## Refining Program

A general pilot-plant refining program was conceived and has a twofold purpose - to obtain data for design and evaluation and to guide demonstration-plant operations. At present, three pilot-plant tools for refining studies are under construction. These are a batch still, an equilibrium flash-vaporization still, and a batch treating unit. Experimental work has not yet been started.

## Crushing, Conveying, and Storage of Oil Shale

Efficient crushing of oil shale is important in relation to the over-all retorting operation - more important than might be suspected from comparison of the crushing cost with other costs of producing oil from shale. The basic requirements of an oil-shale crushing plant are low-cost operation, minimum production of fines, and assurance of a constant supply of crushed shale. In selecting equipment and laying out a plant to meet these requirements, certain physical properties of the rock must be considered, especially its elasticity or rubberlike quality and the tendency of the richer grades to break along the laminations forming long, thin slabs.

At present the crushing plant consists essentially of a 4- by 10-foot apron feeder, a 36- by 42-inch Blake-type double-toggle primary crusher, a hammer-mill type secondary crusher, a gearless gyratory tertiary crusher, two double-deck vibrating screens (for recycle screening and crushing with the secondary and tertiary crushers, respectively) and auxiliary conveying, elevating, and storage equipment. The plant can produce coarse material up to 6 inches, material as fine as minus 3/16 inch, or particle sizes within that range.

To provide desired data on experimental crushing and screening operations, weighing facilities were installed, including a 40-ton truck scale for weighing shale to be feed to the plant and conveyor scales on the product and fines-rejection conveyors. Use of the three scales allows a reasonably accurate material balance to be made on all crushing operations. Another improvement is installation of instruments for measuring electrical power consumption.

In addition to crushing and screening oil shale for pilot-plant and demonstration retorting operations, tests were continued on the 24- by 20-inch Jeffrey Flextooth secondary crusher. This work confirms earlier conclusions that (1) this type of crusher is more effective than the Blake-type jaw crusher for breaking up slabs of rich oil shale and (2), by increasing rotor speed, a high throughput rate can be attained but at the expense of increased production of fines.

## Demonstration Retorting Plant

As soon as it became evident from pilot-plant work that the gas-combustion retorting process had definite promise for large-scale adaptation, plans were initiated for a demonstration plant (see fig. 30) so that data on larger-scale equipment could be obtained for projection to commercial-scale design.

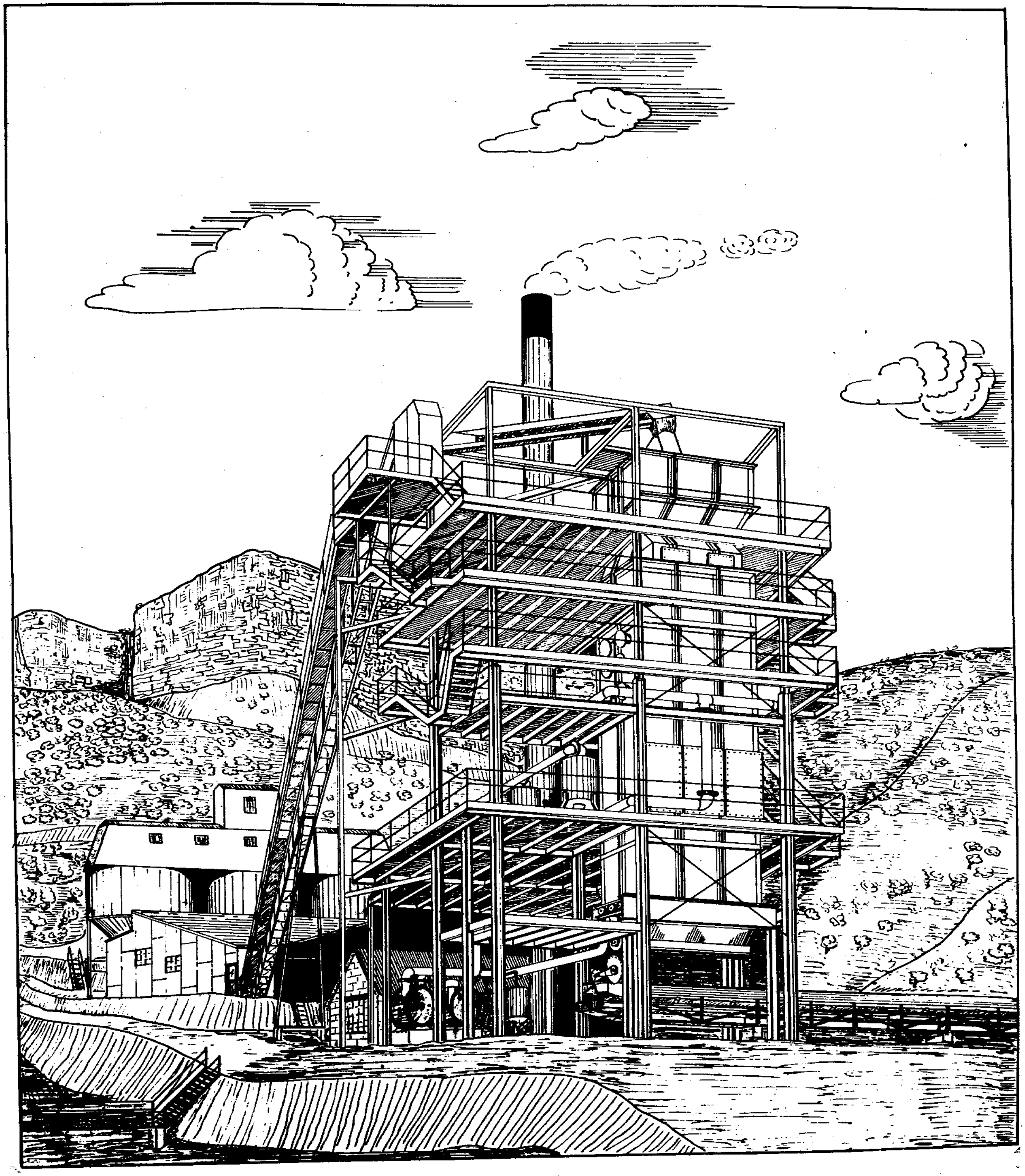

Figure 30. - Artist's sketch of gas-combustion demonstration plant to be built in 1952.

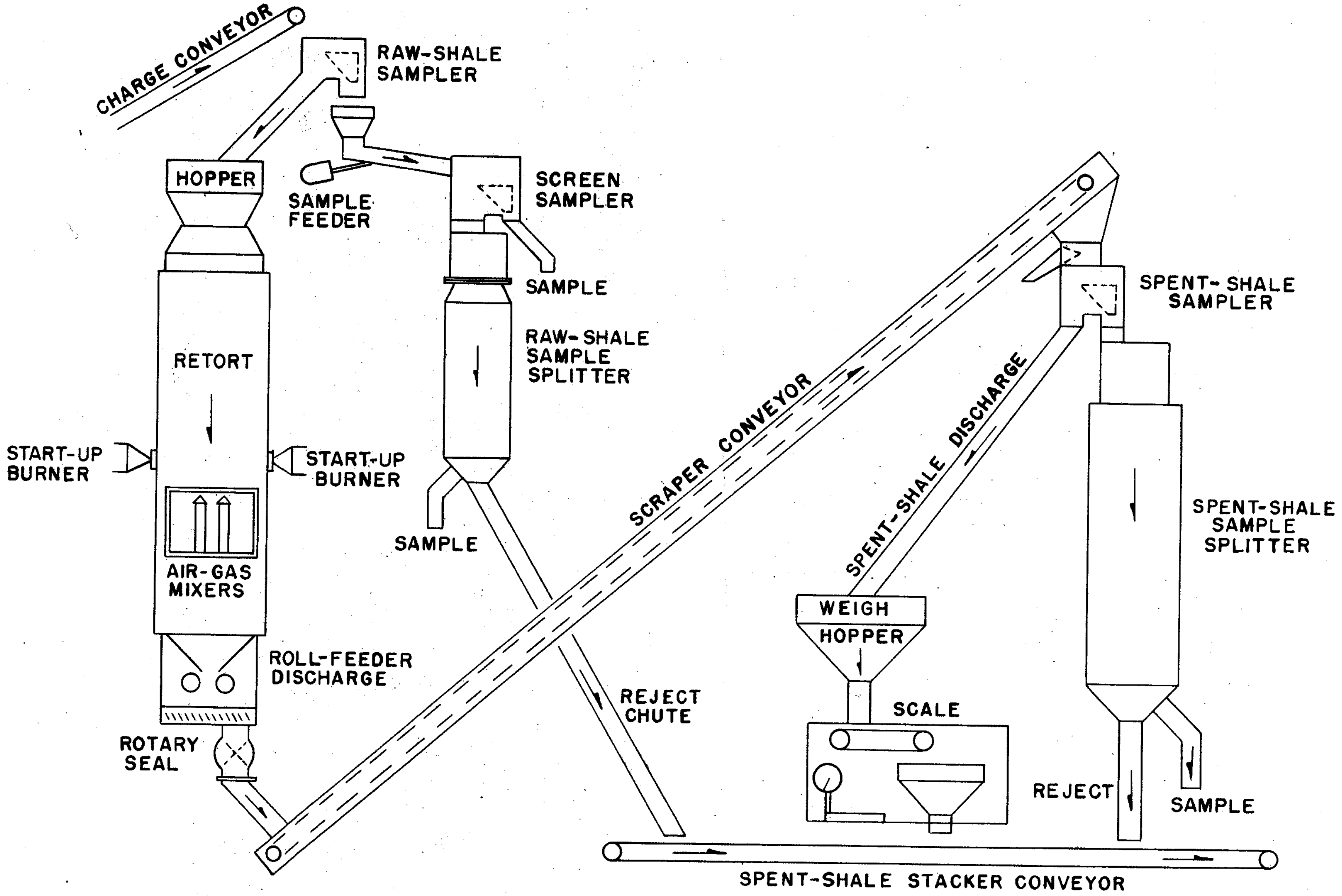

Figure 31. - Shale-handling system, gas-combustion demonstration plant.

A complete set of preliminary drawings and a sample contract for the design, fabrication, and erection of the demonstration plant having a nominal capacity of 150 to 300 tons a day were prepared and copies sent to prospective bidders. The contract was awarded to the Blaw-Knox Construction Co., Chemical Plants Division. Bureau engineers were assigned to the Tulsa, Okla., office of Blaw-Knox to act as consultants in connection with the detailed design and preparation of equipment specifications. The contractor's field-construction organization was set up at Rifle about October 1, and, if delivery and construction schedules are met, the retort should be ready for operation in the summer of 1952.

An important stipulation in the specifications incorporated into the contract provided that the plant should be capable of tests over a wide range of operating conditions and that it should have the flexibility necessary for obtaining the data desired. In general, the specifications provided that the retort should be able to operate at rates of shale throughput ranging from 200 to 450 pounds per hour per square foot of retort cross section and should handle shale assaying 20 to 40 gallons per ton and ranging from 1/4 inch to 3 inches in particle size.

The process to be carried out in the demonstration plant is exactly the same as that described earlier under Pilot-Plant Activities. However, the equipment differs and will be described in the following paragraphs.

After careful study of the N-T-U structure with relation to the proposed plant, it was apparent that it would be advisable to use the old steel supporting structure for the new retort and to utilize as much of the old equipment as possible without imposing limitations on the new process. Structural-steel work will remain substantially intact; but, of course, the old retort vessels will be removed, as well as auxiliary vessels and towers. Gas and air blowers, instruments, and the raw-shale conveying system that were part of the N-T-U plant will be used with the new retort.

In keeping with precedent in expanding from a small-scale plant to a larger one, it is anticipated that problems will arise in connection with the 300-ton-a-day unit that were not encountered in the 6-ton-a-day pilot plant, and experimentation will be required for their solution. Accordingly, it was of primary concern that the retort be designed so that changes could be made conveniently. Another important consideration was provision for obtaining accurate data for the design of commercial units. Other basic requirements of the design are even flow of shale, even distribution of the product gases, and elimination of any obstructions in the vessel that could cause bridging in the shale bed and result in clinkering or coking. Shale movement is controlled by the proper arrangement of roll feeders that remove the spent shale from the base of the retort, and gas flow is controlled by the design of the air-gas mixers and product off-take system.

Figure 31 illustrates the shale handling and sampling system that is to be incorporated into the demonstration plant. To reduce segregation of particle size and promote even flow, the raw shale enters the retort from the charge hopper through a telescoping feed tube. After charging, the material passes by gravity through the preheating, retorting, combustion, and cooling zones and finally is discharged through an adjustable-speed roll feeder that controls the rate of flow through the retort. Escape of gas at this point is prevented by a rotary seal. The spent shale then is elevated by a short scraper conveyor to the sampler and finally is transported to the adjacent canyon by a belt conveyor. As shown in the diagram, a complete sampling system for raw and spent shale is to be provided.

Figure 32 delineates the gas-flow and oil-recovery system. The product mixture of gases, water vapor, and oil mist is drawn from the cool shale bed near the retort top by a wet-type blower. Oil-mist particles agglomerate within the blower, and the liquid is drained to oil run-down tanks. The vapor mixture then passes through a cyclone separator, where most of the remaining oil mist is dropped out. Two centrifugal gas blowers are used for recycling gas through the retort. Drain lines are provided on these blowers to recover any small volume of oil that may separate at this point. Excess gas is vented to the stack.

## Demonstration Shale-Oil Refinery

In keeping with the desire to develop sound methods for processing crude shale oil in the shortest possible time, the Demonstration Refinery (see fig. 33) was designed to be extremely flexible. As a result, the thermal and distillation portions of the plant can carry out a wide variety of operations, ranging from atmospheric distillation to recycle cracking, and including coking, viscosity breaking, and thermal reforming. The treating section of the refinery is designed for treating the naphtha and light gas oil with caustic and sulfuric acid. Provision also has been made for redistillation and doctor sweetening of treated distillates and for the batch springing of sodium cresylate and tar-base sulfate. A recent addition provides facilities for adding tetraethyllead to the finished gasoline.

Before 1951 the demonstration thermal cracking unit had processed crude shale oil and distillates in a variety of conventional thermal refining procedures. Operating conditions were varied widely for each procedure, and product yields and quality under each set of conditions were evaluated. The results of this work have established a range of conditions under which a given process may be carried out to best advantage. They also have shown that some thermal processes are better-suited than others to the refining of shale oil. The fields of investigation thus have been narrowed enough to permit initiation of studies that will establish optimum operating conditions and determine process modifications best-suited to this oil. In brief, the feasibility of refining by thermal means has been established, and it now is possible to direct more attention toward process developments that will give the best possible quality and yields of product.

### Thermal Operations

Investigations were continued on three types of thermal cracking operations that have proved well-adapted to the refining of shale oil, that is, coking, recycle cracking, and viscosity breaking. In two runs the coking process was modified to produce a pitch that shows some promise as a substitute for the coal-tar pitch now used by the steel industry as an additive to the coke-oven charge to improve the quality of blast-furnace coke. Other

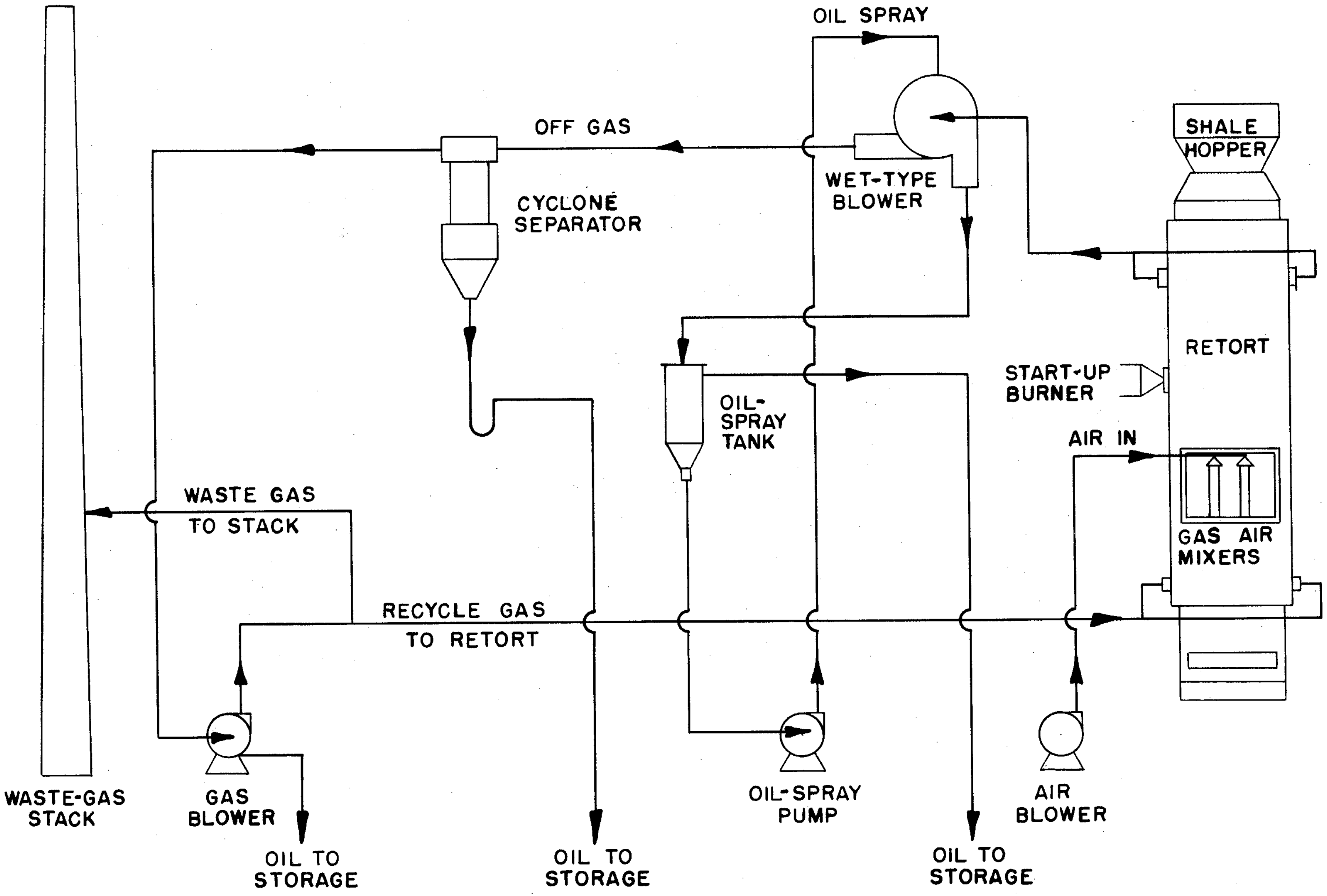

Figure 32. - Oil-recovery system, gas-combustion demonstration plant.

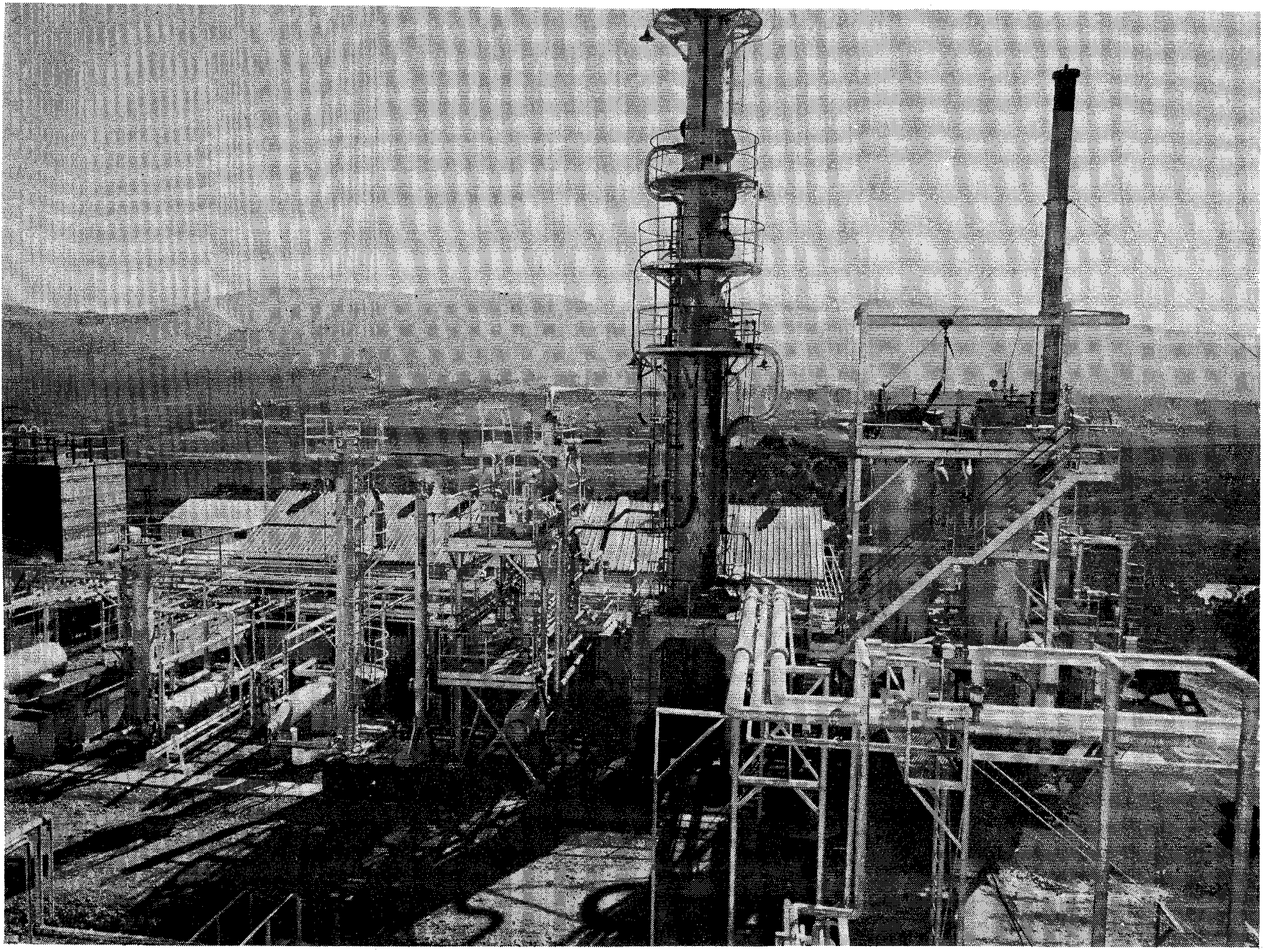

Figure 33. - Demonstration shale-oil refinery.

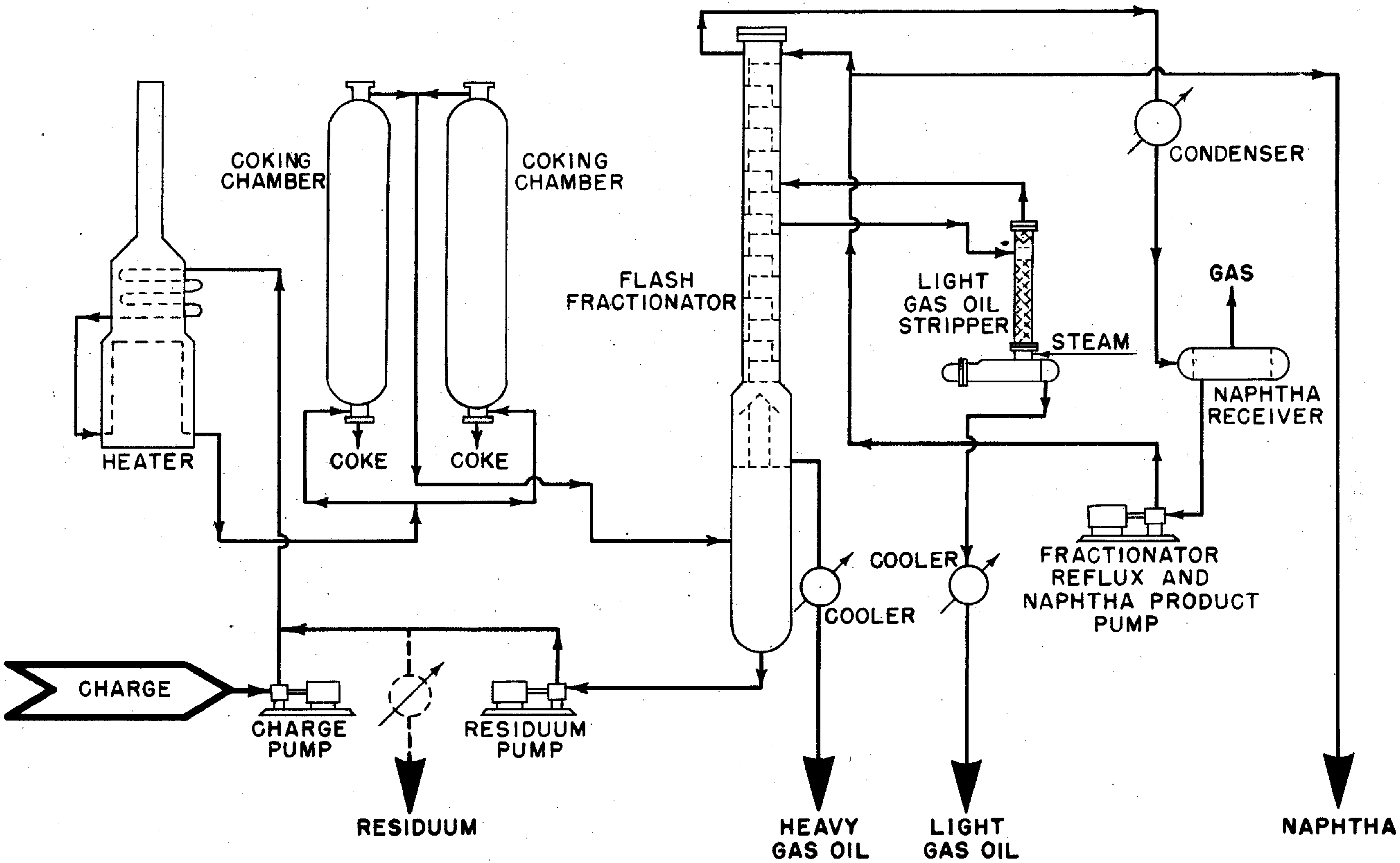

Figure 34. - Once-through and recycle delayed coking of crude shale oil.

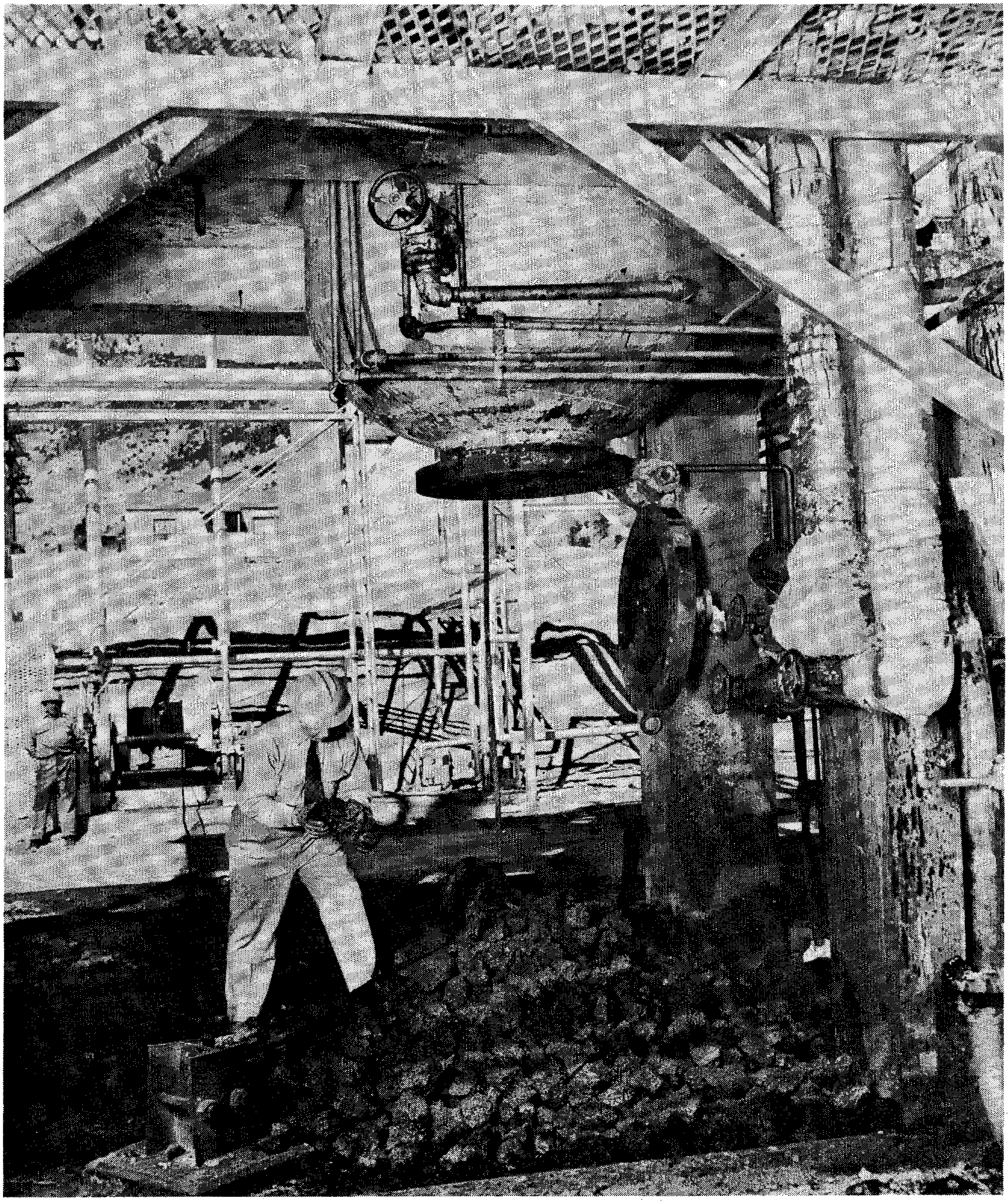

Figure 35. - Shale-oil coke.

thermal operations included thermal reforming of shale gasoline, a process not previously investigated, and preparation of several grades of road oil for service tests.

## Coking

As applied to crude shale oil, coking may be used to produce (1) a combined liquid product suitable for hydrogenation, (2) a synthetic crude having viscosity and pour point suitable for pipeline transportation, or (3) gas oils suitable for further thermal cracking or for use, after treatment, as Diesel fuel.

Six coking runs were made in 1951, using crude shale oil as charge stock. One of these was a once-through operation; three were recycle delayed runs in which flash fractionator bottoms were combined with the crude and returned to the heater, and in the other two runs the crude charge entered the system via the flash chamber, and heater feed was drawn from the same point.

Figure 34 shows the flow for two of these operations. The solid lines indicate the flow in the usual recycle delayed-coking procedure, and the dotted lines outline the changes necessary for a once-through operation. Shale-oil coke or residue is shown in figure 35.

During a part of one once-through run, conditions were so adjusted that pitch instead of coke was produced in the coke chamber. The general characteristics of this pitch are given in table 8.

Under a cooperative agreement with the Geneva Steel Co., a part of this pitch was blended at Geneva with Utah coal. The mixture then was coked in a standard coke oven to determine the ability of the shale pitch to improve blast-furnace coke quality. Coal-tar pitch at present is used exclusively for this purpose. The results obtained at Geneva with shale-oil pitch were highly encouraging.

TABLE 8. - Characteristics of shale-oil pitch

| | |
|---|---|
| Softening point (R and B)....... °F. | 401 |
| Volatile matter ........ wt. percent | 46.4 |
| Benzene-insoluble .............. do. | 50 |
| Total sulfur ................... do. | .44 |
| Nitrogen ....................... do. | 3.95 |

Once-through coking procedures are satisfactory when a synthetic crude for pipeline transportation is desired, or for such special applications as the production of pitch or the over-all reduction of the carbon:hydrogen ratio. For more exacting requirements, such as the production of a combined liquid product suitable for hydrogenation, it is desirable to recycle the heaviest portion of the liquid product. Table 9 details the operating conditions for runs of this type, yields, and liquid-product properties, and table 10 gives the analysis of the gas produced. The yield of total liquid product, as would be expected, is lower than that obtained by once-through coking, but the carbon residue of the heavy gas oil is greatly improved.

Table 11 gives an analysis of coke produced in the operation. This coke is similar in physical characteristics to that produced in the petroleum industry. In cooperation with the Bureau, the Geneva Steel Co. tested shale-oil coke of this type to determine its possibilities as a substitute for low-volatile coal in the manufacture of blast-furnace coke. The tumbler stability and shatter index of the coke produced from the initial blend were good, and, in general, the results of the tests were promising.

TABLE 9. - Recycle delayed coking of crude shale oil

OPERATING CONDITIONS

| | | | |
|---|---|---|---|
| Charging rate: | Raw crude ........................ | bbl. per stream-day | 243.3 |
| | Recycle ........................................... | do. | 32.0 |

| | Heater | | Flash chamber | Fractionator | |
|---|---|---|---|---|---|
| | Inlet | Outlet | Top | Top | Btm. |
| Temperature ........... °F. | 181 | 925 | 771 | 349 | 705 |
| Pressure ......... p.s.i.g. | 250 | 58 | 24 | | |

PRODUCT YIELDS AND PROPERTIES

| | Crude charge | Naphtha | Light gas oil | Heavy gas oil | Coke | Gas | Loss | Product blend |
|---|---|---|---|---|---|---|---|---|
| Yields...........vol. percent | 100.0 | 13.1 | 29.7 | 44.3 | - | - | - | |
| Yields .......... wt. percent | 100.0 | 10.8 | 27.9 | 44.6 | 9.9 | 5.7 | 1.1 | |
| Gravity .............. °A.P.I. | 19.9 | 50.9 | 28.4 | 17.8 | | | | 24.9 |
| Pour point .............. °F. | 85 | | 10 | 90 | | | | 60 |
| Viscosity .............. sec. | | | | | | | | |
| S.U.S. at 100° F. ......... | | | 38.9 | | | | | 60.8 |
| S.U.S. at 130° F. ......... | 132.3 | | 35.2 | 149.6 | | | | 47.1 |
| S.U.S. at 210° F. ......... | 47.7 | | | 46.8 | | | | |
| Sulfur .......... wt. percent | 0.82 | 0.84 | 0.70 | 0.58 | | | | 0.67 |
| Nitrogen ................ do. | 2.2 | 1.03 | 1.82 | 2.32 | | | | 1.94 |
| Tar acids ...... vol. percent | [1] 1.7 | 1.0 | 2.5 | | | | | 1.0 |
| Tar bases ............... do. | [1] 3.7 | 5.6 | 15.5 | | | | | 5.4 |
| Cetane No. .................. | | | 32.9 | | | | | |
| Octane No., M.M. ...... clear | | 66.4 | | | | | | |
| +3 cc. tetraethyllead ..... | | 71.9 | | | | | | |
| Octane No., R.M. ...... clear | | 74.5 | | | | | | |
| +3 cc. tetraethyllead ..... | | 81.5 | | | | | | |
| Hydrocarbon analysis: | | | | | | | | |
| Olefins ...... vol. percent | | 51.0 | 39.5 | | | | | |
| Aromatics ............. do. | | 13.6 | 34.9 | | | | | |
| Paraffins and naphthenes .......... do. | | 35.4 | 25.6 | | | | | |
| A.S.T.M. distillation (corrected to 760 mm. Hg) | | | | | | | | |
| I.b.p. ................ °F. | 263 | 106 | 456 | 395 | | | | 180 |
| 10 percent at ......... do. | 474 | 198 | 488 | 648 | | | | 351 |
| 20 percent at ......... do. | 547 | 241 | 494 | 679 | | | | 437 |
| 50 percent at ......... do. | 684 | 312 | 533 | - | | | | 618 |
| 90 percent at ......... do. | - | 360 | 587 | - | | | | - |
| E.P. .................. do. | 699 | 395 | 638 | 699 | | | | 699 |
| Recovery ...... vol. percent | 59.0 | 99.0 | 99.0 | 30.0 | | | | 69.0 |

[1] Based on total distillate to 580° F.

TABLE 10. - Product-gas analyses[1]

| Operations and charge | Recycle coking N-T-U crude | Recycle cracking N-T-U crude[2] | Recycle cracking gas oil | Viscosity breaking N-T-U crude[2] | Reforming shale-oil naphtha |
|---|---|---|---|---|---|
| Hydrogen | 11.0 | 5.4 | 3.8 | 5.0 | 8.3 |
| Methane | 38.7 | 41.6 | 37.3 | 56.0 | 46.6 |
| Ethane | 13.3 | 19.0 | 16.5 | 14.0 | 13.1 |
| Propane | 7.6 | 10.1 | 13.0 | 2.1 | 4.7 |
| Butanes | 4.1 | 3.1 | 4.1 | .0 | 1.1 |
| Pentanes | 1.8 | .8 | 1.7 | .0 | 1.0 |
| Hexanes | .2 | - | .1 | .0 | .2 |
| Ethylene | 3.3 | 3.6 | 6.5 | 5.6 | 10.4 |
| Propylene | 5.2 | 6.1 | 8.7 | 1.5 | 6.2 |
| Butenes | 3.4 | 3.0 | 5.0 | .2 | 1.9 |
| Pentenes | 3.6 | 1.0 | 2.1 | - | 1.3 |
| Hexenes | 1.0 | .3 | .5 | - | .6 |
| Heptenes | .1 | - | - | - | - |
| Nitrogen | - | - | - | 5.7 | 2.9 |
| Carbon dioxide | .7 | 1.2 | - | 2.0 | .5 |
| Carbon monoxide | 2.6 | 3.1 | - | 5.2 | - |
| Hydrogen sulfide | 3.3 | 2.1 | .9 | 2.6 | 1.0 |
| Molecular weight | 28.2 | 27.6 | 30.9 | 21.3 | 24.7 |

[1] Analyses by mass spectrometer. All expressed in volume percent.
[2] Absorber in operation.

TABLE 11. - Coke analysis (moisture-free)

| | | |
|---|---|---|
| Volatile matter | percent | 10.45 |
| Fixed carbon | do. | 89.06 |
| Ash | do. | 0.49 |
| Total | do. | 100.00 |
| | | |
| Hydrogen | do. | 3.70 |
| Carbon | do. | 87.24 |
| Nitrogen | do. | 4.45 |
| Oxygen | do. | 3.65 |
| Sulfur | do. | 0.47 |
| Ash | do. | 0.49 |
| Total | do. | 100.00 |
| | | |
| Gross heating value | B.t.u. per lb. | 14,979 |
| Net heating value | do. | 14,634 |
| Real specific gravity | | 1.0587 |
| Cell space | percent | 24.5 |
| C:H ratio | | 23.36 |

## Recycle Cracking

Earlier work had demonstrated that the recycle cracking of crude shale oil gives good yields of naphtha but that variations in operating conditions can result in wide variations in the quality and yield of products. Accordingly, a series of runs was made involving different conditions of temperature, pressure, and reaction time in an effort to establish optimum conditions. To achieve this end more runs will be required, but several noteworthy observations have been made.

1. A combination of low reaction-zone pressure with a relatively short reaction time (reaction chamber bypassed) gives excessive deposition of coke in the heater and therefore is impractical from an operating standpoint.

2. Low reaction-zone pressure and a longer reaction time give excellent yields of naphtha having a fair antiknock value, but control of the operation is difficult.

3. The use of higher reaction-zone pressures with a short reaction time (reaction chamber bypassed) gives satisfactory operation and produces a good yield of naphtha having a fair octane number.

4. Maximum attainable pressures in the reaction chamber with consequent long reaction times and low recycle ratio produced a naphtha of relatively good antiknock characteristics but resulted in lower yields.

5. Medium reaction-chamber pressures (150 to 200 p.s.i.g.) with resultant lower reaction times and higher recycle ratios gave better yields of naphtha with good antiknock ratings. This type of operation (see fig. 36 for flow diagram) shows much promise for processing both crude and viscosity-broken shale oil.

Table 12 gives the properties of the crude charge and products for an operation conducted under the medium-pressure conditions. Yields and rates also are given. It will be observed that a naphtha yield of 49.6 volume percent of the charge was attained, together with 45.9 volume percent of residuum. Gas production was 7.7 weight percent of charge. Analysis of the gas is shown in table 10. No operating difficulties of any consequence were encountered in the operation.

Recycle cracking is useful not only for processing crude shale oil but also for obtaining additional naphtha from gas oils produced in such operations as coking and viscosity breaking. As might be expected, the use of the cleaner, more refractory charge stock permits using higher heater-outlet temperatures than when crude shale oil is charged. Table 13 gives product yields and characteristics for a typical run in which a mixture of light and heavy gas oil was used as charge stock and a heater-outlet temperature of 985° F. was maintained. The raw naphtha obtained was 33.5 volume percent of the charge and was lower in sulfur content and slightly lower in nitrogen than that usually obtained by recycle cracking of crude shale oil.

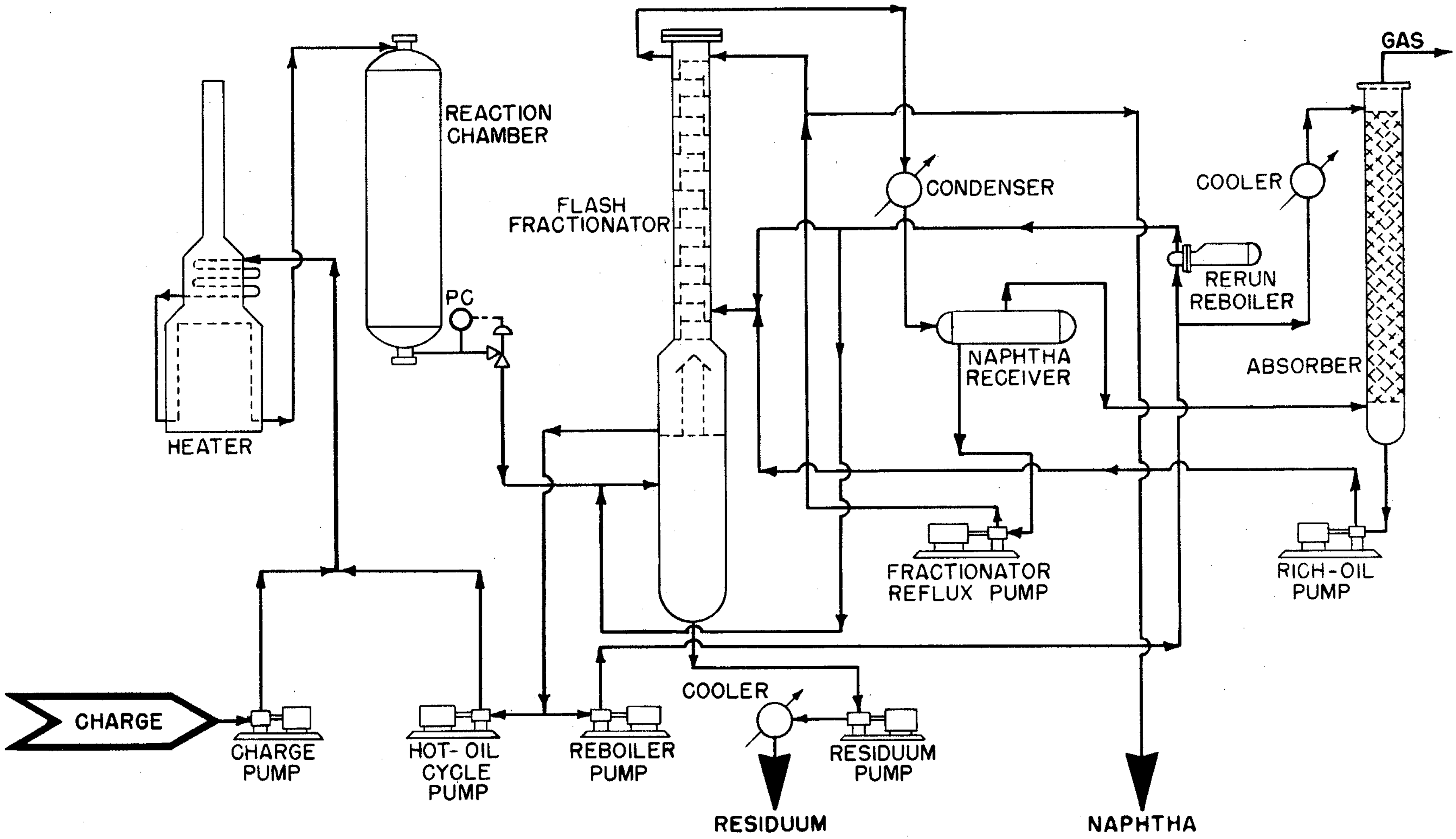

Figure 36. - Recycle cracking of crude shale oil.

## TABLE 12. - Recycle cracking of N-T-U crude shale oil

### OPERATING CONDITIONS

| | | | |
|---|---|---|---|
| Charging rate: | Raw crude | bbl. per stream-day | 96.0 |
| | Recycle | do. | 258.0 |

| | Heater | | Reaction chamber | Flash chamber | Fractionator | |
|---|---|---|---|---|---|---|
| | Inlet | Outlet | Top | Top | Top | Btm. |
| Temperature... °F. | 434 | 920 | 848 | 762 | 386 | 621 |
| Pressure..p.s.i.g. | 460 | 200 | 200 | 64 | | |

### PRODUCT YIELDS AND PROPERTIES

| | Crude charges | Naphtha | Residuum | Gas | Loss | Recycle stock |
|---|---|---|---|---|---|---|
| Yields ........... vol. percent | 100.0 | 49.6 | 45.9 | - | - | - |
| Yields ........... wt. percent | 100.0 | 40.1 | 51.9 | 7.7 | 0.3 | - |
| Gravity ............... °A.P.I. | 19.6 | 55.2 | 4.0 | | | 15.4 |
| Pour point ............... °F. | 85 | | 80 | | | 25 |
| Viscosity ............... sec. | | | | | | |
| S.U.S. at 130° F. ........... | 135.7 | | | | | 40.5 |
| S.U.S. at 210° F. ........... | 47.8 | | 257 | | | 32.8 |
| S.F.S. at 122° F. ........... | | | 739 | | | |
| Sulfur ............ wt. percent | 0.82 | 0.72 | 0.56 | | | 0.76 |
| Nitrogen ................. do. | 2.15 | 1.10 | 3.07 | | | 2.67 |
| Tar acids ........ vol. percent | 1/0.8 | 0.8 | | | | |
| Tar bases ................. do. | 1/4.4 | 6.0 | | | | |
| Octane No., M.M. ........ clear | | 71.0 | | | | |
| +3 cc. tetraethyllead ....... | | 76.5 | | | | |
| Octane No., R.M. ........ clear | | 79.0 | | | | |
| +3 cc. tetraethyllead ....... | | 87.3 | | | | |
| Hydrocarbon analysis: | | | | | | |
| Olefins ........ vol. percent | | 46.4 | | | | |
| Aromatics ................do. | | 17.9 | | | | |
| Paraffins and naphthenes..do. | | 35.7 | | | | |
| A.S.T.M. distillation (corrected to 760 mm. Hg) | | | | | | |
| I.b.p. ................... °F. | 334 | 89 | 2/376 | | | 275 |
| 10 percent at ........... do. | 480 | 143 | 597 | | | 466 |
| 20 percent at ........... do. | 557 | 186 | 696 | | | 484 |
| 50 percent at ........... do. | 693 | 295 | 907 | | | 537 |
| 90 percent at ........... do. | - | 396 | - | | | 679 |
| E.P. ..................... do. | 699 | 405 | 934 | | | 699 |
| Recovery ....... vol. percent | 54 | 91.5 | 54.4 | | | 91.0 |

1/ Based on total distillate to 580° F.

2/ Norwood vacuum distillation corrected to 760 mm. Hg.