

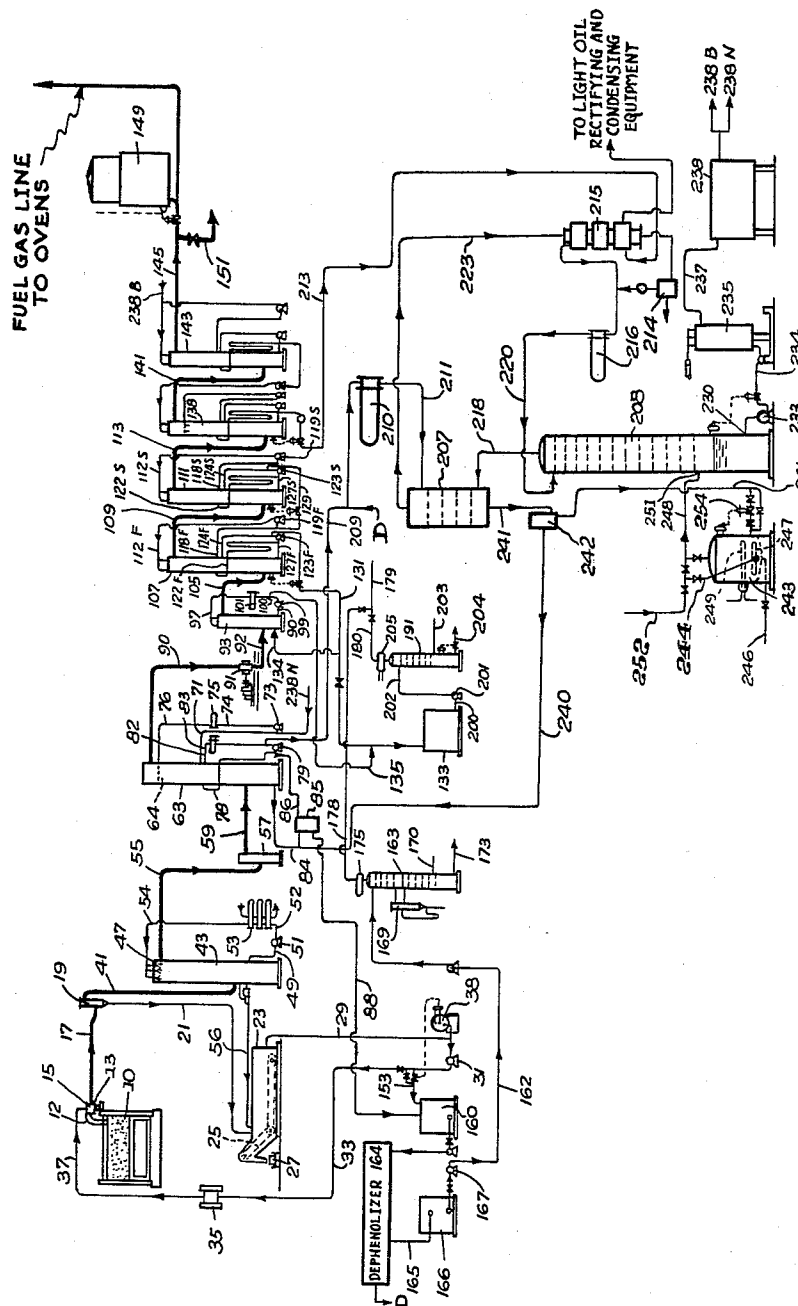
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COKE OVEN GAS BY-PRODUCT RECOVERY

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COKE OVEN GAS BY-PRODUCT RECOVERY

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This invention relates generally to the recovery of the gases from the coking of coal.

When coal and other bituminous materials are heated in a coke oven in the absence of air, large volumes of gas, known as "coke oven gas" are driven off the coal leaving a residue of carbonaceous material. This gas contains various valuable by-products such as ammonia, naphthalene, tar, and light oils such as benzene, toluene, and xylene, which by-products are recovered at the coke plant. The provisions for the recovery of these by-products involves a large capital expense, and efforts are now being made to utilize these provisions and increase their capacity without changing their physical dimensions. Efforts are also being made to automate these units and to decrease the "down" time during which the units are undergoing repairs or maintenance. One of the problems existing heretofore in automating and increasing the capacity of the by-product recovery system has been that the naphthalene compound tends to settle out as a solid and thereby clog the lines.

An object of the present invention therefore is to provide a novel apparatus and process providing a system for the recovery of gases and other materials evolved during the coking of bituminous coal and particularly adapted for the automation of such a system. Another object is to provide novel apparatus and process for removing the naphthalene from coke oven gas prior to the removal of the ammonia from the gas, thereby eliminating the possibility of naphthalene clogging the lines during subsequent steps of material removal from the gas.

A further object is to provide novel apparatus and process for removing naphthalene from the gas in an absorbent oil, for removing the light oil from the gas in an absorbent oil, and for removing the naphthalene and the light oil from the absorbent oil simultaneously with minimum amount of heat and process steam.

A still further object is to provide a novel process and apparatus for removing the ammonia from the gas with two liquors which are kept separated whereby the ammonia is stripped from each liquor separately.

The absorbent oil, known as "wash oil," used in the novel process of the invention is advantageously a petroleum type absorbent oil having a boiling range within the limits of 250° C. and 400° C., preferably within the range of 300° C. to 370° C. A "creosote" type absorbent oil obtained by distillation of coal tar may also be used, but the corrosion problems generally encountered with creosote oil are avoided by use of the petroleum type.

The aqueous liquors are used for removing the ammonia from the gas and are defined herein as "flushing liquor" and "ammonia wash liquor." In accordance with this invention, the ammonia wash liquor may be stripped of its ammonia content and the liquor cooled and recycled for further ammonia absorption without additional treatment, and thereby prevent even its small amount of phenol from going into sewage. This liquor

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may be recirculated because it contains little or no fixed salts such as ammonium chloride.

According to this invention, a naphthalene scrubber, located immediately after the conventional primary coolers and tar precipitators, removes naphthalene from the coke oven gas as soon as possible to prevent deposition of solid naphthalene in the gas piping and coal chemical recovery equipment. With the naphthalene scrubber thus located ahead of the ammonia removal equipment, a minimum quantity of absorbent oil is used for the naphthalene absorption to minimize the introduction of ammonia and ammonia containing compounds into the subsequent light oil recovery system. It is also desirable that the ammonia absorbed by the minor quantity of absorbent oil leaving the naphthalene scrubber be removed before this oil mixes with the major quantity of wash oil from the benzol scrubbers. Contamination of the light oil recovery system with the ammonia containing rich oil from the naphthalene scrubber could be prevented by the use of a separate stripping still for each oil quantity, thereby keeping one absorbed oil entirely separated from the other. Such an arrangement, however, would require a substantially greater quantity of stripping steam than is now used in conventional practice.

Since naphthalene is one of the least volatile materials absorbed from the gas, it is one of the most difficult to strip from the wash oil. For equal quantities of naphthalene and benzene absorbed in wash oil a great deal more stripping steam is required for stripping the naphthalene than for the benzol. In normal benzol washer operation, as known heretofore, about 0.43 pound of naphthalene are removed in the benzol washers per ton of coal carbonized. This quantity will vary, depending upon the temperature of the wash oil and gas in the benzol washers and the efficiency of stripping in the wash oil still, and the above quantity is estimated as being representative of an average condition. The quantity of wash oil circulated over the benzol washers in conventional operation is usually in the neighborhood of 165 gallons of wash oil per ton of coal carbonized. The normal quantity of stripping steam to the stripping still, which is usually operated at 120° C., is about 0.65 pound of steam per gallon of wash oil. This is equivalent to 107 pounds of steam per ton of coal carbonized. Under these conditions, the steam used in the stripping still is sufficient to remove the naphthalene absorbed in the benzol washers when the naphthalene content of the oil entering the stripping still is about 2% by weight. The quantity of naphthalene absorbed in the benzol washer and removed in the stripping still under these conditions is equivalent to about 0.035% by weight of the wash oil circulating over the benzol washers. Under these conditions, the oil entering the stripping still would contain 2.0% by weight naphthalene and the oil leaving the stripping still for return to the benzol washers would contain 1.965% by weight of naphthalene. Thus, it is evident that the removal of naphthalene is limited by the quantity of steam used in the stripping still.

The quantity of naphthalene removed from the gas depends upon the naphthalene content of the debenzolized oil circulated over the scrubbers, the temperature of the absorption, and the quantity of oil circulated. At a given absorption temperature and inlet concentration of naphthalene in the gas, the amount of naphthalene absorbed is determined by the naphthalene content of the wash oil to the scrubbers. With other conditions being equal, therefore, it can be seen that the naphthalene removal from the gas is determined by the quantity of stripping steam used in the stripping still.

The benzol washers are conventionally operated at

slightly higher than atmospheric pressures, usually at about 800 mm. of mercury absolute. Operation at higher pressures, however, offers certain advantages. Operation of the benzol washers at super atmospheric pressure of the gas permits a substantial reduction of the wash oil circulation rate and of the stripping steam. The higher gas pressure makes it possible to enrich the benzolized wash oil leaving the benzol washers to a greater extent, i.e., substantially proportional to the ratio of the absolute pressures. The enrichment of the wash oil when the gas pressure is 1450 mm. Hg absolute, for example, can be about 1.8 times that obtainable at the conventional lower pressure of 800 mm. The higher concentration of light oil constituents in the benzolized wash oil in turn makes it possible to reduce the stripping steam requirements substantially in inverse proportion to the ratio of the absolute pressure. It will be understood, of course, that these pressures carry through the ammonia washers and any other gas treating units beyond the pressure side of the booster which takes the gas from the coke oven and forces it through the units beyond the boosters. This invention functions well with either the conventional or the higher pressure operations.

It has been found that if the small quantity of rich wash oil from the naphthalene scrubber is mixed with the benzolized oil from the benzol washers and the mixture be sent to the stripping still, the total naphthalene to be removed in the stripping still is about 1.39 pounds of naphthalene per ton of coal. This is about 3.25 times the quantity of naphthalene normally required to be removed from the wash oil in the stripping still. If it were attempted to operate in this manner with the reduced quantity of steam required for stripping the light oil products absorbed at the higher pressure, the naphthalene in the benzolized wash oil and debenzolized wash oil build up to the point where it is impossible to obtain satisfactory naphthalene removal in the scrubber and benzol washers. The novel process and apparatus of this invention permits satisfactory removal of the increased quantity of total naphthalene absorbed in both the naphthalene scrubber and the benzol washers by the reduced quantity of stripping steam available, and at the same time minimizes contamination of the wash oil circulating system for the benzol scrubbers with ammonia, tar, sludge, and other impurities that may be picked up by the wash oil in the naphthalene scrubber.

The novel process and apparatus of this invention provides for circulation of a small amount, for example less than ten gallons, of wash oil per ton of coal, over the naphthalene scrubber. To obtain satisfactory contact between this limited quantity of wash oil and the large amount of coke oven gas to be scrubbed, the oil may be recirculated from bottom to top of one or more recirculating stages in the naphthalene scrubber, advantageously at least two recirculated stages. These stages may be provided with packing or sprays.

In accordance with this invention, naphthalene rich wash oil from the naphthalene scrubber is fed to a first stripping still which may consist of from one to ten trays, although it is believed that the optimum number of stripping trays is between two and five. The naphthalene rich wash oil enters the top stripping tray and flows from the bottom stripping tray to the wash oil purifier. The wash oil from the naphthalene stripper is kept separate from the benzolized oil from the benzol washers. The benzolized wash oil from the benzol scrubbers is fed to the upper portion of a second stripping still and flows downwardly through the still. The wash oil flowing from the first stripping still with most of its naphthalene stripped therefrom flows into a wash oil purifier where the wash oil and residual naphthalene are vaporized with heat and live steam and any tar, pitch, sludge, or polymerized material is removed as residue in the wash oil purifier and thus kept out of the wash oil circulated over the benzol washers. The wash oil vapors from the purifier

are fed to the second still and condensed in the latter still. Stripping steam and wash oil vapors enter the bottom of the second still and flow upwardly in counter-current contact with the wash oil from the benzol scrubbers, thus stripping the light oil products from the wash oil from the benzol scrubbers. The wash oil vapors condense in the second still. The steam and light oil vapors then flow from the second still upwardly through the first stripping still and strip the naphthalene from the oil from the naphthalene scrubbers. The combined vapors that leave the top of the first stripping still pass through a conventional vapor to oil heat exchanger, light oil rectifier and light oil condenser. The purified wash oil thus is mixed with the wash oil circulation for the benzol scrubbers. The small amount of wash oil circulated over the naphthalene scrubber is taken from the oil pumped from the base of the wash oil still to the benzol washer. Thus, a small percentage of the wash oil circulation for the benzol washers is continuously bled off for absorption of naphthalene in the naphthalene absorbers; but before this oil is returned to the recirculating system for the benzol washers, any ammonia and other volatile constituents are removed in the first stripping still and any high boiling non-volatile materials are removed as residue in the purifier, thereby removing any contaminants which otherwise would build up in the wash oil system and enter the oil both from the benzol washers and from the naphthalene scrubber. The foregoing purifies the wash oil while removing the normal contaminants and sludge which build up in the benzol washer system as well as the additional contaminants which are absorbed in the naphthalene scrubber. By utilizing the same stripping steam three times in the wash oil purifier, in the second stripping still, and in the fuel stripping still, the quantity of stripping steam required for purifying the wash oil and for stripping the light oil constituents and naphthalene from the wash oil from the benzol washers, and a relatively large quantity of naphthalene from the wash oil from the naphthalene scrubbers, is minimized, and the utilization of the wash oil purifier is increased to take care of the additional contaminants introduced in the naphthalene scrubbers without sacrificing its ability to keep the sludge and non-volatile contaminants in the benzol washer system at a satisfactory level.

In accordance with this invention, the flushing liquor which cools the gases evolved during the coking of coal and removes some phenol therefrom and some ammonia as free ammonia and some as fixed ammonia (such as in ammonium chloride), and the wash liquor which is later used to remove the remainder of the free ammonia from the gas, are kept separate. Thus, when the ammonia is recovered from the liquor, it is necessary to add materials, such as milk of lime, only to the flushing liquor to free the fixed ammonia, since the wash liquor will contain little or no fixed ammonia. The ammonia recovered from both liquors may be combined and used for production of fertilizer or burned. The gas is washed with an absorbent oil prior to the ammonia recovery step to remove the naphthalene from the gas, thereby preventing deposition of naphthalene during subsequent processing of the gas; this washing also removes the major part of the residual phenol from the gas whereby the phenol content of the wash liquor which contains the free ammonia is substantially reduced and phenol may be removed only from the surplus flushing liquor prior to being sent to waste. The gas is also scrubbed with wash oil to remove light oil after the step of washing to remove the ammonia. The naphthalene and the light oil are both stripped from the absorbent oil in a manner wherein the vapors from a light oil stripping still are applied to a still for stripping the naphthalene from the naphthalene rich oil, the stripped absorbent oil from the naphthalene stripping still is then vaporized with steam and the resulting vapors are fed to the light oil stripping still for stripping the light oil from the light oil rich oil,

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and a major portion of the stripped absorbent oil from the light oil stripping still is used for the benzene or light oil scrubbing and a minor portion used for the naphthalene scrubbing.

In a preferred embodiment of this invention, the by-product system is combined with means for rendering the operation of the system automatic. A particular advantage of this by-product system of the invention is the fact that the early removal of naphthalene and the recovery of ammonia as a vapor rather than as a solid salt of ammonia substantially prevents unexpected flow stoppages and renders the process better adapted to automatic control.

The above and further objects and novel features will appear more fully from the following detailed description when the same is read in connection with the accompanying drawing. It is to be understood, however, that the drawing is not intended as a definition of the invention but is for the purpose of illustration only.

The single sheet of drawing schematically illustrates a novel arrangement of apparatus for carrying out the invention.

Turning now to the novel arrangement of apparatus for carrying out the process of the invention, the coal or other bituminous material is heated in a conventional coke oven battery 10 in the absence of air. The gas evolved flows through conduit 12 to a collector main 13. Flushing liquor sprays into the conduits 12 and collector main 13 through injectors 15 cooling the hot gases and condensing some of the tar. The mixture of flushing liquor, gas, and tar flow through conduit 17 to a downcomer 19 where the gases separate from the liquor and tar.

The liquor and tar flow through a line 21 from downcomer 19 to a flushing liquor decanter tank 23 where the tar being heavier than the liquor settles to the bottom and is pumped by way of a conventional line (not shown) to storage. The pitch sludge is conveyed by scraper 25 to cart 27. The liquor overflows through line 29 and is forced by a pump 31 through line 33, a screen 35, and line 37 to injectors 15. Circulating tank 38 serves as a reservoir for the flushing liquor.

The gas flows through a conduit 41 from downcomer 19 to the lower section of a conventional primary cooler 43. The gas ascends the primary cooler countercurrent to the liquid descending from sprays 47. This liquor collects at the lower portion of primary cooler 43 and flows through a line 49 to a pump 51 which recirculates the liquid through a line 52, a cooler 53, and a line 54 back to the sprays 47. Excess liquor and condensed tar also overflow through line 56 to the decanter tank 23. The gas leaves primary cooler 43 through a conduit 55, flows to an electrostatic precipitator 57 which removes substantially all the tar from the gas, and then flows through a conduit 59 to the lower portion of a naphthalene scrubber 63.

The gas ascends naphthalene scrubber 63 countercurrent to the descent of absorbent or wash oil sprayed into the scrubber at sprays 64. Scrubber 63 is illustrated herein as being divided into two sections so that the absorbing oil from sprays 64 collect at the center of the scrubber and flow through conduit 71 to a pump 73 and through line 74, cooler 75, and lines 76 back to sprays 64. A portion of this oil also flows through line 78, a pump 79, line 81, cooler 82 and line 83 in the lower section. The wash oil collects in the bottom portion of the scrubber and flows through line 84 to a decanter 85 where the wash oil is separated from any aqueous condensate. The wash oil is sent by line 86 to pump 79, and the condensate is sent to storage tank 160 through line 88. The gas which leaves at conduit 90 has the naphthalene content so reduced as to substantially eliminate the danger of any naphthalene clogging the apparatus lines during the further processing of the gas. The volume of wash oil that enters the scrubber through line 238 leaves at line 209 as

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an equivalent volume with the naphthalene and higher boiling hydrocarbons therein, i.e., as naphthalene rich oil.

The naphthalene-free gas flows through conduit 90 to a booster 91, which raises the gas to a pressure such that the pressure of the gas leaving the system at line 92 is substantially the pressure required to deliver the gas to the points of utilization at sufficient pressure for use. This compression of the gas raises the temperature of the gas. Accordingly, the gas flows through conduit 90 to the lower portion of final cooler 93 where the gas flows upwardly countercurrent to the flow of water sprayed into the top by way of line 97. The water collects at the bottom of cooler 93 and flows back through line 90, pump 99, line 100, cooler 101, and line 97 into the cooler. The gas flows from cooler 93 through a line 105 to the lower portion of an ammonia washer 107.

The gas flows upwardly through washer 107 and through a line 109 to the lower portion of a second washer 111 similar to washer 107. The gas leaves washer 111 at line 113 substantially free of ammonia. In washer 107, 111 the gas ascending through the washer is contacted with water descending (not shown) within the washer from sprays connected to line 112F and 112S. Each washer is shown herein as having two sections. The water collects at the upper section and flows through line 118F, 118S, pump 119F, 119S, and line 112F, 112S back to the sprays. The excess liquor collecting in the upper section overflows through line 122F, 122S to the suction of pump 123F, 123S where it joins with the liquor being recirculated through line 124F, 124S to sprays in the lower section of the washer. The solution collects at the bottom of the washer and flows through line 127F, 127S to the pump 123F, 123S. The solution from washer 111 also flows through line 124S to line 129 to pump 119F and to washer 107. The solution from washer 107 flows through line 127F to pump 123F and then flows through line 131 to a storage tank 133. The solution from line 131 may alternately flow to tank 133 by way of line 134, the final cooler 93, and line 135.

The gas which leaves washer 111 at line 113 is substantially free of ammonia and flows to a first benzol washer 138 and through conduit 141 to a second benzol washer 143. The gas which leaves washer 143 at conduit 145 is substantially free of valuable by-products such as tar, naphthalene, ammonia, and light oil. This gas may then flow to a suitable gas holder 149 and through line 151 to a consumer for the production of chemicals such as synthetic ammonia or to a steel plant as fuel in open hearth furnaces, etc.

Benzol washers 138 and 143 may be substantially identical to the ammonia washers 107, 111 except that where the gas is washed in the ammonia washers with water the gas in the benzol scrubbers is washed with the absorbent oil. Also, where such ammonia washers usually have two steps of wash, each benzol washer may have three or four stages. The light oil, i.e., the benzene, toluene, xylene components, of the coke oven gas is absorbed from the gas into the absorbent oil.

The foregoing has described the flow of gas from the coke oven battery to the point of utilization and the removal of the valuable constituents from the gas with an absorbing medium, i.e., water or absorbent oil. It will be clear to those skilled in the art that this novel arrangement involves various elements such as coke oven battery 10, decanter tank 23, primary cooler 43, naphthalene scrubber 63, tar precipitators 57, final cooler 93 ammonia washers 107, 111, benzol scrubbers 138, 143 and gas holder 149 that are conventional units for the coking of coal and the recovery of by-products from the gases evolved during the coking.

Considering now the recovery of the by-products from the absorbing medium, the excess flushing liquor flows from recycle line 33 through line 153 to flushing liquor storage tank 160. This liquor contains in solution free ammonia, fixed ammonia (primarily as ammonium chlo-

ride), and phenol, as well as other impurities such as pyridine, hydrogen sulfide, and cyanides. The ammonia is stripped from the liquor in an ammonia still 163; but, in those areas in which the deammoniated liquor can not be released to sewerage without removal of the phenol, the liquor must be sent through dephenolizing stage 164 which may be of any conventional type, a particular desirable type for this use is the dephenolizing system described in our copending application Serial No. 679,701. From the dephenolizing operation, the solution flows through line 165 to a storage tank 166 and through pump 167 and line 162 to the upper portion of ammonia still 163. The milk of lime slurry is added to still 163 by way of a conventional lime leg 169 and steam is added at 170 to strip the ammonia from the solution. The solution substantially free of ammonia and phenol is then released through outlet 173 to sewerage. The steam and ammonia vapors from the upper portion of still 163 pass through a dephlegmator 175 where they are subjected to cooling so that the greater portion of the water vapor is removed from the ammonia vapor. The ammonia vapor then flows through line 178 to a line 179 which is connected to the outlet line 180 of a second ammonia still 191.

This second ammonia still 191 receives the wash liquor which flows from the ammonia washer tank 133 through line 200, pump 201, line 202, to the upper portion of the still. As this liquor descends through the still, steam supplied at inlet 203 strips the ammonia from the liquor. Most of the water vapor is removed from the vapor leaving the still by the dephlegmator 205, and the ammonia vapor flows through line 180 to line 179. The ammonia in line 179 may be sent to a conventional ammonia saturator of the type used in the indirect process of ammonia recovery, if there be a demand for ammonium sulfate or ammonium phosphates. If the demand for such ammonium salts be low the ammonia may then be sent to a boiler or to a flare to be burned.

The foregoing has presented a novel arrangement wherein the flushing liquor which contains both fixed and free ammonia and the solution from the ammonia washers which contains only free ammonia is maintained separate and the ammonia is stripped separately from the solutions. Thus, it is necessary to apply a lime slurry only to the still wherein fixed ammonia is being stripped from the flushing liquor as the solution from the ammonia washers contains little if any fixed ammonia. Also it has been found necessary in accordance with this invention to remove the phenol only from the flushing liquor containing the fixed ammonia as the naphthalene scrubber removes most of the phenol, as well as the naphthalene, which remains in the gas after leaving the primary coolers. For this reason, the concentration of phenol in the solution from the ammonia washers is low and recovery of the phenol from this solution will not be required.

It has been found that 70-90% of the total phenol in the effluents from the coal chemical recovery operations is contained in the flushing liquor. Most of the phenol remaining in the gas after the primary coolers is absorbed in the absorbent oil in the naphthalene scrubber. Thus the ammonia wash liquor will have absorbed therein only between 0-5% of the total phenol content in the coal chemical recovery effluents. Since the phenol content of the deammoniated liquor leaving still 191 at line 204 is low, this liquor can be cooled, and, if desired, without further treatment be recycled to the ammonia washers and thereby prevent even its small content of phenol from going to the sewer. Alternatively, the deammoniated liquor from line 204 may be sent to the quenching station (not shown) for quenching the coke from the coke ovens 10, without any increase in corrosion of surrounding steelwork since the concentration of chlorides and other corrosive salts is very low in this stream.

The removal of naphthalene and light oil from the

wash oil is effected in a novel manner with a pair of stripping stills 207, and 208; the naphthalene being stripped from the wash oil in still 207 and the light oil being stripped from the wash oil in still 208. To this end, the wash oil which flows from naphthalene scrubber 63 through line 209 and which is rich in naphthalene also flows through a preheater 210 and line 211 to the upper portion of still 207. At point D there may also be added the light oil from the dephenolizer when a dephenolizer such as that described in copending application Serial No. 679,701, now Patent No. 2,946,655, is used to remove the phenol from the flushing liquor by extraction in a light oil solvent which solvent is then treated to remove the phenol; and in this manner, the light oil may then be purified to prevent substantial build-up of impurities therein. Furthermore to this end, the wash oil which flows from the benzol washers through line 213 and which is rich in light oil and less rich in naphthalene also flows through a vapor to oil heat exchanger 215 where the wash oil is heated by vapors from still 207, a final heater 216, and a line 220 to the upper portion of still 208. As the light oil rich wash oil descends through still 208, the light oil is stripped from the absorbent oil with steam which is supplied to the still 208 in a manner described hereinafter. The light oil and steam vapors from still 208 are fed by conduit 218 to the lower portion of still 207 and pass upwardly through still 207 to strip the naphthalene from the wash oil which is descending through this still. The combined steam, and naphthalene vapors, and light oil, by way of conduit 223, pass through heat exchanger 215 and, by indirect heat exchange with the light-oil-rich wash oil from line 213 heat this oil. The condensate flows to a water separator 214 where the water is discharged and the oil pumped to a final heater 216. The vapors are sent to conventional rectifying and condensing equipment (not shown).

The absorbent or wash oil stripped of light oil flows from the bottom of still 208 through line 230, pump 233, and line 234, to an indirect cooler 235 where the absorbing medium is cooled to substantially ambient temperatures and then through line 237 to a circulating tank 238. A minor portion of the wash oil is withdrawn from tank 238 and is fed by way of line 238N to naphthalene scrubber 63 as the absorbent oil for the naphthalene scrubber, and a major portion of the wash oil is withdrawn and is fed by way of line 238B to benzol scrubber 143 as the absorbent oil for the benzol washers 138 and 143.

The naphthalene-stripped wash oil from still 207 is conducted by way of line 241 to a wash oil purifier 243 where direct steam through line 244 is injected into this wash oil by way of nozzles 247 and additional indirect heat supplied by way of steam heated coils 249 vaporizes the wash oil and lower-boiling material to leave the resinous high-boiling material as a residue. This resinous high-boiling residue material is discharged through line 246. The vapors from the top of the purifier flow through line 248 to an inlet 251 to wash oil still 208. The wash oil vapors condense in still 208 and the light oil and steam pass upwardly through still 208 countercurrent to the light oil rich wash oil passing downwardly through still 208 and strip the light oil from the wash oil. Additional steam from line 252 may be passed through line 248 if needed.

Normally all of the discharge from still 207 passes through line 241 to purifier 243, the rate of flow being controlled by a conventional level controller 254. An overflow 242 is placed in this line so that in the event less than the output is used at any time, the excess may be fed by way of line 240 to decanter 85.

To illustrate the operation of the above system coke oven gas entered naphthalene scrubber 63 with a naphthalene content of 90 grains per 100 s.c.f. and left the naphthalene scrubber with a naphthalene content of 13 grains per 100 s.c.f. The temperature of the wash oil in the naphthalene scrubber was 30° C. The rate of circu-

lation of wash oil over the naphthalene scrubber was 2.1 gallons per ton of coal carbonized, and this oil was recirculated over each of the recirculating stages at the rate of 200 gallons per ton of coal. Coolers 75 for each recirculating stage maintained the oil at 30° C. The gas entered the benzol washers with a naphthalene content of 13 grains per 100 s.c.f. and left with a naphthalene content of 1.5 grains per 100 s.c.f. The average pressure in the benzol washers was 1450 mm. Hg absolute and the temperature was 25° C. The wash oil from the naphthalene scrubber had a naphthalene content of 10% by weight and was preheated to 120° C. by heater 210, before entering the top tray of a 4-tray stripping still 207. This oil left the stripping still with a naphthalene content of 2% by weight and flowed to the wash oil purifier 243 which was maintained at a temperature of 190° C. by the use of an indirect heating coil 249 using high pressure steam. Low pressure stripping steam flowed through the purifier by way of line 244 and sparger 247 at the rate of 70 pounds of steam per ton of coal. The steam and oil vapor from the purifier entered below a 12-tray still utilized for stripping light oil from the benzolized wash oil from the benzol washers 138, 143. The circulation rate for wash oil to the benzol washers was 91 gallons of wash oil per ton of coal carbonized. The naphthalene content of the wash oil to the benzol washers was 2% by weight and the naphthalene content of the wash oil from the benzol washers was 2.03% by weight. The wash oil pumped from the base of the wash oil still was 93.1 gallons per ton of coal carbonized. This quantity was split into two streams, one stream of 91 gallons per ton of coal was pumped to the benzol washer 143 and the other stream of 2.1 gallons per ton of coal carbonized was pumped to the naphthalene scrubber 63. The oil condensate from a light oil condenser was sent to storage for subsequent rectification and refining. This system, in the naphthalene scrubber, removed naphthalene to a degree that no naphthalene depositions were encountered in the lines and chemical recovery equipment after the naphthalene scrubber. The quantity of wash oil circulated and stripping steam used was reduced substantially below that required for normal operation at lower pressure and with naphthalene scrubbing. The removal of ammonia and volatile compounds from the rich oil from the naphthalene scrubber in the stripping still 207 prevented contamination of the main wash oil circulating system for the benzol washers with these compounds. Vaporization of the wash oil from the naphthalene stripping still in the wash oil purifier 243 removed the traces of tar, pitch, and sludge absorbed in the naphthalene scrubber and at the same time maintained the sludge content of the main wash oil circulating system for the benzol washers at a satisfactory level, averaging about 10 to 15 grains per gallon, as determined by precipitation with isopentane, by continuous bleeding of wash oil from the benzol washer system and returning this bleed by way of the purifier after having passed through the naphthalene scrubber.

The foregoing has presented a novel arrangement for the removal of by-products from the gas evolved during the coking of coal with absorbent oil and ammonia liquors. The naphthalene is removed from the gas early in the process so that the likelihood of the apparatus becoming clogged due to deposition of naphthalene during subsequent treatment of the gas is substantially eliminated. The absorbent or wash oil used for the recovery of naphthalene and light oils is continuously purified and the vapors from this purification are applied first to the wash oil from the benzol scrubbers and then to the wash oil from the naphthalene scrubber. Economy is effected in that each quantity of steam takes part in three operations, namely, stripping the wash oil from high boiling impurities, stripping light oil from wash oil, and stripping naphthalene from wash oil. Efficiency of operation is achieved by removing the absorbent oil to be purified at

the point where the greatest possibility for buildup of resinous materials occurs. Further economy and efficiency is achieved by maintaining the flushing liquor separate from the ammonia wash liquor and separately stripping each liquor of its ammonia content so that the ammonia stripping stills can be made smaller, the lime slurry need be applied only to one of the stills, namely the still to which is fed liquor containing fixed ammonia, and the small quantity of solution to be dephenolized permits economy in the size of dephenolizer for a given size coke plant.

Although the foregoing has illustrated and described the invention in detail, it is to be expressly understood that the invention is not limited thereto. As will now be understood by those skilled in the art, various changes can be made in the design and arrangement of the parts without departing from the spirit and scope of the invention.

The tar precipitators and naphthalene scrubber, for example, can be located in the system beyond or after the booster or compressor. When so positioned, the naphthalene scrubber can additionally serve as a cooler for the gas. Additional advantages of so positioning the naphthalene scrubber are that the scrubbing is accomplished at high pressures, thereby reducing the size required for towers, lines, and pumps, and also thereby reducing the amount of wash oil required for the naphthalene removal and the amount of steam required for the stripping steps. The primary coolers may be of the indirect type and the naphthalene scrubbers, ammonia washers, and benzol washers may be of the packed, spray, bubble plate or perforated plate type.

What is claimed is:

1. A process for the recovery of valuable by-products from the gas evolved from the coking of coal which comprises first contacting said gas with a first quantity of wash oil to remove the naphthalene from the gas by absorption in the wash oil, whereby said first quantity of wash oil becomes rich in naphthalene, thereafter contacting said gas with a second quantity of wash oil to remove light oil from the gas by absorption in the wash oil, whereby said second quantity of wash oil becomes rich in light oil, applying the naphthalene rich wash oil to a first stripping zone where naphthalene is stripped therefrom, applying the light oil rich wash oil to a second stripping zone where the light oil is stripped therefrom, applying the vapors of said second zone to said first zone whereby said vapors strip the naphthalene from the wash oil therein, withdrawing stripped wash oil from said first zone and applying heat and steam thereto whereby the wash oil vaporizes, and applying the vapors of said wash oil and steam to said second stripping zone for stripping the light oils from the wash oil therein.

2. A process for the recovery of valuable by-products from the gas evolved from the coking of coal which comprises cooling said gas with flushing liquor and recovering the flushing liquor, contacting said gas with a minor quantity of wash oil to remove naphthalene from the gas by absorption, thereafter contacting said gas with ammonia wash liquor to remove ammonia from the gas by absorption, subsequently contacting said gas with a major quantity of wash oil to remove the light oil by absorption, applying said minor quantity of wash oil to a first stripping zone, applying said major quantity of wash oil to a second stripping zone, withdrawing stripped wash oil from said first zone, vaporizing said withdrawn wash oil with steam and feeding the vapors therefrom to said second zone to strip the light oil from said major quantity of wash oil, feeding the vapors from said second zone to said first zone for stripping the naphthalene from said minor quantity, removing phenol from said flushing liquor and removing ammonia from both of said liquors.

3. A process for the recovery of valuable by-products from the gas evolved from the coking of coal which

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comprises first contacting said gas with a first quantity of wash oil to remove the naphthalene from the gas by absorption in the wash oil, whereby said first quantity of wash oil becomes rich in naphthalene, thereafter contacting said gas with a second quantity of wash oil to remove light oil from the gas by absorption in the wash oil, whereby said second quantity of wash oil becomes rich in light oil, applying the naphthalene rich wash oil to a first stripping zone where naphthalene is stripped therefrom, applying the light oil rich wash oil to a second stripping zone where the light oil is stripped therefrom, applying the vapors of said second zone to said first zone whereby said vapors strip the naphthalene from the wash oil therein, withdrawing stripped wash oil from said first zone and applying heat and steam thereto whereby the wash oil vaporizes, applying the vapors of said wash oil and steam to said second stripping zone for stripping the light oils from the wash oil therein, whereby the wash oil vapors condense in said second zone, withdrawing the stripped wash oil from said second zone, and dividing said wash oil so withdrawn for use as said first and second quantities.

4. In a process wherein by-products such as naphthalene and light oil are recovered continuously from the gas evolved from the coking of coal by absorption in a wash oil, the improvement which comprises contacting said gas with a first wash oil to absorb the naphthalene therein, thereafter contacting said gas with a second wash oil to absorb the light oil therein, stripping the naphthalene from said first wash oil in a first zone, said first wash oil also being subject to also absorbing high boiling compounds therein, vaporizing with steam in a second zone said first wash oil from said high boiling compounds, applying the vapors so formed to said second wash oil in a third zone to strip the light oil therefrom with said steam and to condense said vaporized wash oil, applying the stripped vapors of light oil and steam to said first zone for stripping the naphthalene from wash oil in said first zone whereby the same quan-

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tity of steam vaporizes the wash oil from high boiling compounds, strips the light oil from the second wash oil, and strips the naphthalene from the first wash oil.

5. The process of claim 4 wherein the stripped wash oil from the third zone is divided in said first and second wash oils for continuing the process.

6. In a process wherein by-products such as naphthalene and light oil are absorbed in a wash oil from the gas evolved from the coking of coal and recovered by stripping the by-products from the wash oil with steam, the improvement which comprises contacting said gas with a first wash oil to absorb the naphthalene from the gas, thereafter contacting said gas with a second wash oil to absorb the light oil from said gas, withdrawing and subjecting wash oil from which the naphthalene has been stripped to steam thereby vaporizing said wash oil, applying the vapors of wash oil and steam to said second wash oil to remove the light oil therefrom as vapors of light oil, and applying the vapors of light oil and steam to said first wash oil to strip the naphthalene from said first wash whereby one quantity of steam serves to vaporize the wash oil from which the naphthalene has been withdrawn, strip the light oil from the second wash oil, and strip the naphthalene from the first wash oil.

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