

TABLE 31. - Properties of hydrotreated heavy naphtha and blended gasoline

	Hydrotreated high-boiling naphtha	Blend of hydrotreated and low-boiling naphthas
Sulfur.....weight percent	0.02	0.13
Nitrogen.....do.	.60	.31
Gum, A.S.T.M.....mg. per 100 ml.	5.2	5.6
Octane number, motor method, clear.....	68	69
Octane number, motor method, +3 ml. tetraethyllead.....	81	79
Octane number, research method, clear.....	75	77
Octane number, research method, +3 ml. tetraethyllead.....	88	88
Hydrocarbon types:		
Paraffins.....volume percent	52	45
Naphthenes.....do.	0	2
Olefins.....do.	6	26
Aromatics.....do.	42	27

Acid-Treating Shale-Oil Naphtha

While hydrotreating produces a shale gasoline of good quality, acid treating still offers some advantages in simplicity, and a study of this process is continuing both at Laramie and Rifle in an effort to improve the method.

A characteristic that frequently appears in acid-treated shale gasoline before it is redistilled is the negative tetraethyllead susceptibility of the material. This phenomenon often has been found to be associated with such hydrocarbons as cyclic olefins, cyclic diolefins, indenenes, fulvenes, and aromatics with unsaturated side chains. The fact that it sometimes occurs in acid-treated shale gasoline but not in untreated gasoline suggests that some such compounds as those listed form in acid treating. Of those listed, aromatics with unsaturated side chains appear most likely to form through alkylation of aromatics with some of the olefins or diolefins present.

To study this phenomenon further, a sample of the polymer formed in acid treating and recovered upon redistillation of the treated stock was fractionated; and properties of the fractions, including octane number, and, where applicable, cetane number, were determined. The distillation curve, octane numbers and sulfur contents of fractions of this polymer are shown in figure 51. Several pronounced peaks occur in the octane rating curve, and analyses show that these fractions have high aromatic contents. Those fractions above 475° F. range upward from 60 volume percent aromatic compounds and contain a large portion of the sulfur originally distributed in the gasoline fractions boiling below 400° F. It is these high-aromatic, high-sulfur-content fractions of the polymer that exhibit negative tetraethyllead susceptibility, as indicated in figure 51, and that, if left in the gasoline after treating,

result in a gasoline of negative lead susceptibility. This suggests that thiophenic sulfur compounds, as well as perhaps aromatic hydrocarbons, are alkylated by some of the olefins or diolefins in the gasoline during low-temperature acid treating, thereby increasing in molecular weight and boiling point to such an extent that they are removed from the boiling range of gasoline and can be separated by distillation. This is borne out by the fact that acid treating without redistillation commonly results in only moderate changes in sulfur content, while acid treating followed by redistillation to the original end point results in large decreases in sulfur content of the gasoline.

Another reaction that may occur during acid treating is alkylation or polymerization of aliphatics to produce higher-molecular-weight aliphatics, which also are separated from the acid-treated stock during redistillation. The evidence for this can be found in that portion of the acid polymer boiling near the end point of the original gasoline, which contains nearly 70 percent paraffins and/or naphthenes and has a cetane number near 60. Some question remains that at least part of this material may have been in the original gasoline and was not formed in acid treating. Further studies are being made to clarify this point.

The results of this work to date indicate that acid treating may have potentialities beyond those commonly expected. There is evidence of typical carbonium-ion type reactions that result in (1) alkylation of the sulfur compounds to higher-molecular-weight products, which can be removed from the gasoline by distillation, and (2) formation of some high-boiling aliphatic compounds, which may be salvaged from the polymer and used as high-cetane blending stocks. Experimental work is being done to determine if conditions for acid treating can be found that will produce a better over-all product than that obtained at the low temperatures now being used. Studies also are being made to determine which components of thermally cracked gasoline react during acid treating. This knowledge may indicate advantageous fractionations that may be made before acid treating to control the type of alkylate or polymer formed.

Solvent Extraction

Work has continued on studies of solvent extraction (see fig. 52) as a means of obtaining catalytic cracking stocks and high-cetane Diesel fuels from shale-oil distillates. It has been found that low molecular-weight carboxylic acids, particularly formic and acetic, are more effective than any solvents used previously in producing raffinates of low nitrogen content and good cetane number. These extracted stocks, prepared from light gas oil, can be used as Diesel fuel or charged to catalytic cracking units with much improved operation over raw gas-oil charge stocks. The best raffinates obtained to date in high yields contain more nitrogen, the troublesome constituent in catalytic cracking stocks, than is desirable; but considerably longer catalyst life has been observed in cracking these stocks than when cracking raw shale-oil distillates. Yields and properties of typical raffinates from formic and acetic acid extraction are shown in table 32. Whether solvent

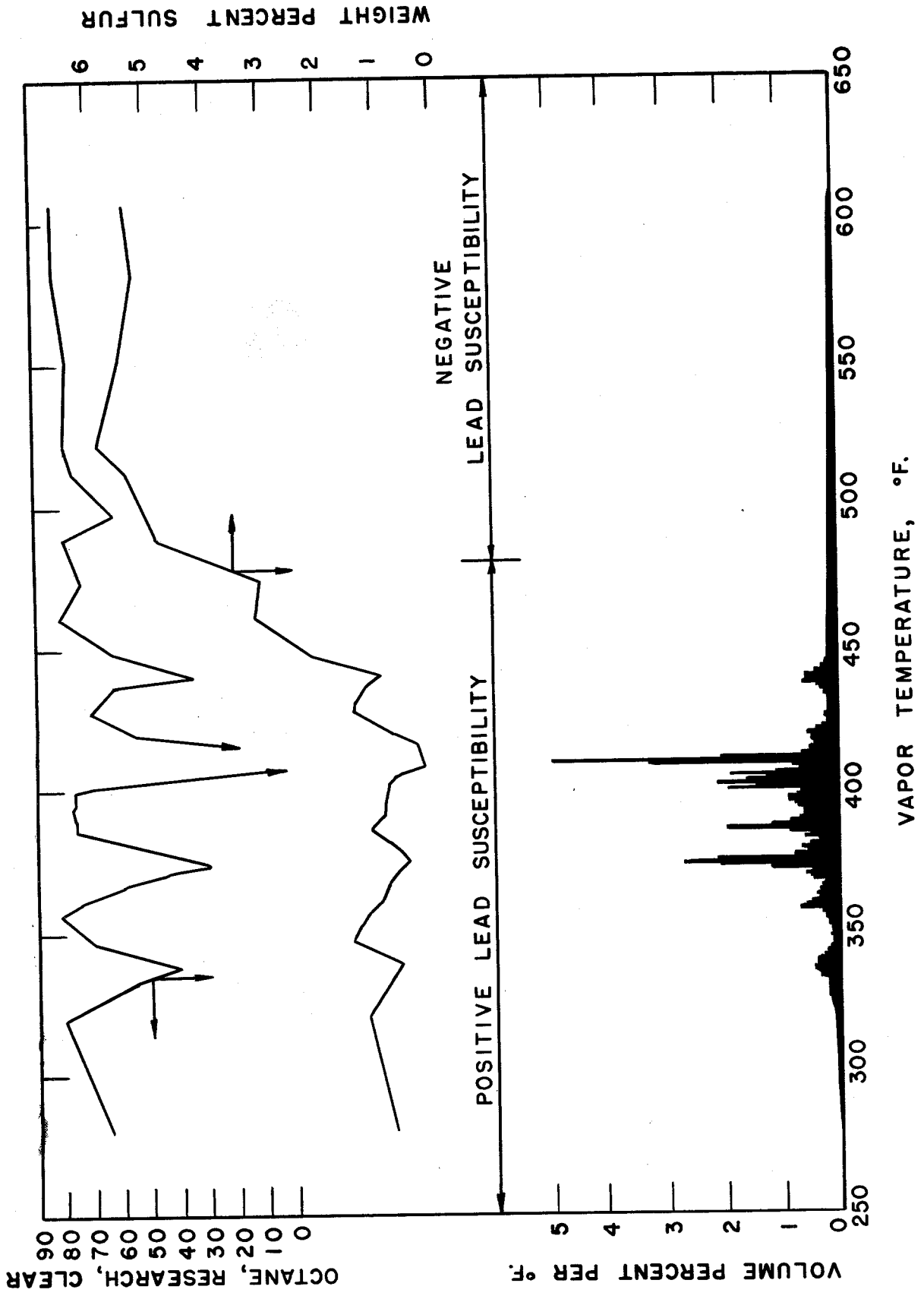


Figure 51. - Properties of fractions of polymer from acid-treated thermally cracked gasoline.

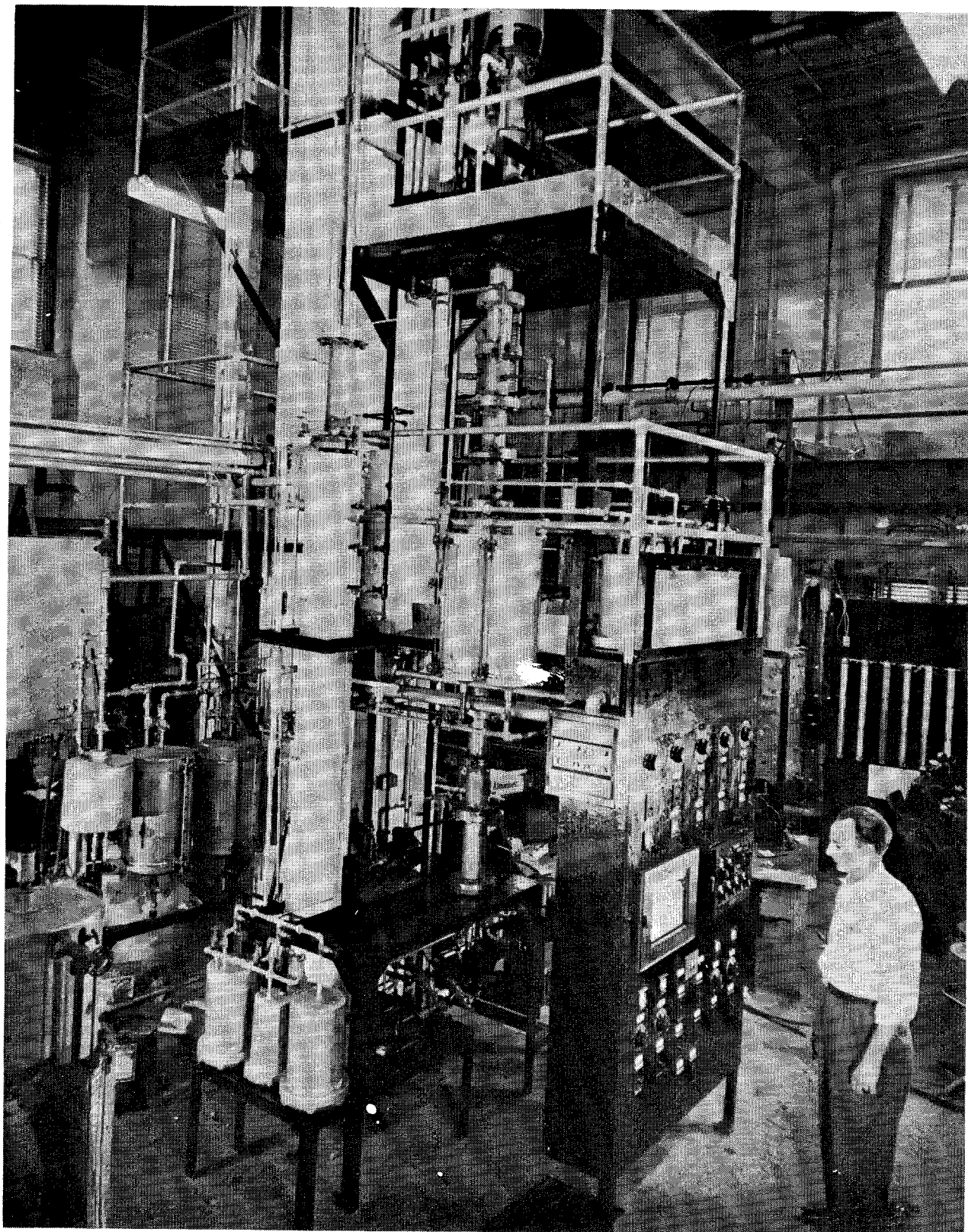


Figure 52. - Continuous solvent-extraction unit.

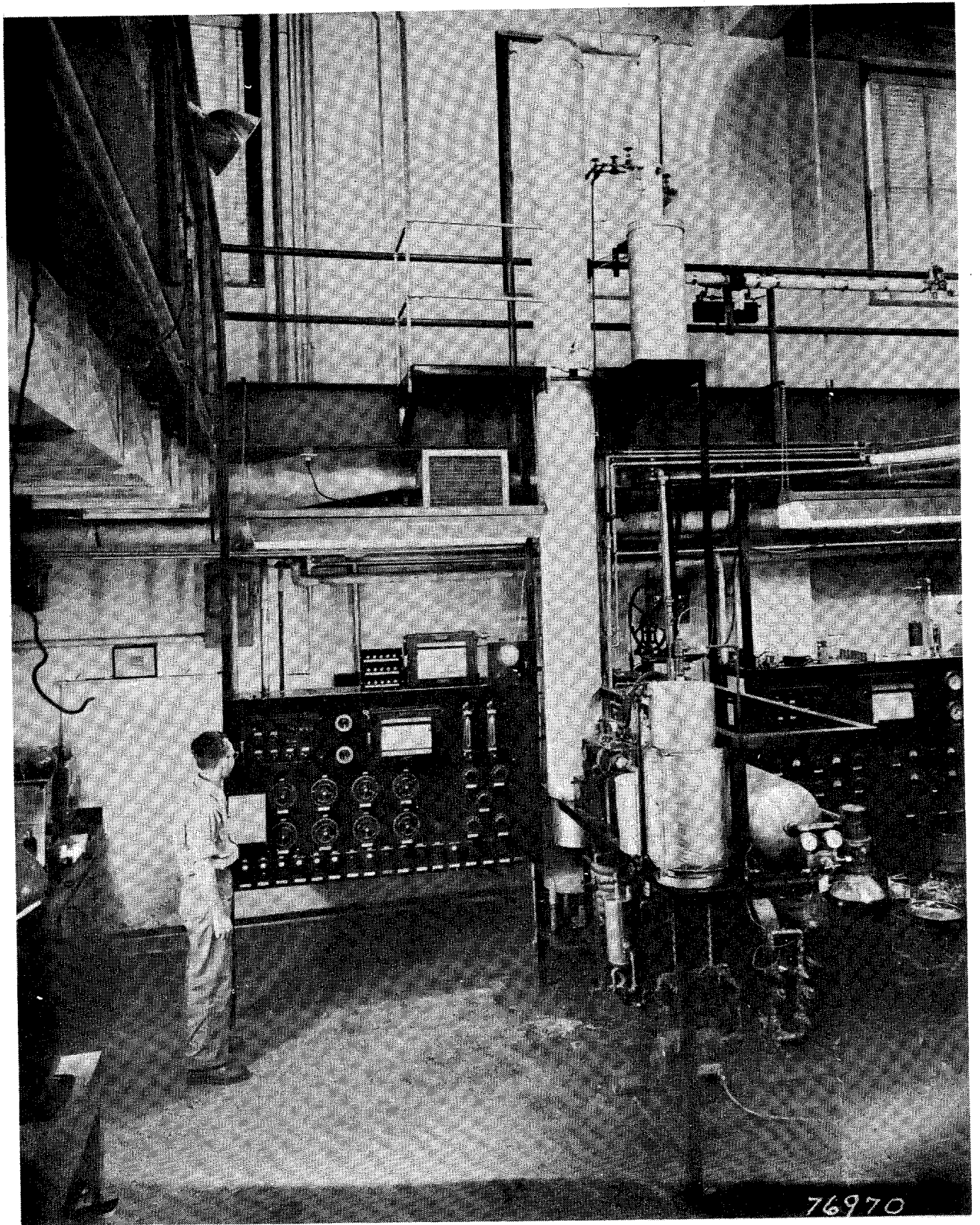


Figure 53. - Fixed-bed catalytic cracking unit.

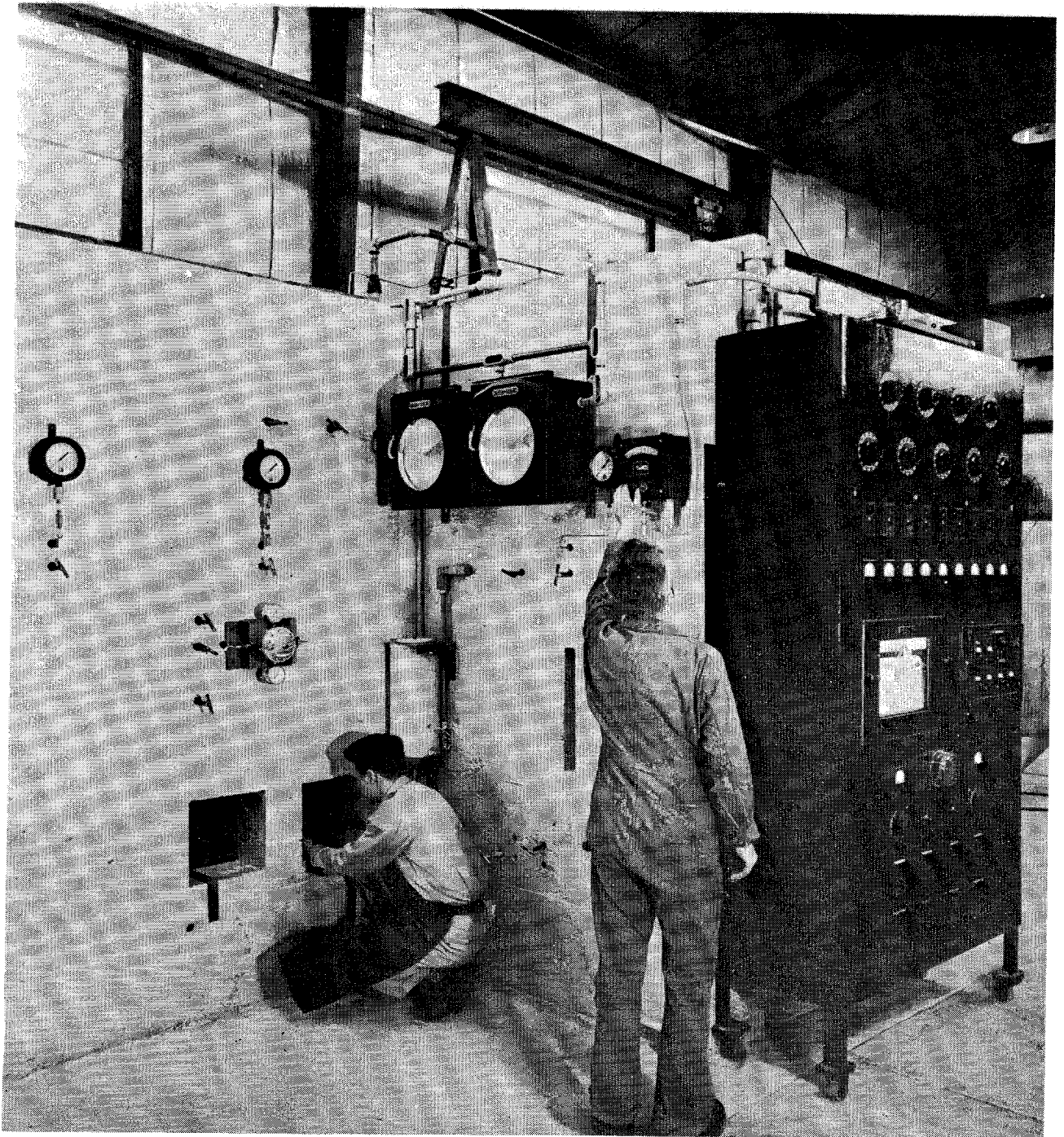


Figure 54. - High-pressure-hydrogenation unit.

extraction can be used to advantage as a shale-oil processing method now is largely a matter of comparative cost.

TABLE 32. - Properties of raffinates from light gas oil

	Charge stock	Raffinates	
		Formic acid	Acetic acid
Solvent.....			
Yield.....Volume percent of charge	100	79.0	77
Gravity..... ^o A.P.I.	30.0	34.6	34.6
Viscosity.....S.U.S. at 100 ^o F.	40.0	37	38
Viscosity.....gravity constant	.861	.843	.842
Sulfur.....weight percent	.77	.73	.82
Nitrogen.....do.	1.37	.22	.36

Catalytic Cracking

Numerous catalysts have been prepared and tested in an effort to improve gasoline yields and catalyst life when cracking shale-oil distillates (fig. 53). However, no catalyst yet has been found that appears to have a pronounced advantage over those commonly used in petroleum processing. Gasoline yields and catalyst life appear to be a direct function of the nitrogen content of the cracking stock, and removal of even small percentages of nitrogen compounds considerably improves catalytic cracking results. As a consequence, recycle gas oil has been found to be a better cracking stock than the virgin gas oil. Recycle oils still contain considerable nitrogen but less than the original charge. In this respect, catalytic cracking differs from thermal cracking, at least at low conversions. In thermal cracking the nitrogen content of the recycle gas oil tends to increase over that in the original charge.

It was shown previously that pyridine-type nitrogen compounds have excellent octane blending values and apparently do not have other properties that are detrimental to quality or cannot be overcome.

If more of these pyridine compounds could be formed in the gasoline by decomposition of high-molecular-weight nitrogen compounds, a gain both in quantity of gasoline and in octane number could be had. Catalytic cracking appears to tend to accomplish this; but, unfortunately, cracking catalysts are poisoned or deactivated rapidly by these nitrogen compounds. Efforts to develop catalysts less affected by nitrogen compounds will continue.

Hydrogenation

Hydrogenation studies have been limited largely to hydrotreating of thermally cracked naphthas, as discussed earlier. This was necessary because a treating process for shale gasoline had to be developed and because past work had demonstrated that heavy shale-oil distillates and crude shale oil could not be hydrogenated effectively at the operating pressures obtainable with the equipment available. To study hydrogenation of these heavier stocks, a unit (see fig. 54) is being built in which higher pressure can be used. Now nearly completed, this unit will make possible a more thorough study of hydrogenation.

Characteristics of Asphaltic Residuums from Shale Oil

Asphaltic residuums of different consistencies were prepared from N-T-U shale oil by (1) vacuum distillation, (2) propane precipitation, (3) thermal cracking, and (4) air blowing. From analyses of these products, the properties of the 100-penetration asphalts were estimated and are shown in table 33. The asphaltic residuum prepared by vacuum distillation of bottoms from the recycle cracking of N-T-U shale oil had lower values for bitumen content, bitumen solubility in carbon tetrachloride, ductility, and viscosity, but it had a higher specific gravity than the other shale-oil asphalts. The propane-precipitated asphalt had the highest ductility and apparently contained the least wax. All of the shale-oil asphalts showed positive spot tests with 100 percent xylene. (The air-blown asphalt was too dark for this test; however, its charge stock had a positive spot.)

TABLE 33. - Properties of 100-penetration asphalts from shale oil

	Type of asphalt			
	Residual	Propane- precipitated	Thermally cracked	Air- blown
Yield from crude oil...weight percent	16	18.8	38.5	31.4
Maximum liquid temperature.....°F.	685		433	455
Ash.....percent	.0	.0	.0	.0
Bitumen.....do.	99.8	99.8	97.5	99.8
Bitumen soluble in CCl ₄do.	99.7	100.0	94.5	100.0
Carbon residue.....do.	20.7	13.8	18.6	15.8
Ductility at:				
77° F., 5 cm./min.....cm.	98	150+	95	
Nitrogen.....percent	2.84	2.72	2.91	
Penetration at:				
32° F., 200 gm. wt., 60 sec.....dmm.	10	11	15	18
60° F., 100 gm. wt., 5 sec.....do.	19	20	24	30
77° F., 100 gm. wt., 5 sec.....do.	100	100	100	100
Penetration at 77° F. of residue from loss-on-heating test.....dmm.	69		67	
Softening point.....°F.	113	111	110	114
Specific gravity, 77°/77° F.....	1.019	1.029	1.053	1.012
Spot test by:				
100 percent xylene.....	Positive	Positive	Positive	1/
Sulfur.....percent	0.57	0.61	0.53	
Viscosity, Furol, at:				
210° F.....seconds	403		155	
275° F.....do.	53		24	

1/ Sample was too dark to detect spot; however, the charge stock had a positive spot with 100 percent xylene.

The shale-oil asphalts differed from petroleum asphalts in several respects. Table 34 compares the vacuum-reduced asphalt from N-T-U shale oil with the corresponding asphalts from four samples of petroleum. The shale-oil asphalt was characterized by a positive spot; low solubility in carbon disulfide (bitumen content) and carbon tetrachloride; low ductility, viscosity, and sulfur contents; and high temperature-susceptibility and nitrogen contents. Based upon appearance, the shale-oil asphalt also contained more wax than the petroleum asphalts.

TABLE 34. - Properties of residual 100-penetration asphalts from shale oil and petroleum^{1/}

	N-T-U shale oil	Petroleum ^{2/}			
		Kern River, Calif.	Byron, Wyo.	Oregon Basin, Wyo.	Tampico, Mexico
Yield from crude oil.....weight percent	16	55	27	45	74
Bitumen.....percent	99.8	100.0	100.0	100.0	99.9
Bitumen soluble in CCl ₄do.	99.7	100.0	100.0	100.0	100.0
Carbon residue.....do.	21	14	25	20	22
Ductility at:					
77° F., 5 cm./min.....cm.	98	100+	100+	100+	595
Fire point.....°F.	695	635	720	655	495
Flash point.....do.	575	540	625	565	
Loss on heating.....percent	.06 to .03	.00	.03	.00	.2
Nitrogen.....do.	2.84	1.18	.61	.66	.52
Penetration at:					
32° F., 200 gm. wt., 60 sec.....dmm.	10	13	19	21	32
60° F., 100 gm. wt., 5 sec.....do.	19	28	33	30	43
77° F., 100 gm. wt., 5 sec.....do.	100	100	100	100	100
Penetration at 77° F. of residue from loss-on-heating test.....do.	69	89	82	85	84
Softening point.....°F.	113	108	112	113	117
Specific gravity, 77°/77° F.....	1.019	1.010	1.024	1.026	1.036
Spot tests ^{3/}	Positive	Negative	Negative	Negative	Negative
Sulfur.....percent	0.6	1.23	3.9	4.8	6.1
Viscosity, Furol, at:					
210° F.....seconds	403	730	1,180	1,300	2,700
275° F.....do.	53	83	140	160	290

^{1/} Estimated from properties of series of asphalts of different penetrations.

^{2/} Reported by Stanfield, K. E. and Hubbard, R. L., Asphalts from Rocky Mountain Crude Oils: Laboratory Preparation and Comparison: Bureau of Mines Tech. Paper 717, 1949, 77 pp.

^{3/} By the Ollienis and heptane-xylene equivalent tests.

The properties of the shale-oil asphalts can be varied greatly by blending and by utilizing different methods of refining. Except for a positive spot test, it appears that asphalts can be prepared from Colorado shale oil that will meet specifications for road oils and asphalts, or other special applications. According to Robertson,^{4/} satisfactory asphalts of the air-blown and vacuum-refined types are manufactured from oil of South African torbanites. Road oils of the rapid- and medium-curing types, which also have positive spot tests, have given good service in the construction of roads throughout southern Africa from Cape Province to the Belgian Congo.

Oil-Shale Research and Analysis

Analytical research on the composition and characteristics of oil shale included: The development and improvement of analytical methods; analyses of representative oil shales from the Demonstration Mine near Rifle, Colo., and from other domestic and foreign deposits; and a study of the constitution of the organic material in Colorado oil shale. The basic data obtained in these studies were used in other projects concerning the extent and richness of oil shale deposits, the mining of Colorado oil shale, and the processing of Colorado oil shale into liquid fuels and other products.

Assays and Miscellaneous Analyses

Some assays and analyses of oil shales from the Green River formation in the vicinity of Rifle, Colo., have been reported in previous annual reports. As shown in figure 55, two series of samples from the Mahogany ledge at the oil-shale mine have been analyzed: A series of 6 grades of shale assaying 10.5 to 75 gallons of oil per ton and 10 samples representing the 9 constituent beds and a composite of the entire Mahogany ledge. Complete results of these analyses, which include petrographic and X-ray examinations, determinations of shale properties, ultimate and oxide analyses, assays and examinations of assay products, and weathering tests, have just been published in Bureau of Mines Report of Investigations 4825. This report presents the most-extensive analytical data available to date on Colorado oil shale and provides a means of estimating the properties of different grades of the oil shale, or of materials obtained by mining one or more of the mineable beds in the Mahogany ledge at the mine.

A total of 3,458 assays was completed on 3,446 samples, principally on samples of Green River oil shale from cores and cuttings of oil and gas wells. For the most part, the assay results were used as a basis for determining the extent and richness of oil shale deposits in Colorado, Utah and Wyoming.

In addition to the miscellaneous analyses mentioned above, improved analytical methods were developed for the combustion and oxide analysis of oil shale and its products. Carbon and hydrogen determinations were made on approximately 770 samples and oxide analyses were completed on 40 foreign oil shales. Recent tests indicated that the curve showing the relation between the specific gravity of Colorado oil shale and its assay oil yield, as presented in the 1946 annual report, was not precisely applicable to the oil shale now being obtained from the oil-shale mine. To prepare a more representative curve, assays and specific gravity determinations are being made on 1-foot core samples extending through the entire Mahogany ledge.

^{4/} Robertson, G. G., The Refining of South African Torbanite Crude Oil: Second Oil Shale and Cannel Coal Conference at Glasgow, Prepr. B. 10, July 1950.

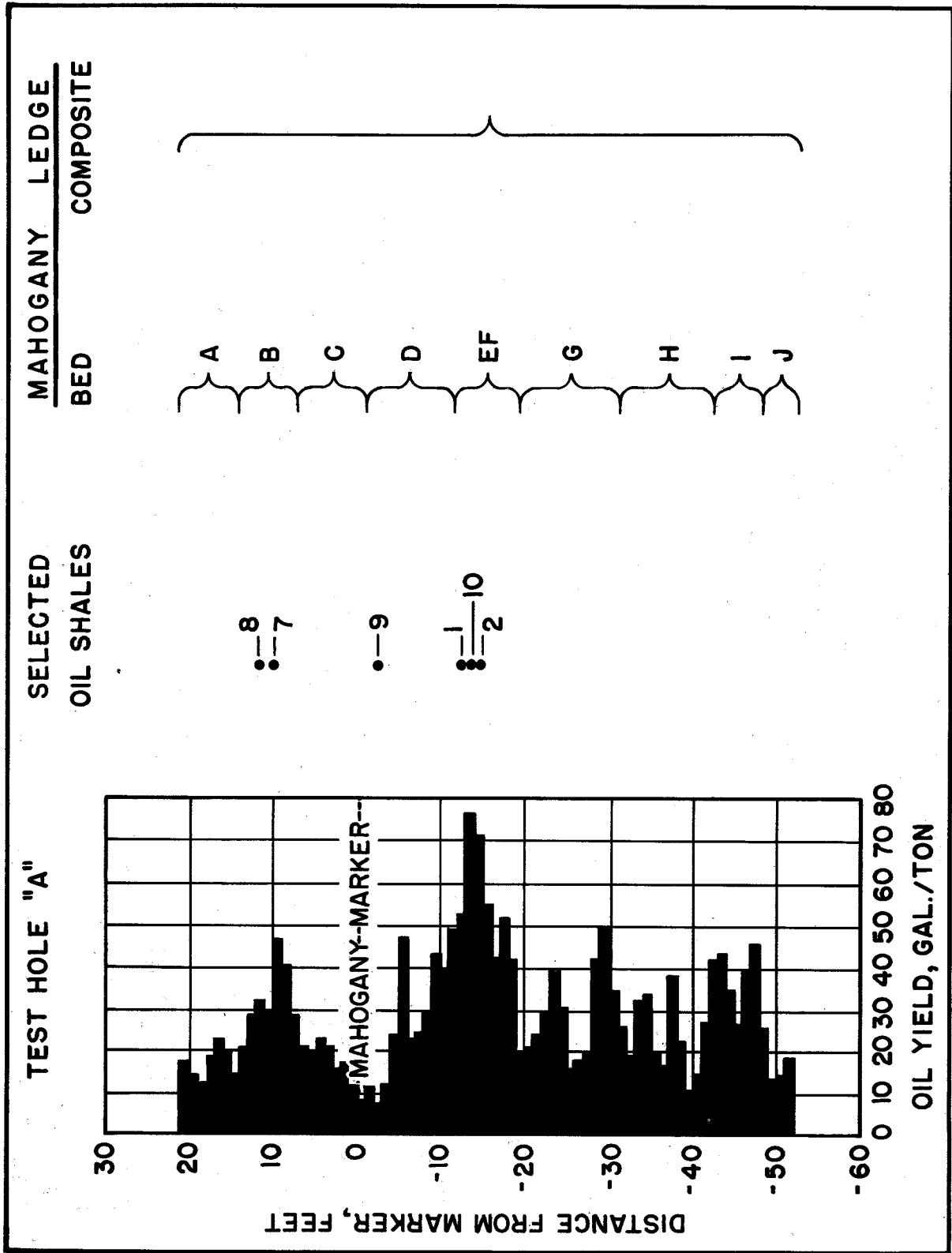


Figure 55. - Source of oil-shale samples with reference to Mahogany marker, Rifle, Colo.

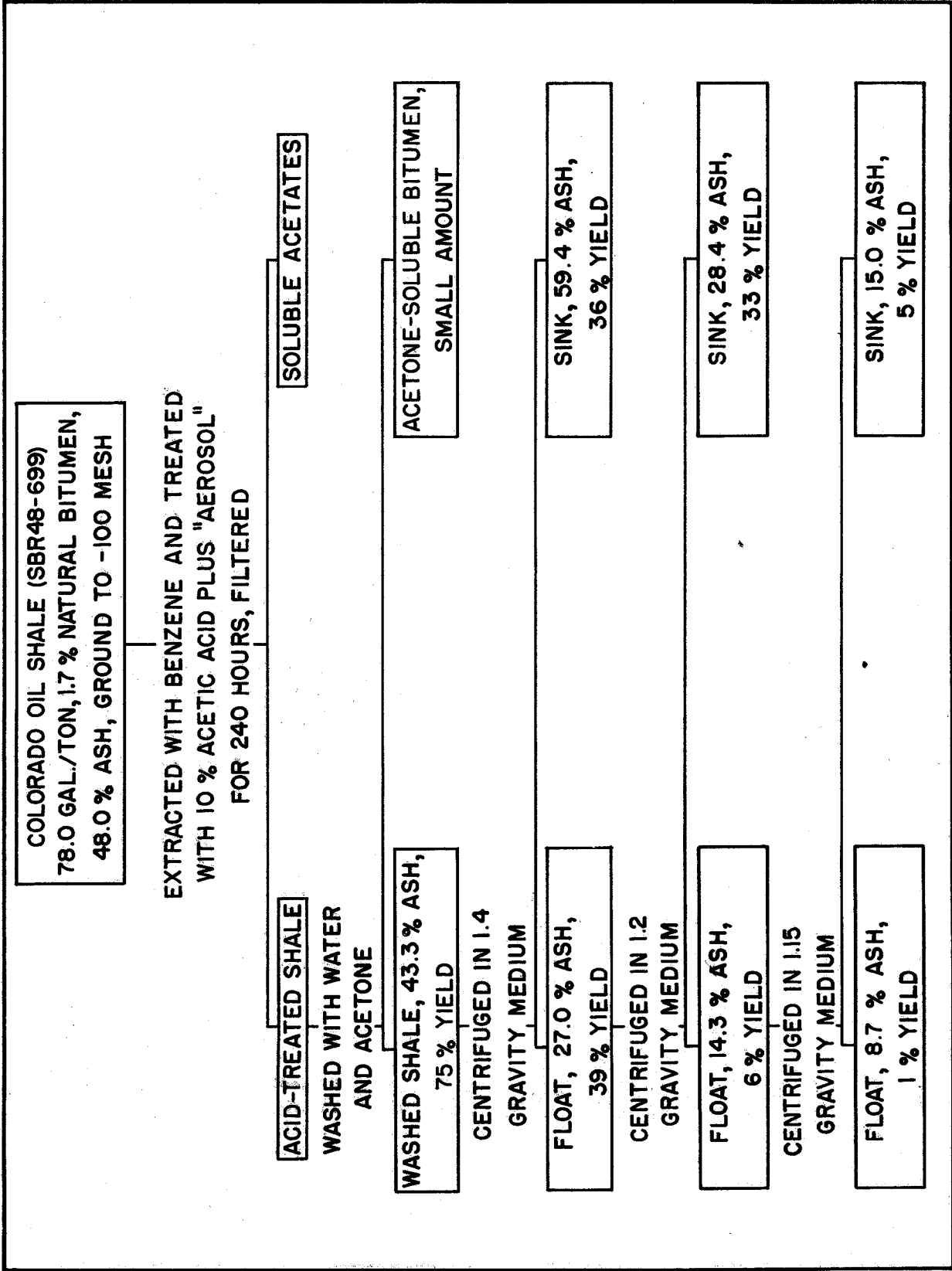


Figure 56. - Scheme for concentrating kerogen in Colorado oil shale.