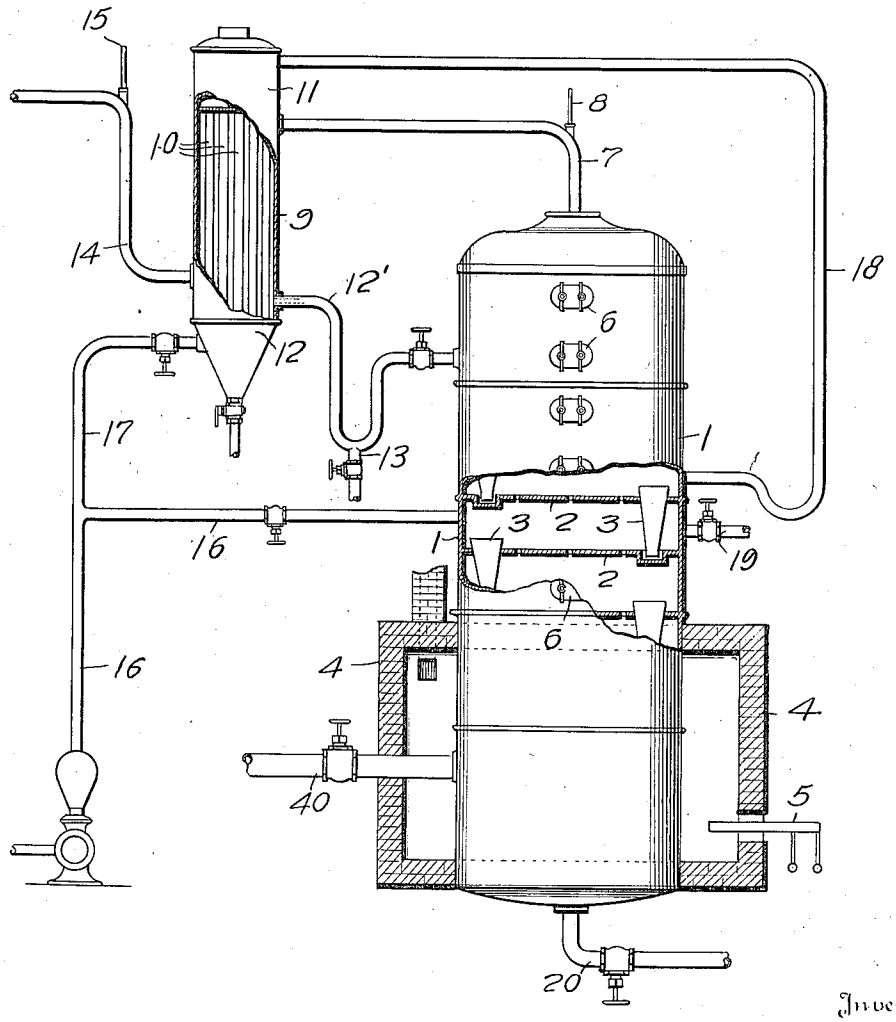
July 8, 1924. 1,501,014

A. McD. McAFEE

DISTILLATION WITH ALUMINUM CHLORIDE

Filed March 29, 1922



Inventor

A. M. McAFEE,

By K. P. McElroy

His Attorney

Patented July 8, 1924. 1,501,014

UNITED STATES PATENT OFFICE.

ALMER McD. McAFEE, OF PORT ARTHUR, TEXAS, ASSIGNOR TO GULF REFINING COMPANY, OF PITTSBURGH, PENNSYLVANIA, A CORPORATION OF TEXAS.

DISTILLATION WITH ALUMINUM CHLORIDE.

Application filed March 29, 1922. Serial No. 547,813.

To all whom it may concern:

Be it known that I, ALMER McDUFFIE McAFEE, a citizen of the United States, residing at Port Arthur, in the county of Jefferson and State of Texas, have invented certain new and useful Improvements in Distillation with Aluminum Chloride, of which the following is a specification.

This invention relates to distillation with aluminum chloride; and it comprises a process of distilling oil with aluminum chloride wherein distillation is performed in a column still having its base at a temperature considerably higher than the temperature at the top and provided with the usual heat economizer accessories used in column stills, the aluminum chloride being introduced into the still at a mid-point in its height and exhausted chloride, with or without substantial quantities of oil, being removed at or near the base, vapors of low boiling oils produced being removed at the top and a feed of oil being introduced at or near such top, the flow of oil so introduced being frequently substantially greater than the amount catalyzed in the column by the aluminum chloride with formation of vapors, the excess of oil in such cases being removed at the base together with exhausted, or nearly exhausted, aluminum chloride; and it further comprises certain apparatus useful in the performance of said process; all as more fully hereinafter set forth and as claimed.

In certain methods now in use for the production of gasoline, or of gasoline and kerosene, from higher boiling oils, a high boiling oil, as for example gas oil, is placed in a still, a small amount of aluminum chloride, often around 5 per cent, is added and the mixture is heated to the temperature of free ebullition under constant agitation. Chemical action of the aluminum chloride on the high boiling oil takes place with development of vapors of low boiling oils (gasoline) at a temperature which is often materially below the boiling point of the oil under treatment. In the case of a gas oil having an initial nominal boiling point of about 600° F., action often starts in at 475° and continues between 500 and 550° F. Practically all of the oil can be converted into low boiling oils with very little loss. The operation results not only in the production of volatile oils but causes certain advantageous changes in the oil undergoing conversion. The volatile oils produced are "saturated" in character, not tending to change or oxidize in storage and not requiring drastic treatment with sulfuric acid for purification. Similarly, the oil in the still, if the operation be interrupted before it is completely converted into oils of lower boiling point, and the aluminum chloride removed, is found to be of improved quality. In another and prior Patent, No. 1,127,465 of February 9, 1915, I have described and claimed a process wherein improvement of oil is effected in this way, a topped oil being distilled with aluminum chloride for a time to produce a certain amount of gasoline, or of gasoline and kerosene, the operation interrupted and the residual oil freed of aluminum chloride. This residual oil is of high grade and is particularly well adapted for use in making medicinal oil and lubricating oils of excellent quality.

In the manufacture of low boiling oils from higher boiling oils in such a conversion method, small amounts of anhydrous aluminum chloride are added to a body of oil in a still and the operation is conducted under vigorous agitation. The aluminum chloride does not dissolve in the whole body of oil to make a uniform solution, but melts down or combines with a portion of the oil to form a heavy liquid which is kept stirred up through, or emulsified in, the rest of the oil by agitation. Aluminum chloride is a volatile body and during the conversion a certain amount of it vaporizes, either as such or in the form of volatile combinations with oily hydrocarbons, and it is therefore usual to cool the vapors produced in the still down to about 350–300° F to condense and return vaporized aluminum chloride, prior to allowing the vapors of low boiling oils to go forward to the final or water cooled condensers. As the operation goes on, the heavy oily liquid in the still changes in character and becomes more and more viscous and tarry. With this change in character comes a diminution in activity. After a time, a sludge containing the spent chloride is removed from the still and sent to a recovery plant to regain active aluminum chloride, fresh aluminum chloride being then charged into the still. As alumi-

num chloride combines with hydrocarbons, this loss of activity may be due to its combination with asphaltic or tarry hydrocarbons to form relatively inactive bodies.

Operating in the way described, the operation is, or may be, continuous as regards the oil, the still being supplied with fresh oil in amount equivalent to the amount removed in vapors. But the operation is not uniform, vapor production in the still at any given time depending somewhat on the age of the charge of aluminum chloride present. As regards the aluminum chloride, the operation is more or less discontinuous.

It is the object of the present invention to provide a method of and means for continuous operation; the operation being continuous not only as regards the oil but as regards the aluminum chloride, and the distillation being made uniform. To this end, I take advantage of certain of the phenomena previously noted. The operation may be so conducted as to give a total, or nearly total, conversion of the oil under treatment to oils of lower boiling point (gasoline or gasoline and kerosene), or it may be so conducted as to convert any desired proportion of the oil into oils of lowered boiling point and give residual oils of improved quality (as in the acknowledged prior patent).

As stated, in the still during the operation some of the aluminum chloride volatilizes and must be condensed and returned to the body of oil in the still. This returned material, formed from volatilized chloride is always of high active nature; unlike that which finally occurs in the sludge, it is an energetic catalyst of the reactions here desired. In a way, it may be said that of the aluminum chloride charged into the still part is in circulation between the vapor and liquid phases and retains its activity, while part occurs in heavy oily combinations, which finally become an inactive sludge. Actually, of course, there is no such sharp distinction, since some of the chloride of the heavy oily liquid vaporizes and some of the returned chloride goes into the sludge and all the chloride ultimately occurs in the sludge. In the present invention, I arrange conditions so as to keep the chloride as far as possible in the active, vaporizable form. To this end, I supply my chloride at an intermediate point in a flow of oil of progressively increasing temperature. In so doing, the heavy oily combinations flow forward with the oil while the vapors formed go backward against the flow. With one end of the system too cool to permit aluminum chloride vapors to escape and the other end hot enough to strip the sludge of volatilizable active chloride as far as possible, it will be seen that the chloride is, to a large extent, kept in the middle of the system and in active form. In practice, I use a device of the type of an ordinary column still; that is, a vertical column provided with the usual crossplates or devices whereby the downward progress of the oil is as a series of boiling or bubbling transverse pools, vapors formed in the still going upward through these pools; and I introduce fresh aluminum chloride at a midpoint. A tower with a packing of coke, shaped clay dividing devices, rings, etc., may be used in lieu of the column, but I regard the latter as best adapted for my purposes. The top of the system is maintained at a temperature low enough to ensure condensation of aluminum chloride vapors and the base of the still is maintained at a relatively high temperature, 600° F. or higher, with of course intermediate gradations of temperature at intermediate points. The aluminum chloride introduced at such an intermediate point is liquefied by the oil and tends, as a liquid, to flow forward and downward with the oil, but its vapors tend to pass upward in countercurrent against the flow of oil. In so doing, as will be seen, aluminum chloride, in so far as it is in active volatile form, is kept in the middle portion of the system. The exit temperature of the vapors from the system is, as usual, kept around 300–350° F. Such aluminum chloride as reaches the base of the still is mainly in the inactive sludgy form and is there withdrawn, together with some, or much, of the oil. If the operation is conducted with the object of producing improved residual oil, the amount of the oil passing out at the base of the column with the exhausted aluminum chloride may be considerable. If it be not, the base of the column may be kept at a considerably higher temperature (such as is used in "tar stills" or coking stills) and in this event, the aluminum chloride reaching the base of the still is "recovered"; its combinations with tarry or asphaltic hydrocarbons are coked or broken up and the chloride liberated as vapor. This vapor ascends the column and takes part in the actions there going on.

The base of the column may be heated in any suitable way, as by placing it in a furnace chamber. This is convenient where high temperatures are required. In a modified form of my invention, heat may be supplied by hot vapors, thereby accomplishing certain additional results.

As is well known, oils may be "cracked" or destructively distilled by exposure to high temperatures with production of a certain amount of vapors of gasoline and kerosene. The condensed products, cracked gasoline and kerosene, are however not liked com-

merically because of their unstable, "unsaturated" nature. In another and prior Patent, No. 1,326,073, I have described and claimed a process of improving the quality of these products wherein the vapors from the cracking still are led through or over a bath of oil and aluminum chloride at a high temperature with the result of "saturating" the vapors of the gasoline and the kerosene, so that the condensed product is of higher grade. Sufficient high boiling oil condenses from the vapors to maintain the bath. As the operation goes on, these condensed oils are converted into lower boiling oil vapors by the aluminum chloride and these vapors join those passing through the bath.

As the vapors from a cracking still are usually at quite a high temperature, 700° F. or higher, they are well adapted for heating the still in the present process and they may be introduced into its base, passing upward in countercurrent against descending oil (and chloride). In so doing, the vapors of low boiling oils are, as in the patent, saturated and improved and join those made in the still from the oil fed thereto. Such high boiling oils as are condensed from the vapors may also be converted by the aluminum chloride, or, where the still is run to make a certain quantity of improved high boiling oil, they may join this. The condensed high boiling oils are improved in character by the aluminum chloride, their "cracked" nature being done away with.

In the accompanying illustration I have shown, mainly in elevation with certain parts in central vertical section, certain apparatus within the present invention and useful in the performance of the stated process.

In this showing, element 1 is a column still of the ordinary type; what is sometimes known as a "beer still." It may be made of iron or steel or other suitable metal. It is provided interiorly with the usual pool forming plates, here shown as perforated plates 2 with tubular connections 3 leading liquid from one plate to another. Around the base of the still it is heated as shown by fire chamber 4 provided with burners 5. All the heat, or some of it, may be supplied by leading in hot oil vapors by conduit 40 which may connect with a cracking still (not shown). Any other suitable method of heating to a high temperature may be used, that shown being merely illustrative. The column is provided with a series of manholes 6, these permitting cleaning. There may be a manhole opposite each plate to provide convenient access thereto. At the top, vapors pass through vapor conduit 7 provided with thermometer 8 to heat economizer 9. As shown, this is provided with tubes 10 passing between headers 11 and 12 forming a vapor space around the tubes. Any condensate formed in this vapor space passes out through trap outlet 12', which may be provided with valved draw-off 13 and which leads back to the still at a high point. Vapors not condensed in the economizer pass forward through conduit 14 provided with thermometer 15 to a suitable condenser (not shown). Oil is sent to the still through pipe 16. As shown, this pipe is valved and directly connected to the still at a middle point. There is another valved connection 17 leading oil into the base of the economizer to pass upward through the tubes therein and by conduit 18 to the still. Aluminum chloride is introduced into the still through valved pipe 19 at a midpoint, that is, a point intermediate the relatively cold top and the relatively hot base. It is best introduced with oil as a magma. At the base of the still is valved outlet 20 through which aluminum chloride sludge and oil may be withdrawn.

The apparatus illustrated and described may be used in various specific ways under the present invention. Presuming that it is employed in the manufacture of gasoline (or of gasoline and kerosene) from gas oil, the gas oil is introduced at 16 and a sufficient amount is sent through the economizer on its way to the still via pipes 17 and 18 to hold the temperature of the vapors emerging through 14, as shown by thermometer 15, at about 300° F. Aluminum chloride is introduced at 19 and acts upon the oil flowing down through the still and entering through pipes 16 and 18, either or both. Aluminum chloride vapors and light oil vapors rise in the still beyond the point of entry of 16 and 18 and are there fractionated, aluminum chloride being returned with downflowing condensates. In part, the aluminum chloride passes down through the still with the oil from 18 entering progressively hotter distilling zones. The tendency is for the vapors to pass upward. As the aluminum chloride-heavy oil combinations pass downward through the still, the aluminum chloride is constantly stripped therefrom, very little in the active form remaining with the oil and reaching 20. This gives an excellent utilization of aluminum chloride in the still. If it be desired to make kerosene as well as gasoline, the operation is managed by maintaining thermometer 8 at about 350° F. and thermometer 15 at about 300° F. and condensate from the economizer is taken off at outlet 13. This condensate will be mostly kerosene.

If the operation is to be so conducted as to give an improved residual oil, as described in the acknowledged patent, the operation is exactly the same, save that the flow of oil through the still is increased so as to have a substantial amount leaving the

system at 20, together with the exhausted sludge.

If heating be done in whole or in part by oil vapors entering at 40, the feed of oil through 16 and 18 may be diminished somewhat to correspond to the amount of oil so introduced.

In the column still, the oil travels downward as a series of successive transverse layers, each feeding the next-below and supplied by the next-above and each of a somewhat higher temperature than the next-above. Vaporization takes place from each layer, partly because of the catalytic action and partly by distillation, and this vaporization is aided by the vapors bubbling through the layer. These vapors include aluminum chloride coming from the hotter oil below; and in the vapor spaces between the transverse liquid layers, vapors of oil and of aluminum chloride have an opportunity to act on each other in the vapor phase.

The liquefied aluminum chloride traveling forward and downward with the oil is filmed out on the plates and a maximum opportunity for vaporization afforded. A sufficient area of contact between the chloride and the oil is thus effected without the use of stirring mechanism, as is a common practice in the conversion of petroleum oils with aluminum chloride. In the column for a time vapors of aluminum chloride and hot liquid oil travel in countercurrent.

The present invention may be employed with other more or less volatile catalysts, such as aluminum bromid, tin tetrachloride, titanium chloride, etc.

What I claim is:—

1. The process of distilling oils with aluminum chloride which comprises establishing and maintaining a vertical downwardly flowing current of oil through a zone of progressively increasing temperature and supplying aluminum chloride thereto at a midpoint.

2. The process of distilling oils with aluminum chloride which comprises establishing and maintaining a vertical downwardly flowing current of oil through a zone of progressively increasing temperature, the top of said zone being at a temperature sufficiently low to hold back vapors of aluminum chloride and the base at a temperature high enough to cause free vaporization of aluminum chloride, and supplying aluminum chloride to said current at a midpoint.

3. In the distillation of oils with aluminum chloride, the process which comprises establishing and maintaining a flow of oil against a countercurrent of aluminum chloride vapors, in a heated zone with temperatures progressively increasing in the direction of the flow of oil and supplying oil and aluminum chloride to said zone at a midpoint.

4. In the distillation of oils with aluminum chloride, the process which comprises leading oil downward through a column still with its base at a temperature of 600° F. or higher and its vapor outlet not above 350° F. and charging aluminum chloride into the downflowing oil at a midpoint.

5. In the catalysis of oils with aluminum chloride, the process which comprises passing aluminum chloride vapors upwardly through successive transverse layers of downwardly flowing hot oil.

6. In the catalyzed distillation of oil with aluminum chloride, the process which comprises passing liquid oil and aluminum chloride vapors in contact in countercurrent, in a heated zone with temperatures progressively increasing in the direction of the flow of oil and supplying oil and aluminum chloride to said zone at a midpoint, the amount of oil so supplied being greater than will be catalyzed to lower boiling oils by the action of said chloride.

7. In the distillation of oils with aluminum chloride, the process which comprises leading oil downward through a column still with its base at a high temperature and its vapor outlet not above 350° F., charging aluminum chloride into the downflowing oil at a midpoint and supplying oil vapors at the base to afford heat.

In testimony whereof, I have hereunto affixed my signature.

ALMER McD. McAFEE.