

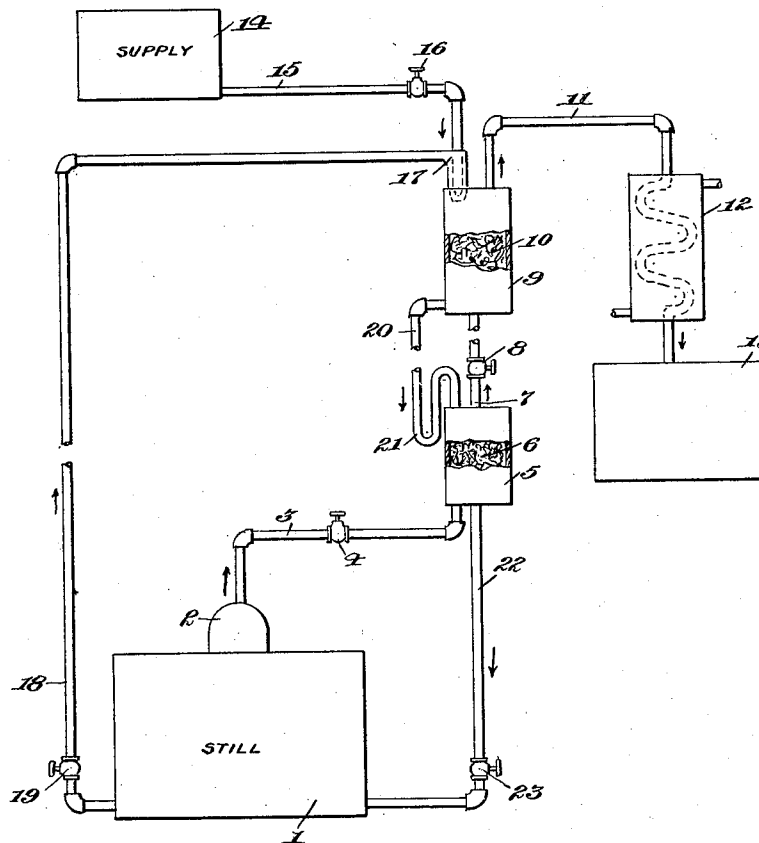
April 29, 1930.

A. SCHWARZ

1,756,887

OIL CRACKING PROCESS

Filed Feb. 25, 1924



Inventor:
Alfred Schwarz,

by

W. H. Weisman

Att'y.

UNITED STATES PATENT OFFICE

ALFRED SCHWARZ, OF MONTCLAIR, NEW JERSEY, ASSIGNOR TO PETROLEUM SAND PRODUCTS CORPORATION, A CORPORATION OF DELAWARE

OIL-CRACKING PROCESS

Application filed February 25, 1924. Serial No. 694,905.

My invention relates to the cracking of oils and more particularly has reference to a cracking process wherein oil in liquid state is maintained over an extended or enlarged area while in contacting relationship with oil vapors in order to insure maintenance of proper reacting conditions, all as more fully hereinafter set forth and as claimed. It has been common practice to distill oils under pressure, the result of the pressure being that certain oils which would vaporize at atmospheric pressure will be maintained in their liquid condition and in accordance with the amount of pressure employed, oils of lower boiling point can be kept in their liquid condition and their vaporization can be prevented at will. If a relatively light oil is to be contacted and caused to react with a relatively heavy oil, a certain pressure may be employed and certain results may be obtained. Since, however, the number of different hydrocarbon compounds present in an ordinary crude oil, fuel oil or the like, is very great, no one pressure or temperature condition can be adjusted to fit them all and while some of them will yield to treatment under a given set of conditions, others will either not disassociate at all or will disassociate into products undesirable as end products. When a certain temperature is reached suitable for the disassociation and reformation of compounds, the molecules of such compounds should be in contact with each other. If it so happens that under that particular temperature some of the hydrocarbons are in the liquid state and some of them are in the vapor state, then such contacting becomes more difficult and ordinary means such as reflux condensers and the like are not suitable to accomplish this result effectively.

It has been the practice heretofore in some of the cracking processes widely employed commercially to distill under pressure and also either partially or wholly condense under pressure and while the reasons for the results obtained in such methods are not fully understood, it has been found that maintaining the pressure through all or part of the condensation apparatus cannot in all cases cause the proper reaction, because if two molecules, say for example—one of fixed gas and the other one of a heavy oil, are intended to combine, the total amount of energy or heat temporarily held by those molecules may be too much for the formation of the new molecules of a desired class. Therefore, heat must be removed and a new set of conditions is evidently required. This may be accomplished by reducing the temperature and reducing the pressure. In reducing the pressure, however, some of the compounds which may be desired to react with other compounds will assume the vapor state and contacting becomes difficult on account of the large volume of vapor compared with the relatively small volume of oil. It, therefore, becomes important to expose large surface areas of the liquid oil to the vapors so formed in order to give opportunity for contacting. To a limited extent such contacting has been achieved in the old processes by running the oil which is condensed in what is known as the "reflux towers" over shelves or blades, but the relative amount of area so exposed is insufficient to effect the contacting of liquid and vapors as contemplated by the present process.

According to my invention, I use steel borings, steel wool or similar material having finely divided surfaces which become coated with the reflux oil and I provide through this means the large areas required. In a tower provided with shelves such as is used at present, I can, by removing the shelves and replacing them with steel borings, increase the contact area between oil and vapor several hundred times. I distill under pressure of, for example,—one hundred pounds per square inch and at cracking temperature, and in this manner I obtain

cracking as is well known in the prior art. Thereafter I release the vapors, however, and pass them over a body of steel borings or the like and I may decrease the pressure and temperature to any desirable degree, that being a matter of practice which is developed in accordance with the oil treated, but by releasing the pressure at the proper time, new conditions are created and by providing the steel borings, I furnish enlarged surface areas for the oil immediately as it condenses and at the prevailing temperature the oil is exposed to the action of vapors passing over the same and, therefore, I create in this manner a condition of constantly varying temperature and pressure, vapor and liquid stages, etc. That is to say, the operating conditions are different from those maintained in the still and further variations occur as the hydrocarbons pass through the enlarged surface areas. Such a treatment will enable the molecules to find a proper condition under which they may react with other molecules and the borings provide the means for physical contact between liquid oil and oil vapor.

Though cracking and distillation of an oil might be simultaneous operations, the cracking should be distinguished from the distillation in that the cracking operation is a distinctly chemical reaction while distillation comprises only the physical separation of already existing compounds from each other. The conditions of operations are therefore different. Oil distillation is accomplished as soon as an oil reaches its boiling point and the vapor leaves the liquid. The separated vapors may be immediately cooled, and the operation is accomplished. But in cracking, the temperatures are raised to a point where the molecules become unstable and ready to either break into small fractions, or where the unstable molecules are enlarged by taking up other molecules or fractions thereof. The boiling point has no direct influence on the reactions taking place but when reactions are desired between liquids and vapor, the greater rarefaction of the vapor must be considered. The time factor in distillation is that time in which a given amount of oil is brought to its boiling point and vaporized, while the time factor in cracking is that time which is required to bring the oil to the temperature of instability of its molecules and the formation of contacts between the resultant unstable molecules with other unstable molecules which are essential for the formation of predetermined compounds. The fact that the oil at the temperature of instability is either in its vapor form or in its liquid form has no direct bearing upon the ability of forming new compounds, but contact is established more easily between liquids and liquids than between vapors and liquids, hence the general tendency to distill

under pressure so that the oils may be maintained in their liquid state.

It is immaterial in distillation whether the temperature is maintained after the vapor is formed because the operation is completed when vapor is formed and the only time necessary is for the physical transportation of the vapor from the still to the condenser. In a cracking operation, however, the temperature should be maintained and adjusted until reaction between the desired portions of the oil has taken place. Otherwise, the heat consumed to bring the molecules to the critical stage of instability is wasted. To merely bring the oil to the temperature of instability is insufficient. To perform a new formation of compounds it is necessary that a given oil should also be contacted with other oils either in the liquid or vapor state. In order to obtain the reaction, therefore, the time required to pass an unstable molecule into contact with another unstable molecule for the two to react is the essential factor in reformation. Since no data is available as a guide in establishing proper temperatures of instability and proper combination of the different molecules, the best that can be done is to give ample opportunity for each molecule to contact with another molecule desirable for combination therewith at a temperature suitable for reaction between the two. This means maintaining each temperature step long enough for each group of molecules capable of reacting at such temperatures to contact with another group of molecules, then changing the temperature to the reaction temperature best suited for another group of molecules, and so on until the desired reactions have been effected.

In further explanation of the above, it must be borne in mind that a molecule may become unstable at a given temperature. Another molecule also unstable at the same temperature may be present and new compounds are formed, whereas if the original molecule had no available affinities within the range of its contacting area, it would return from its unstable condition as the temperature is reduced, back to its stable condition without change. It is very probable that the temperature of instability of a given molecule and its ability to combine with other unstable molecules is far below the temperature of simple cracking. By this temperature of simple cracking I mean the temperature at which a molecule breaks up into smaller fractions without inter-reaction with another molecule.

It can be very readily conceived that when, as is the case in some of the present cracking methods, the pressure is maintained during condensation, some new compounds are formed but in view of the fact that gravitation begins to occur as soon as condensation takes place, the condensed oil will descend and collect into a common pool while the va-

por will rise and collect into a common vapor body so that contacting between liquid oils and vapors still capable of reacting becomes impossible due to the lack of physical contact or, in other words, opportunity for reaction is lacking although the temperature condition may yet be favorable. On the other hand by filling the towers with steel borings or similar sustaining means, the force of gravity is counteracted and opportunity for contacting between vapors and liquids may take place readily.

From the foregoing it appears that in order to form a hydrocarbon compound of a certain predetermined character from other hydrocarbon compounds of a character not suitable for the intended purpose, it is necessary to supply at the moment of formation, the exact chemical balance between hydrogen and carbon which must later on appear in the end product, but in addition thereto the exact formation or cracking temperature is necessary. In a conglomeration of hydrocarbons such as is the case in the oil to be cracked, no one temperature would suit all the compounds available for recombination and it becomes necessary therefore to subject the entire, combination of hydrocarbons to constantly changing temperatures, changing both upward and downward, and to create constantly new physical contacts between molecules.

In carrying out my invention, I distill the oil under pressure as is customary in cracking operations, but instead of passing the vapors through a system of towers as is done at present, under pressure, gradually cooling the same and returning the heavy ends by gravity to the still, thus segregating the lighter ends in their vapor form from the condensed heavier ends, I release the vapors after they leave the still into one or more chambers, which chambers are provided with a multitude of surfaces, such as for example, steel borings, wire netting, or similar substances calculated to provide large surface areas for the heavy oil to condense upon and be held in suspension, thus providing passage for the vapors between and in contact with the oil surfaces to cause chemical reaction. To establish different temperatures and different pressure conditions, I may use a series of tanks or towers and expand the vapors from their initial pressure condition in one or more steps to a lower pressure or to atmospheric pressure, or I may even rarify the said vapors by use of sub-atmospheric pressure. The tanks or towers may be provided with suitable cooling means, either air or water cooling, and I may provide also means such as pumps or injectors and the like to force the reflux oils from lower pressure zone back into a higher pressure zone. I may also provide means for circulating the fresh oil charged to the system through the towers and over the borings and I may also provide

means for circulating part of the heavy liquid oil under treatment in the still through the towers and over the borings.

The invention may be carried out, for example, in the arrangement of apparatus illustrated somewhat diagrammatically in the accompanying drawing. In the drawing reference character 1 indicates a still which may be heated in any known manner. This still is provided with a vapor dome 2 from which a vapor pipe 3, provided with a pressure reducing valve 4, leads to a tank or partial condenser 5 that contains steel borings, steel wool or the like, 6. Vapor outlet pipe 7 leads from the tank 5 through a pressure reducing valve 8, to the tank or partial condenser 9 which also contains steel borings, steel wool or the like, 10. A vapor pipe 11 leads from the tank 9 to the coil condenser 12 and an outlet extends from the lower end of the coil of this condenser to the storage tank 13.

A supply tank 14 for crude oil having feed pipe 15 provided with a valve 16 leads to the conventionally shown spray device or nozzle 17 at the top of the tank 9. A pipe 18 provided with a valve 19 leads from the bottom of the tank 1 through the spray 17.

A return pipe 20 for condensed oils, provided with a trap 21, leads from the bottom of tank 9 to the top of tank 5. A pipe 22 provided with a valve 23 leads from the bottom of tank 5 to the still 1 for return of reflux condensate to the still. If the column of oil in pipe 22 is not of sufficient height to force the condensate into the still, a suitable pump (not shown) may be provided in the line 22.

The operation is as follows:

The oil to be distilled and cracked is introduced into the still 1 and heated to a cracking temperature of 700° F. to 900° F., more or less, and the pressure reducing valve 4 is so set that the pressure of the vapors in the still may reach about one hundred pounds per square inch, whereupon the vapors under reduced pressure enter the bottom of tank 5 through pipe 3 and are in part condensed, the condensed oils spreading upon, and being very minutely subdivided by the steel wool or borings 6, thus obtaining intimate contact between the remaining uncondensed vapors and the condensed oils. The temperature in tower 5 may be maintained between 500° F. and 750° F., more or less, depending on the oil being processed. The condensed oils trickle downwardly and reach the pipe 22 through which they are led back into the still 1 for redistillation. The pressure in tank 5 may be maintained at about thirty pounds per square inch by means of the pressure reducing valve 8, whereupon the vapors again reduced in pressure pass through the pipe 7 into the tank 9 where they are again partially condensed in a similar manner, the reflux oils passing back through the pipe 20 which

is long enough to contain a column of liquid sufficiently high to compensate for the difference in pressures in the tanks 9 and 5. A temperature ranging between 350° F. and 500° F. may be maintained in tower 9, the temperature varying with the boiling point of the ultimate product desired to be condensed in the final condenser 12. The uncondensed vapors or gasoline products pass out through the pipe 11 and are condensed in the condenser 12 and received in the storage tank 13.

Fresh oils are introduced through the pipe 15 from the supply tank 14 and are sprayed over the steel wool in tank 9 and at the same time the heavy residues from the still 1 may be forced by the pressure therein through the pipe 18 and spray 17 into the top of the tank 9 so as to assure intimate contact of vapors and oils, thereby causing the desired reactions to take place and form light boiling oils.

It is, of course, understood that in expanding the oil into its vapor state, such as is the case when the vapors are meeting the inflowing oils, heat is transferred to certain fractions of the oils taking the form of latent heat of vaporization and this in itself forms a cooling means. At the same time entirely new physical arrangements of the different fractions of the oils in relation to each other are made, violent disturbances take place and constantly changing contacting conditions are established.

It is to be understood that any number of combinations of different stages of pressure and temperature can be arranged, that is to say, pressure can be released directly to atmospheric, or can be released in any number of stages until atmospheric conditions are reached but it is not believed necessary to describe more than one form of the invention in order to demonstrate the principle involved. One of the essentials of the process is that appropriate surface area of the liquid is exposed to the vapors formed during the process. I am aware that steel shelves and other means to extend the liquid area exposed have been used heretofore but the relative area of liquid exposed to the vapors was always insufficient and my invention rests partially in the fact that I have recognized that the ideal condition for a cracking operation of this type exists only when there is a sufficiently extensive passage of the vapors over liquid areas to afford sufficient contacts of the vapors with the liquid. In the prior art there is nowhere shown sufficient area of liquid surfaces exposed to cause more than a small amount of the required contacting to take place. It is very desirable to have a unit weight of liquid so divided that its surfaces are exposed to the surfaces of an equal weight of vapor, which condition is best approached by minute subdivision of one of the components in the other.

I claim:

1. The process of producing lower boiling oils from higher boiling oils which comprises distilling the latter at a cracking temperature and under superatmospheric pressure in a cracking zone, passing vapors from said zone under successively decreasing pressures upwardly through successive masses of subdivided solid particles, condensing a portion of the vapors in said masses whereby the condensate is held therein in minutely subdivided form over an extended area, causing the condensate in each mass to move downwardly in counter current to the ascending vapors, and passing further quantities of vapors from said cracking zone under successively decreasing pressures upwardly through said successive masses for intimate contact with the condensates.

2. The process of producing lower boiling oils from higher boiling oils which comprises distilling the latter at a cracking temperature and under superatmospheric pressure in a cracking zone, passing vapors from said zone under successively decreasing pressures into successive masses of subdivided solid particles, condensing a portion of the vapors in said masses whereby the condensate is held therein in minutely subdivided form over an extended area, passing further quantities of vapors from said cracking zone under successively decreasing pressures into said successive masses for intimate contact with said condensate, replenishing the oil in said cracking zone by introducing higher boiling oils into the last of said successive masses, and causing the same to flow through said masses in contact with vapors therein to said cracking zone.

3. The process of producing lower boiling oils from higher boiling oils which comprises distilling the latter at a cracking temperature and under superatmospheric pressure in a cracking zone, removing vapors from said zone, reducing the pressure on said vapors and passing the same under the reduced pressure into a mass of subdivided solid particles, condensing a portion of said vapors in said mass whereby the condensate is held therein in minutely subdivided form over an extended area, passing further quantities of vapors from said cracking zone under reduced pressure into said mass for intimate contact with said condensate, and introducing into said mass of subdivided solid particles hot oil from the cracking zone for contact with the vapors therein.

4. The process of producing lower boiling oils from higher boiling oils which comprises distilling the latter at a cracking temperature and under superatmospheric pressure in a cracking zone, passing vapors from said zone under successively decreasing pressures into successive masses of subdivided solid particles, condensing a portion of the vapors in

said masses whereby the condensate is held therein in minutely subdivided form over an extended area, passing further quantities of vapors from said cracking zone under successively decreasing pressures into said successive masses for intimate contact with said condensate, and passing hot oil from said cracking zone through said masses in counter current flow to the vapors passing there-through.

In testimony whereof I affix my signature.
ALFRED SCHWARZ.