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PERFORMANCE OF A GIRBOTOL PURIFICATION PLANT AT LOUISIANA, MO.

BY L. F. WILLMOTT, H. R. BATCHELDER, L. P. WENZELL, JR., AND L. L. HIRST

United States Department of the Interior — February 1956

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UNITED STATES DEPARTMENT OF THE INTERIOR
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BUREAU OF MINES
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CONTENTS

TABLES

ILLUSTRATIONS

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SUMMARY AND CONCLUSIONS

An ethanolamine purification unit for removing carbon dioxide and hydrogen sulfide from Fischer-Tropsch synthesis gas was installed at the Bureau of Mines synthetic liquid fuels demonstration plant at Louisiana, Mo. The unit was a surplus Radford Girbotol unit from the Missouri Ordnance Works modified for a capacity of 90,000 std. cu. ft. per hour of synthesis gas at 450 p.s.i.g., operating pressure. The hydrogen sulfide loading of the feed gas was specified at 500 grains per 100 cu. ft. The unit was designed by the Girdler Corp. and installed by the Koppers Co.

Initial operations were conducted for 11 days in May 1951. Thereafter 7 additional runs were made, varying in duration from 8 to 54 days. The last run was terminated on May 29, 1953, the total time the plant was in operation being 219 days.

Although scrubbing gas with ethanolamine solution to remove hydrogen sulfide and carbon dioxide has been used extensively in the oil-refining, natural-gasoline, and natural-gas industries and in steel finishing, this report is the first description of semi-commercial-scale application of the process to the purification of synthesis gas produced from coal or coke for Fischer-Tropsch synthesis. A brief account of each run and a summary of the operational data are presented. A material balance is given for a period typical of the operation with a gas produced from coke.

In all runs except the last the gas handled by the unit was from a Kerpely oxygen-blown coke producer and had a hydrogen sulfide content of less than 150 grains per 100 cu. ft. After the first two preliminary runs the unit performed satisfactorily, not only with the gas from the Kerpely producer but also, in the final run, with gas from a coal gasifier; this gas had a hydrogen sulfide content of 600 grains per 100 cu. ft.

From the performance of the Girbotol unit the following conclusions were reached:

1. The Girbotol unit effectively removed the bulk of the carbon dioxide and hydrogen sulfide from synthesis gas produced either from coke or directly from coal.

2. The performance of the unit indicated the need for further research into (a) the causes and control of corrosion of the materials of construction of the unit with such research evaluating the effects of temperature and intermittance of operation and (b) the cause of foaming in the reboiler and means for abating it.

ACKNOWLEDGMENTS

The authors wish to acknowledge the helpful suggestions and comments of H. W. Wainwright of the Appalachian Experiment Station, Bureau of Mines, Morgantown, W. Va., and G. C. Egleson, formerly of that station.

Thanks are due to Dr. R. E. Reitmeier and his associates of the Gas Processes Division, Girdler Corp., who contributed valuable information.

INTRODUCTION

The Bureau of Mines at Louisiana, Mo., operated semicommercial plants to demonstrate two processes for the conversion of coal to oil - the first, direct hydrogenation of coal and the second, gasification of coal followed by Fischer-Tropsch synthesis. An important step in the Fischer-Tropsch or gas-synthesis process was purification of the synthesis gas produced by coal gasification.

The most satisfactory and active catalysts employed in Fischer-Tropsch synthesis are sulfur sensitive, and a maximum concentration of 0.1 grain of total sulfur per 100 cu. ft. in purified synthesis gas is all that can be tolerated. The presence of carbon dioxide also has a deleterious effect on the catalytic hydrogenation of carbon monoxide and, in addition, adversely affects the absorption of organic sulfur in the activated carbon tower of the raw-synthesis-gas purification system.

The planning period for the gasification and purification units coincided with the development of amine gas-scrubbing processes in which the fouled amine solution is regenerated, not by using steam but directly by using the sensible heat of the raw gas that is to be purified;[5] considerable savings are made possible by so doing.[6] These savings are readily apparent when consideration is given to the report[7] that about 60 percent of the cost of diethanolamine operation lies in the cost of the steam needed to regenerate the foul solution. In some of the installations the amine solution is stripped in a tower mounted over the combustion chamber or gasifier in which the raw gas is made, and in others the stripper consists of a flat, rectangular, closed vessel mounted over the gasification or combustion space. In some of these processes copper sulfate is added to the lean amine solution to inhibit corrosion.

However, the construction period for the Louisiana, Mo., gas-synthesis plant also coincided with a period of shortage of durable goods, and this circumstance weighed heavily in selecting and using the surplus Radford Girbotol plant from the Missouri Ordnance Works.

The Girbotol unit was not expected to suffice in itself for removing the sulfur constituents of the gas but rather to lessen the burden on the subsequent iron oxide and activated carbon units for final sulfur cleanup. Thus, the unit was designed to reduce the hydrogen sulfide content of the synthesis gas to 10 to 20 grains per 100 cu. ft. and the carbon dioxide content to 1 to 3 percent.

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[5] Hotchkiss, A. G., and Webber, H. M., A New Heat-treating Atmosphere Producer: Iron Age, vol. 158, No. 21, Nov. 21, 1946, pp. 48-55.

[6] Hotchkiss, A. G., and Webber, H. M., Protective Atmospheres: John Wiley & Sons, Inc., New York, N. Y., 1953, pp. 93-99.

[7] Bureau of Mines, Annual Report of the Secretary of the Interior on Synthetic Liquid Fuels for 1954: Part I, Oil From Coal: Rept. of Investigations 5118, 1955, p. 46.

Originally the intent was to use triethanolamine as the scrubbing liquid in the Girbotol unit, but as a result of laboratory investigations at the Bureau of Mines station at Morgantown, W. Va., the decision was made to use diethanolamine instead. Triethanolamine, which is selective to hydrogen sulfide would facilitate the commercial recovery of sulfur in the acid gas from the unit; however, use of diethanolamine would permit more nearly complete removal of carbon dioxide from the gas and simultaneously remove much of the hydrogen sulfide. Morgantown investigations established that lower residual concentrations of carbon dioxide in the gas would be beneficial not only to the Fischer-Tropsch synthesis process but also to the active carbon absorption process for removing the organic sulfur compounds. Moreover, a sulfur-recovery process became available for which acid gas streams of much lower hydrogen sulfide content would be suitable.[8/]

The results of laboratory investigations of the abosorption of carbon dioxide and hydrogen sulfide in ethanolamine at atmospheric pressure were published in 1935, 1936, and 1941,[9 10 11/] and a report on plant-scale operation was published in 1941.[12/] Laboratory and pilot-plant work on the removal of impurities in synthesis gas under pressure was conducted at Morgantown, W. Va., and the results of this work were published in 1952.[13/] The complete gas-purification operation at Louisiana, Mo., has also been reported.[14/]

DESCRIPTION OF THE MODIFIED RADFORD GIRBOTOL PROCESS

In the Girbotol purification plant gas from the Kerpely coke producer,[15/] the coal gasifier,[16/] or from the synthesis-gas holder was compressed in 1 or 2 horizontal, 2-stage compressors. The discharge pressure was governed by the operating pressure of the synthesis reactor of the gas-synthesis plant. Normally this pressure was 330 to 340 p.s.i.g. and required that the gas be delivered to the Girbotol unit from the aftercoolers of the compressors at 370 p.s.i.g. Normally the temperature of the gas entering the absorber was 100° F.

[8/] Resen, F. L., New Sulfur Process: Oil and Gas Jour., vol. 50, No. 4, 1951, p. 59.

[9/] Bottoms, R. R., and Wood, W. R., The Girbotol Purification Process: Refiner and Natural Gasoline Manufacture, vol. 14, 1935, p. 105.

[10/] Mason, J. W., and Dodge, B. F., Equilibrium Absorption of Carbon Dioxide by Solutions of Ethanolamines: Trans. Am. Inst. Chem. Eng., vol. 32, No. 27, 1936.

[11/] Cryder, D. S., and Maloney, J. D., The Rate of Absorption of Carbon Dioxide in Diethanolamine Solutions: Trans. Am. Inst. Chem. Eng., vol. 37, No. 827, 1941.

[12/] Reed, R. M., and Wood, W. R., Recent Design Developments in Amine Gas Purification Plants: Trans. Am. Inst. Chem. Eng., vol. 37, No. 363, 1941.

[13/] Wainwright, H. W., Egleson, G. C., Brock, C. M., Fisher, J., and Sands, A. E., Removal of Hydrogen Sulfide and Carbon Dioxide From Synthesis Gas Using Di- and Tri-Ethanolamine: Bureau of Mines Rept. of Investigations 4891, 1952, 19 pp.

[14/] Wenzell, L. P., Jr., Dressler, R. G., and Batchelder, H. R., Plant Purification of Synthesis Gas: Ind. Eng. Chem., vol. 46, 1954, pp. 858-862.

[15/] Willmott, L. F., Batchelder, H. R., and Tenney, R. F., Production Operating Experience With Oxygen in the Kerpely Producer at Louisiana, Mo.: Bureau of Mines Rept. of Investigations 5108, 1955, 16 pp.

[16/] Dressler, R. G., Batchelder, H. R., Tenney, R. F., Wenzell, L. P., Jr., and Hirst, L. L., Operation of a Powdered-Coal Gasifier at Louisiana, Mo.: Bureau of Mines Rept. of Investigations 5038, 1954, 35 pp.

Figure 1 is a photograph of the purification unit. The central tower is the absorber, and that on the right is the regenerator. The small vessel between the two is the oil-entrainment separator. The two bottom horizontal vessels are the heat exchangers. Above them is one of the solution coolers and above it the reboiler.

In figure 2, a flow diagram of the unit, synthesis gas is shown entering the unit at the middle of the left side of the diagram. The gas passed first through an entrainment separator, which removed any oil or moisture carried over from the compressors. The gas next entered the base of the absorber and was scrubbed countercurrently with lean diethanolamine solution, which entered the absorber through a distribution ring above the packing. The absorber was a 30-inch-diameter tower packed with 35 feet of 1-1/4- by 1-1/4-inch stoneware Raschig rings.

Scrubbed gas left the top of the absorber through another separator, which separated entrained solution from the gas and returned it into the base of the absorber. A bull's-eye, sight-flow indicator showed the amount of entrained liquid being returned. Excessive flow indicated foaming in the absorber. The temperature of the diethanolamine solution was adjusted to give an outlet-gas temperature of 105° F., thus insuring the right humidity for hydrogen sulfide removal in the iron oxide towers, the next step in the purification train.

The rich diethanolamine solution flowed under absorber pressure through a liquid-level control valve and thence to the tube sides of 2 solution heat exchangers in series and into the top of the reactivator operated at approximately 12 p.s.i.g. In passing through the two solution heat exchangers the rich diethanolamine solution was warmed by the lean solution flowing on the shell sides. Its temperature on entering the reactivator was approximately 205° F.

Rich diethanolamine solution flowed downward through the reactivator over 13 successive trays. The bottom tray collected the liquid and diverted it to the far end of the shell side of the reboiler. Heat was supplied to the diethanolamine solution by steam on the tube side of the reboiler, the amount of steam delivered being controlled by the indicating pressure controller. The temperature of the solution in the reboiler was approximately 240° F. Natural gas was admitted to the reboiler at a rate of approximately 1,000 c.f.h. to reduce foaming and assist in stripping the solution.

Liberated carbon dioxide, hydrogen sulfide, and water vapor passed from the top of the reactivator into the shell side of the acid-gas cooler. Water vapor was condensed and returned to the reactivator at the top, the 16th tray, after passing through a drip leg which acted as a seal. The rate was approximately 2 g.p.m. Water was used as the cooling medium, and the rate of flow (about 120 g.p.m.) was adjusted so that the temperature of the acid gas was held at 150° F. Acid gas was released to the low-pressure relief header by a back-pressure controller set to maintain 10 to 12 p.s.i.g. in the reactivator. A low-pressure relief header carried the acid gas to the flare stack.

The stripped diethanolamine solution collecting in the base of the reactivator was continuously released through the shell sides of 2 solution heat exchangers and 2 solution coolers to the suction of 2 triplex pumps, 1 or both of which were used to deliver lean diethanolamine to the absorber. In the heat exchangers the temperature of lean diethanolamine was reduced to 170° F. and in the solution coolers to 105° F. After passing through the second heat exchanger and before it entered the first solution cooler, a small side stream of lean diethanolamine was taken and delivered to a decanter for continuous clarification of the solution.

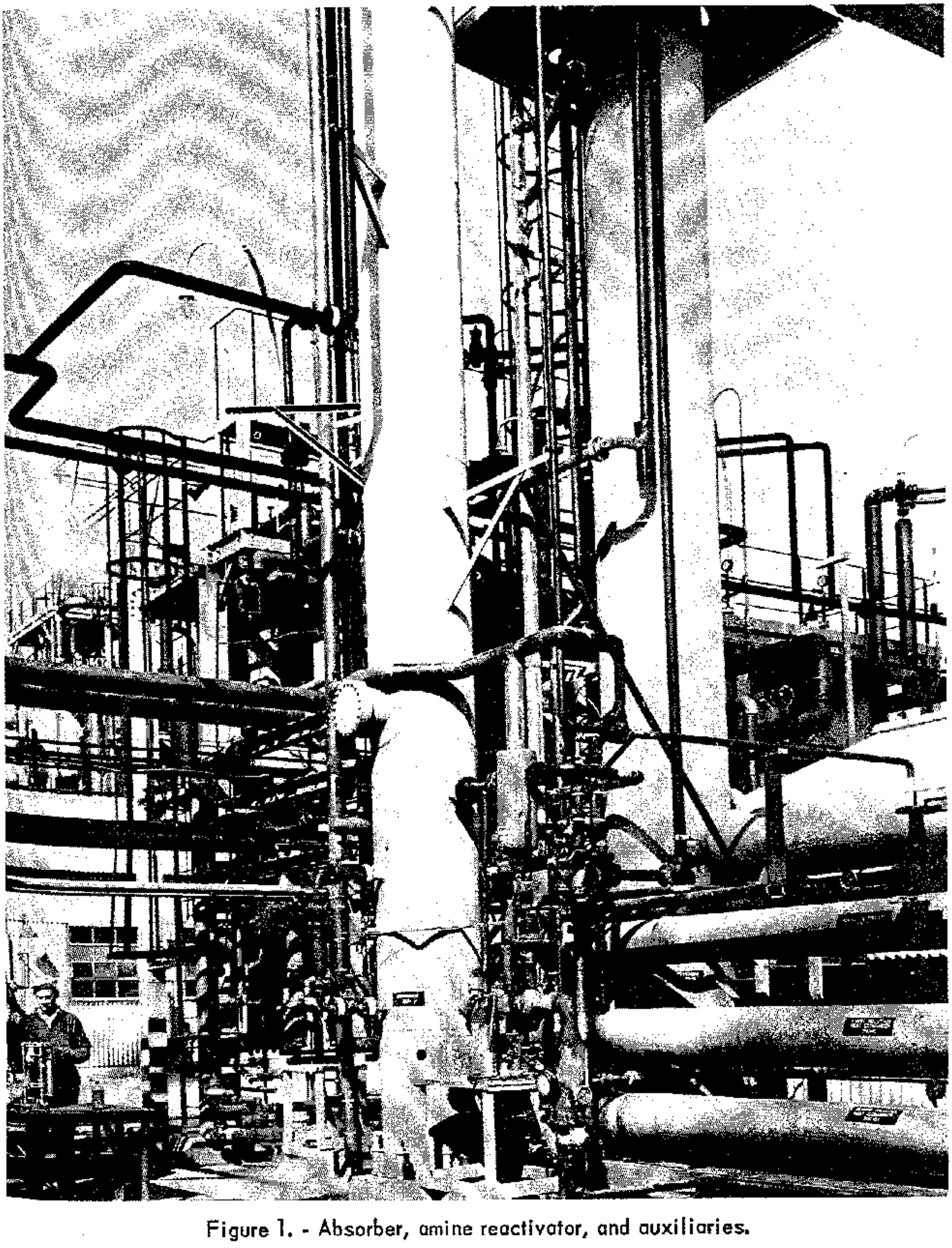

Figure 1. - Absorber, amine reactivator, and auxiliaries.

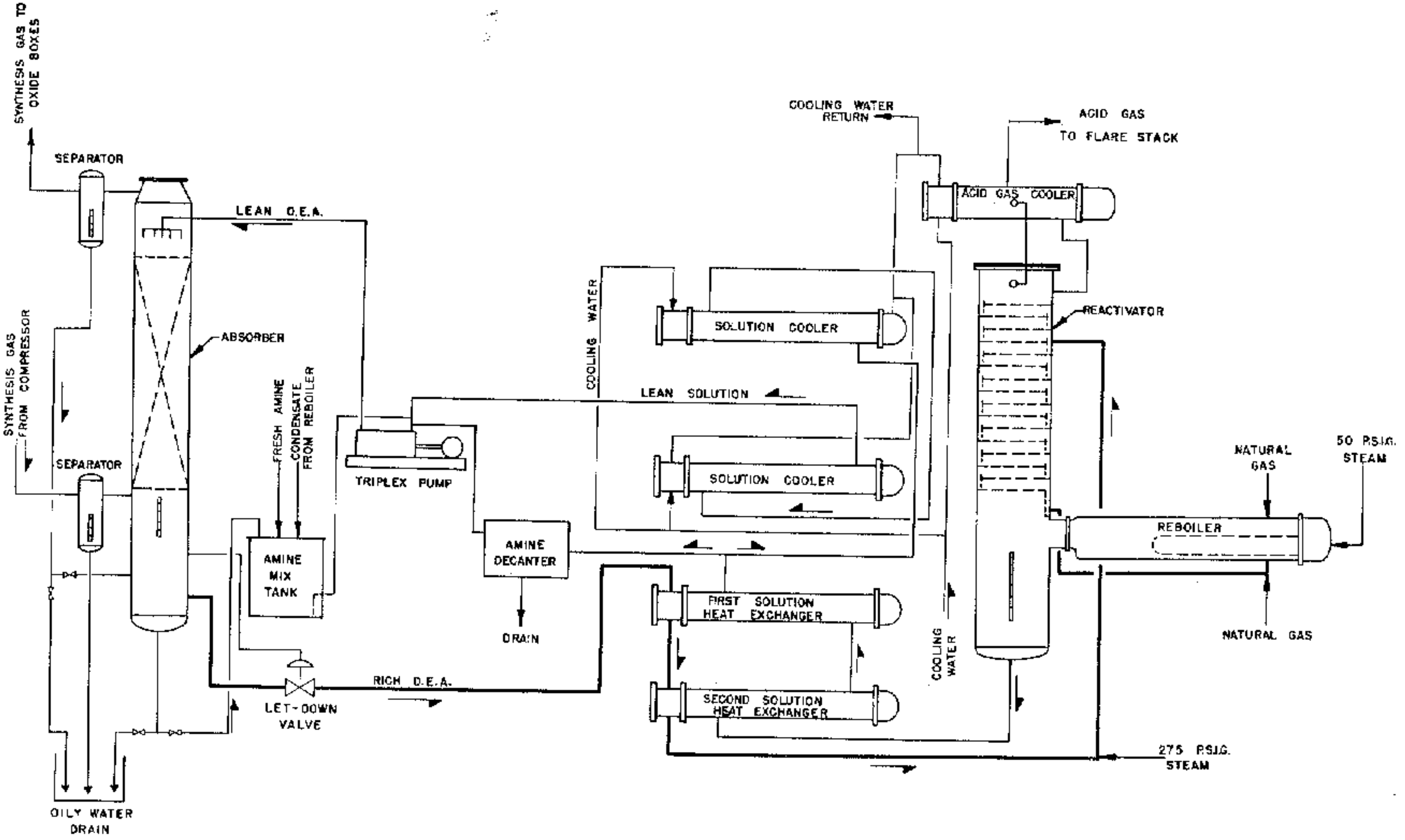

Figure 2. - Flowsheet of the process

The rate of flow of lean solution to the absorber was indicated on a flow indicator and in the base of the reactivator a gage glass indicated the liquid level.

OPERATIONAL DATA AND DESCRIPTION OF OPERATIONS

The following is a brief description of the purification runs that were made:

Run 1

This 8-day run served to train operators, determine mechanical performance, and produce a gas with which to test the performance of the iron oxide towers for residual hydrogen sulfide removal. These towers followed the Girbotol unit in the purification train. No attempt was made to obtain maximum removal of carbon dioxide and hydrogen sulfide. In general, the unit was operated to produce an off gas containing 3 to 5 percent carbon dioxide and 15 to 30 grains of hydrogen sulfide per 100 cu. ft. at a gas-flow rate from the absorber ranging from 65 to 75 M c.f.h.

Amine solution was lost during the run, necessitating frequent additions of both fresh amine and reboiler steam condensate to maintain the solution volume and the desired amine concentration. Good stripping of the rich amine was not possible because of flooding of the reactivator tower at any reboiler temperature higher than that attained with 20 p.s.i.g. steam. It was suspected that the heat exchangers were not adequate, thus limiting the temperature of the rich solution entering the top of the reactivator and placing an excessive heat load on the reboiler.

The automatic speed control on the raw gas compressors did not function satisfactorily at the speed at which a single compressor was required to operate to deliver the requisite quantity of gas. Fluctuations in compressor speed caused upsets in the absorber tower and loss of amine solution. On the other hand, 2 compressors on the line performed better than only 1 as their reduced speeds were within the range of satisfactory tachometer control.

During most of the run the absorber pressure was 400 p.s.i.g., but toward the end of the run it was reduced to 325 p.s.i.g. Earlier in the run some sticking of the feather valves of the compressor occurred, which was eliminated when the operating pressure was lowered and two compressors were used. A possible explanation is that the quantity of nongaseous impurities passing through each valve was considerably reduced.

Run 2

This run of 19 days was interrupted several times by tar deposits in the valves of the gas compressors and in auxiliary equipment. Much the same difficulty of solution loss was experienced as in run 1, amine being carried over from the reactivator into the flare stack seal. The loss was reduced when it was found that, in constructing the plant, the inlets to the reactivator of the rich solution and the reflux from the acid-gas cooler had become transposed. At the same time that this was corrected, the bypass around the acid-gas cooler back-pressure regulating valve was partly opened, the valve having been found to be undersized. This further reduced the loss of solution.

An attempt was made to increase the circulation of diethanolamine from 35 to 70 g.p.m., but excessive vibration of the piping with attendant breakages forced a return to the lower rate.

As in run 1, it was difficult to maintain the liquid level in the reactivator system. The level could not be held constant when the reboiler steam pressure was increased above 22 p.s.i. Consequent low reboiler rates resulted in poor stripping of the rich amine and poor removal of both carbon dioxide and hydrogen sulfide. There was also evidence of sludge accumulations in the system.

Operating with approximately 90,000 std. cu. ft. per hour feed gas containing 15 to 16 percent carbon dioxide and 130 to 140 grains of hydrogen sulfide per 100 cu. ft. and with a circulation of 36 g.p.m. of 35-percent diethanolamine resulted in a scrubbed gas containing about 2-1/2 percent carbon dioxide and 10 grains of hydrogen sulfide. The absorber pressure was 350 p.s.i.g.

Run 3

During this run the gas purified in the Girbotol unit was used, after further purification with iron oxide, alkalized iron, and activated carbon, in Fischer-Tropsch synthesis throughout the first run of the gas-synthesis plant.

Before the run was begun the Girbotol unit was cleaned, particularly the tube bundles of the heat exchangers and solution coolers, which were pulled and cleaned. The reactivator was emptied of amine and thoroughly flushed with water.

Diethanolamine solution used in the previous runs had become contaminated with a fine, heavy, black sludge and some oily matter. The oil was apparently carried over in the gas from the compressors, and changes were made to the inlet-gas separator on the absorber to correct this condition. The sludge was partly iron sulfide, and this may have formed by the reaction of rust in the system with hydrogen sulfide in the gas. The sludge, however, was not analyzed for the presence of organic sulfur compounds. It settled quite rapidly so batch decantation from a 500-gallon tank was decided on for initial clean-up of the amine solution before the run began. During a short down period toward the end of the run provision was made to withdraw 150 gallons of solution each day, allow it to settle, and then pump the clarified solution back into the system. The reactivator had a capacity of 380 gallons, of which 250 gallons was held in the trays with the balance in the reboiler and base of the reactivator.

Although fluctuations in liquid level in the reactivator were believed to be attributable to the dirty solution hampering liquid flow in the trays, foaming in the reboiler also was thought to be a cause. In consequence, a connection was made to admit natural gas to the shell side of the reboiler. When the run began 1,500 cu. ft. per hour of natural gas was admitted over the surface of the boiling amine solution in the reboiler, and it was then found possible to raise the pressure of the steam to the reboiler to 30 p.s.i.g. Considerable reduction in fluctuations of liquid level in the reactivator and better stripping of the rich diethanolamine at the higher steam pressure resulted also.

From the beginning of the run the concentration of amine was brought up to and maintained at 45 percent and the circulation rate held at 40 g.p.m. Treating gas containing 16.7 percent carbon dioxide and 130 grains of hydrogen sulfide per 100 cu. ft., the Girbotol reduced these impurities to an average of 1.5 percent carbon dioxide and 2.0 grains hydrogen sulfide per 100 cu. ft. The rate of feed gas was 75 M std. cu. ft. per hour and the absorber pressure was 350 p.s.i.g.

Run 4

Clarity of the diethanolamine solution was maintained by the intermittent decantation procedure established near the end of the previous run. Liquid-level fluctuations in the base of the reactivator, however, continued to be a source of trouble. It was noted in particular that the problem was aggravated by the intermittent additions of clarified amine or when condensate was added to compensate for losses of water distilled from the system.

In previous runs serious fouling of the amine cooler and heat exchangers had occurred. Before this run the exchangers were thoroughly cleaned and treated with chromite inhibiter. No trouble was experienced with these units during the run.

A temperature indicator, for the reactivator, installed in the control room contributed to closer control of the system. A new liquid trap in the synthesis-gas line on the inlet side of the absorber reduced the amount of oil contaminating the amine solution. Losses of diethanolamine again coincided with pressure upsets in the system.

The concentration of amine averaged 44 percent, and the circulation rate was 39 g.p.m. The thiosulfate content remained at less than 0.2 percent equivalent of the diethanolamine solution. Treating gas containing 16.6 carbon dioxide and 105 grains of hydrogen sulfide, the unit reduced these impurities to 1.8 percent carbon dioxide and 1.5 grains hydrogen sulfide per 100 cu. ft. The feed-gas rate was 74 M cu. ft. per hour, and the absorber pressure was 345 p.s.i.g.

In this run period 46 million cubic feet of raw gas was treated from which 7 million cubic feet of carbon dioxide was removed.

Run 5

This run was made to test alterations to the system and to study further the activated carbon towers. The gas-synthesis plant was not operated during this period.

One alteration was the installation of a continuous settling system for the amine. The decanter was connected to a bleed stream flowing at 10 to 15 gallons per hour, equivalent to treating the entire liquid in the system once a week. The amine was cleaned up satisfactorily, and trouble in fluctuations in liquid level in the reactivator was reduced.

Another alteration was installation of a continuous makeup stream for water lost by vaporization from the reactivator. The original method was direct, intermittent addition of condensate into the vapor space of the reboiler, there being a connection from the 30 p.s.i.g. steam side of the reboiler to the solution side. By this means very little heat was added to the solution side, but the intermittent addition of water upset conditions until the additions of condensate had thoroughly mixed with the entire circulating system. Steam at 275 p.s.i.g. was substituted for condensate, and finally the addition point was changed to the rich amine line immediately before it entered the reactivator. By using the 420° F. steam much more heat could be added for the same amount of added condensate. Before this alteration was made the temperature of the rich solution going to the top of the reactivator was approximately 195° F., and after the change had been made the temperature was 212° to 219° F. This change made for smoother operation of the reactivator because, by adding the heat to the rich solution, its stripping began in the upper trays, and flow of acid gas upward through the tray was reduced to the point where it could not appreciably retard the flow of solution downward through the tray.

The third alteration was the installation of a second lean amine cooler. It is shown in figure 2 as the top cooler in the tier. As can be seen in figure 1, the solution cooler is not housed, and the first operation in warm weather had indicated that at the cooling-water temperatures prevailing and at the 40-gallon-per-minute circulation rate it was not adequate to maintain the desired temperature of the amine to the absorber. This temperature is important because it, in turn, controls the temperature and humidity of the gas going to the iron oxide towers at optimum values for best performance of the iron oxide. Installation of the second cooler in series with the original one permitted this closer temperature control of the amine.

Another alteration was the installation of a meter to measure the quantity of water supplied to the amine coolers. Also, the hairpin-type tubes of the reactivator reboiler were cleaned.

Gas feed rate to the Girbotol unit for the first 8 days was 45,000 cu. ft. per hour of a 51-percent nitrogen gas with 8 percent carbon dioxide content and 30 grains of hydrogen sulfide per 100 cu. ft. The gas was from the Kerpely coke producer, operating on low air blast. With a diethanolamine concentration of 45 to 50 percent and a circulation rate of 40 g.p.m. the gas cleanup in the Girbotol unit was substantially complete. The carbon dioxide content was reduced to less than 1/2 percent and hydrogen sulfide to less than 1/2 grain sulfur per 100 cu. ft. The absorber pressure was 350 p.s.i.g.

Oxygen blast was then applied to the Kerpely producer and the gas feed rate to the purification plant was increased to 80,000 cu. ft. per hour. The carbon dioxide content of the raw gas was 19-1/2 percent, and the hydrogen sulfide was 72 grains per 100 cu. ft. With 45 percent diethanolamine circulating at 38 g.p.m., stable Girbotol operation reduced these impurities to 4-1/2 percent carbon dioxide and 3 grains hydrogen sulfide per 100 cu. ft.

Run 6

The principal objective of this run was to supply the Gas-Synthesis Plant with a steady flow of 65,000 cu. ft. per hour gas containing less than 0.1 grain of sulfur per 100 cu. ft. and not more than 3 percent carbon dioxide.

Diethanolamine losses during this operating period were quite small, except on occasions of pressure upsets in the system. There was no indication of chemical deterioration of the amine solution, except for an increase of thiosulfate from 0.2 to 0.4 percent diethanolamine equivalent. The continuous decanter maintained the solution free of sludge.

During this run the amine concentration was maintained at 44 percent and the circulation rate at 38 g.p.m. Treating gas containing 18.4 percent carbon dioxide and 75 grains of hydrogen sulfide per 100 cu. ft., the Girbotol unit reduced these impurities to an average of 3.0 percent carbon dioxide and 3.0 grains of hydrogen sulfide per 100 cu. ft. The rate of feed gas was 75.8 M cu. ft. per hour, and the absorber pressure was 350 p.s.i.g.

Run 7

This run was made to supply synthesis gas to the Fischer-Tropsch reactor.

As a result of the previously described changes that had been made, operation of the Girbotol unit was extremely smooth. Its performance, however, was less satisfactory than in previous runs. Inspection of the diethanolamine circulation system at the conclusion of the run indicated the cause. The sprays in the absorber tower distribution ring were found to be partly plugged. In addition, the Raschig rings in the tower were coated with tarry material, and some of the rings were broken.

The amine solution remained clear and the thiosulfate of an equivalent of 0.5 percent of diethanolamine. Small losses of diethanolamine were noted, larger losses occurred with pressure upsets in the system.

Operating with approximately 72 M cu. ft. per hour of feed gas containing 19.4 percent carbon dioxide and 75 grains of hydrogen sulfide per 100 cu. ft. and with a circulation rate of 41 g.p.m. of 41-percent diethanolamine resulted in a scrubbed gas containing about 4.2 percent carbon dioxide and 2.1 grains of hydrogen sulfide per 100 cu. ft. The absorber pressure was 340 p.s.i.g. During the run 88,600,000 cu. ft. of gas was fed to the Girbotol unit, and a total of 13,900,000 cu. ft. of carbon dioxide was removed.

Run 8

This was the first run during which gas produced directly from coal by dust gasification was treated in the Girbotol plant. All previous Girbotol operations had been confined to treating gas of much lower hydrogen sulfide concentration that was generated from coke in the Kerpely producer. This necessarily short run gave good reason to believe that gas from coal could be purified readily and probably almost as economically as gas from the producer.

It was also found that the Girbotol unit was capable of removing a considerable portion of the organic sulfur compounds in the raw feed gas, an average of 20 grains per 100 cu. ft. at the inlet being reduced to 1-1/2 grains at the outlet of the absorber tower. The sulfur compounds, however, were not identified; consequently, it was not known whether the organic sulfur was tying up amine as an unregenerable compound. No attempt was made to strike a balance between the organic sulfur taken out of the system in the acid gas from the regenerator and the organic sulfur disappearing from the raw synthesis gas in the absorber.

During this run the average concentration of diethanolamine was 38.6 percent, and the circulation rate was 43.4 g.p.m. Treating raw gas at an average flow of 52,000 cu. ft. per hour, containing 17.8 percent carbon dioxide and 600 grains of hydrogen sulfide per 100 cu. ft., the gas leaving the Girbotol absorber contained only 0.15 percent carbon dioxide and 2.35 grains of hydrogen sulfide per 100 cu. ft. This excellent scrubbing performance in the absorber tower must be attributed to the cleaning of the Raschig rings and tower sprays in preparation for the run and the higher L/G ratio at which the absorber was operated. In the previous runs this ratio of amine circulation to feed gas was usually about 32; in this run it was 50.

DISCUSSION OF OPERATIONS AND RESULTS

A summary of the data obtained from each run is shown in table 1. The effect of higher pressure steam for regenerating the rich amine is evident in the carbon dioxide content of the lean amine. However, approximate mass transfer coefficients indicate that, owing to other variables, the better stripping did not result in increased absorber efficiency. The effect of ratio of free amine to carbon dioxide in feed gas on the percentage of carbon dioxide removed is quite pronounced. The trend is shown graphically in figure 3, the curve being a plot or results obtained

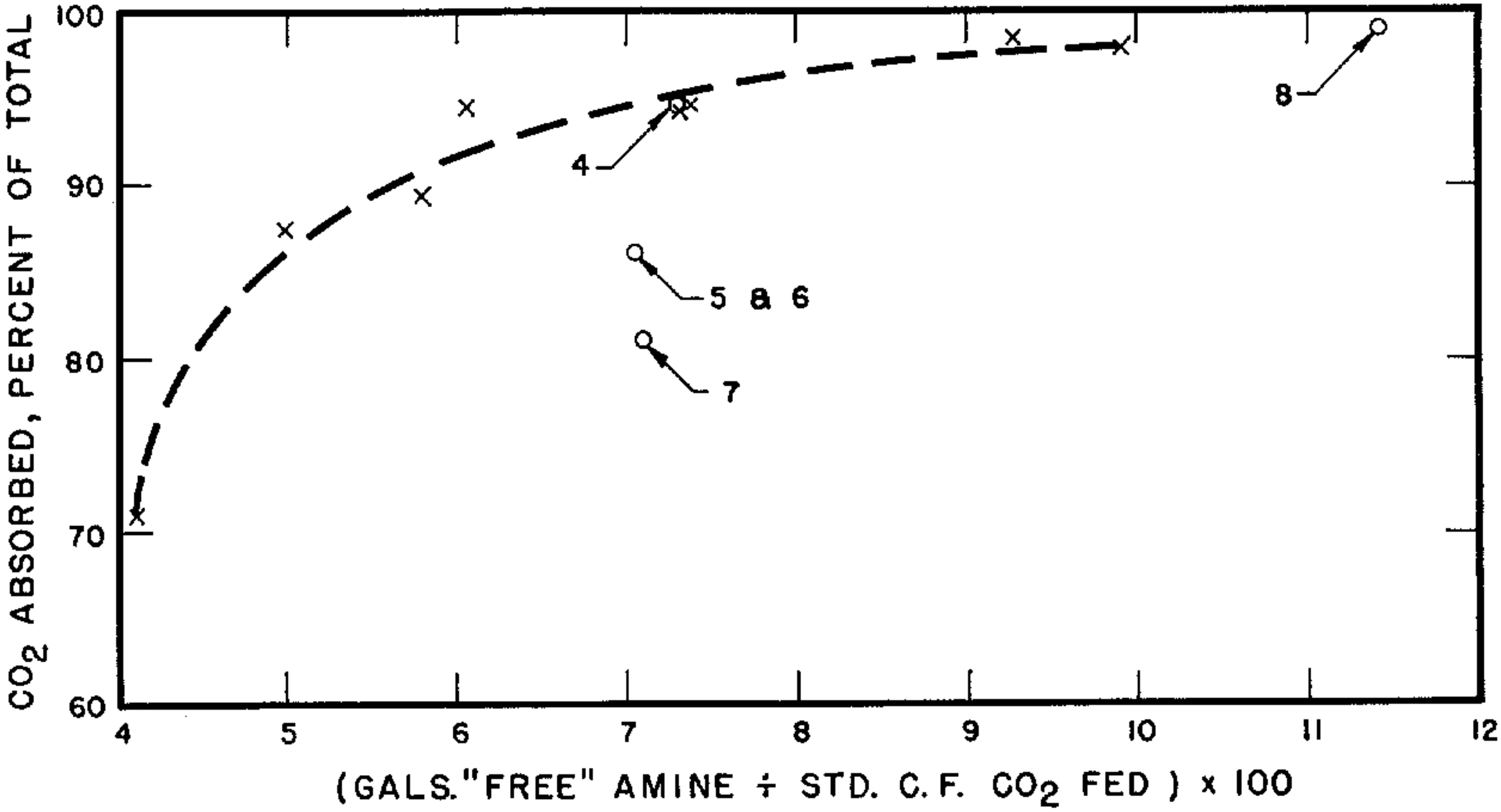

Figure 3. - Performance curve.

during runs 1, 2, and 3. The results of the other runs are identified by their corresponding numbers, those for runs 5, 6, and 7 being departures from the trend.

As mentioned previously, at the termination of run 7 the absorber was opened for inspection. Over half of the spray head was plugged, and the packing and the tower wall were coated with a black deposit. Some of the Raschig rings were broken. The tower was emptied, the spray ring and packing were cleaned, broken rings were eliminated, and enough new packing was added to bring the packing level to within 12 inches of the spray assembly. The entrainment separator on the scrubbed-gas outlet line was also cleaned, as it too contained the same black coating as the packing. Probably the condition of the absorber during run 8 was more comparable to its condition during runs 1 to 4 than during the runs succeeding these. Consequently, it is not unreasonable to assign to contamination one reason, at least, why the scrubbing performances of runs 5-7 lie outside the curve of figure 3.

The scrubbing performance represented by the curve (runs 1-4) was made when the average free amine concentration was 37.3 percent. In runs 5-7 the average concentration was 43 percent. Other investigators have reported[17/] that with increase in amine concentration the increase in viscosity tends to produce films of greater thickness and thus counteracts the effect of increased concentration, the net effect depending on the comparative magnitude of the influence of the two variables. Thus, it may or may not be significant that the better scrubbing achieved during run 8 coincided not only with the removal of the effects of contamination but also with a reduction in amine concentration to 38 percent or very close to that obtained during the runs on which the curve of figure 3 is based.

Figure 4 shows diagrammatically typical operating conditions of the system when synthesis gas from coke is scrubbed and figure 5 the operating conditions with gas produced in the coal-dust entrainment gasifier.

Carbon dioxide and hydrogen sulfide balances were made throughout the runs and are presented for each run in table 1. Calculations for a typical balance and analytical methods are presented in the Appendix.

[17/] Cryder, D. S., and Maloney, J. O., The Rate of Absorption of Carbon Dioxide in Diethanolamine Solutions: Trans. Inst. Chem. Eng., vol. 5, 1941, p. 827.

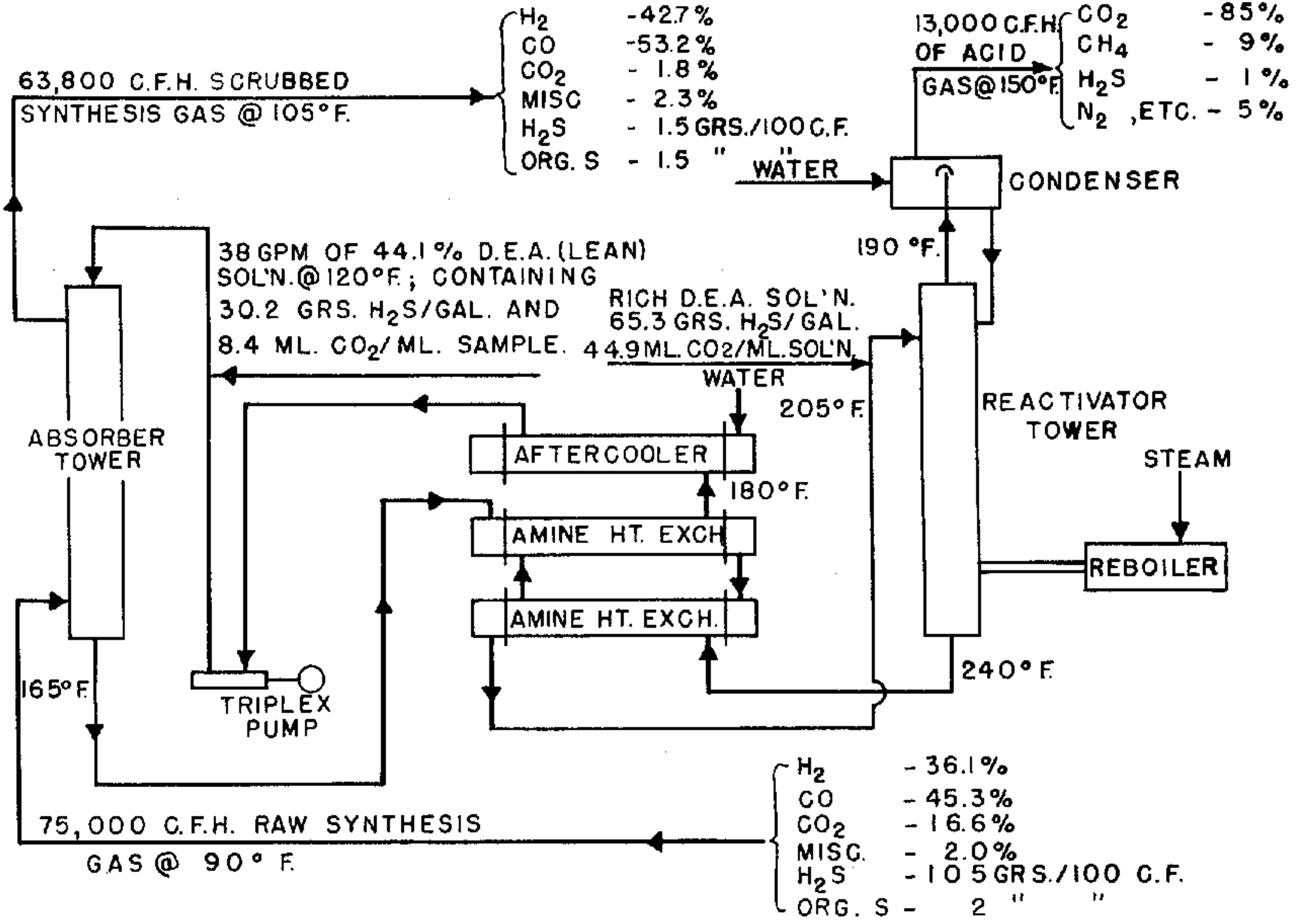

Figure 4. - Typical operating conditions when scrubbing gas produced from coke.

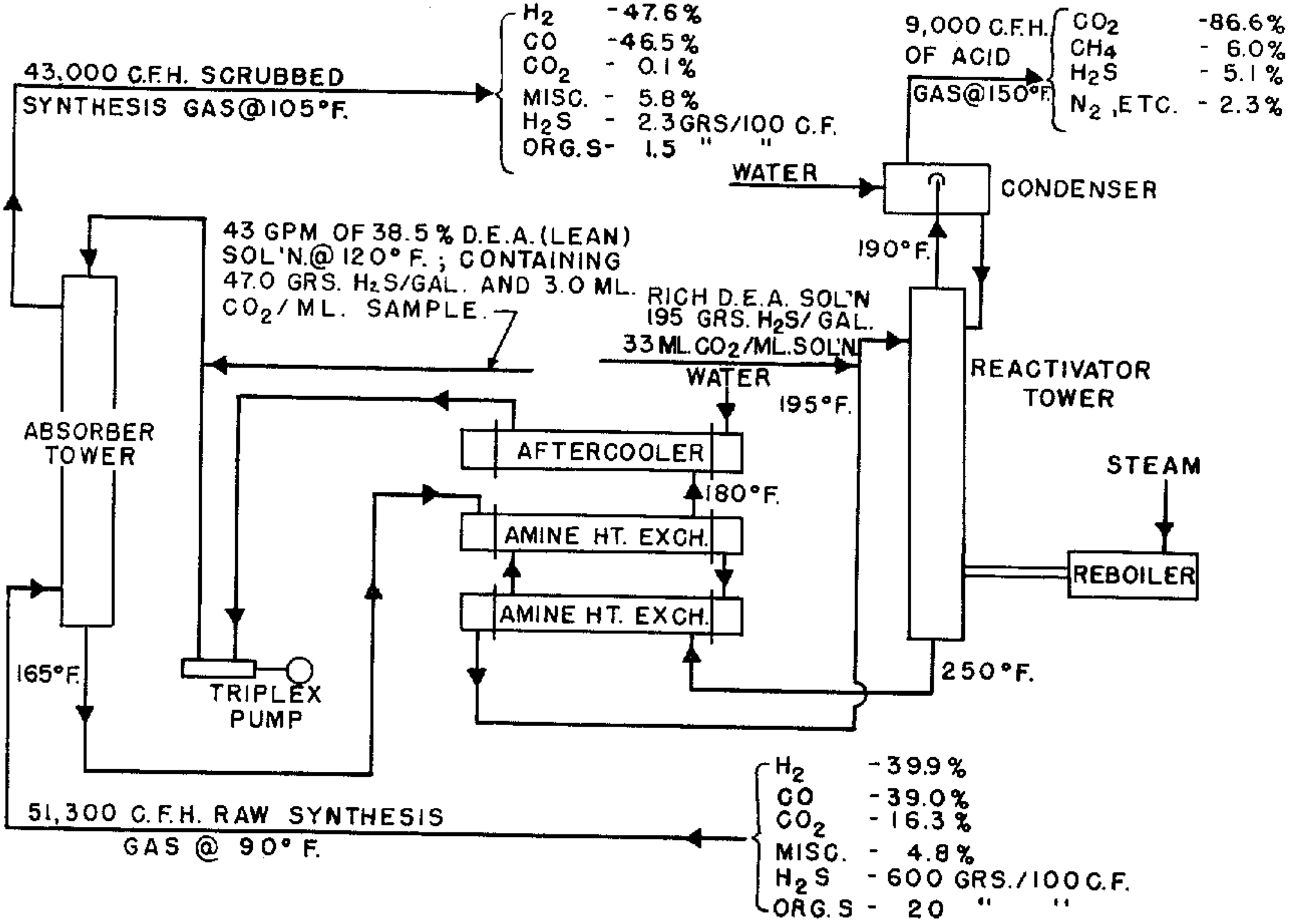

Figure 5. - Typical operating conditions when scrubbing gas produced from coal.

TABLE 1. - Summary of operating data

Run No.	1	2	3	4	5	6	7	8
Date	5/29/51-6/8/51	7/9/51-8/3/51	8/23/51-9/14/51	10/16/51-11/18/51	4/10/52 5/15/52	5/25/52-6/28/52	12/3/52-1/25/53	5/22/53-5/29/53
Purpose of run	Purification only, to train operators.	Purification only.	Purification and synthesis	Purification and synthesis	Purification only, to work out steaming cycle for activated carbon towers.	Purification and synthesis.	Purification and synthesis.	Purification only.
Changes made to equipment before or during run	-	Reversal of reflux and rich DEA inlets on reactivator.	Natural gas connected to reboiler. Heat exchanger and solution cooler cleaned. Reactivator emptied and flushed. Amine solution clarified.	Batch amine decanter installed.	Continuous decanter; continuous water makeup; second solution cooler installed; reboiler cleaned.	-	-	Raschig rings removed from absorber and cleaned. Absorber spray nozzles cleaned.
Gas feed ....cu.ft./hr.	72,200	87,000	75,000	74,000	79,500	75,800	71,900	53,000
Purified gas ....do.	65,000	75,800	63,500	63,000	66,500	63,800	60,500	42,800
Feed-gas analysis:								
H_2...................percent	36.5	36.9	36.5	36.1	37.6	38.9	38.7	40.1
CO ....do.	48.0	46.3	45.0	45.3	41.4	41.4	40.2	38.0
CO_2....................do.	14.1	15.0	16.7	16.6	19.5	18.4	19.4	17.8
Misc. ....do.	1.4	1.8	1.8	2.0	1.5	1.3	1.7	4.1
H_2S ....grains/100 cu.ft.	121	130	130	105	72	75	75	600
Gas analysis, outlet absorber:								
CO_2 ....percent	4.6	2.5	1.5	1.8	4.5	3.0	4.2	0.15
H_2S ....grains/100 cu.ft.	16.0	12.0	2.0	1.5	3.0	3.0	2.1	2.35
DEA circulation........ g.p.m.	28	36	40	39	38	38	41	43.4
DEA concentration .... percent	27	35	45	44	45	44	41	38.6
Reboiler pressure.....p.s.i.g.	20	20	25.0	28.0	30.0	31.0	31.0	32.0
Pressure of absorber....do.	400	350	350	345	350	350	340	370
Pressure on reactivator.do.	10.5	12.0	12.0	12.5	13.0	13.0	13.0	13.0
Temp. gas from absorber....°F.	100	105	115	105	105	105	105	104.5
Acid content of DEA:								
Rich (from absorber):								
H_2S............. grains/gal.	42	55.0	85	65	43	52	55	196
CO_2 ...cu.ft./gal. of sample	4.8	6.2	6.0	6.0	6.3	6.2	5.2	4.4
Lean (to absorber):								
H_2S .... grains/gal.	16	16.5	50	30	20	30	38	47
CO_2 ...cu.ft./gal. of sample	0.9	1.3	1.1	1.1	0.8	0.5	0.5	0.4
Total raw gas to Girbotol .... million cu.ft.	19.0	39.7	18.0	46.0	42.1	63.7	88.6	10.0
Total purified gas..... do.	17.0	34.5	15.3	39.1	35.3	53.6	74.7	8.2
Ratio L/G ....Gal. sol./M c.f. feed gas	23.2	24.8	32.0	31.2	28.7	30.0	34.2	50.1
CO_2 balance...percent of input	90.4	94.9	101.6	102.8	100.2	108.0	101.3	113.3
H_2S balance ....do.	56.7	79.9	87.5	119.4	94.9	91.3	79.4	124.7

APPENDIX

Typical Material Balance

The following material balance for the Girbotol absorber is included as being typical of those made for each purification run. Period: December 7, 1952, to January 19, 1953 (1,032 hours). Average data for period.

a. Feed gas to absorber: 74,036 M std. cu. ft.
CO_2 = 19.4 percent
H_2S = 75 gr./100 cu. ft.
CO_2 = 14,360 M std. cu. ft.
H_2S = 7,930 lb.

b. Lean gas from absorber: 62,300 M std. cu. ft.
CO_2 = 4.2 percent
H_2S = 2.1 gr./100 cu. ft.
CO_2 = 2,620 M std. cu. ft.
H_2S = 190 lb.

From gas analysis and flows:

CO_2 removed from gas = 11,740 M std. cu. ft. or
11,380 std. cu. ft. per hour in 1,032 hours
H_2S removed from gas = 7,740 lb.

c. Amine: 41 g.p.m.
Rich: CO_2 = 5.2 cu. ft./gal. solution
H_2S = 54.9 gr./gal.
Lean: CO_2 = 0.5 cu. ft./gal. solution
H_2S = 37.1 gr./gal.

From amine analysis and flow:

CO_2 picked up by amine = 11,930 M std. cu. ft.
H_2S picked up by amine = 6,460 lb. or 6.3 lb./hr.

Balance

$$\frac{CO_2 \text{ in lean gas} + CO_2 \text{ picked up by amine}}{CO_2 \text{ in rich gas}} \times 100 = 101.3 \text{ percent}$$

$$\frac{H_2S \text{ in lean gas} + H_2S \text{ picked up by amine}}{H_2S \text{ in rich gas}} \times 100 = 83.9 \text{ percent}$$

Analytical Methods

Before the first run of the Girbotol unit sampling connections were installed. A supply of sampling bombs was obtained for collecting samples of feed, scrubbed, and acid gas under pressure.

The sampling schedule was as follows:

(1) Feed gas, for carbon dioxide and hydrogen sulfide, three times daily.
(2) Scrubbed gas, for carbon dioxide and hydrogen sulfide, three times daily.

(3) Rich amine, for carbon dioxide and hydrogen sulfide, three times daily.
(4) Lean amine, for carbon dioxide, hydrogen sulfide, and percentage of diethanolamine, three times daily.
(5) Acid gas, for carbon dioxide and hydrogen sulfide, once daily.
(6) Lean amine, for thiosulfate, as required.
(7) Total sulfur in feed and scrubbed gas by platinum spiral method,[18] as required. The samples were sent to the plant laboratory for determination.

In addition, the plant operators were instructed in analytical procedures and performed plant-control determinations as required in order to obtain a more rapid check on plant operations. The following plant analyses were made:

1. Total apparent hydrogen sulfide in rich and lean amine solutions by oxidation in an acid medium with standard iodine solution.

2. Free diethanolamine in rich and lean solutions by titration with standard sulfuric acid, using methyl red indicator.

3. Determination of hydrogen sulfide in gas mixtures by the Tutweiler method, using appropriate size of Tutweiler burettes and concentration of iodine solution, depending on whether the sample was feed gas, scrubbed gas, or acid gas.

4. Carbon dioxide by Orsat analysis.

Tables were supplied so that the operators could directly convert the volumes of the titrations into the terms applicable to the determinations - grains per gallon, percent diethanolamine, or grains per 100 cu. ft.

In the plant-control determinations of total apparent hydrogen sulfide in amine solutions, extra precautions were taken to guard against loss of hydrogen sulfide on addition of acid and before the titration with iodine. A quantity of standard iodine estimated at only slightly less than that required to oxidize the hydrogen sulfide present in the sample was measured and acidified. The sample was then added and the titration quickly completed.

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[18] Sands, A. E., Wainwright, H. W., and Egleson, G. C., Organic Sulfur in Synthesis Gas: Occurrence, Determination, and Removal: Bureau of Mines Rept. of Investigations 4699, 1950, 51 pp.