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PROCESS AND APPARATUS FOR TREATING HYDROCARBON OIL

Filed Feb. 6, 1925

Fig. 1.

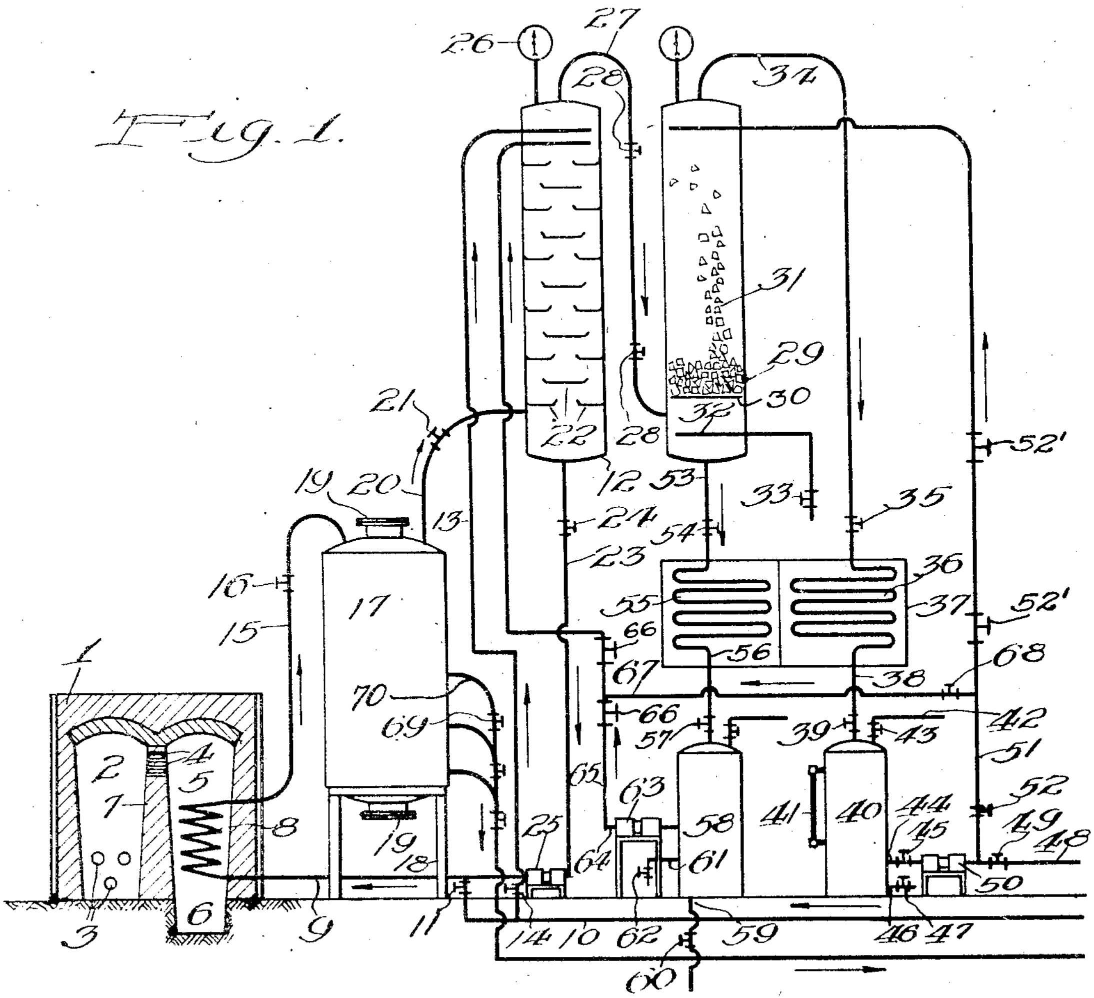
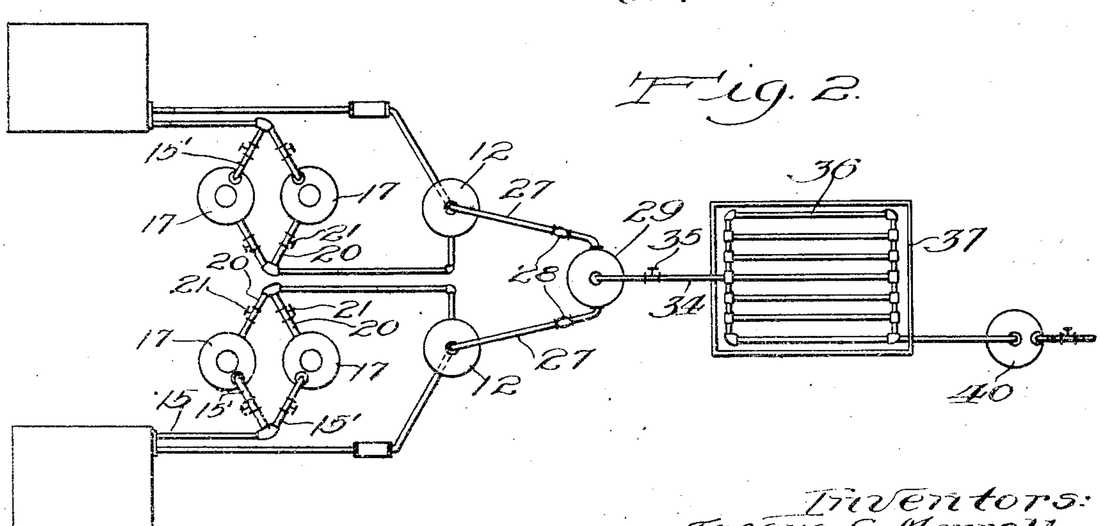


Fig. 2.



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PROCESS AND APPARATUS FOR TREATING HYDROCARBON OIL

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This invention relates to a process of hydrocarbon oil conversion and refers more particularly to the production of low boiling point fractions from higher boiling point oils, which low boiling point fractions are suitable for commercial use.

During the past few years, countless attempts have been made by oil refiners to produce end point gasoline as a direct product of a cracking process. Various of these attempts have been more or less sucessful, but not practical to any marked degree, owing to the instability of the final product, which would develop color and odor on standing. It is the specific embodiment of the present invention to produce as a direct product end point gasoline conforming to all the specifications for commercial gasoline as to boiling point range, including end point.

Briefly describing our invention, it primarily consists in removing the hydrocarbon vapors discharging from the top of the dephlegmator of an oil cracking process or from a plurality of dephlegmators connected into intercommunicating units or in the form of a battery. These vapors, either under the same pressure as is maintained in the dephlegmator or dephlegmators or under a substantially reduced pressure down to say atmospheric, are subjected to mixture with steam in a separate fractionating column, said steam and vapors co-mingling physically with each other to form a steam hydrocarbon vapor mixture in this fractionating tower. The steam is preferably introduced for the purpose of maintaining the vapors in a vaporous state and preventing premature condensation of the major portion of the product at a given temperature, and also to permit these hydrocarbon vapors to condense simultanenously with the condensation of the steam, that is, the steam being mixed physically with the vapors in the form of a mixture, and condensing the mixture simultaneously, will cause each to be condensed in the physical presence of and contact with the other to secure the utmost stability in the final or hydrocarbon liquid product, per se, and when subjected to a subsequent treatment. Separation of the hydrocarbon liquid and water may take place beyond the condenser, and the fact is to be noted that the water is darker in color and contains a certain amount of the impurities normally present in pressure distillate which has been condensed without admixture with steam.

As pointed out above, the vapors from the dephlegmator or dephlegmators may have their pressure reduced in their passage to the fractionating column, and said physical co-mingling of steam and vapors in the fractionating column may take place at a pressure around atmospheric or slightly above.

The various advantages, objects and utility of the present invention may be apparent from the following detailed description, but it may be well to here point out that the invention possesses a very great economical feature over present processes which consist in withdrawing the vapors from a number of dephlegmators forming part of a battery of interconnected oil cracking units and condensing said vapors and later subjecting the liquid distillate to redistillation. According to our invention we propose to subject these vapors without substantial condensation to fractionation in the presence of steam. The basic novelty of the present invention, however, it is to be completely understood, is not necessarily confined to treating the vapors from a plurality of dephlegmators, but it is to be understood that the novelty resides in the introduction of steam into a zone in which the hydrocarbon vapors from a dephlegmator are introduced without previously undergoing any substantial condensation.

In the drawing, Fig. 1 is a diagrammatic side elevational view of an apparatus for carrying out our invention, and Fig. 2 is a top plan diagrammatic layout illustrating the incorporation of the idea of a single fractionating zone serving a number of independent dephlegmators.

In the drawing, 1 designates a side-fired furnace provided with the combustion chamber 2 heated by means of the burners 3, the gases of combustion passing through the flues 4 into the tube chamber 5, the spent gases being exhausted through the stack 6.

The combustion chamber 2 and tube chamber 5 are separated by means of the bridge wall 7. In the tube chamber is positioned a continuous coil of connected tubing 8, being supplied with oil through the connecting feed line 9, having communication with the raw oil feed line 10, in which latter is interposed the valve 11. The raw oil, instead of being fed directly to the heating coil 8 may be discharged into the upper portion of the dephlegmator 12 through the line 13, in which latter is interposed a valve 14.

It is to be understood also that the feed of raw oil to the system may be split, part of same being fed directly to the dephlegmator and another part being fed directly to the heating coil. The oil passing through the heating coil is heated to a conversion temperature, for instance, 750 to 950° F., more or less, and is discharged into the transfer line 15, in which is interposed a valve 16 discharging into the top of a vertical reaction chamber 17 supported on the supports 18. This vertical reaction chamber may take the form of a vertically elongated drum or shell, having upper and lower manhole plates 19 for the purpose of cleaning. The lighter fractions of the heated oil being discharged into the reaction chamber 17 through the transfer line 15 will vaporize and will discharge through the vapor outlet 20, in which is interposed the valve 21, discharging into the lower portion of the vertical dephlegmator 12, which is provided with the perforated pans 22. It is to be understood, of course, that the pans 22 are merely shown diagrammatically and that any form of plate, pan or packing to retard the upward flow of vapors and to give contact between the vapor and liquid as is usually employed in this art today would be suitable.

The vapors in their obstructed travel upwardly through the dephlegmator 12 are subjected to physical contact with the raw oil where such has been introduced, thus condensing the heavier fractions of said vapors, said condensate being returned by means of the reflux return line 23, in which is interposed valve 24. This reflux may be entirely withdrawn from the system and discharged to storage, or it may be returned either under a hydrostatic head pressure or under a forced or applied pressure by means of the pump 25 to the combined feed line 9. A pressure gauge 26 is provided on the dephlegmator 12.

Describing particularly some of the features of this invention, the vapors which do not condense in the dephlegmator 12 discharge from the top of said dephlegmator into the vapor line 27, in which is interposed the valves 28, which preferably take the form of pressure reducing valves, the discharge end of said vapor line 27 discharging into the lower portion of a vertical fractionating column 29. This vertical fractionating column 29 may be provided with the perforated base plate 30 and any suitable form of packing 31 may be employed as is usually used in fractionating columns in this art. As pointed out, directly adjacent the point of introduction of the vapors to the fractionating column 29 is a steam inlet pipe 32, in which is interposed a valve 33, said steam inlet being connected with any suitable source of steam supply, either of the saturated or superheated type.

Further describing the tower 29, it may be any suitable type, such as the packed, pan, plate, or bubble type. The steam and vapors physically co-mingle with each other in the lower portion of the fractionating tower 29 passing upwardly, their flow being retarded by means of the elements 31 and discharging at the top thereof into the line 34, in which is interposed valve 35 communicating with the condenser coil 36 in condenser box 37, the condensing coil 36 communicating by means of the line 38, in which is interposed the valve 39 with the combined receiver and separator 40. This combined receiver and separator 40 may be provided with the usual sight-glass 41, uncondensible gas outlet 42 controlled by valve 43, and liquid outlet 44 controlled by valve 45. The liquid discharge 44 is the discharge for the oil distillate, and a second discharge 46 controlled by valve 47 is provided for the purpose of withdrawing the water. The oil withdrawn through the pipe 44 may be withdrawn to storage through the pipe 48, the valve 49 being opened, or it may be returned by means of pump 50 to the line 51, the valve 52 being opened, said line 51 discharging into the upper portion of the fractionating column 29. By returning the portions of the pressure distillate to the upper portion of the fractionating tower 29, a uniform or regulated temperature may be maintained therein, and the subjection of the vapors coursing upwardly through said fractionating tower 29 coming in direct contact with the cooled distillate may condense the heavier fractions of said vapors.

The liquid condensate from said fractionating tower 29 may discharge through the line 53, in which is interposed valve 54, communicating with the cooling coil 55 in the condenser box 37, after which it may discharge through the line 56; in which is interposed valve 57 into what may be termed the pressure distillate bottoms receiver and separator 58. This receiver 58 may be provided with the discharge drain 59 controlled by valve 60, for the purpose of removing the water which stratifies in said receiver. The liquid oil in said receiver may be withdrawn through the line 61 controlled by valve 62 and sent to storage for further refining, or it may be withdrawn by means of the pump 63 interposed in the line 64 and returned through the line 65, in which is interposed valve 66, to the upper portion of the dephlegmator 12 for the purpose of assisting in the condensation of the heavier fractions of the vapors coursing upwardly therethrough. The liquid returning through the line 51 may be bypassed through the line 67, the valve 68 being opened and valve 52′ closed, which line 67 has connection with the line 65 for the purpose of introducing to the top of the dephlegmator 12 a lighter gravity oil for the purpose described.

Referring to Fig. 2, we have illustrated the use of our invention in connection with a number of oil cracking units interconnected into the same battery. A number of alternately connected reaction chambers may be used with diverting lines 15′ branching out from the transfer line 15 with suitable valves interposed in said lines 15′, the purpose being to operate the process continuously over long periods of time and allow for freely cutting in a new tank 17 while simultaneously cutting out another one. It may be here pointed out that Fig. 2 is not an identical plan layout of the side elevation shown in Fig. 1. The vapors from either of the chambers 17 discharge into either of the vapor lines 20 controlled by the valves 21 into the dephlegmator 12. It is to be understood that although we have illustrated two units in this particular battery, the invention is adapted to be utilized in connection with units of say five each in the battery, with, of course, the understanding that any number may be utilized. The vapors discharging from the top of the dephlegmators 12 through the vapor lines 27 and past the pressure reducing valves 28, pass into a single fractionating column 29 common to a plurality of dephlegmators.

Describing now the operation of our invention, the raw charging stock may be introduced either directly into the heating coils or into the upper part of the dephlegmator 12, and said oil heated in its passage through the heating coils to a cracking or conversion temperature, for instance, between 750° and 950° F., said heated oil being discharged into the reaction chamber 17, where the lighter fractions thereof separate in the form of vapors and where the unvaporized residue builds up in a substantial body composed of unvaporized liquid and precipitated free coke. The unvaporized liquid residue may be withdrawn from time to time through the residue draw-off line 70 controlled by valve 69, a plurality of these lines being provided at various heights on the reaction chamber for the purpose of providing discharge for the liquid at various heights when the free coke has built up inside the chamber.

The vapors discharging through the vapor line 20 are dephlegmated in the dephlegmator 12, the reflux being returned to be reheated, together with raw oil where the latter has been introduced to the dephlegmator.

The vapors remaining uncondensed after passage through the dephlegmator discharge through the line 27 into the lower portion of the fractionating tower or column 29. On the system previous to this point a pressure of from three to several hundred pounds above atmospheric has been maintained. This pressure is preferably reduced by means of the reducing valves 28 materially below the pressure maintained on the balance of the system, preferably around atmospheric. It may, of course, be slightly above. The vapors discharging through the bottom of the vapor line 27 physically co-mingle with the steam, and this mixture courses upwardly through the fractionating tower 29 countercurrent to the flow of liquid distillate, where same is returned through the line 51.

One of the primary purposes for the introduction and physical mixing of the steam and vapors in this fractionating column 29 is to prevent any substantial condensation therein, although in order to most effectually fractionate the vapors therein, some condensation must take place, and therefore portions of the distillate may be returned through the line 51 to provide reflux and at the same time act as a cooling medium. It is understood, of course, that the reaction chamber 17, dephlegmator 12 and fractionating column 29 may be insulated if desired.

The reduction in pressure between the dephlegmator 12 and fractionating column 29 may be only that amount which will permit good separation of the finished liquid product from the fractionating column, or, as pointed out, the pressure may be reduced to atmospheric. It may be good operating practice to condense the final product under a few pounds pressure above atmospheric. In any case, the pressure upon this end of the system is controlled by a suitable valve on the final receiver and separator 40, which also acts as a gas outlet. It is a known fact in the fractionation of vapors in a cracking system that it is easier to secure a clean separation of lighter fractions such as gasoline at low pressures than it is at high pressures.

The steam assists in lowering the temperature necessary to keep the hydrocarbons in a vapor state and prevents premature condensation. The primary and major purpose for the introduction of steam is to produce a gasoline-like product which per se is more stable than a product the vapors of which have not been mixed with steam, and also, such a product will be more amenable to treatment to produce a stable, marketable product. This result is brought about in a great measure by the physical co-mingling and condensation of hydrocarbon vapors and steam.

It has been the experience of applicants covering a period of several years that in order to treat cracked gasoline-like products without redistillation by chemical means and especially by what is referred to as the sulphuric acid method of treatment, these cracked gasoline-like products for the most part must be distilled in the presence of steam. Further, when these cracked gasoline-like products were fractionated from a crude distillate, using fire alone, and then subjected to chemical treatment, in spite of the use of every precaution, the product is almost invariably unstable with respect to color and odor. On the other hand, when these cracked distillates are redistilled and condensed in the presence of steam, the resultant product usually remains waterwhite, stable, and is perfectly marketable.

At the lower pressure employed in the fractionating tower 29, some heavy ends will condense out, the process being practically one of fractional condensation, along with some condensed water, both liquids being withdrawn through the cooler 55 into the receiver 58, where the water is separated and withdrawn through the line 59.

It must be here understood that the following method of further refining the liquid oil product collected in the receiver 40 has been found preferable.

This liquid oil product may be first subjected to a water wash followed by treatment with a solution of litharge in caustic soda, referred to as plumbite solution, and then treated with sulphuric acid of concentration varying from 85% up to 95%, the latter referred to as concentrated sulphuric acid, usually known as 66° Baumé acid. The acid sludge is then drawn off after a period of agitation, the gasoline is then thoroughly water washed, neutralized with caustic soda, and finally, it has been advisable to treat with a small amount of fuller's earth or like absorbent. The gasoline may be filtered through a column of this earth, or a simple means of treatment is to agitate with the earth, previously allowing practically all of the water to settle out. Any earth which remains suspended is washed out of the gasoline by agitating with water. In some cases, it has been advisable to substitute a plumbite solution for the caustic soda in the above treatment. This plumbite solution consists of a solution of litharge in caustic soda.

It may be advisable under certain circumstances to treat with absorbents alone, this being perfectly feasible with the gasoline product obtained by this process.

Finally, it is to be pointed out that although some commercial systems have attempted to produce end point gasoline from a cracking system, for the most part they have been unsuccessful in later treating this gasoline into a commercial, waterwhite and stable product.

We are well aware that heretofore, various inventions have been perfected relating to the redistillation of liquid distillate in the presence of steam, and we differentiate therefrom in that we subject the vapors without any intended or substantial condensation to actual physical contact with said steam, preferably under a reduced pressure. It is to be noted that our invention is carried out as part of a continuous process and without any material change in present equipment.

By the term "end point gasoline," we mean gasoline having an end point of or below 437° F.

We claim as our invention:

1. A process of hydrocarbon oil conversion, consisting in subjecting the oil to conditions of conversion temperature and superatmospheric pressure to cause substantial vaporization, subjecting the vapors to dephlegmation while maintained under superatmospheric pressure, removing the uncondensed vapors and physically commingling same with steam to cause an intimate mixture of the steam and vapors, causing said mixture to have an obstructed upward passage through a fractionating zone, in then condensing the mixture and separating the water and oil after condensation, returning portions of the condensed vapors free from water to the fractionating zone to condense the heavy ends of the mixture, and returning the resulting condensate under an applied pressure to the zone of dephlegmation.

2. A process of hydrocarbon oil conversion, consisting in subjecting the oil to conditions of conversion temperature and superatmospheric pressure to cause substantial vaporization, subjecting the vapors to dephlegmation while maintained under superatmospheric pressure, removing the uncondensed vapors and physically commingling same with steam to cause an intimate mixture of the steam and vapors, causing said mixture to have an obstructed upward passage through a fractionating zone, in then condensing the mixture and separating the water and oil after condensation, withdrawing portions of the condensed vapors free from water under an applied pressure and discharging same into the zone of dephlegmation.

3. A process of hydrocarbon oil conversion, consisting in subjecting the oil to conditions of conversion temperature and superatmospheric pressure in a battery of interconnected oil cracking units to cause substantial vaporization, dephlegmating the vapors under superatmospheric pressure, passing the uncondensed dephlegmated vapors to a single fractionating zone prior to any substantial condensation of the vapors, introducing steam to said fractionating zone in physical contact with the vapors, obstructing the up-

ward travel of said mixture through the fractionating zone, condensing the mixture, separating the water and collecting the oil, employing portions thereof as a dephlegmating medium for the vapors.

4. In an apparatus for treating oil, consisting in an elongated passageway, mounted in a heating means, an enlarged reaction chamber communicating therewith where substantial separation of vapors takes place, a dephlegmator communicating with the vapor space of said reaction chamber, a fractionating means, means connecting the vapor space of said dephlegmator with said fractionating means, means in said connecting means for controlling the vapor pressure, means for introducing steam to said fractionating means to be mixed with the vapors therein, obstructing means in said fractionating means retarding the upward flow of said vapor-steam mixture, means for condensing the uncondensed mixture and means for returning portions of the condensed oil free from water to the fractionating and dephlegmating means.

5. In apparatus for hydrocarbon oil conversion, the combination with a battery of oil cracking units comprising a plurality of heating and conversion means, each of the latter having a vapor space, a dephlegmator communicating with each vapor space, of a single fractionating means connected with the vapor space of the dephlegmators, means in the connections between the plurality of dephlegmators and single fractionating means for regulating the pressure on the system, means for introducing steam to said single fractionating means to mingle in physical contact with the vapors, condensing means and means for forcing, under applied pressure, the return of portions of the oil condensate free from water to each of the dephlegmators or single fractionating means.

6. A process for treating cracked hydrocarbon oil vapors comprising subjecting such vapors to dephlegmation in a zone maintained under a superatmospheric pressure, passing the uncondensed dephlegmated vapors to a fractionating column, preventing premature condensation of the major portion of the dephlegmated vapors in said fractionating column by introducing steam to physically commingle with the vapors in said fractionating column, causing the commingled steam and vapors to have an obstructed passage through said column, maintaining the commingled steam and vapors in said column under a substantially atmospheric pressure, subjecting the commingled steam and vapors subsequent to their passage from said column to condensation, and thereafter effecting a separation of the resultant water and distillate.

7. A process for treating cracked hydrocarbon oil vapors comprising subjecting such vapors to dephlegmation in a zone maintained under a superatmospheric pressure, passing the uncondensed dephlegmated vapors to a fractionating column, preventing premature condensation of the major portion of the dephlegmated vapors in said fractionating column by introducing steam to physically commingle with the vapors in said fractionating column, causing the commingled steam and vapors to have an obstructed passage through said column, maintaining the commingled steam and vapors in said column under a substantially atmospheric pressure, subjecting the commingled steam and vapors subsequent to their passage from said column to condensation, and thereafter effecting a separation of the resultant water and distillate, and returning portions of the resultant distillate to the zone of dephlegmation maintained under superatmospheric pressure.

8. In the art of hydrocarbon oil conversion, the improved method of treating the cracked vapors which comprises subjecting the vapors to initial dephlegmation, subjecting the dephlegmated vapors to fractionation in the presence of steam to separate pressure distillate bottoms therefrom, separating the pressure distillate bottoms from the water condensed from the steam in such fractionation, condensing the fractionated vapors and remaining steam, separating the resultant pressure distillate from the water, and returning portions of the pressure distillate to the initial dephlegmation step as a cooling medium.

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