

RESEARCH AND DEVELOPMENT, PETROLEUM AND OIL-SHALE  
EXPERIMENT STATION, LARAMIE, WYO.

The 1950 annual report gave the results of experimental retorting of oil shale at higher-than-normal temperatures to produce aromatic oils and unsaturated gases from which many critical chemicals or high-octane gasoline can be made. Additional research has shown that an entrained-solids system has promise for either high-temperature or normal retorting at throughput rates many times greater than those of other known retorting processes. A small pilot plant is being constructed to continue the development of this process.

Shale-oil refining research was devoted to the development of processes for bettering the quality of thermally cracked gasoline produced by the Demonstration Plant at Rifle, the improvement of distillate stocks for Diesel fuels or catalytic-cracking stocks, and further studies of low-pressure hydrogenation. Advancements have been made in each of these techniques.

Studies of the constitution of the organic material in Colorado oil shale, by degrading it into smaller organic fragments for analysis and identification, indicate that it consists predominantly of nonbenzenoid structures. A comprehensive report was published on composition and properties of Colorado oil shales.

Knowledge of the composition of shale oil was augmented during the past year by publications on pyrroles identified in shale-oil naphtha, gum formation in gasoline, and the determination of nitrogen in shale oil and by technical society presentations of mass spectral correlations in composition studies, crude-oil analyses, and the composition of high-temperature retorted oils. The development of analytical methods and additional composition studies are continuing.

Byproduct tar acids and tar bases from the refining of shale-oil distillates were purified, and their composition was determined.

#### Oil-Shale Retorting Research

The development of a process for retorting oil shale at high temperatures has received most attention during the past year, both because of the nature of the products that can be produced in this manner and the fact that the type of retort that appears most suitable for this high-temperature operation shows promise in the normal retorting temperature range as well. Before deciding upon a tentative design for a small pilot plant, three methods of retorting at high temperatures were studied. These were: The inclined-surface retort, somewhat similar to a conventional coal-carbonization retort, except that the retort tube was set at an angle to permit continuous gravity flow of shale; a single-vessel, fluidized-bed retort; and an entrained-solids retort in which the shale was carried into and out of a heated, vertical furnace by an entraining gas or steam. Of the three methods, the entrained solids retort appears to offer the best possibility of enlargement to pilot-plant and commercial-plant size, and a small pilot plant is now being constructed on this principle.

## Entrained-Solids Retort

A diagrammatic sketch of the bench-scale equipment used in developing this retorting method is shown in figure 46. This process, which embodies pneumatic solids transport (fig. 47) in conjunction with rapid heating to high temperatures, promises the highest production rate per unit size of equipment of any retorting process yet investigated. Conditions are excellent in this system for obtaining high rates of heat transfer. It also offers the possibility of using the autothermic cracking principle by introducing controlled amounts of oxygen in the entraining gas, thus obtaining partial combustion and generation of heat within the retort, much as is now done in cracking hydrocarbon gases to produce ethylene. This variation, if successful, will lessen the quantity of heat that must be transmitted through the retort walls.

In the bench-scale equipment it was possible to determine minimum flow rates of entraining fluid, maximum shale-feed rates, heat-transfer areas required, and furnace temperatures necessary for satisfactory, high-temperature retorting. These data were then applied to the design of a small pilot plant, now being constructed, in which an extensive study of the process can be made. Very high shale throughputs are believed to be possible in this bench-scale equipment, and quantities ranging upward to 4,000 pounds and more per hour per square foot of retort cross-sectional area are expected. This compares with throughputs of 200 to 400 pounds per hour per square foot of cross-sectional area found to be obtainable in the best pilot plants reported to date for conventional retorting. Whether or not such high throughputs can be obtained in larger equipment will be determined as the development work progresses. Higher heat-transfer rates have been achieved in this system than are commonly obtained in other retorts depending largely on conduction for heat transfer, for this system allows heat transfer by radiation and convection, as well as conduction. One disadvantage of an entraining system is the necessity for using finely ground shale. This adds to the cost of shale preparation. The use of a carrier fluid also results in dilution of the product gases and vapors, thus adding to recovery costs if a fixed gas is used. However, if it is found economical to use steam as a carrier medium, at least part of this disadvantage can be overcome. It was found in the bench-scale unit that higher heat-transfer rates could be obtained when using steam than when using gas as a carrier, which is an additional advantage.

### Products from High-Temperature Retorting

The type of shale oil produced by conventional retorts at moderate temperatures has been discussed in previous reports, but the potentialities of oil produced at high temperatures has not been generally appreciated. Not only could this oil be used to supply high-octane blending stocks for upgrading shale gasoline produced by other methods; but, because it is almost completely aromatic, it appears very attractive as a chemical raw material. The gas produced contains a high percentage of ethylene, one of the more important basic chemicals, as well as other components of possible chemical value. Table 28 shows the yields of some products that could be obtained from one 20,000-ton-per-day oil-shale plant using high-temperature retorting.

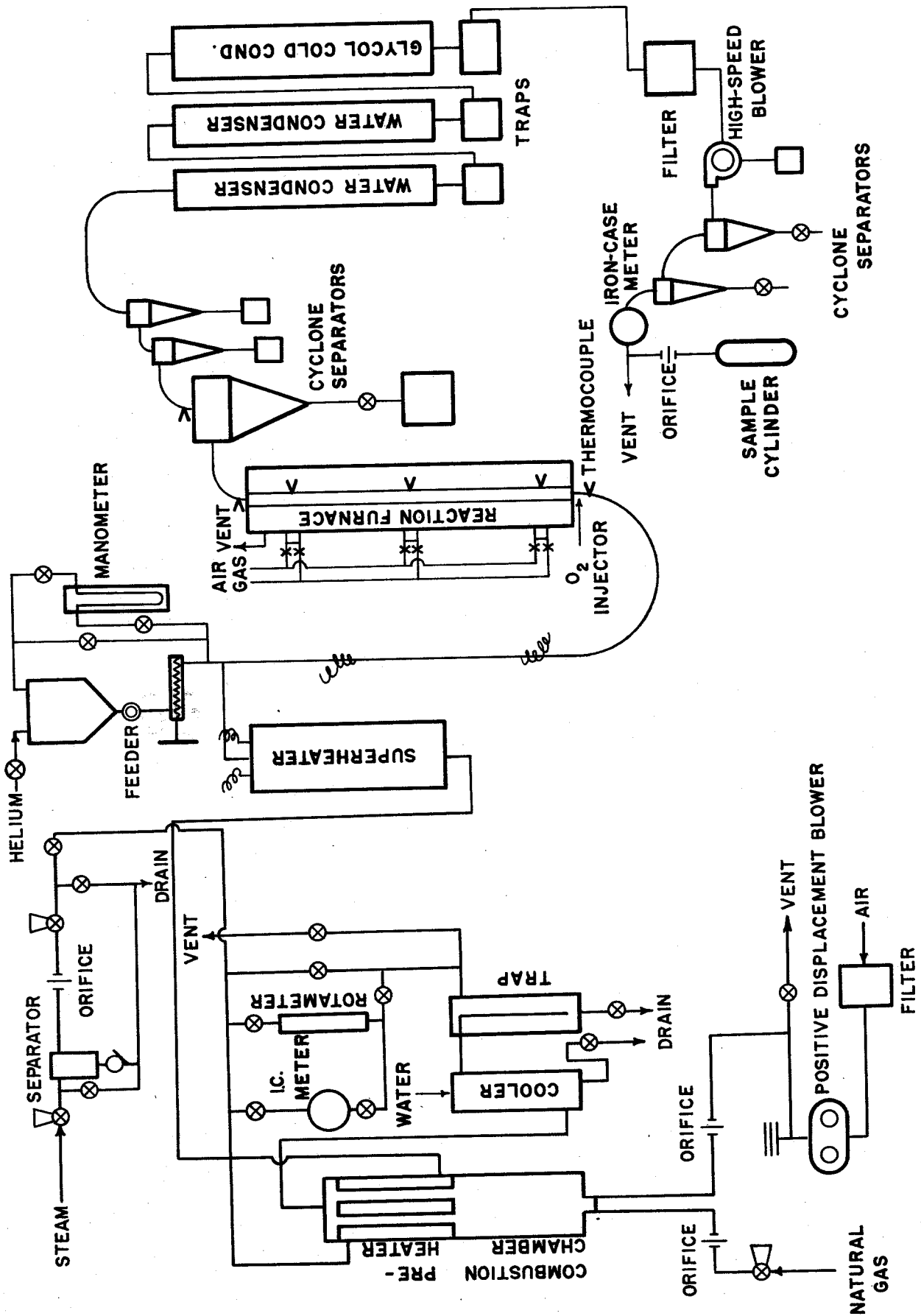


Figure 46. - High-temperature entrained-solids retort.

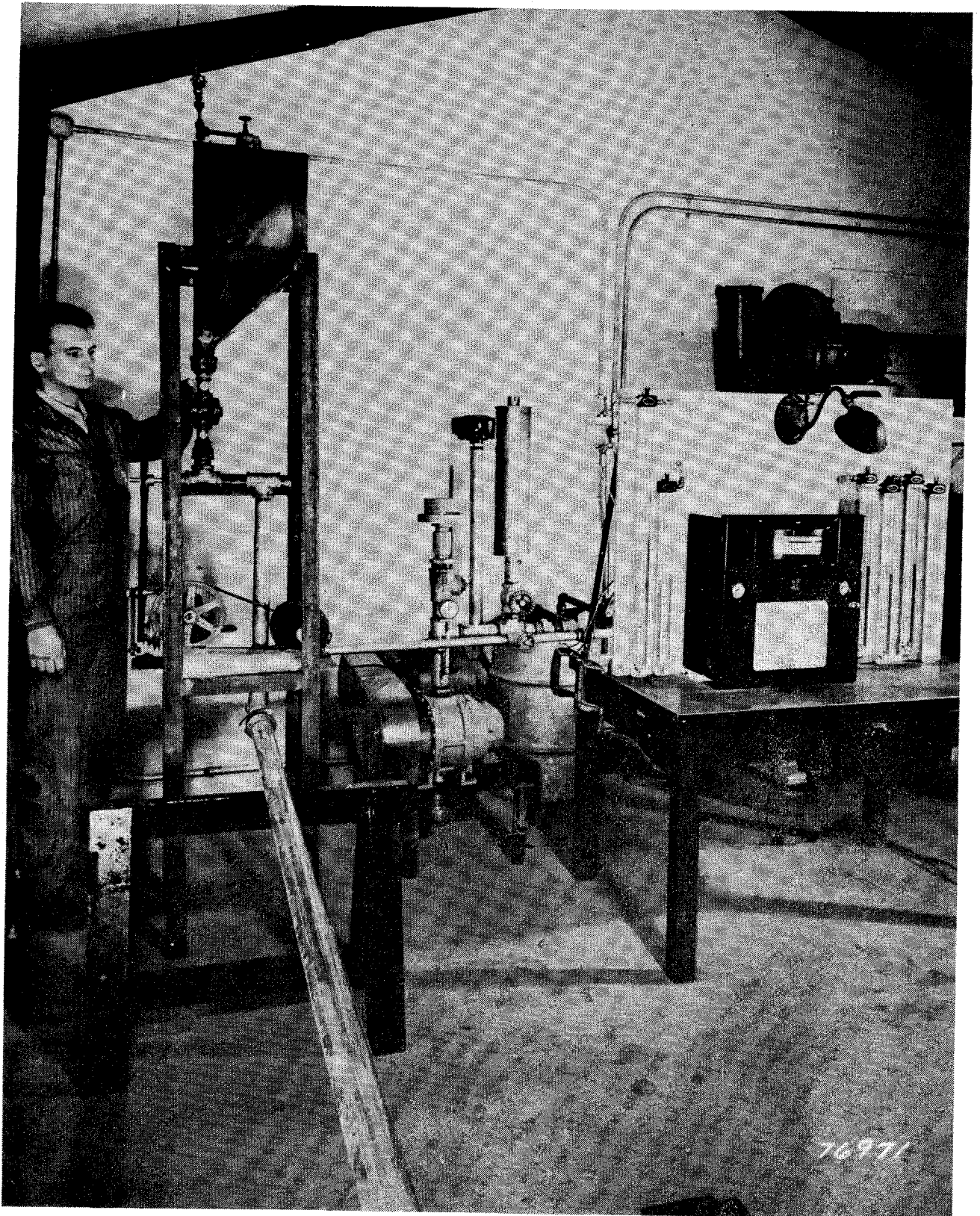


Figure 47. - Apparatus for studying flow characteristics of entrained oil shale.

TABLE 28. - Potential production of some chemicals from a 20,000-ton-per-day high-temperature retorting plant

Chemical	1949 United States production 1,000 gal.	Potential yearly production from oil-shale plant <sup>1/</sup>	
		1,000 gal.	Percent of 1949 production
Benzene.....	2/157,200	11,780	7.5
Toluene.....	2/82,200	5,340	6.5
Motor benzene.....	2/23,400	2,020	8.6
Xylenes.....	2/57,100	3,180	5.6
Solvent naphtha.....	3/5,100	1,310	26.2
Crude tar acids.....	3/12,400	790	6.4
	(1,000 lb.)	(1,000 lb.)	
Naphthalene.....	2/235,000	24,800	10.5
Ethylene.....	2/1,280,000	209,200	16.3

<sup>1/</sup> Based on 310 operating days per year on 30-gallon-per-ton shale.

<sup>2/</sup> Ewell, R. H., Chem. Ind., vol. 67, 1950, pp. 726-30, 743.

<sup>3/</sup> U. S. Tariff Commission, Synthetic Organic Chemicals, Rept. 169, 1949.

Benzene is in critical supply at present. It is one of the most important organic chemicals both in quantity consumed and variety of products in which it plays an essential part. Although used directly as a solvent and gasoline additive, it finds its greatest use as a chemical raw material. The major derivatives are styrene, phenol, nylon, aniline, synthetic detergents, chlorobenzenes, and nitrobenzene. These find ultimate outlets in many phases of industry: Synthetic rubber, resins, plastics, medicinals, dyes, insecticides, textiles, detergents, explosives, and others. Most of the present supply of benzene comes as a byproduct from high-temperature carbonization of bituminous coal to produce coke for the steel industry. As a result, the supply from this source is inflexible, for it is a function of the quantity of steel produced. Oil shale offers a supplemental source of this valuable commodity.

Ethylene is one of the basic raw materials in the chemical industry, being the starting point for the manufacture of almost an endless list of products. The major ones are ethyl alcohol, ethylene oxide, ethyl benzene, ethyl chloride, ethylene dichloride, and ethylene dibromide, each of which enters into the manufacture of still other products. With benzene, it is used to produce styrene, one of the major ingredients of some types of synthetic rubber. It has been calculated from laboratory processing data that one 20,000-ton-per-day, high-temperature retorting plant could produce enough nitration-grade benzene to yield, when reacted with ethylene from the process, 49,600 short tons of styrene annually, equivalent to 25 percent of the styrene produced in the United States in 1949. There would remain, for other chemical use, 177,000,000 pounds of ethylene annually.

Naphthalene also is in short supply, and this process offers a source of this chemical. It is used principally in manufacturing phthalic anhydride,

an intermediate in alkyd resin production. One plant of the stated size would produce about 10 percent of the total naphthalene entering the chemical market in 1949.

Other products of importance to the chemical industry that may be produced in appreciable quantities are tar acids, tar bases, propylene, butylenes, toluene, xylenes, and higher molecular weight aromatics.

### Shale-Oil Refining Research

For the past year efforts have been directed largely to developing methods for treating thermally cracked shale gasoline and to improving distillate stocks for use as Diesel fuels or catalytic cracking stocks. As background for the gasoline-treating research, extensive studies were made of the properties of this type of gasoline and the polymer formed when it was acid-treated. This work has resulted in the development of a catalytic treating method which appears to have advantages over those previously used. It indicates also that low-temperature acid treating itself may be essentially a catalytic treating process and suggests lines of investigation that may result in improved acid-treating techniques. Solvents have been found that are more effective in preparing catalytic cracking stocks and Diesel fuels from shale-oil distillates than those studied in the past. Equipment has been assembled for use in extending the study of the hydrogenation of shale oil and shale-oil distillates to pressures above 1,500 p.s.i., the maximum safe operating pressure of equipment available for past studies. This new equipment, now virtually ready for operation, will permit a more complete evaluation of the hydrogenation process as a method for refining shale oil.

### Properties of Thermally Cracked Gasoline

Gasoline prepared at the Demonstration Plant at Rifle, Colo., by thermally cracking N-T-U gas oil was separated into 20 fractions of approximately 5 volume percent each, and those properties of these fractions that are important in gasoline specifications were determined. It was found that sulfur compounds and gum-forming constituents were concentrated largely in the high-boiling portion of this gasoline, as shown in figures 48 and 49, respectively, while octane numbers, as shown in figure 50, varied widely over the boiling range. A small part of the sulfur can be removed by washing with dilute sodium hydroxide, as indicated by the shaded areas in figure 47, but the major portion of it is unaffected by such treatment. The peaks of sulfur content occur in fractions corresponding in boiling points to the thiophenic sulfur compounds that have been identified in other thermally cracked shale naphthas.

The gum content and octane ratings vary periodically, the low octane numbers occurring in fractions taken near the boiling points of normal aliphatic hydrocarbons and the high values near the boiling points of aromatic and cyclic olefinic hydrocarbons. In general, the high-gum-content fractions are identical with high-octane fractions. This suggests that a major contribution to gum-forming proclivities of shale gasoline may be made by cyclic olefins, cyclic diolefins, or unsaturated aromatics. These types of

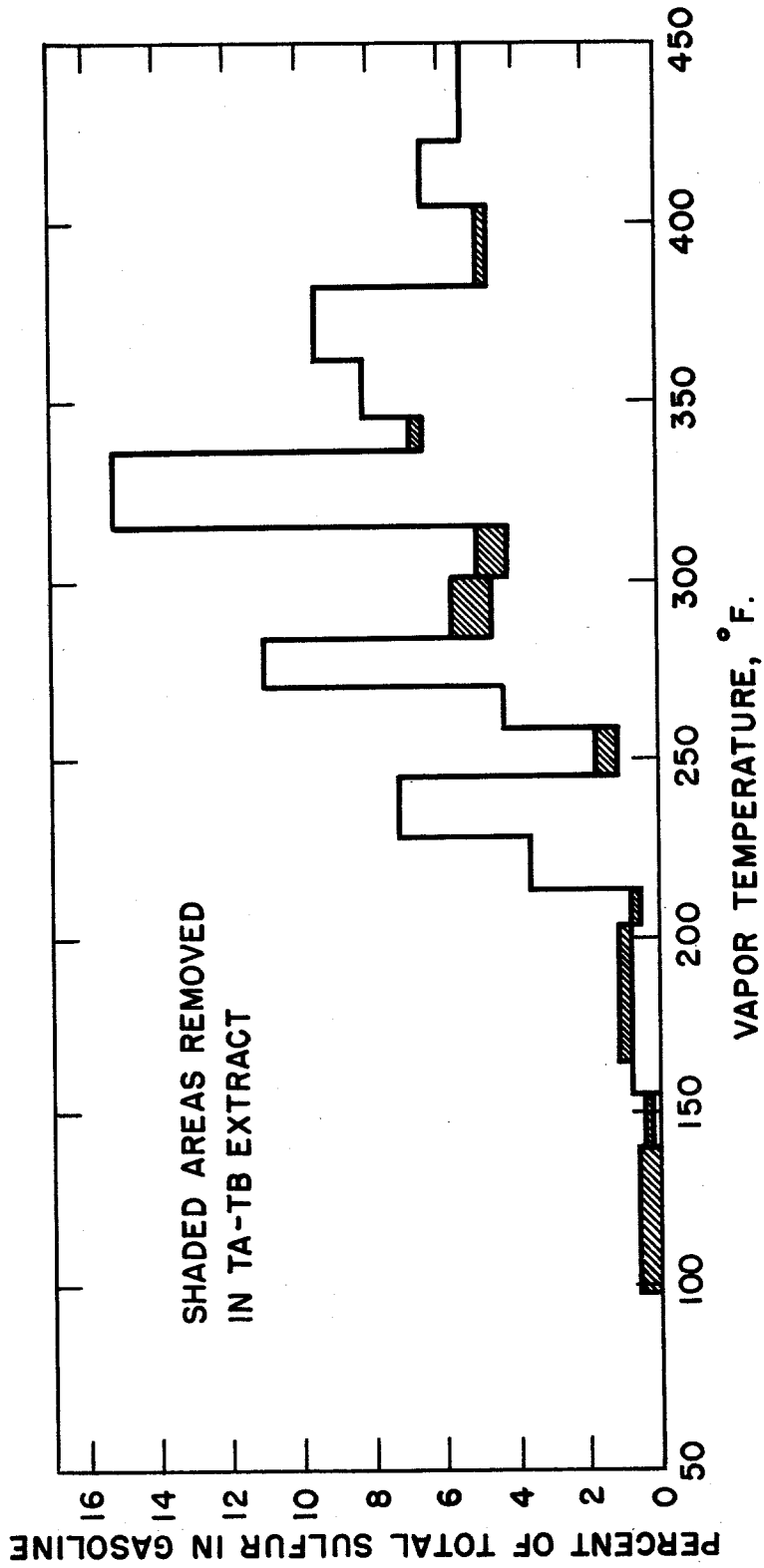


Figure 48. - Distribution of sulfur in thermally cracked gasoline.

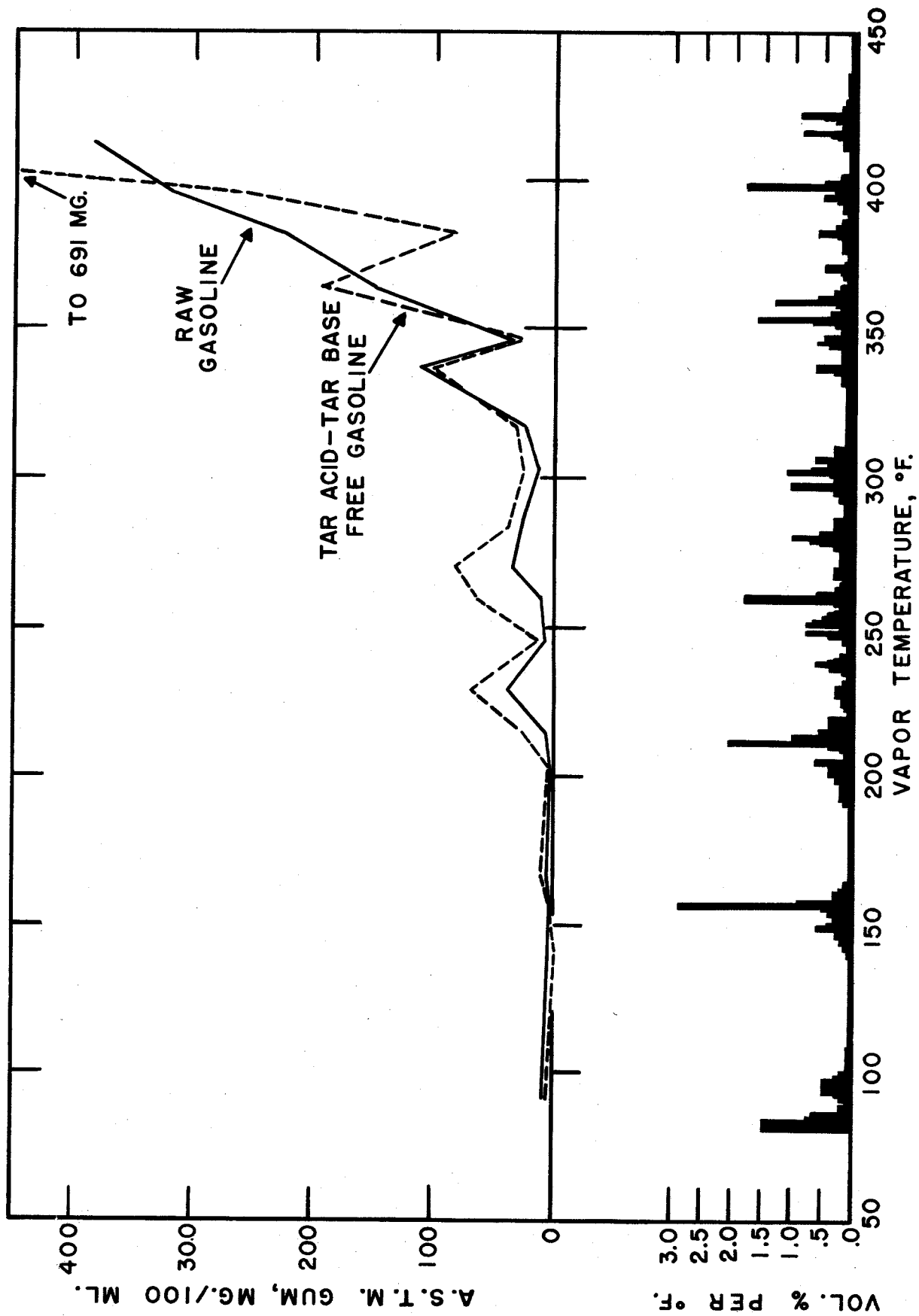


Figure 49. - Distribution of gum and distillation of thermally cracked gasoline.



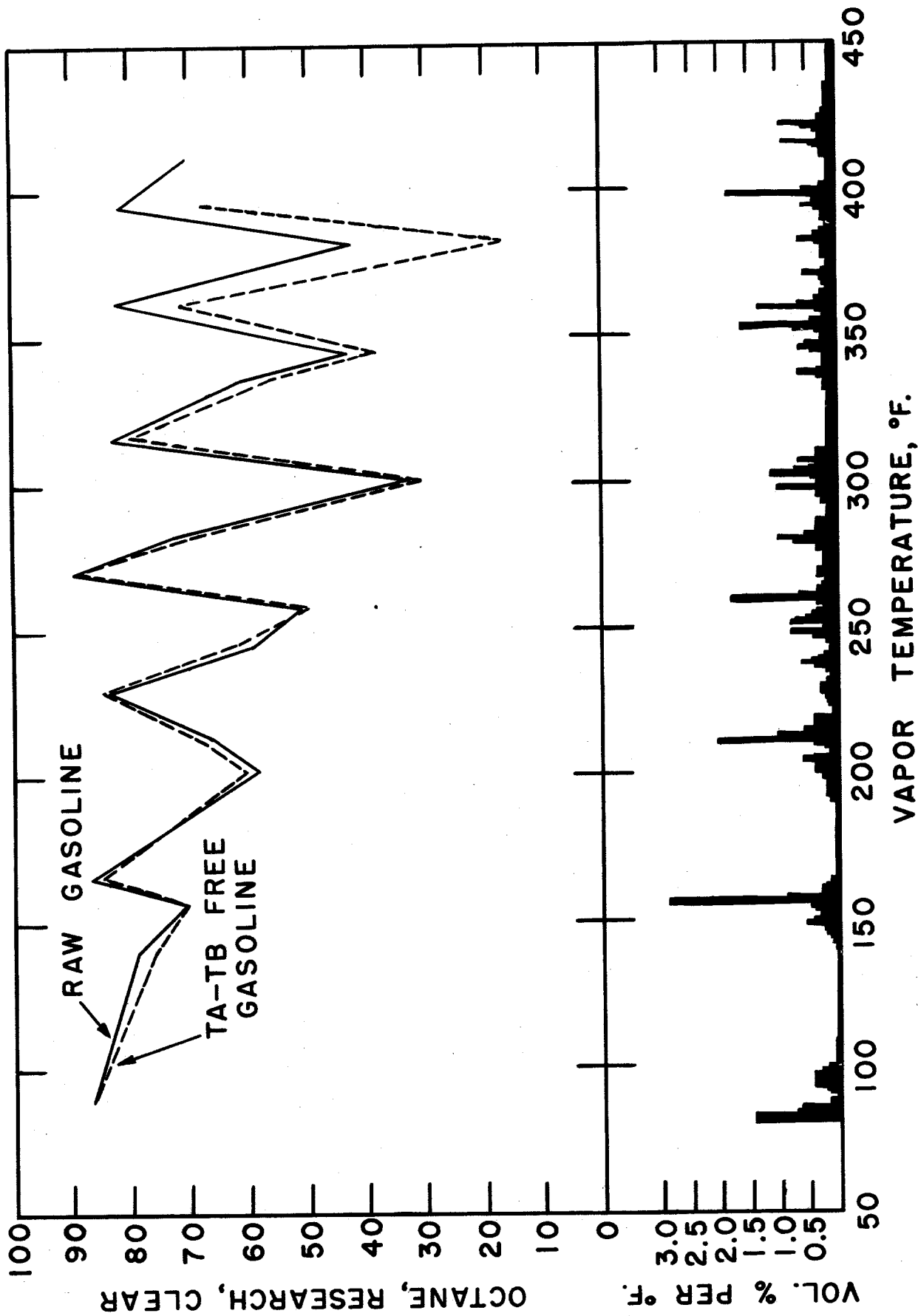


Figure 50. - Octane ratings of fractions of thermally cracked gasoline.

hydrocarbons all have high octane numbers and have been found, in petroleum research, to be bad gum formers, particularly cyclic diolefins and unsaturated aromatics.

Removal of tar acids and tar bases in most instances increased the gum content of the treated fractions. This may be due partly to a gum-inhibiting effect of these materials, but it appears more probable that the treating procedure itself provided opportunity for the unstable components to react to form gum through oxidation and other reactions, thus resulting in higher gum contents in the tar-acid-tar base free fractions. Removal of tar acids and tar bases resulted in an appreciable decrease in octane number in those fractions having a high nitrogen content. As the tar-base content of all fractions is much greater than the tar-acid content, this octane-number effect probably is a function of the amount of tar bases, largely alkyl pyridines, removed from each fraction. This effect is illustrated by the dotted curve in figure 50.

A considerable saving both in octane number and in volume of gasoline would result if tar bases could be left in shale gasoline, and research work has been done to determine if they have detrimental properties making their removal mandatory. So far, with the exception of odor and possibly color stability, no property of these tar bases has been proved to be detrimental. They burn satisfactorily in an internal-combustion engine without producing acid gases that would cause corrosion and seemingly do not contribute appreciably to gum formation. That they do make a worthwhile contribution to octane number is evident from table 29, which shows the calculated blending octane number of the tar acid-tar base component of various boiling-range fractions of this gasoline. In the highest-boiling range fraction, over 20 volume percent of the fraction is made up of tar bases, which means that a large volume loss, as well as a large octane-number loss, is suffered when they are removed. However, by acid treating they are automatically removed, and it may not be economical to recover and replace them in the gasoline. With the recent widespread interest in pyridines, particularly vinyl and methyl ethyl, for use in manufacturing pharmaceuticals, plastics, and synthetic rubber, these tar bases may have value as chemical raw materials.

TABLE 29. - Octane blending value of tar acid-tar base components of shale gasoline

Boiling range, °F.	Volume percent in fraction		Research octane blending value
	Tar acids	Tar bases	
284-301.....	0.3	3.7	143
301-315.....	.5	1.5	120
315-336.....	.2	5.2	123
336-346.....	.1	11.3	94
346-360.....	.1	4.6	122
360-380.....	.0	19.0	126
380-395.....	1.4	12.9	188
395-411.....	1.7	20.2	145

Properties of these 5-percent fractions show that thermally cracked shale gasoline can be separated advantageously into two portions, whose properties are shown in table 30. The fraction boiling below 258° F. and representing approximately 50 volume percent of the total has low sulfur, nitrogen, and gum contents and good octane numbers, while the fraction boiling above 258° F. contains a major portion of the undesirable constituents. The light naphtha requires only a mild treatment to make a good gasoline blending stock, while the heavy fraction needs severe treatment. By separating the light naphtha before treatment, savings in volume of materials and in size of treating equipment can be made that will be reflected in the cost of treatment.

TABLE 30. - Properties of low-boiling and high-boiling fractions of thermally cracked gasoline

	Boiling range, °F.	
	98-258	258-417
Volume percent of total gasoline.....	50.1	49.9
Sulfur.....weight percent	.19	1.06
Nitrogen.....do.	.17	1.64
Gum, A.S.T.M. ....mg. per 100 ml.	3	1,600
Gum, copper dish.....do.	10	5,000
Octane number, motor method, clear.....	70.0	66.0
Octane number, motor method, +3 ml. tetraethyllead....	76.8	72.3
Octane number, research method, clear.....	79.2	73.4
Octane number, research method, +3 ml. tetraethyllead.	88.2	79.3
Hydrocarbon type:		
Paraffins.....volume percent of neutral oil	34	29
Naphthenes.....do.	8	6
Olefins.....do.	52	37
Aromatics.....do.	6	28

#### Hydrotreating of Heavy Naphtha

Studies have been made to determine suitable processing conditions for refining the heavy naphtha portion of shale gasoline, using cobalt molybdate catalyst. It has been found that, at temperatures of 950° to 980° F., pressures from 600 to 800 p.s.i., hydrogen flow rates from 2,000 to 3,000 cubic feet per barrel of feed, and space velocities from 5 to 7.5 volumes of charge per volume of catalyst per hour, good recoveries can be obtained of a naphtha containing very little sulfur and gum. Nitrogen is not completely removed under these conditions.

Table 31 shows the properties of a hydrotreated heavy naphtha and of a blend of this product with the light naphtha previously separated from the raw gasoline.