METHOD OF REMOVING AND DISPOSING OF AMMONIA FROM COKE OVEN GAS

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

When coal is heated in a coke oven in the absence of air, large volumes of the gases, known as coke oven gas, are evolved leaving a residue of carbonaceous material known as coke. Heretofore, ammonia, naphthalene, tar, and light oils such as benzene, toluene, and xylene have been recovered from the gas as by-products. The systems for recovery of these by-products are known as coal-chemical recovery systems. The equipment and operations for these systems have required large capital expenditures when those by-products are recovered from the gas. In general, these systems have included a cooling apparatus such as primary and secondary coolers, naphthalene recovery apparatus, ammonia recovery apparatus, either as ammonia or as a salt of ammonia, and light oil recovery equipment.

In recent years, the economic feasibility of recovering ammonia from coke oven gas and marketing it as ammonia or as a salt of ammonia has become questionable because of synthetic ammonia processes which have created an over supply of the product.

By the present invention it is proposed to treat the coke oven gas in a manner such that the ammonia is removed therefrom and disposed of by burning without causing air pollution rather than recovering the ammonia for use as a marketable product.

As a further consideration for improving the overall operation of coal-chemical recovery system operation, there is the problem of maintaining the system in continuous operation for extended periods without encountering unavoidable shutdowns for repairs and maintenance. One of the most acute problems with respect to avoiding shutdowns that has been encountered heretofore has been the tendency of the naphthalene compound contained in the gas to settle out and thereby clog the lines. Such clogging by the naphthalene compounds has increased the operating cost of the coal-chemical systems. Furthermore, efforts have been made to automate these systems, but because of the clogging of the naphthalene, these efforts have not been completely satisfactory.

In connection with these systems, in addition to the questionable economics of recovering and marketing the ammonia as a salt, such as ammonium sulfate, the formation of such ammonia salts in the system has also been a deterrent toward achieving an efficient system. The primary difficulties encountered in the systems such as, for example, ammonium sulfate in locations not adapted to receive the solids, have been that the sulfate crystals tend to settle out and clog the lines such that servicing of the equipment may be necessary.

Accordingly, it is an object of the present invention to provide a novel apparatus and process arranged so that the ammonia is ultimately disposed of and the naphthalene removed from the coke oven gas at a point in the system such that the tendency of the naphthalene to clog the lines is substantially eliminated.

It is a further object to provide a novel apparatus and method for removing the naphthalene from the coke oven gas by various suitable absorbing agents such that efficient use is made of the recovered naphthalene and wash oil and also the absorbent.

It is another object to provide an apparatus for removing the ammonia from the coke oven gas and thereafter burning the same in a manner such that the burning does not cause air pollution.

It is a further object to provide a novel apparatus and method for using the ammonia removed from the gas in a manner such that a portion is recirculated back into the system either as a gas or in water solution to increase the amount of hydrogen sulfide and hydrogen cyanide removed from the gas and burning the ammonia with the remaining portion of the hydrogen sulfide and cyanides.

The present invention may be applied to different modifications of coal-chemical systems varying in accordance with the ultimate product it is desired to recover from the gas and the manner in which the products are used in the system.

In carrying out the invention, the naphthalene is removed from the gas in a naphthalene scrubber located after the conventional primary coolers and tar precipitators but before the ammonia washers for removing the ammonia from the gas so as to prevent the deposition of solid naphthalene in the ammonia washer piping and equipment. With the removal of the naphthalene ahead of the ammonia removal equipment, a minor quantity of naphthalene absorbent material may be used to minimize the introduction of ammonia and ammonia containing compounds into the subsequent by-product recovery system when such absorbent material is used therein.

The selection of the wash oil used in the naphthalene scrubber is determined by the economics of the system in which the present invention is incorporated.

In this connection, it is to be mentioned that it is usual to recover light oils from the coke oven gas as a by-product. Economic studies on coal-chemical systems have indicated that under some circumstances, it is not economically feasible to recover the light oil in the gas, but to use the light oil contained in the gas for its heating value. The absorbent used in the removal of this naphthalene, known as wash oil, may be fuel oil of a petroleum type, or a conventional petroleum type oil or a "creosote" type absorbent oil obtained by distillation of coal tar.

If the light oil is not recovered, any of the above described wash oils may be used. However, the selection of the wash oil will again be determined by the availability of the particular wash oil at the site of the installation, the purpose for which the naphthalene is to be used, costs, and other factors.

When it is not desired to recover the naphthalene as a marketable product, the petroleum fuel oil with the naphthalene absorbed therein, after passing from the naphthalene scrubber, may be used as a source of fuel for firing furnaces or the like in an integrated steel plant. In this manner, the naphthalene is used for its heating value along with the fuel oil.

If a conventional wash oil is used as an absorbent for naphthalene, it is circulated through the naphthalene scrubber in the usual manner so as to remove the naphthalene, and thereafter the naphthalene-containing wash oil is stripped of the naphthalene in a rectifier and reused. The naphthalene vapors originating from the rectifier are recirculated to the primary cooler to contact the gases
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coming from the battery of ovens such that the naphthalene content reaches an equilibrium and is separated from the gas along with the tar that condenses out therein.

The use of a tar distillate as an absorbent for naphthalene also may be advantageous since the naphthalene-containing tar from the naphthalene scrubber may be treated in a still to separate the naphthalene from the naphthalene-containing tar distillate and the naphthalene vapors therefrom returned to the primary coolers so as to function in the manner as specified above in connection with the use of conventional wash oil. The de-naphthaleneized tar distillate is recycled to the naphthalene scrubber.

The coke oven gas, after removal of the naphthalene in the naphthalene scrubber, is passed into ammonia washers and therein contacted and washed with a wash liquor which, in accordance with the present invention, is water. The water absorbs the ammonia and, as well as limited quantities of certain other impurities such as hydrogen sulfide and hydrogen cyanide, is removed from the gas.

The ammonia-containing wash water is then introduced into ammonia stills for the purpose of stripping the ammonia therefrom and the water recirculated or discharged to waste. The recovered ammonia and the other impurities in one form of the invention are thereafter immediately passed into an oven located preferably at the base of the gasholder stack and burned under controlled conditions such that the formation of oxides of nitrogen is substantially prevented. Fuel to assist in burning the gas may be obtained from any suitable source such as, for example, the previously treated coke oven gas, natural gas, or the like.

In a further embodiment of the invention, the ammonia may be used as an agent for purifying the gas by increasing the quantities of hydrogen sulfide removed from the coke oven gas. Normally, the percentage of hydrogen sulfide removed from the gas by the washing treatment in the ammonia washers varies between 20 and 40 percent. In accordance with the present invention, it is proposed to increase these quantities removed to between 60 and 80 percent.

This is accomplished by circulating the ammonia-containing water through an ammonia purifier prior to passing the washing into the stripping still as described above and by controlling the purification such that substantially all of the impurities such as hydrogen sulfide, hydrogen cyanide, and carbon dioxide are removed from the liquor and removing only a portion of the ammonia. The portion of the liquor, equal to the net amount removed from the gas before enrichment in the purifier and the hydrogen sulfide, hydrogen cyanide, and carbon dioxide are then burned in the Dutch oven. The remaining ammonia in the wash water is subsequently circulated into the ammonia stills where the ammonia is stripped therefrom and, if necessary, passed through a dephlegmator. The recovered ammonia is thereafter recirculated to a location preceding or to the forward washing stage of the ammonia washer such that it mixes with the coke oven gas. In this manner, the recirculated ammonia and the ammonia usually contained in the coke oven gas react within the ammonia washers so as to form greater quantities of ammonium sulfide and ammonium cyanide than when only the ammonia contained in the gas is present. Thereby, the quantities of hydrogen sulfide removed from the gas are increased. The increased hydrogen sulfide removal may be obtained also by dispersing the ammonia vapors in the water to form a solution and returning this ammonia enriched solution to the system at the upstream end (with respect to gas flow) of the ammonia removal system.

The above and further objects and novel features will appear:

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

Turning now to the drawing of 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 is sprayed into the conduits 12 and collector main 13 through injectors (not shown) cooling the hot gases and condensing some of the tar. The mixture of flushing liquor, gas, and tar flows through conduit 17 to a conventional battery 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 in a conventional manner to storage. The liquor flows through line 29 to a circulating tank 30, and is forced by a pump 31 through line 33, screen 35, and line 37 to the collecting main 13.

The gas flows through a conduit 41, from downcomer 19, to the lower section of the primary cooler 43, and ascends therethrough countercurrent to the liquid descending from the sprays 45. The liquor for the sprays 45 collects in the lower portion of the primary cooler 43 and flows through a line 47 to a pump 51 which circulates the liquid through a line 53, a cooler 55, and a line 57 back to the sprays 45.

The gas leaves the primary cooler adjacent to the upper end thereof through a conduit 61 and flows to a secondary cooler 63. The gas ascends cooler 63 countercurrent to the liquid descending from sprays 65. Liquor for the sprays 65 is provided from the lower portion of the primary cooler 43 by way of lines 67, level control valve 69, and line 71 which enters the lower portion of the secondary cooler 63. The flushing liquid collects in the lower portion of the secondary cooler 63 and flows through line 73 to a pump 75 which circulates the liquor through line 77, cooler 79, and line 81 to the sprays 65. Excess liquor overflows through line 83, level control valve 85, and line 87. Connected to the line 87 is a line 89 through which the liquor flows through a valve 91 and line 93 to an ammonia liquor storage tank 95 from whence it will be treated as to separate the free ammonia, hydrogen sulfide, pyridine, and cyanide from the liquor such that these ingredients may be burned to a manner more fully to be described below. These liquors also may contain phenol in varying quantities and in the event the quantities are sufficiently great such that the de-ammoniated liquor may not be released to sewerage without removal of the phenol, the liquor is sent through a dephenolizing stage.

To this end, there is provided a dephenolizing system 97 which is connected into the lines 87 and 93 by way of valves 99 and 101. Thus, when the valves 99 and 101 are opened and the valve 91 is closed, the excess liquor from coolers 43 and 63 will be treated by the dephenolizing system 97. This system may be of any suitable type such as, for example, of the type described in the assignee's copending application, Serial No. 679,701.

The gas leaves the secondary cooler 63 through conduit 103 and flows to a drier 105 which may be of the electrostatic precipitator type, which removes substantially all of the tar from the gas and then flows through a conduit 107 to a lower portion of the naphthalene scrubber which is maintained at a temperature between about 10° to 55° C. The gas ascends within the naphthalene scrubber 109 countercurrent to the descent of the wash oil sprayed into the ammonia washers 107. The ammonia vapors in the water to form a solution and returning this ammonia enriched solution to the system at the upstream end (with respect to gas flow) of the ammonia removal system.

The above and further objects and novel features will appear:

The single sheet of drawing schematically illustrates a novel arrangement of the apparatus for carrying out invention.
As illustrated, the wash oil is introduced into the system through line 127 and is circulated through the naphthalene scrubber 109 and discharged into the line 125 in a manner as above described.

In accordance with the present invention, there may be used wash oils having different characteristics such as a fuel oil having a viscosity of 50 to 90 SSV at 100°F, a boiling point range from 280 to 480°F; a more or less conventional wash oil having a boiling point ranging from 300 to 470°F; or a "creosote" type wash oil. Therefore, the manner in which the naphthalene enriched wash oil is disposed of may vary in accordance with various considerations such as economics, facilities, marketing, etc. Accordingly, there is provided by the present invention a system readily adaptable to meet different conditions.

Considering first the use of a fuel oil having the above described characteristics, fuel oil is introduced into the scrubber as above described and naphthalene is absorbed from the gas. As is well known, the naphthalene is readily combustible and may be burned and used for its heating values. Accordingly, by the present invention, rather than rectifying the naphthalene enriched fuel oil as has been the usual practice heretofore, it is discharged from the line 125 by way of valve 129 and line 131 into a fuel oil storage tank (not shown) and mixed with the conventional fuel oil used for firing furnaces or other equipment used in steel making. In this manner, the naphthalene is used to increase the volume of the fuel oil.

In those instances where conditions dictate, it may be desirable to use conventional petroleum wash oil described above. To this end, there is connected to the line 125 a wash oil rectifying system comprising a naphthalene stripping still 132, which is connected to the line 125, by way of valve 141 and line 143. Hence, when the valve 129 is closed and the valve 141 is open, the naphthalene enriched wash oil flows into the upper end of the stripper 137 and descends therein countercurrent to the steam introduced in the lower portion thereof through pipe 145. The wash oil collects in the lower portion of the still 137 and is recirculated to the naphthalene scrubber spray 111 by way of line 147, cooler 149, line 151, and line 153.

The naphthalene vapors leave the still 137 from the upper end thereof and flow through line 155 to a point in the gas stream ahead of cooler 43. To prevent clogging in the line 155, the temperatures of the vapors are maintained above that at which the naphthalene settles out. The naphthalene vapors, including any phenol collected therein, are again contacted with the main stream of coke oven gas evolved at the battery 10 and the naphthalene vapors condense thence in the primary cooler such that they reach an equilibrium and the naphthalene is separated from the gas in the primary cooler along with the condensed tar. In this manner, the naphthalene is disposed of in the flushing liquor decanter along with the condensed tar by way of line 52 into the tank collecting in flushing liquor decanter 23.

Since a large quantity of the flushing liquor from decanter 23 is evaporated into the gas stream at the conduit 12 and main 13 and since this water condenses from the gas at coolers 43 and 63, there normally occurs a depletion in the quantity of liquor in the decanter 23 and circulating tank 50 and an increase in volume in coolers 43 and 63. To maintain the liquor condensate in the decanter 23 and the tank 30 at the desired level, the primary cooler and secondary cooler condensates are returned thereto from the primary cooler 43 by way of line 67, line 48 and line 52 and from cooler 63 by way of lines 59 and 51. Tar condensate in coolers 43 and 63 is returned to the decanter tank 50 at the same time by way of line 67 and line 48. By this means, the flushing liquor decanter 23. To prevent an accumulation of these salts, they are removed in solution at a rate equal to their collection rate in the flushing liquor system and returned through line 59 to the primary cooler 43.

It is to be understood that the naphthalene vapor leave the top of the stripping still 137 may be treated in a more or less conventional manner. For example, to recover the naphthalene as a marketable product or alternatively, it may be mixed with fuel oil in the steel mills, and thereby used for its heating value. In either of these processes, the temperatures in the still 137 are maintained between 100 and 150°C and at a pressure ranging from 760 to 500 mm. of mercury absolute.

In the event a "creosote" wash oil such as a tar distillate having a boiling range of 200 to 400°C is used, the valve 157 is opened and the creosote wash oil is introduced in the line 127, flows to the sprays 111 and 113, and is circulated through the naphthalene scrubber in the manner described in connection with the petroleum fuel oil absorber. The operating temperature of the scrubber is maintained in a range between 10 and 55°C and the fresh creosote oil is added at a rate of between 0.02 and 0.06 gallon per 1000 cubic feet of gas treated. This quantity of the naphthalene in the creosote wash oil may vary between a range of from 0.0 to 50 grams per liter. The naphthalene enriched "creosote" wash oil is collected in the lower portion of the naphthalene scrubber 109 and flows into the stripper 137 by way of the line 121, pump 123, line 125, through valve 141 (valve 129 is closed) and line 143.

The steam is introduced into the still 137 through the line 145 such that the naphthalene is separated from the tar distillate or creosote wash oil which collects at the lower portion of the still and is recycled back to the sprays 111 and 113 of the naphthalene absorber 109 by way of line 147, cooler 149, line 151, and line 153. The naphthalene vapors are discharged from the top of the still through the line 155 to the primary coolers by way of conduit 41 and mixed with the coke oven gas evolved in the batteries 10. The naphthalene vapors mix with the coke oven gas in the primary cooler such that the naphthalene reaches an equilibrium and is separated from the gas along with the condensed tar. In this manner, the naphthalene is disposed of in the flushing liquor decanter 23 along with the condensed tar from the primary and secondary coolers 43 and 63 by way of lines 48 and 50 respectively.

The substantially naphthalene-free gas leaves the naphthalene scrubber through conduit 161, which raises the gas to a pressure sufficient to deliver the gas to the further points in the system for further treatment. The gas is discharged from the booster 161 under pressure through the conduit 163 to the lower portion of a final cooler 162. The gas ascends in the final cooler 165 countercurrent to the flow of water into the top thereof by way of sprays 164. The water collects at the bottom portion of the cooler 165 and is recycled back to the sprays 164 by way of the line 169, pump 171, cooler 173, and line 175. The gas flows from the final cooler 165, through a conduit 177, to the lower portion to a first one of a possible series of ammonia washers 179 such as 179a, 179b, 179c and 179d.

Each of the washers is similarly constructed and are connected by conduits 191 extending from the upper end of one washer to the lower portion of the other, such that the gas flows through each of the washers 179 countercurrent to the water descending from sprays 183 such that the ammonia is absorbed from the gas. As illustrated, the wash water is introduced through the line 185 and flows to the spray 183 of the last of the ammonia washers 179, in with respect to gas flow by way of line 187, pump 189, and line 191b containing water collects at the lower portion of each of the washers 179—a, b, c, and d and is recycled to the sprays by way of the lines 187 and line 191. The excess ammonia-con
taining water overflows through line 193—c, level control valve 195, and line 197a and/or the adjacent washer 179—c where it joins the water being circulated through the sprays 183 of the washer by way of the lines 187, pump 189, and line 191 similarly to the washer 179—d. Each of the four ammonia washers is interconnected in a similar manner such that the excess ammonia-containing water is ultimately collected in the washer 179—a. This excess ammonia water overflows through line 199, level control valve 201, and line 203. The line 203 is connected with the line 169 of the recycling system of the final cooler 165. However, it may also by-pass final cooler 165 and flow directly to line 209.

Hence, the ammonia-containing wash water is contacted with the gas entering the final cooler 165 so as to cool the gas and also to remove some of the ammonia. The water containing the ammonia collected in the final cooler 165 and ammonia washers 179—a, b, c, and d overflows through line 209 and valve 207. When the valve 211 is closed and valve 207 is open, the ammonia containing liquor flows through line 213 to the ammonia liquor collecting tank 95.

The gas which leaves the washer 179—d through the conduit 215 is substantially free of ammonia. If it is desired to recover the light oils, the substantially ammonia-free gas is circulated into the light oil washer 217 countercurrent to the sprays 219 of wash oil which is circulated therethrough by way of line 221. The light oil-containing wash oil collects at the bottom of the washer 217 and is pumped by suitable means to a system (not shown) for separating the light oil and wash oil. The light oil washing and the system for separating the oil may be similar to that described in the assignee's copending application Serial No. 711,380, filed January 27, 1927 which is now Patent No. 2,961,065.

The gas substantially free of ammonia, tar, naphthalene, and light oil leaves the washer 217 through the conduit 221 by way of the now open valve 223 and line 225 to the gas holder 227, or through line 229 when the valve 231 is open for use as fuel in the steel making procedure.

Under some circumstances, it may not be desired to recover the light oil from the coke oven gas. To this end, the valve 224 is closed and the valve 226 is open such that the gas flows through the conduit 225 directly to gas holder 227 or through the conduit 229 to the steel mills.

Turning now to the ammonia wash water stored in the tank 95, the wash water contains the liquid collected by way of the conduits 93 and/or 213 and contains in solution the ammonia, both free and fixed, hydrogen sulfide, hydrogen cyanide, carbon dioxide, and other impurities removed from the coke oven gas as it circulates through the ammonia washers 179—a, b, c, and d and the primary and secondary coolers 43 and 63. The wash water in the tank 95 flows through the line 233, pump 235, line 236, open valve 238, and line 275 to the upper portion of an ammonia stripping still 237. As the wash water descends through the still 237, steam supplied at the inlet 239 strips the ammonia from the liquor. The ammonia vapors leave the top of the still 237 through line 243, open valve 266, line 267, dephlegmator 269, line 271—a, valve 272—b which is connected to the line 245.

Heretofore, it has been the practice to utilize this ammonia to make salts such as ammonium sulphate and ammonium phosphate. In accordance with the invention, the ammonia which had been removed from the coke oven gas is now burned. Ammonia ordinarily does not support combustion when it is in the presence of large quantities of water or steam vapors. However, if the moisture content of the ammonia is properly controlled, ammonia will burn with a yellow flame in an atmosphere of air or oxygen, in accordance with the following equation:

\[
4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}
\]

The products of such combustion are mainly nitrogen and water. However, traces of oxides of nitrogen are also formed and these oxides can pollute the atmosphere if present in sufficient quantities. In accordance with this invention, therefore, the ammonia is burned under conditions that minimize the formation of oxides of nitrogen.

The combustion of ammonia in air is self-sustaining in as much as the gross heat of combustion of ammonia releases 9668 B.t.u.'s per pound of ammonia burned. The ammonia vapors leaving the still contain carbon dioxide, hydrogen sulfide, and hydrogen cyanide and water vapors. The quantity of water vapor is controlled by the dephlegmator 269 as is well known in the art.

These vapors are introduced into the Dutch oven 247 located at the base of a chimney 249. This Dutch oven has been pre-heated in a manner described below. Accordingly, the ammonia burns to form nitrogen and water. Sufficient air is provided in the oven 247 to support self-sustaining combustion of the ammonia vapors. The quantity of air used of course will be dependent on the oven characteristics as will be recognized by one skilled in the art. Insufficient air will burn the ammonia in only a partial decomposition of the ammonia present. On the other hand, an excess of air tends to lower the flame temperature and may cause the flame to extinguish.

In connection with the flame temperature, it has been found that self-sustaining combustion of the ammonia vapor with a minimum formation of oxides of nitrogen is achieved at temperatures ranging between about 760 to 980° C. Conveniently, initial heat of the oven may be provided by way of a fuel to achieve the desired temperature. This fuel may be of any type readily available at the site of the installation. As shown, the fuel may be in the form of natural gas or fuel oil which may be introduced at the inlet 251 or recovered coke oven gas from the holder 227 which is introduced through the inlet 253 connected to the line 255. When the flame temperature at which self-sustaining combustion for the ammonia vapors is reach, the fuel supply may be cut off and the ammonia will continue to burn.

The ease at which self-sustaining burning of the vapors is achieved is to some extent determined by the water vapor content thereof. The water vapor acts in the nature of a diluent absorbing some of the heat of combustion of the ammonia vapors. The ratio of steam to ammonia has been varied from 3:7:1 to 1:1 without encountering any difficulties in obtaining decomposition of ammonia. When the ratio of water vapor to ammonia is high, it may be advisable to provide additional fuel to maintain a desired temperature in the oven. The water content of these vapors as pointed out above, is controlled by the dephlegmator 269 which functions to control the dew point. In this connection, it is also to be noted that the ammonia vapors which include carbon dioxide tend to react and form ammonia-carbon dioxide complexes such as ammonia bicarbonate and/or ammonium carbonate which crystalize out and may clog the vapor line. To prevent this, the temperatures of the ammonia vapors are maintained above about 70° C. To achieve this temperature at which the complexes do not form the dew point is set at a lower limit of about 70° C. At this dew point, the equilibrium constant for these ammonia-carbon dioxide complexes is such that the material does not crystalize in the lines.

The combustion of the ammonia still vapors after de-
phlegmation to 95° C. is exemplified by the following examples shown in Table I.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Air Nat. gas NH₃ CO₂ H₂S H₂O</th>
<th>Furnace Temp. °C</th>
<th>NO in the gas grams/200 ft³</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>76.6 7.8 2.3 1.0 0.0 12.3</td>
<td>9,085</td>
<td>N.D. Complete dep. of NH₃</td>
<td>Insufficient air for complete combustion</td>
</tr>
<tr>
<td>2.</td>
<td>51.6 1.2 2.4 2.7 0.0 33.9</td>
<td>1,015</td>
<td>N.D. Incomplete dep. of NH₃</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>68.8 0.5 3.4 1.6 0.0 20.3</td>
<td>890</td>
<td>N.D. Complete dep. of NH₃</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>34.0 4.9 5.1 1.7 0.0 21.3</td>
<td>660</td>
<td>N.D. Flue out.</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>76.9 5.5 2.7 12.2 0.0 14.5</td>
<td>980</td>
<td>N.D. Do.</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>77.1 6.6 2.4 1.0 0.2 12.7</td>
<td>980-1,010</td>
<td>2.9</td>
<td>Complete dep. of NH₃</td>
</tr>
<tr>
<td>7.</td>
<td>77.0 6.6 2.4 1.0 0.2 12.7</td>
<td>980</td>
<td>2.9</td>
<td>Do.</td>
</tr>
<tr>
<td>8.</td>
<td>52.0 0.0 12.6 6.1 3.4 20.9</td>
<td>1,003</td>
<td>2.9</td>
<td>Do.</td>
</tr>
<tr>
<td>9.</td>
<td>52.3 0.0 12.6 6.2 3.4 20.9</td>
<td>810</td>
<td>N.D. Do.</td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>53.3 0.0 7.6 2.0 0.0 24.1</td>
<td>650</td>
<td>N.D. Flue out.</td>
<td></td>
</tr>
</tbody>
</table>

The oxides of nitrogen in the above examples were determined after cooling of the flue gases to 40 to 50° C. by means of a water spray and analyzed in accordance with the Shaw method as described in Analytical Edition of Industrial and Engineering Chemistry, volume 8, page 162, May 15, 1936.

In order to minimize the formation of oxides of nitrogen, the Dutch oven is constructed such that the vapor has only a short residence period within the oven at these temperatures. To this end, the rate of burning is advantageously carried out such that there is a heat release of between 20,000 and 150,000 B.t.u.'s per hour per cubic foot of combustion volume in the oven at temperatures ranging between 760° C. and 980° C. It has been found that within these ranges of heat release and temperature that the oxides of nitrogen resulting from the combustion of the impure ammonia released in quantities of from 50 to 1,000 parts per million varying in accordance with the rate of heat release and the flame temperature. Of course, it will be understood that these figures will vary depending on the construction and the design of the oven.

From the foregoing description, it can readily be seen that by the present invention substantially complete combustion of the ammonia vapors is accomplished without causing air pollution by (1) maintaining the temperatures of the impure ammonia vapors in the feed lines to the oven above a lower limit of about 70° C. so as to prevent clogging of the line; (2) maintaining the oven at a temperature between 760 and 980° C.; and (3) maintaining the residence time of the products of combustion of the ammonia vapor such that there is produced between 20,000 and 150,000 B.t.u.'s per hour per cubic foot of combustion volume in the oven.

As is well known, if large quantities of hydrogen sulfide and hydrogen cyanides remain in the coke oven gas, these impurities may render the gas unsuitable for use in steel making. As a further modification, it is proposed to use a portion of the ammonia content collected in the wash water so as to increase the percentages of hydrogen sulfide and hydrogen cyanides removed from the coke oven gas.

To accomplish this, there is incorporated into the system as disclosed, an ammonia purifier 256. The wash water containing the ammonia and other impurities is introduced from tank 85 into the upper portion of the purifier 256 by way of the line 233, pump 235, line 236, open valve 257 (the valve 238 is now closed) and line 259. Stripping steam is supplied to the purifier 256 through inlet 261. If desired, additional steam may be supplied midway of the purifier by means not shown. The top temperature of the purifier is maintained between 50 and 90° C. and preferably between about 50 and 70° C. to allow a portion of the ammonia and a major portion of the other impurities substantially equal to the quantity produced in the system to pass out of the top of the purifier and flow through the line 263 and line 258 scribed above. The hot liquor descending through the purifier is substantially depleted of hydrogen sulfide and cyanides but because of the control of temperatures within limits at the top of the purifier, only a portion of the ammonia has been removed and, therefore, ammonia remains in the liquid which collects at the base of the purifier. The hot liquor containing this portion of ammonia flows to the upper portion of the ammonia stripping still by way of the line 267, pump 269, level control valve 271, open valve 273. and line 275. The ammonia is stripped from the liquor as it descends through the still 237 by the steam supplied at the inlet 239.

The ammonia vapors flow through the line 243, open valve 266, line 267, through a dephlegmator 269, to a line 271c and open valve 274 (valve 271b is in line 271c is closed). For the purpose of contacting the coke oven gas as it circulates through the system, there is connected at spaced intervals along the line 271c, a line 273a, a valve 275a, and a line 277 communicating with the conduit 159; a line 279, a valve 281, and a line 283 communicating with the line 61; and a line 285, a valve 287, and a line 289 communicating with the line 41. Hence, by opening any of the valves 275a, 281, or 287, the nitrogen ammonia gas may be selectively introduced into either the final cooler 165, secondary cooler 63, or primary cooler 43. Similarly, a condensate high in ammonia content may be produced in dephlegmator 269 and transferred through line 290 and through valve 291 to line 197 which feeds it to line 187. The condensate may also be fed through appropriate lines either to line 169 connected to final cooler 165 or to line 73 connected to cooler 63 so as to increase the ammonia content in the water in washer 179, cooler 165, or cooler 63. This results in obtaining a greater removal of the acid gas impurities.

As a result of recycling the ammonia from the stills back to the coolers or washer, there is an additional quantity of hydrogen sulfide removed from the coke oven gas.

Variations and modifications may be made within the scope of the claims and portions of the improvements may be used without others.

What is claimed is:

1. A process for treating gas evolved from the coking of coal which comprises contacting the gas with a wash oil for removing substantially all of the naphthalene from the gas, thereafter contacting the naphthalene-free gas with water to absorb substantially all of the ammonia and a portion of the water soluble impurities therefrom, stripping the ammonia and said water soluble impurities as vapors having a water vapor to ammonia ratio ranging between about 3.7:1 to 1:1 from said water, and burning said ammonia under temperature and heat-evolving conditions substantially precluding the formation of oxides of nitrogen.

2. The process as defined in claim 1 in which the gas
is contacted with a petroleum fuel oil having a viscosity in S.S.U. units at 100° F. ranging between 50 and 90 and a boiling point ranging between 280 and 480° C.

3. The process as defined in claim 1 in which the gas is contacted with petroleum wash oil having a boiling point ranging between 300 and 370° C.

4. The process as defined in claim 1 in which the gas is contacted with a distillate of tar having a boiling point ranging between 200 and 400° C.

5. The process as defined in claim 3 in which the naphthalene-rich wash oil is applied to a stripping zone so as to recover separately naphthalene vapor and wash oil by the use of steam, and said naphthalene vapor is recirculated to contact the gas stream prior to contacting the gas with wash oil.

6. The process as defined in claim 4 in which the tar distillate wash oil containing absorbed naphthalene is applied to a stripping zone so as to recover separately the tar distillate wash oil and naphthalene vapor by the use of steam, the recovered tar distillate wash oil is recirculated to contact the gas stream, and said recovered naphthalene is recycled to contact the gas stream prior to contacting the gas with wash oil.

7. In a process for treating gas evolved from the coking of coal which comprises the sequence of steps of cooling the gas and thereafter contacting said gas with a wash oil so as to remove substantially all of the naphthalene from said gas, thereafter contacting the denaphthalized gas with water so as to absorb substantially all of the ammonia and a portion of the water soluble impurities from said gas, stripping the ammonia and said water-soluble impurities as vapors having a water vapor-to-ammonia ratio ranging between about 3.7:1 to 1:1, introducing said vapors into a burning zone at a temperature above 70° C. whereby the formation of ammonia-carbon dioxide complexes is substantially precluded from said water, and burning said ammonia vapors at a temperature ranging between 760° C. and 980° C. with a residence time in the burning zone producing a heat release of between about 20,000 and 150,000 B.t.u.’s per hour per cubic foot of combustion volume.

8. In a process for treating coke oven gases, the improvement which comprises scrubbing the coke oven gas with water to absorb the ammonia therein; thereafter stripping the ammonia from said water as ammonia vapors having a water vapor to ammonia ratio ranging between about 3.7:1 to 1:1 and at a temperature of about 70° C. and burning the ammonia vapors so obtained from said water at a temperature ranging between 760° C. and 980° C. with a residence time in the burning zone producing a heat release of between about 20,000 and 150,000 B.t.u.’s per hour per cubic foot of combustion volume.

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