

July 21, 1942.

H. K. SUTHERLAND

2,290,654

AZEOTROPICAL DISTILLATION WITH ANTIMONY TRICHLORIDE

Filed Dec. 24, 1940

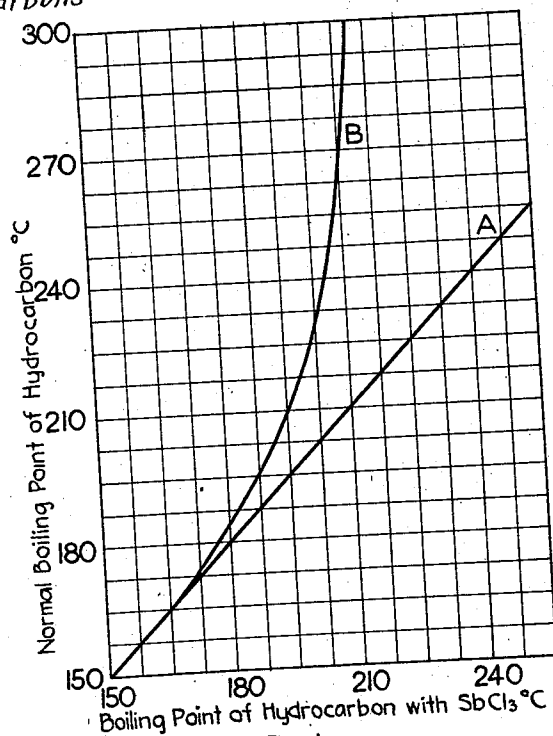
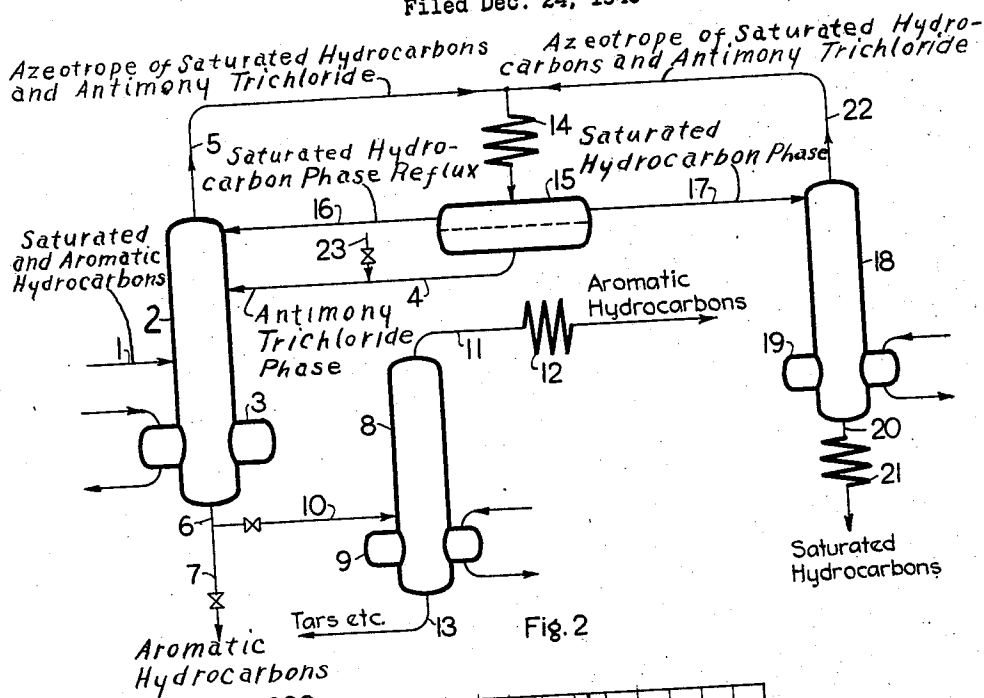


Fig. 1

Inventor: Harry Kennon Sutherland

By his Attorney: J. W. Russell

UNITED STATES PATENT OFFICE

2,290,654

AZEOTROPICAL DISTILLATION WITH
ANTIMONY TRICHLORIDE

Harry Kennon Sutherland, Berkeley, Calif., assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

Application December 24, 1940, Serial No. 371,468

9 Claims. (Cl. 202-42)

This invention relates to a process for the separation of aromatic hydrocarbons from saturated hydrocarbons. More particularly, it relates to a process whereby said hydrocarbons are separated by utilizing my discovery that saturated hydrocarbons form low boiling mixtures with antimony trichloride.

The primary sources of these hydrocarbon compounds are either petroleum or coal tar distillates, and since they always occur in admixture therein, their separation is a matter of considerable technical importance.

It is an object of my invention to produce hydrocarbon fractions of high paraffinicity and low aromaticity on the one hand, and of high aromaticity and low paraffinicity on the other hand, employing physical processes. It is a further object to prepare fractions of high aromaticity or paraffinicity by azeotropically distilling hydrocarbons from mixtures containing them with antimony trichloride. It is still another object to provide a process for the separation of aromatic and saturated hydrocarbons having substantially identical boiling temperatures.

I have found that narrow-boiling mixtures of aromatic and saturated hydrocarbons can be separated into their components which, under normal conditions, have vapor pressures so close to each other as to make separation by ordinary fractional distillation as a practical matter exceedingly difficult, if not impossible. My process comprises distilling such mixtures of saturated and aromatic hydrocarbons to be separated in the presence of antimony trichloride under conditions causing relatively low boiling mixtures of antimony trichloride and saturated hydrocarbons to be distilled overhead while the aromatic hydrocarbons remain behind.

By low boiling mixtures I mean mixtures of hydrocarbons and antimony trichloride that distill overhead at lower temperatures than are required to distill the hydrocarbons of the mixture in the absence of antimony trichloride.

I have discovered that antimony trichloride forms low boiling mixtures with saturated hydrocarbons, which mixtures boil at temperatures below the normal boiling temperature of the hydrocarbons. With aromatic hydrocarbons antimony trichloride apparently neither forms low boiling mixtures nor depresses their boiling points to any substantial degree. Thus the saturated hydrocarbons may be taken overhead together with the antimony trichloride while the aromatic hydrocarbons remain behind.

The amount of antimony trichloride employed

may be just that amount required to cause all of the non-aromatic hydrocarbons to be distilled overhead, although somewhat smaller amounts or even an excess may be used. An excess, if used, may accumulate in the bottom products. I prefer to employ such an amount of antimony trichloride that substantially none of it is withdrawn as liquid at the bottom of the distillation zone for two reasons: In the first place, aromatics are thus not kept in long contact with antimony trichloride, which is an active Friedel-Crafts catalyst; and the second reason is that substantially pure aromatics can be withdrawn from the distillation zone without necessitating further separation from the antimony trichloride as by distillation. Thus redistillation of the aromatic hydrocarbons may be required only when it is desired to remove slight amounts of color bodies sometimes produced. However, such colored bodies may frequently be removed by other methods, such as acid or clay treatment or both.

The amount of antimony trichloride necessary to form low boiling mixtures with the saturated hydrocarbons present in the column depends upon the particular hydrocarbon fraction under consideration. This amount is, of course, a function of the percent of saturated hydrocarbons in the feed as well as the boiling range of the feed. However, it may be said in general, the percentage of saturates being equal, that the higher boiling the fraction treated, the greater the quantity of antimony trichloride required.

The following examples are illustrative: A straight-run gasoline fraction, boiling between 190 and 202.8° C., which contained 83% saturated hydrocarbons and 17% aromatic hydrocarbons, required a feed rate of antimony trichloride equivalent to about 4% by volume of the hydrocarbon feed rate to form low boiling mixtures with all of the saturated hydrocarbons present. Another fraction containing 85% saturated hydrocarbons and 15% aromatic hydrocarbons, boiling between 235 and 239° C., required a quantity of antimony trichloride equivalent to about 28% of the feed by volume. While the above figures are typical examples of required amounts of antimony trichloride for definite mixtures of different boiling ranges, it is necessary to determine experimentally the optimum quantity of antimony trichloride required for any given hydrocarbon mixture. This is easily determined by continuously increasing the antimony trichloride admitted to the distillation column employed for separating aromatic and saturated hy-

drocarbons according to my process until it just begins to appear in the bottom product. A quantity of antimony trichloride just short of this amount is generally the optimum.

It appears probable that the low boiling mixtures formed between antimony trichloride and saturated hydrocarbons are azeotropic mixtures; however, I do not wish to limit my invention to the correctness of any theory regarding its mechanism, nor to operations wherein the composition of the distillate corresponds to the lowest boiling composition attainable with antimony trichloride and the particular hydrocarbons encountered.

My process is especially applicable to straight-run petroleum distillate fractions, which fractions normally contain only small amounts of unsaturated non-aromatic hydrocarbons, if any, but it is not necessarily limited thereto. It may also be applied to hydrocarbon mixtures of other origin such as coal tar distillates or cracked petroleum distillates. In the case of cracked materials it is advantageous first to remove unsaturated non-aromatic compounds such as olefins and diolefins, as for example by conventional sulphuric acid treatment, polymerization, and the like. It is preferable to pre-remove these olefins to prevent their polymerization, and the formation of tars and other undesirable contaminants when in contact with the antimony trichloride, when such polymerization is desired. In certain cases the presence of appreciable amounts of olefins under these conditions may result in the alkylation of aromatics, antimony trichloride being a Friedel-Crafts catalyst.

My process is particularly applicable to the separation of mixtures of aromatic and saturated hydrocarbons, at least a major portion of which boils above 175° C. but not above 350° C., and it is preferably applied to mixtures having initial boiling temperatures above 190° C. When applied to such fractions my process effects a clean separation between aromatic and saturated hydrocarbons with relatively low reflux and plate requirements.

It is desirable that mixtures to which my process is applied possess relatively narrow boiling ranges, otherwise separation may be hindered by the presence in the distillate of aromatics boiling at temperatures approximately the same as those of the low boiling mixtures of normally higher boiling saturates, if fractions of considerable breadth are treated. For complete separation, the permissible breadth of the fraction depends upon the particular fraction under consideration, as may be recognized from a consideration of Figure 1 of the drawing, which is a graph illustrating the relationship at substantially atmospheric pressure between the normal boiling point of saturated hydrocarbons and their boiling point with antimony trichloride, compared to the boiling points of aromatic hydrocarbons of the same boiling points, which, as far as is known, do not form azeotropes with antimony trichloride. The boiling points of the hydrocarbon with antimony trichloride are plotted as the abscissa, while the normal boiling points of the hydrocarbon are plotted as ordinates. Curve A applies to aromatic hydrocarbons, while curve B applies to saturated hydrocarbons. From Figure 1 it can be seen that the greater the spread between two corresponding points of the curves, the easier is the separation of hydrocarbons having the corresponding boiling temperature.

Figure 1, or similar graphs obtained at pres-

ures other than atmospheric, may be employed for determining maxima of boiling ranges of hydrocarbon mixtures, which maxima should not be exceeded for clean separation, as illustrated in the following examples:

Assuming that it be desired to separate a fraction boiling from 210 to 240° C. into saturated and aromatic hydrocarbons: Since the saturated hydrocarbons go overhead while the aromatic hydrocarbons remain in the column, the factor determining whether a given separation is practicable is the difference in the boiling point between the highest boiling saturated hydrocarbon and the lowest boiling aromatic hydrocarbon. The following table indicates values read from Figure 1:

	Without antimony trichloride	With antimony trichloride
Highest boiling saturate.....	240	207
Lowest boiling aromatic.....	210	210

It is evident that clean separation can be effected in this case if fractionation equipment is available permitting a separation of components boiling 3° C. apart, which is the difference in the boiling temperature between the highest boiling saturated hydrocarbon and the lowest boiling aromatic hydrocarbon.

The same general principles can be applied to determine if any given separation is practicable.

In operating my process, it is advantageous to remove from the distillation zone moisture and air, as the presence of these substances tends to catalyze tar formation, possibly due to the formation or presence of small quantities of olefins in the feeds. I have found that if olefins, moisture and air are excluded, any one of which may cause tar formation, this reaction is practically completely arrested and consequently it is possible to produce aromatics and saturates of a high degree of purity.

A preferred manner in which to carry out my process is illustrated in Figure 2 of the accompanying drawing, which figure represents a flow diagram showing the most important steps of my process.

A feed containing saturated and aromatic hydrocarbons, such, for example, as a straight-run gasoline boiling between 210 and 240° C., is continuously admitted via line 1 to a primary bubble tower or other suitable fractionation column 2 equipped with reboiler 3. The gasoline may be admitted either in the liquid or vapor phase. Just sufficient antimony trichloride to form low boiling mixtures with all of the saturated hydrocarbons in the column continuously enters column 2, via line 4. Temperatures in column 2 are controlled by means of reboiler 3 so that the antimony trichloride vaporizes and the paraffinic fraction of the gasoline is in the vapor state while the aromatic portion is liquid. Necessary amounts of heat input can be controlled most readily by observing the vapor temperature at the top of the column, which temperature should be about equal to or lower than the initial boiling temperature of the distillate; or else by analyzing the end products obtained from the column.

The low boiling mixtures formed between the saturated hydrocarbons and antimony trichloride are taken overhead, while aromatic hydrocarbons are withdrawn from the bottom of fractionating column 2, via line 6, whence they may be taken to storage, via line 7. However, it often is

desirable to redistill the aromatics which for this purpose may be admitted to redistillation column 8, equipped with reboiler 9, via lines 6 and 10. Vaporized aromatics are then taken overhead via line 11, passing on to condenser-cooler 12, thence to storage not shown, while unvaporized residue comprising high boiling tars, etc., is removed from column 8, via line 13.

The low-boiling mixtures pass from the top of fractionating column 2, via vapor line 5 to condenser-cooler 14, thence to separator 15. In separator 15 two phases separate, a heavier antimony trichloride-rich phase, and a lighter hydrocarbon-rich phase. The former is returned to the upper portion of column 2 through line 4. The hydrocarbon-rich phase may be divided into two portions, one returning to the top of column 2, via line 16, as reflux, and the other being fed via line 17 to fractionation column 18, equipped with reboiler 19.

The feed admitted to column 18 via line 17 contains saturated hydrocarbons in excess of the amount which can form low-boiling mixtures with the quantity of antimony trichloride present. This excess is withdrawn from the bottom of column 18, via line 20, through cooler 21 to storage not shown. The low-boiling mixtures which are formed in column 18 return overhead via line 22, and condenser-cooler 14, to separator 15. Ordinarily these vapors have the same composition as the low-boiling mixtures from column 2 and therefore behave in the same manner.

Occasionally it may be desirable to operate column 18 under different pressure or temperature conditions from those of column 2, thus influencing the composition of the vapors passing off the column 18. It then may be advantageous to condense and separate the vapors in a system independent of cooler 14 and separator 15. But even in this case the fundamental operation remains the same, the antimony trichloride-rich phase being returned to column 2, and a portion of the hydrocarbon-rich phase being conducted to column 18 as reflux. Antimony trichloride make-up is provided via line 23.

For simplicity, pumps, heat exchangers, bypasses, vents and other auxiliary equipment have not been shown in the drawing, the application of which will be evident at once to anyone skilled in the art.

Example

A fraction of a straight-run kerosene having a true distillation range of 230-236° C. and containing 16.8% aromatic hydrocarbons, was continuously fractionated in an apparatus similar to that illustrated in Figure 2. The main column corresponding to column 2 of the drawing was equivalent to 30 theoretical plates, while a second column corresponding to column 18 was equivalent to 10 theoretical plates. The hydrocarbon reflux ratio maintained in the main column was approximately 1:1, while the reflux ratio to the second column was approximately 5:1. Sufficient antimony trichloride was added initially to form azeotropes with all the saturated hydrocarbons present in the column according to the procedure suggested above. Operating this unit under these circumstances, the fraction withdrawn from the second column contained no antimony trichloride and less than 1% aromatic hydrocarbons, while the fraction withdrawn from the bottom of the first column contained only 3.7% by weight of saturated hydrocarbons.

I claim as my invention:

1. In a process for separating a mixture comprising aromatic and saturated hydrocarbons, at least a portion of which boils above 175° C., to produce two fractions, one of which is rich in saturated hydrocarbons and the other rich in aromatic hydrocarbons, the steps of distilling said mixture in the presence of an amount of antimony trichloride effective to improve said separation under conditions to form an overhead fraction containing antimony trichloride and a residual fraction.

2. In a process for separating a mixture comprising aromatic and saturated hydrocarbons, of which mixture at least a portion boils between 190° C. and 350° C., to produce two fractions, one of which is rich in saturated hydrocarbons and the other rich in aromatic hydrocarbons, the steps of distilling said mixture in the presence of an amount of antimony trichloride effective to improve said separation under conditions to form an overhead fraction containing antimony trichloride and a residual fraction.

3. In a process for separating saturated hydrocarbons from aromatic hydrocarbons and olefinic hydrocarbons in a mixture containing them, at least a portion of which mixture boils above 175° C., the steps comprising removing said olefinic hydrocarbons, distilling the remaining hydrocarbons in the presence of an amount of antimony trichloride effective to improve said separation under conditions to form an overhead fraction containing antimony trichloride and saturated hydrocarbons and a residual fraction containing aromatic hydrocarbons.

4. In a process for separating a hydrocarbon liquid comprising aromatic and saturated hydrocarbons, the initial boiling point of which is above 175° C., the steps of distilling said liquid in the presence of an amount of antimony trichloride effective to improve said separation under conditions to form an overhead fraction containing antimony trichloride and saturated hydrocarbons, and a residual fraction containing aromatic hydrocarbons, the boiling point of the lowest boiling aromatic hydrocarbon contained in said liquid being higher than the boiling point of the low-boiling mixtures formed between the highest boiling saturated hydrocarbons contained in said liquid and antimony trichloride.

5. A process for separating a mixture comprising aromatic and saturated hydrocarbons having an initial boiling point of at least 175° C., comprising the steps of admitting to a first distillation zone said mixture and an amount of antimony trichloride effective to improve said separation, withdrawing from the lower portion of said distillation zone a liquid fraction rich in aromatic hydrocarbons, withdrawing from the upper portion of said first zone a vapor fraction rich in saturated hydrocarbons and containing antimony trichloride, cooling said vapor fraction to effect its condensation and separation into two liquid phases, an upper predominantly hydrocarbon phase and a lower predominantly antimony trichloride phase, returning a part of said upper phase to the upper portion of said first distillation zone, introducing the remaining portion of said upper phase to a second distillation zone, returning said lower phase to said first distillation zone, withdrawing from the lower portion of said second distillation zone a liquid rich in saturated hydrocarbons, withdrawing a vapor consisting essentially of antimony trichloride and saturated hydrocarbons from the top of said sec-

ond distillation zone and cooling said vapors to effect their condensation and separation into two liquid phases, an upper predominantly saturated hydrocarbon phase and a lower predominantly antimony trichloride phase, said lower phase being returned to said first distillation zone for use in another cycle.

6. The process according to claim 1, wherein said process is operated continuously.

7. The process according to claim 1, wherein said fraction rich in aromatic hydrocarbons is separated from high-boiling impurities by a distillation step.

8. The process according to claim 1 wherein said antimony trichloride is employed in such an

amount that substantially all of it is taken overhead.

9. In a process for separating a hydrocarbon mixture at least a portion of which boils above 175° C., and which comprises aromatic and saturated hydrocarbons of approximately the same boiling temperatures, to produce two fractions, one of which is rich in saturated hydrocarbons and the other rich in aromatic hydrocarbons, the step of distilling said mixture in the presence of an amount of antimony trichloride effective to improve said separation under conditions to form an overhead fraction containing antimony trichloride and a residual fraction.

HARRY KENNON SUTHERLAND.