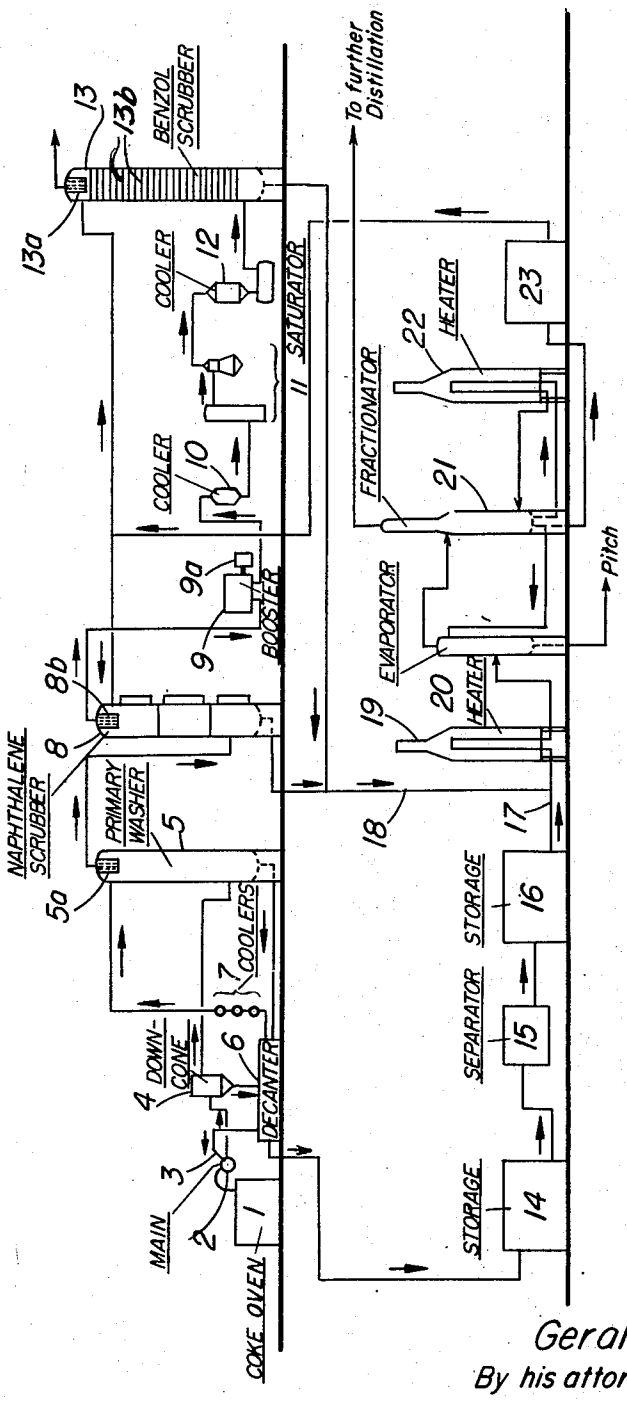
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METHOD FOR COKE-OVEN BY-PRODUCT RECOVERY

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METHOD FOR COKE-OVEN BY-PRODUCT RECOVERY

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6 Claims. (Cl. 196—8)

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This invention pertains to an improved method for the recovery of by-products from hot coke oven gases and in particular to a method and apparatus for the recovery of light oils therefrom.

In the production of coke, hot carbonaceous materials such as coal, lignite, peat or the like are heated in the absence of air with the production of certain gaseous by-products. Among these are tars, hydrocarbons such as light oils, naphthalene, various lower paraffins and olefins, and nitrogenous compounds such as ammonia and hydrogen cyanide, as well as hydrogen and oxides of carbon.

The recovery of many of these materials, especially the light oils which contain valuable aromatic compounds such as benzene, toluene and xylenes, is economically desirable.

In the processes generally used for the recovery of the light oils, tar and ammonia, and a least to a certain extent, naphthalene, are first separated from the gases. The gases are then scrubbed with a wash oil, usually of petroleum origin, which absorbs the light oils. The pressures at which such scrubbing is generally carried out range from about 0.5 to about 1.5 p. s. i. g. With relation to the quantity of wash oil used, in normal practice from about 35 to about 55 gallons of wash oil flow through a normal scrubber per gallon of light oil recovered.

To separate the light oils from their absorber oil, general practice calls for a steam stripping operation. This involves the use of considerable quantities of steam and is expensive. In the past, suggestions have been made that the separation be carried out by distillation, but in the ordinary process, with its relatively high ratio of wash oils to light oils, such an expedient has been even more expensive than steam stripping, in most instances.

It is an object of the present invention to provide a process whereby light oils can be recovered from coke oven gases with less expense than has been possible hitherto.

It is another object of the present invention to provide a process for the separation of light oils from coke oven gases wherein steam stripping is eliminated.

It is another object of the present invention to provide a process for the recovery of light oils from coke oven gases by scrubbing with an absorber oil wherein the separation of light oils from the mixture of absorber oil and light oil by distillation is made practical.

It is a further object of the invention to provide a method for the recovery of by-products from

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hot coke oven gases wherein the gases are scrubbed with an absorber oil to separate naphthalene therefrom and in a second treatment are scrubbed with an absorber oil to remove light oils therefrom and characterized in that the separation of the light oils from their absorber oil and naphthalene from its absorber oil may be carried out by codistillation.

Other objects of the invention will appear from a consideration of the following specification and claims.

According to the invention, the above objects are attained by compressing the gases, after they have been cleansed of tar and naphthalene and before treatment to remove light oils, to above about 5 p. s. i. g., preferably above about 30 p. s. i. g., and advantageously from about 50 p. s. i. g. to about 100 p. s. i. g. At this pressure, and usually at a temperature of from about 20 to about 40° C., the gases are scrubbed with an absorber oil for the removal of their light oil content.

By the term "absorber oil," I mean an oil having an initial point (atmospheric distillation) above about 225° C. and an end point not higher than about 400° C. which will take up light oils from the coke oven gases. Preferably the absorber oil will have an initial point of about 230° C. and end point of about 300° C. Such absorber oils may, for example, be of petroleum origin or may be creosote oils derived from the distillation of coal tar itself.

The invention is particularly useful in a process such as that disclosed and claimed in my copending application Serial No. 161,325, filed May 11, 1950, for "Method and Apparatus for Coke Oven By-Product Recovery," where the coke oven gases having been cooled and cleansed of tar are first treated with an absorber oil which is continuously revivified by distillation for the absorption of naphthalene therefrom and where the resulting mixture of naphthalene and absorber oil is combined with a heavy carrier and distilled to produce the naphthalene and the purified absorber oil.

When the present invention is used in such a process, the mixture of light oil and absorber oil may be combined directly with the naphthalene-absorber oil-heavy carrier mixture and the combined streams distilled in one operation with the production of naphthalene, light oils and a revivified absorber oil. The cooperative relationship between such process and the present invention is particularly close because when a continuously revivified absorber oil is used, it is pos-

sible to employ a bubble plate scrubbing column for the separation of the light oils from the gases without fear of the plates clogging up with polymerized absorber oil or sludge. The use of bubble plate scrubbing columns is more adaptable to relatively high pressure operation than spray or packed type apparatus which ordinarily must be used because of the sludge problem and because the lower pressure drop of spray or packed type columns is more suitable for low pressure systems. In turn, the use of pressures in excess of 30 p. s. i. g. enables the amount of scrubbing oil to be reduced to the point where the quantity of material which must be handled in the distillation column is sufficiently small that the heat requirements will be less than those necessary to carry out steam stripping.

As pointed out in my said copending application Ser. No. 161,325, by the term "heavy carrier" is meant a liquid hydrocarbon carrier having an end point above the end point of the absorber oil and one, at least a portion of which will remain liquid when the absorber oil is vaporized. The carrier may be of petroleum origin or may be a coal tar. Examples of suitable carriers are coke oven by-product tar, and Bunker C fuel oil of petroleum origin.

The proportion of carrier in the distilland should generally be not less than about 2% by weight. One function of the carrier is to insure that no particles of tar or pitch carried into subsequent distillation equipment will remain on any hot surface and there polymerize to coke. The minimum percent specified is considered the least quantity which will perform this function.

Where the boiling point range of the carrier is such that a part of it is vaporized with the absorber oil, the total quantity of carrier added must be such that the fraction which will remain liquid upon vaporization of the absorber oil constitutes not less than 2% of the distilland.

There is no upper limit to the quantity of carrier which may be added, but if the carrier is added solely for the purpose of preventing the coking of entrained tar and pitch, in general no more than the amount required for that purpose will be added.

It will be understood that the boiling point of the absorber oil is dependent on the nature of the carrier used and the one must be chosen with due regard to the other. Thus, if by-product tar is used as a carrier, the boiling range of the absorber oil must be such that its end point is below about 335° C., in order that the absorber oil may be readily purified of the phenanthrene and anthracene normally present in coal tars by distillation.

The exact pressure which is used in the light oil scrubbing tower is subject to considerable variation. The stated lower limit of 5 p. s. i. g. has been found to be approximately the lowest pressure at which a bubble plate scrubbing column may be used to advantage. Where distillation rather than steam stripping is to be used to separate the light oil from its absorber oil, a pressure of above about 30 p. s. i. g. will generally be necessary for economic operation. As may readily be appreciated, there is no upper limit other than that dictated by the apparatus available. Advantageously the light oil scrubber will be operated at from about 50 p. s. i. g. to about 100 p. s. i. g.

Theoretically it is desirable to conduct the absorption at the lowest temperature possible. In practice, the scrubbing tower is usually operated at between 20° C. and 40° C.

The quantity of absorber oil used in the light oil scrubbing will depend on operating pressures and temperatures. By way of example, however, at a pressure of 50 p. s. i. g. and a temperature of 30° C. about 10 gallons of wash oil are necessary, per gallon of light oils recovered.

In the preferred embodiment of the invention, the absorber oil used is a creosote oil having a boiling point range (atmospheric distillation) of from about 230° C. to about 300° C. and produced from the coke oven gases themselves. Moreover, in the preferred embodiment, the gases are first contacted with water to remove tar and then with a creosote absorber oil to remove naphthalene. The tar removed from the gases is used as the heavy carrier and is combined with the naphthalene rich absorber oil and the light oil rich absorber oil. This mixture is then fractionated into its various components.

In the drawings, the figure is a flow diagram of a coke oven by-product recovery system according to the preferred embodiment of the invention.

Referring to the figure, the hot gases issuing from coke oven 1 are at a temperature of about 800° C. They pass into a collecting main 2 where they are met with a spray of aqueous flushing liquor introduced through an injector 3. By contact with this liquor, their temperature is reduced to from about 60° C. to about 100° C., a portion of the ammonia in the gases is absorbed and some of the tar and naphthalene is condensed. The foul flushing liquor together with its tar and naphthalene and the absorbed ammonia passes through a downcomer 4 into a decanter 6. In the decanter, it separates into a tar layer and a water layer, the water layer being reused as flushing liquor in the collecting main 2.

The gases move from downcomer 4 to a primary cooler 5 where they are again contacted with an aqueous spray. The liquid for the primary cooler sprays may also be drawn from decanter 6 and may be cooled as by passage through coolers 7. As they emerge from the top of the primary cooler, the gases pass through an entrainment removal device 5a provided at the top of the primary cooler. At this point, the gases are at a temperature of from about 20° C. to about 40° C. Their naphthalene content may be from about 50 to about 250 grains per hundred cubic feet.

From the primary cooler, the gases are sent through a naphthalene scrubber 8 where they are met with a stream of creosote absorber oil produced from the by-products themselves. Details of operation of a preferred type of naphthalene scrubber are described in my copending application Serial No. 161,325.

Moving out of the naphthalene scrubber 8, the gases whose naphthalene content is now reduced to from about 1 to about 5 grains per hundred cubic feet pass through an entrainment removal device 8b and are delivered to the suction side of a system of boosters and intercoolers designated as 9 in Fig. 1. The boosters may be driven by a steam turbine 9a. In the booster system, the pressure of the gases is raised to above about 30 p. s. i. g., usually to from about 50 to about 100 p. s. i. g. As a result of this compression, the temperature of the gas is raised. From the booster system, the gas is delivered to an intermediate cooler 10 where its temperature is reduced to from about 50 to about 80° C. At this

temperature, the gas is delivered to a conventional ammonia saturator 11 where the ammonia is removed. Leaving the ammonia saturator, the temperature of the gases is still from about 50 to about 80° C. They are therefore passed to a final cooler 12 wherein their temperature is again reduced to from about 20 to about 40° C. At this temperature and at a pressure which is still above about 50 p. s. i. g., the gases are passed upwardly through a light oil or benzol scrubber 13 where they are contacted with a creosote wash oil of the same nature as that used in the naphthalene scrubber 8. The benzol scrubber 13 preferably contains a number of bubble plates 13b, since, as pointed out above, the use of a bubble plate scrubbing tower is particularly adapted for pressure operations. At the exit from the benzol scrubber, the gases are run through an entrainment removal device 13a and emerge clean and dry and ready to pass directly to the fuel mains and burners or to further processing systems.

As pointed out above, the decanter 6 contains a water layer and a tar layer. The tar layer is drawn off and charged to a wet tar storage tank 14. Emerging from storage tank 14, the tar passes through a centrifugal separator 15 where it is cleansed of water and solid impurities. The clean tar is charged to a dry tar storage tank 16. From there, it is combined with the naphthalene rich absorber oil drawn from the bottom of naphthalene scrubber 8 and the light oil rich absorber oil drawn from the bottom of light oil scrubber 13 and charged to a fired pipe still heater 19. There, the temperature of the combined streams is raised and they are delivered to an evaporator 20 for the separation of pitch. Details of evaporator 20 may be found in my said copending application Ser. No. 161,325. The bottoms from the evaporator 20 are drawn off and may be sent to pitch storage, not shown.

The overhead from the evaporator 20 may be charged to a fractionator 21 for the separation of the absorber oil from the lower boiling components.

A portion of the bottoms from the fractionator 21 consisting of a creosote oil which should contain less than 1% of naphthalene may be refluxed to the evaporator 20. A second bottoms stream from the fractionator 21 may be passed through a reboiler 22 and recharged to the bottom of fractionator 21. A third bottoms stream from fractionator 21 may be charged to a creosote oil storage tank 23 for further use in scrubbers 8 and 13.

The overhead from fractionator 21 may be charged to further distillation equipment for separation into its components in any convenient manner, as for example in a system similar to that shown in my said copending application Ser. No. 161,325.

It will be understood that the mixture of light oil and absorber oil need not be delivered to distillation apparatus as in the process described, but may be steam stripped. In such case the pressure in scrubber 13 need be maintained only above about 5 p. s. i. g.

As pointed out, the system described, wherein the light oil is removed from the gases under a pressure of above about 30 p. s. i. g., results in many savings where considered by itself. The benefits to be obtained from the invention are increased, however, when the gases are further processed at high pressure after leaving the light oil scrubber. For example, the gases leaving the light oil scrubber may be subjected to hypersorption with activated carbon at elevated pressures for the recovery of ethylene, hydrogen cyanide and other light components. such processes are not usually economical where the gas leaving the light oil scrubber is boosted to processing pressure for this purpose alone. On the other hand, where the gases have already been compressed prior to light oil absorption, the cost of the compression is borne partly by the increased efficiency of the light oil absorption, and in part by the additional materials subsequently recovered, with the result that the process as a whole becomes economically practicable.

Although the recovery system described above is, in my opinion, the most efficient method of employing my invention, it is to be understood that the invention is not limited to use in such a system. Thus, for example, it is not necessary that the light oil rich absorber oil from the light oil scrubber be combined and codistilled along with a naphthalene rich absorber oil and a heavy carrier. Moreover, it is not necessary that the absorber oil used be a creosote oil or that, if a heavy carrier is used, it be a coke oven by-product tar. Similarly, while it is considered that a bubble plate scrubbing tower will be most effective at the pressures involved, it is obvious that other types of apparatus may be used with varying degrees of effectiveness, without departing from the invention.

What I claim is:

1. In a process for the recovery of by-products from hot coke oven gases, a combination of steps which comprises removing tar from the gases, subsequently compressing the gases, contacting the gases at a pressure of above about 30 p. s. i. g. with a substantially naphthalene and light oil free absorber oil having an initial point above about 225° C. and an end point not higher than about 400° C. to remove light oils therefrom with consequent enrichment of said absorber oil and distilling at least a portion of the light oil rich absorber oil to separate light oils therefrom, said distillation being conducted solely by indirectly heating said light oil rich absorber oil.

2. In a process for the recovery of by-products from hot coke oven gases, a combination of steps which comprises removing tar from the gases, contacting the gases with a substantially naphthalene-free absorber oil having an initial point of above about 225° C. and an end point not higher than about 400° C. for the removal of naphthalene therefrom, subsequently compressing the gases, contacting the gases at a pressure of above about 30 p. s. i. g. with a substantially naphthalene and light oil free absorber oil having an initial point of above about 225° C. and an end point not higher than about 400° C. to remove light oils therefrom with consequent enrichment of said absorber oil and distilling at least a portion of the light oil rich absorber oil to separate the light oil therefrom, said distillation being conducted solely by indirectly heating said light oil rich absorber oil.

3. In a process for the recovery of by-products from hot coke oven gases, a combination of steps which comprises removing tar from said gases, contacting the gases with a substantially naphthalene-free absorber oil having an initial point above about 225° C. and an end point not higher than about 400° C. for the removal of naphthalene therefrom with consequent enrichment of said absorber oil, contacting the gases at a pressure of above about 30 p. s. i. g. with a substantially light oil and naphthalene free absorber oil having an initial point above about 225° C. and

an end point not higher than about 400° C. to remove light oils therefrom with consequent enrichment of said absorber oil, and distilling said light oil rich absorber oil and said naphthalene rich absorber oil in admixture with a liquid hydrocarbon carrier having an end point greater than the end point of the absorber oil, at least a portion of which carrier will remain liquid when the absorber oil is vaporized, said distillation being conducted solely by indirectly heating said mixture.

4. In a process for the recovery of by-products from hot coke oven gases, a combination of steps which comprises removing tar from the gases, subsequently compressing the gases, contacting the gases at a pressure above about 30 p. s. i. g. with a substantially naphthalene and light oil free creosote absorber oil having an initial point above about 225° C. and an end point not higher than about 400° C. to remove light oils therefrom with consequent enrichment of the absorber oil and distilling the light oil rich absorber oil to separate light oils therefrom and to revivify said absorber oil, said distillation being conducted solely by indirectly heating said light oil rich absorber oil.

5. In a process for the recovery of by-products from hot coke oven gases, a combination of steps which comprises removing tar from said gases, contacting the gases with a substantially naphthalene-free creosote absorber oil having an initial point above about 225° C. and an end point not higher than about 400° C. for the removal of naphthalene therefrom, subsequently compressing the gases, contacting the gases at a pressure of above about 30 p. s. i. g. with a substantially naphthalene and light oil free creosote absorber oil having an initial point above about 225° C. and an end point not higher than about 400° C. to remove the light oils therefrom

with consequent enrichment of the absorber oil and distilling the light oil rich absorber oil to separate light oils therefrom and to revivify said absorber oil, said distillation being conducted solely by indirectly heating said light oil rich absorber oil.

6. In a process for the recovery of by-products from hot coke oven gases, a combination of steps which comprises removing tar from said gases, contacting the gases with a substantially naphthalene and light oil free creosote absorber oil having an initial point above about 225° C. and an end point not higher than about 335° C. for the removal of naphthalene therefrom with consequent enrichment of said absorber oil, contacting the gases at a pressure above about 30 p. s. i. g. with a substantially naphthalene and light oil free creosote absorber oil having an initial point above about 225° C. and an end point not higher than about 335° C. to remove light oils therefrom with consequent enrichment of said absorber oil and distilling the tar previously separated in admixture with the naphthalene rich absorber oil and the light oil rich absorber oil to recover the naphthalene and light oil therefrom and to revivify the absorber oil, said distillation being conducted solely by indirectly heating said mixture.

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