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PROCESS FOR OBTAINING VALUABLE PRODUCTS FROM SOLID CARBONACEOUS MATERIALS

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The present invention relates to the art of producing valuable products from carbonaceous materials, particularly coal, and comprises more specifically an improved process for producing valuable products by an improved hydrogenation process. The invention will be fully understood from the following description and the drawing.

The drawing is a semi-diagrammatic view in sectional elevation of an apparatus suitable for carrying out the improved process.

Referring to the drawing, reference numeral 1 denotes a mill of any preferred form adapted to reduce coal or other similar carbonaceous material to a finely divided state and to incorporate the ground coal into a fluid suspension in oil which is introduced by line 2. The fluid mass is forced by pump 3 through line 4 into a hydrogenation chamber 5, which is adapted to withstand pressures of 20 to 200 atmospheres or higher when at an elevated temperature of 800 to 950° F., in the presence of free hydrogen. The chamber or drum may be heated in any preferred manner, such as by means of electric heaters 6 or otherwise, and the contents is kept in continual agitation by means of a stirring mechanism 7.

A gas rich in free hydrogen is forced into the drum by pipe 8, and vapor and gas escape through a vapor line 9 to a partial condenser preferably in the form of a rectification tower 10, with cooling coil 11 at the top, heating coil 12 at the base and bell-cap plate 13, or their equivalent, therebetween. Vapor and gas are conducted to final condenser 14 and condensate is separated from gas by means of a separator drum 15. The distillate is withdrawn to storage (not shown) by line 16 and gas is removed by line 17 to a purifier 18, which may comprise an oil-scrubbing system or equivalent means for dissolving the major quantity of hydrocarbon constituents and hydrogen sulfid from the gas. Purified gas is recompressed by booster 19 and a part is returned by line 20 to drum 5 after preheating in coil 11 and an exchanger 21 or otherwise. Fresh hydrogen is added by line 22.

Condensate from condenser tower 10 is cooled in cooler 23 and discharged into an accumulator 24 or withdrawn by line 24a to storage (not shown). The accumulator may be held under pressure below drum 5 and liberated gas is conducted by line 25 to purifier 18, above described.

While the present process is preferably operated on ashless or deashed coal or other carbonaceous material, such materials are not required, and if a material containing mineral matter is used, it is preferred to withdraw a stream of oil from drum 5 by line 26 to eliminate non-carbonaceous impurities. The withdrawn oil is cooled in exchangers 27 and 21 and gas released from a separation drum 28. Mineral matter is then separated from the oil preferably in a continuous or semi-continuous manner by a rotary filter 29 or equivalent centrifugal or settling means. The separated oil may be returned by line 29a to drum 5 and may be used to carry in fresh carbonaceous matter, if desired, but it is preferred to send a part of the oil to accumulator drum 24 by line 29b for further treatment, as will be disclosed.

Oil is withdrawn from accumulator 24 and forced by pump 30 through a mixer or extractor 31 together with a suitable solvent introduced by means of pump 32 and capable of dissolving oxygen-containing impurities, particularly phenolic bodies from the oil in addition to nitrogenous impurities and other impurities of an asphaltic character. The extractor may be of any suitable design, making use of the counter-current principle, if desired. Solvent and purified oil are separated in drum 33 and the former is returned for recirculation by line 34 or discarded or may be treated for the recovery of the extract in apparatus (not shown).

Purified oil is conducted to a still or other suitable apparatus for removing the traces of the solvent. If the solvent used is relatively low boiling, a still 35 is preferred, and if otherwise, then apparatus will be adapted to effect the separation by means of some other property of the specific solvent, as will be understood. Traces of the low boiling solvent are removed by line 36 and sepa-

5 rately collected while the oil is forced by pump 37 through a heating coil 38 and into a second hydrogenation drum 39 which may be similar in design to drum 5. Oil may be withdrawn from the drum and circulated through coil 38 by line 40 and gas rich in hydrogen is forced into the drum by line 41 which receives its supply from the compressor 19. A part of the hydrogen may be added to coil 38 by line 42.

10 Any preferred method for recovery of the hydrogenated oil may be used and in the drawing, vapor and gas are taken from the drum by vapor pipe 43 to partial condenser 44 and final condenser 45. The condensate from condenser 44 is cooled in cooler 46 and discharged into a separator drum 47 from which the distillate is taken to storage (not shown) by line 48. Light condensate from condenser 45 is also discharged into a separator 49 from which the oil is taken to separate storage by line 50 and gas from both drums 47 and 49 is conducted by pipe 51 to the purifier 18 for recirculation. If desired, the method of recovery of the oil, shown in Ser. No. 379,914 filed July 22, 1929 by P. L. Young, may be used.

15 In the operation of the present process, coal or other solid carbonaceous material is subjected to the action of hydrogen at a pressure in considerable excess of atmospheric, preferably from 20 to 200 atmospheres or higher, and at a temperature from about 600° F. to about 850° F. in a primary hydrogenation zone. Under the influence of such conditions, the solid material is liquefied. Light oil boiling below about 400° F. is produced but preferably in relatively small quantities. Middle oil, in the form of distillate, is also produced together with heavy liquid material from which ash is separated, if ash be present in the original solid. The heavy oil may be recirculated to the primary hydrogenation or liquefaction zone but it is preferred to pass this oil, either admixed with the middle oil or alone, to an extraction stage in which oxygen-containing impurities, such as, for example, phenolic bodies, are removed. Nitrogenous material and asphaltic products may also be extracted. The solvents preferred are low boiling materials immiscible with the oil, such as aqueous solutions, caustic soda, carbonate or other alkalis, or alcohols such as methyl and ethyl or liquid sulfur dioxide, but other solvents such as glycerine or glycol, preferably with water, or inorganic or organic acids such as acetic acid or esters, may be used. Solvents may be used successively, if desired, to remove the several impurities above indicated and these extracts may be recovered from the solvents in any appropriate manner, such as acidification of the alkali or distillation of the solvent.

It is generally advisable to remove traces of the solvents remaining in the oil before the secondary hydrogenation step. This latter step may be carried out in a variety of different ways, either with or without catalytic materials, but their use is of great advantage and they may be suspended in the drum in finely divided form or packed in lump form in the drum. The preferred catalysts are metallic oxides and their mixtures, such as chromium and molybdenum oxide and oxide of other polyvalent metals. Temperature is generally from 700° F. to 950° F. and pressure, as before, in considerable excess of atmospheric, preferably from 20 to 200 atmospheres or higher. There is some light oil formation but this is generally and preferably under 15% or 20% or even 5% or 10% of the oil fed when it is desired to make high-grade lubricating oils. The remaining oil is converted, with a small loss in the form of gas, to oil suitable for lubricating purposes and is in every respect equal or superior to the best grades of petroleum lubricants when reduced to the proper viscosity and flash. It should be noted that operating the secondary hydrogenation process at a relatively higher temperature results in a copious production of low boiling oils which are suitable for motor fuels.

This invention is not to be limited by any theory of the mechanism of the process nor by any illustration of the manner in which it is preferably operated but only by the following claims in which it is desired to claim all novelty inherent in the invention.

We claim:

1. An improved process for obtaining valuable products from solid carbonaceous materials, comprising liquefying such solid material under the influence of hydrogen at a pressure in considerable excess of atmospheric pressure and at an elevated temperature, contacting a part of the liquefied product with a solvent capable of removing a substantial portion of the oxygen-containing impurities, subsequently subjecting the purified oily product to hydrogenation treatment and recovering a fraction suitable for lubricating purposes therefrom.

2. An improved process for producing valuable heavy oil from coal, comprising subjecting finely divided coal to treatment with a gas rich in free hydrogen under pressure in considerable excess of atmospheric pressure at an elevated temperature, withdrawing a heavy oily material, removing inorganic material therefrom, washing the oil with a substantially immiscible solvent capable of removing oxygen-containing impurities therefrom, subjecting the oil substantially free of oxygen-containing impurities to a second treatment with a gas rich in free hydrogen at pressure in considerable excess of atmospheric and at an elevated temperature and

recovering an oil suitable for lubricating purposes therefrom.

3. Process according to claim 2 in which the first hydrogenation treatment is in the absence of a catalyst and the second hydrogenation treatment is in the presence of a suitable catalyst.

4. Process according to claim 2 in which pressure during the hydrogenation steps is in excess of about 20 atmospheres, temperature in the first of such steps is from about 600 to 850° F. and temperature in the second of such steps is from about 700° F. to about 950° F.

5. Process according to claim 2 in which traces of the solvent are removed from the oil prior to the second hydrogenation step.

6. An improved process for obtaining increased yields of valuable lubricants from coal and other solid carbonaceous materials, comprising the steps of liquefying the solid material by the action of hydrogen at a pressure above about 20 atmospheres and at a temperature between about 600 and 850° F. interadjusted with pressure whereby phenolic bodies are unreduced, removing such phenolic impurities from the liquefied product and subjecting the purified oil to a second stage of hydrogenation whereby the oil is further refined for lubricating purposes.

7. Process according to claim 6 in which the first hydrogenation step is carried out without the aid of catalysts and the second hydrogenation step is accomplished under the influence of a suitable catalyst immune to sulfur poisoning.

8. Process according to claim 6 in which a pressure of about 200 atmospheres is employed in the liquefaction stage and temperature is adjusted to a point where liquefaction is rapid, but below the phenol reducing temperature.

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