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TREATMENT OF CARBONACEOUS MATERIAL

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This invention relates to the treatment of carbonaceous materials such as black or brown coals and certain cellulosic materials in a state of fine division or powder and in an unoxidized or oxidized condition with a hydrocarbon oil at a comparatively low temperature for the purpose of obtaining a charging stock suitable for cracking the solid residue obtained by driving off all the volatiles being a coke if coking coals are used for finely divided carbon if non-coking coals are used, such residue in either case being substantially free from pitches, tars, etc.

An essential feature of the present invention resides in using oil of a particular grade, this being judged by its distilling range of temperatures, such range being approximately the same as that within which the volatiles in the coal or other carbonaceous material are capable of being driven off under the prevailing conditions, that is to say from an intimate mixture of the coal and the oil. Generally, therefore, although not necessarily in every instance, the distillation regarded from the point of view of the oil is completed at or about the same temperature as that of the end point of the oil. Regarded from the point of view of coal, for instance, the temperature at which the bulk of the volatiles are driven off from the coal in the oil and coal mixture is lower than that usually necessary for coal distillation and generally does not exceed about 380° C. (vapour temperature).

Preferably the oil is used in amount approximately equal to or greater than the amount by weight of fine coal or equivalent carbonaceous material employed in admixture with it, but I do not restrict myself to such amounts; on the one hand I may use less, provided it is sufficient to prevent destructive distillation of the coal and oil mixture, and on the other hand I may use so much as to render it practicable to stop the distillation short of arriving at a solid residue and to utilize the still fluid residue for other purposes, as for example as a liquid fuel or as a basis for manufacture of such a fuel.

It is well known that even in low temperature coal distillation a temperature of about 350° C. to 400° C. is required for the liquid products to commence to distil and that the products continue to distil over at from 500 to 600° C. leaving coke as a residue. In either high or low temperature distillation of coal as ordinarily practiced about one half the liquid distillate is pitch—a difficult product to market—and the percentage of light spirit is quite small. Also in ordinary oil cracking processes there is always

a heavy asphalt residue. According to the present invention, however, the temperature at which the distillate commences to come over is low in comparison with the end point of the distillation, and the distillation is generally completed around 350° C. to 400° C. (vapour temperature) but there may be instances in which this temperature should be exceeded.

I am well aware that it has been proposed to distil powdered coal in an oil having a high initial boiling point whereby certain of the volatiles in the coal become distilled off under the initial boiling point of the mineral oil, the oil itself being drained from the coal or filtered and used over and over again. In this case the oil acts mainly as a carrier. I am also aware of the proposal to de-ash coals with heavy oils and drive off the oil to obtain primarily an ash-free coal; in this latter case tars and pitches and the products of low temperature coal distillation are obtained with the heavy mineral oil cracked by destructive distillation. I, however, have found that by using mineral oils that have approximately the same distilling range as the volatiles in the coal or oils having a substantial fraction with such distilling range under the prevailing conditions, a better conduction of heat is secured than in any process heretofore described and thereby enable the coal to give a materially increased percentage yield of light hydrocarbon products and at the same time enable the mineral oil to be partially converted into lower boiling products with increased yields of hydrocarbon oils as compared with the percentage obtainable from either by distilling the oil and coal separately and adding their respective fractions. There is in this case little if any of the products of low temperature coal carbonization in the distillates obtained. If the mixture is heated down to bone dryness, there are practically no pitches, tars or asphalt, no naphthalene or anthracene and little if any carbon compounds of the double ring series in the distillate. In most instances small or negligible percentages of tar acids have been found and the distillate obtained consisting mostly of hydrocarbons is subject to cracking by any of the usual commercial systems to petrol or light hydrocarbons. By taking the distillate from the first topping operation and re-distilling this with fresh powdered coal and repeating this step, the distillate can be used in this manner until, on cracking, a full one hundred per cent. or more of petrol is obtained using the oil as the basis of calculation. Cracking of the distillate obtained by my process does not however form part of my invention.

While I do not wish to be bound to any special theory in explanation of the materially larger yield of distillate when using mineral oils of low boiling point or oils containing at least a substantial low boiling point fraction, I wish to call attention to the work of Pictet on Coal (Ann. de Chim. et de Physique 1918, vol. 10, page 249, published by Masson et Cie., Boulevard Saint-Germain 120, Paris) in which he "advanced a hypothesis based on his well-known researches on the distillation of coal, in vacuo, according to which petroleum has at least in part been formed from coal by slow distillation at low temperatures" (Gurwitsch—Scientific Principles of Petroleum Technology, page 222, published by Chapman & Hall, 11 Henrietta Street, London). My process conforms to a considerable extent to the same theory in that the distillation of the coal particles is conducted slowly at low temperatures and by taking place under oil at low temperatures permits the coal to yield petroleum hydrocarbons additional to those in the mineral oil used.

It is known that coal will ordinarily give by low temperature distillation about 25 gallons per ton of a liquid distillate of which about half is pitch. If, however, the oil used be a mineral oil having about the same distilling range as the coal in accordance with the process of the present invention, one can obtain an additional 20 to 30 per cent of more by volume of liquid distillate (using the original oil as the basis of calculation).

In carrying out the invention use may be made of catalytic matter naturally present in the coal (such as alkaline clays, oxides of iron, etc.). The volume and characteristics of the distillate and of the residue vary considerably with different catalysts and with the amount of them used, and I prefer a petroleum or other soap to assist in the distillation and to keep the particles in suspension during distillation, or I may constantly stir the mixture or agitate it by means of air or gas.

In order that the invention may be clearly understood and readily carried into effect I will now describe the same by means of examples of procedure, as follows:—

First example

Coal was ground so that 85% passed through a 200 mesh screen and was intimately mixed in a tank by means of a high-speed stirrer with an equal quantity by weight of a fuel oil of about .895 sp. gr. On heating in a still to a temperature corresponding to the end point of the fuel oil, namely about 380° C. to 400° C. there was obtained an increase of from 20 to 36% of distillate as compared with the original volume of oil used. On one occasion about 2½% by weight of crude petroleum soap or other soap was used, whereas on another occasion no soap was used but the mixture was kept stirred during the distillation. The pressure distillate was free from or contained only negligible percentages of those products usually obtained in low temperature distillation, and the residue in the case of a coking coal was coke and in the case of a non-coking coal was a fine dry carbon powder.

Second Example

Equal quantities by weight of fuel oil of .895 sp. gr. and powdered coal prepared so that 85% passed through a 200 mesh screen were intimately mixed in a tank with a high speed stirrer and conveyed to a still. The still was first heated to about 290° C. the fire withdrawn and air passed through the mixture and so regulated

that the temperature did not exceed 400° C. This being an exothermic reaction no further heat is required and the operation can be made continuous by those skilled in the art by withdrawing the devolatilized coal intermittently and replacing the withdrawn carbon mass by pumping in fresh coal and oil mixture prepared as above and continuing the blowing of air through the mass. Sufficient pressure can be maintained if desired to prevent too rapid volatilizing of low boiling fractions. Such oil as remains in the withdrawn devolatilized carbon can be centrifuged and the remaining oil be driven off in a low temperature carbonization retort. Likewise it must occur to those skilled in the art that in the first example part of the oil can be distilled off and the mixture freed of excess oil, centrifuged and the balance of oil driven off in a low temperature carbonization retort, or the heavy carbon mass carried direct to a retort as conditions warrant. The pressure distillate from the still and from the centrifuge and from the retort are mixed together or handled separately and may serve as charging stock suitable for cracking.

In the first example above, I have referred to using petroleum soap or other soap as a stabilizer. I may add this ready-made to the coal and oil mixture or I may make it in situ by blowing an oxidizing gas into the mixture of finely divided coal and oil in the presence of an alkali or alkaline salt or by subsequently neutralizing the product by an alkali or alkaline salt solution.

The coal may be pre-oxidized at ordinary temperatures by mixing the coal in finely ground condition with just sufficient water to allow free oxidation and then blowing ozone or a mixture of ozone with air or oxygen through the mass. This oxidized product can then be stirred thoroughly with or into oil either with or without a catalyst and distilled and cracked in liquid or vapour phase in the usual manner. In either case there is an increase in liquid distillate with less carbon as residue. It seems from results obtained with ozone that by proper regulation and proper use of catalysts one can obtain with oils products that are almost entirely liquid except for relatively small amounts of carbon as by-product, which is the opposite of the present hydrogenation process.

In the foregoing process I may use not only or not solely comminuted coals or shales of all kinds or grades including anthracite, lignite, peat, pitches, asphalts, etc., but I may even use other carbonaceous materials such as Bagasse, sugar beet waste, straw, sawdust, cornstalks, etc. Such materials may be pre-oxidized as above described or may be unoxidized or the two types of material may be used in any suitable proportions. I may also use suitable animal or vegetable oils instead of or in admixture with mineral oils.

Constant stirring of the mixture undergoing distillation in the still is advantageous and the pressure may be sub- or super-atmospheric or at the ordinary pressure. The distillation may be carried out with or without the aid of steam or air or both.

With regard to stopping the distillation short of reaching a solid residue I may for instance employ the oil and coal in the ratio of about two to one by weight and slowly distil off about 50% to 60% of distillates and use the remainder as a liquid fuel.

What I claim is:—

1. The production of liquid hydrocarbon distillates comprising distilling at relatively low temperatures a mixture of about equal parts by weight of finely divided solid carbonaceous material containing volatile hydrocarbons and a mineral oil having a wide distilling range of temperatures approximating to that of the volatiles in the carbonaceous material under the conditions of the process with an end point of about 380° C. to 400° C.

2. The production of liquid hydrocarbon distillates comprising distilling finely divided carbonaceous material containing volatile hydrocarbons with a substantially equal quantity by weight of mineral oil having a wide distilling range of temperatures approximating to that of the volatiles in the carbonaceous material used under the conditions of the process, the maximum temperature attained not exceeding about 380° C. to 400° C.

3. The production of liquid hydrocarbon distillates comprising distilling at relatively low temperatures a mixture of about equal parts by weight of finely divided solid carbonaceous material containing volatile hydrocarbons and a mineral oil having a wide distilling range of temperatures approximating to that of the volatiles in the carbonaceous material under the conditions of the process with an end point of about 380° to 400° C., the distillation being continued until the residue is solid, whereby in addition to liquid distillate a solid fuel product substantially free from pitches, tars or asphalt is obtained.

4. The production of liquid hydrocarbon distillates comprising distilling a mixture of about equal parts by weight of finely divided solid carbonaceous material containing volatile condensible hydrocarbon constituents and a mineral oil having a wide distilling range of temperatures approximating to that of the volatiles in the carbonaceous material used under the conditions of the process and terminating at about 380° C., the distillation being conducted within the temperature range specified until the residue is solid, whereby a liquid distillate suitable for cracking is obtained and a solid residual fuel product substantially free from pitches, tars or asphalt.

5. The production of liquid hydrocarbon distillates comprising distilling a mixture of finely divided coal and commercial fuel oil of about 0.895 specific gravity and of wide distilling range in about equal parts by weight under conditions such that substantially all of the oil and of the volatiles in the coal are distilled off simultaneously as a condensible distillate throughout a distilling range terminating at about 380° C.

6. The production of liquid hydrocarbon distillates by low temperature distillation of an intimate mixture of about equal parts, by weight of oil and finely divided solid carbonaceous material containing volatile condensible hydrocarbons, comprising mixing the finely divided solid with a mineral oil having a wide distilling range the same as that of the volatiles in the coal and terminating at about 380° C., and subjecting the mixture in the presence of a catalyst to distillation within the range of temperatures specified.

7. The production of liquid hydrocarbon distillates by low temperature distillation of an intimate mixture of about equal parts by weight of oil and finely divided solid carbonaceous material containing volatile condensible hydrocarbons, comprising mixing the finely divided solid with

a mineral oil having a wide distilling range the same as that of the volatiles in the coal and terminating at about 380° C., and subjecting the mixture in the presence of a catalyst to distillation within the range of temperatures specified and simultaneously oxidizing part of the oil.

8. The production of liquid hydrocarbon distillates by low temperature distillation of an intimate mixture of about equal parts by weight of oil and finely divided solid carbonaceous material containing volatile condensible hydrocarbons, comprising mixing the finely divided solid with a mineral oil having a wide distilling range the same as that of the volatiles in the coal and terminating at about 380° C. subjecting the mixture in the presence of a catalyst to distillation within the range of temperatures specified and simultaneously producing petroleum soap in the distilling mixture by oxidizing a part of the oil and neutralizing the resultant fatty acid.

9. The process of obtaining liquid hydrocarbon distillates by low temperature distillation at only slightly super-atmospheric pressures, which process comprises intimately mixing in about equal parts by weight finely divided carbonaceous material containing volatile condensible constituents with a mineral oil, having a wide distilling range with end point of about 380° C. conducting the distillation within the specified temperature range until a substantial part of the mixture has passed over as condensible distillate and retaining the remainder of the mixture as liquid fuel.

10. The process of obtaining liquid hydrocarbon distillates by low temperature distillation at only slightly super-atmospheric pressures, which process comprises intimately mixing in about equal parts by weight finely divided carbonaceous material containing volatile condensible constituents with a mineral oil, having a wide distilling range with end point of about 380° C., conducting the distillation within the specified temperature range, periodically withdrawing part of the exhausted material and replacing it with fresh oil and coal mixture.

11. The process of obtaining liquid hydrocarbon distillates by low temperature distillation at only slightly super-atmospheric pressures, which process comprises intimately mixing in about equal parts by weight finely divided carbonaceous material containing volatile condensible constituents with a mineral oil, having a wide distilling range with end point of about 380° C., conducting the distillation within the specified temperature range, initiating the distillation by applied heat, and thereafter regulating the temperature by a stream of air passed through the mixture.

12. The process of obtaining liquid hydrocarbon distillates by low temperature distillation at only slightly super-atmospheric pressures, which process comprises intimately mixing in about equal parts by weight finely divided carbonaceous material containing volatile condensible constituents with a mineral oil, having a wide distilling range with end point of about 380° C., conducting the distillation within the specified temperature range and in the presence of a catalyst.

13. The production of liquid hydrocarbon products from a mixture of coal and oil comprising mixing the coal in a finely divided state with at least an equal weight of oil having a wide distilling range corresponding to that of the volatiles in the coal and terminating at about 380° to 400° C., and subjecting the mixture to distillation within the temperature range specified in the pres-

ence of a catalyst and at slightly super-atmospheric pressure.

14. The production of liquid hydrocarbon products from a mixture of coal and oil comprising mixing the coal in a finely divided state with at least an equal weight of oil having a wide distil-

ling range corresponding to that of the volatiles in the coal and terminating at about 380° to 400° C., passing steam through the mixture and subjecting it to distillation within the temperature range specified in the presence of a catalyst.

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