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U. S. JENKINS ET AL.

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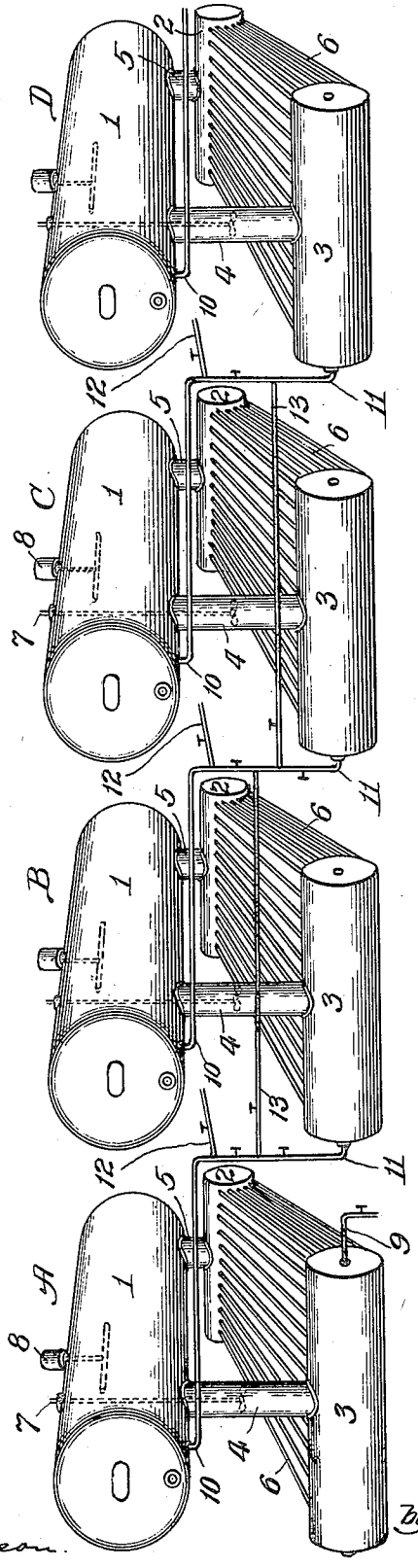

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METHOD OF TREATING HEAVY HYDROCARBONS.

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To all whom it may concern:

Be it known that we, ULYSSES S. JENKINS and STEPHEN SCHWARTZ, citizens of the United States, residing at Arkansas City, in the county of Cowley and State of Kansas, have invented certain new and useful Improvements in Methods of Treating Heavy Hydrocarbons, of which the following is a specification.

This invention relates to a method of treating heavy hydrocarbons, and more particularly to improvements in methods adapted chiefly for cracking fractions of crude oil, having a boiling point of 550 degrees Fahrenheit and upward at atmospheric pressure, and is an improvement upon the inventions disclosed in United States Letters Patent Nos. 1,226,526 and 1,247,883.

Among the objects of our invention is the provision of a method for destructive distillation of heavier fractions of crude oil than gasoline with the purpose of manufacturing gasoline therefrom; further to secure a method of carrying on destructive distillation of fractions of crude oil under pressure suitable to cause a chemical change of the crude oil fractions into gasoline, whereby the output of the apparatus used for such purpose is greatly increased for a given time; further to eliminate the waste of time heretofore necessary in cleaning carbonaceous matters from the pressure stills; further continuously removing that part of the heavy oils from the pressure stills which cannot be successfully treated under pressure on account of their high carbon contents being near the point of coking; further to effect a great saving of fuel by utilizing to a large degree the heat transmitted to the body of the oils; further to apply a plurality of pressure stills in a battery, treating the oil successively in the stills, decreasing its pressure, and volume and increasing its gravity in the successive stills, removing continuously from the last still that part of the oil which does not yield a desirable quantity and quality of condensable vapors and gases, and feeding fresh oil to the first still and passing oil successively from one still to the next; and such further objects, advantages and capabilities as will later more fully appear.

In order to more fully understand our invention, reference is had to the accompanying drawing in which is illustrated in perspective a battery of four pressure stills, in which is omitted feed pumps, furnaces, storing tanks, condensers, service pipe lines, etc., which are only accessory devices of pressure stills, their operation and purpose being well known to those skilled in the art.

In the drawings, it will be seen that the apparatus for carrying out our improved method comprises a battery of pressure stills designated at A, B, C, and D, (there being preferably four in number), each still being of the type fully disclosed in United States Letters Patent No. 1,226,526 and 1,247,883. The construction of these stills will not be gone into in detail, but sufficient for the present application it is stated that they consist of the main barrel or drum 1, the forward drum 2, and the rear drum 3, the latter of which is connected to the main barrel 1 by means of the leg 4, and the former of which is connected to the barrel 1 by means of the connecting neck 5. The drums 2 and 3 are in communication with each other by means of the upwardly inclined circulating tubes 6. Mounted within the leg 4 is the mechanical circulating device indicated generally at 7, the function of which is to create a positive circulation throughout the barrel 1, the drums 2 and 3, the connecting legs 4 and 5, and the tubes 6. In order to remove the condensable gases and vapors from the barrels 1, there is provided the adjustable artificially cooled vapor take-off indicated generally at 8. 9 indicates the nozzle for charging fresh oil into the drum 3, while 10 designates the overflow nozzle through which the oil may be conducted from the barrel 1 to the drum 3 of the next succeeding still, 11 designating the nozzle in the next succeeding still, through which the oil enters the drum 3. Each of the respective stills has the same constructive features, and hence it is sufficient to describe only one thereof. For the further details of the construction of these stills, reference is had to the United States patents cited above. It is, however, here further stated that we, if desired, may provide the by-passes or pipes 12, through which oil may be conducted to a receiver pending the time that it is to be injected into the next succeeding drum 3. In order that any of the stills may be cut out of action for the purpose of repairs and the like, without interrupting the operation of the remaining stills, there are provided the pipes 13 connecting the out-

flow pipe from one still to the inflow pipe to the next alternate still; it being understood, of course, that suitable valves will be arranged in these pipes to make possible the transfer of oil from one to the other, as desired.

In the present state of the art of pressure distillation, the pressure stills are charged with a certain number of barrels of heavy oil to a certain level. After charging a still, the oil is heated to temperature of 600 degrees Fahrenheit and upwards, depending on the quality of the oils used in the stills, and by throttling the vapor outlet of such stills a pressure is built up in the still, by the oil vapor. The resulting vapors are condensed in suitable manner known in the refining of oils and yield a product which is termed as pressure distillate. This pressure distillate contains a greater or less percentage of gasoline and undecomposed or partially decomposed constituents of the original heavy oil charged to the still. The pressure distillate is then subjected to treatment with chemicals as sulphuric acid and sodium hydroxide, and subjected to a fractional distillation with the aid of steam. All these operations are carried on in the manner of routine crude oil refining, therefore a detail discussion of the same is omitted.

As the distillation of the charge progresses, the quantity of oil in the pressure still diminishes, and the quality of the remaining oil rapidly deteriorates, being reduced to the point where the oil suddenly decomposes into carbon or coke and fixed gases; the yield of gasoline decreasing in the overhead pressure distillate.

This point is generally reached after sixty percent of the charged oil is distilled under pressure; then it becomes necessary to remove the residue which is known as "still bottoms," which amounts to approximately thirty-five percent of the charged oil, the difference of five percent representing the losses of the operation in fixed gases.

The inside of the stills, especially on the surfaces exposed to the greatest heat of the furnace, will contain carbonized oil and hard coke baked onto the steel plates, notwithstanding the use of very ingenious devices inside of the still to scrape the walls during the distillation of only sixty percent of the original oil charged; after which it becomes necessary to clean the "still" before starting another "batch" run. To avoid coke, excessive cleaning and delays of the above method, we carry out the pressure distillation of heavy fractions of crude oil in pressure stills, such as shown in the accompanying drawing and described in United States Letters Patent referred to above.

In the present specification and claims the term "gravity" refers to "specific gravity" unless otherwise qualified.

In the pressure "stills," operated in the batch system, the run is finished after the amount of the charge is reduced to a percentage which is practical for a given pressure "still" and process, and the gravity of the pressure "still" bottoms gradually increased, while the pressures and temperatures must be changed from the beginning of the distillation to the finish of the run. In order to keep away from a gradual decrease of the gasoline percentage in the pressure distillate, our pressure distillation, conducted in accordance with the present invention, consists in successive reduction of the heavy oils, using preferably four pressure stills in series, continuously charging the battery with fresh oil and continuously removing that part of the heavy oil from the battery which is not apt to give the desired good results.

We accomplish the destructive distillation of fractions of crude oil, heavier than gasoline, in successive stages and carry it to a point where the residuum of any fractions of the crude oil, heavier than gasoline, will be changed into a product similar to the heaviest fraction of crude oil made in the routine manufacturing of, e. g. fuel oil, and will say that this end product has a specific gravity corresponding from 10 to 20 Baumé degrees, a flash point in an open cup tester 275 degrees Fahrenheit or above; a cold test 40 degrees Fahrenheit or below. It should be understood that our method does not limit as an end product a fuel oil exactly as the above specifications, because such a fuel oil subjected to suitable pressures and temperatures will yield a certain amount of gasoline and a heavier residuum than 10 to 20 Baumé degrees, and the question of the quality of this residuum fuel oil of the process should be determined by the conditions of the demand for certain qualities and quantities of such a residual fuel oil as the remainder of the pressure distillation of the heavy crude oil fractions.

In the operation of a battery of continuous pressure "stills" in accordance with our invention, we charge the units of the battery with a heavy crude oil fraction, say having a boiling point 550 degrees Fahrenheit and a gravity 34 degrees Baumé. After the "stills" are brought to 700 degrees Fahrenheit and 135 pounds pressure, the releasing of the vapors into the condenser box, connected with the stills, begins and pressure distillate of 50 degrees Baumé gravity, with 75% gasoline conversion, is received at the end of the coil (not shown in drawing). At this point the gravity of the oil, which is in the pressure "still" and kept in constant circulation with the mechanical circulator 7 is about 28 to 29 Baumé degrees. Then we start to feed into the first pressure "still" fresh, preferably preheated 34 degrees

Baumé gravity oil, (if we started with the same kind oil) through the nozzle 9 from a storage which is not shown in the drawing. Neither have we shown the pump which accomplishes this feeding, nor the preheater since these parts are commonly known to those versed in the art. At the same time we remove from the bottom of the still through nozzle 10, such an amount that the gravity of the liquid contents of the first still shall be kept constantly at a gravity of 28 to 29 degrees Baumé. The outflowing oil removed from the liquid of the still can be conducted into a receiving tank (not shown) through a pipe line, suitable valves being inserted into the pipe line between nozzles 10 of the first and second still up to the time when the liquid content of the second still rises to a specific gravity corresponding to say 25 or 26 degrees Baumé.

At this time we change the direction of the outgoing oil from the first still into the feed nozzle 11 of the second still, and simultaneously remove such a quantity from the liquid content of the second still that its gravity shall be kept constantly between say 25 to 26 Baumé, with the 28 to 29 Baumé oil coming from the first still. The outgoing 25 to 26 Baumé degree oil from the second still is forwarded through the by-pass to a receiver till the liquid content of the third still of the battery is reduced to a gravity say 20 to 22 Baumé degrees. The same operation is repeated on the fourth "still" which has been reduced to a gravity of 16 to 17 degrees Baumé and kept constantly at this gravity with the overflowing 20 to 22 gravity bottoms of the third still. The heavy crude oil fraction which entered the battery at a gravity say 34 Baumé is therefore successively forwarded to the last still of the battery and its specific gravity successively is increased during this passage. The volume of the fresh oil passing from one still to the other is also reduced, certain percentage of pressure distillate being made from it in each still and removed as overhead distillate, until finally the last remainder of the oil is so heavy in gravity on account of chemical changes that it cannot be used to advantage in the process. This part of the oil is continuously removed from the battery. Usually there is about 20 to 30 percent of the original volume of heavy crude oil fraction left as such a residium,—in some cases less than this amount, depending upon the physical and chemical properties of the original heavy crude oil fraction.

If the first member of the battery of stills gave the highest conversion of gasoline at 700 degrees Fahrenheit from a 34 Baumé gravity gas oil, the next following still in which the residual oil of the first still was kept at 26 to 28 Baumé gravity, required only 685 degrees Fahrenheit temperature in the oil in the still to give an equally high conversion of gasoline from the 26–28 Baumé residuum; with the next reduction of gravity to 24 Baumé there was only 670 degrees Fahrenheit heat required to reach a conversion of this residuum equal to any of the preceding stills, having a lower gravity residual oil.

The yield of gasoline is very sensitive to temperature changes and with increasing gravities of gas oil or fuel oil decreasing temperatures are necessary to maintain a uniform yield of gasoline and to keep the amount of by-products of the chemical reaction, such as permanent gases and coke forming carbonaceous matters, down to the the minimum.

From the first still to the last still of the continuous battery the oil is heated under pressure in the stills of the series and circulates at high velocities such as 200 feet per minute and upward in the heated tubes 6, the front connecting neck 5, the longitudinal barrel 1, and the rear connecting leg 4, which is connected with the rear transverse drum 3. This circulation of the oil in each still of the series keeps the chemically precipitated carbon particles in suspension and prevents the coking of the oil in the tubes, distributes the heat transmitted to the oil in the entire body of the oil enclosed in the still, even in the last still where the highest concentration of the suspended carbonaceous matter occurs. This end product of the battery carries away all the carbon precipitated during the pressure distillation, the mechanical circulation prevents the deposition of these carbon particles on to the tubes or other surfaces, hence the explanation of the long time period of running of such a continuous battery of pressure stills without cleaning. Furthermore the bottoms of the stills overflowing from one to the other are at high temperatures when entering the next still, hence a great saving of fuel compared with the batch run pressure stills.

During the operation the gravities, after once adjusted in the single stills, are under easy control, through regulation of the feed oil for still number one. While the temperatures and pressures for each successive still in a continuous battery are decreasing, yet as the gravities of the still bottoms are constant for each still during the operation, the temperature and pressures are constant also for each still. In consequence of the constant gravities, temperatures, and pressures for each still during the continuous run, the overhead pressure distillate is of uniform quality and quantity for each still. We do not wish to limit our method of adjusting the gravities in the continuous destructive distillation of fraction of crude oil heavier

than gasoline to the above illustrated case, but the difference between each successive member of the battery could be greater or less than 3 to 4 degrees Baumé; yet we have found this proportion to give good results in practicing this method on an industrial scale. In this case there is generally 5 to 8 pounds pressure difference between each member of the series, accomplishing the flow of oil from one still to the other if there is no oil level difference applied between the stills to promote the flow of oil from one still to the other, also a temperature difference from 20 to 40 degrees Fahrenheit between the successive members of the battery.

From all stills the vapors are released through a valve and are taken up through the adjustable vapor takeoff as it is described in the United States Letters Patent No. 1,226,526 and No. 1,247,883, at a point most conducive to the removal of the most condensable vapors. Each still has its own circulating propeller mechanism driving the oil enclosed in the stills through the heated tubes at proper velocities.

In practical application of this process we have found that one pressure still in batch running gave a return of 35 percent gasoline from the pressure distillate collected from the still. We found also that this pressure distillate is such high grade material that it does not require a treatment with chemicals as is necessary for other pressure distillates, but a fractional distillation with the aid of steam gives a good grade gasoline, free of bad odor and color. We found that a certain still of certain dimension was able to handle 250 barrels of 34 Baumé gas oil before the tubes needed cleaning in batch running, while in a series of stills in accordance with the present invention, the same stills gave a capacity ten times larger for the same time period of run and needed but a slight cleaning. In a battery we prefer to have by-passes, illustrated at 13, between the stills so that each still might be taken out from the series for cleaning and repairs, while the others not needing such are under heat and pressure.

Having now described our invention, we claim:—

1. The method of continuous destructive distillation of fractions of crude oil, which consists in supplying oil to a plurality of pressure stills in a series, heating said stills, removing gases and vapors from each of said stills, feeding fresh oil into the first still when the gravity of the oil being treated therein has increased to a predetermined gravity, withdrawing from said first still some of the oil being treated therein, and then after the gravity of the oil in the second still has increased to a predetermined gravity higher than that of the first still adding to the second still oil removed from the first still so as to maintain the gravity substantially constant in the individual stills, but each higher than in the preceding still.

2. The method of continuous destructive distillation of fractions of crude oil which consists in supplying oil to the first of a plurality of pressure stills in a series, and successively passing the remaining oil from each still to the next still, successively increasing the gravities in the respective stills of the series constantly during the run, to the gravity where the resulting fuel oil does not give the desired amount of gasoline, continuously removing this fuel oil from the series of stills, and maintaining substantially constant the oil gravities of the idividual stills with oil selectively fed thereinto from the next preceding still.

3. The method of continuous destructive distillation of fractions of crude oil, which consists in supplying oil to a plurality of pressure stills in a series, maintaining the oil in said stills under pressure so that the pressure in each succeeding still is less than that in the preceding still, and maintaining the gravity of the oil and the temperature and pressure substantially constant in the individual stills.

4. The method of continuous destructive distillation of fractions of crude oil, which consists in supplying oil to a plurality of pressure stills in a series, drawing off overhead pressure distillate until the gravity of the oil in the various stills rises to predetermined amounts which successively increase in value in the respective stills, maintaining the gravity of the oil in the first still substantially constant by adding fresh oil, and maintaining the successively higher gravities of the remaining stills substantially constant by adding to each thereof oil of a lower gravity taken from the next preceding still.

5. The method of continuous destructive distillation of fractions of crude oil, which consists in supplying oil to a plurality of pressure stills in a series, removing overhead pressure distillate from each still until the gravity of the remaining oil is increased to successively increased predetermined amounts in the several stills, and maintaining such increasing predetermined amounts substantially constant by adding to each still oil of a lower gravity taken from the next preceding still.

6. The method of continuous destructive distillation of fractions of crude oil, which consists in supplying oil to a plurality of pressure stills in a series, removing overhead pressure distillate from each still until the gravity of the remaining oil is increased to successively increasing predetermined amounts in the several stills, maintaining such increasing predetermined amounts substantially constant by adding to each still oil of a lower gravity taken from the next

preceding still, and withdrawing from the last still oil of a gravity so high as not to give a profitable yield of gasoline.

7. The method of continuous destructive distillation of fractions of crude oil, which consists in supplying oil to a plurality of pressure stills in a series, removing overhead pressure distillate until the gravity of the remaining oil is increased to successively higher predetermined amounts in the several stills, maintaining the gravity of the oil in the first still substantially constant by adding fresh oil thereto of lower gravity, maintaining the successively increasing gravities of remaining stills substantially constant in each still by adding thereto oil of a lower gravity from the next preceding still, and removing oil from the last still of a gravity so high as not to give a profitable yield of gasoline.

8. The method of continuous destructive distillation of fractions of crude oil, which consists in supplying oil to a plurality of pressure stills in a series, maintaining the gravity of the oil and the pressure and temperature substantially constant in each still, the gravity increasing but the temperature and pressure decreasing in value in the series of stills, the gravity in the last still being the highest and the temperature and pressure the lowest that will give a profitable yield of gasoline.

9. The method of continuous destructive distillation of fractions of crude oil, which consists in supplying oil to a plurality of pressure stills in a series, withdrawing overhead pressure distillate from each still until the gravity of the remaining oil in the first still is increased to a certain predetermined value, maintaining this value substantially constant by adding to the first still fresh oil and withdrawing therefrom a portion of said remaining oil, then as soon as the gravity of the oil in the next succeeding still is increased to a predetermined value greater than that of the oil in the first still, diverting the oil being drawn from the first still to cause it to flow into the second still and at the same time withdrawing some of the remaining oil from the second still, whereby to maintain the gravity of the oil in the second still substantially constant at said greater value than that in the preceding still, and continuing these steps throughout the remaining stills until the gravity of the oil in the last still is the greatest that will give a profiable yield of gasoline.

10. The method of continuous destructive distillations of fractions of crude oil, which consists in supplying oil to several pressure stills in a series, maintaining during the run, substantially constant gravities in each member of the series increasing successively in the series to the gravity where the resulting fuel oil does not give the desired amount of gasoline, continuously removing this fuel oil from the series of stills, and keeping down the oil gravities of the stills with fresh oil fed continuously to the stills.

11. The method of continuous destructive distillation of fractions of crude oil, which consists in supplying oil to several pressure stills in a battery, feeding fresh oil to the series of stills, mechanically circulating the contents of each still, passing the volume of the fresh oil charged to the battery of stills from one still to the other, continually increasing its gravity and decreasing its volume, removing the generated vapors and gases at a point most conducive to the separation of the most condensable gases and vapors from the stills, releasing the vapors and gases of each still into a condenser under atmospheric pressure, and removing continuously from the last still of the series that part of the oil which does not furnish the desired good quality and quantity of condensable vapors and gases.

In witness whereof, we hereunto subscribe our names to this application in the presence of a witness.

ULYSSES S. JENKINS.
STEPHEN SCHWARTZ.

Witness as to U. S. Jenkins:
C. B. STEWART.