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2,428,467

TWO STAGE AZEOTROPIC DISTILLATION OF TOLUENE WITH METHANOL


Application June 4, 1941, Serial No. 396,532

6 Claims. (Cl. 202—42)

1. It has long been known that toluene is present in varying amounts in petroleum fractions of gasoline boiling point and particularly in those gasolines originating from vapor phase cracking or other high temperature cracking operations.

It has lately been discovered that the gasoline produced by the catalytic vapor phase cracking process known as the Houdry process and described in the patents of Eugene Houdry and associates is particularly rich in toluene.

According to a co-pending application, Serial No. 351,716, filed August 7, 1940, any aromatic hydrocarbon present in a petroleum fraction may be substantially wholly recovered, and in relatively high purity, by distilling, in the presence of a suitable azeotrope forming agent, a suitably selected cut of that petroleum fraction, which cut is substantially free of aromatic hydrocarbons of higher boiling point than the sought for aromatic hydrocarbon. A method of determining the cut point to be used in the fractionation for preparing such selected petroleum fraction is taught therein. It has been found, by examination of numerous types of commercial gasolines, including catalytically cracked, thermally cracked, and straight run gasolines, that a reasonably well fractionated petroleum fraction of about 245°F. end boiling point, (A. S. T. M.), contains substantially all of the toluene originally present, and substantially no higher boiling aromatic hydrocarbons, and that by azeotropic distillation of that 245°F. end boiling point fraction in the presence of methanol, yields of toluene of the order of 90% of the toluene present could be obtained, and the toluene so recovered would be of a relatively high purity, of the order of 90 or 95% to 98%. Reference above to "a reasonably well fractionated petroleum fraction of about 245°F. end boiling point (A. S. T. M.)." of course, means that the petroleum fraction had an end boiling point of 245°F. when measured according to testing specifications of the American Society for Testing Materials. Throughout this specification, the abbreviation A. S. T. M. should be taken to mean the same as the above, that is, that the tests or measurements referred to are taken according to the specifications of the American Society for Testing Materials.

This invention has for its object the provision of a process for this operation whereby the maximum economy of operation is obtainable, combined with a minimum loss of toluene and a minimum of operative steps. This object and other objects in part obvious and in part pointed out hereinafter are attained by the process here set forth.

To understand this process, reference is made to the drawings attached to this specification, Figure 1 of which shows in diagram form the basic process and Figure 2 of which shows a modification of one portion of the process.

Turning to Figure 1 we find gasoline containing, among other things, toluene, stored in tank 3, which is forwarded by pump 4 through heater 5 to fractionator 6, where, under reflux introduced at 7 and heat from reboiler 8 it is topped of that portion boiling between the initial boiling point and 200°F. (A. S. T. M.). The overhead distillate is removed by pipe 9 to pipe 10 and storage tank 11. The remaining topped gasoline is forwarded by pump 12 and pipe 13 to a second fractionator 14, where, under reflux introduced at 15 and heat from reboiler 16 a fraction corresponding to that boiling between 200°F. and 245°F. (A. S. T. M.) is removed as an overhead distillate. The bottoms product, that portion of the gasoline from 245°F. to end point (A. S. T. M.) is removed by pipe 17 and passes through pipe 18 to tank 11. The condensed overhead product of fractionator 14, comprising the 200°F. to 245°F. (A. S. T. M.) fraction of the gasoline is taken from receiver 18 by pump 19 and passed through pipe 20 and heater 21 to fractionator 22, where under reflux introduced at 23 and heat from reboiler 24 and overhead product comprising that portion of the gasoline between 260°F. and 215°F. (A. S. T. M.) is removed, to collect in receiver 25 and pass through pipe 26 and pipe 10 to tank 11. The bottoms product of fractionator 22, comprising the 215°F. to 245°F. (A. S. T. M.) cut of the original gasoline, withdrawn by pipe 27 is cooled by passage through heat exchanger 28 and cooler 29 to storage in tank 30 and comprises the toluene-containing feed for the azeotropic distillation step by the process.

In very many instances the preparation of the hydrocarbon mixture fed to the process may be much simplified. Non-azeotropic hydrocarbons lighter than those normally found in the 215-245°F. cut will, of course, readily distill therefrom, particularly in the presence of an azeotrope forming substance without carrying away toluene. Benzene, if present, will form with the azeotrope forming substance a constant boiling mixture sufficiently below any formed with toluene that it may be sent away along with the non-azeotropic materials. When large amounts of those materials lighter than about 215°F. A. S. T. M. end boiling point are present, they would preferably be separated as shown to avoid the imposition of their distillation and heat load upon the azeotropic distillation steps. On the other hand, many appropriate starting materials do not contain enough of these lower boiling materials to render their separate removal prior to the azeotropic distillation economical. In such instances the charge preparation may consist only of that step shown still 14 of Figure 1, wherein all of the original gasoline charge of
boiling point higher than that of a 245° end point (A.S.T.M.) gasoline is separated and discarded, the steps carried out in stills 6 and 22 of Figure 1, which are merely for the purpose of removing light ends, being omitted entirely.

The next step for the recovery of toluene in high purity is an azotropic distillation of the 245° F. end point (A. S. M.) cut in the presence of added methanol. This is practiced by passing the close cut gasoline fraction through pipe 39 and heater 41 into fractionator 32 in the presence of an added amount of methanol derived either from tank 33 and introduced by pipe 34 or derived from further process steps and introduced by pipe 35, or both. In fractionator 32, under the influence of reflux introduced at 36 and heat from the reboiler 37, the gasoline cut is separated into an overhead product comprising a large portion of the non-aromatic hydrocarbons and all of the added methanol, which passes through pipe 39 and condenser 38 to receiver 40, and a bottoms cut containing practically all of the toluene and some of the non-aromatics, which passes through pipe 41, cooler 42, tank 43, and pipe 44 to a second step of azotropic distillation. Cooler 42 and tank 43 are, of course, provided in a balanced continuous operation the bottoms cut from 32 may pass directly to the second distillation step. This second azotropic distillation step is accomplished in fractionator 45 under the influence of reflux introduced at 46 and heat from reboiler 41, in the presence of methanol added by pipe 48. The overhead product from this operation, comprising the non-aromatic hydrocarbons and the methanol passes through pipe 49 and condenser 50 to receiver 51. From each of the receivers 40 and 41, a sufficient amount of condensed product is withdrawn and returned as reflux to the respective tower at points 36 and 46, and the remaining overhead product condensate is combined, flowing through pipe 52 to be mixed with water entering through pipe 53, the whole then passing through pipe 54 into settler 55. The upper layer in 55 constituting discarded non-aromatic hydrocarbons is withdrawn through pipe 56 and returned through pipe 10 to tank 11, while the lower layer, methanol-water, passes through tank 57 and heater 58 into alcohol recovery distillation is shown, all portions prior to the placing of the 215-240° F. (A. S. T. M.) cut in tank 29 being the same and all portions beyond the "crude" toluene storage tank 58 being the same. This modification takes advantage of the discovery that water-methanol is an additive for azotropic distillation of better ability for this operation than methanol alone.

The closely cut gasoline passes from tank 29 through pipe 72 and heater 73 to fractionator 74 being first mixed with aqueous methanol from pipe 75. Makeup methanol may be added from tank 76. In fractionator 74, under the influence of reflux introduced at 77 and heat from reboiler 78 an overhead product is taken off through pipe 79 and condenser 80 to receiver 81. Bottoms product, constituting, as before, all of the toluene and some of the non-aromatic hydrocarbons in the charge is taken through pipe 82, cooler 83, tank 84, and pipe 85 to fractionator 86. In this operation, aqueous methanol having been introduced by pipe 75, water separates within fractionator 74 and is collected on trap tray 87 and removed through pipe 88 and cooler 89 to accumulator 90. Bottoms product from fractionator 74 proceeding to fractionator 88 through pipe 85 is admixed with aqueous methanol from pipe 91. In fractionator 88 under the influence of reflux introduced at 82 and heat from reboiler 87, a bottoms oil is formed, constituting the methanol and non-aromatic hydrocarbons is formed to pass through pipe 94 and cooler 95 to receiver 96.

As before, the water, from the aqueous methanol charged fractionator 86 is collected by trap tray 97 and passes through cooler 98 and pipe 99 to accumulator 90. As before, bottoms product from fractionator 88, constituting about 90% or more of the toluene originally present in the gasoline, and having a purity of about 98% or higher, passes through pipes 100 and cooler 101 to tank 88.

Of the overhead product collected in receivers 81 and 96, such portion as is not returned for reflux at points 77 and 82 is withdrawn through pipe 102 to mixer 103 where it meets water coming from gas holdover through pipe 104, and is delivered into separator 105. The top from 105 constituting methanol-free non-aromatic hydrocarbons passes through pipe 106 to disposal with other discarded non-aromatic hydrocarbons. The aqueous-methanol layer from 105 is taken through pipe 107 and forced by pump 108 into pipe 15 for reuse in the process. In this version of the process methanol and water are both circulated continuously within the process.

The successful operation of this process as a whole, for the high recovery of toluene of high purity, depends upon carefully effected process steps and controls. Those for the preparation of the gasoline fraction have already been discussed. Those for the azotropic distillation step will now be taken up. An increase in the amount of methanol present in such distillation leads to increases in the percent of toluene present in the bottoms, but beyond a certain optimum, simultaneously leads to increasing toluene lost into overhead distillate. It has been found that the optimum amount of methanol to be added for such distillation lies between a minimum of about 5% by volume of the volume of non-aromatic hydrocarbons present plus 28% by volume of the volume of toluene, and a maximum of about 120% by volume of the non-aromatics plus 56% by volume of the toluene.

It has further been found that the amount of reflux utilized has a very pertinent bearing.
With even a really good fractionating, such as with a tower of about 24 theoretical plates, a reflux ratio of about 10:1 (reflux:overhead product) or above will give about 100% recovery of toluene as a bottom product of about 70% concentration on initial feeds of around 20%, while with optimum methanol addition and reflux ratios of 8:1 or above it is relatively easy to obtain 70% mixtures up to bottoms product of about 98% or more purity and still recover about 90% or more of the toluene present at reasonable heat loadings, an increase in percent recovered beyond this calling for rises in the reflux ratio and correspondingly increased heat load.

Further, it has been found that because of the inter-relation of the optimum amount of methanol, and the optimum reflux ratio, that the choice of the most economical scheme of operation, i.e. whether one-stage or two-stageazeotropic distillation, depends upon the amount of toluene present in the starting material. The total amount of material to be sent overhead, and consequently the total heat demand of the process, is greater for a one-stage process than for a two stage process if the concentration of toluene in the initial feed is less than about 40 percent by volume, while above this concentration, the heat demand of a single stage process is less. Consequently, while the process shown in the drawings and described above shows an azeotropic distillation operation consisting of two steps, the concentration of the feed to each, it is to be understood that, depending upon the toluene content of the closely-cut gasoline, a single step may be utilized if desirable.

When toluene content of the 245°F. A. S. T. M. end boiling petroleum stock is so high as to indicate a single step toluene recovery system, the indicated amount of methanol will be utilized in this single step recovery. That is, the methanol added will be not less than

\[ M = \frac{86}{100 - T} + 287 \]

nor more than \[ M = \frac{120}{100 - T} + 567 \], where \( T \) is volume percent of toluene in charge stock and \( M \) is percent by volume, based on original charge stock, of methanol added. For example, for 100 bbls. of a charge stock containing 40% toluene, the added methanol would be not less than \( \frac{86}{100 - 40} + 28 \) (40) = 82.6 barrels, nor more than \( \frac{120}{100 - 40} + 56 \) (40) = 94.4 barrels.

When the toluene content of the 245°F. A. S. T. M. stock is low enough to indicate a two step toluene recovery system, the calculation of the total added methanol for both steps of the toluene recovery will be the same, but the amount to be added in the first toluene recovery step would be only a fraction, usually about 60-75% of the total. Consequently, the statement of minimum and maximum methanol addition above made applies as well to a two-stage toluene recovery as to one-stage toluene recovery.

In its simplest form, then, the process is merely one of two distillation steps, in the first of which there is prepared a toluene-containing petroleum fraction of about 245°F. (A. S. T. M.) end point and in the second which toluene is recovered therefrom in a single distillation step under azeotropic conditions as outlined. Further, as pointed out above, either of these may be elaborated for economic reasons. Under some circumstances dictated by proportional presence of light ends in the original charging stock it may be advisable to include light ends removal in the preparation. Also, under certain circumstances of toluene concentration, as outlined herein, it may be advisable to perform a two stage toluene separation rather than to attempt the accomplishment of this operation in a single step.

Throughout this specification there is made use of the terminology which speaks of a certain petroleum fraction being the "215-245°F. (A. S. T. M.) cut" and the like. By this is meant a fraction of the gasoline boiling between the temperatures 215°F. and 245°F. as observed in the standard A. S. T. M. distillation of the gasoline.

This application is directed to similar subject matter to that disclosed and claimed in applications of Theodor A. Petry, John L. Biles and William V. Betts, Serial No. 351,716, filed Aug. 7, 1940, and Serial No. 400,196, filed June 28, 1941. The invention disclosed and claimed in those applications is senior to the inventions disclosed and claimed herein.

This application is also directed to subject matter similar to that disclosed in an application of Theodor A. Petry, Henry D. Knoll and Russell R. Lee, filed Feb. 5, 1941, which became Patent No. 2,332,493, issued on Oct. 19, 1943. The subject matter disclosed and claimed in said patent is senior to the invention disclosed and claimed herein.

We claim:

1. That method of recovering substantially all of the toluene present in a toluene-containing petroleum fraction and recovering said toluene in a high purity of 90% or more, comprising the steps of first distilling the petroleum fraction to segregate therefrom a charge fraction of approximately 245°F. end boiling point measured according to the specifications of the American Society for Testing Materials, containing substantially all of the toluene originally present, and then distilling that charge fraction in the presence of an added amount of methanol which is not less than about \[ M = \frac{86}{100 - T} + 287 \] where \( M \) is the added methanol, expressed as volume percent of the charge fraction and \( T \) is the volume percent of toluene in the charge fraction, in which the charge fraction contains less than about 40% by volume of toluene, and the charge fraction is first distilled in the presence of a portion of the methanol to yield a first distillation residue containing substantially all of the toluene and having a toluene concentration substantially more than 40 percent, and that residue is then distilled in the presence of the remainder of the methanol to yield a second residue substantially all of the toluene in a condition of relatively high purity.

2. That method of recovering substantially all of the toluene present in a toluene-containing petroleum fraction in a high purity of 90% or more which comprises the steps of, first distilling the petroleum fraction to segregate therefrom a charge fraction of approximately 245°F. end boiling point measured according to specifications of the American Society for Testing Materials, containing substantially all of the toluene originally present, and then distilling that charge fraction in the presence of an added amount of methanol which is not less than about \[ M = \frac{86}{100 - T} + 287 \] where \( M \) is the added methanol, expressed as volume percent of the charge fraction and \( T \) is the volume percent of toluene in the charge fraction, in which the charge fraction contains less than about 40% by volume of toluene, and the charge fraction is first distilled in the presence of a portion of the methanol to yield a first distillation residue containing substantially all of the toluene and having a toluene concentration substantially more than 40 percent, and that residue is then distilled in the presence of the remainder of the methanol to yield a second residue substantially all of the toluene in a condition of relatively high purity.
ume of toluene, and the charge fraction is first distilled in the presence of a portion of the methanol and water to yield a first distillation residue containing substantially all of the toluene and having a toluene concentration substantially more than 40 percent, and that residue is then distilled in the presence of the remainder of the methanol and water to yield a second residue substantially all of the toluene in a condition of relatively high purity.

3. In a process for recovering, in a state of high purity of 90% or more, substantially all of the toluene present in a gasoline petroleum fraction, in which, initially such a petroleum fraction is distilled having present in the fraction an amount of toluene less than 40% by volume but containing substantially all of the toluene originally present and having an end boiling point of about 245°F, secondly, methanol is added to said petroleum fraction, thirdly, the azetotropic mixture is distilled to boil off the methanol with a portion of the non-aromatic compounds and leave a product enriched in toluene, fourthly, additional methanol is added, and fifthly, the azetropic mixture is again distilled to boil off the additional methanol with the remainder of the non-aromatic compounds and leave a substance substantially all of the toluene, the impurities which consist of limiting the amount of methanol added to an amount within a range defined by the lower limit \[ M = \frac{68.100 - T}{100} + 287 \] and the upper limit \[ M = \frac{120.100 - T}{100} + 587 \] where \( M \) is the volume percent of methanol (based on charge fraction) and \( T \) is the volume percent of the toluene in the charge fraction, and limiting the amounts of methanol added in the first stage of azetotropic distillation to a range of 60M to 75M and in the second stage of azetotropic distillation to a range of 25M to 40M.

4. That method of recovering substantially all of the toluene present in a toluene-containing petroleum fraction and recovering said toluene in a high purity of 90% or more, comprising the steps of first distilling the petroleum fraction to segregate therefrom a charge fraction of approximately 245°F, end boiling point containing substantially all of the toluene originally present, and then distilling that charge fraction in the presence of the added amount of methanol vapor and azeotropic methanol which is not less than about \( M = \frac{68.100 - T}{100} + 287 \) where \( M \) is the added methanol, expressed as volume percent of the charge fraction and \( T \) is the volume percent of toluene in the charge fraction, in which the charge fraction contains less than about 40 percent by volume of toluene, and the charge fraction is first distilled in the presence of a portion of the methanol to yield a first distillation residue containing substantially all of the toluene and having a toluene concentration substantially more than 40 percent, and that residue is then distilled in the presence of the remainder of the methanol to yield as a second residue substantially all of the toluene in a condition of relatively high purity.

5. That method of recovering substantially all of the toluene present in a toluene-containing petroleum fraction and recovering said toluene in a high purity of 90% or more, comprising the steps of first distilling the petroleum fraction to segregate therefrom a charge fraction of approximately 245°F, end boiling point containing substantially all of the toluene originally present, and then distilling that charge fraction in the presence of the added amount of methanol vapor and azeotropic methanol which is not less than about \( M = \frac{68.100 - T}{100} + 287 \) where \( M \) is the added methanol, expressed as volume percent of the charge fraction and \( T \) is the volume percent of toluene in the charge fraction, in which the charge fraction contains less than about 40 percent by volume of toluene, and the charge fraction is first distilled in the presence of the added amount of methanol to yield a first distillation residue containing substantially all of the toluene and having a toluene concentration substantially more than 40 percent, and that residue is then distilled in the presence of the remainder of the methanol to yield as a second residue substantially all of the toluene in a condition of relatively high purity.

THEODOR A. PETRY, RUSSELL LEE, JOHN L. BILES, WILLIAM V. BETTS.

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