

May 9, 1961

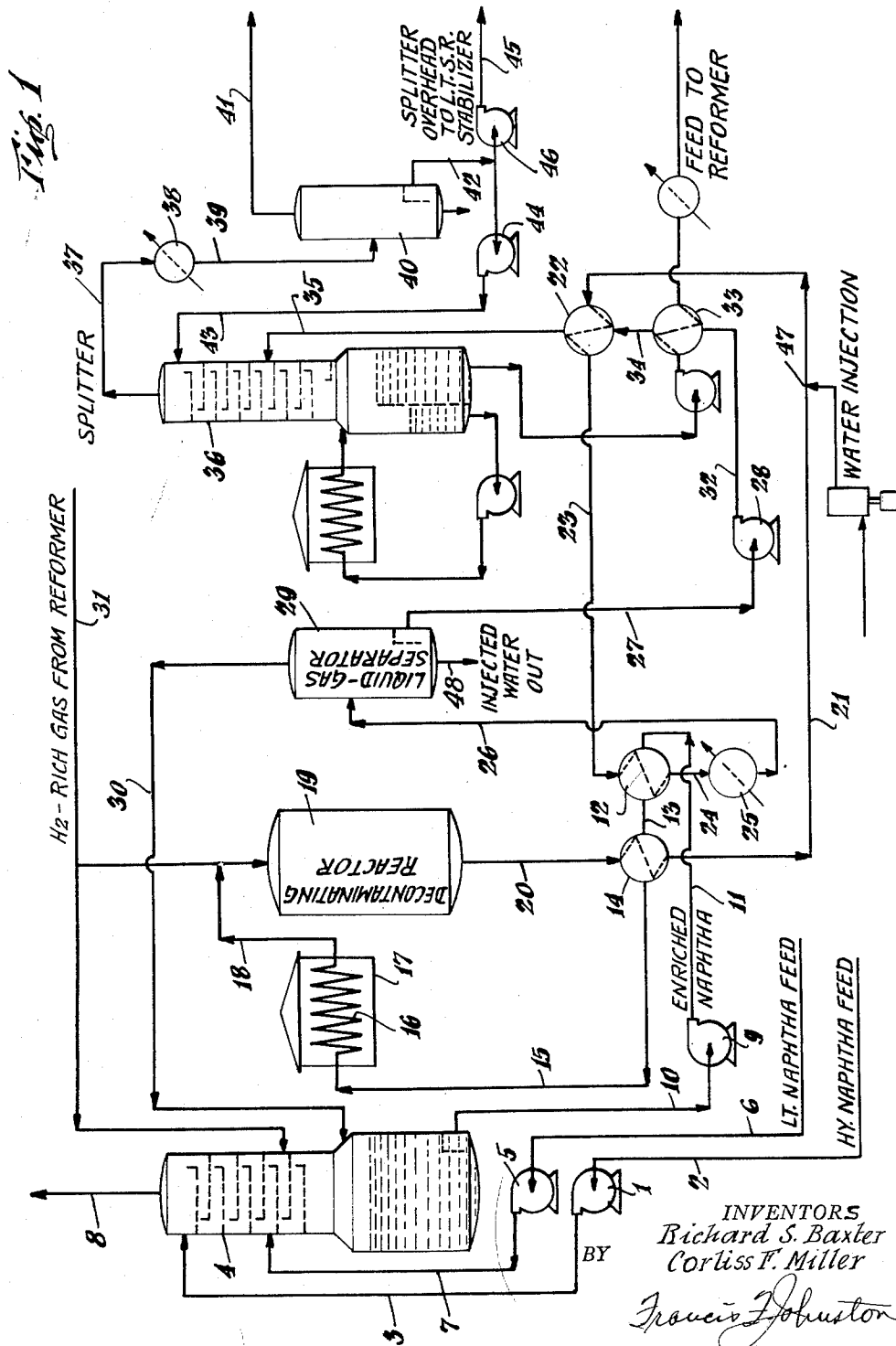
R. S. BAXTER ET AL

2,983,675

MAINTAINING SUBSTANTIALLY CONSTANT PRESSURE DIFFERENTIAL
DOWNSTREAM OF A HYDROGENATING REACTOR

Filed July 5, 1957

2 Sheets-Sheet 1



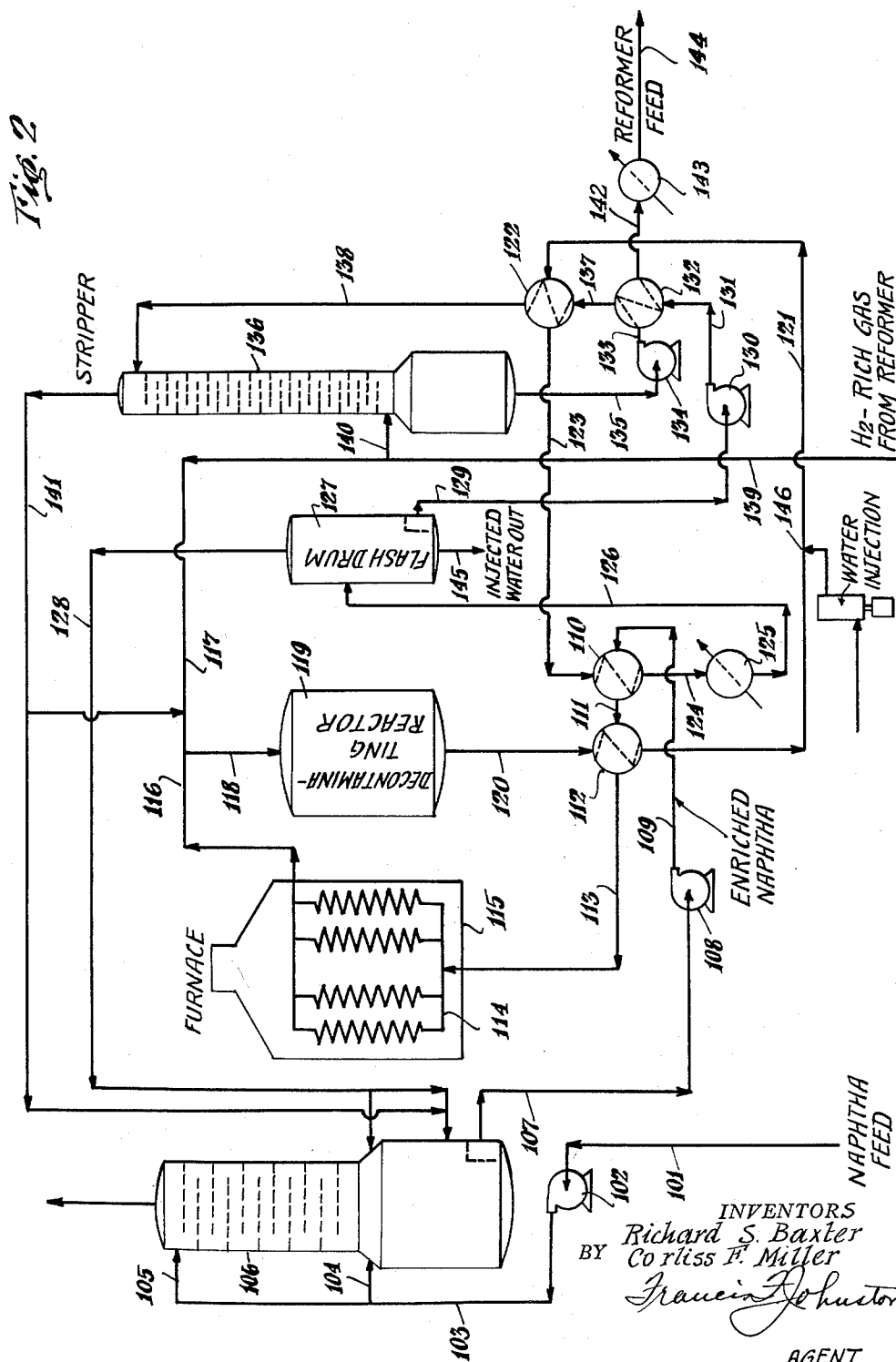
May 9, 1961 R. S. BAXTER ET AL 2,983,675
MAINTAINING SUBSTANTIALLY CONSTANT PRESSURE DIFFERENTIAL
DOWNSTREAM OF A HYDROGENATING REACTOR
Filed July 5, 1957 2 Sheets-Sheet 2

2,983,675

MAINTAINING SUBSTANTIALLY CONSTANT PRESSURE DIFFERENTIAL
DOWNSTREAM OF A HYDROGENATING REACTOR

Filed July 5, 1957

2 Sheets-Sheet 2



1

2,983,675

**MAINTAINING SUBSTANTIALLY CONSTANT
PRESSURE DIFFERENTIAL DOWNSTREAM
OF A HYDROGENATING REACTOR**

Richard S. Baxter, Detroit, and Corliss F. Miller, Trenton, Mich., assignors to Socony Mobil Oil Company, Inc., a corporation of New York

Filed July 5, 1957, Ser. No. 670,136

5 Claims. (Cl. 208—212)

The present invention relates to the choking and the corroding of piping and valves downstream of hydrogenating reactors treating hydrocarbon mixtures containing nitrogen and chlorine compounds and, more particularly, to the choking and corroding of piping, valves and ferrous alloys downstream of a naphtha pretreater employed for the removal of sulfur as hydrogen sulfide from the naphtha feed to a reformer.

Before discussing the locations at which choking and corroding of piping and valves occur downstream of a reactor, employed in hydrogenating hydrocarbons admixed with organic sulfur, nitrogen and chlorine compounds and the means by which such choking and corrosion of ferrous piping and valves can be reduced if not eliminated, it is believed desirable to discuss two flow sheets illustrative of the operations in which the aforementioned difficulties arise.

Illustrative of the operations beset by choking and corroding of piping downstream of a hydrogenating reactor treating a mixture of hydrocarbons containing nitrogen and chlorine, is the pretreatment of naphtha to remove sulfur and nitrogen prior to reforming the pretreated naphtha.

Figure 1 of the drawings is a highly schematic flow sheet showing the flow of liquids, vapors and gases in the pretreatment of naphtha prior to reforming in which the effluent from the hydrogenating reactor is heat exchanged first with the feed naphtha, then with bottoms of a splitter and again with the feed naphtha before being introduced into a flash drum or other means for separating hydrocarbons having four or more carbon atoms per molecule from hydrogen, hydrogen sulfide, and hydrocarbons having less than four carbon atoms per molecule.

Figure 2 of the drawings is a highly schematic flow sheet showing the flow of liquids, vapors and gases in the pretreatment of naphtha vapor prior to reforming in which the effluent from the hydrogenating reactor is heat exchanged first with the feed naphtha, then with the bottoms of a stripper, and again with the feed naphtha before being introduced into a flash drum or other means for separating hydrocarbons having four or more carbon atoms per molecule from hydrogen, hydrogen sulfide, and hydrocarbons having less than four carbon atoms per molecule.

The flow sheets Figures 1 and 2 are not limiting but merely illustrative of the localities at which plugging and corrosion of piping occurs downstream of a reactor in which hydrocarbons contaminated with nitrogen and chlorine compounds are hydrogenated. In general, choking of piping occurs at that point in the piping downstream of the hydrogenating reactor at which the reactor effluent is first cooled to about 450° F. or below 450° F.

The flow sheet of Figure 1 is illustrative of a unit in which heavy naphtha is drawn by pump 1 through pipe 2 from a source not shown and discharged through pipe 3 to the top of absorber 4. Pump 5 draws light naphtha through pipe 6 from a source not shown and discharges

2

the light naphtha into pipe 7 through which the light naphtha flows to absorber 4.

In absorber 4 the naphtha to be treated, i.e., the feed naphtha flows downwardly countercurrently to the upwardly flowing gases flowing from the liquid-gas separator 29 through line 30 and from the reforming unit (not shown) through line 31. The contact of the naphtha feed with the gases removes a major portion of the entrained hydrocarbons having four or more carbon atoms per molecule from the gases providing an enriched naphtha.

The enriched naphtha is drawn from absorber 4 by pump 9 through line 10. Pump 9 discharges the enriched naphtha into pipe 11 at slightly above the pressure of decontaminating or hydrogenating reactor 19. The enriched naphtha flows along pipe 11 to heat exchanger 12 where it is in indirect heat exchange relation with effluent from reactor 19 as hereinafter described. From heat exchanger 12 the enriched naphtha flows through pipe 13 to heat exchanger 14 where the enriched naphtha is in indirect heat exchange relation with effluent from reactor 19. From heat exchanger 14 the enriched naphtha flows through pipe 15 to coils 16 in furnace 17.

In furnace 17 the enriched naphtha is heated to a reaction temperature of about 600° to about 800° F. for sulfur removal by hydrogenation of the organic sulfur compounds. From coil 16 the heated enriched naphtha flows through pipe 18 to reactor 19. Hydrogen-rich gas flowing from a reformer unit (not shown) or other source of gas containing at least 25 percent and preferably at least 60 percent hydrogen is mixed with the heated enriched naphtha in the proportion of about 250 to about 500 standard cubic feet (s.c.f.) per barrel.

The heated enriched naphtha and hydrogen-containing gas flow downwardly through reactor 19 in contact with a (preferably) sulfur-insensitive hydrogenating desulfurization catalyst, e.g., a mixture of oxides of cobalt and molybdenum on alumina. Contact with such a catalyst decomposes the organic sulfur compounds to hydrocarbons and hydrogen sulfide. Organic nitrogen compounds are decomposed to the hydrocarbon and ammonia. Organic chlorine compounds are decomposed to the hydrocarbon and hydrogen chloride. The reactor effluent comprising hydrogen, hydrocarbons, ammonia, hydrogen sulfide and hydrogen chloride flows from reactor 19 through pipe 20 to heat exchanger 14. Thence through pipe 21 to heat exchanger 22 where the reactor effluent is in indirect heat exchange relation with condensate from liquid-gas separator 29 flowing through pipe 34.

From heat exchanger 22 the reactor effluent flows through pipe 23 to heat exchanger 12 where it is in indirect heat exchange relation with enriched naphtha flowing through pipe 11. From heat exchanger 12 the reactor effluent flows through pipe 24 to condenser 25. From condenser 25 the reactor effluent cooled to a temperature at which hydrocarbons having four or more carbon atoms per molecule are condensed flows to liquid-gas separator 29.

In liquid-gas separator 29 the uncondensed hydrogen, hydrogen sulfide, hydrocarbons having less than four carbon atoms per molecule and other non-condensable gases are vented through line 30 and flow to absorber 4. The condensed hydrocarbons are drawn from separator 29 through pipe 27 by pump 28 and discharged into pipe 32. The condensate from separator 29 flows through pipe 32 to heat exchanger 33 where the condensate is in indirect heat exchange relation with the bottoms of splitter 36, the feed to the reformer unit (not shown). From heat exchanger 33 the separator condensate flows through pipe 34 to heat exchanger 22 where the separator condensate is in indirect heat exchange relation with reactor effluent flowing through pipe 21. From heat ex-

changer 22 the separator condensate flows through pipe 35 to splitter 36.

In splitter 36 an overhead is taken through pipe 37 to condenser 38. From condenser 38 the splitter overhead flows through pipe 39 to accumulator 40. In accumulator 40 the components of the splitter overhead boiling below butane are vented to refinery fuel system or recovery through line 41. The components of the splitter overhead boiling above butane flow from the accumulator through pipe 42 and in part are pumped to splitter 36 through pipe 43 by pump 44 and the balance is pumped through pipe 45 by pump 46 to the light straight run stabilizer (not shown).

In the flow sheet designated Figure 2 a stripper is substituted for the splitter of Figure 1. Thus naphtha feed is drawn through pipe 101 by pump 102 from a source not shown and discharged into pipe 103. The feed naphtha flows partially through pipe 104 and partially through pipe 105 into absorber 106 in which it contacts in countercurrent flow gas flowing from stripper 136 and gas-liquid separator 127. From absorber 106 the enriched naphtha is drawn through pipe 107 by pump 108 which discharges into pipe 109.

The enriched naphtha flows along pipe 109 to heat exchanger 110 where it is in indirect heat exchange relation with the effluent from hydrogenating reactor 119 flowing through pipe 120. From heat exchanger 110 the enriched naphtha flows through pipe 111 to heat exchanger 112 where the enriched naphtha is in indirect heat exchange relation with reactor effluent flowing through pipe 120.

From heat exchanger 112 the enriched naphtha flows through pipe 113 to coils 114 in furnace 115. In furnace 115 the enriched naphtha is heated to reaction temperature which for hydrosulfurization is about 600° to about 800° F. From coils 114 the heated enriched naphtha flows through pipe 116 to pipe 118. Hydrogen-rich gas flowing from a reformer unit (not shown) through pipe 117 (when desirable a portion or all of the gas flowing from stripper 136 through line 141 can be diverted through line 146 and mixed with the hydrogen-rich gas flowing through line 117) is mixed with the hot enriched naphtha in pipe 118 at the rate of about 250 to about 650 s.c.f. per barrel of enriched naphtha.

The enriched naphtha and hydrogen-containing gas flow downwardly through hydrogenating reactor 119 in contact with a hydrogenating desulfurizing catalyst such as a mixture of oxides of cobalt and molybdenum supported on an alumina carrier. In the hydrogenating reactor hydrogen sulfide, ammonia and hydrogen chloride are produced. These gases, together with the naphtha feed and the excess hydrogen-containing gas, designated reactor effluent, flow through pipe 120 to heat exchanger 112 discussed hereinbefore.

From heat exchanger 112 the reactor effluent flows through pipe 121 to heat exchanger 122 where the reactor effluent is in indirect heat exchange with the condensate from gas-liquid separator 127 flowing through pipe 137 from heat exchanger 132.

From heat exchanger 122 the reactor effluent flows through pipe 123 to heat exchanger 110 where it is in indirect heat exchange relation with enriched naphtha as discussed hereinbefore. From heat exchanger 110 the reactor effluent flows through pipe 124 to cooler 125 where the reactor effluent is cooled to a temperature at which the C₄ and higher hydrocarbons are condensed.

The cooled reactor effluent flows from cooler 125 through pipe 126 to gas-liquid separator 127. The gaseous portion of the cooled reactor effluent, i.e., hydrogen, hydrogen sulfide, hydrocarbons boiling below butane and other non-condensable gases is vented from separator 127 through line 128 and flows therethrough to absorber 106 as discussed hereinbefore.

The condensed reactor effluent flows from separator 127 through pipe 129 to the suction side of pump 130. Pump 130 discharges the reactor effluent condensate into

pipe 131 through which the condensate flows to heat exchanger 132. In heat exchanger 132 the condensate is in indirect heat exchange relation with the bottoms of stripper 136 flowing through pipe 133.

From heat exchanger 132 the condensate flows through pipe 137 to heat exchanger 122 where the condensate is in indirect heat exchange relation with the total reactor effluent flowing through pipe 121. From heat exchanger 122 the condensate flows through pipe 138 to stripper 136.

To assist in stripping gaseous components of the reactor effluent from the condensate a portion of the hydrogen-rich gas flowing through line 139 to line 117 is diverted to stripper 136 through line 140.

All overhead comprising hydrogen, hydrogen sulfide and hydrocarbons having less than four carbon atoms per molecule is taken through line 141 to absorber 106 or to reactor 119 as discussed hereinbefore.

A bottoms is drawn from stripper 136 through pipe 135 by pump 134 and pumped through pipe 133, heat exchanger 132 and pipe 142 to cooler 143. From cooler 143 the stripper bottom flows through pipe 144 as reformer feed to a reforming unit (not shown).

In light of the foregoing discussion of the flow sheets Figures 1 and 2 the problems of the obstruction of piping and corrosion of ferrous alloys downstream of the hydrogenating reactor can be discussed with greater clarity.

In a unit employing the equipment and heat exchanger train illustrated by the flow sheet Figure 2 a pressure differential of 10 p.s.i. increased to 125 p.s.i. across heat exchanger 110 (Figure 2) after three months of operation. The unit was shut down and approximately 750 pounds of deposits removed. When the unit was put on stream the pressure differential across heat exchanger 110 (Figure 2) was 40 p.s.i. Following a second shutdown and removal of deposits the pressure drop across heat exchanger 110 decreased to 10 p.s.i. Within one week after putting the unit back on stream the pressure drop across heat exchanger 110 had increased to 25 p.s.i. It is to be noted that the temperature of the total reactor effluent is reduced to below 450° F. in heat exchanger 110.

In a unit employing the equipment and heat exchanger train illustrated in Figure 1 corrosion was observed in the splitter overhead pumps after only sixty days operation. Heavy deposits also had built up in the piping connecting these pumps as well as in heat exchangers 22 and 12.

It was found that these deposits were saline in nature and comprised predominantly ammonium chloride. Consequently, it was not surprising to find that these deposits can be removed by flushing the critical portions of the system with water. However, the indiscriminate use of water produces other equally troublesome difficulties.

Probably the most important limiting factor in the use of water to eliminate or at least markedly reduce the amount of water-soluble salts deposited in the equipment, heat exchangers, piping and the like downstream of a hydrogenating reactor treating a hydrocarbon feed containing nitrogen compounds and chlorine compounds decomposable under reactor conditions is the water content of the effluent from the decontaminating unit, i.e., the decontaminated feed to the reformer unit. Many platinum-type catalysts are water-sensitive. The presence of more than a limiting amount of water in the feed to platinum-type reforming catalyst results in the loss of activity. Thus, the manufacturer of one platinum-type catalyst recommends that the amount of water in the feed to a reforming unit in which that platinum-type catalyst is used not exceed 40 p.p.m. Many operators, however, limit the concentration of water in the feed to a reforming unit employing that particular platinum-type catalyst to a maximum of 20 p.p.m.

A further difficulty accompanying the use of indiscriminate amounts of water to reduce or eliminate the

deposit of water-soluble salts in the system downstream of a decontaminating reactor is the result of saturation of the vaporous or gaseous portion of the effluent with the excess water. The water introduced into the gaseous portion of the effluent returns to the absorber and destroys the operational balance. Water carried over mechanically to the fractionating system interposed between the liquid-gas separator of the decontaminating unit and the entrance to the reforming unit gathers in the trays of the fractionating unit and destroys the fractionation balance of the towers. Thus, it becomes evident that there are critical limits to the amount of water which can be introduced into the system downstream of the decontaminating reactor when removal of the salt deposits is to be accomplished without taking the unit off-stream.

The lower critical limit is the minimum amount of water required to remove the deposits of water-soluble salt as a solution which will not be supersaturated at the temperatures to which it is subjected before being withdrawn from the system. The upper critical limit is the maximum amount of water which can be used without disrupting the balance of the fractionating operations downstream of the reactor.

Thus, in a refinery operating a decontaminating unit such as illustrated in Figure 1, it was found that continuous injection of water at any point between reactor 19 and heat exchanger 22 at the rate of about 1.5 gallons per minute (g.p.m.) or at the rate of about 1.75 to about 2.0 gallons per barrel of naphtha throughout would keep the heat exchangers 22 and 12 substantially free from water-soluble salt deposits. The point selected for injection of water is one where the temperature of the effluent is higher than about 450° F.

It is preferred to inject hot water, i.e., water having a temperature of at least about 180° F. However, the injection of steam is not satisfactory since the salt deposit must be dissolved in and carried in solution in the liquid water. Hence, the maximum temperature of the water injected is that at which the injected water will remain liquid at the pressure existing downstream of the point of injection. It has been found that a satisfactory source of water for injection is boiler feed water having a temperature of about 220° F. under a pressure of about 600 p.s.i.g.

It has been found that when hot water is injected at the rate of about 1.5 g.p.m. or about 0.25 gallons per barrel of feed to the decontaminating reactor at a point such as 47 (Figure 1) or 146 (Figure 2) practically all of the water can be drawn-off at the gas-liquid separator 29 (Figure 1) or 127 (Figure 2) through pipes 48 and 145 respectively. Thus, while injecting hot water at the rate of 10.5 g.p.m. into the reactor effluent stream at 146 water was drawn from the flash drum at 145 at the rate of 9 g.p.m. No water appeared in the stripper bottoms and only minor amounts of water appeared in the absorber. The minor amounts of water which appeared in the absorber did not interfere with the steady operating conditions of the unit.

When injecting hot water, e.g., boiler feed water under 600 p.s.i.g. at a temperature of 220° F. into the total effluent at the rate of 10.5 g.p.m., i.e., at the rate of 0.75 gallon per barrel of feed to the decontaminating reactor no difficulties arose in the operation of either the stripper or the absorber. However, in another plant the injection of hot water at the rate in excess of 0.5 g.p.m. was found to result in an excessive amount of water in the feed to the reforming unit. That is to say, when water was injected at the rate of 1 g.p.m., i.e., 0.16 gallon per barrel of feed to the decontaminating reactor it was found that the water in the charge to the reformer was present in a concentration of 84 p.p.m. greatly in excess of the maximum recommended by the catalyst manufacturer. Accordingly, it is necessary to inject hot water downstream of the decontaminating reactor and upstream of the point at which the temperature of the

reactor effluent first reaches 450° F. at a rate not exceeding about .4 gallon per barrel of feed to the decontaminating reactor and preferably about .25 to about .35 gallon per barrel of feed to the aforesaid reactor. The minimum amount of water injected into the effluent stream downstream of the decontaminating reactor is the minimum amount of water in the liquid state under the conditions of temperature and pressure existing in the system downstream of the reactor required to maintain a substantially constant pressure differential between a point in the system upstream of the point at which the temperature of the reactor effluent stream first is reduced to about 450° F., hereinafter designated the 450° point and a point downstream of the 450° point. The maximum amount of water to be injected is that amount of which at least 85 percent can be drawn-off upstream of fractionating equipment.

While the injection of water such as boiler-feed water or other water having a pH of 7 is satisfactory for the maintenance of substantially constant pressure differential across heat exchangers and the like downstream of the point at which the temperature of the reactor effluent first is lowered to about 450° F., corrosion of ferrous metals in contact with the reactor effluent is not eliminated or reduced to a negligible rate. Accordingly, it is preferred to inject water containing a buffer or an alkaline agent and having a pH of at least 8 in sufficient amount to maintain the pH of the system at about pH7 to 7.2. The material which accomplishes the purpose while introducing the fewest difficulties is ammonia. Accordingly, it is referred to inject solutions of ammonia having an ammonia concentration such as to produce aqueous solutions of about 26° Baume at the rate of about 1 to about 2.5 gallons for 10,000 barrels of oil per day.

While water can be injected continuously to remove water-soluble salts deposited downstream of the 450° point, it is preferred to inject the water intermittently. Intermittent injection of water into the system reduces the possibility of injected water being carried over into the fractionating system. To ensure the presence of water in the liquid phase downstream of the 450° point, it is necessary to inject water at a rate greater than that at which it can be vaporized under the conditions of temperature and pressure downstream of the 450° point and rejected with the absorber off-gas. Intermittent injection of water rather than continuous injection of water is preferred since intermittent injection of water allows the recycled water (in the gas-liquid separator gas) to be rejected during the period when water is not injected. The injection preferably is repeated only after the gaseous phase is substantially free of water from the previous injection. Intermittent injection of water results in the rejection of recycled water without resort to interfacial control systems and without the danger of disrupting fractionating tower operation because of water levels on the tower trays. The injection of water preferably is effected within a period of from about 10 minutes to about two hours.

We claim:

1. A method for pretreating a reformer feed stock containing sulfur, nitrogen, and chlorine compounds as contaminants which comprises reacting said feed stock with hydrogen under desulfurizing conditions thereby producing an effluent stream comprising hydrocarbons, hydrogen and water-soluble material derived from said contaminants, injecting hot water into said effluent stream while the said stream is at a temperature in excess of about 450° F. and under a pressure sufficient to maintain said water in the liquid phase, cooling said mixed stream of effluent and water to a temperature at which C₄ and higher hydrocarbons are condensed, separating from said cooled mixed stream, (a) a gaseous fraction, (b) an aqueous fraction containing said water soluble material

7

in solution and (c) a liquid hydrocarbon fraction comprising C₄ and higher hydrocarbons.

2. The method as set forth in claim 1 in which the separated liquid hydrocarbon fraction contains not more than 15% of the injected water.

3. The method as set forth in claim 1 in which the liquid hydrocarbon fraction is fractionated to provide a reformer feed stock containing not more than 40 p.p.m. water.

4. The method as set forth in claim 1 in which said hot water is injected into said effluent stream intermittently for periods of from about ten minutes to about two hours at a temperature of about 180° F. and said injection of water is repeated only after the gaseous fraction separated from said reaction effluent is substantially free of water.

8

tion of water is repeated only after the gaseous fraction separated from said reaction effluent is substantially free of water.

5. The method as set forth in claim 1 wherein the injected water contains ammonia in solution and is at a temperature of at least 180° F.

References Cited in the file of this patent

UNITED STATES PATENTS

2,162,933	Bolinger et al. -----	June 20, 1939
2,529,790	Waddill -----	Nov. 14, 1950
2,758,064	Haensel -----	Aug. 7, 1956
2,785,120	Metcalf -----	Mar. 12, 1957