

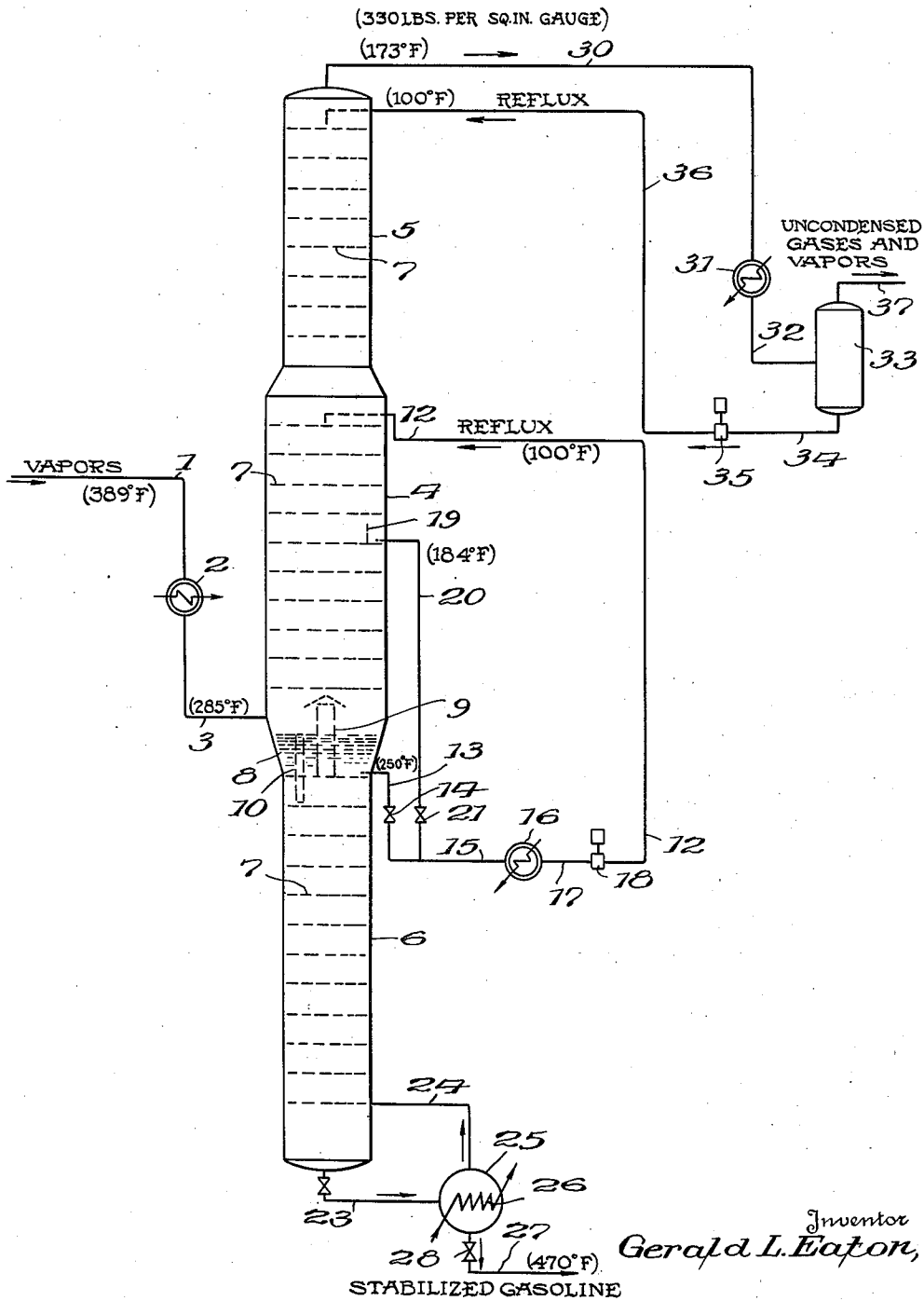
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FRACTIONATION OF HYDROCARBON VAPOR MIXTURES

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FRACTIONATION OF HYDROCARBON VAPOR MIXTURES

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1 Claim. (Cl. 196—11)

This invention relates to a process of and apparatus for fractionating hydrocarbon mixtures, more particularly mixtures of normally liquid and normally gaseous hydrocarbons such as are produced in processes of cracking hydrocarbon oils.

As is well known, the products obtained in oil-cracking processes contain, in addition to constituents having boiling points above the normal gasoline boiling-point range, considerable quantities of normally gaseous materials such as butane, butylenes, propane, propylene, ethane, ethylene, methane and hydrogen. The separation of the higher boiling members of this series from gasoline constitutes a definite problem in the art, a problem which has been made somewhat more critical by the development of processes for effecting cracking and polymerization of C₃ and C₄ hydrocarbons to gasoline-like materials. If the gasoline hydrocarbons are removed from the vapors by simple condensation, sharp separation is impossible; either the condensed gasoline is highly unstable and contains undesirable quantities of normally gaseous materials or an undesirable amount of hydrocarbons having 5 or more carbon atoms per molecule remains uncondensed.

It is usually desired to retain a certain amount of the C₄ hydrocarbons in the stabilized gasoline, the exact amount depending upon the vapor pressure specifications for gasoline, which, of course, vary in accordance with the seasons. It will be obvious that if this entails a failure to condense C₅ and heavier hydrocarbons, considerable inefficiency will result, and where, as is now frequently the case, it is desired to deliver the higher boiling constituents of the uncondensed gases to a cracking or polymerizing zone, the presence of C₅ and heavier hydrocarbons in the mixture thus delivered is undesirable.

In the prior applications of Povl Ostergaard, Serial No. 52,717, filed December 3, 1935 and Serial No. 103,947, filed October 3, 1936, there are described and claimed certain improvements in fractionating hydrocarbon vapors of the character referred to hereinabove, comprising a combined condenser-stabilizer for removing stabilized gasoline from hydrocarbon gases containing the same, such as the gases leaving the main gas-oil fractionator of an oil cracking unit either of conventional type or of the so-called gas-reversion or gas-recycling type. This combined condenser-stabilizer essentially consists of two fractionating columns normally superimposed one

upon the other, with means for introducing hydrocarbon vapors of the character described at a point intermediate the two columns. The upper column serves primarily as a condenser and dephlegmator wherein the vapors are contacted with cool reflux condensate. This reflux medium is obtained by withdrawing unstabilized gasoline condensate from the intermediate portion of the tower, cooling it and recirculating it to the upper portion of the condensing column. Excess unstabilized condensate drawn from the base of the condensing column is delivered to the lower or stabilizing column, and heat is supplied to the base of the stabilizing column, usually through the medium of a boiler of more or less conventional type. During its passage downwardly through the stabilizing column, the condensate from the upper or condensing column is rectified and stabilized, the vapors liberated during stabilization being returned to the upper or condensing column.

The above system has proved extremely advantageous in practice, as a means for recovering stabilized condensate from oil-cracking units, both of conventional type and of the so-called gas-reversion type. It has certain very important practical advantages over a simple rectifying column of conventional type as well as over other prior art devices. One of these advantages resides in the fact that cooling is effected at a higher temperature level than is true of the ordinary rectifying column. To illustrate this more fully, it will be remembered that in the ordinary rectifying column as applied to vapors of this type, some form of cooling is provided at the top of the column. This may be either a small coil located in the head of the column, or it may comprise a separate condenser receiving vapors from the top of the column, together with means for recirculating condensate thereby obtained into the head of the column. In order for such a rectifying column to work efficiently, a temperature differential must be maintained throughout the column and this means that the temperatures of the outlet vapors will be low, not far removed from atmospheric. This in turn means that temperature differential between the vapors leaving the top of the column and the recycled reflux is low; and it is difficult to supply adequate cooling on account of this low temperature differential.

In the Ostergaard condenser-stabilizer, on the other hand, the stabilized condensate which is to be returned as reflux is withdrawn from an inter-

mediate portion of the column at a temperature substantially higher than that maintained in the upper portion of the column, so that there is a very large temperature differential between the temperature of the side stream as withdrawn from the column and the temperature of the same material when returned as reflux; this vastly increases the ease and economy of operation.

The Ostergaard system also has the advantage that the cooling is applied to a liquid stream rather than to a vapor stream and is somewhat more efficient on that account.

It must be conceded, however, that notwithstanding the definite practical advantages of the Ostergaard condenser-stabilizer, there is a slight theoretical disadvantage in the Ostergaard system as specifically shown in the aforesaid prior applications. For utmost efficiency of fractionation, regardless of other considerations, a rectifying column should be truly countercurrent in principle, with a uniform gradual equilibrium change from tray to tray through the entire column. It will be obvious that withdrawal of a side stream from the column and return of this side stream after cooling to a high point in the column involves some theoretical upsetting of the equilibrium conditions within the tower, for it is obvious that the side stream or reflux cannot be precisely in equilibrium with the vapors at the point of re-entry into the column. The vapors at the point of re-entry should contain considerably less of the higher boiling constituents present than the vapors and liquid at the point of withdrawal. Consequently, the reflux material in the Ostergaard system inevitably contains a slightly higher proportion of high boiling, i. e. gasoline, constituents than is desirable for utmost fractionating efficiency.

It will be understood, of course, that theoretical fractionating efficiency is not always the most important consideration. There are many instances in which designs embodying some slight variation from theoretical fractionating efficiency are found to be of practical advantage under given conditions and that is true of the Ostergaard system.

I have found that the advantages of the Ostergaard system may be retained, and a more nearly perfect theoretical fractionating efficiency attained, by a simple modification of the Ostergaard system.

In accordance with my invention, mixed hydrocarbon vapors of the character referred to hereinabove, such as vapors produced in the cracking of hydrocarbon oils from which constituents heavier than gasoline have been removed, are introduced into a condenser-stabilizer column differing from the Ostergaard column in that three instead of two sections are provided. The two lower sections are substantially identical in construction and operation to the two sections of the Ostergaard condenser-stabilizer. However, I also provide a third section superimposed upon the intermediate or condensing section and provided with means for condensing or dephlegmating the vapors reaching the top of this third section to produce a condensate which is then returned to the head of the third section as a cooling and reflux medium therefor.

The bulk of the cooling is supplied by withdrawing a side stream and returning it to the intermediate section, as in the Ostergaard system. Additional cooling and rectification is,

however, provided in the upper or third section, the primary purpose being to correct any lack of proper equilibrium at the top of the intermediate section and thereby to insure that all normally liquid constituents desired to be included in the stabilized gasoline fraction are condensed and held within the column and do not pass out in uncondensed form.

This system is of especial advantage in all instances where the character of the vapors is such that use of the Ostergaard system tends to leave a small amount of gasoline constituents uncondensed in the overhead product from the column.

In order that my invention may be more clearly set forth and understood, I now describe, with reference to the drawing illustrating and forming part of this specification, various preferred forms and manners in which my invention may be practiced and embodied. In the drawing,

The single figure is a more or less diagrammatical and conventionalized elevational view of a condensing and stabilizing column, adapted for the performance of the process of my invention.

Referring to this drawing, a mixture of hydrocarbon vapors containing gasoline constituents and lighter normally gaseous constituents are shown entering the system through a line 1. In a preferred specific embodiment of the invention, these vapors constitute the overhead product from the main fractionator (not shown) of an oil cracking or gas polymerization unit, being free or substantially free from constituents boiling above the normal gasoline boiling-point range and containing, in addition to hydrocarbons having boiling points within the gasoline boiling-point range, considerable quantities of lower boiling constituents, such as hydrocarbons having not more than four carbon atoms per molecule.

These vapors are first introduced into an indirect heat exchanger or cooler 2 wherein their temperature is substantially reduced. The partly cooled vapor is then passed through a line 3 into the lower part of a fractionating column 4 which, as shown, comprises the mid-section of a fractionating column also having upper and lower sections 5 and 6, respectively. Each of the sections 4, 5 and 6 is internally provided with suitable gas and liquid contact devices such as bubble cap trays 7, which may be of conventional design. The mid-section 4 and the upper section 5 of the column are in open communication, but a weir device 8 is provided between the mid-section 4 and the lower or stabilizing section 6. A suitable weir device, as illustrated in the drawing, is provided with a vapor conduit 9 and a liquid downflow pipe 10.

Relatively cool reflux oil, obtained as set forth hereinbelow, is introduced into the upper portion of the mid-section 4 through a line 12. As the vapors pass upward through the mid-section 4, they are met by a descending flow of relatively cool reflux condensate introduced as aforesaid, resulting in the condensation of unstabilized gasoline, which collects in the weir device 8. A portion of the condensate thus obtained is withdrawn from the weir device 8 through a line 13 having a valve 14 and is delivered through a line 15 to an indirect cooler 16. The cooled condensate leaving the cooler 16 passes through a line 17 to a pump 18 which in turn delivers it to the line 12 into the upper portion of the mid-section 4.

Alternatively, reflux for the mid-section 4 may

be provided by withdrawing a portion of the internal reflux from a trap tray or weir device 19 located above the point of introduction of the vapors into the mid-section 4. Reflux condensate thus withdrawn passes through a line 20 having a valve 21 and communicating with the line 15, and is cooled in the cooler 16 before being returned by the pump 18 through the line 12 into the upper part of the mid-section 4, as before.

Unstabilized condensate collecting in the weir device 8 and not withdrawn through the pipe 13 passes through the downflow pipe 10 into the lower or stabilizing section 6 of the column, the base of which is in communication through a valved liquid line 23 and a vapor-return line 24 with a re-boiler 25 of conventional design. The re-boiler 25 is provided with an internal coil 26 or other means for supplying heat thereto. Stabilized gasoline is withdrawn from the bottom of the re-boiler 25 through an outlet line 27 having a valve 28.

During its passage downwardly through the lower section 6, the unstabilized condensate is rectified and stabilized to remove constituents too light to be included in the final gasoline product. These constituents, in vapor form, re-enter the mid-section 4 through the vapor line 9.

Vapors uncondensed in the mid-section 4 pass upward into the upper section 5 of the column, where they are subjected to further cooling and rectification. In the instance shown, such cooling and refluxing is effected by withdrawing uncondensed vapors from the top of the column through a line 30 leading to a condenser 31, which in turn communicates through a line 32 with a vapor-separator 33. Condensate collecting in the separator 33, as a result of the cooling effected in the cooler 31, is withdrawn through a line 34 leading to a pump 35, which in turn delivers the cool reflux condensate through a line 36 into the top of the upper section 5 of the column.

In passing upward through the column 5, the vapors from the mid-section 4, undergo further rectification, the temperature and amount of reflux supplied being sufficient to prevent the escape from the top of the column in uncondensed form of constituents desired to be retained in the final gasoline product. Thus any C₅ hydrocarbons which are retained in the reflux supplied through the line 12 and which may be vaporized in the upper portion of the mid-section 4 are condensed and held back in the upper section 5 of the column.

While the specific temperatures maintained at different points in the unit will vary in accordance with the results desired and in accordance with the character of the vapors charged, the following temperatures, observed in connection with a typical operating instance, will serve to illustrate and exemplify my invention more specifically:

	° F.
Vapors entering through line 1.....	389
Vapors passing through line 3.....	285
Side stream, where withdrawn through line 13.....	250
Side stream, where withdrawn through line 20.....	184
Reflux returning through line 12.....	100
Vapors leaving through line 30.....	173
Reflux returning through line 36.....	100
Stabilized gasoline withdrawn through line 27.....	470
Pressure 330 pounds per square inch gage.	

For convenience these temperatures have been indicated on the drawing, but it will be understood from the foregoing that they are merely illustrative and are not to be construed as limiting the invention to this specific instance.

The foregoing temperatures were observed in connection with an operation in which 6205 mols per hour of vapors of the character indicated were supplied through the line 1. From these vapors there was recovered 1250 mols per hour of stabilized gasoline free from C₃ hydrocarbons and containing 8.1 per cent by volume of C₄ hydrocarbons. The net overhead vapors leaving the separator 33 through the line 37 amounted to 4955 mols per hour, constituted as follows:

Constituents	Mols per hour	Mol percent
H ₂ S.....	90	1.8
Methane.....	950	19.2
Ethane and ethylene.....	1000	20.2
Propane and propylene.....	2400	48.4
Butane and butylenes.....	500	10.1
Heavier hydrocarbons.....	15	0.3

Whereas the stabilized distillate in this instance amounted to 500 barrels per hour, the reflux supplied through the line 12 amounted to 915 barrels per hour, and the reflux supplied through the line 36 amounted to 450 barrels per hour.

From the above figures, it will be evident that my invention makes it possible to obtain a remarkable sharp separation of stabilized gasoline from vapors of the character indicated. Propane is entirely excluded from the stabilized gasoline, while the net overhead products contain an exceptionally small percentage of C₅ and heavier hydrocarbons.

As will be evident from an inspection of the temperatures given in connection with the specific example described, the major portion of cooling required for the tower is supplied in the condenser 16, where the temperature drop is large as compared with the temperature drop through the cooler 31. Where the cooler 2 is dispensed with, a still larger temperature drop in the cooler 16 will occur.

While I have described my invention hereinabove with respect to a preferred form and embodiment, for purposes of illustration and exemplification, and with respect to a specific operating example, it will be understood by those skilled in the art that my invention is not limited to the details thereof, but may variously be practiced and embodied within the scope of the claims hereinafter made.

What I claim is:

A method of condensing stabilized gasoline from vapors comprising a mixture of hydrocarbons having boiling points within a gasoline boiling-point range and hydrocarbons having lower boiling points, such as are produced in oil-cracking operations, which comprises introducing such vapors, previously freed of constituents having boiling points higher than are normally included in gasoline, into the lower portion of a condensing and rectifying zone, withdrawing reflux condensate from said zone, cooling it and returning it at a higher level in said zone as a cooling and refluxing medium therefor, delivering another stream of reflux condensate from said first-mentioned rectifying zone into a second rectifying zone, the lower portion of which is heated to a temperature sufficient to effect stabilization of the gasoline condensate passing therethrough, delivering vapors liberated in said second recti-

5 fying zone to said first-mentioned rectifying zone,
delivering vapors from said first-mentioned rec-
tifying zone into a third rectifying zone wherein
condensation and rectification of gasoline con-
stituents in the vapors entering from the first-
mentioned rectifying zone is effected, withdraw-
ing uncondensed vapors from the upper portion
of said third rectifying zone, cooling said vapors
to condense the heavier portions thereof, return-
ing at least a portion of the condensate thereby

obtained to the said third rectifying zone as a
cooling and refluxing medium and in such quan-
tities and at such a temperature as to effect con-
densation from the vapors traversing said third
rectifying zone of substantially all gasoline hy-
drocarbons contained therein, and returning re-
flux condensate from said third rectifying zone
to said first-mentioned rectifying zone.

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