May 24, 1932. E. C. HERTHEL **1,859,966**

ART OF CRACKING HYDROCARBONS

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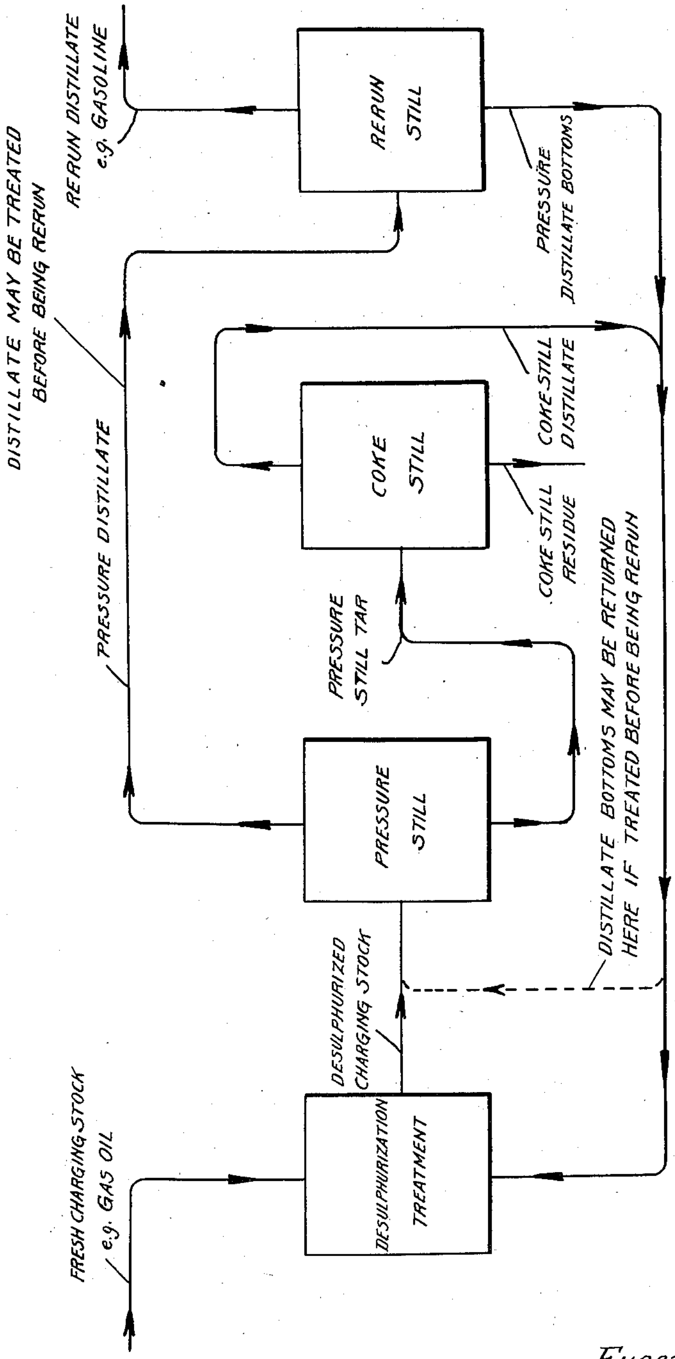

Fig. 1

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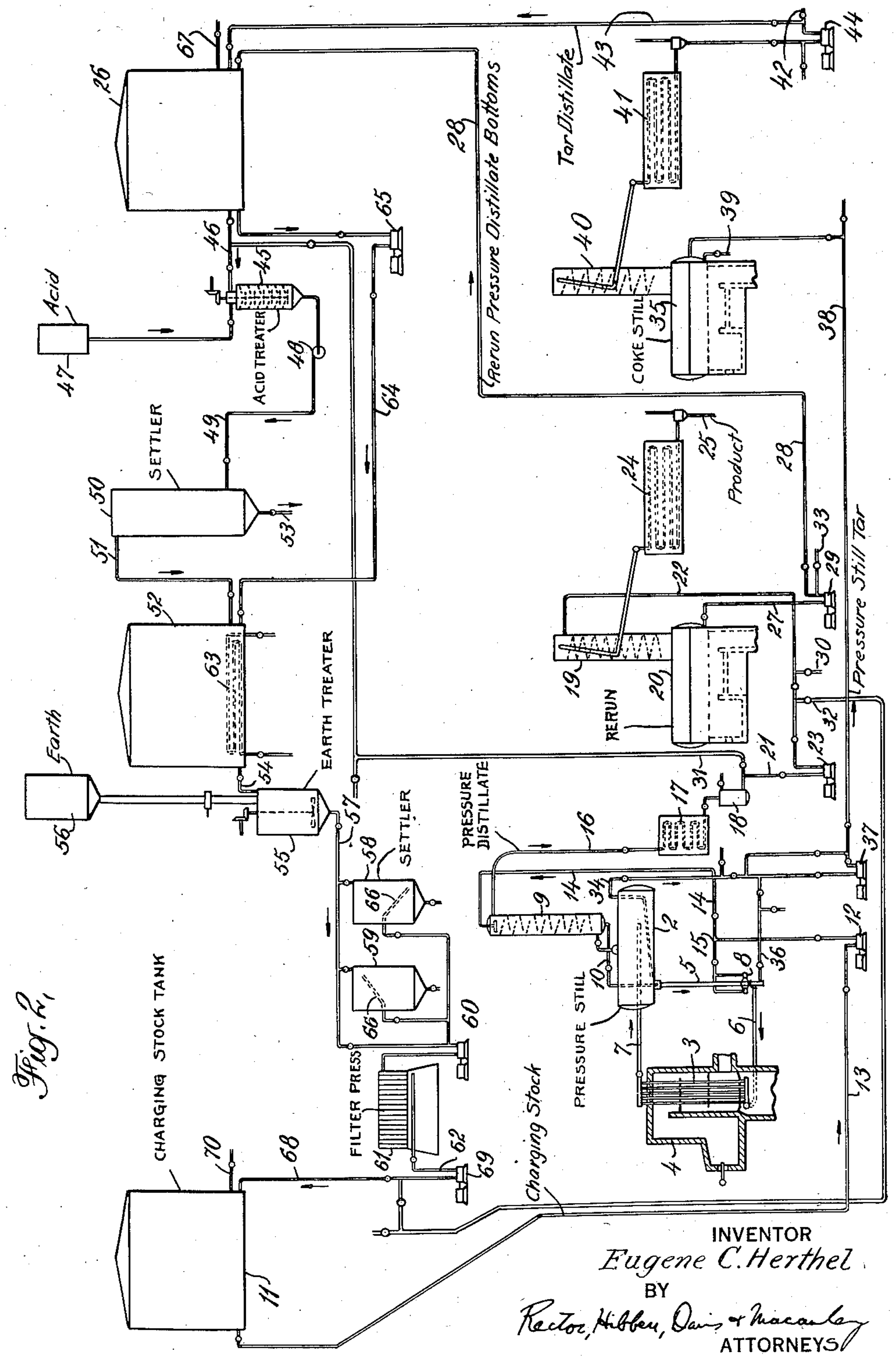

Fig. 2.

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UNITED STATES PATENT OFFICE

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ART OF CRACKING HYDROCARBONS

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This invention relates to improvements in cracking heavier hydrocarbon oils, such as gas oil, fuel oil and heavy residues, for the production of lighter hydrocarbon oils, such as gasoline and pressure distillates, therefrom by distillation under pressure.

In the cracking of heavier petroleum oils in pressure stills for the production of gasoline or pressure distillates, there are formed during the cracking operation certain constituents of an asphaltic or pitch-like character. With continuation of the cracking operation, the amount of such constituents increases and there is a tendency for deposits of carbon or coke to form on the heated walls of the still, thus necessitating the shutting down of the still for cleaning purposes between successive runs. The shutting down of the pressure still, the withdrawal of the charge therefrom, the cleaning of the still, the recharging of the still and the preliminary heating of the still to bring the fresh charge up to cracking conditions, all require time, and the total amount of time so required in ordinary commercial operations means a corresponding reduction in the proportion of the time when the still is operating for carrying out the desired cracking operation.

According to the present invention, the deposition of pitch or carbon on the heating surfaces of the pressure still is prevented or greatly reduced, so that overheating or danger of failure of the heating walls is correspondingly prevented or reduced, and the time of useful operation in a single run prolonged with correspondingly increased continuity of operation, reduced loss of working time and increased production per still per day.

When a pressure still is charged with gas oil or other charging stock to be subjected to cracking and the charge is heated to the cracking temperature, the cracking takes place in a gradual and progressive manner and the lighter constituents produced by the cracking operation which go to make up the pressure distillate are removed from the still progressively during the cracking operation. Other constituents, such as heavier hydrocarbons formed by the cracking operation, may remain and mix with the charge in the still. A small amount of asphaltic or pitch-like constituents is progressively formed. Such constituents appear to be of varying properties and characteristics. For the most part they remain in solution in the charge during the early portion of the run and they may remain completely in solution during the early portion of the run. With gradual and progressive cracking of the charge, however, the amount of such asphaltic or pitch-like constituents gradually and progressively increases until eventually the amount of such constituents increases beyond the saturation point. As the charge becomes supersaturated there is an increased danger of deposit of pitch or carbon on the heating walls of the still, with corresponding danger of overheating and failure of the heated walls if the still is not shut down at more or less frequent intervals to remove this deposit.

The pitch content of the pressure still charge may be regulated by the introduction of fresh feed and the withdrawal of pitch-laden tar so that concentration of pitch-like constituents in the still charge as a whole may be maintained below the saturation point. The pressure still tar, when operating in this manner, contains a substantial percentage of lighter oil and it is customary to subject the pressure tar to some distillation process to recover the content of lighter oil for return to and retreatment in the cracking operation. For example, the tar may be distilled to dryness at atmospheric pressure in a coke still, the major portion of the pitch-like constituents contained in the pressure tar remaining in the still as coke. The distillate from such operation may then be returned to the pressure still, together with fresh charging stock, for further cracking treatment. It is also customary to redistill or fractionate crude pressure distillates, and the heavier ends or bottoms from such redistillation or fractionation treatment are frequently returned to the pressure still for further cracking treatment.

In charging stock which contains sulphur, certain of the sulphur compounds appear to undergo cracking to form sulphur-containing constituents, probably of an asphalt-like character, which are particularly objectionable. Analyses of the carbon deposits on the heating walls of cracking stills indicate that certain of these sulphur-containing constituents have a preferential affinity for the heated surfaces, or tend to separate out on such surfaces, and cause deposits containing both iron and sulphur in proportions approximating those of iron sulfide. Separation of certain of the more objectionable sulphur-containing compounds from the pressure still charge or pressure tar is exceptionally difficult as they have boiling points closely approximating those of the pressure still charging stock. Accordingly, while the majority of the less objectionable pitch-like constituents in the pressure tar may be converted into coke or left behind as an undistilled residue on redistillation the more objectionable sulphur-containing compounds tend to remain in the distillate. If this distillate is returned to the pressure still for further cracking treatment the complete cycle tends progressively to increase the concentration of the more objectionable sulphur-containing compounds in the pressure still charge. Similarly a large part of the sulphur-containing compounds which are carried over from the pressure still with the crude pressure distillate become concentrated in the heavier portions of the pressure distillate on redistillation or fractionation.

According to the present invention, the fresh pressure still charging stock is treated to remove the more objectionable sulphur-containing compounds before introduction to the pressure still. The proportion of such compounds present in the pressure still charge during the cracking operation due to the sulphur contained in the fresh charging stock is thereby materially reduced. While the removal of the greater part of the sulphur compounds from the fresh charging stock may be readily accomplished by ordinary refining methods, a sufficiently vigorous treatment to remove the most refractory sulphur compounds is not commercially practicable from an economic standpoint, and where only a part of the sulphur compounds are removed by pretreatment of the charging stock, those which remain become concentrated in the pressure still charge, as above described, on reintroduction of distillates from the tar or of heavier portions of the pressure distillate to the pressure still. Further, according to the present invention, however, both such tar distillates and heavier portions of the pressure distillate, to the extent that they are returned to the pressure still for further cracking treatment, are subjected to a desulphurizing treatment before reintroduction to the pressure still.

In order to convert the crude pressure distillates from the usual pressure cracking operations into marketable products, such as gasoline or motor fuel, it is generally necessary, in addition to redistillation or fractionation, to further treat the distillate, for example with an acid and alkali, to remove the sulphur and unstable unsaturated compounds which decompose on prolonged standing and exposure to sunlight to form gummy and resinous bodies. In some cases, crude pressure distillates are treated to remove the sulphur and gum-forming constituents prior to a redistillation operation. This method of operation is of particular value, for example, where it is advantageous to combine redistillation of the crude pressure distillate with the redistillation of other oils or distillates not requiring further treatment. Where the crude pressure distillate is treated in this manner prior to redistillation, the pressure distillate bottoms may advantageously be returned directly to the pressure still without further treatment. The desulphurizing treatment applied to the fresh charging stock may advantageously be combined with the similar treatment of tar distillates to be recycled, as well as with any further treatment of the heavier portions of the pressure distillate bottoms, as where the crude pressure distillate is not subjected to a desulphurizing operation before redistillation or fractination.

By treating the stocks to be recycled to the pressure still to remove more objectionable sulphur-containing compounds, in accordance with the present invention, the average concentration of such constituents in the average pressure still charge may be repressed without requiring unusual or expensive treatment of the fresh charging stock.

The desulphurizing treatment may be carried out by any of the known methods, such as agitation with sulphuric acid and subsequent neutralization of the oil with an alkaline solution. One particularly advantageous method of carrying out the desulphurizing operation, however, is intimately to contact the oil with sulphuric acid in a mechanical treater as hereinafter described, and after separating any remaining acid and acid sludge, to remove any remaining acid compounds by treatment with a clay or fuller's earth, the clay or fuller's earth with the constituents absorbed therein being separated from the oil either directly or after settling by a filtering operation or other suitable treatment.

The invention will be further described in connection with the accompanying drawings, illustrating in a diagrammatic and somewhat conventional manner, one particularly advantageous embodiment of the improved method of operation of the invention and arrangement of apparatus adapted for the practice of the invention, but it is intended and will be understood that the invention is illustrated thereby but is not limited thereto. In the drawings:

Fig. 1 is a flow sheet diagrammatically illustrating the sequence of steps in a preferred method of operation according to the present invention.

Fig. 2 shows an arrangement of apparatus, partly in section and partly in elevation, adapted for the practice of the invention.

Referring to Fig. 2, the pressure still shown is of the general type described and illustrated in U. S. Patent No. 1,285,200 issued to Sinclair Refining Company on an application of E. W. Isom filed November 19, 1918, and comprises a bulk supply tank 2, a battery of heating tubes 3 arranged in a suitable furnace 4, and circulating connections 5, 6 and 7 whereby oil may be circulated by the pump 8 from and to the bulk supply tank through the battery of heating tubes in which it is heated to a cracking temperature. The vapors generated in the cracking operation pass through the reflux tower 9, and reflux condensate, together with unvaporized fresh oil when fresh oil is introduced to the refluxing operation, is returned to the cracking still through connection 10. Fresh charging stock may be supplied to the reflux tower from the tank 11 by the pump 12 through lines 13 and 14. A portion of the fresh charging stock may be introduced to the still through the circulating pump bearings by branch connection 15 to cool and lubricate the same. Vapors escaping from the reflux tower 9 pass through line 16 to condenser 17, from which condensate passes to receiver 18 which may be of the usual type employed in connection with pressure cracking stills. The crude pressure distillate withdrawn from receiver 18 may be charged directly to the reflux tower 19 on the rerun still 20, through connections 21 and 22 by means of the pump 23, and fractionally distilled therein. The vapors generated in the rerun still are passed to the condenser 24 from which the distillate of the desired end point is discharged through connection 25, for example, to storage or to a further treating operation. The rerun still 20 may be utilized to redistill crude pressure distillate from a battery of pressure cracking stills, the additional crude pressure distillate from such other cracking operations being introduced thereto through connection 30. The rerun pressure distillate bottoms may be passed directly to the storage tank 26 through lines 27 and 28 by the pump 29. Where it is desirable to subject the crude pressure distillate to a desulphurizing treatment prior to the redistilling operation the crude pressure distillate may be discharged directly to the desulphurizing operation from receiver 18 through connection 31 and this desulphurized stock, together with any other oil requiring distillation, may be introduced to the rerun still through the connection 32, the bottoms from such redistillation being discharged through connection 33. Tar may be withdrawn from the pressure still through line 34, either continuously or intermittently during the cracking operation, to maintain the pitch concentration of the pressure still charge below the saturation point. The pressure tar so withdrawn may advantageously be charged directly to a coke still 35, one of several, preferably operated at substantially atmospheric pressure. The sensible heat contained in the pressure tar may thus be utilized to assist in the evaporation of the volatile constituents upon lowering of pressure. The pressure still, for example, may be operated under a pressure of 100 to 150 pounds per square inch. Connection 36 is provided for draining the pressure still at the end of the run, and the pressure tar so withdrawn may be pumped to a coke still by the pump 37 through connection 38. The coke stills and rerun stills may be of the ordinary shell type provided with reflux towers and mounted in suitable furnace structures. The coke still 35 is provided with a valved connection 39 for withdrawing heavy residue when it is not desired to continue the distillation to "coke". The vapors generated in the still 35 pass through the reflux tower 40 to the condenser 41. The distillate may be withdrawn through valved connection 42 or passed directly to the tank 26 through pipe 43 by the pump 44. In addition to the crude pressure distillate bottoms and coke still distillate supplied to the tank 26 through connections 28 and 43 respectively, fresh oil may be supplied thereto through valved connection 67. The tank 26 is connected with the mechanical treater 45 by valved connection 46. The mechanical treater consists of a series of cells located one above another and with rotary disks or baffles carried by a vertical shaft. These rotary disks are arranged at approximately the center of each cell between side baffles. When the disks are rapidly rotated the oil and acid which are introduced in separate streams from tanks 26 and 47, respectively, flowing onto the highest disk at the top of the treater, are caused to intermingle as they flow down over successive disks and are thrown by centrifugal force against the walls of the apparatus, their intermixture being promoted by the resulting impact. The mingled oil and acid are collected by the side baffles and delivered to the next lower disk. Leading from the bottom of the treater is an outlet for the oil and acid tar which are pumped by the pump 48 through the pipe 49 to the settler 50, or to the first of a series of settlers. In such settlers the acid-tar separates from the oil and the oil overflows through the pipe 51 either to another settling tank or a receiving tank 52 for the acid-treated oil, while the acid sludge collecting in the bottom of the settling tank is drawn off through connection 53 and pumped for example, to an acid recovery plant. From the tank 52 the acid-treated oil passes through the pipe 54 to the mixing apparatus 55 to which clay or fuller's earth from the storage bin 56 is supplied in regulated amounts. The acid-treated oil, before being subjected to the earth treatment, may advantageously be heated, for example approximately to 175° F., and a steam coil 63 is provided in tank 52 for this purpose. The treated oil is thoroughly agitated with the clay or fuller's earth and when the treatment is completed, the oil and earth are pumped by pump 60 through the line 57 to a pressure filter 61 from which the finished oil is discharged at 62. In the treatment of oils containing relatively less refractory sulphur compounds, the acid treatment may be omitted and the earth treatment relied upon entirely. By-pass connection 64 and pump 65 are provided to supply oil from the tank 26 directly to the receiving tank 52. The earth and oil mixture from the treater 55 may be permitted to settle before being subjected to the filter pressing operation and only the relatively clear oil charged to the filter press. The earth and oil mixture from the treater 55 may accordingly be directed to either of the settlers 58 or 59 and after standing the required length of time the settled oil may be withdrawn through the swing lines 66. The filtered oil is delivered to the charging stock storage tank 11 through line 68 by the pump 69. The tank 11 is provided with valved connection 70 through which additional substantially sulphur-free oil may be supplied, such as the rerun pressure distillate bottoms obtained when the crude pressure distillate is subjected to a desulphurizing treatment prior to its redistillation and which accordingly may be returned to the cracking operation without further desulphurizing treatment.

It will be apparent that the present invention provides an improved process by which the pressure still charge, in cracking operations in which portions of the products of the pressure distillation are recycled, may be kept in equilibrium as to sulphur content, particularly as to the more objectionable sulphur-containing compounds, and by which the equilibrium content of sulphur and sulphur compounds can be kept at a value materially promoting the economy and efficiency of the pressure still operation.

I claim:

1. The improvement in the cracking of heavy hydrocarbon oils for the production of lighter hydrocarbon oils therefrom, comprising distilling the heavy hydrocarbon oils under pressure and at a cracking temperature, supplying fresh oil to this cracking operation and withdrawing tar therefrom, subjecting the tar withdrawn from the cracking operation to distillation at a lower pressure, subjecting the distillate from the tar distillation to a desulphurizing treatment, and returning the desulphurized tar distillate to the first mentioned cracking operation.

2. The improvement in the cracking of heavy hydrocarbon oils for the production of lighter hydrocarbon oils therefrom, comprising distilling the heavy hydrocarbon oils under pressure and at a cracking temperature, supplying additional heavy oil to this cracking operation and withdrawing tar therefrom, subjecting the tar withdrawn from the cracking operation to distillation at a lower pressure, commingling the distillate from the tar distillation with fresh oils, subjecting the tar distillate and admixed fresh oil to a desulphurizing treatment and supplying the desulphurized oil mixture to the first mentioned cracking operation.

3. The improvement in the cracking of heavy hydrocarbon oils for the production of lighter hydrocarbon oils therefrom, comprising distilling the heavy hydrocarbon oils under pressure and at a cracking temperature, supplying additional heavy oil to the cracking operation and withdrawing tar therefrom, subjecting the tar withdrawn from the cracking operation to distillation at a lower pressure, subjecting the distillate from the tar distillation to a desulphurizing treatment, returning the desulphurized tar distillate to the first mentioned cracking operation, and subjecting the additional heavy oil to be supplied to the first mentioned cracking operation to a desulphurizing treatment.

4. The improvement in the cracking of heavy hydrocarbon oils for the production of lighter hydrocarbon oils therefrom, comprising distilling the heavy oils under pressure and at a cracking temperature, fractionating the crude pressure distillate obtained from this cracking operation, commingling a heavier fraction from the fractionation of the crude pressure distillate with fresh oil and subjecting the oil mixture to a desulphurizing treatment, introducing the desulphurized oil mixture to the first mentioned cracking operation, and withdrawing tar therefrom.

5. The improvement in the cracking of heavy hydrocarbon oils for the production of lighter hydrocarbon oils therefrom, comprising distilling the heavy hydrocarbon oils under pressure and at a cracking temperature, supplying additional heavy oil to this cracking operation and withdrawing tar therefrom, fractionating the pressure distillate and subjecting the tar withdrawn from the cracking operation to distillation, recycling a heavier fraction from the fractionation of the crude pressure distillate and the distillate from the tar distillation to the first mentioned cracking operation, and sub-

jecting the additional oil to be supplied to the cracking operation and the fractions to be recycled to a desulphurizing treatment before supplying them to the first mentioned cracking operation.

6. The improvement in the cracking of heavy hydrocarbon oils for the production of lighter hydrocarbon oils therefrom, comprising distilling the heavy hydrocarbon oils under pressure and at a cracking temperature, supplying additional heavy oil to this cracking operation and withdrawing tar therefrom, subjecting the crude pressure distillate obtained from the cracking operation to a desulphurizing treatment and fractionating the desulphurized pressure distillate, subjecting the tar withdrawn from the cracking operation to distillation, subjecting the distillate from the tar distillation together with additional heavy oil to be supplied to the cracking operation to a desulphurizing treatment, and introducing the desulphurized additional heavy oil and tar distillate together with a heavier fraction of the desulphurized pressure distillate to the first mentioned cracking operation.

In testimony whereof I have subscribed my name.

EUGENE C. HERTHEL.