

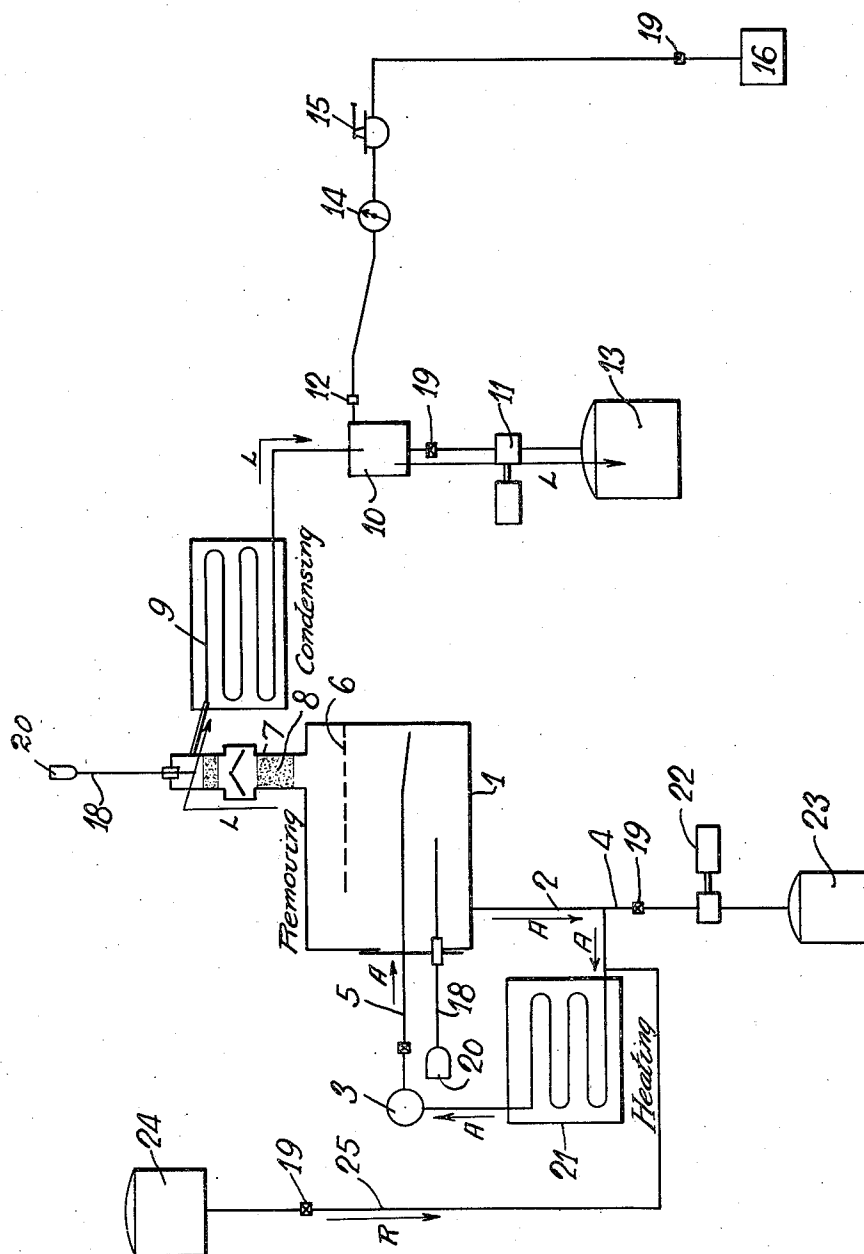
Feb. 12, 1935.

W. L. NELSON ET AL

1,990,664

PROCESS FOR THE PRODUCTION OF HYDROCARBONS

Filed Jan. 18, 1929



Inventors
 Wilbur L. Nelson and
 George H. Fancher
 By their Attorneys
 Warfield & Watson

UNITED STATES PATENT OFFICE

1,990,664

PROCESS FOR THE PRODUCTION OF
HYDROCARBONSWilbur L. Nelson, Oil City, Pa., and George H.
Fancher, Golden, Colo.

Application January 18, 1929, Serial No. 333,418

21 Claims. (Cl. 196—77)

This invention relates to a process for the production of high-boiling hydrocarbon compounds, more particularly for the production of lubricating oils, and includes correlated improvements and discoveries whereby the operation of such process is enhanced.

It is an object of the invention to provide a process whereby lubricating oils may be produced from materials of little value, and hence to provide a process of economical import.

Another object of the invention is to provide a process for the production of lubricating oils of high quality and with the attending formation of only a small amount of other and lighter hydrocarbon material.

A further object of the invention is to provide a process in accordance with which various residua arising in the oil industry are thermally decomposed with the production of lubricating oil.

Furthermore, the invention is capable of ready commercial application and may well be adapted to operation in a continuous manner.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others thereof, which will be exemplified in the process hereinafter disclosed, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention reference should be had to the following detailed description taken in connection with the accompanying drawing, in which the figure shows diagrammatically an arrangement in accordance with which the invention may be practiced.

It is well known that heretofore hydrocarbon material has been thermally decomposed for the purpose of obtaining light products, as gasoline and kerosene. In the operation of these processes, pressures above atmospheric and high temperatures are employed.

In the practice of the process according to this invention, the hydrocarbon material is thermally decomposed by subjecting to a high temperature and at a reduced pressure. The hydrocarbon materials which may be utilized are those which contain substantially no material volatile at a temperature lower than 680 degrees F. at atmospheric pressure. The high temperature and reduced pressure are maintained upon the body of hydrocarbon material until the thermal decomposition is completed. The products arising within the thermal decomposition zone are removed immediately therefrom in order to prevent secondary reactions with a tendency to break down the compounds of high boiling point which are desired in accordance with the invention for incorporation in lubricating oil, and cooled below the tem-

perature of thermal decomposition. That which remains may be run from the operation while in a molten condition or the operation may be carried to an extent where a coke is formed.

The hydrocarbon materials which may be used for charging are various topped residua, resulting from commercial distillation operations upon petroleum, of which mention may be made of residua from cracking operations, from vacuum distillations, from the distillation of shale oil, from shale and naturally occurring residua, as the asphalts.

These residues, or starting hydrocarbon materials, with the probable exception of the residua from vacuum distillations, may contain compounds which are volatile and will distill at the high temperature and reduced pressure employed in this process. However, they yield very little, if any, distillate when heated to 680 degrees F. at atmospheric pressure, and are satisfactory starting materials for the thermal decomposition which results in the obtainment of lubricating oils.

The temperature which may be advantageously used is at least as high as 700 degrees F., and the pressure is maintained between 700 mm. and 1 mm. of mercury. Particularly advantageous results are obtained when operating at pressures below 300 mm. absolute, and more specifically at a pressure of about 30 mm. absolute.

In the carrying out of the process, it may be operated, for example, as a batch process. When it is so operated, the hydrocarbon material which may be a naphthenic base reduced crude, is charged into a suitable still and thermally decomposed by heating to a high temperature, as above 700 degrees F. The material which distills over, while bringing the hydrocarbon material up to the thermal decomposition temperature, is collected separately. The material is then held at the high temperature and under the reduced pressure for the period of thermal decomposition, with immediate removal of the volatile products from the thermal decomposition zone and cooling thereof to a lower temperature. The period during which the temperature and pressure conditions are maintained may be determined either from the standpoint of the yield desired, or until any product ceases to be formed under those conditions. The whole system—still, condenser, etc.—are held under the reduced pressure conditions, and when the operation is completed the residue is removed, either in a molten condition or as coke.

An arrangement of apparatus in which the process may be practiced is shown in the figure and consists of a still 1 having rising therefrom column 7, both the column and the still being provided with temperature indicators 18, which may be thermocouples (pyods), with the leads going to millivoltmeters 20. Passing from the bottom

of the still is a pipe 2, which leads through a heating coil 21 to a pump 3, by means of which the material undergoing treatment may be caused to circulate and return to the still through a pipe 5 as indicated by arrows marked A. The pipe 2 is also connected with a pipe 4, which may be utilized for removing the contents of the still in a molten or fluid condition through a pump 22 to a tank 23. Near the upper portion of the still there is positioned a screen 6 to break up foam and prevent its passage to the column. To increase the contact between the rising vapors and the descending liquid in the column, for the purpose of scrubbing out entrained heavy material, there is placed therein a packing 8, giving large surface, such as a ring packing. From the column the vapors pass through a condenser 9, which may be either air or water cooled; thence into a first receiver 10, and thence through a pump 11 into a second or storage receiver 13 as indicated by arrows marked L. Between the two receivers is a valve 19 (which designation is also used with respect to other valves placed about the system) in order that the collected material in the second receiver may be drawn off without disturbing the conditions of vacuum under which the system is operating. The receiver 10 is provided with a valved outlet 12, which connects with a vacuum pump 16 having connected therebetween a pressure gauge 14 and a vacuum regulator 15. The feed may be from a reservoir 24 by gravity through a pipe 25 to pipe 2 as indicated by the arrow marked R. The construction of the system throughout is to be with full consideration of the pressure and temperature conditions attending the operation.

As illustrative examples of a manner in which the invention may be carried into practice, the following are given:

Example I

796 parts of a Kansas naphthenic base reduced crude obtained by previously topping by flash at 680 degrees F. with steam in vacuum were placed in a still, and the temperature raised to about 700 degrees F. as rapidly as practicable. The log of this run is as follows:

Time p. m.	Still temperature ° F.	Barometer mm. Hg	Vacuum mm. Hg	Absolute pressure mm. Hg
12:43-----	695	741	731	10
1:17-----	750	741	731	10
1:29-----	752	741	731	10
1:51-----	755	741	731	10
2:21-----	750	741	731	10
2:57-----	753	741	731	10
3:16-----	746	741	731	10
3:55-----	750	741	731	10

The first drop was obtained at a temperature of 695 degrees F. and up to the time that the temperature became constant at 750 degrees F., 19 parts or 2.4% of the charge had distilled over, this being due to increase in temperature rather than to thermal decomposition. During the time that the temperature and pressure remained practically constant, namely, at 750 degrees F. and 10 mm. mercury absolute, there was obtained 223 parts of a crude lubricating oil product, representing about 28% of the charge. The crude lubricating oil which was the product of thermal decomposition at constant temperature and pressure had a viscosity of 271 seconds Universal Saybolt at 100 degrees F. It had good color, contained substantially no wax and was treated with sulphuric acid in the usual way,

After treatment, the product had a viscosity of 442 seconds Universal Saybolt at 100 degrees F. or a viscosity of a superheavy motor oil. The specific gravity at 60 degrees F. was 0.9113.

Example II

775 parts of a coastal reduced crude were charged into a still and the temperature gradually raised to a point above 700 degrees F. and under a reduced pressure of 235 mm. mercury absolute. The log of this run is as follows:

Time p. m.	Still temp. ° F.	Barometer mm. Hg	Vacuum mm. Hg	Absolute pressure mm. Hg
2:36-----	703	737	502	235
3:13-----	750	737	491	233
3:23-----	750	737	504	233
3:42-----	755	737	513	233
3:49-----	741	737	504	237
4:00-----	750	737	500	237

As a result of subjecting this reduced crude to a temperature of 750 degrees F. and under a reduced pressure of 235 mm. mercury absolute, there was obtained 442 parts of a crude lubricating oil distillate. This represents about 57% of the original charge. There was no distillate obtained during the period of raising the temperature to 700 degrees F. The charging material accordingly yielded a product only by thermal decomposition. The viscosity of the product prior to treatment was 92 seconds Universal Saybolt at 100 degrees F.

Example III

614 parts of a California naphthenic base reduced crude obtained by topping under vacuum at a high temperature, but below cracking temperature and with steam were charged into a still. The log of this run is as follows:

Time a.m.	Still ° F.	Barometer mm. Hg	Vacuum mm. Hg	Absolute pressure mm. Hg
10:37-----	774	740	700	40
11:07-----	774	740	701	39
11:37-----	774	740	701	39
11:50-----	774	740	701	39
12:58 p.m.-----	775	740	696	44

As a result of the thermal decomposition at a practically constant temperature of 774 degrees F. and a practically constant pressure of about 39 mm. mercury absolute, there was obtained 298 parts of a crude lubricating oil distillate which represents about 47% of the charging stock. The crude lubricating oil was heavy and of good color. The viscosity was 1222 seconds Universal Saybolt at 100 degrees F. and 75 seconds Universal Saybolt at 210 degrees F. The crude stock was treated with sulphuric acid in the usual way and there was obtained a lubricating oil having good color, no odor and a viscosity of about 105 seconds Universal Saybolt at 210 degrees F. The specific gravity at 60 degrees F. was 0.9343. This oil therefore was an extra heavy lubricating oil.

As hereinbefore mentioned, one way in which the process may be carried out is in accordance with a batch method. However, the process is not so limited inasmuch as it may also be carried out as a continuous process. When operating in a continuous manner the residuum or reduced crude is heated in a system of tubes to the tem-

perature of thermal decomposition. The residuum so heated may then pass into an evacuated chamber in which it is allowed to remain for a suitable length of time to accomplish the

5 separation of heavy volatile products of decomposition from the undecomposed material. The material which is undecomposed may be recirculated through the heating tubes at the same temperature as that used for the heating of the
10 original stock. Further, a small amount of the undecomposed material may be taken from the evacuated chamber as a process residue, and a small amount of fresh charging stock may be admitted to the recirculating stream before this
15 stream enters the heating coils and after it leaves the evacuated chamber.

The process further may be practiced in the manner above described for continuous operation, with the exception that there is no recirculation of undecomposed material. In accordance with this mode of procedure, the original stock is continuously fed to the heating coils and the undecomposed material is continuously removed from the evacuated chamber.

25 Furthermore, the process may be practiced in accordance with either of the two above continuous methods with an additional processing which consists in charging the residue from the continuous process into an auxiliary coking still. In
30 this still the residue is thermally decomposed under the temperature and pressure conditions hereinbefore outlined and the processing is continued until the residue is a coke.

In this process for the production of lubricating oils by thermal decomposition of residuums
35 under practically constant conditions of high temperature and reduced pressure, the products rising from the thermal decomposition are rapidly removed from the zone of thermal decomposition and cooled below such temperature.
40 The removal of the products may be aided through the use of steam or inert gases, whereby heavier products may be removed from the zone of decomposition without an increase in temperature.

45 Furthermore, with the charging stock there may be admixed various alkaline agents such as lime, caustic soda and caustic potash. These materials being introduced into the still along
50 with the charging stock, subject the stock and the resulting products to a chemical treatment which facilitates the subsequent treatment of the distillate obtained.

In accordance with our process, there have
55 been obtained yields of from 30% to 60% of untreated lubricating oil stocks. Economic value of the process has already been alluded to, inasmuch as the raw material used, for example, topped residues from atmospheric petroleum distillations and also from vacuum distillations and the residues from commercial cracking processes is practically of no value. It is sometimes sold as a heavy fuel oil and is sometimes burnt under the stills in the plant and in general may be
60 considered a waste product. The residues used do not yield any material amount of a distillate when heated at 680 degrees F. and at atmospheric pressure. When these residues are heated under vacuum at 680 degrees F., they will yield a distillate, but there will remain a material varying between 10% and 50% which cannot be distilled under the highest vacuum at a temperature of 680 degrees F. It is such a residue which is
65 contemplated as the charging stock for this process, and accordingly the process makes possible a

substantial yield of lubricating stock by thermal decomposition from materials which, by methods heretofore used, would not yield any lubricating stock.

Certain heavy hydrocarbons have heretofore
5 been broken down into lighter weight hydrocarbons by using great pressures and high temperatures. It has not been considered possible to do this without high pressures and those hydrocarbons which did not break down under high
10 pressures have been in many instances thrown away. The present invention permits the breaking down of heavy hydrocarbons under reduced, i. e., sub-atmospheric pressures, including certain hydrocarbons which may not be broken
15 down by the old high-pressure methods. The term "heavy hydrocarbon" used in this specification and in the claims refers to those which are susceptible to the low-pressure method and includes:

I. Reduced or topped crude oil (fuel oil) which may have as constituents wax distillate, cylinder stocks and tar;

II. Any residues that may arise in regular processing operations and which are heavier
25 than those mentioned in I;

III. Cracked fuel oils or residues; and

IV. Natural tars or asphalts which are mined or residues prepared from these.

Since certain changes may be made in carrying
30 out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which as a matter of language might be
40 said to fall therebetween.

Having described our invention, what we claim as new and desire to secure by Letters Patent, is:

1. A process for the production of lubricating oils, which comprises thermally decomposing
45 a heavy hydrocarbon material at a high temperature and under pressure less than atmospheric, and maintaining such temperature and pressure during a period of thermal decomposition.

2. A process for the production of lubricating
50 oils, which comprises thermally decomposing a heavy hydrocarbon material at a high temperature and at a pressure less than 600 mm. absolute, and maintaining such temperature and pressure during a period of thermal decomposition.

3. A process for the production of lubricating oils, which comprises thermally decomposing a heavy hydrocarbon material at a high temperature and a pressure of about 30 mm. absolute.

4. A process for the production of lubricating
60 oils, which comprises thermally decomposing a heavy hydrocarbon material at a temperature above 700 degrees F. and under pressure less than atmospheric, and maintaining such temperature and pressure during a period of thermal decomposition.

5. A process for the production of lubricating oils, which comprises thermally decomposing a heavy hydrocarbon material at a temperature above 700 degrees F. and at a pressure less than
70 600 mm. absolute, and maintaining such temperature and pressure during a period of thermal decomposition.

6. A process for the production of lubricating oils, which comprises thermally decomposing a
75

heavy hydrocarbon material at a high temperature and under pressure less than atmospheric, and maintaining such temperature and pressure during a period of thermal decomposition, and rapidly removing and cooling volatile decomposition products below the temperature of decomposition.

7. A process for the production of lubricating oils, which comprises thermally decomposing a heavy hydrocarbon material at a high temperature and under pressure less than atmospheric, and maintaining such temperature and pressure during a period of thermal decomposition, circulating the hydrocarbon material through the thermal decomposition zone, and rapidly removing and cooling volatile decomposition products below the temperature of thermal decomposition.

8. A process for the production of lubricating oils, which comprises thermally decomposing a heavy hydrocarbon material at a temperature above 700 degrees F. and under pressure less than atmospheric, and maintaining such temperature and pressure during a period of thermal decomposition, circulating the hydrocarbon material through the thermal decomposition zone, and rapidly removing and cooling volatile decomposition products below the temperature of thermal decomposition.

9. A process for the production of lubricating oils, which comprises thermally decomposing a heavy hydrocarbon material at a temperature above 700 degrees F. and at a pressure less than 600 mm. absolute, maintaining such temperature and pressure during a period of thermal decomposition, circulating the hydrocarbon material through the thermal decomposition zone, and rapidly removing and cooling volatile decomposition products below the temperature of thermal decomposition.

10. A process for the production of lubricating oils, which comprises thermally decomposing a heavy hydrocarbon material, substantially non-volatile at 680 degrees F. and atmospheric pressure at a temperature above 700 degrees F. and under pressure less than atmospheric, and maintaining such temperature and pressure during the period of thermal decomposition.

11. A process for the production of lubricating oils, which comprises thermally decomposing a heavy hydrocarbon material, substantially non-volatile at 680 degrees F. and atmospheric pressure at a temperature above 700 degrees F., and at a pressure less than 600 mm. absolute, and maintaining such temperature and pressure during the period of thermal decomposition.

12. A process for the production of lubricating oils, which comprises thermally decomposing a heavy hydrocarbon material, substantially non-volatile at 680 degrees F. and atmospheric pressure in the presence of an alkali, at a temperature above 700 degrees F. and under reduced pressure less than atmospheric, and maintaining such temperature and pressure during the period of thermal decomposition.

13. A process for the production of lubricating oils, which comprises thermally decomposing a heavy hydrocarbon material, substantially non-volatile at 680 degrees F. and atmospheric pressure, in the presence of an alkali, at a temperature above 700 degrees F. and at a pressure less

than 600 mm. absolute, and maintaining such temperature and pressure during the period of thermal decomposition.

14. A process for the production of lubricating oils, which comprises thermally decomposing a heavy hydrocarbon material, substantially non-volatile at 680 degrees F. and atmospheric pressure at a temperature above 700 degrees F. and at a pressure less than 600 mm. absolute, maintaining such temperature and pressure during the period of thermal decomposition, and rapidly removing and cooling the volatile decomposition products below the temperature of thermal decomposition.

15. A process for thermally decomposing heavy, liquid hydrocarbon material, which comprises heating such material at a high temperature under pressure less than atmospheric for the period of thermal decomposition while rapidly removing the arising vapors.

16. A process for thermally decomposing heavy, liquid hydrocarbon material, which comprises heating such material at a high temperature above 700 degrees F. and at a pressure less than 600 mm. absolute for the period of thermal decomposition, and rapidly removing the arising vapors.

17. A process for thermally decomposing liquid hydrocarbon material, which comprises heating a heavy hydrocarbon material which is substantially non-volatile at 680 degrees F. and atmospheric pressure to a temperature above 700 degrees F. and at a pressure less than 600 mm. absolute for the period of thermal decomposition, and rapidly removing the arising vapors.

18. A process for the production of lubricating oils, which comprises subjecting heavy hydrocarbons to a temperature and a sub-atmospheric pressure at which they are substantially non-volatile, but at which they can be thermally decomposed, for a period of time sufficient to cause thermal decomposition thereof and rapidly removing the decomposition products.

19. A process for the production of lubricating oils, which comprises subjecting to a temperature greater than 700° F., and a pressure of less than 300 mm. absolute, a charge of material containing heavy hydrocarbons which are non-volatile under the conditions employed, for a period of time sufficient to cause thermal decomposition of said heavy hydrocarbons.

20. A process for the production of lubricating oils, which comprises subjecting a heavy hydrocarbon material which is substantially non-volatile at temperatures in the neighborhood of 680° F. and at atmospheric pressure, to a temperature greater than approximately 700° F., and to a pressure less than approximately 600 mm. absolute for a period sufficient to cause thermal decomposition, and rapidly removing the decomposition products.

21. A process for the production of lubricating oils, which comprises subjecting a heavy hydrocarbon material, which is substantially non-volatile at 680° F. and at atmospheric pressure, to a temperature above 700° F. and to a pressure less than 12 mm. absolute for a period of time sufficient to thermally decompose the material.

WILBUR L. NELSON.
GEORGE H. FANCHER.