METHOD FOR THE FRACTIONATION OF MIXTURES CONTAINING DICYLOPENTADIENIEN AND OTHER MATERIALS

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The invention relates to the fractionation of liquid mixtures containing dicyclopentadiene and other materials having a lower boiling point than dicyclopentadiene.

One object of this invention is to develop an improvement in the method of operation by which valuable pure products, especially pure dicyclopentadiene may be obtained with a high yield.

Further objects of the invention can be seen from the following specification of the invention and the description of the drawings which show schematically an apparatus for the realization of the invention.

Mixtures especially suitable for treatment according to the invention are the fore-runnings which are obtained by distillation of materials containing dicyclopentadiene with remaining materials of a lower boiling point of which carbon disulphide takes the greatest part (35-45% of the fore-runnings). The materials of lower boiling point include non-saturated aliphatic compounds. Although it was known that the fore-runnings of benzene contain valuable materials, the method has been developed until now to frac-
tionate the fore-runnings of benzene into useful pure materials or fractions. All efforts to separate useful mate-
rials by fractional distillation of the fore-runnings were in vain. Consequently, until the present invention, it was not possible to separate the fore-runnings of benzene and the latter were mostly added to the tar fraction used for road tar.

The present invention is based on the perception that the decomposition of dicyclopentadiene at increased temperatures is the reason for the difficulties in the fractiona-
tion of the fore-runnings of benzene. It is generally known that dicyclopentadiene decomposes at increased temperatures, especially near its boiling point (170°C.), forming monocyclopentadiene with a boiling point of 41°C. This decomposition is due to this decomposition which fractionates in colourless fractions at the base in order to obtain the necessary recirculation, results in the generation of low boiling hydrocarbons in practically all boiling ranges of the constituents of the feedstock which interfere with the normal process of fractionation and inter-
mingling with the distillates generated. For the same rea-
sions it is practically impossible to obtain pure dicyclopentadiene from the fore-runnings of benzene by normal distillation methods used in the tar industry, because even higher boiling materials are formed by polymerisation of the reactive medium at an increased temperature, and higher boiling materials also intermingling with the dicyclopentadiene fraction.

The new method for fractionation of the fore-runnings of benzene and other liquid mixtures containing dicyclopentadiene and other materials with a lower boiling point than dicyclopentadiene is characterized in that the volatile fractions are evaporated from the feedstock to at least a remain-
der which contains the main portion of dicyclopentadiene but is practically free of components boiling at a lower point than dicyclopentadiene, whereby the vola-
tilisation temperature lies below the decomposition point of dicyclopentadiene and almost no water vapours are present. After that the products of the distillation and the possible remainders are separated to form the desired fractions.

According to the invention the primary evaporation of the feedstock is carried out at a temperature below the boiling point of the constituents of the feedstock, which, under normal conditions, are liquid in the applied pres-
sure range. This temperature is advantageously not to exceed 25°C. and preferably it should be below 15°C. Using these low temperatures the stability of the dicyclo-
pentadiene is secured on one hand, and on the other the vapour pressure is so low that only a very small portion of dicyclopentadiene evaporates, so that the remaining or nearly the whole portion of dicyclopentadiene in the feedstock is enriched in the remainder of the primary evaporation.

According to the invention, the conditions concerning the temperature and the steam pressure of dicyclo-
pentadiene for the primary evaporation of the feedstock, i.e. the evaporation of its low boiling constituents, can be realized in different ways. For instance, a distillation under decreased pressure can be performed together with a fractionation and condensation of the vapours pro-
duced. Another method is to evaporate the low boiling materials by leading a carrier gas almost free of water through or above the liquid feedstock, preferably inside an insulated or heat protected container and after that containing these low boiling gas parts, the carrier gas by suitable adsorption or absorption means, said car-
rier gas being advantageously recirculated.

As carrier gas, an inert gas, preferably purified coke oven gas, may be used according to this invention.

The carrier gas enriched with the vaporizable mate-
rials is, according to this invention, brought into contact with the adsorption means, such as activated coal, silica gel, etc. The materials retained by the adsorption means may be distilled by steam, after which the adsorption means are dried and cooled, preferably by first hot, and later cold, partial flow of the carrier gas before these adsorption means may be re-used for the removal of the evaporated impurities from the carrier gas.

According to this invention it is advantageous to provide the adsorption means in a number of chambers arranged in series between which coolers may be arranged for the withdrawal of heat arising from the adsorption of the low boiling carrier gas. According to this, the adsorption may be performed at an advantageous low temperature. It would be advantageous to use two or more series of adsorbers which serve alternately for the retaining of con-
stituents of the carrier gas, the gas from one adsorber series to another can be set forth with such constituents of the feedstock evaporate, so that these adsorbers can separately be adsorbed and recovered.

A further object of the invention is to prevent the absorbed materials from the carrier gas by chemical con-
version in case the carrier gas is recirculated through the evaporator, the absorbers and the adsorbers. These materials are, for instance, unsaturated hydrocarbons which are washed out by concentrated sul-
furic acid at a suitable point of the gas recirculation.

The dicyclopentadiene and benzene contained in the feedstock may, if desired, also be evaporated and con-
densed or be removed from the carrier gas.

A preferred mode of operation according to the in-
vention is to continue the evaporation without any water until only a remainder is obtained which contains di-
cyclopentadiene and benzene. This remainder is then to be distilled by steam fractionation, so that at first a benzene fraction and afterwards a pure dicyclopentadiene fraction may be obtained.

This mode of operation has the advantage that a de-
composition of dicyclopentadiene to monocyclopenta-
diene and the formation of higher polymerisation-pro-
ducts is prevented, this fact resulting in a higher yield of dicyclopentadiene. Furthermore the gum or syrup like remainder is almost free of dicyclopentadiene which can in a pure concentration be removed in the distillation.

In case that monocyclopentadiene is contained in the feedstock, the latter before entering the primary zone of evaporation will especially be treated with heat at a temperature not exceeding 100°C. in a closed container without any evaporation or without considerable evaporation, in order to convert the monocyclopentadiene to dicyclopentadiene, which may be obtained as described above. It is also of advantage to remove, before the primary evaporation is started, from the feedstock the acid constituents such as hydrogen sulphide, hydrocyanic acid, etc.
Further objects of the present invention may be seen from the following description of a preferred embodiment of the invention according to the accompanying drawing in which there is shown a plant designed according to the invention and adapted for the fractionation of dicyclo-pentadiene: the feed stock, for instance the fore-runnings of the rectification of crude benzene, is drawn from the storage tank 1 to the mixer 2 where it is treated with lime or lime water in order to absorb the acid constituents such as hydrocyanic acid, hydrogen sulphide, etc. After the solid media and the watery solution have been removed, the mixture is brought into a closed container 3 in which it is heated to a temperature of less than 100° C. without considerable evaporation so that any monocylo-pentadiene in the stock may be converted to dicyclo-pentadiene.  

Coming from the heating container 3 the stock is then conveyed through the duct 4 into an evaporator 5 into which a duct 6 issues at the base a carrier gas, for instance cleaned coke oven gas in a finely divided state. After the carrier gas has passed through the content of the container 5 it escapes, together with the evaporated constituents of the stock, through the pipe 7 and then reaches either one of the other groups of four adsorption containers 10, 11, 12, 13 or 14, 15, 16, 17, depending on the valves 8 or 9 used. Both groups of adsorption containers are constructed in an identical manner and are used in turn as described in the following. Inside the adsorption containers, which are preferably brick lined, an adsorption material such as activated coal is suitably arranged, for instance on huddles. The gas enters the adsorption container at the top and flows through the adsorption materials from the top to the bottom. The bottom part of one adsorption container is connected with the top part of the next container by means of a pipe line 18 in which a cooler 19 is arranged controlled by two valves 20 and 21 fixed outside on both sides of the cooler. After the gases have passed over the container they enter the next at the top. After the gas has passed the last adsorption container 13 or 17 of one or the other group of adsorption containers, it flows being freed from its load, through the pipe line 25 controlled by the valves 23 and 24 and is condensed into a scrubber 26 in which the gas is treated with concentrated sulphuric acid and if necessary with other materials suitable to extract certain constituents of the gas. After that the gas reaches the cooler 27 and from there flows to a blower 28 which is connected with the duct 6 fixed at the evaporation container 5 by means of a duct 29 controlled by a valve 30. It has been seen that the carrier gas is rectified by means of the blower 28.  

The evaporator 5 is advantageously insulated against heat from the outside so that the evaporation can take place at very low temperatures. As soon as the upper adsorber group 10, 11, 12, 13 or, for instance, loaded by retaining vaporizable constituents of the carrier gas, the valves 8 and 23 are closed and the valves 22 and 24 of the lower adsorber group are opened so that the contents of this adsorber group may be loaded. After the valve 31 has been opened, steam coming from the pipe line 32 is conveyed into the adsorber 10 from the top. The vapos expelled from the adsorption materials are conveyed through the pipe line 33, in which the media expelled from the adsorption material may be condensed if occasion arises, together with water. 

One of advantage to treat the adsorption containers 10, 11, 12, 13 one after the other with steam in the described way and to obtain the expelled vapours preferably in separate fractions. As soon as the adsorption materials are regenerated, in other words, after the retained media have been expelled therefrom the steam supply is interrupted by operation of a valve 31 and the valve 36 is opened so that the carrier gas, having been heated by the heater 37 can enter the adsorber 10 through the pipe line 39 after the valve 38 has been opened. The at first hot and later on cold carrier gas causes the water within the adsorption materials to be removed and the materials to be dried and cooled so that these materials may be reused for the adsorption of components of the carrier gas. The treatment of the other adsorbers is performed in the same way. This remaining vapor is conveyed through the pipe line 41 into a still 42 after the valve 40 has been opened. In this still 42 the remainder is fractionated with which is led through the pipe line 43. The vapours leave the columns 42 at the top through the pipe line 44 and are conveyed to a condenser 45 from which the condensate can be removed through the line 46 for further use.  

The operation of the described plant may be performed as follows: in the mixer 2 four tons of certain fore-runnings of benzene are mixed with 50 kg. of lime (lime milk). After the solids and the watery solution have been removed the liquid reaches the heater 3, in which the materials are heated to a temperature of 80° C. for four hours. After cooling, the stock is conveyed to the evaporator 5. For five hours cleaned coke oven gas at a temperature of about 15° C. is fed into the evaporator at a rate of 5 cu. m./minute, simultaneous, the temperature of the liquid decreases to less than 0° C. caused by the evaporation. The volatile-laden gas is conveyed through the upper adsorber group, each adsorber containing 2.5 tons of activated coal, and is separated from this gas after that through the lower group. Between the different adsorbers the gas is cooled to 15° C. After the gas flow has been interrupted, steam is conducted through each adsorber for one hour and afterwards hot carrier gas is directed through the lower group. The balance of the 10 tons is 2.9 tons of unusable residues.  

In practical operation the amount of carrier gas which is contained in the feed stock and escape when the stock is evaporated. This carrier gas surplus is at a suitable point continuously or in certain intervals removed from the circulating carrier gas flow and in case that cleaned coke oven gas is concerned it may be fed back into the gas duct leading to the by product plant. When the carrier gas loaded with the evaporated constituents is conveyed through several adsorbers, filled for instance with activated coal, a fractionation of the constituents occurs due to the adsorption of certain constituents in certain constituents gather in certain adsorbers. By treating the different adsorbers individually in order to expel the retained media, pure fractions may be obtained. The adsorber materials and the temperature of the adsorbers should advantageously be chosen in such a way that a fraction of methylcyclo-pentadiene may be obtained from the adsorbers. 

Having thus described the present invention so that others skilled in the art may be able to understand and practice the same, I state that what I desire to secure by Letters Patent is defined in what is claimed. 

What I claim is: 

1. In the fractionation of fore-runnings obtained in the rectification of crude benzene and comprising substantial amounts of liquid mixtures of dicyclopentadiene, substantially amount of carbon disulphide, some benzene and other vaporizable materials having a boiling point lower than that of dicyclopentadiene, the improvement which comprises vaporizing the lower boiling material mixture at a temperature exceeding 25° C. while retaining the major portion of the dicyclopentadiene in the residue. 

2. The method of claim 1 wherein the residue is steam distilled. 

3. The method of claim 1 wherein the vaporization of said lower boiling media carried out at a temperature below 0° C. 

4. The method of claim 1 wherein the vaporization 85 is carried out under decreased pressure.
5. The method of claim 1 wherein the vaporization is carried out by contacting said mixture with a carrier gas which is substantially free of water.

6. The method of claim 1 wherein the vaporization is carried out by contacting said mixture with an inert carrier gas which is substantially free of water.

7. The method of claim 6 wherein said inert gas is coke oven gas.

8. The method of claim 1 wherein said mixture is heated, prior to evaporation of said low-boiling media, to a temperature not exceeding 100° C. without substantial evaporation to convert any monocylo-pentadiene present in said mixture to dicyclo-pentadiene.

9. The method of claim 1 wherein acid constituents in said mixture are eliminated prior to vaporization of said low boiling media by treating said mixture with a member of the group consisting of lime and lime milk.

10. The method of claim 1 wherein the vaporization is carried out by contacting said mixture with an inert carrier gas which is substantially free of water, the vaporized media being subsequently removed from said carrier gas by passage thereof through absorbing media.

11. A method of fractionating the fore-runnings obtained in the rectification of crude benzene, said fore-runnings comprising a liquid mixture containing substantial amounts of dicyclo-pentadiene, substantial amounts of carbon disulfide, some benzene and other vaporizable materials having a boiling point lower than that of dicyclo-pentadiene, said method comprising the steps of first removing acid constituents from said fore-runnings, thereafter heating said fore-runnings to a temperature not exceeding 100° C. to convert any monocylo-pentadiene present in the mixture to dicyclo-pentadiene, evaporating the lower boiling media from said fore-runnings at a temperature not exceeding 25° C. while retaining the main portion of the dicyclo-pentadiene in the residue.

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