

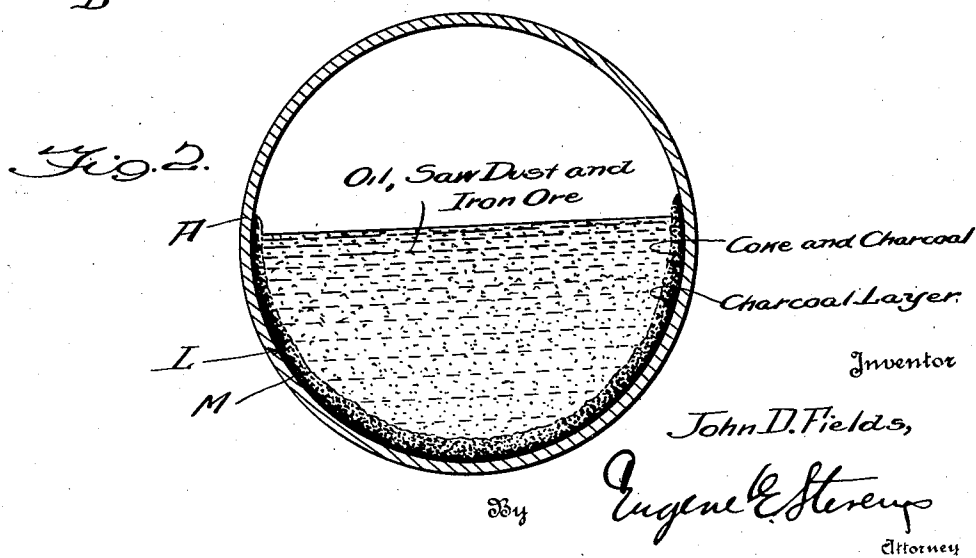
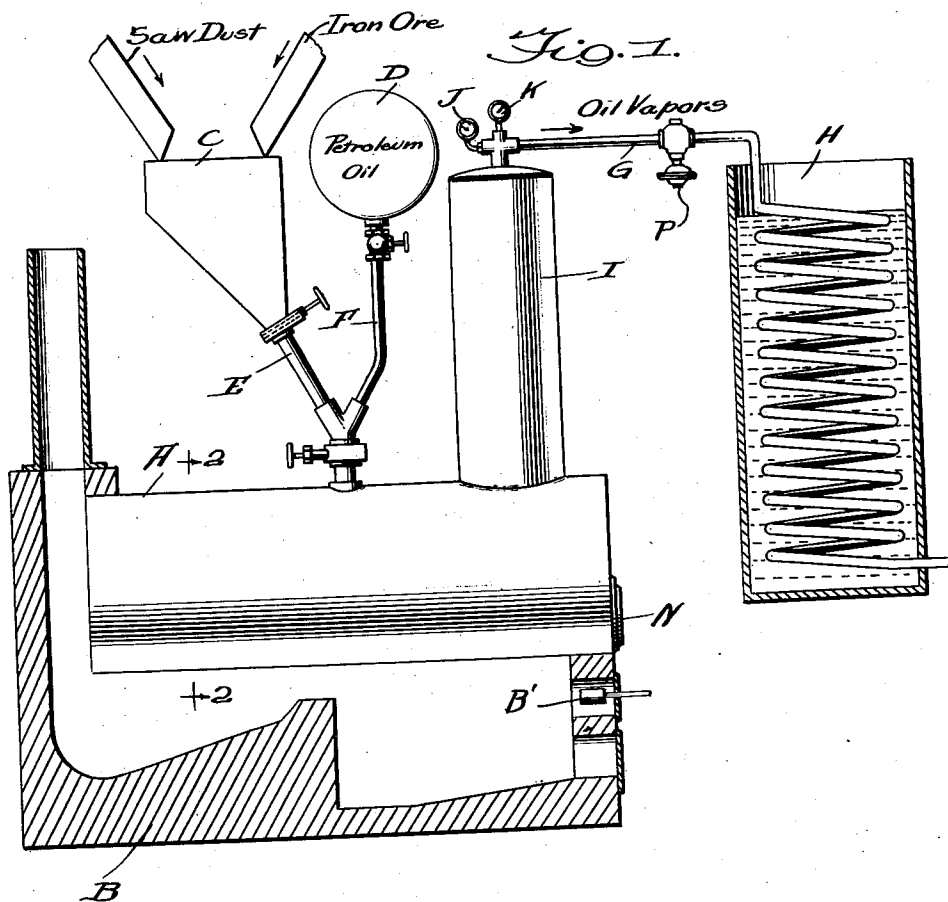
June 28, 1932.

J. D. FIELDS

1,864,720

METHOD OF DISTILLING HYDROCARBONS AND PRODUCING COKE AND PRODUCT THEREOF

Filed June 29, 1931



UNITED STATES PATENT OFFICE

JOHN D. FIELDS, OF LOS ANGELES, CALIFORNIA

METHOD OF DISTILLING HYDROCARBONS AND PRODUCING COKE AND PRODUCT THEREOF

Application filed June 29, 1931. Serial No. 547,795.

This invention resides in the provision of a method of distilling hydrocarbons particularly the petroleum group, together with solid cellulosic vegetable matter and a ferrous material for the purpose of producing low boiling and other desirable oil fractions, and a hard strong residual coke and other useful products.

An object of the invention is to provide a method of the character described which may be readily and economically carried out in a particularly efficacious manner to obtain in a single operation a comparatively great yield of low boiling and other petroleum fractions and a residual ferruginous carbon or coke, having properties enabling its complete and easy removal from the still and rendering it of great value as a fuel and reducing agent in metallurgical and other operations.

Another object is to produce with a method of the character described a hard ferruginous coke, characterized by constituents and properties of carbon derived both from the vegetable matter and the petroleum and having a high tensile and compressive strength, whereby the product is particularly well suited for use in blast furnaces.

With the foregoing objects in view, together with such other objects and advantages as may subsequently appear, the invention hereof resides in the steps and features hereinafter set forth and claimed, but it is to be understood that variations in said method may be resorted to within the scope of claims herewith appended.

In carrying out the method of this invention, comminuted iron ore, finely divided vegetable matter and a petroleum hydrocarbon are placed in a suitable still and subjected to such temperatures and pressures as will effect the distillation of said substances and the formation of residual ferruginous coke as will be hereinafter more fully explained.

The iron ore before addition to the other substances is reduced to such a state of pulverization or fineness that when added to said substances will be held in suspension by the vegetable matter, a fineness of from 150 to 200 mesh having been found satisfactory.

The organic or vegetable matter is also finely divided and may consist of various substances capable of giving alcohol, acetic acid, acetone and phenols when subjected to destructive distillation. Kelp, beet pulp, sugar cane waste, saw dust and other solid carbohydrate or cellulosic vegetable refuse and substances of similar character are satisfactory, but any vegetable matter capable of being converted into charcoal may be utilized. Vegetable matter in a green or natural state (i. e. containing a substantial percentage of water) is preferable. The vegetable materials above listed consist largely of cellulose or other solid carbohydrate material and are relatively poor in proteins, and are substantially free from sulphur. Such vegetable materials are hereinafter included in the expression "a cellulosic vegetable matter". Vegetable materials having these characteristics are generally preferred in the process, since they tend to give good coke.

The hydrocarbon may be of any character desired. However, a particular hydrocarbon which may be employed, is one, for example comprising petroleum having a high boiling point, say of approximately 600 degrees Fahrenheit (315° C.) and of either asphalt or paraffin base.

It should be noted that the iron ore, vegetable substance and hydrocarbon may be combined in various proportions dependent on the characteristics of said substances and the nature of the products thereof desired.

A sufficient amount of the petroleum oil is always employed so that (at temperatures well above the liquefying point of the oil) the mixture of the oil, sawdust or other comminuted vegetable matter used, and iron ore, is a liquid mass. It is to be understood that the oil itself may be freely liquid, semi-solid or even solid at normal room temperature or at some lower temperature. However, a specific proportion is 10 parts of iron ore, 10 parts of vegetable substance (say green wood sawdust) and 80 parts of a petroleum hydrocarbon.

In such an example, the combined amounts of the vegetable matter (e. g. sawdust) and iron ore, represent only a minor fraction of

the amount of the hydrocarbon. Further the proportions of vegetable material and iron ore, as given in this example are about the maximum which I would recommend under any circumstances.

Such a mixture as here described is (at least when hot) a freely liquid mass, which flows as a liquid and can readily be handled as a liquid, by means of a centrifugal pump or the like, and is not a paste or a solid material slightly moistened with an oily liquid.

In distilling the mixture of said substances, various pressures and temperatures may be used provided such temperatures and pressures are sufficient to carbonize or char the said vegetable matter, separate the low boiling fractions and reduce the residuum to a ferruginous coke. A temperature of from 350 to 400 degrees Centigrade (or 662 to 752° F.) has been found sufficient but higher temperatures may be used where heavier fractions are to be produced. As to the pressures, a pressure of 100 pounds per square inch with a temperature of 400° C. has proven satisfactory, although variations of the pressure may be resorted to as desired.

Upon heating the mass sufficiently to produce destructive distillation of the vegetable matter (the iron ore and hydrocarbon being present), the volatile products such as essential oils and acids from the vegetable matter and the low boiling fractions of the hydrocarbon will distill over, the liberation of the gases and vapors agitating the mass. Petroleum distillates are formed during the operation contemporaneously from both the vegetable matter and the hydrocarbon, which distillates will pass off together. The distillates are treated in the usual manner to effect the separation thereof into desired products.

Distillation treatment is continued until solid coke remains in the still, and the hydrocarbon and vegetable substances are reduced to a solid, including organic carbon or charcoal derived from said vegetable substance and carbon derived from the decomposition of petroleum hydrocarbons which may also contain other substances.

This residual solid product of distillation, is, generally speaking, a hard black coke having a high tensile and compressive strength. Such a product is considered of great value in blast furnace operations yet is useful for many other metallurgical and for any of the purposes for which coke is commonly used.

It is important to note that owing to subjecting the mixture aforesaid to the previously qualified distilling temperatures, in one operation, a quantity of residual charcoal is formed from the vegetable matter before the formation of mineral to carbon (petroleum coke), with the result that a protective layer of such charcoal is deposited on the inner surface of the still. In this way, adhesion of

the mineral carbon residuum, which would result if the mineral carbon came into intimate contact with the interior surface of the still, is eliminated and the whole mass of coke may therefore be readily removed from the still. The coke does not rigidly adhere to the still bottom, as does the petroleum coke formed in the usual oil cracking stills. This property is hereinafter referred to in stating that the coke is "non-adhesive". As is well known petroleum coke as usually heretofore prepared adheres tenaciously to the bottom and sides of the still (see economic paper 9, U. S. Bureau of Mines, pages 28-29).

To insure this action and to prevent the particles of iron ore from precipitating to the bottom of the mass during the distilling operation, the fine ore is thoroughly admixed with the finely divided vegetable matter previous to being added to the petroleum hydrocarbon, so that the ferruginous particles will cling to and be supported by the vegetable matter and therefore be distributed throughout the mass.

During the latter portion of the distilling operation, the residuum will have cooked to substantial dryness, leaving a hard coke in the still, in a readily removable state, and the oil practically all distills off, so that the final coke is low in volatile matter.

The said ferruginous particles being held in suspension during the distilling action will remain thoroughly distributed throughout the body of coke as the latter forms in the bottom of the still, thus rendering the formed coke highly heat-conductive so that it will serve to protect the walls of the still against burning out during the final stages of drying out the coke, and which also serves to hasten the driving off of the final volatiles from the coke residuum. The heating is preferably continued to leave dry coke in the still.

The process can be carried out in an apparatus such as shown in the accompanying drawing, in which Fig. 1 shows a side elevation, partly in section, of the essential parts. Fig. 2 is a section, on the line 2-2 of Fig. 1, the connections being omitted.

A represents a boiler or still, heated by fire in the fire place B, heated in any convenient manner, as by oil or gas burner B'. A mixture of sawdust and iron ore is fed from the bin C through the tube E. Petroleum oil from overhead tank D, flows through valved pipe F. The oil, sawdust and iron ore flow into the still or boiler A, to fill the same to the desired level. The several pipes are provided with suitable valves.

On heating the mixture, the vapors evolved pass through pipe G to condenser H, and are therein condensed.

The vapors, on leaving the still A, pass up through a tower or dephlegmator I, wherein heavier fractions may condense and fall back

into the still. At J is shown a temperature indicator and at K is a pressure gauge.

At P is shown an automatic pressure valve which allows the vapors to pass to the condenser, only so long as the pressure in the outlet of I is above some predetermined amount, for example 100 lbs.

As shown in Fig. 2, a thin layer of the charcoal is formed at M, while the bulk of the ferruginous coke containing some charcoal is supported thereon, as shown at L.

A manhole N is provided for removing the coked residue from the still at the end of the process.

It will now be seen that by the simple and inexpensive expedient of adding small amounts of a solid cellulosic vegetable substance and the iron ore to petroleum to be distilled to the point of substantially complete coke formation of the still residuum, I am able to produce in one continuous operation improved distillates and low boiling fractions and also a valuable carbon or coke including the heretofore bothersome and more or less useless still residuum, the easy and clean removal of which from the still is also made possible by such additions.

I do not restrict myself to the proportions as given, but I preferably use, in all cases, oil in amount much greater than the vegetable material and much greater than the iron ore.

The coke formed is, as stated above highly suitable for blast furnace operations. It is even superior to good grade coal coke, which ordinarily contains around 10 to 12% of siliceous ash. My coke product is about as strong as good grade coal coke as commonly now used in blast furnaces.

Cracking still coke and coking still coke as heretofore commonly made, are all soft, i. e. they have no substantial compressive strength or tensile strength. These cokes also are high in volatile matter, say 8 to 12%, usually around 10 to 11%. Cracking still coke from any of the prior processes, is very largely (75-80%) fines, and the lump coke is very weak. This material has heretofore been used to some extent, for making electrical carbon (after suitable refining) or for a reducing agent (in various chemical or metallurgical processes) but the great bulk of the cracking still coke has been used as fuel under the stills. Cracking still coke and coking still coke are both very variable in sulphur content, depending on the original oil being treated, and in most cases the petroleum coke of the prior art contained between 1.5 and 4% S. average about 2% S. For most metallurgical purposes, coke containing over 1% S. will not be accepted.

Refined coking still coke usually contains below 1% S. and is generally below 1.5% (sometimes below 1%) volatile matter. It has not sufficient strength to be usable in blast furnaces (for which purpose it of course

could not be used commercially on account of the cost).

Coking still coke, although obtainable in the form of lumps, contains so much volatile matter that it cannot be heated without softening and running somewhat like cannel coal. When burned it produces great volumes of smoke.

The addition of the iron ore is to harden the coke formed. This of course increases the ash content of the coke, but iron in the coke is not objectionable in metallurgical processes, nor in most of the other uses of coke, except in the manufacture of electrical carbon.

This application is in part continuation of my copending application 432,910, filed March 3, 1930.

In said prior application I have claimed the process of cracking petroleum and producing coke, by mixing a small proportion, say 15-20% of cellulosic material (wood sawdust, etc., as herein described) but without the addition of the iron ore and heating the mixture as in the present disclosure, as well as the coke product formed. Such coke formed is not so hard and strong as the coke produced when the iron ore is added, as in the present case.

I claim:

1. The method consisting in distilling a petroleum hydrocarbon to coke, in the presence of a solid cellulosic vegetable substance, and iron ore, the petroleum being initially in amount greater than either of the other materials.

2. The method consisting in adding a mineral oil to a much smaller amount of a mixture of comminuted solid vegetable matter of very low protein content and finely divided iron ore, and effecting cracking distillation of said mixture, with coke formation.

3. The method consisting in mixing an excess of mineral oil and a mixture of comminuted solid vegetable matter and finely divided iron ore in such proportion as to form a pumpable fluid oily mass and effecting a distillation of such mixture to the point of coke formation.

4. The method which consists in subjecting a liquid pumpable flowable mixture of petroleum, finely divided iron ore and comminuted solid cellulosic vegetable matter to distillation at a sufficient temperature and under a sufficient pressure to release low boiling distillates from the mixture, then continuing the pressure and heat treatment to the extent necessary to destructively distill the vegetable matter and crack the high boiling petroleum fractions, and to produce a ferruginous coke in the still.

5. The method of producing ferruginous coke consisting in subjecting a mixture of petroleum, iron ore and a cellulosic vegetable substance proportioned to constitute a liquid

mass to a temperature sufficient to drive off the volatiles of the mixture and form a dry hard carbon residual containing mineral and vegetable carbon.

5 6. The method consisting in subjecting not over one part of a mixture of comminuted iron ore and a vegetable substance in a green or natural state mixed with at least four
10 parts of a liquid petroleum residuum, to distillation at temperatures and under pressures sufficient to release the distillates and low boiling fractions from the mixture, then continuing the heat and pressure treatment of
15 the mixture to the extent necessary to effect cracking of the oil with coke formation to form a hard ferruginous coke product.

7. The method of converting the residuum derived from the distillation of petroleum into a coke of high tensile and compressive
20 strength, consisting in distilling several parts of the petroleum residuum together with only one part of a mixture of an iron ore and a vegetable cellulosic substance that is reducible to charcoal when subjected to the tempera-
25 tures employed in the coke-forming distillation of the petroleum.

8. The method consisting in admixing finely comminuted iron ore with comminuted solid vegetable matter, adding one part of
30 the mixture to several parts of petroleum and subjecting the mass to temperatures sufficient to drive off volatiles and to produce a hard dry coke of high heat conductivity.

9. A process of making hard coke during
35 the cracking and distilling of petroleum oil, which comprises mixing relatively small amounts of solid comminuted cellulosic vegetable material, and iron ore, with a relatively larger amount of a petroleum oil, and heating
40 the mixture in a still to crack and distill the oil, and carrying the distillation to coke formation.

10. A process which comprises well mixing comminuted woody material and finely powdered iron ore, adding such mixture to a substantially larger amount of a petroleum oil which contains high-boiling fractions, heating a bulk of such mixture in a still, while
50 under superatmospheric pressure during a part at least of the heating operation, and continuing the heating past the stage of forming charcoal from said woody material, to the stage of coke formation.

11. A process of simultaneously making
55 hard coke and a distillate containing gasoline, which comprises mixing solid cellulosic vegetable matter yielding aliphatic organic compounds on destructive distillation, with petroleum hydrocarbons and iron ore, in such
60 proportions as to form a liquid oily mass capable of being pumped, and heating the mixture in a still to distill off light hydrocarbon oils from the petroleum hydrocarbons, while simultaneously distilling off volatile materials from the said vegetable matter, which

distillation products are adapted to be blended to produce a gasoline containing distillate, and continuing the distillation until a hard coke containing mineral carbon and vegetable carbon, and which does not stick to the metal
70 walls of the retort, is produced.

12. A process of simultaneously making hard coke and a distillate containing gasoline, which comprises mixing relatively small but substantial amounts of woody material
75 and added iron oxide with petroleum hydrocarbons, and heating the mixture in a still to distill off the petroleum hydrocarbons while simultaneously distilling off volatile compounds from the said woody material, which
80 distillation products are adapted to be blended to produce a gasoline containing distillate, and continuing the distillation until a hard coke containing vegetable carbon which does not stick to the metal walls of the retort, is
85 produced.

13. The method of simultaneously producing petroleum distillates and high grade coke which comprises subjecting a mixture of several parts of petroleum and one part of a composition containing comminuted solid vegetable matter consisting largely of carbohydrate which on heating will char in the solid state, mixed with added iron oxide, to cracking and destructive distillation and continuing the process sufficiently to form a solid mass of coke.

14. The method of simultaneously producing petroleum distillate and high grade coke which comprises subjecting a mixture of one part of comminuted woody material and iron ore and several parts of a petroleum oil, to cracking and destructive distillation with coke formation; condensing the vapors evolved and recovering a ferruginous petroleum coke containing charcoal from said woody material.

15. The method of simultaneously producing petroleum distillate and high grade coke which comprises subjecting a mixture of one part of a mixture of iron ore and comminuted solid carbonizable carbohydrate vegetable matter and several parts of a petroleum oil to heat under superatmospheric pressure, the heat being sufficient to carbonize the vegetable matter and to crack the petroleum oil and form coke therefrom, condensing the distillate and recovering a petroleum coke containing vegetable carbon.

16. The method of simultaneously producing oil distillate and high grade coke which comprises subjecting a mixture of one part of a mixture of iron ore with comminuted woody matter and at least four parts of petroleum hydrocarbon oil while under superatmospheric pressure, to the influence of heat sufficient to carbonize the woody matter and to crack the hydrocarbon oil with coke formation, condensing the evolved vapors and
125

recovering a ferruginous petroleum coke containing vegetable carbon.

17. The method of simultaneously producing petroleum distillate and high grade coke which comprises subjecting a mixture of one part of a mixture of iron ore with fine solid carbonizable carbohydrate vegetable matter and several parts of a high boiling petroleum oil to a temperature between about 350 and 400° C. while under a pressure of approximately 100 pounds per square inch, condensing the evolved vapors and recovering a strong ferruginous petroleum coke containing vegetable carbon.

18. The method of simultaneously producing petroleum distillate and high grade coke which comprises subjecting a mixture of a high boiling petroleum oil, with iron ore and comminuted woody matter, in such proportions as to form a flowable mass, to a temperature between 350 and 400° C., and under superatmospheric pressure of several atmospheres, condensing the evolved vapors and recovering a strong ferruginous petroleum coke containing vegetable carbon.

19. The herein described process which comprises subjecting a liquid flowable mixture containing a high boiling petroleum oil with a substantial but minor fraction only of its weight of a mixture of fine solid carbonizable carbohydrate vegetable matter and iron ore, while under superatmospheric pressure, to heat at least sufficient to destructively distill said vegetable matter, and condensing the vapors evolved, and continuing the distillation sufficiently to leave a solid mass of coke-like solid material.

20. The herein described process which comprises subjecting a liquid flowable mixture containing a high boiling petroleum oil with a substantial but minor fraction only of its weight of a mixture of wood sawdust and iron ore, while under superatmospheric pressure, to heat at least sufficient to destructively distill said sawdust, and condensing the vapors evolved, and continuing the distillation sufficiently to leave a solid mass of coke-like solid material.

21. The herein described process which comprises subjecting a liquid flowable mixture containing a high boiling petroleum oil with a substantial but minor fraction only of its weight of a mixture of comminuted kelp and iron ore, while under superatmospheric pressure, to heat at least sufficient to destructively distill said kelp, and condensing the vapors evolved, and continuing the distillation sufficiently to leave a solid mass of coke-like solid material.

22. A ferruginous petroleum coke made by distilling to coke a liquid flowable mass of not over one part of a mixture of vegetable cellulosic matter and iron ore and at least four parts of mineral oil residuum, and which coke does not adhere to the walls of the still.

23. A ferruginous petroleum coke, made by distilling to coke, under superatmospheric pressure, a liquid flowable mass of a small proportion of vegetable cellulosic matter and iron ore, with several times as much of a petroleum oil, which coke does not adhere to the walls of the still.

24. A ferruginous petroleum coke having the properties of the product produced by distilling to coke, an admixture of several parts of high boiling petroleum oil and one part of a mixture of carbonizable vegetable carbohydrate material and iron ore, such product being a strong, hard, black coke-like material containing the carbonized residue of said vegetable material.

JOHN D. FIELDS.

85

90

95

100

105

110

115

120

125

130