PART I

PROCESSING, COAL-TO-OIL DEMONSTRATION PLANTS, LOUISIANA, MO.

The two Coal-to-Oil Demonstration Plants at Louisiana, Mo. - less than 100 miles above St. Louis on the Mississippi River - are the first such units in the United States and probably the most-advanced of their type anywhere.

Centrally located with respect to the Nation's major coal fields, their prime function is to apply the results of laboratory research and development on a scale that will translate those results into the cost and engineering information required by private industry for commercial operations. Through research laboratories at Bruceton, Pa., and Morgantown, W. Va., the basic reactions and processes are discovered and developed. Through demonstration plants, the processes are proved.

Dedicated on May 7, 1949, the demonstration plants employ two basically different processes for converting coal to liquid fuels: (1) the direct hydrogenation or Bergius process and (2) the gas synthesis or modified Fischer-Tropsch process. The Hydrogenation Demonstration Plant was completed and placed in operation during 1949, and the initial units of the Gas-Synthesis Demonstration Plant also were completed and operated.

Coal-Hydrogenation Demonstration Plant

The general design and process flow of the 200- to 300-barrel-per-day coal-hydrogenation plant was covered in last year's report. The flow diagram is resubmitted for ready reference (see fig. 2). Construction work started by the Rechtel Corp. during the summer of 1947 was essentially completed early in the year, when for better economy the Bureau's engineering, maintenance, and operating personnel took over the job of completing odds and ends of the construction and the mechanical testing of the equipment before break-in operations. The demonstration-plant activities involve three fields: (1) Mechanical equipment development and testing, (2) training of personnel in high-pressure hydrogenation techniques, (3) obtaining of products, with process and economic data.

The plant has served and is further serving the important function of equipment development and testing. Considerable unit and some over-all plant operation has been accomplished. It will be noted that many parts of the plant have already been proved and certain other features have required redesign of the order and magnitude that would be expected for a new high-pressure process.

Test Operations

The distillation area (see fig. 3) was completed first by the contractor. To test and break in the equipment and controls and to give the operators experience in this type of work, a special Oklahoma City crude petroleum oil was used as a basic feed stock. This oil simulated the liquid-phase cold catchpot product, and the distillate fractions could be used later for the vapor-phase hydrogenation runs after proper fractionation and blending. Several runs were made. In the first runs the fractions were reblended and returned as fresh feed. The final run was made to obtain a naphtha-gas-oil blend for vapor-phase hydrogenation and bottoms suitable for liquid-phase hydrogenation. The operability of the equipment as designed (see fig. 4) and the training program proved to be adequate and effective. No unusual equipment failures and difficulties were experienced. Owing primarily to the type of materials to be processed and the relatively small size of the plant, it was definitely ascertained that most of the controls and the off-gas and product lines

must be steam-traced and insulated. These refinements were made during the past summer, preparatory to the first liquid-phase hydrogenation run.

The hydrogen- and nitrogen-gas manufacturing and compression area, mainly a part of the former Missouri Ordnance Works, was reactivated and operated during the same period to test the equipment and to train newly recruited operators. This part of the plant also was operated intermittently as required for high-pressure nitrogen testing of the hydrogenation plant. Later, hydrogen was supplied for the break-in and actual runs. This equipment has given dependable service, and the redesign of equipment and control system interconnecting the old and new plant areas proved to be entirely satisfactory. At present a new small six-stage compressor is being installed in the hydrogen hyper-compressor building to provide a continuous small supply of nitrogen at high pressure for use during the hydrogenation runs.

Pressure testing of the hydrogenation plant proper was the next major task. Some specific comments regarding the test experience may be of value.

The reflex sight glasses used for auxiliary level indication on cold pressure vessels were not safely operable on hydrogen at 10,300 pounds per square inch. However, they are useful for checking levels during 1,700-pounds-per-square-inch nitrogen test operation.

A number of high-pressure thermowells were found to be defective, causing the tips to collapse from external pressure. Examination of other thermowells showed that many were drilled eccentrically, having little metal at the tips. The vendor replaced these thermowells with new ones drilled from the tip end and seal-welded.

The seal welds on the side connections on high-pressure sample bombs failed under test and were replaced with pressure welds. Numerous leaks occurred in pressure vessel head seals and were corrected by refacing the head groove and using new perfect delta gaskets with an aluminum covering.

When the high-pressure 13,300-pound-per-square-inch-gage tests of the vapor-phase unit were completed, the pressure was reduced to 1,600-pounds-per-square-inch gage for a "dummy" run. Using nitrogen in place of hydrogen at this lower pressure, the operators gained valuable experience, and the equipment was given a break-in test. The preheater furnace was lighted and dried out, along with the converter insulation. Hot-line growth was studied.

The system was next pressured to 10,300-pounds-per-square-inch gage with hydrogen. The temperature was raised slowly to 835° F. and held there to activate the catalyst in the vapor-phase converter (fig. 5). After activation of the catalyst, the temperature was reduced, and a vapor-phase hydrogenation break-in run was made using a 43° A. P. I. gasoline-naphtha-gas-oil blend prepared from the Oklahoma City crude petroleum oil. The charge during the petroleum hydrogenation run was made up of a blend of 11 percent of 61° A. P. I. straight-run gasoline, 31 percent of 47° A. P. I. naphtha, and 58 percent of 39° A. P. I. gas oil. A total of 29,360 gallons of this blend, with 2,960 M cubic feet of 95 percent hydrogen make-up gas was charged during the 4-day run. Although operating conditions were varied to gain information concerning the operation of controls (see figs. 6, 7, and 8) and the product, the average run conditions were as follows:

		P.s.i.g.
Pressure	- Stall inlet	9,750
	- Hydrogen feed	9,975
	- Recycle compressor suction	9,715
	- Recycle discharge	10,000

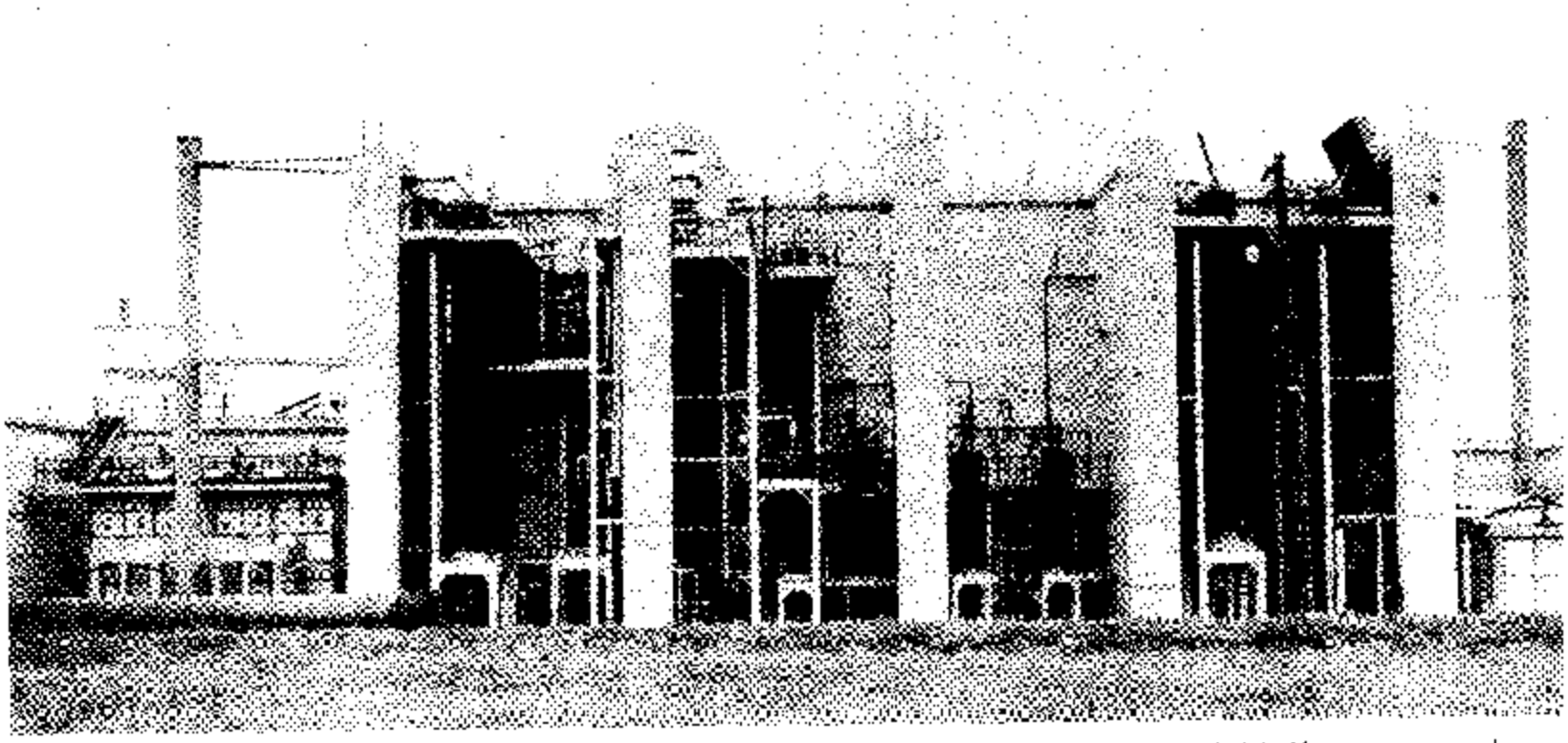


Figure 5. - Rear view of high-pressure stalls. Left three are liquid-phase; right three, vapor-phase.

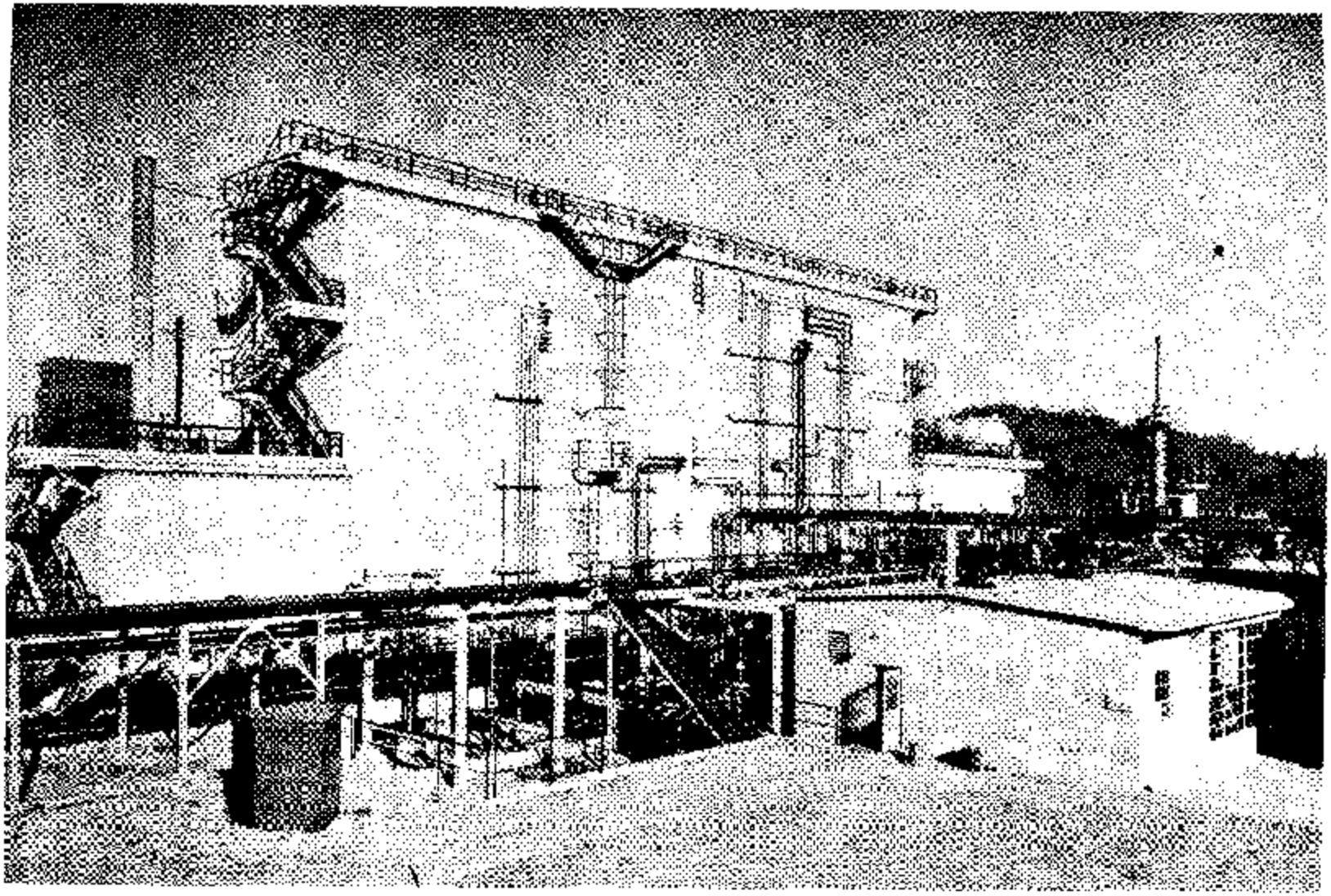


Figure 6. - High-pressure area with control house, protective stall structure, and pipeways.

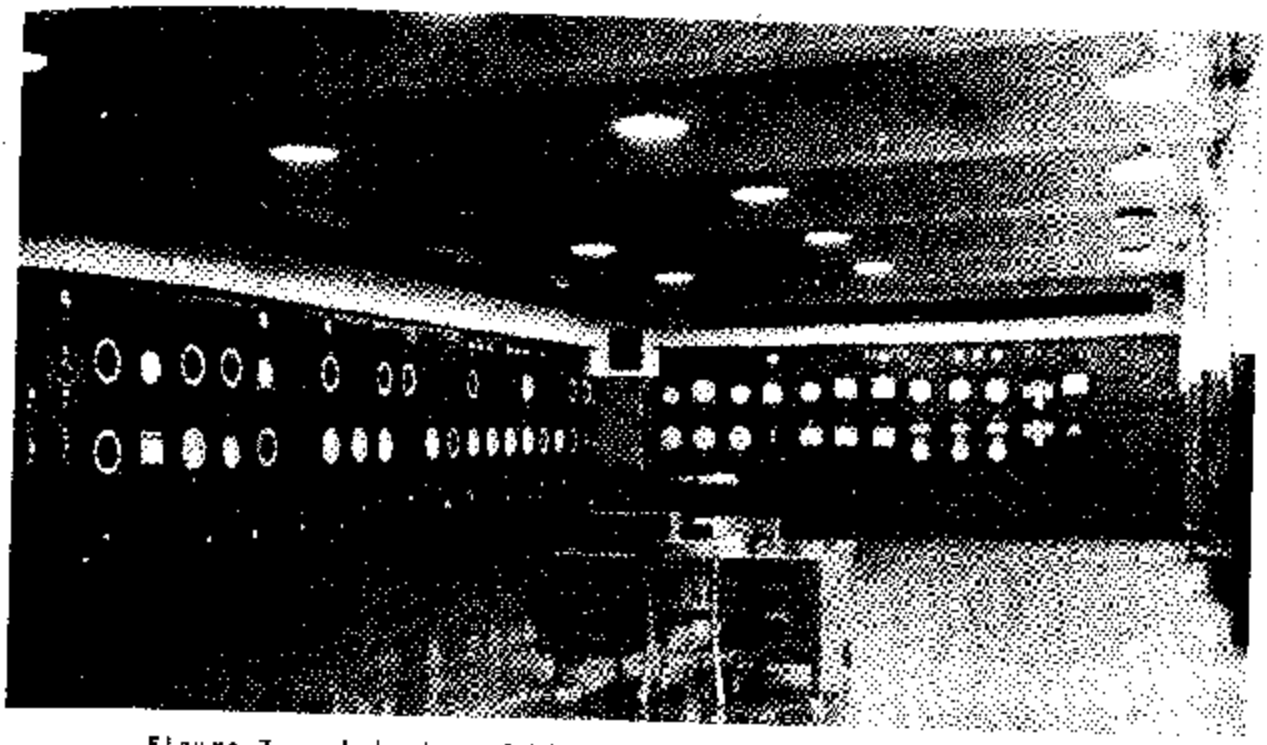


Figure 7. - Interior of high-pressure control house, showing liquid-phase instruments.

Figure 8. - Vapor-phase instruments in high-pressure control house.

		°F.
Temperature	- Preheater inlet.....	395
	- Preheater outlet.....	721
	- Catalyst beds,.....	699
	- Cold catchpot.....	92

Hydrogenation at temperatures above 720° F. produced a light product higher than 70° A. P. I. The distillation unit was put on stream to fractionate the hydrogenated product into its components.

The products and yields obtained were:

	°A.P.I.	Gal.
Gasoline.....	66	15,725
Wash oil (naphtha)....	48	5,840
Bottoms.....	43	4,280
Off-gases.....		975 Mcf

Owing to a leak that developed during the run, the losses were very high, and an accurate material balance could not be made.

Distillation curves showed that the quantity distilling over at 400° F. was increased from 25 percent in the feed to 65 percent in the hydrogenated product, in one pass through the converter. The gasoline cut had an octane number of 63 by the A.S.T.M. D357-48 C.F.R. motor method.

The feed vapor-phase hydrogenation stock then was changed to a lignite-tar distillate oil in order to produce a specification Diesel fuel. This stock was prepared from a 15° A. P. I. North Dakota lignite-tar oil by removing the low-boiling portion and the asphaltic material unsuitable for hydrogenation over the Welhelm K-536 catalyst. The portion used represented 70 percent of the raw oil and had a gravity of 12° A. P. I.

The lignite-tar distillate was charged to the unit without any purging of petroleum oil. The total charge, including the petroleum in the system, was made up as follows:

	Gal.
Lignite-tar distillate.....	12,225
Petroleum oils in system.....	5,480
Hydrogen make-up gas.....	2,930 Mcf

During the first 20 hours of operation, the bottoms from the hydrogenation-product distillation were recycled. During the balance of the run the distillation bottoms were sent to storage and then returned as total feed to hydrogenation. In this manner the run was divided in two passes to aid in reducing the tar-acid content, which was 52 percent in the distillate. After the second pass the hydrogenation-product distillation bottoms met the boiling-range requirements for a Diesel fuel oil, but three additional passes were required to reduce the tar-acid content to less than 2 percent. At this level the acids are easily removed by washing with caustic soda. Although temperatures were varied during the run to obtain the optimum reduction of tar acids, the average operating conditions were as follows:

		P.s.i.g.
Pressure	- Stall inlet.....	9,725
	- Hydrogen feed.....	10,550
	- Recycle compressor suction.....	9,690
	- Recycle compressor discharge.....	10,100

		°F.
Temperatures	- Preheater inlet	390
	- Preheater outlet	730
	- Catalyst beds	727
	- Cold catchpot	91

The products and yields obtained were:

	Gal.
Gasoline	8,835
Wash oil (naphtha)	615
Diesel fuel oil	4,520
Slop oil	520
Off-gases	955 Mcf

Owing to the leak referred to under the petroleum run, the losses were very high, and an accurate material balance could not be made.

Distillation curves showed that the quantity distilling over at 400° F. was increased in one pass by 85 percent as compared to 40 percent for the petroleum. The gasoline had an octane number of 65 by the motor method. This gasoline has given satisfactory service during the past 6 months at this station in all types of motor vehicles formerly using regular motor-grade gasoline.

The bottoms from the product distillation were finished for Diesel fuel oil. Following is a comparison of the properties of the Diesel fuel oil produced with the specifications used by one of the large western railroads for the purchase of Diesel fuel from petroleum:

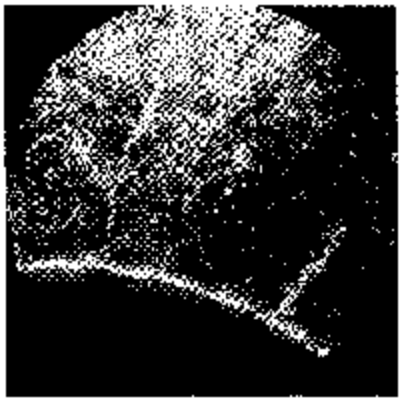
	Louisiana test run	Railroad specifications
Gravity A. P. I.	38.5	32 - 40
Boiling range - 10 percent	440°	425 - 500° F.
- 90 percent	578°	540 - 620° F.
- End point	644° F.	675 max.
Recovery	97%	90%
Viscosity at 100° F.	33.5 ssu	35 - 45 ssu
Flash point (PM)	194° F.	150° F. min.
Pour point	10° F.	5° F.
Ash	0.002%	0.01% max.
Cetane number	56	50 min.
Carbon residue (10 percent bottoms)	0.06%	0.25 max.

This fuel was used successfully on a 200-mile trial run in a Diesel-electric locomotive (fig. 1) hauling a loaded eight-car passenger train to and from the plant during the dedication ceremony.

The operation cited is of particular interest because it represents successful operation of the first 700-atmosphere hydrogenation plant in this country. It is also noteworthy that this first run was made without delay or serious interruption, although none of the operating crew had had actual experience with similar operations.

While the plant was found to be generally operable during the run, it was determined that the diaphragm-type, low-differential-pressure instruments were not satisfactory for flow, level and low-pressure differential measurements. These instruments now are being replaced with high-pressure mercury meter bodies which have already given satisfactory service with controllers. It was also found that

Unused tubing



Used tubing

Ruptured tubing

Figure 9. - Photomicrographs of unused and used tubing, and photograph of ruptured tubing.

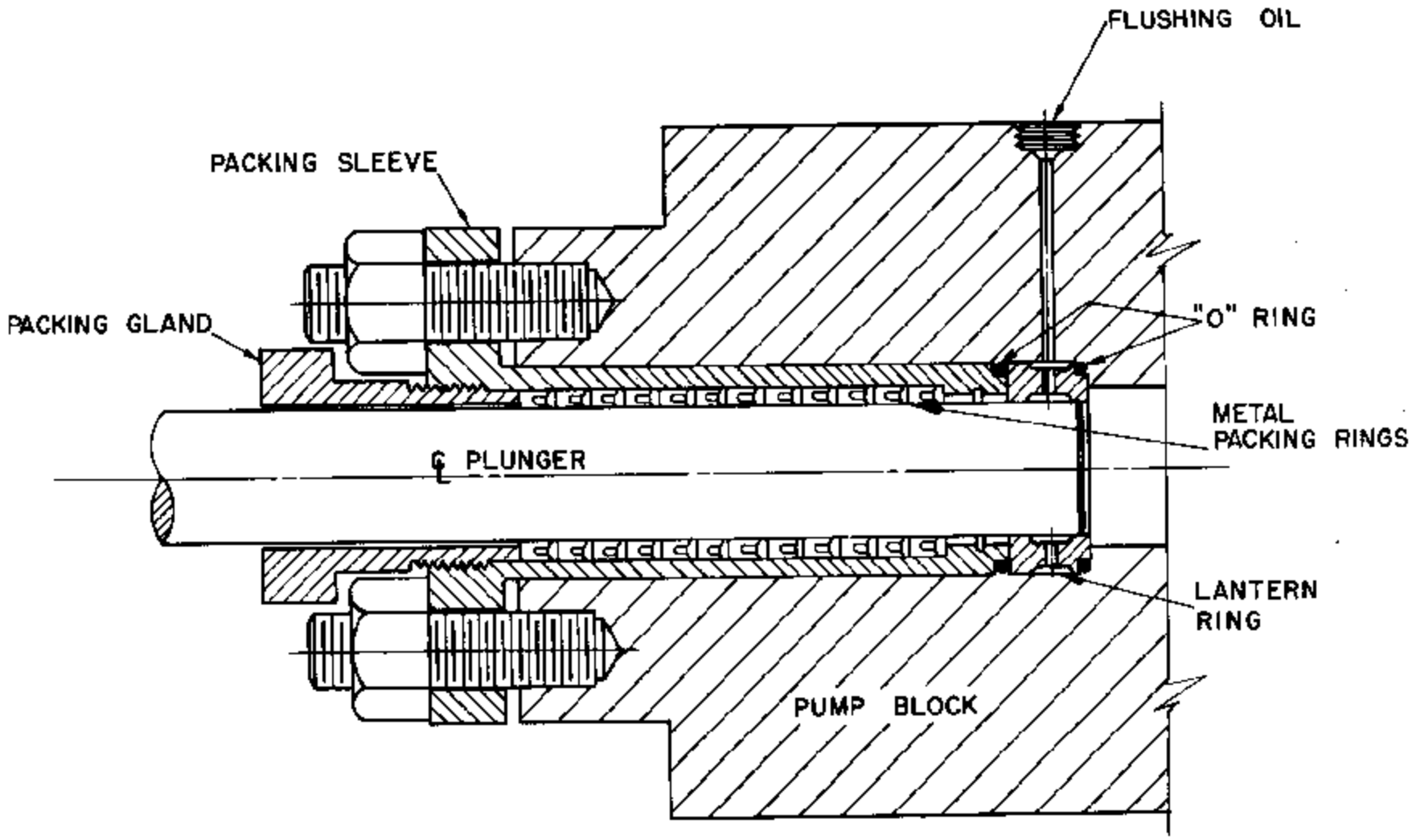


Figure 10. - Cartridge-type chamber for paste injection pump.

the Bourdon tubes on the 20,000-lb.-range pressure gages and transmitters must be replaced with a more sturdy design tested for 30,000 lb.

Following the initial vapor-phase run, the unit was put in safe stand-by condition for the May plant-dedication ceremonies. After the dedication the work was resumed, and all available operating and maintenance personnel was engaged in pressure-testing the liquid-phase hydrogenation unit. After repeated testing and repairs to vessel heads and pipe fittings, the system withstood the 13,300-pound-per-square-inch-gage nitrogen strength and tightness tests. Shortly afterward it was discovered that where 3/8-inch nozzles were welded to larger piping the welds lacked complete penetration. A new technique had to be developed, requiring insertion of back-up rings, which were drilled out after welding was completed. All such piping had to be returned to the fabricators for rewelding and reannealing.

Failure of instrument tubing at the 10,000-pound-per-square-inch pressure level necessitated thorough rechecking of several samples taken from stock and service. Internal cracks were found in both the used and unused tubing, indicative of faulty fabrication procedures. Figure 9 is a photomicrograph showing the radial cracks starting at the internal diameter and a section of the ruptured tubing.

Leakage and cracking of welds acting as the seal for threaded plugs and tubes in pump and heat-exchanger blocks resulted in redesign of this joint. It was found necessary to incorporate full-pressure welds for this duty without allowing for any assistance from the thread holding force. All seal welds throughout the plant had to be replaced with full-strength pressure welds.

During the 3 months that this work was being done all of the injection pumps were put through prolonged break-in runs to stop leakage around the blocks, valves, and plungers. Satisfactory operation finally was obtained on all pumps except the motor-driven vertical triplex, variable-stroke pump, and the paste pumps.

Several types of soft packing, Teflon block, chevron packing and two types of metallic packing were tried on the variable-stroke pump, and each leaked badly in flushing oil service. Also, the plungers were scored. For this high-speed pump, the solution seems to be the use of close-fitting, packless, bronze sleeves.

On the slow-moving paste injection pumps, moderate to satisfactory success was achieved with either metallic or chevron packing. A metal packing consisting of bronze wedge and sealing rings was developed by Bureau engineers, and it seems to be the right approach to the problem. For quick replacement the packing rings were assembled in a removable cartridge, as shown in figure 10. Accurate alinement and rigid frame are absolute necessities for the success and long life of the close-fitting packing, and the pump manufacturer was called in to assist with improvement of these pumps. For additional paste-pump capacity, one of the two available German paste-injection pumps is being reconditioned, and plans are under way for procuring the necessary fluid drive and for installing the pump as a spare unit. Meanwhile, chevron packing is being used with improved results to charge low-solid-content tar oil at 10,000-pounds-per-square-inch into the liquid-phase unit.

Intensive efforts also were made to complete installation and rearrangement of instrumentation, connect the emergency light and power system, and complete the steam-tracing and insulation of pipe lines.

After repairs and retesting of the plant, extensive 1,600-lb. nitrogen dummy runs were performed on the liquid-phase hydrogenation unit to test and calibrate instruments, particularly the hot and cold catchpot level control systems. When this testing and the welding in the area were completed, further full-pressure

hydrogen circulation runs were made to check the instruments, preheater firing and general plant tightness before the first tar-oil run was started. As a result of the first hydrogen test runs, it was found necessary to reface all of the preheater return bends and tube ends and to remove the insulating-box covers from the preheater and insulate the bends separately to prevent hydrogen leaks and subsequent fires.

The liquid-phase hydro unit was in continuous operation from October 12 to December 6. Coal-tar oil was circulated through the system to the hot catchpot let-down and back to the unit, at full normal pressure and with a preheater outlet temperature at 450° F, for the first 3 weeks. During this period, the general reliability of the equipment and its tightness were ascertained. The operators obtained further experience while continuous efforts were being made to get the instruments, particularly the control valves, working satisfactorily. It also was proved that the injection pumps would operate without excessive leakage for periods up to 2 weeks on a set of chevron packing. The contents of the hot catchpot ran over on October 25, and the hot-tar oil circulation phase of the run had to be prolonged considerably to clean deposits from the lines, instruments, vessels, and recirculating compressors (see fig. 11). During the period after this disturbance, the operators gained reliable experience in cleaning equipment of heavy-oil and naphthalene deposits and in operating without instruments, particularly catchpot level-control equipment. As a result of this experience, too, it is now known to be possible to control the hot catchpot level quite accurately by hand, using the vapor- and liquid-level thermocouples in V-9 hot catchpot. Likewise, safe levels can be maintained by hand in the cold vessels by frequent let-downs to a point where some gas is released to the let-down receivers.

The level-control equipment and the hydrogen circulators were frequently cleaned of tar during this period. Even though this additional experience was obtained with hand-controlled levels, it was possible to start raising the converter temperatures gradually by November 7. The first hydrogenation products appeared at a temperature of approximately 750° F. From November 10 to 17 the plant was operated smoothly, hydrogenating tar oil at a temperature of 850° F. in the converters to produce naphtha-wash oil, middle-oil, finishing oil and some light-oil bottoms. This operation is typified by the following data (tables 9 and 10), which were abstracted from the operational sheets for November 16, 1949.

TABLE 9. - Operating conditions

Pressure	10,130 p.s.i.g.
Recycle hydrogen	80% purity
Paste-oil injection	20,160 gal./day - 14 gal./min.
Naphtha injection	1,727 gal./day
Wash-oil injection	1,623 gal./day
Catalyst used	1,008 lb./day, 2% MoO_3 on charcoal

Gas flows:	Cu. ft. per day
Total hydrogen to stalls	6,120,000
Hydrogen bypassed	15,384,000
Total hydrogen to preheater	2,832,000
Hydrogen to inlet of preheater	648,000
Hydrogen to 2d pass of preheater	2,184,000
Hydrogen for cooling and agitation	3,288,000

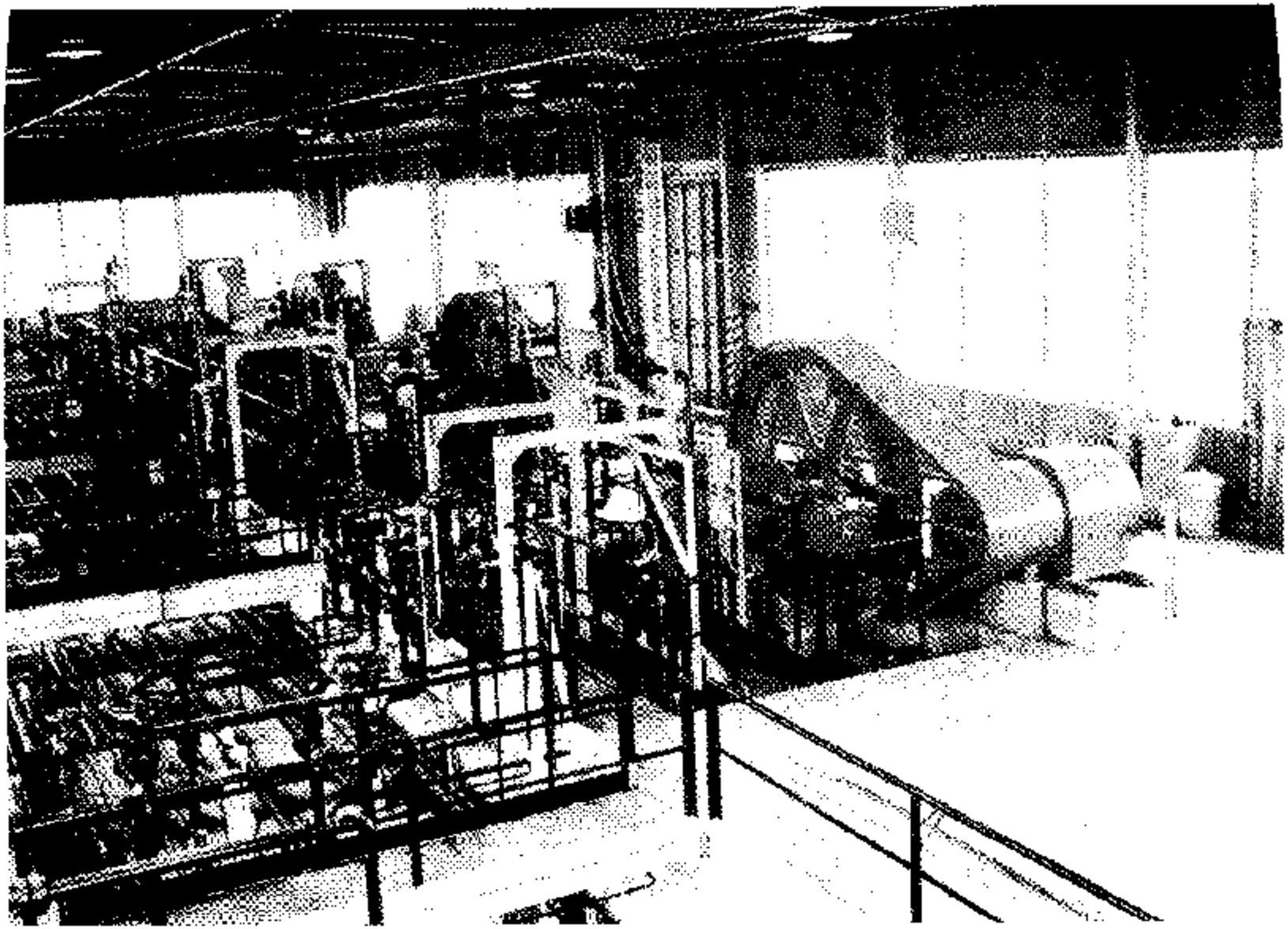


Figure 11. - Motor- and turbine-driven hydrogen recycle booster compressors. Note high-pressure valves and piping.

TABLE 9. - Operating conditions (Cont'd.)

	°F.		
Temperatures:			
Preheater inlet	151		
Preheater outlet	611		
First converter:			
Top zone	858		
Middle zone	856		
Bottom zone	854		
Second converter:			
Top zone	851		
Middle zone	848		
Bottom zone	844		
Hot catchpot	702		
Cold catchpot	125		
	In gal.		
Throughputs (gal./day):			
Pasting-oil injection	20,160		
Water injection	1,300		
Gasoline injection 1/	1,727		
Wash-oil injection 1/	1,623		
Products from hydro (gal./day):			
Heavy-oil let-down	10,297	51%	
Cold catchpot product	9,863	- net make	49%
	1,727	- inj. gasoline	
	11,590		
Products from still (C-701) gal./day:			
Gasoline	1,950		
	1,727	- inj. gaso.	14.5%
	123	- gaso. made	1.0%
Naphtha	2,113		17.7%
Middle oil	2,477		20.8%
Flushing oil	620		5.2%
Light-oil bottoms	4,858		40.8%
	11,918	- Total product from still	
	328	- Reject wash oil as feed to still	
	11,590	- Total product from hydro	

1/ The wash-oil scrubber is a closed circuit, and the material entering and leaving this system does not become part of the new product from the Hydro Plant. The injection gasoline used to change the gravity of the cold catchpot product to aid water separation is subtracted from the net gasoline produced.

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TABLE 10. - Characteristics of oil streams

	Pasting oil	Heavy-oil let-down	Cold catchpot product	Gaso. from still	Naphtha from still	Middle oil from still	Flushing oil from still	Light-oil bottoms from still
Distillation								
I.B.P.	428° F.		180° F.	106° F.	350° F.	240° F.	480° F.	584° F.
5 percent	512		250	158	-	516	538	608
10 percent	578		314	190	390	534	550	618
20 percent	618		420	226	408	542	560	638
30 percent	36% @ 660°		560	302	426	554	575	14% @ 684°
90 percent			83% @ 680°	404	468	578	602	
End point		No distillate at 550° F.		416	516	602	646	
Recovery, percent				91	99.5	97	98.5	
Specific gravity @ 60°	1.19	1.34						1.10
A.P.I. @ 60°			10.3	44.6	17.0	9.2	7.4	
Asphalt, percent	12.1	13.0						
C_6H_6 insolubles, percent	26.4	26.9						
Viscosity S.U. @ 210°F.	85 Sec.	709 Sec.						

On November 17 the make-up hydrogen compressor had to be shut down for a small repair, and the unit pressure was reduced somewhat. After the pressure was raised back to the normal 10,000-pounds-per-square-inch, the temperatures in the first converter became excessive, necessitating a partial emergency pressure release. Neither the converter shells or line temperatures became excessive, however, and when normal converter temperatures again prevailed, the plant pressure and temperatures again were raised slowly to resume hydrogenation.

First Liquid-Phase Run With Coal

For some time very reactive coke deposits existed in the first converter, tending toward excessive local reaction temperatures (900°-1,000° F.). These reaction zones or pockets became dormant by November 23, allowing normal tar-oil hydrogenation operations to be lined out for some time preliminary to the introduction of coal paste. The first coal paste containing 10 percent Rock Springs coal was introduced (see fig. 12) November 24, and in 20 hours the coal was raised to 25 percent in the paste. All operating conditions remained very much the same as reported for the coal-tar operation, except that the new products were from coal rather than from destructive hydrogenation of tar. The mechanical performance of the paste-preparation equipment and the paste-injection pumps seemed actually to improve with the addition of coal to the tar oil. The operation of instruments remained satisfactory, particularly those used for temperature control in the converters. The coal-paste phase of the run was continued successfully for 8 days and was terminated after the limited supply of Rock Springs coal previously obtained to break in the coal-preparation plant was exhausted. During this operation data were obtained regarding

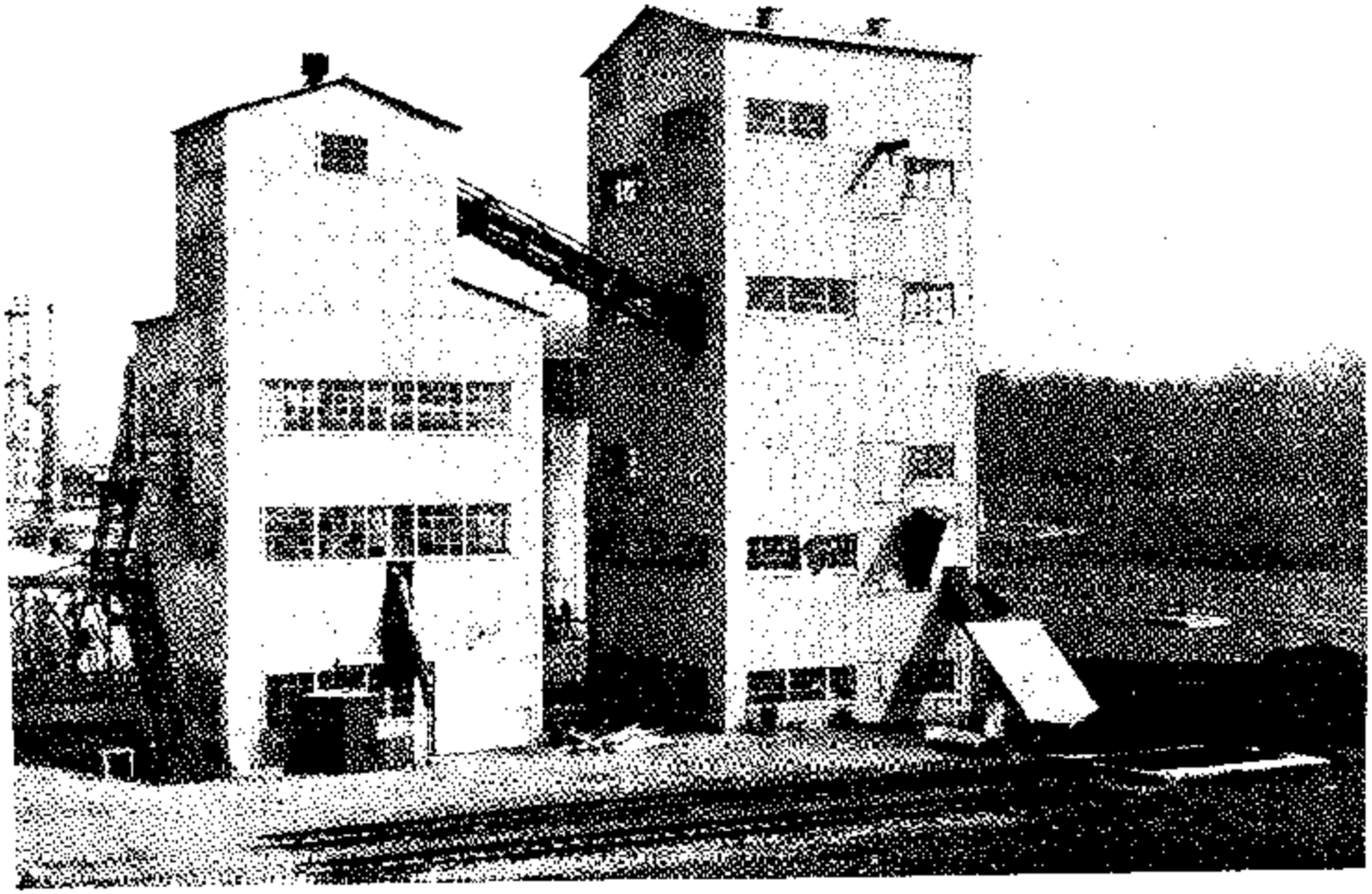

Figure 12. - Raw coal enters through coal-preparation plant at right and is conveyed to paste-preparation plant at left where it is mixed with heavy oil and catalyst.

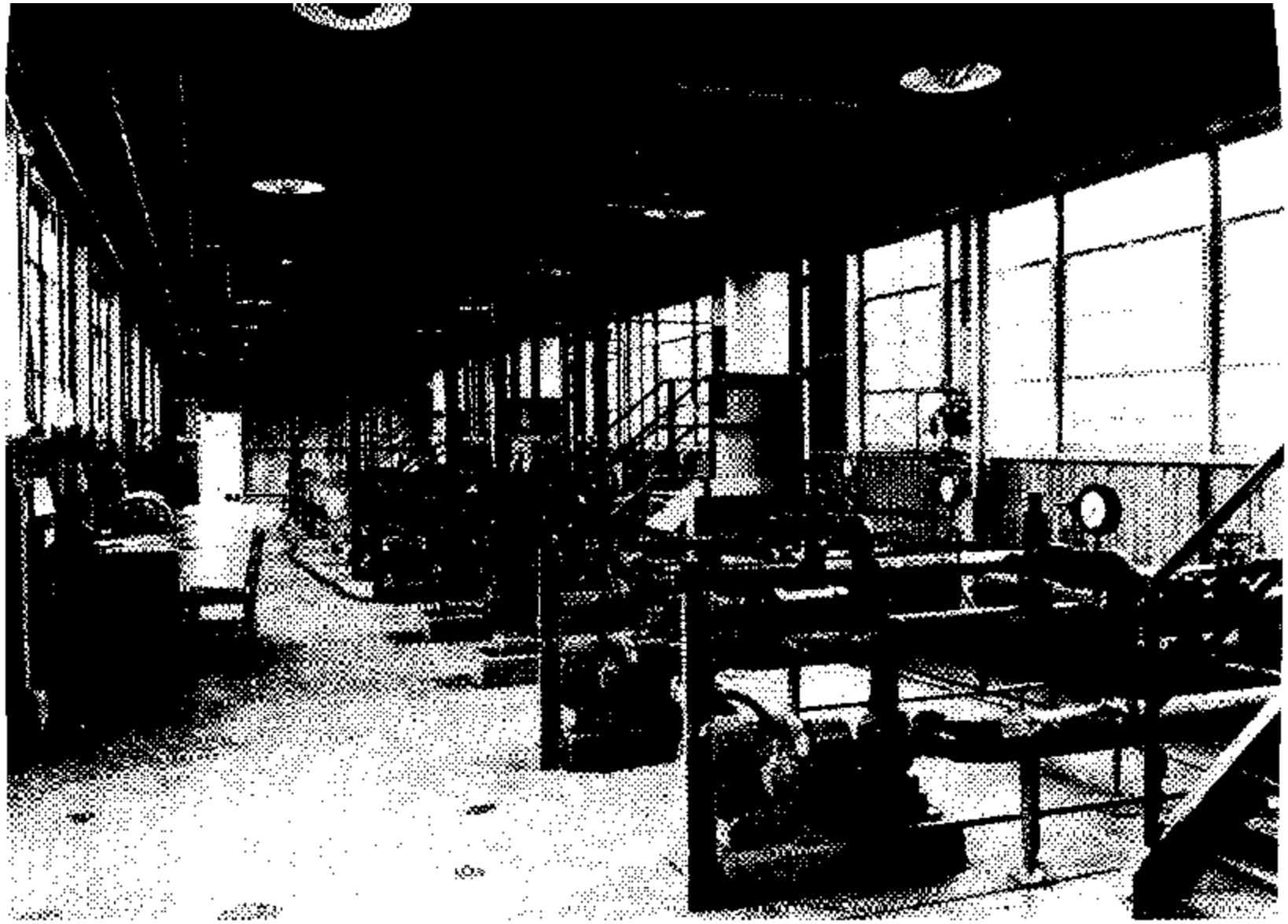

Figure 13. - Inside heavy-oil pump house. Heavy oils are transferred for process use or storage by these pumps.

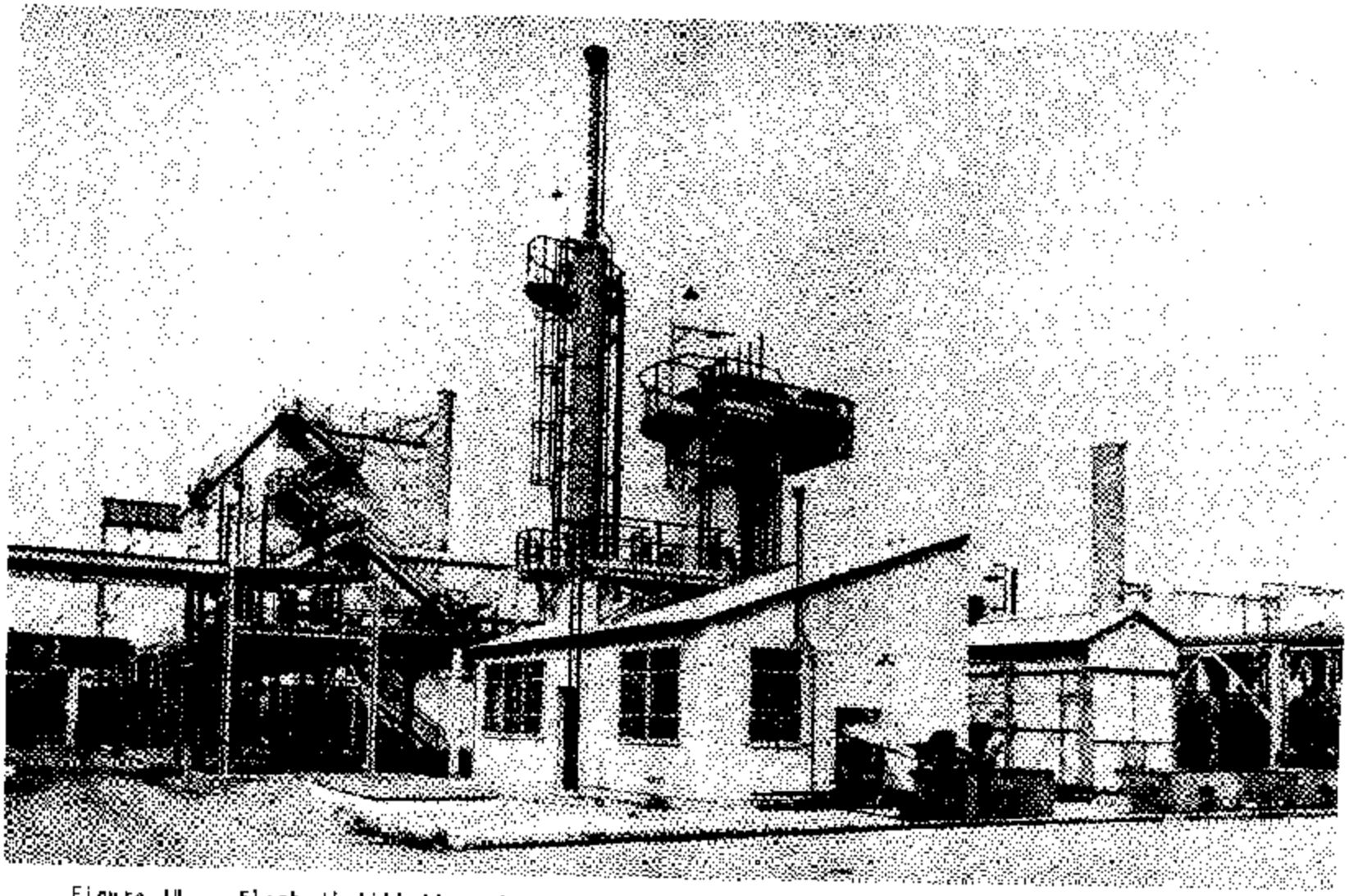

Figure 14. - Flash-distillation plant. Oil is recovered from hydrogenation residue by flash vaporization with superheated steam.

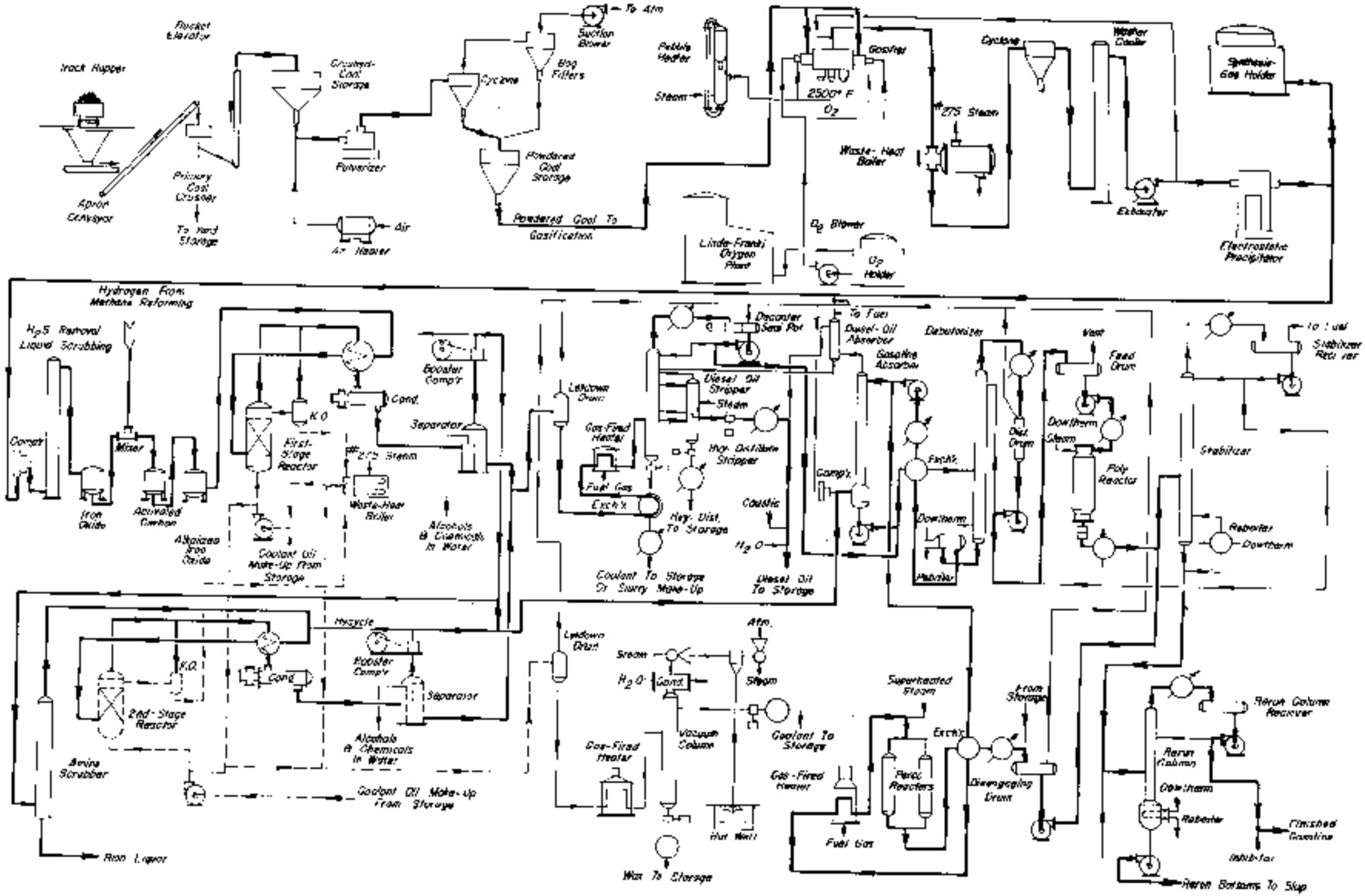

Figure 15. - Process flow diagram of Gas Synthesis Plant.