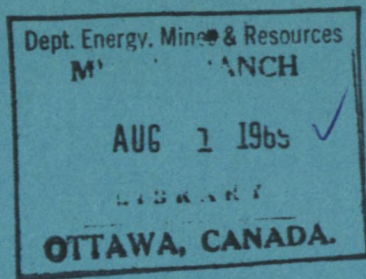


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MINES BRANCH

DEPARTMENT OF MINES

OTTAWA, CANADA.

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STATUS OF HYDROGENATION OF PETROLEUM, BITUMEN, COAL TAR AND COAL

by

T. E. Warren

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STATUS OF HYDROGENATION OF PETROLEUM, BITUMEN, COAL TAR  
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by T. E. Warren\*

Introductory

The purpose of this paper is to describe the chief processes for the hydrogenation of coal, coal tars, bitumen and petroleum, and to draw some conclusions concerning their applicability to Canadian fuels.

Information for this paper has been obtained from a complete review of technical periodicals, text books and abstracts published since 1914; from the results of experimental work by the writer on the hydrogenation of Alberta bitumen, low temperature coal tar, and peat; and incomplete review of patents; and from communications from members of organizations engaged in hydrogenation. The subject is not one which lends itself readily to theoretical analysis; and for this reason the large numbers of investigators have been compelled to obtain their data empirically. Most of this data has resulted from brief programmes of experiments, the conditions of which differ fundamentally from those of the large scale developments. Successful processes have been developed by the I. G. Farbenindustrie in Germany, and the Standard Oil Company in the United States. During the past year the Imperial Chemical Industries Ltd. has been operating a 10 ton-per-day-plant at Billingham, England. These companies, however, have disclosed only part of their operating methods, and have kept secret such essential details as the composition of the catalysts, their methods of preparation, and manner of use. In addition, their patents are difficult to interpret. Therefore, in preparing the following report, it has been necessary to select critically from different sources of information. A bibliography of literature references not cited in the text is appended.

In its broadest sense, the term "hydrogenation" includes any treatment with hydrogen. The hydrogen may react with the predominating constituent of the material treated, with a constituent present in comparatively small amount, or may not react at all; but by its presence may influence other reactions. As generally applied to fuels, the term includes any combination of these influences.

Chemical reactions involved in hydrogenation is illustrated by the following description of the effect of temperature and of

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hydrogen on high-boiling paraffin hydrocarbons. (1) The large molecules of which these are composed, under the influence of high temperature, break into two or more smaller molecules, of which at least one is unsaturated. The unsaturated molecules have a tendency to unite to form large aggregates which split and reunite still further until a solid coke-like material is formed. However, if sufficient hydrogen can be added to the unsaturated primary products, they lose the tendency to unite, and remain as light oils and gas instead of forming coke. As an illustration, the cracking processes, in which petroleum oils are heated without the addition of hydrogen, usually produce a considerable yield of coke, but the new commercial process of oil hydrogenation does not. The hydrogen reacts more completely and quickly if it is at a high pressure, and if hydrogenating catalysts are present.

Although the hydrogenation of coal and coal tars is similar, it is complicated by the presence of impurities and the complexity of the hydrocarbon structure. By the new catalytic processes, however, oxygen, nitrogen, and sulphur are removed as water, ammonia, and hydrogen sulphide respectively.

#### HYDROGENATION PROCESSES

Of the several suggested processes for hydrogenation the Bergius process was the first to demonstrate the possibility of hydrogenating coals and oils commercially. Later, the I. G. Farbenindustrie and the Standard Oil Company brought out a new process which has many advantages over the earlier Bergius process. Although all these processes are essentially the same they differ in some details, and for this reason a brief description of each is given.

##### The Bergius Process:

In 1913, Bergius was granted a patent, according to which petroleum spirit could be made from heavy hydrocarbon oils (2) at a temperature of 450°C., and under hydrogen pressure of more than 20 atmospheres. In a later patent (3) an initial pressure of 100 atmospheres was specified. At about the same time, during experiments on the production of artificial coal from cellulose, Bergius found that coal could be, to a large extent, converted into liquid oils by hydrogenation. This process was the subject of British Patent No. 18232 of August 1, 1914. After the war, Bergius' American patents for coal and oil hydrogenation were assigned to the Chemical Foundation, Inc., and were offered for sale in October, 1930. (4).

In 1912, after his first laboratory experiments, Bergius received the support of the A. G. fur Petroleumindustrie, and in 1916, a group of German financiers and technologists formed the Konsortium fur Kohlenchemie which later began operations under the name of the Erdol and Kohlenverwertung A.G. In 1922, the Erdol and Kohlenverwertung entered into negotiations with the Royal Dutch Shell Company, which resulted in an agreement in connexion with the international rights of the Bergius process (5). Bergius' plant at Rheinau was developed



to a large scale through its use, up to 1922, for the hydrogenation of oils(6). After 1922, it was used in part for experiments on coal hydrogenation and by 1926 a unit had been constructed which was capable of treating 100 tons of coal per day(7). Subsequently the I. G. Farbenindustrie obtained the hydrogenation rights in Germany, and Bergius discontinued work on the subject.

The process finally developed at Rheinau by Bergius was as follows:(8) Coal was powdered to less than 0.1 inch size and mixed with about 40 per cent of its weight of oil from a previous cycle and 5 per cent of ferric oxide. The mixture was pumped through a heat exchanger into a horizontal reaction chamber. The temperature of the reaction chamber varied with the material charged, and was usually 450 to 490°C. for coal. Hydrogen at about 200 atmospheres pressure was admitted through a heat exchanger at the inlet end of the reaction chamber. Both liquid and vapour passed to the exit end of the reaction chamber where the gas (hydrogen and other gases) was removed and recycled after the light oils had been condensed from it. The liquid was passed to a second and third reaction chamber of similar construction, but operating at different temperatures(9). The liquid product from the third stage was fractionated. Sulphur was removed from the coal as iron sulphide by the iron oxide added in the charge. The time of contact of the charge in the various stages is uncertain. It was probably about one hour in each stage. Longer times of contact were used in the earlier small scale experiments

The yields obtained from a typical coal by the Bergius process, including carbonization of the residue from hydrogenation, are as follows(8):

<u>Product</u>	<u>Yield as weight per cent of coal charged</u>
Neutral refined motor spirit (boiling range, 86 - 446°F)	15.0
Diesel oil and creosote oil	20.0
Lubricating oil	6.0
Fuel oil	8.0
Gas	23.5
Coke	24.0
Water	7.5
Ammonia	0.5
Loss	5.5
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	110.0

The total is greater than 100 per cent by the amount of hydrogen (5 per cent) and of iron oxide (5 per cent) added to the original charge.

Although the plant at Rheinau operated commercially on oil during the war, the process of coal hydrogenation described above never passed the experimental stages. It had the fundamental faults; (a) that the rate of addition of hydrogen was not great enough, (b) that sulphur was removed as solid iron sulphide, the accumulation of which interfered with recycling, and (c) that oxygen-containing



compounds such as cresols were not changed which resulted in a large refining loss.

The Process of the I. G. Farbenindustrie:

The development of the Bergius process was to some extent paralleled up to 1926 by that of the I. G. Farbenindustrie. Later this company obtained the hydrogenation rights in Germany and continued the experiments on a large scale. At present, a plant is being operated commercially at the Leunawerke of the I. G. near Merseburg in the brown coal district. It has a capacity of about 10,000 barrels per day and uses as a raw material brown coal tar and petroleum oils (10).

Although the present process of the I. G. has been developed from that of Bergius, it differs in that special catalysts are used. These increase the velocity of the hydrogenation reaction so that the throughput is increased and coke formation eliminated, and bring about the conversion of oxygen-containing compounds to hydrocarbons, and the elimination of organic sulphur as hydrogen sulphide. The catalysts are not removed after one passage through the apparatus, as was the iron oxide in the older process, but are continually recycled (11).

Since conflicting statements have been made concerning the operating details of the I. G. process, it is not possible to describe them with certainty. They are thought by the writer to be as follows:

The untreated tar is mixed with the catalyst and passed through coils 4 inches in diameter and 1,000 feet long. Hydrogen is introduced at the inlet to the coils at a pressure of about 3,000 pounds per square inch. The final temperature attained in the preheater is about 425°C. when coal tar is being treated. The solid-liquid-gas mixture passes to the reaction chamber, a cylinder 58 feet high and 2½ feet in internal diameter (10). In the reaction chamber, the pressure is about 3,000 pounds per square inch and the temperature, which varies with the different materials, is about 455°C. for coal tar. The gas is removed from the top of the reaction chamber and the light oil which it contains is condensed or absorbed under pressure. The uncombined hydrogen is passed through a purifying train, its pressure increased to 3,000 pounds per square inch, and it is returned to the inlet end of the preheating coil. The liquid containing the catalyst is continuously pumped from the bottom of the reaction chamber, mixed with fresh charging stock and passed to the inlet of the preheater. A second stage of hydrogenation may be used for further treatment of the light oil product (11).

The Standard oil hydrogenation process of the Standard Oil Company, which is probably identical in principle, is stated to be so flexible that by changing conditions of temperature, pressure, duration, and catalysts, products ranging from lubricating oils to anti-knock gasoline can be produced in the same equipment (12).



When operating on coal tars or petroleum oils there is no solid product. All of the charge leaves the apparatus as liquid or gas. It is possible to produce more than 75 per cent by weight (approximately 100 per cent by volume) of gasoline from coal tar or low-grade petroleum residues by repeated recycling. The process is on a commercial basis in the United States where the Standard-I. G. Company has erected a 5,000-barrel-per-day plant for the hydrogenation of petroleum. The first plant at Bayway, N.J., has been duplicated at Baton Rouge, La., where commercial operation began early in 1931 so that the process as applied to petroleum has apparently gone beyond the large scale experimental stage(11).

From the description of the process, it has been seen that continuous operation is possible only if all of the charging stock can ultimately be removed as vapour from the reaction chamber, unless fresh quantities of catalyst are continuously supplied. Accordingly, coal or other materials containing matter which cannot be volatilized do not readily lend themselves to the process. Pastes of powdered coal and oil are said to have been hydrogenated by the I. G. by a procedure similar to the one described(11), but it is not probable that any appreciable part of their gasoline production comes from this source.

#### Combined Processes:

Many combinations of hydrogenation with other operations are possible. One of these, suggested by Bergius, and used to some extent by the I. G. Farbenindustrie, is the combination of a coke oven and hydrogenation plant (14). Hydrogen formed at the end of the coking run is used to hydrogenate coal tar so that the unit is self-contained.

The Standard-I. G. Company uses the hydrogenation plant as auxiliary equipment in oil refineries. Natural gas or gas from a cracking process is combined with steam to produce hydrogen. The residue from cracking is hydrogenated(12). Asphalts and asphalt-base residues may in some cases be economically hydrogenated to such an extent that they may be distilled without coke formation and later be converted to gasoline by one of the cracking processes (11).

#### THE WORK OF THE BRITISH FUEL RESEARCH BOARD

The only organization operating a semi-commercial scale unit which publishes its results is the British Fuel Research Board. In 1924 the Board made plans to study hydrogenation, especially as applied to British coals, and in 1925 work with small bombs was begun at the Fuel Research Station. An agreement was also made with the International Bergius Company by which experiments were carried out at Rheinau to test the suitability of British bituminous coals for hydrogenation.

In February, 1927, a continuous plant capable of treating one ton of coal per day was put into operation at the Fuel Research Station. It was very similar in construction to that of Bergius at Rheinau. In operating, powdered coal was mixed with oil or tar and iron oxide to make a stiff paste which was forced by a hydraulic press into the first of three reaction chambers to which hydrogen



under pressure was also supplied. The mixture was passed through the three reaction chambers in series to a separator and condenser from which the gas was passed through a second condenser and scrubber to the gas holder. The bombs were heated in lead baths to ensure close temperature control. Since 1927, work has been continued using both the plant and the laboratory-scale bombs, on a variety of investigations. Until recently, the plant has been run under the conditions of the Bergius plant in 1927. Various amounts of iron oxide and varying temperatures as well as different coals were tried. Coal has also been distilled at 430°C. in a current of hydrogen at high pressure using iron oxide as a catalyst. The yield and quality of the oil produced in this was better than that obtained by passing hydrogen and charge together through the bomb. The new method has not been carried out continuously.

Other experiments have concerned the hydrogenation of tar and oils, the partial hydrogenation of non-coking coals to produce coking coals, and the production of hydrogen.

The reports of the Fuel Research Board are received about a year after the work has been completed and no detailed description has been compiled. However, the conclusions are free from commercial interest and are based on a large fund of information. In the report covering the work to March 31st, 1928, the following statements are made: " - - - - - with our present knowledge it is safe to assume that the cost (of producing oil directly from coal) would be considerably greater than the price at present ruling for imported oils although it should be less than the price of imported oils which ruled in 1917-18"; " - - - - - improvements to reduce the cost of working may be expected, notably in the cost of hydrogen production or in the recovery and re-use of the hydrogen in the gaseous products of the process".

#### COST CALCULATIONS

In 1927, H. Bruckmann, who was president of the Erdöl und Kohlenverwertung A. G. - the organization controlling the Bergius interests - stated that the cost of treating one metric ton of coal by the Bergius process was 71 marks (5). The valuable product obtained from the treatment was 65 per cent by weight of crude oil which contained 25 per cent of gasoline, 30 per cent of Diesel oil, and 10 per cent of lubricating oil based on the original coal. These figures were used by A. C. Fieldner(15) to show that the cost of gasoline produced directly from coal would be about 26 cents per gallon\* in the refinery in Germany, and about 40 to 50 cents at the refinery in America. Fieldner's calculations were based on the assumption that the crude oil produced from coal hydrogenation would be cracked to yield 50 per cent of gasoline.

Under normal conditions gasoline is worth 7 to 9 cents per gallon at the refinery in the United States(15). The Standard-I.G. process for oil hydrogenation, as has been previously noted, is expanding. It is apparent, therefore, that even if the raw material has no value the cost of processing cannot be greater

\*In quoting the paper by A.C.Fieldner, the writer has assumed that the figures relating to costs are based on U.S.gallons. The cost per Imperial gallon may be obtained by multiplying by 1.2.



than 9 cents per gallon, U.S.

This apparent contradiction in the estimation of costs, is, in part, explained by the fact that the processes of coal and oil hydrogenation yield different products. In the hydrogenation of oil a charging stock of low value is converted to 75 per cent by weight of gasoline. In the case of coal the yield is only 25 per cent by weight of gasoline unless further steps are taken(5). For instance, if Bruckmann's estimate for processing a metric ton of coal (2,205 pounds) be assumed to apply to the processing of a metric ton of oil, the cost per Imperial gallon of gasoline produced is 8.05 cents.

It is possible to make an approximate calculation of two of the most important items of expense in the I. G. and Standard-I. G. processes, namely, equipment charges and hydrogen cost.

The cost of large hydrogenation plants, calculated from the data of different writers, varies between \$700. and \$2,500 per barrel of 35 Imperial gallons daily capacity(16,10,17,5). If the cost assumed to be \$2,000 per barrel per day and the depreciation and maintenance charges to be 15 per cent, the charge per Imperial gallon for this item is 2.45 cents.

A recent review of methods of hydrogen production gives the cost of hydrogen by the reaction of steam with natural gas as 11.0, 14.1, and 17.2 cents per thousand cubic feet, when the cost of natural gas was 5, 15, and 25 cents per thousand cubic feet respectively(18). Natural gas can be transported in pipe lines for 2.5 cents per thousand cubic feet per 100 miles so that the three costs represent the value of waste natural gas at 200, 600, and 1,000 miles respectively(19). Where the cost of electric power is 15 dollars per horse-power year, and the overall efficiency of motor and compressor is 50 per cent, the cost of compressing 1,000 cubic feet of hydrogen from one atmosphere to 200 atmospheres is 1.94 cents for power. Assuming other charges, i.e. labour, fixed charges, etc. on the compressor to be 4.0 cents per thousand, the total cost for hydrogen compressed to 3,000 pounds per square inch is about 21 cents per thousand. In the production of gasoline from coal tar, about 4 per cent of hydrogen is combined(20). Assuming an equal amount to be lost in compression, scrubbing, etc., the cost of hydrogen per Imperial gallon of gasoline is 3.02 cents.

The combined cost of the two items is, therefore, 5.47 cents per Imperial gallon. While it is obvious that much of the calculation was based on uncertain data, and that there are additional items of expense, the figure shows that it is reasonable to expect that the production of gasoline from petroleum residues and coal tars can compete under some conditions with the distillation and cracking methods used at present.

Officials of the Imperial Chemical Industries have stated that gasoline could be produced by their process in England for 14 or 15 cents per Imperial gallon, of which 4 cents is the cost of the coal(21). Imported gasoline is taxed 16 cents per gallon so that the process could be operated commercially at a profit if manufactured



gasoline were exempt from taxation. Since it would benefit the coal-mining industry and help to relieve unemployment in England the process is the centre of much interest. By comparison with the calculations of Bruckmann<sup>(5)</sup> and Fieldner<sup>(15)</sup> it is seen that the estimated cost of the direct production of gasoline from coal has fallen from 31 cents per Imperial gallon in 1927 to 14 cents in 1931.

#### The Application of Hydrogenation to Canadian Fuels:

In central Canada it is probable that the process will first be used as an adjunct to the plants refining imported petroleum oils. Since this phase is already developed and in use commercially in the United States, it may be adopted very soon. The use of lignite and peat as raw materials presents interesting possibilities but depends on further development of an adaption of hydrogenation to these materials.

In Alberta, bituminous coal and bitumen are possible raw materials<sup>(22,23,24)</sup>. A recent estimate, made by the Alberta Research Council<sup>(25)</sup> of the cost of separating one ton of bitumen from bituminous sand is \$4.20. Assuming \$1.80 as the cost of mining and transporting to the separation plant a sufficient quantity of bituminous sand to produce one ton of bitumen, the value of one ton of bitumen becomes \$6.00 — which is greatly in excess of the cost of a ton of coal. Therefore, although there is every indication that the cost of hydrogenation will be much lower for bitumen than for coal, it is difficult to predict to what extent (if any) motor fuel may be produced cheaper from bitumen than from coal. Further laboratory and large-scale work will be necessary before data concerning the comparative costs can be obtained.

Hydrogenation is economically possible only on a large scale. Therefore in the case of small-scale developments for obtaining gasoline from bitumen some combination of topping and cracking processes, using the residue as paving material, would be preferable to a small hydrogenation unit.

In the Maritime Provinces, imported petroleum and native bituminous coal are the principal materials for consideration. The coal might be directly hydrogenated or, more probably, carbonized to coke or semi-coke and tar. The tar could then be hydrogenated to produce motor fuel. Shale oil, due to its comparatively high cost of production, is only remotely to be considered as a source of material for hydrogenation.

The hydrogenation processes will probably attain full development only after the supply of natural petroleum has become appreciably depleted. However, it is impossible to predict when commercial operation on any given material will begin as estimates of the reserve of petroleum cannot be made with certainty, and improvements in hydrogenation are to be expected. The expansion of the industry to coal and other raw materials will probably be a gradual one following the development of oil hydrogenation which, in the United States and Germany, has already begun.



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