmospheres are not thermodynamically necessary. Thus, for example, Sweeny and Voorhies (38) write the reactions:



and calculate the equilibrium constant-temperature-pressure relationships from low-temperature specific-heat measurements. Their calculations show that in the temperature range 450-480°C. a pressure of hydrogen of approximately 10 atmospheres is sufficient to obtain a commercially satisfactory yield (about 50 per cent conversion per pass), assuming that the reaction rates are large enough so that equilibrium may be reached in one pass at a reasonable space velocity. However, much higher hydrogen pressures,—namely, 200 to 500 atmospheres—are found desirable in vapor-phase hydrogenation of oils. It is possible that much higher temperatures exist on the surfaces of the catalysts than in the gas phase, owing to the net exothermicity of the oil-hydrogenation reactions, and at such higher temperatures correspondingly greater pressures of hydrogen would be necessary for a satisfactory yield. It is, however, more probable that the desirability of a pressure of 200 to 500 atmospheres of hydrogen is determined by reaction rates at the catalyst surface, rather than by thermodynamic relationships.

REFERENCES

- (1) ALCHUDZAN, A. A.: *J. Gen. Chem. (U.S.S.R.)* **4**, 1168 (1934).
- (2) ANDO, S.: *J. Soc. Chem. Ind. Japan* **39**, 278-80B (1936).
- (3) BOOTH, N., AND WILLIAMS, F. A.: *J. Inst. Fuel* **11**, 493 (1938).
- (4) *British Fuel Research Board Report for the Year Ended 1936*, p. 151. H. M. Stationery Office, London (1936).
- (5) Reference 4, pages 142-4.
- (6) *British Fuel Research Board Report for the Year Ended March 1937*, pp. 149-51. H. M. Stationery Office, London (1937).
- (7) Reference 6, pp. 118-20.
- (8) *British Fuel Research Technical Paper 40*, "The Hydrogenation Cracking of Tars," Part I, Preliminary Experiments. H. M. Stationery Office, London (1935).
- (9) *British Fuel Research Board Report for the Year Ending March 1935*, p. 102. H. M. Stationery Office, London (1935).
- (10) GESELLSCHAFT FÜR TEERVERWERTUNG M.B.H.: German patent 661,003 (June 10, 1938).

- (11) GLASS, J., AND HINSHELWOOD, C. N.: *J. Chem. Soc.* **1929**, 1815.
- (12) GRIFFITH, R. H.: *Nature* **137**, 538 (1936).
- (13) GRIFFITH, R. H.: *Trans. Faraday Soc.* **33**, 408-16 (1937).
- (14) GRIFFITH, R. H.: *Contact Catalysis*, pp. 88-9. Oxford University Press, London (1936).
- (15) HALL, C. C., AND CAWLEY, C. M.: *J. Soc. Chem. Ind.* **56**, 303-8T (1937).
- (16) HINSHELWOOD, C. N., CLUSIUS, K., AND HADMAN, G.: *Proc. Roy. Soc. (London)* **A128**, 88 (1930).
- (17) HIRST, L. L., AND OTHERS: *Ind. Eng. Chem.* **31**, 869 (1939).
- (18) HOLLINGS, H., BRUCE, R., AND GRIFFITH, R. H.: *Proc. Roy. Soc. (London)* **A148**, 186 (1935).
- (19) HORTON, L., KING, J. C., AND WILLIAMS, F. A.: *J. Inst. Fuel* **7**, 85 (1933).
- (20) I. G. FARBENINDUSTRIE A.-G.: German patent 619,739 (October 12, 1935).
- (21) INTERNATIONAL HYDROGENATION PATENTS CO., LTD.: British patent 452,915 (September 1, 1936).
- (22) I. G. FARBENINDUSTRIE A.-G.: German patent 677,104 (June 19, 1939).
- (23) KING, J. G.: *J. Inst. Fuel* **9**, 323 (1936).
- (24) KING, J. G.: "The Hydrogenation Cracking of Tars," in *Science of Petroleum*, pp. 2156-61. Oxford University Press, London (1938).
- (25) KINGMAN, F. E. T., AND RIDEAL, E. K.: *Nature* **137**, 529 (1936).
- (26) KÖRÖSY, F.: *Trans. Faraday Soc.* **33**, 416-25 (1937).
- (27) LEOPOLD, A.: *Ann. combustibles liquides* **14**, 513-30 (1939).
- (28) MAILLARD, A.: *Ann. combustibles liquides* **9**, 1013 (1934).
- (29) MORIKAWA, K., AND YAMAGATA, K.: *J. Soc. Chem. Ind. Japan, Suppl. Bind.* **41**, 434-6 (1938).
- (30) MORIKAWA, K., ABE, R., OKAMURA, T., AND YAMAGATA, K.: *J. Soc. Chem. Ind. Japan, Suppl. Bind.* **41**, 431-4 (1938).
- (31) MORGAN, G., AND VERYARD, J. T.: *J. Soc. Chem. Ind.* **57**, 152 (1938).
- (32) MAXTED, E. B., AND MOON, C. H.: *Trans. Faraday Soc.* **32**, 769 (1936).
- (33) PIER, M.: *Trans. Faraday Soc.* **35**, 967-79 (1939).
- (34) PIER, M.: *World Petroleum Congr., London, 1933, Proc.* **2**, 290.
- (35) POTT, A., BROCHE, H., NEDELMANN, H., SCHMITZ, H., AND SHEER, W.: *Glückauf* **69**, 903 (1933).
- (36) STORCH, H. H., FISHER, C. H., EISNER, A., AND CLARKE, L.: *Ind. Eng. Chem.* **32**, 346 (1940).
- (37) STRAIN, H. H.: *J. Am. Chem. Soc.* **60**, 1268 (1938).
- (38) SWEENEY, W. J., AND VOORHIES, A.: *Ind. Eng. Chem.* **26**, 195-8 (1934).
- (39) VALLETTE, F.: *Bull. soc. encour. ind. nat.* **135**, 353 (1936).
- (40) VARGA, J., AND MAKRAY, I.: *Brennstoff-Chem.* **17**, 81-3 (1936).
- (41) WARREN, T. E., BOWLES, K. W., AND GILMORE, R. E.: *Ind. Eng. Chem.* **11**, 415 (1939).
- (42) INTERNATIONAL HYDROGENATION PATENTS CO., LTD.: British patents 442,440 (February 3, 1936), 450,473 (July 20, 1936), 457,211 (November 24, 1936); French patents 779,872 (April 13, 1935), 785,245 (August 5, 1935), 787,520 (September 24, 1935), 794,437 (February 17, 1936), 816,955 (August 21, 1937). HOLYOD, R., COCKRAM, C., AND IMPERIAL CHEMICAL INDUSTRIES, LTD.: British patent 427,883 (April 29, 1935). MATHEWS, M. A., PARSONS, L. G. B., AND IMPERIAL CHEMICAL INDUSTRIES, LTD.: British patent 440,456 (December 21, 1935). I. G. FARBENINDUSTRIE A.-G.: German patents 654,024 (December 10, 1937),

- 671,183 (February 1, 1939), 678,808 (July 24, 1939); British patent 472,538 (September 20, 1937).
- STANDARD-I.G. Co.: U. S. patent 2,098,400 (November 9, 1937).
- (43) INTERNATIONAL HYDROGENATION PATENTS Co., LTD.: British patents 442,573 (February 11, 1936), 444,779 (March 27, 1936), 455,313 (October 10, 1936), 455,453 (October 19, 1936), 477,944 (January 10, 1938); French patents 793,436 (January 24, 1936), 794,936 (February 28, 1936), 814,334 (June 21, 1937).
- I. G. FARBENINDUSTRIE A.-G.: British patents 473,082 (October 6, 1937), 488,651 (July 7, 1938); French patent 830,135 (July 21, 1938); German patents 614,916 (June 25, 1935), 633,185 (July 21, 1936), 657,703 (March 11, 1938), 658,651 (April 8, 1938), 664,385 (August 30, 1938), 666,065 (October 8, 1938), 678,485 (July 17, 1939), 670,717 (January 24, 1939), 678,622 (August 3, 1939); U. S. patents 1,996,009 (March 26, 1935), 2,005,192 (June 18, 1935), 2,006,996 (July 2, 1935), 2,039,259 (April 28, 1936).
- STANDARD-I. G. Co.: U. S. patents 2,002,997 (May 28, 1935), 2,058,789 (October 27, 1936), 2,159,511 (May 23, 1939).
- YORKSHIRE TAR DISTILLERS, LTD.: British patent 435,192 (September 13, 1935).
- DEUTSCHE HYDRIERWERKE A.-G.: German patent 611,922 (April 9, 1935).
- (44) INTERNATIONAL HYDROGENATION PATENTS Co., LTD.: French patents 793,464 (January 25, 1936), 793,779 (January 31, 1936), 794,437 (February 17, 1936), 826,454 (March 31, 1938).
- STANDARD OIL COMPANY OF INDIANA: U. S. patent 2,033,737 (March 10, 1936).
- MELAMID, M.: U. S. patent 2,110,887 (March 15, 1938).
- (45) COMPAGNIE MINES VICOIGNE, NEOUX, ET DROCOURT: British patent 447,930 (May 28, 1936); French patents 787,211 (September 19, 1935), 792,711 (January 10, 1936).
- INTERNATIONAL HYDROGENATION PATENTS Co., LTD.: British patent 457,198 (November 23, 1936); French patent 793,108 (January 16, 1936).
- VIEUX, C.: British patents 442,023 (January 20, 1936), 446,494 (April 28, 1936).