W. F. RITTMAN AND C. B. DUTTON.

TREATMENT OF HYDROCARBONS.

APPLICATION FILED FEB. 5, 1917.

1,365,604. Patented Jan. 11, 1921.

FIG. 1.

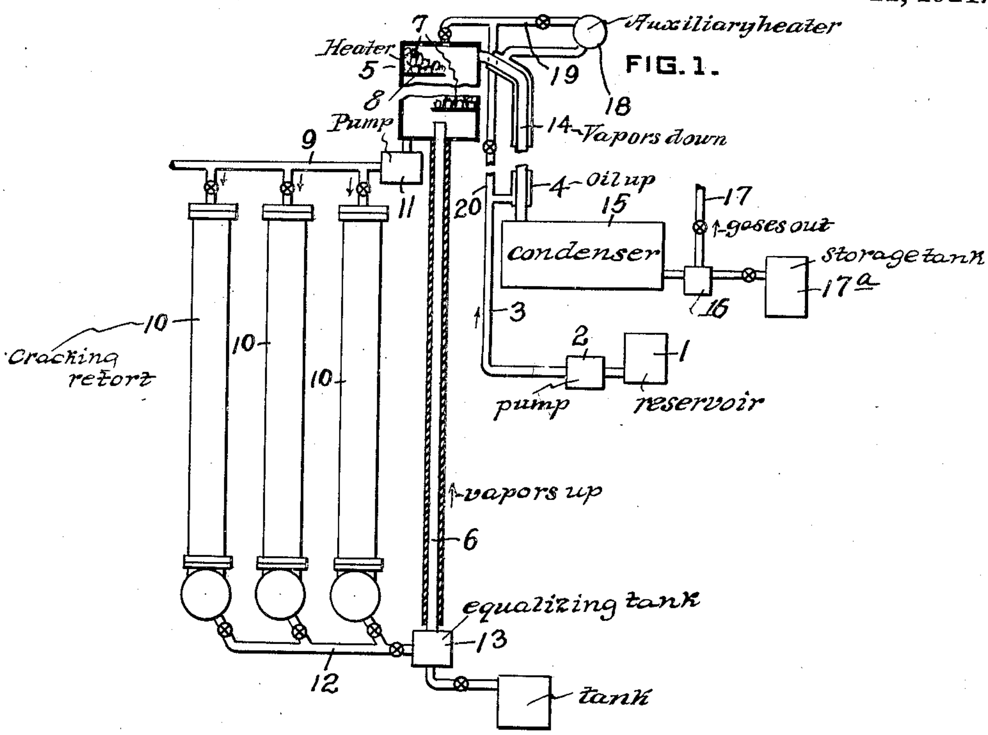
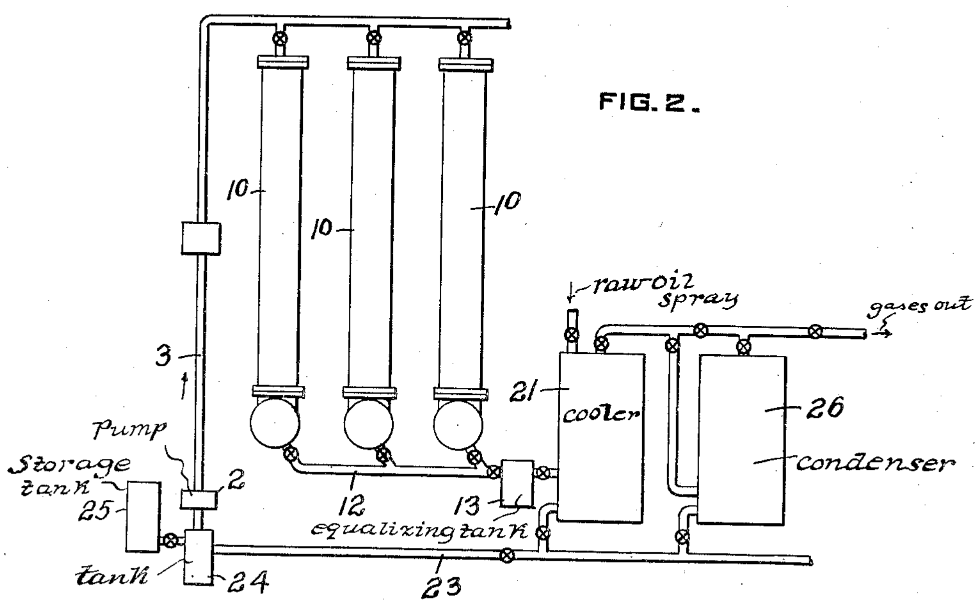


FIG. 2.



WITNESSES

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TREATMENT OF HYDROCARBONS.

1,365,604. Specification of Letters Patent. **Patented Jan. 11, 1921.**

Application filed February 5, 1917. Serial No. 146,727.

To all whom it may concern:

Be it known that we, WALTER F. RITTMAN and CLARENCE B. DUTTON, residing at Pittsburgh, in the county of Allegheny and State of Pennsylvania, citizens of the United States, have invented or discovered certain new and useful Improvement in the Treatment of Hydrocarbons, of which improvement the following is a specification.

It is a well known law of physical chemistry that a pronounced tendency of substances to react is dependent upon the nature of such substances and the distance of the system of which they are components from a state of equal equilibrium. This tendency to react is counterbalanced by chemical inertia or the tendency to continue in *statu quo*, which latter tendency decreases with increase of temperature. Hence, in processes involving chemical reactions, operating conditions should be selected which will bring the system to which they are applied nearer to the desired composition. This is of importance as increasing temperature may bring the system farther from or nearer to the desired composition. For example, too high a temperature applied to the decomposition of heavy hydrocarbons would carry decomposition beyond that necessary to form the desired low boiling hydrocarbon products and reduce same to coke and permanent gases.

The vapor phase cracking or decomposition process recognizes and applies these principles to the cracking of heavy hydrocarbons. In the operation of the vapor phase cracking process, an unbalanced system of hydrocarbons is introduced into the upper end of a retort in a vaporous condition, or such vaporous condition is created immediately after introduction of a liquid, into such retort. This unbalanced system, while in a vaporous state, is then subjected to temperature, ranging above the point at which the cracking begins to occur, which for most hydrocarbons will be in excess of 350° C. A particular temperature is selected for an operation sufficient to overcome the chemical inertia of the system as introduced and to supply heat sufficient to break down the hydrocarbons into new molecular formations which tend to readjust themselves with respect to each other to form a system in which the products desired to be produced, as for example, low boiling hydrocarbon, or low boiling aromatic hydrocarbons will be present in commercial quantities or proportions. This chemical change is aided by the continued maintenance of a substantially uniform pressure of the hydrocarbons broken down or cracked which pressure it has been found should be super-atmospheric and preferably in excess of 30 lbs. per square inch for the attainment of satisfactory results.

As the unbalanced system, influenced by the temperatures and pressures employed, tends to approach a state of stable equilibrium, a certain percentage of any given constituents is not exceeded. In other words, in a hydrocarbon system produced by heat, pressure and time, there is a great diversity of components consisting, for example, of fixed hydrocarbon gases such as methane, ethane, ethylene, butane, etc., and hydrogen, as well as more readily condensible hydrocarbons such as those having boiling points ranging above 30° C. to heavy complex molecules of high boiling point, and only a certain proportion of any given commercial group will be found present as the system approaches equilibrium. It is possible to create therefore, only a certain percentage of the desired low boiling products in a single stage of the operation, this proportion remaining practically constant for the particular type of liquid hydrocarbon or hydrocarbon vapors fed into the retort so long as the conditions, *i. e.* temperature, pressure, rate of feed, etc., creating same continue constant. Starting out with a given quantity of raw material only a certain percentage will be converted into the desired end products in a single passage of such quantity through the cracking apparatus.

The cycle of operation, therefore, can be tersely summarized as follows: An unbalanced system is introduced and made to approach a balanced system; this system is then withdrawn and the desired components or products separated out. The remainder or a selective portion thereof, which is again an unbalanced system, is returned in due course to the cracking apparatus for further cracking and is there made to again approach a balanced system, then withdrawn from the cracking apparatus and the desired products again separated out, and the process repeated. As the operation has been carried on heretofore, the cycle above described has been intermittent in character, and resulted in the loss of heat contained in the oil, necessitated additional installation for carrying out the same steps and involved a loss of time returning the unbalanced system for cracking treatment. For example, the system of hydrocarbon vapors after passage from the retort were conducted to an ordinary refinery type of multiple tube condenser, uncondensed gases passing thence through a scrubber, and then into a gas holder. The product condensed through the agency of a natural cooling medium, was passed into a receiving tank and afterward to a still where the separation of desired low boiling product was made by fractional distillation. The heavy or high boiling fraction of the product *i. e.*, usually that boiling above 200° C. was then pumped back into the oil feeding means as an unbalanced system for further treatment or cracking. This process was repeated over and over until the maximum conversion had been obtained for a quantity of raw or starting material.

In the accompanying drawing forming a part of this specification, Figure 1 is an elevation of a form of apparatus adapted for the practice of the invention described herein, the retort heating means being omitted, and Fig. 2 is a similar view of a modification of the improved apparatus.

In the practice of the invention, the raw oil to be treated is drawn from the reservoir 1 or any other suitable source by a pump 2, and forced through a pipe 3, and the outer member 4 of a preliminary heat exchanger, and from the preliminary heat exchanger into the upper portion of the main oil heater 5. As the raw oil passes down through the heater it encounters a counter current of highly heated cracked vapors escaping from the pipe 6. In order to insure the efficient inter-change of heat between the raw oil and the upwardly moving vapors, any suitable means known in the art are employed for dividing the oil into small streams or films. As for example, masses 7 of small pieces of refractory material are arranged on grids 8 suitably supported in the shell of the heater. From the heater 5 the heated oil passes through the pipe 9 into the upper ends of the retorts 10. In order to prevent back pressure from the retort entering the heater 5, any suitable means may be coupled into the pipe 9, preferably a pump indicated at 11, as such pump will insure the feed of the oil in the main heat-exchanger 5 into the retorts.

The retorts are heated by any suitable means, preferably a furnace of the type or construction shown and described in application filed Feb. 5, 1917, Serial Number 146,725, so that the oil fed into the retorts will be vaporized substantially instantaneously as it enters the upper ends of the retorts, the vapors raised to or approximately to, cracking temperature and finally subjected to a cracking temperature which will be dependent on the end product desired. While being heated as stated, the vapors are subjected to pressure also dependent upon the end product desired, and attained by regulating the rate of flow of oil into the retort, and the discharge from the retort on the apparatus hereinafter described. The products of the reactions in the retort, escape into a common conduit 12, and pass into an equalizing tank 13.

In the passage from the retorts to the tank 13, only vapors of very high boiling oils will be condensed, and these with any other carbon formed in cracking will be retained in the tank 13, while the other vapors will flow up through the pipe 6 into the heater 5. It is preferred that the pipe 6 should be covered with a non-conducting material to minimize condensation therein. Any vapors not condensed by contact with the raw oil in the heat exchanger 5 escape through the pipe 14, forming the inner member of the heat exchanger through which the raw oil passes, as before stated, and enters the condenser 15. The condensed oil and gases will pass through the trap 16 from which the gases escape through pipe 17, while the oil passes on into a storage tank 17[a].

The vapors flowing up through the pipe 6 will be a mixture of hydrocarbons differing widely as regards their boiling points, and as it is desired to segregate the vapors of hydrocarbons having a boiling point above that of the end product desired, as for example, gasolene, the raw oil entering the heat exchanger 5 should be at a temperature not higher than that of the desired end product, so that vapors of the hydrocarbons having a higher boiling point will be condensed and be returned to the retorts with the crude oil for recracking. In case the raw oil is not heated to the desired temperature by the vapors flowing from the heat exchanger 5 to the condenser, an auxiliary heater 18 may be arranged in the pipe 19 connecting the member 4 of the preliminary heater with the heat exchanger 5. To insure a more efficient regulation of the temperature of the raw oil in the heat-exchanger 5, a by-pass 20 can be employed for admitting cold raw oil in the heat exchanger. In the form of apparatus shown in Fig. 2, the hot vapors from the mixing or equalizing tank 13 are passed into a cooling chamber 21, wherein a temperature is maintained sufficient to condense from such mixed vapors flowing from the tank 13, those vapors having such a high boiling point as to require re-cracking. In case the natural radiation from the walls of this cooling chamber 21 will not reduce the temperature of the vapors sufficiently to condense out the products requiring re-cracking, raw oil may be sprayed onto the upper ends of this cooling chamber 21 in sufficient quantities to reduce the temperature of the vapors to the desired point above stated. The lower portion of this tank is connected by a pipe 23 to a tank 24 from which these cracked products which require re-treatment may be pumped back into the upper ends of the retorts, the tank 24 being connected to a storage tank 25 containing raw oil. The uncondensed vapors flow from the receptacle 21 into a condenser 26 where all the condensible vapors are condensed out, while the gases and uncondensed vapors are conducted to a gasometer, or preferably to absorbers for the extraction of the wild gasolene.

We claim herein as our invention:

1. The process herein described which consists in vaporizing a hydrocarbon having a high boiling point, subjecting such vapors to a temperature and pressure for a period of time for the formation of the desired low-boiling-point end product, condensing out from the cracked vapors undesirable high-boiling point hydrocarbons, segregating from the remaining hydrocarbons those having boiling points above that of the desired low-boiling-point end product, condensing the remaining vapors and re-cracking the hydrocarbons so segregated.

2. The process herein described which consists in vaporizing a hydrocarbon having a high boiling point, subjecting such vapors to a temperature and pressure for a period of time for the formation of the desired low boiling point end product, condensing out from the cracked vapors undesirable high-boiling-point hydrocarbons, subjecting the remaining vapors to contact with raw oil heated to the temperature of the boiling point of the low-boiling-point end product desired, thereby condensing hydrocarbons having a higher boiling point, cracking the raw and cracked oils and condensing the vapors having the desired low boiling point.

3. The process herein described of cracking heavy hydrocarbon oils which consists in vaporizing the oil, subjecting the vapors to cracking conditions, viz.—duration of treatment, a cracking temperature (350° C. or higher), and maintained superatmospheric pressure (30 lbs. per square inch or more)—suitable for the formation of the particular low-boiling-point end-product desired, discharging the reaction products of the cracking through a conduit into a receptacle, thereby condensing and collecting the undesirable high-boiling-point oils, bringing the uncondensed vapors from said receptacle into contact with the raw heavy hydrocarbon, thereby condensing and mixing with said raw hydrocarbon, hydrocarbons having a higher boiling point than that of the low-boiling end product, subjecting the mixture to vapor cracking as above specified, and condensing the vapors having the desired low-boiling-point.

4. The process as claimed in claim 3 in which the raw oil is heated to a temperature corresponding to the boiling point of the end-product desired before coming into contact with the uncondensed vapors.

5. A process as claimed in claim 4 in which the raw oil is preliminarily heated by vapors passing through the condenser.

In testimony whereof, we have hereunto set our hands.

WALTER F. RITTMAN.
CLARENCE B. DUTTON.