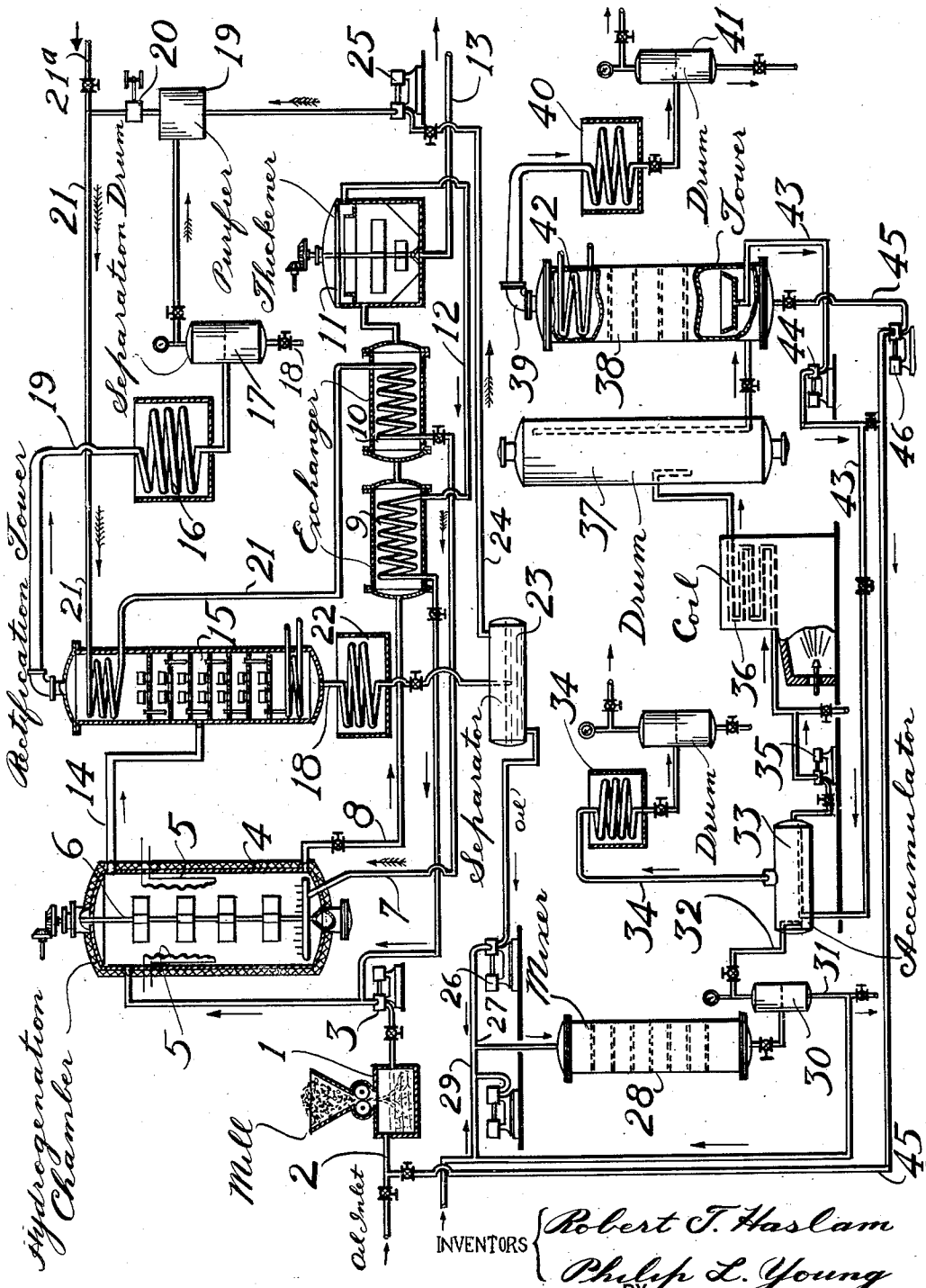
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PROCESS FOR OBTAINING VALUABLE PRODUCTS FROM SOLID CARBONACEOUS MATERIALS

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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 substances, particularly coal, and comprises specifically an improved process for producing valuable low boiling distillates suitable for motor fuels. The process will be fully understood from the following description and the drawing which illustrates one form of apparatus suitable for the invention.

The drawing is a semi-diagrammatic view in sectional elevation of an apparatus constructed according to this invention and shows the flow of materials.

In an application Serial No. 375,675, filed July 2, 1929, Edward B. Peck disclosed a process for producing valuable light distillates from carbonaceous materials, among which coal is included, by first hydrogenating the coal so as to produce a suitable middle oil fraction, then cracking the oil so produced to form gasoline and tar of which the latter is returned for further hydrogenation.

It has been found, however, that unless hydrogenation is intense, the middle oil contains impurities apparently chiefly of a phenolic nature although other oxygen-containing and some nitrogen-containing substances are present. In this improved system, it is proposed to hydrogenate carbonaceous materials such as coal and other solid or semi-solid tarry or asphaltic materials under moderate conditions of hydrogenation and subsequently to remove such phenolic or other impurities before cracking as in the peck method. It is preferred to liquefy the coal under hydrogenation conditions with a very limited production of oil boiling below 400° F. and to produce the bulk of the light oil in the subsequent cracking operation.

Referring to the drawing, reference character 1 denotes a mill for reducing the coal or other carbonaceous material to a finely divided state. Oil is added to the finely divided coal by means of a pipe 2 either from an external source or as will be described below and the fluent mass is forced by pump 3 into a hydrogenation chamber 4. The chamber may be of any preferred design but should be provided with some means such as electric heaters 5 for raising temperature to the point where reaction begins. Generally the reaction will produce sufficient heat thereafter but in some circumstances, addition of heat is necessary. The drum should also be capable of withstanding high hydrogen pressure, for example, of 200 atmospheres or higher at temperatures in the neighborhood of 800 or 950° F. A stirring means 6 is also provided.

Hydrogen or a gas rich in free hydrogen is forced into the drum by means of line 7 and if the carbonaceous material used contains ash, it is preferable to prevent accumulation by withdrawing a part of the mass from the drum, for example, by means of line 8. The mass withdrawn is cooled in exchangers 9 and 10 and is discharged into a separation means 11 which is shown in the drawing as a thickener, although centrifuges or filters preferably of continuous types may be used alone or together with the thickener to separate the ashy mineral matter from the tarry oil which is returned to the hydrogenation drum by line 12. A sludge of mineral matter is withdrawn from the thickener by line 13 and discarded or oil recovered therefrom in any suitable manner.

Distillate and gas from the hydrogenation oven 4 are withdrawn by vapor line 14 to a condenser 15 which is preferably in the form of a rectification tower. Light oil and gas escape from the condenser to a second condenser 16 wherein the oil is condensed and gas and oil are separated in drum 17. The oil is withdrawn by line 18 to storage (not shown) and the gas is taken to a purification system indicated at 19. Purified gas is then recompressed by compressor 20 and recirculated by line 21 to hydrogenation drum after preheating in condenser 15 and ex-

changer 10 or otherwise. Make-up hydrogen may be added by line 12*a*.

Heavy distillate or middle oil condensed in condenser 15 flows through cooler 22 and into a gas separator 23 which is held at a pressure below that of drum 4 so that released gas is conducted by line 24 and booster 25 to the purification system, as described before. The oil is then forced by pump 26 through line 27 and into a mixer 28 which may be of any preferred type capable of thoroughly agitating and contacting two immiscible liquids. A suitable solvent is forced into the mixer by line 29 and the thoroughly agitated liquid mass is discharged into a separator drum 30. The solvent is withdrawn by pipe 31 and may be recirculated through mixer 28 or removed to storage and recovery of the extract. The purified oil is drawn from the separator drum 30 by pipe 32 and is conducted to an accumulator 33 which is heated preferably by injection of hot oil and traces of the solvent if a low boiling solvent has been used and may be removed by vapor pipe 34 and condensed.

The oil is then forced by pump 35 through a cracking coil 36 and preferably into a digestion drum 37 for further cracking. Cracked products are withdrawn from the drum and separated in tower 38 into at least three cuts, light distillate oil, heavy distillate which has a boiling range too high for use as a motor fuel, and a tarry residue. The light distillate is removed by line 39 to condenser 40, gas separator drum 41 and storage (not shown). Heavy distillate is condensed by cooling coil 42 in the tower 38 and is trapped out and returned to accumulator tank 33 by line 43 and pump 44 or to drum 4. Unvaporized tar may be returned to hydrogenation drum 4 by means of pump 45 and pipe 46.

In the operation of the process, solid or semi-solid carbonaceous materials are liquefied under the action of high pressure hydrogen, and although it is preferred to use ashless or deashed materials, it is not necessary. The coal or other material is reduced to a finely divided state, incorporated in an oil, which may be wholly or in part a product of prior operation, and is hydrogenated under pressure in excess of about 20 atmospheres and preferably above 100, say at 200 atmospheres or higher, even 500 atmospheres. Temperatures may be generally maintained by the heat of the reaction but it is sometimes necessary to add some heat and should be held at from about 600° F. to 950° F. although preferably at about 700° F. At more elevated temperatures there is a more copious production of light oils boiling below say 400° F., but we prefer to limit this to a relatively small quantity. It has been noted that at higher pressures, temperatures may be relatively higher.

Pure hydrogen may be used in the hydrogenation step or gas rich in hydrogen, and such gas is recirculated in a relatively large excess, over the quantity actually required to combine with the oily mass. The effluent gas is preferably purified before recirculation by any suitable means for elimination of the major part of the hydrocarbon and sulphurous constituents. Scrubbing under high pressure with oil has proved to be satisfactory and such treatment may be followed by a wash with alkali, if desired.

The middle oil, boiling above commercial motor fuel, is cooled and purified by washing or extracting with suitable immiscible solvent to remove the major quantity of the phenolic and other oxygen-containing, as well as nitrogen-containing, impurities. While we prefer aqueous alkali such as caustic soda or carbonate, other solvents such as glycol or glycerine, alcohol, acetic acid and inorganic acids and organic esters may be used. Some of these, such as glycol and alcohol, are preferably used in aqueous solution. Liquid sulphur dioxide may be used, if desired. The treating system may be countercurrent and the use of successive treatment with two or more of the solvents indicated or their equivalents, is contemplated. It is generally desirable to remove the last traces of solvent from the oil and the method indicated is satisfactory for low boiling solvents, but for high boiling solvents the method preferred must depend on the particular characteristics of the solvent, as will be understood.

Cracking is accomplished preferably at pressures in excess of atmospheric and at temperatures between about 750° and 1100° F., either in the liquid or vapor phase according to well known methods. The tarry residue produced by cracking is preferably returned to the hydrogenation step.

The phenolic and other oxygen-bearing materials and also the nitrogenous impurities extracted by the solvent may be recovered by any known method, for example, if caustic soda has been used as the solvent, the extracts may be recovered by acidification. These products may be used as such in many ways, for example, as a preservative for wood or as a cheap disinfectant or the like or the materials may be refined, as will be understood.

This invention is not to be limited by any theory of the mechanism of the process nor by the particular method of cracking and hydrogenation, although the specific method disclosed is preferred, nor by any example of the method given merely for illustrative purposes, 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 low boiling oils from solid carbonaceous

material, comprising subjecting such material to the action of hydrogen at a decomposition temperature and at a pressure in excess of about 20 atmospheres, whereby an oil containing phenolic impurities is produced, removing a substantial portion of such impurities from a part of the oil and cracking the purified oil whereby substantial quantities of low boiling oil are produced.

2. An improved process for obtaining valuable low boiling oils from solid carbonaceous materials, comprising liquefying such material by the action of a gas rich in hydrogen at a pressure in excess of 100 atmospheres, whereby an oily liquid of intermediate boiling range containing oxygen-bearing impurities is produced, washing such oil with a solvent immiscible therewith and capable of removing a major portion of the oxygen-bearing impurities and subsequently cracking the purified oil whereby a substantial yield of low boiling oil is produced together with a tarry residue.

3. Process according to claim 2 in which the solid carbonaceous material is liquefied under relatively low liquefying temperature conditions whereby the production of oil boiling below about 400° F. is small and phenols are unreduced.

4. Process according to claim 2 in which the quantity of distillate oil of an intermediate boiling range, above 400° F., produced by the hydrogen treatment is in substantial excess of the quantity of oil boiling below 400° F. produced during such step.

5. Process according to claim 2 in which an aqueous solvent is used to wash the intermediate boiling oil prior to cracking.

6. Process according to claim 2 in which aqueous alkali is used to extract impurities from the intermediate boiling oil prior to cracking.

7. Process according to claim 2 in which tarry residual oil produced during cracking is returned to the hydrogenation step.

8. An improved process for producing low boiling oils from coal, which comprises liquefying the coal by hydrogenation whereby the major quantity of the carbonaceous material is converted into an oil boiling above about 400° F. and containing impurities of a phenolic nature, removing such phenolic impurities, cracking the purified oil whereby low boiling oil and tar are produced and returning the tar to the hydrogenation step.

9. Process for the production of valuable products from coal, comprising liquefying the coal by the action of high pressure hydrogen at temperature approaching, but below that at which phenolic impurities are reduced, whereby a major quantity of the liquefiable material is converted into a heavy oily product boiling above about 400° F. and a minor quantity is converted into a light oil boiling below 400° F., separately collecting such fractions, removing phenolic impurities from the heavy oily product, cracking the phenol-free heavy oil to produce light oil boiling below about 400° F., and a tarry residue, blending the low boiling fractions from the two operations and returning the tarry residue to the liquefaction step with fresh coal.

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