

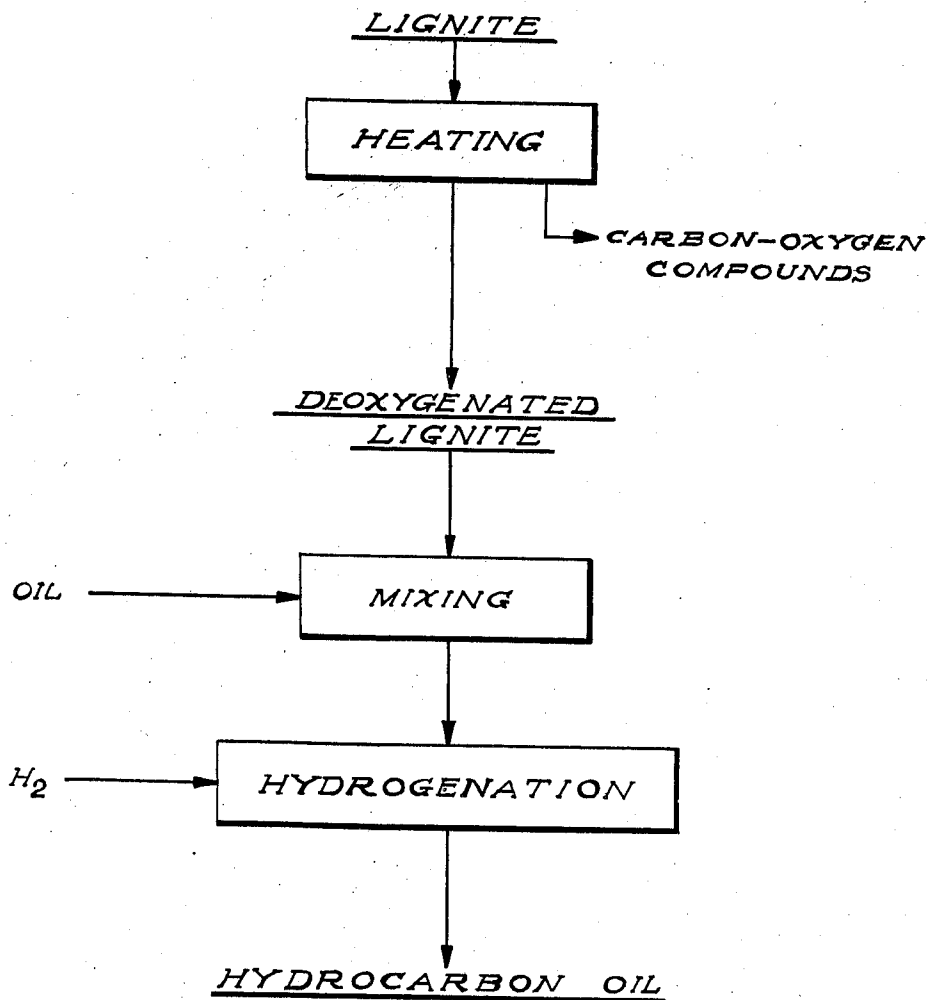
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HYDROGENATION OF HIGH OXYGEN COAL

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## UNITED STATES PATENT OFFICE

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## HYDROGENATION OF HIGH OXYGEN COAL

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## 1 Claim. (Cl. 196—53)

Anthracite coal is extremely difficult to hydrogenate. It is highly deficient in hydrogen as compared with the hydrogen content of liquid hydrocarbons and is very dense, hence difficult for hydrogen to penetrate the ground coal during the hydrogenation process. Bituminous coal is much less difficult to hydrogenate, nevertheless it contains certain components which are resistant to hydrogenation. One of these is fusain. Proposals have been offered to reduce the fusain content of bituminous coal by grinding and separating the finest portion or dust, the latter being somewhat richer in fusain than the balance of the coal. This method of separation is, however, incomplete. Durain is also difficult to hydrogenate, although not quite so resistant as fusain. It has been proposed however, to remove durain from coal by hand picking operation, since the durain has a dull appearance and the content of durain in the coal feed stock may be considerably reduced by this treatment. These methods of pretreatment, however, are rather costly. Lignite, on the other hand, is quite readily hydrogenated to yield liquid products. Owing to its high content of oxygen which usually will exceed 15 percent and frequently 20 percent or higher, the consumption of hydrogen used in the liquefaction process is excessive. Since hydrogen is costly to produce, this results in a cost for the entire treatment which at the present time appears to be prohibitive.

In the United States the lignite deposits constitute perhaps one-third of the total resources in solid fuels. Of this amount of lignite, for example, some six hundred billion tons are located in deposits in the State of North Dakota. Many of these deposits can be mined by the stripping or pit method and the mining cost therefore should be relatively low. Being more amenable to reaction by hydrogen than solid fuels more advanced in carbonization, the problem of commercial hydrogenation of lignite appears simpler than that of similar treatment of bituminous or anthracite coal. However, the presence of so much oxygen in lignite constitutes, as indicated, a drawback through undue consumption of the costly element hydrogen.

It may be noted in connection with the foregoing that the formation of lignite from peat is accompanied by the evolution mainly of water and is thus a dehydration. The formation of bituminous coal from lignite is accompanied by the evolution of great quantities of carbon dioxide and is thus a deoxidation, while the conversion of bituminous coal to anthracite involves

the formation of great quantities of methane and is thus a dehydrogenation.

It is an object of the present invention to utilize the solid fuel which has passed from the peat stage and before it has entered into the bituminous stage to such a degree that substantial conversion to fusain and durain has occurred. The raw material of the preferred form of the invention therefore is lignite in its various forms, ranging from the near-peat stage to the beginning of the bituminous stage or at least to the point of incipient bituminization. It is an object, however, to treat the lignite prior to hydrogenation in such a manner as to eliminate a considerable part of its oxygen content, such oxygen content being not that part which comes off as water but the oxygen which is otherwise combined, such as that which appears during bituminization as carbon dioxide. It will be understood that the quantity of oxygen eliminated will depend largely upon the temperature of the treatment and the time to which the lignite is exposed to this temperature, as will be explained more fully below.

The deoxidation step according to the present invention is carried out by heating the lignite to eliminate first water and then oxygen as carbon dioxide or possibly in some cases or to some extent at least as carbon monoxide. Various proposals have been made for drying lignite and carbonizing it more or less, but such proposals do not disclose a feature of my invention which is rapid heating to deoxygenate without formation of a substantial content of carbonized bodies difficult of hydrogenation. In other words, I seek to eliminate a considerable part of the oxygen of lignite without applying heat in such a sustained manner that the slower stages of carbonization occur and material difficult to hydrogenate results.

In carrying out the invention lignite may be ground and dried using, for example, a continuous drying method brought about by passing a stream of the lignite material through a drying chamber which may be of the rotatable type. The lignite then is brought into a deoxygenating chamber where it is rapidly heated with expulsion of oxygen as carbon dioxide, the temperature varying somewhat with different grades of lignite, but ordinarily being somewhat above 350° C., preferably about 360° C. the foregoing step preferably being conducted at atmospheric pressure. Higher temperatures than these can be used in some cases, depending upon the speed of travel of the stream of lignite through the deoxygenating zone, while in other cases sub-

stantially lower temperatures may be used, especially if the lignite contains its oxygen in a less firmly bound condition.

It will thus be understood that there is a time factor involved which may be utilized for the purpose of deoxygenation without undue carbonization. By arranging the process so as to have the lignite travel through the heating zone as a continuous stream it may be brought to the requisite temperature rapidly and quickly discharged therefrom. It is advisable to protect the discharging lignite from the action of air by covering the discharge end of the reaction chamber and possibly in some cases flooding it with an inert gas.

Preferably the deoxygenated lignite is allowed to flow into a container which is charged with tar or heavy oil serving as a pasting oil. The putty or pasty material which is obtained in this way, after being ground if necessary, is conveyed to the hydrogenation apparatus. The pasting oil which is prepared for reception of the deoxygenated lignite preferably is kept hot so as to be thin enough to allow rapid submersion of the lignite. The contents of the container so utilized if desired may be agitated in a suitable manner.

Owing to the variation in the properties of lignite it will be impossible to lay down any definite conditions for deoxygenation without carbonization, it being desirable to test each grade of lignite to determine its facility of deoxygenation and tendency to carbonization and to carry out the heating step to accomplish the maximum amount of deoxygenation below the stage of carbonization to materials difficult of hydrogenation.

A mixture of the deoxygenated lignite and pasting oil in about equal proportions or varying more or less according to the density or compactness of the lignite particles may thus be secured. It is conveyed to an apparatus equipped for hydrogenolysis in liquid phase, being introduced into the hydrogenator or reactor with hydrogen at at least 100 atmospheres pressure and preferably 200 atmospheres or higher. There it meets with a body of oil containing a catalyzer, for example one of the molybdenum chromium type, and undergoes the liquefying action of hydrogen, the overhead being taken off as a mixture of light and heavy oils. This process of treatment is of the sump oven type.

The overhead from this operation is preferably distilled to yield three fractions, namely, naphtha, medium oil and tar oil or tar. The latter preferably forms the basis of the pasting oil required as previously noted. The naphtha is subsequently treated by gas phase hydrogenation to give a hydrofined product, as will be subsequently described. The fraction above the naphtha, which is somewhat similar in boiling range to a mixture of kerosene and gas oil, preferably is separated by fractionation and later submitted to gas phase hydrogenation.

In various parts of the world shale deposits exist in the neighborhood of lignite deposits. As one modification of the invention I may utilize shale oil, combining the treatment of shale distillates with those obtained from lignite liquefaction. Thus shale may be distilled in any suitable way and the distillate separated by fractional distillation into naphtha, medium oil and tar oil. All of these are very crude products, since shale yields highly unsaturated and unstable liquid products that are far from being suitable as volatile liquid fuels.

A schedule of treatment which will illustrate

this phase of the invention is the following. Distill shale as noted and separate the distillate into:

1. Shale spirit.
2. Shale medium oil.
3. Shale tar.
4. Total overhead from liquid phase hydrogenation of mixture of lignite and tar, preferably a mixture of lignite, lignite tar and shale tar.
5. Lignite spirit from operation 4.
6. Lignite medium oil from operation 4.
7. Lignite tar from operation 4.
8. Mix medium oils 2 and 6 and subject to gas phase hydrogenation.

9. Mix products 1 and 5 and light overhead product from 8 and hydrofine or hydroform this as the case may be to obtain a motor spirit possessing high anti-knock qualities.

10. Excess of product 3 and product 7 over the requirements of pasting oil for the lignite hydrogenation may be subjected to liquid phase hydrogenation to obtain lighter products followed by gas phase hydrogenation to yield light oils, specifically motor spirit; the latter preferably being incorporated with product 9.

While I have given these specific illustrations of the invention, the invention may be varied in a considerable number of ways and I believe that such deviations from the foregoing, as will now be evident to those skilled in the art, should form a part of the present invention. For example, some phases of hydrogenolysis do not require catalysts, while others are conducted to very great advantage by using catalytic material, especially that which is recognized as sulphactive or resistant to sulphur poisoning. Among such catalysts molybdenum and tungsten are particularly useful, however, other catalysts less costly may be used in their stead or admixed therewith. In the liquid phase hydrogenolysis the catalyst is preferably finely divided and employed in sump oven procedure, while in gas phase hydrogenolysis the catalyst if used preferably is incorporated with magnesium oxide, zinc carbonate, and the like, and made up into small masses such as cubes which can be charged into the hydrogenating reactor. Furthermore, the exact order of mixing and treating the various distillates may vary, as will now be evident. Refining methods other than hydrofining may be used in some cases, including sulphuric acid and alkali treatment, and the like.

The foregoing invention, therefore, in its preferred aspects will be seen to contemplate the evaluation and utilization of vast deposits of lignite, especially in conjunction with a similar evaluation and utilization of shale deposits. Were it not for the gumming qualities of shale oil and the tremendous losses resulting in refining to remove gum-forming constituents, shale oil might have come into use to some extent in the past as a motor fuel, but always these obstacles have confronted those interested in the exploitation of shale and have proved difficult to overcome. The present process provides means of utilizing the very valuable qualities of shale oil without refining losses. The structure of shale oils is such that their conversion by hydrogenolysis to anti-knock spirit of great value is feasible and when such stock is incorporated with that obtained from the hydrogenolysis of lignite, very valuable motor spirit and even kerosene or lubricating oils may be expected. This result, moreover, is obtained from solid fuel deposits which heretofore have been considered of a very low grade character and commercially unworkable

so long as an abundance of ordinary petroleum is at hand.

Descriptive of the co-hydrogenation or hydrogenolysis of liquid fuels from different sources, as for example, from lignite and shale, I prefer to use the term interhydrogenation or interhydrogenolysis, the product derived thereby being termed an interhydrogenolate. Thus in the treatment by hydrogen under gas phase conditions of a mixture of crude spirit derived from shale distillation and from lignite hydrogenolysis I may, for example, carry out the operation at a temperature of 1,000° F. and a hydrogen pressure or rather a total pressure of a hydrogen-containing gas of, say 200-400 atmospheres, whereby cyclicization and other conversions and reactions take place with the formation of anti-knock bodies in abundance. A product so obtained would be termed an interhydrogenolate. In using the term uncarbonized or substantially uncarbonized, I do not mean to indicate that some sintering and possibly a slight amount of carbonization may take place, but have in mind to convey by the term uncarbonized that the structure of the lignite has not been so altered by carbonization reactions as to become materially re-

sistant to hydrogenation. In like manner the use of the term deoxygenated lignite should not convey that oxygen has been entirely removed, since this ordinarily is impossible without carrying the reaction too far into the stage of carbonization. The term deoxygenated, therefore, means that some part, presumably a substantial part of the oxygen of the lignite has been removed.

What I claim is:

Process of liquefying lignite to form useful liquid hydrocarbon oils, which comprises rapidly heating the lignite in the absence of added reducing gases and at approximately atmospheric pressure to a temperature at least in the lower part of the range normally used for carbonization, maintaining the lignite at this temperature for a time sufficient to remove oxygen combined with carbon of said lignite and insufficient to cause appreciable carbonization or liquefaction of the lignite, incorporating the deoxygenated non-carbonized material with a pasting oil, and subjecting the mixture to the action of hydrogen at high temperature and under high pressure.

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