<u>INFORMATION CIRCULAR</u>

<u>DEPARTMENT OF COMMERCE - BUREAU OF MINES</u>

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RECENT DEVELOPMENTS IN THE PRODUCTION OF
MOTOR FUELS FROM COAL[1]

By A. C. Fieldner[2]

INTRODUCTION

It is with some diffidence that I venture to address the Montreal Section of Society of Chemical Industry on the subject of motor fuel from coal at a time when crude petroleum is produced in greater quantities than at any time in history, and at a time when the known reserves exceed all expectations, even the optimistic estimates of the Committee of Eleven of the American Petroleum Institute. Not only are new fields being discovered in America at an embarrassing frequency but sources outside of the North American Continent show unmistakable signs of adding materially to the world's sources of oil. Were it not for the tremendous scientific and technical importance of the work done in the past few years in trans-forming coal into liquid motor fuels, I should prefer to let this subject rest until a more propitious time, such as prevailed some years ago, when the gasoline consumptive curve was rising rapidly and the production curve was slowing in its upward trend. That was the period which stimulated the researches which resulted in tetra-ethyl-lead and anti-knock gasolines on this side of the Atlantic and in methanol, synthetic gasoline and hydrogenation of coal on the other side. Some of you will recall a symposium on Motor Fuels and Oil Conservation held at the Chemists' Club in New York in September, 1925. Dr. R. L. Brown and I presented a paper at this session on "Complete Utilization of Coal and Motor Fuel[3], in which we pointed out that coal was the most likely raw material source of gasoline substitutes if and when needed. We grouped the present and future processes for obtaining motor fuel from coal in three classes, namely:

(1) The carbonization of coal, including the gas manufacturing and coking industry, and low temperature carbonization.

(2) The hydrogenation and liquefaction of coal by the Bergius process.

(3) The complete gasification of coal and conversion of the resulting gases by pressure synthesis into methanol, "synthol," and other liquid combustibles.

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[2] Chief Chemist, U. S. Bureau of Mines, Washington, D. C.
[3] Fieldner, A. C., and Brown, R. L., Complete Utilization of Coal and Motor Fuel: Oil, Paint and Drug Reporter, October 5, 1925, pp. 12-13; Blast Furnace and Steel Plant, Vol. 14, No. 138, 1926.

We showed that the light oil from coal carbonization, although an import
local source of the benzol constituent of blended motor fuels used in the vicini
of coke ovens, could never be more than a relatively small supplementary source
supply; and that for a primary source of supply we would be obliged to look to
more or less complete conversion of coal to liquid fuels by the hydrogenation
coal, or synthesis from water gas. Let us now review the status of these proc
at that time (September, 1925) and the developments that have taken place in the
2-1/2 years that have elapsed to date. We shall first discuss the supplementary
sources of motor fuel.

## Supplementary Sources of Motor Fuel

Motor benzol from coke and gas works:- Approximately 2.5 gallons of ref
motor benzol is obtained per ton of coal carbonized in by-product coke ovens
1923, for the United States this amounted to 95 million gallons (38 million ton
coal carbonized) which was 1-1/4 per cent of the 6600 million gallons of gaso
used. In 1926, coke oven benzol amounted to 112 million gallons which was
cent of the 11 billion gallons of gasoline used. Hence motor benzol becomes
more insignificant as the years go by.

Low-temperature carbonization:- Low temperature carbonization of coal
often cited as a process which will add to our future motor fuel supply. In
process coal is heated to 450° to 700° C. instead of 1000° to 1300° C. The tar
yields are from 20 to 30 gallons, or two or three times that obtained in high
temperature carbonization. Also, the tar resembles petroleum in some respect
Low-temperature tar consists of one-third to one-half tar acids and higher phe
and the remaining substances are hydrocarbons - saturated, unsaturated, and
It does not contain benzene, toluene, naphthalene, or anthracene, and very li
phenol or cresol, all of which are found in high-temperature tar. From 1 to
gallons of light oil may be scrubbed from the gas, and another gallon or two
distilled from the tar, the total yield being from 2 to 4 gallons per ton o
However, refining losses due to high content of unsaturated compounds bring
net yield of motor fuel to about the same as for high-temperature carbonizat
namely, 2-1/2 gallons per ton of coal. The low-temperature tar itself may be
cracked in pressure-stills with a yield of about 20 or 25 per cent motor fuel
Hence, even with this cracking, low-temperature carbonization of coal can no
expected to yield more than 7 to 12 gallons per ton carbonized. The main prod
of low-temperature carbonization is necessarily a smokeless solid fuel and it
the success in popularizing the solid fuel that the future of this process dep
assuming that a technically successful process is developed. Much capital ha
expended on both sides of the Atlantic in large scale experimentation. Comme
success has not been achieved yet although material progress has been made in
last five years. But as stated before, the amount of by-product motor fuel th
may be obtained from this source can not be more than supplementary in amount
which will depend on the market for the solid fuel. The picture has not chang
any respect from that presented in 1925.

Gasoline from oil-shale:- In the estimate of potential oil resources,
large deposits of oil shale must not be neglected. In the United States alo
is estimated that reserves of some 390 billion tons are in sight that will

of 15 gallons per ton. This amount of shale would mean a total of 135
barrels of shale oil, a reserve of possible fifteen or twenty times the
oil reserves available by the usual pumping methods. However, oil from
is highly unsaturated and the refining losses are larger than with petroleum.
is known of the mining and refining costs and interest in shale is at a low
due to our flood of flush petroleum and the rapid technical development of
afying coal. The unfavorable location of shale deposits with reference to cen-
of population, the low yields as compared to coal, the startling developments
synthetic processes, all militate against the early use of shale in the declin-
period of petroleum production. Generally speaking, I am therefore inclined to
shale as a source of oil secondary to coal.

Primary sources of motor fuel from coal:- Let us turn, now, to a considera-
of primary sources of motor fuel from coal, that is, processes in which a
fuel is the principal product of the process. These are (1) the hydrogena-
and liquefaction of coal, and (2) the conversion of coal to water gas which is
turn converted by catalytic methods into synthetic motor fuels. Research and
mical development along these lines constitute one of the most brilliant chap-
of modern chemistry and engineering. The practical achievements already
mplished are noteworthy and they show the unexpected utilitarian application
is so often made of research conducted solely for the advancement of science.
ther Bergius, when he sought to produce artificial coal from cellulose by the
lication of temperature and pressure, nor Sabatier when he studied the effect of
talysts on the reaction between carbon monoxide and hydrogen had any idea of pro-
ing motor fuels for future generations.

The Bergius process:- Dr. Frederich Bergius, the inventor of the process
the hydrogenation and liquefaction of coal, states that the direct addition of
rogen to coal was first carried out in his laboratory in Hanover in 1913, as a
ult of some three years study of the chemical nature of coal. In his first
periments he attempted to prepare an artificial coal by subjecting cellulose to
high pressures in steel bombs kept at elevated temperatures, thus simulating
geological processes of nature but speeding up the reactions by using higher
peratures. The product thus obtained resembled anthracite. Further studies on
possible constitutional formulae for coal in turn led Bergius to the conclusion
coal itself was made up largely of a class of chemical compounds which, under
tain conditions of temperature and pressure, could be made to take up hydrogen
be converted into liquid and gaseous compounds. Experiments along this line in
and 1913 resulted in obtaining a considerable degree of liquefaction when
ried out with the coal in small glass lined steel bombs of one and two liter
city. Parallel experiments with oil instead of coal showed that heavy oils and
could also be cracked and hydrogenated under pressure with large yields of
saturated hydrocarbons. Temperatures of 350 to 400° C. and pressures of 100
spheres of hydrogen were employed. Even in these early experiments as much as
per cent of the coal was converted to gaseous liquid and soluble compounds.
ble in benzene). Outbreak of the World War in 1914 stopped further develop-
on the hydrogenation of coal, although during the war period, especially near
end of the war, large scale experimental work on the cracking of heavy oils[4] was

Bergius, F., Neue Methode zur Verarbeitung von Mineralöl und Kohle: Zeit. f.
Angew. Chemie, Vol. 34, p. 341 (1921).

undertaken at Mannheim-Rheinau, which was followed at the close of the war with renewed experimentation on the hydrogenation of coal. It was not until 1921 that the principal difficulties in developing high pressure apparatus on a technical scale were overcome, and a systematic examination of various types of coal and lignite were undertaken.

## Theory of Process

In normal bituminous coal the ratio of hydrogen to carbon is approximately 16 to 1, while in petroleum the ratio is about 8 to 1. Hence in the conversion of coal to oil it is necessary to double the quantity of hydrogen. In the ordinary coking process coal begins to decompose at 350° - 400° C. (662° - 752° F.), giving off gaseous and liquid products and leaving a solid residue richer in carbon. The heavy complex organic molecules composing coal split off water, carbon dioxide, saturated hydrocarbons of the methane series and also unsaturated hydrocarbons which tend to polymerize and form solid products. The ultimate result of coking coal is to break down the organic substances to gas and coke with very little liquid product. Now, according to Bergius[5], if hydrogen is present at high pressure during this initial breaking-down of the complex coal molecules, hydrogen attaches itself at once at the points of rupture in the molecular bonds, thus preventing polymerization and combination of the unsaturated cracked products into high molecular weight solids. According to Bergius,[6] hydrogenation begins at relatively low temperatures and after treatment at 300° to 350° C. (572° - 662°F.) the product is still solid, though it has taken up a fairly large amount of hydrogen and is a sort of pitch with a fairly high melting point. This product becomes liquid if treatment is continued at a temperature of 450° C. (842° F.).

Summarized in a few words, the process of liquefaction of coal is cracking the coal molecules with simultaneous absorption of hydrogen, or possibly absorption of hydrogen, followed by splitting up of large molecules into smaller ones with continued addition of hydrogen.

That hydrogen is absorbed in the reaction is definitely shown both by increased hydrogen content of the products and by the reduction of pressure in the bomb during the process.

## Influence of Temperature and Time

According to Bergius[7], the temperature range favorable to maximum liquefaction of coal is rather narrow, being between 450 and 480° C. (842° - 896° F.) for most coals. Higher temperature speeds up the reaction but a limit is soon reached at about 480° C. above which coke is formed. Below 450° C. the rate of reaction is slow and the output of liquid hydrocarbons decreases. Longer periods of treatment compensate for lower temperatures within certain ranges. The optimum maximum pressure is between 150 and 200 atmospheres.

5. Bergius, F., Die Verflüssigung der Kohle: Zeit. Verein Deutscher Ingenieur, Vol. 69, Oct. 17, 1925, Nos. 42 and 43.

6 Bergius, F., Die Aussichten der Olerzeugung aus Kohle: Internationale Bergwirtschaft, Vol. 1, Oct.-Dec. (1925).

7 See Reference 5.

## Influence of Dispersing Medium

Attention has been called to the narrow temperature range in which lique-
[fac]tion can take place. Close temperature control is therefore necessary to obtain
[desir]able yields of oil. While such control is possible without use of liquid dis-
[pers]ing agents in the coal in very small scale experiments such as the two-liter
[bomb,] in technical scale operations it was found necessary to mix the coal with oil,
[coal t]ar or other liquid medium to conduct away the exothermic heat of reaction and
[prev]ent overheating of the individual coal particles. Also this liquid medium is
[requi]red in the continuous operation of the process to permit pumping the coal into
[the p]ressure cylinders.

## Suitability of Various Types of Coal
### for Liquefaction

Table 5 taken from a paper by Bergius gives results of "Berginization" of a
[numb]er of coals of various types ranging from anthracite to lignite. These tests
[were t]aken by Bergius as representative from several thousand such tests made at
[Mann]heim-Rheinau using the 2-liter rotary bomb or a larger 40-liter bomb. Some of
[these] tests were made with the coal dispersed in oil; others were made on the coal
[alon]e. Examination of this table and consideration of other experimental evidence
[show] that the younger rank coals such as brown coal, lignite, and sub-bituminous
[coals] are most completely liquefied or leave the smallest amount of residual carbon.
[A Ger]man brown coal left an ash-free residue of only one per cent; a German gas-
[flame] coal, approximately 10 per cent; a flame coal, 15 per cent; and semi-anthra-
[cite] 45 per cent. Anthracites containing more than 85 per cent carbon give very
[poor] yields of oil. In other words, our highest priced coals such as anthracite,
[and] smokeless semi-bituminous are poor coals for conversion to oil. The most
[easi]ly liquefied coals would appear to be the non-coking and sub-bituminous coals
[of Il]linois, Missouri, Iowa, Colorado, Wyoming, Montana, Utah, Washington, and
[othe]r Western States. It is probable that the brown lignites of Saskatchewan, the
[Dak]otas and Texas can be almost completely liquefied.

It is evident also from Table 5 that the per cent of ash has no major
[infl]uence on liquefaction yields. The yield is in proportion to the organic matter,
[and t]he ash is simply so much inert diluent to be handled in the process. Since
[the B]ergius process can utilize low rank, poor quality coal for the production of
[oil,] it would be an excellent outlet for the fines which are now so difficult to
[sell] at many mines; that is, when an oil shortage renders the process profitable.

TABLE 5.— Some results of a series of liquefaction tests with the 2-liter and the 40-liter bombs.

(According to Bergius)

| Coal No. | Exp. No. | As received analysis of water-free coal | | | V. M. in pure coal | Results | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Ash | Free carbon | Vol. matter | | Oil yield in % of | | Residual coal in % of | |
| | | | | | | as rec'd coal | pure coal | as rec'd coal | pure coal |
| Rheinisch-Westfälische Bituminous Coal | | | | | | | | | |
| 201 | 1553 | 5.3 | 58.0 | 36.7 | 38.7 | 45.7 | 50.8 | 18.8 | 21.1 |
| 204 | 1546 | 4.6 | 62.8 | 32.6 | 34.2 | 42.5 | 44.5 | 25.0 | 26.3 |
| 206 | 1478 | 31.6 | 49.5 | 18.9 | 29.4 | 36.4 | 55.8 | 10.3 | 15.7 |
| 210 | 1539 | 6.2 | 83.0 | 10.8 | 11.5 | 43.3 | 46.7 | 37.6 | 43.0 |
| 216 | 1565 | 6.0 | 73.0 | 21.0 | 22.4 | 51.4 | 54.7 | 26.4 | 28.1 |
| 209 | 1534 | 4.0 | 70.0 | 26.0 | 27.0 | 42.3 | 44.0 | 27.0 | 28.0 |
| 213 | 1550 | 9.5 | 75.5 | 15.0 | 16.6 | 35.7 | 37.8 | 26.3 | 29.5 |
| Other German Coals | | | | | | | | | |
| 252 | 913 | 13.2 | 66.8 | 20.0 | 23.0 | 36.0 | 41.5 | 18.0 | 20.8 |
| 221 | 1789 | 24.0 | 54.5 | 21.5 | 28.3 | 43.0 | 60.0 | 13.3 | 18.5 |
| 232 | 389 | 11.0 | 50.5 | 38.5 | 43.3 | 56.0 | 63.0 | 3.2 | 3.5 |
| 228 | 1858 | 8.0 | 56.5 | 35.5 | 38.5 | 68.0 | 80.0 | 0.6 | 0.7 |
| Foreign Coal | | | | | | | | | |
| 1 | 1346 | 14.8 | 55.0 | 31.2 | 36.2 | 52.0 | 60.2 | 26.0 | 29.8 |
| 101 | 1457 | 18.3 | 48.3 | 33.4 | 40.8 | 48.0 | 61.0 | 7.9 | 10.0 |
| 104c | 1461 | 6.0 | 60.5 | 33.5 | 35.7 | 62.2 | 66.7 | 8.3 | 8.9 |
| 108a | 1471 | 7.5 | 73.5 | 19.0 | 20.5 | 43.0 | 46.8 | 22.2 | 24.1 |
| 110b | 1496 | 23.3 | 45.7 | 31.0 | 40.5 | 38.2 | 48.8 | 16.4 | 21.0 |
| 116 | 1521 | 7.7 | 63.0 | 29.3 | 31.8 | 56.0 | 64.0 | 11.4 | 13.0 |
| 302 | 1674 | 44.0 | 37.0 | 19.0 | 34.0 | 29.0 | 53.0 | 8.1 | 14.7 |
| *303 | 1595 | 16.8 | 37.8 | 45.4 | 54.5 | 39.0 | 48.0 | 4.3 | 5.3 |
| 308 | 1655 | 16.5 | 32.5 | 51.0 | 61.0 | 37.0 | 44.0 | 8.6 | 10.3 |
| 499 | 1633 | 14.8 | 43.6 | 41.6 | 48.8 | 56.0 | 66.0 | 1.0 | 1.7 |
| 406 | 1430 | 15.0 | 45.0 | 40.0 | 47.0 | 64.3 | 75.0 | 0.9 | 1.1 |
| 723c | 1884 | 4.7 | 76.8 | 18.5 | 19.4 | 47.2 | 48.0 | 34.6 | 35.2 |
| 802 | 1761 | 14.7 | 48.5 | 36.8 | 41.9 | 54.4 | 77.5 | 3.1 | 4.4 |
| Peat | 1391 | 2.0 | 32.0 | 66.0 | 67.3 | 35.0 | 35.7 | 18.0 | 18.4 |

* Peat

## Hydrogenation of Low Temperature Coke

It is possible to combine low temperature carbonization with "Berginization" semi-coke. This may prove to be an advantageous combination for brown coals lignite, because the low temperature carbonization removes some 40 to 50 per of inert water and carbon dioxide and the usual low temperature tar, and a porous friable semi-coke which is readily ground fine and almost completely fied.

Distribution of Oxygen of Coal in Berginization Products.-- The organic of the coal substance is found in the products principally as water but also carbon dioxide, phenols, and tar acids, the proportions of carbon dioxide and increasing in the hydrogenation products of the younger coals.

Distribution of Nitrogen of Coal in Products.--The nitrogen of the coal goes into the gas as ammonia and partly into the oil in the nitrogen bases. Since gaseous ammonia does not suffer decomposition as in the coking process, the of ammonia is three times as much.

Sulfur Distribution in Products.--Sulfur is found in various forms in both oil under hydrogenation conditions where no steps are taken to fix the sulfur. However, if about 5 per cent pulverized iron oxide is mixed with the coal then the light oil fractions are practically free from sulfur, and the fractions retain but a very small amount. The $H_2S$ in the gas can be removed by the usual methods.

Gas Yields in Berginization Process.--The gas yields of the Berginization process are from 15 to 25 per cent by weight of the coal substance, depending on the of coal and the method of treatment in the process. The gases consist principally of $CH_4$ and its homologues; unsaturated hydrocarbons are practically absent according to Bergius. In normal operation the gas yield from a ton of coal is practically equivalent in total B.t.u. to that obtained in standard coke oven practice.

## Continuous Process on Semi-Commercial Scale

The first step in the commercial adaptation of the coal hydrogenation process by Bergius was to develop a continuous method of feeding the coal into the pressure apparatus and withdrawing the products continuously. This problem solved by mixing the finely pulverized coal with some of the heavier oils from process, thus forming a thick paste which could be handled with a pump. The oil also seemed to distribute the heat more uniformly through the mass during the reaction. Oil amounting to about 40 per cent of the weight of the coal was found adequate for this purpose. The coal paste is forced into the two steel autoclaves 1000 Kg. per 24 hour capacity in series against a pressure of 150 atmospheres by specially constructed pump. Hydrogen is forced into the same autoclaves by another pump. The autoclaves are heated to the reaction temperature by gas burners underneath or by a lead bath, and the mixture is agitated by an internal rotating

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stirrer. The first autoclave serves to preheat the mixture up to the reaction temperature, and the second autoclave is the reaction chamber proper. The reaction products leave the autoclave through a pipe and are cooled in a condenser. Expansion to atmospheric pressure takes place through a valve and the gases are separated from the liquid and solids in a separator.

The effluent is a black mobile liquid containing the inorganic matter of the coal plus any undecomposed carbonaceous matter in suspension. This product is first distilled to remove the water and light oils, and then centrifuged while warm to separate the solid residue from the oil. The solid residue which contains some residual oil is distilled down to coke, and the distillate added to the oil product from the centrifuge for refining in the same manner as petroleum, except that phenol and tar acids are separated in the usual manner of the tar distiller.

## Products of Berginization

The yield obtained from a typical gas-flame-coal of 6 per cent ash, in U.S. gallons per short tons of coal are given approximately as follows:

|  | Gallons |
|---|---|
| Motor fuel | 48 |
| Diesel engine and creosote oils | 54 |
| Lubricating oil | 16 |
| Fuel oil | 22 |
| Total refined products | 140 |

Information on the exact composition of these various oils is lacking as yet. Bergius states[8] that the motor fuel fraction is a mixture of aliphatic, aromatic and hydro-aromatic compounds. Olefines are absent, and but very little sulfuric acid is required in refining to produce stable, water-white motor fuel free from undesirable odor. Ormandy and Craven[9] examined the light-oil fraction distilling from 40° to 160° C. (104° - 356° F.) obtained in the hydrogenation of an English coal. The yield of gasoline was approximately 10 per cent of the weight of the coal (34 gallons per short ton). The washing loss was only 1 per cent, and the gasoline consisted of unsaturates 3.1, aromatics 7.6, naphthenes 51.7, and paraffins 37.6 per cent.

According to Broche[10], the Bergin oil obtained from a brown coal semi-coke contained cyclic compounds, about 22 per cent being phenols.

8  See reference 5.
9  J. Inst. Petroleum Tech., 12, 77 (1926).
10 Broche, Hans, Neure Arbeiten über den Bergius Process und die Chemische Structur der Kohle: Brennstoffchemie, Vol. 7, pp. 140-1 (1926).

## Effect of Catalysts

Although catalysts are not essential for the hydrogenation and liquefac-
of coal, yet Bowen and Nash[11] have shown that

Nickel and iron oxides have a marked catalytic influence. Under
comparable conditions, up to 45.64 per cent of oil products was ob-
tained with nickel oxide catalyst and up to 30.95 per cent with iron
oxide, all experiments in the absence of liquid media. The proportion
of phenols and bases in the oils obtained with these two oxides was
approximately the same, irrespective of the oil yield, and mean values
were 9.21 per cent phenols and 6.41 per cent bases.
    The light fractions obtained were not fully saturated and their
amount depended on the maximum temperatures employed.

Fierz-David[12] also found that $Ni(OH)_2$ speeded up the reaction, and the
have recently patented a number of catalysts for this reaction. From these
other workers it is evident that the 5 per cent iron oxide added by Bergius to
sulfur and avoid polymerization of hydrocarbons by the influence of sulfur
compounds, may also aid in the hydrogenation process. Reports from other investi-
also indicate that some unsaturated hydrocarbons may be expected in Bergin

## Large Scale Commercial Apparatus

As may well be imagined, the development of large-scale technical apparatus
the "Berginization" of coal required the expenditure of a tremendous sum of
and the application of no end of mechanical ingenuity in overcoming the
problems involved in treating coal at temperatures of 450 to 500° C. (842 - 932°F.)
pressures of hydrogen up to 150 or 200 atmospheres. Three to four million
are said to have been expended at Mannheim-Rheinau in experimental work.
commercial scale units used were large double-walled steel reaction chambers,
inches internal diameter and 26 feet long. Such a unit is said to be capable
liquefying 20 tons of coal in 24 hours. The inner wall is about 0.6 inch thick
the outer wall 2 inches. In the annular space between the walls, preheated
nitrogen gas is circulated under a pressure slightly greater than that of the
nitrogen (150 atmospheres) within the autoclave. By this ingenious method an even
ing of the autoclave is obtained under exact temperature control. Also loss of
nitrogen through the walls of the autoclave is retarded. By means of heat
exchangers the heat in the reaction products leaving the autoclave is recovered in
heating the nitrogen and the incoming charge. The final additional heat required
the process is obtained by circulating the nitrogen through coils of iron pipe
immersed in a heated lead bath.

Bowen, Arthur R., and Nash, Alfred W., The Thermal Decomposition of coal in
presence of Catalysts and under Hydrogen Pressure: Fuel in Science and
Practice, Vol. 5, pp. 361-64 (1926).
Fierz-David, H. E., Liquefaction of Wood and Cellulose and some general re-
marks on the Liquefaction of Coal: Jour. S. C. I., Vol. 44, pp. 942-44 (1925).

## Source of Hydrogen Required in Process

The amount of hydrogen required for one ton of coal is approximately 5 per cent of the weight of the coal. Fortunately, this hydrogen need not be pure. The presence of other gases simply requires a corresponding higher total gas pressure so that the partial pressure of the hydrogen is up to the required pressure. Eighty to 85 per cent pure hydrogen can be used. It is possible, therefore, to make use of coke-oven gas given off during the last part of a coking period, but owing to the obvious limitations in tying up a "Berginization" plant with coke production, Bergius proposes to obtain the necessary hydrogen from the reaction gases of the process itself. These gases consist largely of methane ($CH_4$) which may be decomposed with water vapor at 1100° C. (2012° F.) to yield hydrogen and carbon monoxide according to the following reaction:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (1)$$
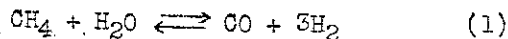
The products of this reaction are then mixed with additional water vapor and passed over an iron oxide catalyst at a temperature of 700° - 900° C. (1292° F.) yielding carbon dioxide and additional hydrogen. The carbon dioxide is washed out with water under pressure by well-known methods leaving four volumes of hydrogen for each volume of methane in the original gas. Similar reactions take place with the others in the gas. In practice a gas is obtained containing about 85 per cent hydrogen plus some undecomposed hydrocarbons, carbon monoxide, carbon dioxide, and nitrogen. About two-thirds of the reaction gases are consumed in producing the hydrogen required for the process, and the remaining third is sufficient to furnish the heat required in the hydrogen-producing process.

## Expenditures on the Development of the
## Bergius Process

The amount of money expended in developing the Bergius process at Mannheim-Rheinau is almost beyond comprehension. H. Bruckmann, President of the Erdöl und Kohleverwertung, A. G. Berlin, in a recent paper[13] states that the investment in the experimental plant amounted to 12 million gold marks, and that the 15 years experimental work consumed some 28 million marks. These figures do not include work of the I. G. at Leuna in recent years, of which I will speak later.

## Cost of Process

Bruckmann also has stated that the total costs of the process are estimated at 71 marks for 650 Kgs. of crude oil. This would be

$$\frac{1000}{650} \times \frac{71}{4} = \$27.73 \text{ per metric ton crude oil}$$

or

$$\frac{27.73}{6.5} = \$4.27 \text{ per bbl. crude oil.}$$

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13 Coal Liquefaction and Its Importance in World Economy: The Mining Journal,
Vol. 160, pp. 69-70, 94, 116. (1928)

a 50 per cent yield of gasoline on complete cracking of this crude, the
the gasoline would be about 26 cents per gallon at the refinery. It must
bered that these figures are for German conditions. In this country with
higher investment and labor costs it would be much higher, probably 40 to 50 cents
tion. Of course, these figures are mere guesses, but they show the utter
sibility of approaching competition with petroleum gasoline costing 7 to 9
at the refinery, the prevailing present day costs in the United States.

### Recent Developments on Coal Liquefaction
### by the I. G.

However, in spite of the apparent cost of the hydrogenation process, the
sche Analin and Soda Fabrik, one of the I. G. Farben Industrie group, who
ed to commercial success the synthesis of ammonia and of methanol, also attacked
problem of coal liquefaction, with all the financial, scientific and technical
ources for which this organization is famous. Obviously, the long experience of
I. G. staff in conducting research on catalytic reactions, in applying high-
sure technique, and in the production and purification of hydrogen, gives them
emendous advantage in the rapid development of a technical scale liquefaction
cess.

The essential difference in the Badische process of coal liquefaction from
of Bergius is in the admixture of suitable catalytic materials with the coal
order to control and vary the products obtained. According to Dr. C. Krauch[14],
ector, I. G. Farbenindustrie, Ludwigshaven, catalysts are introduced in definite
ases of the hydrogenation according to the products desired. For example, they
so operate that the main products are low boiling simple hydrocarbons, and they
can cause more or less of these to be of the aromatic series, thus producing
ectly an anti-knock motor fuel. Dr. Krauch does not name the catalysts used.
patents taken out by the I. G. in the past two years[15] claim as catalysts nitro-
in the combined state as $NH_4$ sulfide, nitrides such as those of Si or Ti or $NH_3$,
or without inert solids or auxiliary catalysts such as Fe or Co; molybdenum
pounds such as molybdic acid, $NH_4$ molybdate or Mo sulfide with or without $NH_3$,
o, ZnO, MgO, activated C, coke, $SiO_2$, Al $(OH)_3$, Ca $CO_3$ or clay; sulfides of the
als of the Fe group or of sulfates, sulfites or other suitable S compounds;
omic and tungsten compounds are also mentioned.

British Patent 247,585 specifies hydrogenation of crude cresylic acid or
her distillates, residues, or conversion products from coal or similar materials
the presence of Co sulfide, or sulfides of Ni, Fe, Mn, Zn, or Al.

Technical and Economic Considerations on Processing with Special Reference to
   High-Pressure Processes: Petroleum, Vol. 23, 1927, pp. 1213-1216; 1240-1248.
Hydrogenizing coal, etc., Brit. Patent 247,582, Feb. 14, 1925; C. A. Vol. 21,
   1927, p. 643; British Patent: 247,583, 247,584, 247,585, 247,586; 247,587.

British Patent 247,586 specifies a process for hydrogenating crude coal, brown coal, wax, and coumarone resins and the like in the presence of Mo compounds.

The I. G.'s commercial coal liquefaction plant was completed last year at Leuna, near Merseberg. It is now supposed to be in commercial operation and its annual capacity is said to be 120,000 tons of oil. The raw material for hydrogenation is brown coal, very cheaply mined by stripping methods.

Frank A. Howard and Robert T. Haslem of the Standard Oil Development Co., who recently visited the Leuna plant state "that they left with the feeling that the applied sciences of chemistry and engineering can face the future with calm assurance in the conviction that the world will never want for automotive fuel at a reasonable price so long as coal is available."

## Synthetic Fuels from Water Gas

The Bergius process for the hydrogenation and liquefaction of coal, converts coal into a crude low grade oil from which by further refining methods similar to those used in the petroleum industry, gasoline, kerosene, Diesel-engine fuel-oil, and pitch are obtained. Parallel with this development has been the conversion of coal into gasoline substitutes, by way of complete gasification to water or coke with subsequent conversion of this gas into alcohols or hydrocarbons.

This conversion is possible by the use of suitable catalysts, and under certain conditions of temperature and pressure, which cause the hydrogen and carbon monoxide of water gas to react chemically and form alcohols or hydrocarbons according to the catalyst and conditions of the process.

## Historical

Following the work of Sabatier and Senderens[16] in the years 1896 to 1902 the formation of methane from carbon monoxide and hydrogen in the presence of finely divided nickel at temperatures of about 300° C. (572° F.), and the work of Haber shortly thereafter on the use of high pressures for the synthesis of ammonia from hydrogen and nitrogen, it was a logical sequence for research to be undertaken on the catalytic hydrogenation of carbon monoxide with the aid of high pressure. In 1913 the Badische Anilin and Soda Fabrik took out a patent[17] on the catalytic hydrogenation of carbon monoxide at high pressure. Water gas containing an excess of carbon monoxide was heated to about 400° C. (752° F.) and 120 atmospheres pressure in the presence of metal oxide catalysts. Under these conditions a liquid separating into an oily layer and a watery layer consisting of organic acids, aldehydes, and ketones. Evidently the war stopped further research in Germany and nothing was published until 1923, when Fischer and Tropsch[18], of the Institute for Coal Research at Mülheim-Ruhr, reported obtaining a mixture of oily and watery

16  Sabatier and Senderens, Ann. Chem. Phys. Vol. 4, 418 (1905).
17  German patent 293,787 (1913).
18  Fischer, Franz, and Tropsch, Hans, Brennstoff-Chemie, vol. 4, (1923), p.
      vol. 5, (1924), pp. 201, 217.

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...ds from water gas containing an excess of hydrogen instead of an excess of monoxide as specified in the Badische patent. Also the oily layer did not ...st of hydrocarbons but largely of the higher alcohols, ketones, and aldehydes, ...some higher fatty acids. The watery layer contained the lower alcohols and ...ones. The relative amount of oily and watery liquids was influenced by the ...ength of the base with which the iron catalyst was alkalized. Fischer and ...sch gave the name "Synthol" to the mixture of compounds comprising the oily ...

The publication of Fischer and Tropsch's paper did not create much general ...rest in the subject of synthetic compounds from water gas. But in 1925 the ...ortation of synthetic wood alcohol or methanol, as it is more properly called, ...Germany caused the chemical world to sit up and take notice that the commercial ...duction of pure methanol from water gas was not a mere laboratory dream. It ...ears that the Badische Anilin and Soda Fabrik started commercial manufacturing ...1923.

While the general procedure of the Badische process was similar to Fischer's ...thol" process, the product was different. Instead of a mixture of oxygenated ...nic liquids, they obtained pure methanol, an important industrial chemical, and ...s a much lower grade motor fuel than gasoline, yet it could be used for this ...pose if need be.

At about the same time that the news of the Badische methanol process be-...public, it was reported that the French also had worked out a similar or ...tically identical process, and early in 1925 Patart[19] published a paper des-...ing his process. In the same year Audibert, another French investigator, ...ished a paper describing his own experiments on the production of methanol from ...on monoxide and hydrogen using one or more of a number of catalysts, including ...oxide or oxides of chromium, vanadium, manganese, tungsten, uranium, lead and ...th.

All of these methods involved the compression of the reacting gases to 150 ...ore atmospheres, and the product was either all alcohol or mixtures of ...enated organic compounds with only minor quantities, if any, of hydrocarbons ...lar to those found in gasoline. It remained for Franz Fischer and his ...ociates of the Institute for Coal Research at Mülheim-Ruhr to discover a catalyst ...the direct production of actual gasoline hydrocarbons from water gas. This ...covery was first announced by Fischer and Tropsch in 1926[20]. They succeeded in ...thesizing petroleum hydrocarbons by passing water gas at atmospheric pressure ...catalysts of finely divided cobalt or iron either alone or mixed with metallic ...de promoters, such as $CrO_3$, $CuO$, $ZnO$, $UO_3$, or $BeO$, at temperatures of about 270° ...(517° F.). Although this hydrocarbon process is yet in the laboratory stages it ...of great interest since it produces actual paraffin oils of various degrees of ...atility, depending on the catalysts and conditions of the process.

...tart, Georges, A New Field of Catalysis under High Pressure: Commercial
Synthesis of Methanol: Chimie et Industrie, vol. 13 (1925), pp. 179-85.
...ischer, Franz, and Tropsch, Hans, Brennstoff-Chimie, vol. 7 (1926), p. 97.

## The Hydrocarbon Process

Fischer's theory of the hydrocarbon reaction is that carbides richer in carbon than $M_3C$ are formed momentarily and these react immediately to form hydrocarbons with the hydrogen, or, perhaps carbides and hydrides form simultaneously the catalyst surface and react with each other.

The oxygen of the carbon monoxide is removed as carbon dioxide and water. The raw materials for this reaction may be water gas, blast furnace gas and hydrogen, natural gas and steam, or coke oven gas and steam.

One important drawback is the necessity for removing all sulfur from the gas, as sulfur poisons the catalyst. Fischer has patented a method[21] for converting the organic sulfur compounds in the presence of hydrogen into hydrogen sulfide by means of contact metals, such as lead, tin, or their reduced chromates at 400°. The $H_2S$ is then removed in the usual manner.

From Franz Fischer's work[22] it appears that cobalt is a better catalyst than iron in that it induces reaction at a lower temperature, it being important to maintain the temperature as low as possible to avoid methane formation.

Addition of other metallic oxides to either Fe or Co in proportion of 1:1 to 3:1 increased the rate of conversion considerably. However, these additions did not influence the relative proportions of higher paraffins formed; they merely increased the speed of conversion.

Addition of alkali to the catalyst increased the condensation of $CH_2$ groups to higher boiling hydrocarbons. For example 1 Fe : 1 CuO catalyst gave mainly volatile gasolines. Addition of $\frac{1}{2}$ to 2 per cent $K_2CO_3$ gave considerable proportions of high boiling oils and paraffin, whereas $Na_2CO_3$ addition gave an intermediate kerosene-like product. The stronger base caused the greater condensation.

Life and Regeneration of Catalyst[22]- The original active surface of the catalyst may be destroyed by a gradual sintering together of the particles. The prevention of this sintering is one of the objects of the oxide mixture. Solid paraffins coat the catalyst in some cases. These can be removed by extraction with solvents, steaming or slow oxidation with air. This latter treatment improves the activity of the catalyst due to alternate oxidation and reduction.

Optimum Temperature of Reaction[22].--The optimum temperature for iron catalyst is said to be 300° C. Reaction becomes too slow below 300° C. The cobalt catalyst is most effective at 270° C., although the reaction velocity does not diminish much down to 250° C. Nickel catalyst with suitable additions will induce reaction as low as 160° C., but even at this low temperature the product is mostly methane. Attempts to increase reaction velocity by raising temperatures above the optimum mentioned led to rapid increase in the proportion of methane with all of these metals.

21 Canadian Patent 266,382, Dec. 7, 1926. British Patent 254,288, Jan. 20, 1927.
22 Brennstoff-Chemie, Vol. 6 (1925), p. 233; vol. 7 (1926), p. 97.

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Gas Velocity[22].--Increasing gas velocity depressed methane formation, but decreased the percentage conversion. Optimum velocity is a compromise between two factors. Unfortunately, Fischer and Tropsch fail to give any data what gas velocity through the catalyst mass. This is an important omission from actical point of view, and prevents making estimates on size and capacity of an trial plant.

Products and Yields.--The products obtained according to Fischer's 1925 and papers are summarized as follows:

1. Residual gas, largely methane, ethane, carbon dioxide, water vapor, and unchanged constituents of the original gas.

2. "Gasol" - propane, butane and small amounts of the corresponding olefines.

3. Gasoline - Sp. Gr. $\frac{15^\circ}{4^\circ}$ 0.6718; gross calorific value, 11,360 calories per gram; 96.4 per cent distills up to 180° C., largely composed $C_6H_{14}$ and $C_7H_{16}$.

4. Synthetic petroleum - Sp. gr. $\frac{15^\circ}{4^\circ}$ 0.7804; 83 per cent distills between 170° C. and 330° C.

Fischer does not give quantitative yields of each product but calls attention to the theoretical yield assuming the following ideal reaction:

$$3CO + 3H_2 = CO_2 + H_2O + 2 CH_2$$
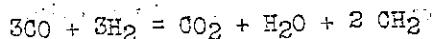
this reaction he calculates a theoretical yield of 190 grams hydrocarbons from cubic meter of water gas. If all these hydrocarbon products are of the gasoline ction, then the total theoretical yield from 1000 cubic feet of water gas would 8 gallons.

The best actual yield reported by Fischer is 100 grams of liquid containing solid products from 1 cubic meter of water gas which was repeatedly circulated the catalyst. One hundred grams is 52.6 per cent of the theoretical yield of grams, or 0.9 gallons per 1000 cubic feet of water gas. This yield includes and heavy oil.

Work of Elvins and Nash.--Shortly after Fischer and Tropsch's first paper 1925, Elvins and Nash[23], of Birmingham University, corroborated the fact that quid hydrocarbons could be obtained from CO and $H_2$, although their yields were small compared to Fischer's. However, they found oxygenated organic compounds ell as oils and later Fischer stated that he and Tropsch also found oxygen con ning substances in amounts so small that they were not worth mentioning. In mber, 1927, Elvins[24] published another paper giving small-scale laboratory re ts obtained with a catalyst composed of 60 parts $Co_2O_3$, 30 parts $CuO$, 45 parts

Fuel in Science and Practice, Vol. 5 (1926), p. 263.
Elvins, Oliver C., Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen: Chemistry and Industry, Vol. 46 (1927), pp. 473 T - 478 T.

$MnO_2$, made by igniting the mixed nitrates and then reducing at 410° C. in hydrogen. Working with catalyst volumes of 50 to 84 c.c. and space velocities of gas mixture of 55 to 240 c.c. per c.c. catalyst, per hour, Elvins' maximum conversion of CO to liquid hydrocarbons was only 2 to 3 per cent of the carbon monoxide passed over the catalyst. Both gaseous and liquid products showed unsaturation and waxy yellowish solids and substances resembling vaseline were deposited in the cold end of the reaction tube on certain of the experiments. Increasing the ratio of hydrogen to carbon monoxide from, 43 per cent $H_2$ and 56 per cent CO, to 73 per cent $H_2$ and 26 per cent CO, increased the water formed and the ratio of saturated to unsaturated hydrocarbons. These conclusions were corroborated by Fischer in a very recent paper. Elvin obtained his best yields at temperatures of 280° to 305° C. No liquids were obtained at 317° C.

Fischer and Tropsch's Recent Work.--Elvins' recent paper was followed by another by Fischer and Tropsch[25] in which they give the composition of the "gasol" "gasoline" and "petroleum" fractions obtained in their semi-commercial scale synthetic plant, and claim that Elvins' results show that he was dealing with a catalyst of low activity as evidenced by the low yields and high temperatures. Fischer and Tropsch state that further work during the past two years with semi-large scale equipment furnished them a sufficient amount of products for complete examination, this paper being a preliminary report of results. They confirm the aliphatic nature of the products, but find the proportion of olefines much greater than indicated in the first paper. Evidently the degree of unsaturation depends on the catalyst and the experimental conditions. In the case of a "gasol" (casinghead gasoline) produced with an iron-copper catalyst, after 24 hours use, the unsaturation content was 26.5 per cent; after 65 hours use the unsaturation increased to 36 per cent. The hydrogenating action of the catalyst decreased with time.

The crude gasoline fraction (boiling from 60 to 185° C.) contained 65 per cent unsaturates. Removal of the unsaturates with sulfuric acid treatment left behind a sweet smelling saturated oil consisting of n-octane, n-nonane and iso-nonane. Naphthenes and ring compounds were absent. The gasoline despite its high unsaturation value remained colorless in air and did not form any gums. Fischer believes the absence of gum formation indicates absence of any diolefines, i.e., hydrocarbons with more than one double bond.

The amount of unsaturated hydrocarbons as indicated by the iodine number can be controlled to a considerable degree by the catalyst and experimental conditions chosen. As for example, a synthetic petroleum fraction of only 8.7 iodine number, was obtained by using a cobalt-copper catalyst, a reaction temperature of 190° C. and an initial gas of 1CO to $4H_2$.

25 Fischer, Franz and Tropsch, Hans, Composition of Products Obtained in Synthesizing: Brennstoff-Chemie Vol. 9 (1928), pp. 21-24.

The influence of rate of gas flow on the saturation of oily reaction ucts was shown by an experiment with an iron-copper catalyst, where in one the oil had an iodine number of 11.5, doubling the gas velocity with other itions constant gave an oil with an iodine number of 34.9. Thus the unsatura- content was tripled. In another case, with an iron-copper catalyst which had in use for a very long period, a yellow-colored oil was obtained having an line number of 64.7, also indicating a decrease of hydrogenating activity with

The total amount of water soluble organic substances was usually small, not than 2 or 3 per cent of the total yield of organic products. They consisted dehydes and ketones, principally acetone.

Bureau of Mines Work[26].--At the Detroit meeting of the American Chemical ety, September 6-10, 1927, Smith, Davis and Reynolds presented some preliminary quantitative laboratory scale experiments conducted at the Pittsburgh riment Station of the Bureau of Mines. Of the various catalysts tried, the wing four were fairly active, viz: $Co-Cu-Cr_2O_3$; $Co-Cu$; $Co-Cu-UO_3$; $Co-Cu-Mn_2O_3$. only attempts at quantitative measurements were made with the $Co-Cu-Mn_2O_3$ lyst which had the same elements but in different proportions from those used vins, as seen in the following table.

### Comparison of Catalyst Compositions.
### Per Cent by Weight.

|  | $Co_2O_3$ | CuO | $MnO_2$ |
|---|---|---|---|
| Elvins | 60 | 30 | 45 |
| Bureau of Mines | 60 | 7 | 13 |

Evidently the Bureau's preparation was much more active than Elvins, for the eau obtained a maximum yield of 124 gms. of hydrocarbons higher than methane, or ms. from butane up, per cubic meter of gas passed over the catalyst once, as ared to Elvins' best reported yield of 10 gms. of liquid and solid hydrocarbons. the Bureau's space velocities were higher, 160 c.c. as compared to Elvins' c.c. per c.c. catalyst per hour. The Bureau's yields were probably equal to or ter than the yields reported by Fischer in his first papers, i.e., 100 gms of id and solid hydrocarbons per cubic meter of gas, circulated repeatedly over catalyst. The Bureau's best yields were obtained over a short temperature e, viz: 270 to 280° C. This agrees with Fischer's report on cobalt catalysts is somewhat lower than Elvins' temperatures of 280 to 305° C.

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ith, D. F., Davis, J. D., Reynolds, D. A. The Synthesis of Higher Hydro- carbons from Water Gas: Ind. & Eng. Chem. Vol. 20, pp. 462-4.

## CONCLUSIONS

By way of summary, we may say that the scientific and commercial [illegible] ments in the conversion of coal to motor fuel have exceeded our wildest [illegible]

The Leuna werks of the I. G. has an installed annual capacity of [illegible] tons methanol and 120,000 tons of crude oil from coal. In the Ruhr dist[rict] Gesellschaft für Teerverwertung has installed a 40,000 ton per annum plan[t] hydrogenating tars. France is now installing methanol plants, and in the [United] States, Lazote, Commercial Solvents, and others have successfully develop[ed] commercial manufacture of methanol for American needs for solvent and che[mical] purposes.

Although methanol is quite inferior to gasoline it can be used for [illegible] fuel. The Fischer hydrocarbon process is yet in the laboratory stage, bu[t illegible] distinct possibilities. The next five or ten years will undoubtedly sho[w illegible] advance both in direct hydrogenation of coal and in the hydrogenation of [illegible] monoxide. Predictions are dangerous. Nevertheless, I believe that for m[ost] production from coal the Bergius process or some modification such as that [illegible] I. G. will prove most economical and that the synthesis of liquid fuels fr[om illegible] will be limited to utilization of by-product gases and natural gas remote [illegible] other markets.

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