

It is planned, through changes, to obtain a more favorable converter-slenderness ratio and better temperature measures to alleviate solids formations in the converters and to attain higher light-oil space-time yields. Eventually it is planned to use individual thermocouples installed through the converter shell rather than the present pyrometer arrangement, which generally gives slow response to temperature change and in itself is conducive to coking. The hot heavy-oil let-down circuit is being activated to improve liquid velocity in the converters. It is also hoped to secure liquid-phase catalysts (which are more effective than copperas, possibly molybdenum-bearing materials, and nickel) and to develop a more effective way of applying catalysts in the plant, so that the reactions will generally proceed smoothly in the direction of light oils and less frequently in the reverse direction toward polymerized, more-or-less unhydrogenable asphalts.

Considerable work is planned for this winter to complete installing most of the new-type injection pumps for all services. The general problem of proper winterization of equipment, especially instrumentation, will be studied while North Dakota lignite is being processed, to solve many difficulties that interfere with smooth, efficient, year-round operation of the demonstration plant and the coal-hydrogenation process, as it might be applied commercially. These problems must be properly solved to facilitate collection of complete and accurate engineering data and make the hydrogenation process commercially attractive.

Comparative Evaluation of Hydrogenation of Two Typical Midwestern Coals, Western Kentucky and Illinois No. 6

Preliminary operating and yield data for the liquid-phase processing of Western Kentucky No. 11 bed and Illinois No. 6 coals were presented in the 1951 report. The data have since been critically reviewed and evaluated. The study has reaffirmed the preliminary findings and conclusions, namely:

1. Yields, throughputs, and product distribution are substantially as predicted.
2. Both coals hydrogenate readily to a high degree of liquefaction and good yields of light oils.
3. Owing to difference in distribution within the coal body, the ash in the Illinois coal was not reduced to as low a level by heavy-medium separation as by simple washing of the Western Kentucky coal.

In addition, much new information has been obtained, such as the following:

1. The hydrogen consumption for equal production of light oils is approximately the same for both coals.
2. The organic residue (unconverted coal) is equal in quantity for both coals at the same conversion temperature and about the same for equivalent makes of light oils, although there is a tendency toward a higher quantity in processing the Illinois coal.
3. Conversion of the Illinois coal to light oils begins at a lower temperature than for the Western Kentucky coal, but the increased conversion per degree in temperature rise is greater for the latter; therefore, at high conversion to light oils, higher temperatures are required for the Illinois coal.
4. The yield of asphaltic materials is low for both coals, and the reduction with rise in temperature is the same for both coals.

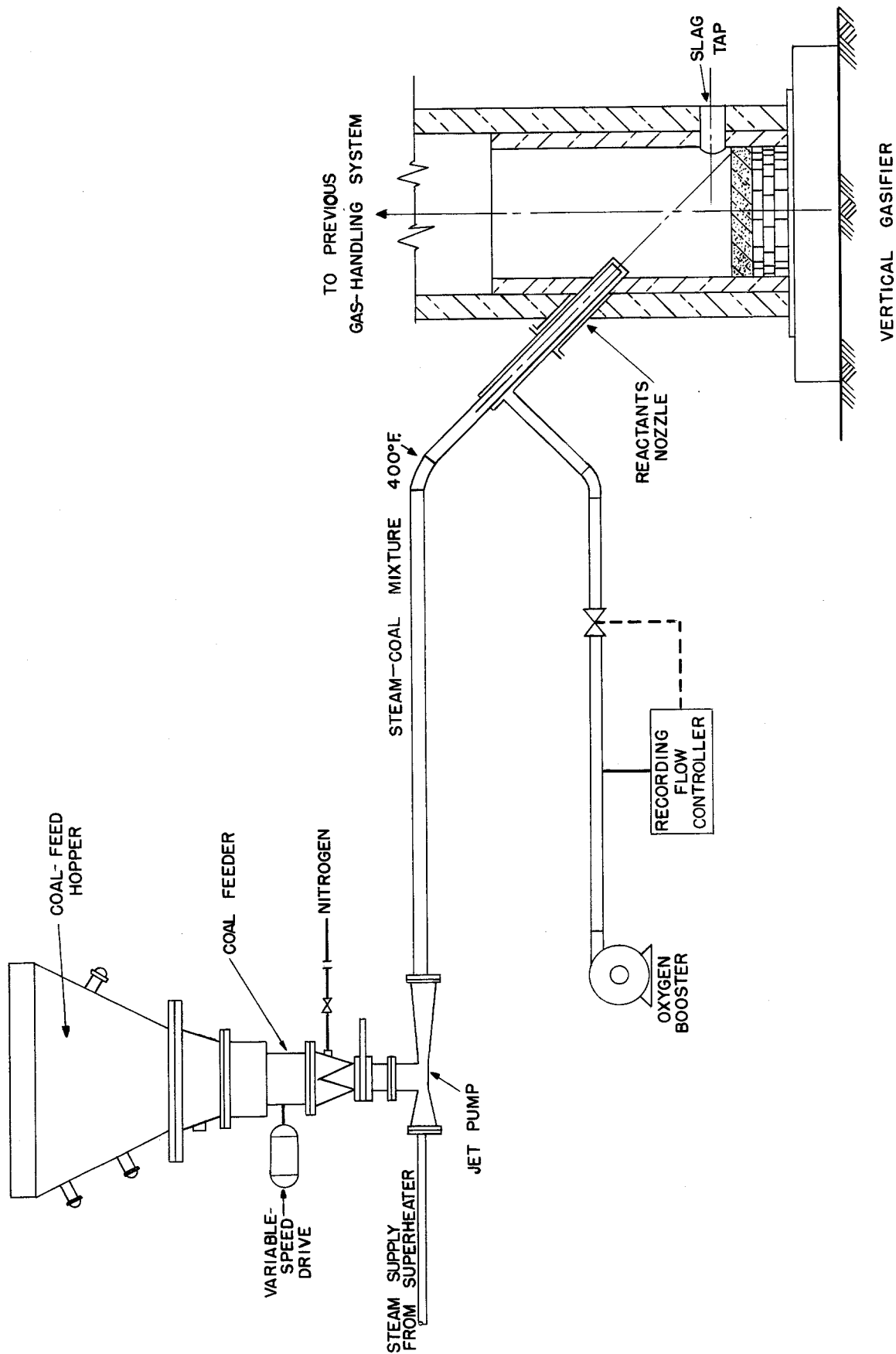


Figure 11. - Vertical gasifier-feed-system diagram.

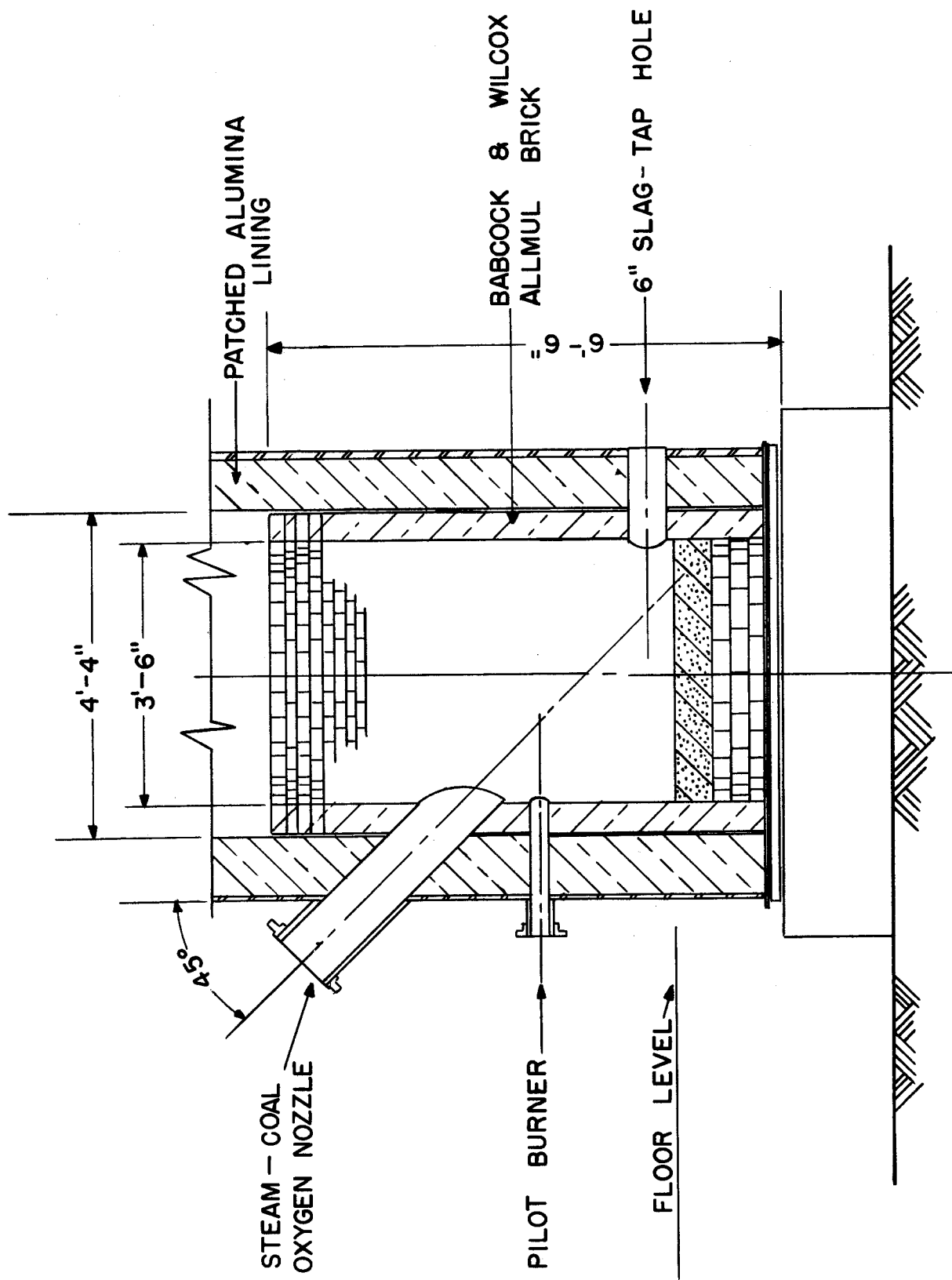


Figure 12. - Lower section of vertical gasifier.

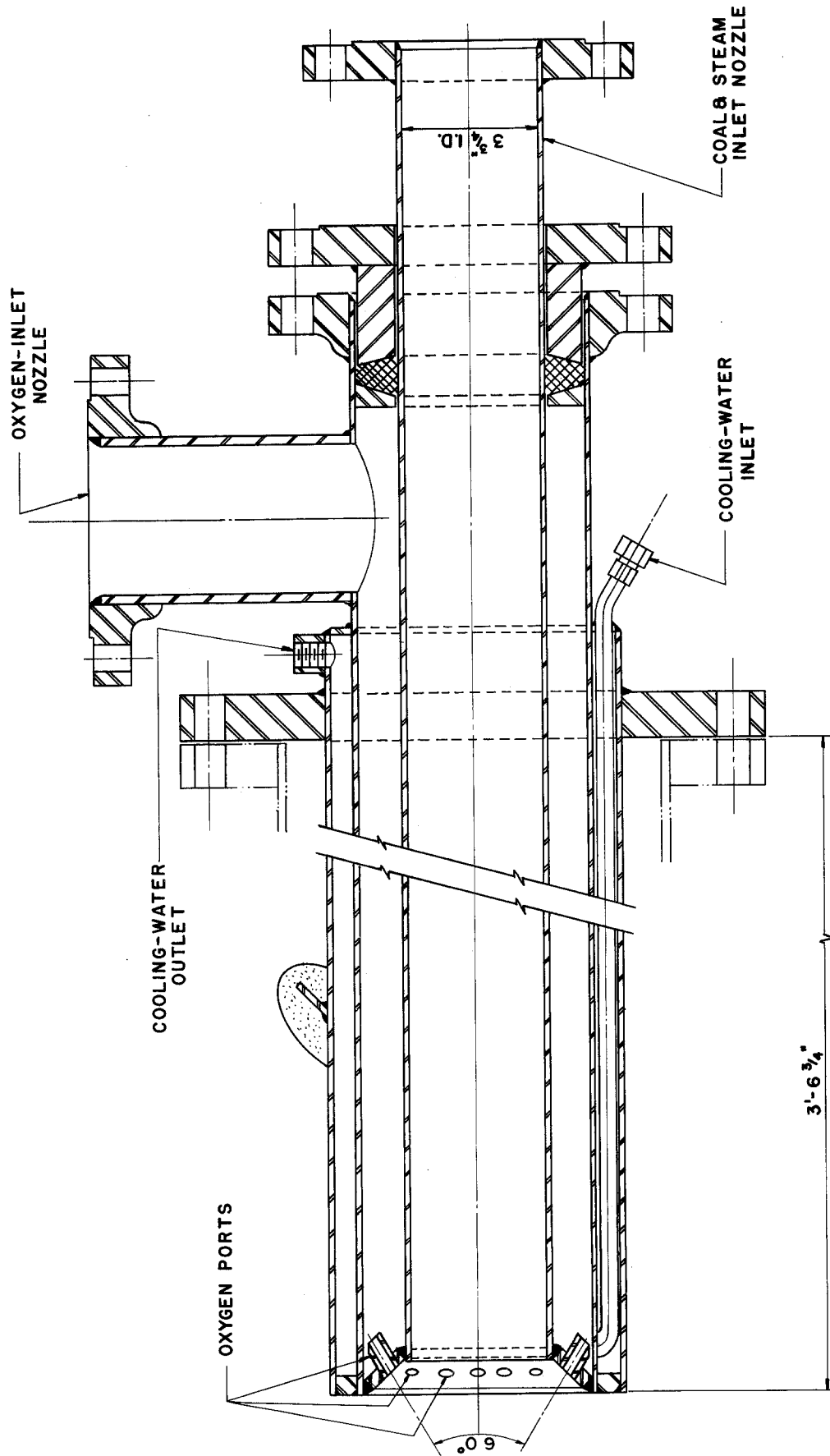


Figure 13. - Reactants nozzle for vertical gasifier.

5. Gasification increases with rising temperature and light-oils yield at equal rates for both coals.

6. The yield of low-boiling tar acids is slightly higher from the Western Kentucky coal at equal yields of light oils.

Gas-Synthesis Demonstration Plant

Coal Gasification

The alumina-lined vertical gasifier put in operation last year was tested further in a new series of runs. It will be recalled that this unit was fed with an oxygen suspension of coal through one nozzle and superheated steam was admitted through another. There was evidence that the velocity of steam addition affected the operating results, and changes were made that permitted use of lower steam velocities. Early indications were that this change was distinctly beneficial, but every attempt to confirm it by further work was unsuccessful. The results from this unit were quite erratic, probably due to progressive damage to the refractory in the lower section and the consequent effect on the degree of mixing of the steam with the oxygen-coal stream. Thus, although changes were made in oxygen-coal ratio, steam-coal ratio, and, as mentioned above, steam velocity, it was impossible to establish any consistent relationship between the operating conditions and the results.

Near the end of these operations, one run was made on a mixture of air and oxygen to tell whether a gas suitable for ammonia synthesis could be produced in this way. The results of this test were only qualitative, but it appeared that this type of operation should be entirely feasible.

All of the preceding work had been done on a Rock Springs, Wyo., coal, which had been used in the work on the Koppers gasification unit. To establish the feasibility of intermittent slag tapping, a run was made with a specially selected Illinois No. 6 coal from Christian County, with an ash of quite low-fusion temperature (about 2,300° F.). With the new coal, serious difficulty was encountered with "flash-backs" in the oxygen transport line, a trouble that had been completely eliminated with the Rock Springs coal by increasing the transport velocity. The flow velocity was increased, the oxygen purity was decreased by dilution with air, and the transport pipes were thoroughly grounded to eliminate static-electricity accumulations. After these changes, it was possible to continue the run for two periods without further difficulty from flash-back.

When attempts were made to tap the accumulated slag, it was found that, although a small amount of quite fluid slag was recovered, solid material seemed to be blocking further withdrawal of slag. Increases in operating temperature did not overcome this.

After the run ended, inspection of the interior showed that there had been extensive "peeling" of the lining in the lower section and that there was, in the bottom of the gasifier, a large accumulation of refractory material, which undoubtedly prevented slag tapping.

Obviously, the lower section needed extensive repairs, and it was decided that revisions in the system should be undertaken at the same time. Several possibilities were considered, and the system finally chosen is shown in the flow diagram (see fig. 11) and in the drawing of the gasifier base (see fig. 12). The nozzle used for injecting reactants is also shown in figure 13.

Briefly, the new system was as follows: A rotary coal feeder, equipped with variable-speed drive, was attached to the bottom of the existing coal feed hopper and delivered coal at a controlled rate into the top of a steam-jet pump. The process steam, superheated to 1,000° F., passed through the nozzle of the jet pump, picked up the coal as it was fed, and transported it in steam suspension to the gasifier. This steam-coal mixture, at about 400° F., passed through the center pipe of the reactants injection nozzle. The oxygen, at a rate controlled by a recording flow controller, passed into an annular section surrounding the steam-coal pipe of the nozzle, then through a number of small ports set at 45° to the flow of the steam-coal mixture.

The reactants injection nozzle was set into the gasifier at an angle of 45° from the vertical, aimed to strike the slag on the floor of the gasifier a few inches in front of the slag tap hole.

The lower section of the gasifier was repaired with patching refractory and then a single course of high-temperature brick laid up to protect the patches. The upper section of the gasifier and the gas-handling system were unaltered.

Three runs have been made on this revised system. The first was extended over about 9 days, during which approximately 210 tons of coal and 3.9 million cubic feet of oxygen were fed. About 80 percent of the carbon in the coal was converted to gas, and about 13-1/2 million standard cubic feet of gas was produced containing 15 percent CO₂, 40 percent CO, and 40 percent H₂. Mechanically, operation of the unit was gratifyingly smooth, and gas was being produced for 210 out of the 216 hours elapsed time. Coal used was Illinois No. 6 with low-fusion ash, previously mentioned, and tapping of the slag was quite satisfactory. During this run the unconverted coal was a serious burden on the filter beds in the water-circulation system; it was felt that conversions would have to be increased to reduce the amount of this material, or the filter beds would have to be altered.

Examination of the gasifier after the operation showed rather serious local erosion directly opposite the reactants nozzle and some damage by slag to the refractory in areas adjacent to this point.

In an attempt to minimize the erosion effect, some special impingement blocks were inserted at the point of maximum wear, and a new run was begun under somewhat more severe conditions to achieve the desired higher-carbon conversions. This run was on for 6 days, during which some difficulty was encountered with slag tapping, and was shut down when "hot spots" were found on the outside opposite the reactants nozzle. Again, mechanical operation of the unit was good, the conversion was increased somewhat, and the expected gas production was achieved. Operation of the filter beds at the higher conversion was distinctly improved, and it is felt that minor revisions will make these continuously operable at reasonable carbon conversions.

Inspection of the unit, however, showed that the impingement blocks had become dislodged and that there was appreciable erosion of the refractory surrounding and behind these blocks. Inclusion of this refractory in the slag undoubtedly caused the tapping difficulties, and it is encouraging that the removal of slag went as well as it did in spite of this.

Plans are being formulated for installing a second reactants nozzle diametrically opposed to the existing one. The oxygen, steam, and coal flows will be divided equally between these two nozzles, and it is hoped that the reduced velocity and the impact of the two streams in the center of the gasifier will minimize the

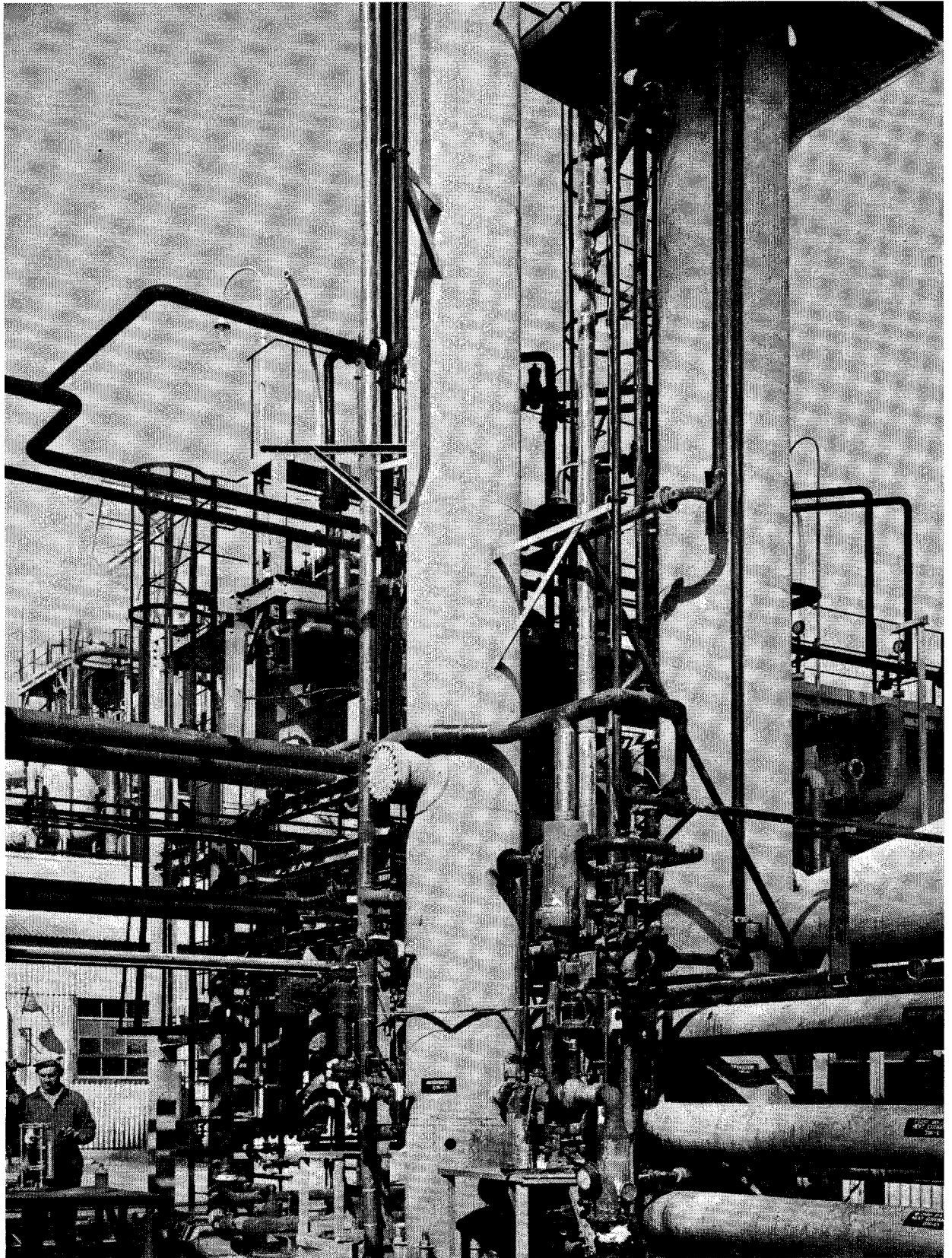


Figure 14. - Amine scrubber, reactivator, and auxiliaries.

damage to the refractory. Although the necessary preliminary work for this change is being pursued, one further modification of the existing gasifier was tried. This consisted of installation of a water-cooling coil behind the brickwork at the point of maximum erosion. When this work was completed, the unit was started under about the same conditions as in the previous run and continued on stream for 7 days. Mechanical operation was satisfactory, and the slag tapping proceeded smoothly. The carbon conversions and gas makes were substantially as anticipated. At conclusion of the run, the gasifier interior was inspected; it was found that the cooling coil had not adequately prevented the local erosion previously noted. The work necessary to permit installation of the second reactants nozzle is being pushed as rapidly as possible in the light of this result.

Operation of Oxygen Plant

The oxygen plant was operated during the year as required to supply oxygen for the coal-gasification trials or for operation of the Kerpely producer. Substantially no major mechanical difficulties were encountered, and there was no period during which the work was delayed owing to lack of oxygen. During the year the unit operated for 3,800 hours and produced 82 million cubic feet of oxygen. Repairs, revisions, and replacements have been continued to increase ease of operation or safeguard against accidental interruption.

Operation of Kerpely Producer

The Kerpely producer was operated approximately 1,590 hours during the year to supply gas for trials in the purification unit and to make feed gas for the synthesis unit. Very little operating difficulty was encountered during this time although, on inspection after the final shut-down, it was found that some brickwork in the top of the unit had been dislodged. The required repairs are minor; except for the changes, as in the oxygen plant, to improve ease or reliability of operation, little work is contemplated. During operating periods almost 1,800 tons of coke and 28 million cubic feet of oxygen were consumed to produce 107 million cubic feet of $\text{CO} + \text{H}_2$.

Operation of Purification Unit

The purification unit was operated 66 days in all during the year, partly to continue the study of its operation and performance and partly to purify gas as required for the synthesis unit. The amine scrubber, reactivator, and auxiliaries are shown in figure 14; their operation represents the initial step in the purification train. In the early stages at quite high gas rates, some trouble was encountered with the amine reactivator. The cause of this difficulty was never clearly defined; but some changes were made, and no trouble has been encountered since. Again the revisions that have been made are primarily those that led to improvement in the ease or continuity of operation and in no case involved major changes in the fundamental operation. An additional amine cooler has been installed to permit operations at high rates during the summer months when cooling-water temperatures are high. During the later periods, it was found possible to treat almost 70,000 standard cubic feet per hour of synthesis gas, purified to about 4 percent CO_2 , with the total sulfur content less than 0.03 grain per 100 cubic feet. To permit study of the relationship between the previously completed laboratory work on carbon adsorption of organic sulfur and the results achieved in the plant units, a small parasite carbon tube has been installed in the plant. This study will be carried on, as time permits, when the purification unit is in operation and should lead to a better basis for large-scale plant design.

Just before the end of the scheduled operation of the purification unit, the first iron oxide tower for removing residual hydrogen sulfide began to pass small quantities of sulfur. This tower has been in constant service in first position since the purification unit was first put on stream. Up to the time it began to pass sulfur, it had treated 170 million cubic feet of gas and removed approximately 570 pounds of sulfur. This tower was packed with 110 cubic feet of sponge containing 9 pounds of oxide per cubic foot. This material can be expected to remove about 0.6 pound of sulfur per pound of oxide. The calculated capacity would be $110 \times 9 \times 0.6$, or 594 pounds of sulfur. Thus, the total sulfur capacity of the tower was almost precisely that which had been calculated when the plant was designed.

Theoretical Studies of Coal Gasification

The mathematical studies of the kinetics of coal gasification have been continued throughout the year. After an extensive review of the previously published information on reaction rates, a mechanism for the reaction of coal with oxygen and steam was developed, and equations were set up expressing the change with time in each of the variables involved. As has been pointed out previously, the resulting calculation is extremely complex and tedious and would be impractical without some high-speed computer, such as the I.B.M. card-programmed electronic computer in use at the Bureau of Mines Pittsburgh Station. As might be expected, when the actual computation was initiated, it was found that revisions in the method would be necessary to permit successful calculation of the results. This somewhat increased the time and effort required for computation and reduced the number of individual cases that could be considered. However, 12 cases have been completely calculated, which cover the normal range of oxygen-coal and steam-coal ratios, gasifier heat loss, and the like. A description of the mechanism has been compiled, and the calculated results have been computed.

It is hoped that comparison of these calculated results with those actually obtained experimentally by various groups working in this field will lead to revisions in the method that should make it suitable for use in actually predicting the results of a given gasifier under given operating conditions. Furthermore, it is believed that this comparison will lead to better understanding of the factors affecting operation of a gasifier, permit improvements in the experimental studies, and provide a sounder basis for the design of any commercial units. Further calculations will be undertaken to extend the range of coverage and to verify questionable points, and the direct comparison between calculated and experimental results should be feasible shortly.

Future Plans

Work on development of a coal-gasification unit at Louisiana, which will be reliably operable and at the same time give the desired carbon conversion and raw materials economy, will be vigorously prosecuted. As soon as this goal is approached, actual purification of synthesis gas made from coal will be tested. It is believed that there will be little difference between this and the producer-gas purification.

Catalyst Fusion and Reduction

The catalyst produced in 1951 was largely consumed in the preliminary testing operations and in synthesis runs 1 and 2. Early in 1952 catalyst-fusion operations were resumed, and additional quantities of doubly promoted, fused synthesis catalyst were produced. All of the catalyst produced to date has been the fused iron oxide type promoted by potash and magnesia, which has been found suitable for use in the partly expanded bed-synthesis process. In 1952 approximately 44,400 pounds of 6- to 20-mesh fused synthesis catalyst was produced.

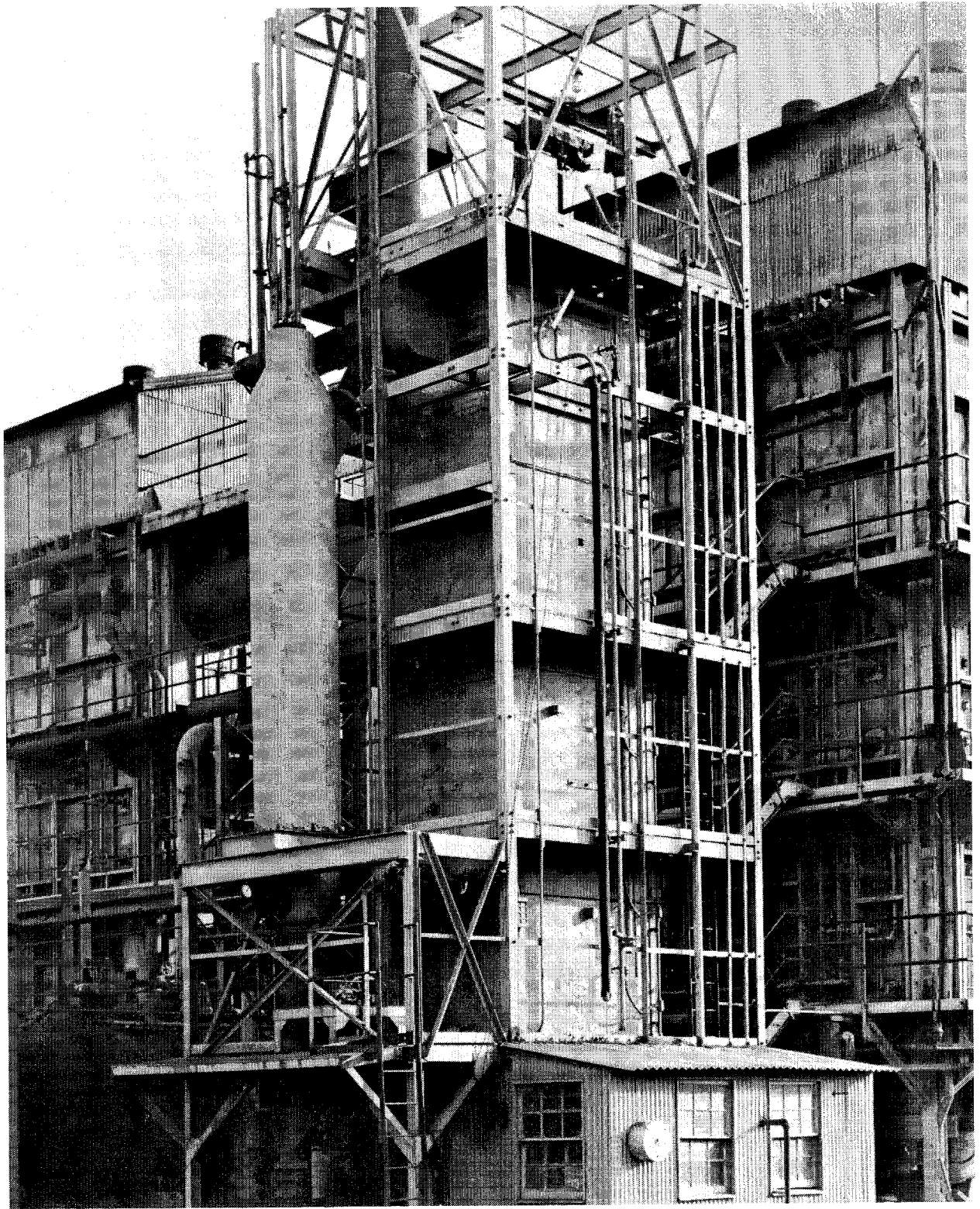


Figure 15. - Catalyst-reduction unit, hydrogen-heating furnace (center), and reduction vessel (left of center).

As has been reported previously, the molten catalyst was blown with air to obtain a desired ferrous oxide-ferric oxide ratio approaching that in pure magnetic iron oxide (magnetite). Although variations in this ratio did occur from batch to batch, they were not excessive, and composition of the catalyst was very close to the following analysis:

| | <u>Percent</u> |
|-------------------|----------------|
| Total iron | 67.09 |
| Ferrous oxide ... | 30.57 |
| Ferric oxide | 61.95 |
| Silica | 1.16 |
| Magnesia | 4.46 |
| Potash | .60 |

Some improvements were made in the Catalyst Fusion Plant to achieve greater safety and improve handling of the solidified pigs of fused catalyst. In fused-catalyst manufacture using water-cooled electrodes, there is always the possibility that a water leak may occur and the water come in contact with the molten mass of catalyst, with a resultant formation of steam and splashing of molten catalyst. To prevent injury to the operators, a steel enclosure has been constructed around the catalyst-fusion station. In actual operation, this steel enclosure did not interfere with the catalyst-fusion operation and did prevent some accidents caused by spattering of the molten catalyst.

An improvement in the method of fastening the iron-fusion ignition wire to the water-cooled electrodes was devised. This very simple device consisted of a sleeve welded into the water-cooled electrode at the proper height from the bottom of the electrode. The ignition-wire cable was inserted through this sleeve, and the wires were spread apart and held fast by means of a drift pin driven into the sleeve. This ingenious device saved much time in operation.

In 1952, 44,417 pounds of sized, unreduced catalyst was produced at \$0.13 per pound. This cost does not include amortization of the plant but does include all other known elements of cost, such as materials, labor, utilities, and miscellaneous expenses.

The catalyst-reduction unit was operated during the early part of 1952 to produce enough reduced catalyst for synthesis run 3 and again during the summer to produce two reactor charges of the reduced catalyst for future runs. This unit is shown as figure 15. During April approximately 18,500 pounds of fused catalyst was reduced with hydrogen in a batchwise operation to yield about 13,600 pounds of reduced catalyst. The catalyst was stored under a sulfur-free heavy oil and employed in synthesis run 3. In August and September an additional 34,600 pounds was reduced to yield about 27,200 pounds of reduced catalyst. As in the previous operation, this reduced catalyst also was stored under oil.

The catalyst-reduction operations proceeded in a fairly smooth manner. As in previous operations, the hydrogen gas was produced in the Coal-Hydrogenation Plant and had been scrubbed under high pressure to remove carbon dioxide. Some variations do occur in the carbon dioxide content, but the slightly longer reduction period tends to compensate for them. Reduction of the catalyst averaged 82 to 84 percent, which is believed adequate for normal activity.