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RECOVERY METHOD FOR CYCLIC VAPOR PHASE REACTION PRODUCTS

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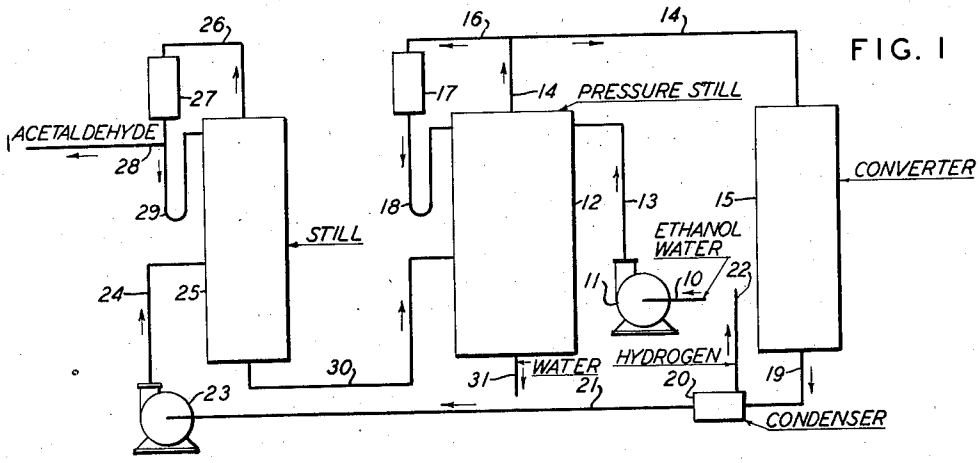



FIG. 1

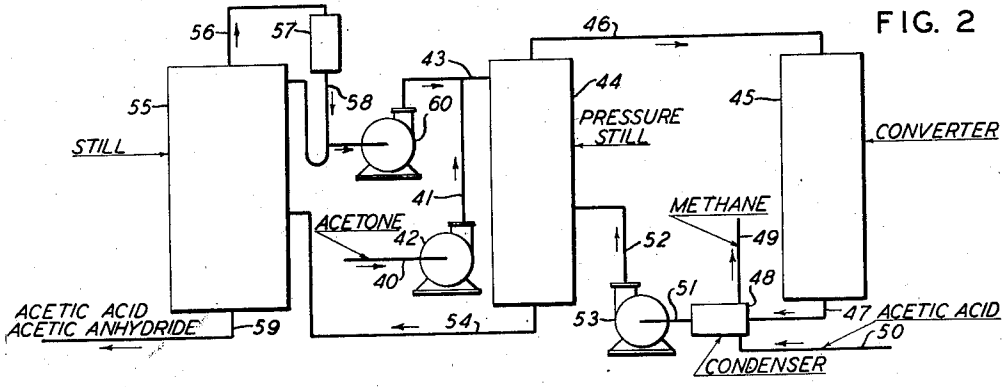



FIG. 2

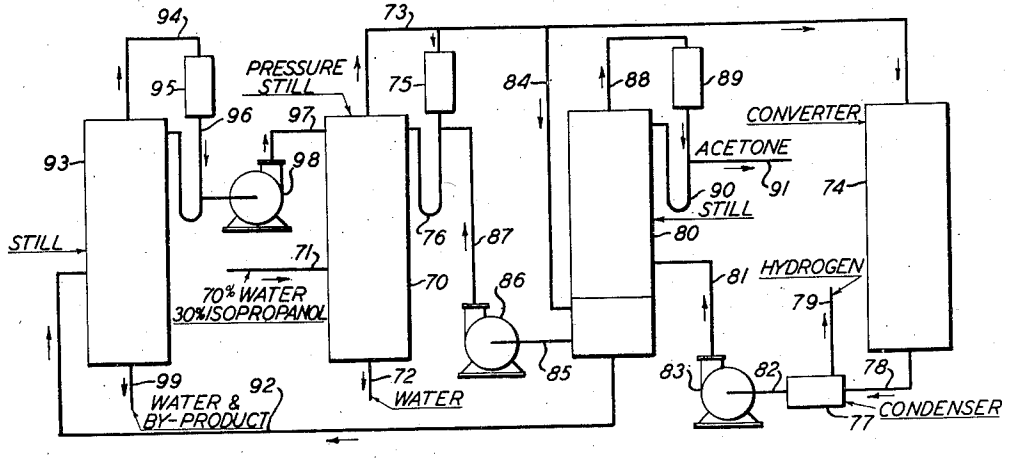



FIG. 3

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## RECOVERY METHOD FOR CYCLIC VAPOR PHASE REACTION PRODUCTS

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6 Claims. (Cl. 260—550)

This invention is an improvement in distillation processes for use in those cyclic vapor phase reaction systems wherein substantially pure unreacted material is recovered and fresh reactant material is introduced.

In a process where a substantially pure material is vaporized and supplied to a converter in which a partial conversion of the starting material to other products takes place, after which the reaction mixture is separated by rectification, the accepted practice is to recover the unreacted material in liquid form from the distillation operation and to revaporize it and return it to the converter in admixture with fresh material to make up for that consumed in the reaction. In the commercial operation of such processes, especially where the percent conversion of the material into other products is low, the cost of the vaporization of the material supplied to the converter may be very large, and, in some cases, this heat requirement actually determines the practicability of the process.

By the method of the present invention, the vaporization of the recovered material from the rectification system may be avoided, and under most conditions the make-up material also may be vaporized without consuming any more heat than is normally required to operate the rectification system. A further economy effected by this invention consists in the reduction in size or elimination of condensers on the stills operating under positive gauge pressure, in which the unreacted material is recovered.

The essence of the invention consists in supplying the converter with the recovered starting material, in vapor form, directly from the rectification system. In general, the make-up starting material (taking the place of that reacted) may also be supplied to the converter in vapor form directly from the rectification system without requiring additional heat for vaporization by using it as part or all of the reflux for the still.

For example, in the process for the manufacture of acetaldehyde from ethanol, ordinarily, the ethanol (or its aqueous azeotrope) is vaporized and passed continuously into a converter where about 25% of it is reacted, largely through dehydrogenation, to form acetaldehyde. The converter product is condensed and passed into a still where the acetaldehyde is continuously removed. The converter product, now stripped of acetaldehyde and consisting largely of unreacted ethanol, is passed into a second still where the ethanol is purified by rectification which may require a reflux ratio of, say, about 3 to 1. Three-fourths of the ethanol supplied to the converter is the distillate from this still, the remaining one-fourth being fresh ethanol added to make up for that converted to acetaldehyde and by-products.

By operating the second still under enough pressure to force the ethanol vapor through the converter, the recovered ethanol may be removed in vapor form and passed directly into the converter. Thus three-fourths of the heat ordinarily required to vaporize the ethanol supplied to the converter may be saved. If the fresh (make-up) ethanol is added to the second still on the top plate, as reflux, the heat ordinarily required for vaporizing the remainder of the converter feed can be saved as well. In this way, the fresh ethanol added to make up for that consumed in the process replaces part of the reflux heretofore obtained by condensation of distillate, and this part of the distillate, formerly condensed, is diverted to the converter feed as vapor.

If it is desired that the still in which the unreacted material is recovered be as small as possible, it may be made large enough in diameter only to handle the vaporized converter feed, all reflux being supplied by fresh material and the distillate from a still operating under atmospheric pressure and supplied with the rest of the crude recovered material.

Another application of this operation may be the manufacture of acetic anhydride by a process in which acetone is vaporized, passed through a converter in which about 12% is converted to ketene, which is reacted with acetic acid, and the products condensed. The condensate is ordinarily fed to a continuous still which removes acetone as a condensed distillate and which may require a reflux ratio of about 1 to 1. By the process of this invention a second still is installed in series with the first, and preceding it, operating under enough pressure to force the acetone vapor evolved therefrom through the converter. The products of reaction mixed with acetone flow into this still where half of the acetone is removed (in vapor form), and thence from its base to the atmospheric pressure still where the remainder of the acetone is rectified. The acetone distilled in the atmospheric pressure still is returned as reflux to the preceding still along with fresh acetone added to make up for that consumed in the reaction. In this way all of the reflux for the preceding still is furnished from other sources (than the vapors being rectified in the still itself), and the material vaporized therein is only the acetone fed to the converter.

It is obvious that if the fresh acetone, added to make up for that consumed, contains higher boiling impurities which should not be allowed to pass into the reaction zone, but which will not affect the acetic anhydride produced, the fresh acetone may be introduced into the second still where it is rectified before passing as reflux to the first still supplying the vapor to the converter. Of course, if the acetone contains other impurities, such as water or low-boiling liquids, it should be separately fractionated before being introduced into the system.

In those processes which require the raw material to be rectified prior to introduction into the cycle, it is often advantageous to employ the still used for this purpose for feeding the vapor directly to the converter. The reflux for this still may be furnished by the still itself, or may be supplied from an atmospheric pressure still which recovers the unreacted material from the converter product. If the percent conversion of the material to the desired product is sufficiently small, as is the case with both of the acetaldehyde and acetic anhydride processes described above, all of the reflux necessary for the operation of the still supplying vapor to the converter may be obtained from the recovery still operating under atmospheric pressure. However, where the conversion of the material is very high, and the raw material must be rectified before use, the still supplying the converter with vapor must furnish part of its own reflux. Such an application is encountered in the process of making acetone by the vapor phase catalytic dehydrogenation of isopropanol.

In this process, the isopropanol or its aqueous azeotrope is passed in vapor form through a converter where from 70% to about 90% is converted to acetone and hydrogen, depending on the conditions of reaction. The converter product is condensed and the hydrogen separated therefrom, and the acetone is distilled from the converter product under atmospheric pressure. The converter product, now substantially free of acetone, is passed into a second atmospheric pressure still where the isopropanol (water azeotrope) is distilled from whatever by-products and excess water may be present, and supplied to a third still as reflux. In the third still, the raw isopropanol containing higher boiling materials (usually excess water) is rectified and the vapor from the still passed directly to the converter. This still is, of course, operated at sufficient pressure to provide the desired vapor flow through the converter.

The accompanying drawing diagrammatically illustrates the flow of materials in the embodiments of the invention, described above, in which:

Figure 1 illustrates a process for producing acetaldehyde by the dehydrogenation of ethanol;

Figure 2 illustrates a process for producing acetic anhydride by the decomposition of acetone to form ketene, and its reaction with acetic acid; and

Figure 3 illustrates a process for producing acetone by the dehydrogenation of isopropanol.

Referring to Figure 1, the azeotropic mixture of ethanol and water is passed through a line 10 into a pump 11 by means of which it is forced into a continuous still 12 as reflux therefor, through a line 13. In the still 12 the azeotropic mixture is vaporized and passes upward through a line 14 to a converter 15. Since the reflux supplied through the line 13 is insufficient to operate the still 12 at a reflux ratio of about 3 to 1, part of the vapor in the line 14 is diverted through a line 16 to a condenser 17 where it is condensed and returned through a line 18 as additional reflux to the still 12. In the converter 15 about one-fourth of the ethanol is converted into acetaldehyde and hydrogen and a small amount of by-products. This mixture passes through a line 19 to a condenser 20 where the mixture of ethanol, acetaldehyde and by-products is condensed and passes through a line 21, with the hydrogen being removed through a line 22. The converter product in the line 21 is forced by means of a pump 23 through a line 24 and into a still 25. In the still 25 the acetaldehyde is removed and passes through a line 26 in vapor form to a condenser 27. In the condenser 27 the acetaldehyde is condensed and leaves the system through a line 28, part of the acetaldehyde being returned through a line 29 to provide reflux for the still 25. From the base of the still 25 the mixture of ethanol, water and by-products is passed through a line 30 to the still 12. (Since the still 25 must be operated under pressure, usually about 30 pounds gauge, in order to condense the acetaldehyde without employing refrigeration, the mixture from the base of this still may be introduced into the still 12 without employing a pump in the line 30.) The water and most of the by-products leave the still 12 at its base through a line 31 while the ethanol-water azeotropic mixture leaves the still 12 in vapor form through the line 14, and thus the cycle is completed. Since one of the by-products of this process is ethyl acetate which will accumulate in the system, it is common practice to subject the mixture flowing in the line 30 to a periodic fractionation. Ordinarily it is not necessary to remove the ethyl acetate more often than once in about five or six days with the process running continuously.

Referring to Figure 2, acetone from a line 40 passes through a line 41 by means of a pump 42 and into a line 43. From this line the acetone passes into a still 44 as reflux therefor. In the still 44 the acetone is vaporized and passes to a converter 45 through a line 46. In the converter 45 about 12% of the acetone is decomposed to form ketene and methane, and from the converter 45 the unreacted acetone and products of decomposition pass through a line 47 to a condenser 48. The methane formed in the converter 45 is removed through a line 49 and the ketene is reacted with acetic acid supplied through a line 50 to form acetic anhydride, (or the ketene is reacted otherwise to form other products capable of separation from acetone by distillation). The mixture of acetic anhydride, acetic acid, acetone and by-products leaves the condenser 48 through a line 51 and is pumped into the still 44, operating under positive gauge pressure, through a line 52 by means of a pump 53. In the still 44 approximately one-half of the acetone is removed by rectification and returns to the converter 45, in vapor form, through the line 46. The acetic anhydride, acetic acid, by-products, and the unrectified half of the acetone pass out of the still 44 through a line 54 to a still 55. In the still 55 the remainder of the acetone is removed through a line 56 and condensed in a condenser 57. From the condenser 57 part of the liquid acetone returns as reflux to the still 55 through a line 58, the remainder passing through the line 43, by means of a pump 60, as reflux to the still 44. From the still 55 the acetic anhydride, acetic acid

and by-products, substantially free of acetone, are removed through a line 69 for use or further separation. Since only about half of the acetone is removed in the still 44, the mixture leaving its base has a boiling point low enough to permit the use of low pressure steam (such as 15 to 20 pounds gauge) for heating, whereas high pressure steam (175 to 200 pounds gauge) is required to operate the still 55, because of the high boiling points of acetic acid and acetic anhydride. However, if all of the acetone is rectified in one still, high pressure steam is required for the entire heating load. Thus, this operation effects a further economy in reducing the consumption of high pressure steam, which is always more costly to produce than steam under relatively low pressures.

Referring to Figure 3, an aqueous mixture containing about 30% isopropanol passes into a still 70 operating under positive gauge pressure, through a line 71. In the still 70 the isopropanol-water azeotropic mixture is distilled and the excess water is removed from the base of the still 70 through a line 72. The azeotropic mixture, in vapor form, passes through a line 73 to a converter 74, part of the vapor from the line 73 passing into a condenser 75 where it is condensed and returned to the still 70 as reflux through a line 76. Between about 70% and 90% of the isopropanol vapor which passes through the line 73 into the converter 74 is converted to acetone and hydrogen, and the mixture passes from the converter 74 to a condenser 77 through a line 78. From the condenser 77 hydrogen is removed through a line 79 and the converter product, in liquid form, is passed into a still 80 through lines 81 and 82 by means of a pump 83. Since the converter product is lower boiling than the isopropanol-water vapor supplied under positive gauge pressure to the converter 74 through the line 73, part of the vapor in the line 73 may be diverted through line 84 to a heating coil in the still 80 in place of part of the vapor condensed in the condenser 75. From the heating coil in the still 80 the condensed vapor from the line 84 passes through a line 85 to a pump 86 where it is returned as reflux to the still 70 through lines 87 and 76. In the still 80 the acetone is separated and passes through a line 88 to a condenser 89 from which part is returned to the still 80 through a line 90 as reflux. The other part is withdrawn through a line 91 for use. From the base of the still 80 the unconverted isopropanol, water and by-products are withdrawn through a line 92 and passed into a still 93. In the still 93 the isopropanol is removed as the azeotropic aqueous mixture through a line 94 to a condenser 95 from which part returns to the still 93 through a line 96 as reflux. The remainder of the azeotropic mixture passes to the still 70 as reflux through a line 97 by means of a pump 98, and thus the cycle is completed. The water and by-products in the still 93 are removed from the base through a line 99.

The above applications of the invention are only illustrative, and many variations thereof will be apparent to those skilled in the art. For example, the system described in which acetone is made from isopropanol may be altered to operate in a manner more like the one described for the production of acetic anhydride. Thus, in Fig. 3, the vapors to the converter 74 could be obtained from the still 93, by operating it under sufficient pressure, and the reflux therefor could be provided by the still 70, operating under atmospheric pressure. The feature of supplying the heat to the still 80 by condensing isopropanol vapor from the line 84 may be omitted, if desired. Its use, however, requires the still 70 to be operated under positive gauge pressure so that the vapor in the line 84 will have a temperature above the boiling point of the liquid in the base of the still 80. If the heating coil in the still 80 can not be made large enough to provide the desired rate of heat transfer the coil may be incorporated in a separate heat exchanger outside of the still 80 with a pump provided for circulating the liquid from the base of the still 80 through the heat exchanger and return.

Other modifications of the invention will be apparent and are included in the invention as described by the appended claims.

I claim:

1. In a cyclic vapor phase reaction process wherein the unreacted material is separated from products of reaction by means of rectification, the step of avoiding separate vaporization of the material supplied to the vapor phase reaction, which comprises adding fresh material in place of at least part of externally condensed reflux to a rectifying column in which unreacted material is being separated from less volatile liquids, recovering the unreacted material in vapor form from the rectifying column, and passing the material into the vapor phase reaction without condensation.

2. In a cyclic vapor phase reaction process wherein the unreacted material is separated from products of reaction by means of rectification, the step of avoiding separate vaporization of the material supplied to the vapor phase reaction, which comprises separating at least part of the unconverted material from the reaction products in one rectification column and introducing the separated material into a second rectification column, along with fresh material in place of externally condensed reflux therefor, and returning the vapor therefrom to the vapor phase reaction without condensation.

3. In a cyclic vapor phase reaction process wherein the unreacted material is separated from products of reaction by means of rectification, the step of simultaneously avoiding separate vaporization of the material supplied to the vapor phase reaction and securing purification of the fresh material added to the cycle, which comprises separating by rectification at least part of the unconverted material in vapor form from the less volatile reaction products mixed therewith and, after condensation, introducing the separated material into a second rectification column near the top thereof in place of at least part of the externally condensed reflux therefor, and rectifying the fresh material in said second column and returning the vapor therefrom to the vapor phase reaction without condensation.

4. In the cyclic process for making acetaldehyde by the vapor phase dehydrogenation of ethanol wherein the unreacted ethanol is separated by rectification from the products of reaction mixed therewith, the step of avoiding separate vaporization of the ethanol supplied to the vapor phase reaction, which comprises adding fresh ethanol in place of at least part of externally condensed reflux to a rectifying column, in which ethanol is being separated from water, and recovering the ethanol in vapor form from the rectifying column and passing it into the vapor phase reaction without condensation.

5. In the cyclic process for making acetic an-

hydride by the vapor phase decomposition of acetone to form ketene and its subsequent reaction with acetic acid, wherein the unreacted acetone is separated from the products of reaction by means of rectification, the step of avoiding separate vaporization of the acetone supplied to the vapor phase reaction, which comprises separating at least part of the acetone from the reaction products in one rectification column and introducing the separated acetone into a second rectification column along with fresh acetone in place of externally condensed reflux therefor, and returning the vapor therefrom to the vapor phase reaction without condensation.

6. In the cyclic process for making acetone by the vapor phase dehydrogenation of isopropanol wherein the unreacted isopropanol is separated by rectification from the products of reaction mixed therewith, the step of simultaneously avoiding separate vaporization of the isopropanol supplied to the vapor phase reaction and securing purification of the fresh isopropanol added to the cycle, which comprises separating by rectification at least part of the isopropanol in vapor form from the less volatile reaction products mixed therewith and, after condensation, introducing it into a second rectification column near the top thereof in place of at least part of the externally condensed reflux therefor, and rectifying the fresh isopropanol in said second column and returning the vapor therefrom to the vapor phase reaction without condensation.

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