

CHARACTERIZATION OF A UTAH TAR SAND BITUMEN

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INTRODUCTION

Until recently, tar sand deposits have been of relatively little importance as an energy resource. Increasing demands for energy have prompted a greater effort to utilize the energy stored in bituminous sandstone deposits. The inaccessibility of the bitumen, which is generally impregnated in subsurface sandstone, and the high viscosity of the bitumen present major problems with recovery. The high viscosity, heteroatom content, and molecular weight cause problems with utilization. Knowledge of the composition of tar sand bitumens would facilitate the accurate prediction of the chemical and physical behavior of these bitumens in recovery and refining processes.

Recently, several studies have been made to determine the properties of tar sand bitumens. Wood and Ritzma (1) and Gwynn (2) have studied several Utah bitumens. Camp (3) has made a comprehensive study of the Athabasca tar sand deposits. Speight (4) has studied the effects of thermal cracking on Athabasca bitumens. Generally, the analysis of the total bitumens included physical properties, elemental analysis, distillation, and infrared spectroscopy. Detailed analysis of the chemical composition of a total bitumen is difficult because of the complexity of these samples. Separation of the total bitumen into simpler fractions would facilitate compound-type characterization.

This study presents the results of a preliminary examination of a P.R. Spring, Utah, tar sand bitumen. Physical properties, elemental analysis, and distillation data are given and compared to literature values for other P.R. Spring samples. The separation of the bitumen, using selected techniques developed in our laboratory (5-9), into acid, base, neutral nitrogen, saturated, and aromatic hydrocarbon fractions is described. The analytical results of the separation are compared with those for high-boiling petroleum residues separated in a similar fashion. This comparative information could provide an evaluation of the bitumen for processing because more is known of the processing characteristics of petroleum fractions than of tar sand bitumens.

EXPERIMENTAL

Description of Bitumen Sample

The core that was extracted to produce the bitumen came from Colvert No. 1, NW $\frac{1}{4}$ SE $\frac{1}{4}$, sec. 35, T. 15 S., R. 22 E., Uintah County, Utah. The tar-bearing sand occurred in the P.R. Spring deposit, Douglas Creek Member, Green River Formation of Tertiary age. Core samples from Colvert No. 1 showed that tar-bearing sand occurred intermittently between the depths of 64 and 162 feet. Approximately 2-inch sections were taken from each foot between 84 and 117 feet, combined, and exhaustively extracted with benzene in a Soxhlet extractor. The benzene extract was filtered through a 4.0 to 5.5- μ fritted glass disk funnel, and the benzene was removed by vacuum distillation (75 to 80°C, 40 to 50 mm Hg). The recovered bitumen was used for property measurements and as the starting material for the separation into defined fractions.

Simulated Distillation of Bitumen Sample

The boiling-range distribution of the recovered bitumen was determined by simulated distillation gas-liquid chromatography using the procedure of Poulson et al (10). Boiling points are determined by calibration with a mixture of n-paraffins ranging from C₁₁ to C₄₂. The upper limit for boiling-point determination in this analysis is about 540°C (1000°F).

Separation of the Bitumen into Defined Fractions

The procedure was an extension of one developed for the separation of high-boiling petroleum cuts into five fractions--acids, bases, neutral nitrogen, saturates, and aromatics (5). This separation and the further division of the first three fractions into subfractions is shown schematically in Figure 1.

A 20-g sample of the bitumen was dissolved in cyclohexane and charged to a column containing 50 g of Amberlyst* A-29 anion exchange resin on top of 50 g of Amberlyst 15 cation exchange resin (Rohm and Haas). The column was exhaustively eluted with cyclohexane to remove nonreactive material. The resins were removed from the column, separated, and placed in individual Soxhlet extractors. The acids were extracted from the anion resin with 1) benzene, 2) 60% benzene-40% methanol, 3) 60% benzene-40% methanol saturated with carbon dioxide at < 0°C, 4) 5% acetic acid-95% benzene. These last two solvent mixtures were applied manually rather than by the usual Soxhlet reflux because they do not form azeotropes. The bases were removed from the cation resin in a similar fashion using the solvents 1) benzene, 2) 60% benzene-40% methanol, 3) 8% isopropyl amine-55% benzene-37% methanol. These seven subfractions were retained separately for analysis and labeled, respectively, acids I, II, III, and IV and bases I, II, and III.

The neutral nitrogen compounds were removed from the acid- and base-free bitumen by chromatography in cyclohexane on FeCl₃/Attapulugus clay, packed in a column above Amberlyst A-29. The ratio of sample to FeCl₃/Attapulugus clay to anion resin was 1:13:17. Nitrogen compounds were recovered by successive column elution with 1,2-dichloroethane and 40% methanol-60% benzene to provide two subfractions. The methanol was removed from subfraction II, after which the ferric chloride was removed from the fraction by dissolving the sample in 1,2-dichloroethane and contacting the sample with the A-29 resin.

Saturated and aromatic hydrocarbons were separated from the acid-, base-, and neutral nitrogen-free bitumen by adsorption chromatography using silica gel as the adsorbent and cyclohexane as the eluting solvent. The cutpoint was made at two bed volumes. Aromatics were desorbed with 60% benzene-40% methanol.

Analysis of Defined Fractions

The separation procedure provided four acid subfractions, three base subfractions, two neutral nitrogen subfractions, saturated hydrocarbons, and aromatic hydrocarbons. Infrared analysis was employed for those functional groups that have definitive bands for which an average molecular extinction coefficient could be estimated. Table 1 lists the infrared bands and the apparent integrated absorption intensities used (7). Peak area was measured by planimetry. Quantitative IR spectra were measured in methylene chloride with 0.5-mm NaCl cells, using either a Perkin-Elmer 521 or 621 infrared spectrophotometer. Molecular weights of the individual fractions were determined by vapor-pressure osmometry in benzene.

*Reference to specific brand names or models of equipment is made for information only and does not imply endorsement by the Bureau of Mines.

TABLE 1. - Infrared assignments
and apparent integrated absorption intensity

	Wavenumber cm^{-1}	$l/\text{mole cm}^{-2} \times 10^4$
Phenols	3500-3640	0.5
Carbazoles	3420-3510	0.7
Carboxylic acids	1700-1790	1.5
Amides	1640-1700	1.5

Basic nitrogen was titrated according to the procedure of Buell (11). A Beckman Model 1063 potentiometric titrimeter with calomel and glass electrodes was used to titrate the bitumen solution with 70 percent perchloric acid in dioxane. The solvent system was 2:1 benzene:acetic anhydride. End points were determined at the inflection point of the curve. Calibration data allowed calculation of the percentage of titratable nitrogen in the sample. The half-neutralization potential (HNP), the potential of the curve midway through the titration, provides information on the strength of the bases.

Saturated hydrocarbons were examined with a CEC-21-110B mass spectrometer. The standard method for group-type analysis (12) was used to classify compounds according to structure.

RESULTS AND DISCUSSION

Properties of the Bitumen

The sandstone core from which the bitumen was extracted remained consolidated throughout the extraction. The extracted organics represented 5.27 weight percent of the core. The filtration of the bitumen to remove fine inorganic materials was adequate, as evidenced by ash content of only 0.17 weight percent. Specific and API gravities and elemental analysis for this bitumen, along with literature values for other P.R. Spring bitumens are given in Table 2.

TABLE 2. - Comparative properties of P.R. Spring bitumens

Property	Sample					
	A This study (core)	B Main canyon seep (2)	C Core 79 to 83 ft (2)	D Core 137 to 141 ft (2)	E Outcrop sample no. 69-13E (1)	F Outcrop sample no. 67-1A (1)
Specific gravity 60/60	.998	.974	.995	1.004	1.016	.969
API gravity	10.3	13.8	10.7	9.4	8.3	14.5
Elemental analysis (weight percent)						
Carbon	84.44				80.0	86.0
Hydrogen	11.05				9.5	10.9
Sulfur	.75	.34	.33	.40	.45	.36
Nitrogen	1.00	.77	.88	1.08	1.0	.67
Oxygen(a)	2.59					
C/H (atomic ratio)	.637				.702	.657
S/N (weight ratio)	.75	.44	.38	.37	.45	.54

(a) Determined by difference.

The bitumens selected for comparison are all from the P.R. Spring deposit of the Green River Formation. Samples B, C, and D were described by Gwynn (2) and E and F by Wood and Ritzma (1). Sample B is a surface seep from the Main Canyon. Samples C and D are core extracts, probably from the Douglas Creek Member. Samples E and F are outcrop extracts, again from the Douglas Creek Member. Although differences in gravity are apparent, there is no obvious correlation of gravity with surface or subsurface samples. The nitrogen content is variable among the samples and is another indicator of the variations in composition between samples. All samples are characteristically low in sulfur, as compared to bitumen samples from southern Utah or Athabasca that typically contain between 2 and 6 percent sulfur (1-4). The carbon-hydrogen atomic ratio of .637 indicates that the study bitumen is of average weight and aromaticity. Gwynn reports that the average carbon-hydrogen atomic ratio for 23 P.R. Spring samples is .635. Sulfur-nitrogen weight ratios of the P.R. Spring bitumens in Table 2 are less than 1, which is typical of both tar sand bitumens and crude oils.

The viscosity of the study bitumen was not determined. The study bitumen was semi-solid at room temperature (penetration 148) and only slightly fluid at 80°C. Thus, conventional viscosity measurements were not applicable. Standardized methods for the workup of the bitumen and the determination of viscosity have not been developed. Such methods must recognize the effect that entrained solvents and the loss of light ends during solvent removal have on viscosity. Camp (3) indicates that variations in these two phenomena are significant factors in the variations of viscosities from sample to sample.

Boiling-Point Distribution--Simulated Distillation

The boiling-point distribution of the material in the bitumen was determined using simulated distillation by gas-liquid chromatography. This technique has several advantages over conventional assay distillations. It is rapid and can analyze very small samples (30 mg). The boiling-point determination is extended by 120°C over that of the standard Bureau of Mines crude oil analysis (BMCOA). The relatively short contact time at higher temperatures minimizes the possibility of thermal cracking, which produces artifacts and alters the distillation curve. The amount of solvent that is entrained in the bitumen can be accurately determined so that its effects on other properties can be calculated or estimated. Complete removal of the extracting solvent is nearly impossible, and its presence in the bitumen affects the amount of recovery, the elemental analysis, and the viscosity.

Simulated distillation affords the option of choosing cutpoints for calculation of the boiling-range distribution. For purposes of comparison with other bitumens, cutpoints were chosen to coincide with the fraction for the BMCOA distillations. The GLC conditions used for the present analysis are designed to analyze the high-boiling portions and will not accurately resolve constituents boiling below 125°C. Hence, fractions 1 through 4 were combined in the calculation.

The simulated distillation results are given in Table 3, column A, along with literature values for the distillations of the P.R. Spring samples described in Table 2. The 0.4 percent material appearing in Fraction 1-4 for this study bitumen is the entrained benzene left from the extraction procedure. One advantage of the simulated distillation is quickly apparent--an additional four fractions (16 through 19) are displayed, giving more information about the bitumen. For the first 15 fractions, the simulated distillation results approximate those reported by Gwynn (2) in that no material boils below 250°C and the percentage of >420°C residue is high. The values reported by Wood (1), however, vary significantly in that substantial amounts of light ends are shown with very little material boiling between 275 and 420°C. These values

TABLE 3. - Distillation data for P.R. Spring bitumens

Fraction	Cut point, °C	Sample					
		A (a)	B	C	D	E	F
		This study (core)	Main Canyon seep (2)	Core 79 to 83 ft (2)	Core 137 to 141 ft (2)	Outcrop sample no. 69-13E (1)	Outcrop sample no. 67-1A (1)
1-4	125	0.4				2.2 ^(b)	
5	150					2.4	
6	175					1.2	
7	200					1.2	1.4
8	225					1.4	6.5
9	250	0.5				5.9	64.4
10	275	1.0				31.1	3.1
11	308	2.1	1.9	1.6	3.1		
12	336	2.8	2.3	2.2	2.8	0.2	
13	364	4.1	3.1	2.9	4.5	2.2	
14	392	3.2	3.4	5.6	4.1	2.5	
15	420	5.1	9.5	11.8	12.5	2.6	3.4
Residue		(80.8)	75.8	74.8	71.0	47.1	21.3
16	448	6.4					
17	476	8.1					
18	504	7.1					
19	532	8.1					
Residue		51.1					

(a) Simulated distillation data. All others are actual distillation.

(b) The total value of 2.2 was found in fraction 4.

suggest that thermal cracking occurred during the atmospheric distillation stage; thus the large fractions below 275°C are probably cracked products that do not reflect the original composition of the bitumen. These results point out the dangers and difficulties of obtaining boiling-point distributions of heavy bitumens by distillation and suggest that a different approach such as simulated distillation should be considered.

Separation of the Bitumen

The P.R. Spring bitumen was separated according to the flow diagram in Figure 1. Acidic compounds were isolated by using an anion exchange resin in the quaternary ammonium hydroxide form. Because the system is nonaqueous, complete ion exchange does not occur but rather an association between acidic types and the basic resin can be expected. Conversely, the bases are separated because they associate with the cation resin used in the sulfonic acid form. The acids were removed from the resin sequentially by exhaustive elution with a series of solvents with increasing polarity. The strongest acids require the most polar desorbing solvent and would appear in the later fractions. The bases were removed from the cation resin with similar elutions with solvents of increasing polarity. Thus, subfractions III and IV of the acids and sub-fraction III of the bases would contain the strongest acids and bases, respectively.

Neutral nitrogen compounds were removed by contacting the acid- and base-free bitumen with ferric chloride/Attapulgus clay in a column system. Nonreactive hydrocarbons were eluted with cyclohexane. Most nitrogen complexes were eluted from the column with

1,2-dichloroethane, and the complexes were subsequently broken when contacted with the A-29 resin in the bottom of the column. Complexes which were strongly adsorbed to the clay (subfraction II) were recovered by elution with benzene and methanol. Iron-nitrogen complexes are unstable in methanol, and so the A-29 resin does not retain the iron during the elution. Therefore, methanol had to be stripped from the sample before it was contacted with A-29 resin to remove the iron. This procedure provided two neutral nitrogen fractions for analysis.

The hydrocarbons portion, which contains some neutral oxygen and sulfur, was separated into saturates and aromatics by adsorption chromatography on silica gel. Elution of the saturates with two bed volumes of cyclohexane gave a satisfactory separation of saturates and aromatics. The UV absorbance at 270 nm for the eluant in 1-cm cells was 0.20, indicating minimal overlap of aromatics in the saturates. The aromatic hydrocarbons were recovered from the gel by exhaustive elution with 60% benzene-40% methanol.

The initial separation, which provides the percentage of total acids, bases, neutral nitrogen, saturates, and aromatics, gives information that could be useful in determining the value of a bitumen as a refining feedstock. Table 4 lists data for these five major fractions from the P. R. Spring bitumen and compares it with similar data from five petroleum residues. Data on the petroleum residues was obtained by USBM-API RP 60 as an extension of the studies of heavy

TABLE 4. - Gross composition of selected bitumens

Fraction	Residue sample					
	P.R. Spring > 225°C	Wil- mington > 485°C	Red Wash > 545°C	Recluse > 750°C	Gach Saran > 675°C	Prudhoe Bay > 675°C
Acids	15.4	10.7	6.0	5.9	12.1	10.0
Bases	12.3	13.3	10.2	8.3	14.2	15.7
Neutral nitrogen	18.5	20.4	10.8	17.4	23.2	12.6
Saturated hydrocarbons	25.7	18.4	51.8	40.8	25.6	32.9
Aromatic hydrocarbons	24.9	35.1	10.9	24.8	18.7	23.4
Recovery	96.8	97.9	94.4	97.2	93.8	94.6

distillate fractions. Comparisons of the bitumen with these residues must be made with the recognition that the residues have higher initial boiling points than the bitumen; i.e., the bitumen contains more low-boiling material. Examination of high-boiling distillate cuts (5, 6, 8, 9) has shown that nonhydrocarbons (acids + bases + neutral nitrogen) are concentrated in the high-boiling fractions. In general, the nonhydrocarbon content of the residue is twice that of the 500-600°C cut, which is in turn twice that of the 400-500°C cut. Table 4 shows that the nonhydrocarbon content of the bitumen is high--second only to the Gach Saran residue--even though the bitumen contains 30 to 50 percent material in the 275 to 500°C boiling range which is absent in the residues. This suggests that a comparable initial-boiling-point residue of the P.R. Spring bitumen would have an unusually high content of nonhydrocarbons.

An additional experiment provided semiquantitative data to show the high nonhydrocarbon content of a comparable residue from the bitumen. The hydrocarbon portion (saturates and

aromatics) of the bitumen was examined by simulated distillation, which showed that 85 percent of these hydrocarbons boiled below 532°C. Because these hydrocarbons represent 50.6 percent of the bitumen, the 85 percent below 532°C represents 43.0 percent of the bitumen. The simulated distillation of the total bitumen shows 48.9 percent boiling below 532°C (Table 3). Of this 48.9 percent, 43.0 percent is hydrocarbon, leaving 5.9 percent as nonhydrocarbon. Calculations based on these data show that a > 532°C residue of the bitumen would have a nonhydrocarbon content of 84 percent, as compared to a nonhydrocarbon content of 27 to 50% for comparable petroleum residues. The unusually high nonhydrocarbon content suggests that additional problems would be incurred in refining processes which are typically sensitive to nonhydrocarbons.

Another major difference between the tar sand bitumen and the petroleum residues is suggested in Table 4. In all the petroleum samples, the base content is higher than the acid content. In the P.R. Spring sample the acids are higher than the bases. This could be an indicator of the differences in oxidation, maturation, or origin for the tar sand bitumen as compared to crude oils.

Analysis of Defined Fractions

Acid, base, and neutral nitrogen compounds were eluted from their respective adsorbents by gradient elution. These fractions were examined further for functional groups by infrared spectroscopy. Only those functional groups that were characteristic and that were sufficiently resolved from other bands to be integrated could be used. These bands with their apparent integrated absorption intensities (B) are listed in Table 1. All carbonyl absorption between 1700 and 1790 cm^{-1} was attributed to carboxylic acids because other carbonyl compounds such as esters and ketones are not retained by the resins and would not be present in the nonhydrocarbon concentrates. A carbonyl band that occurred about 1700 cm^{-1} could be classified as either acids or amides by examining the spectrum taken in THF; THF will break up the association of acids, and the free acid carbonyl band will shift to a higher wavenumber (13).

The results of the infrared analysis of the nonhydrocarbon compounds are given in Table 5.

TABLE 5. - Infrared analysis of nonhydrocarbon concentrates

Fraction	Wt. percent of bitumen	Molecular weight	Weight percent of fraction				Unidentified by IR
			Carboxylic acids	Phenols	Carbazoles	Amides	
Acids I	4.8	1240	4	9	34	40	13
II	2.2	1161	28	20	18	33	1
III	4.0	853	60	6	7	10	17
IV	4.4	(850 est.)	39	4	17	9	31
Bases I	2.0	855			trace	67	33
II	1.5	(900 est.)				55	45
III	8.8	952				17	83
Neutral nitrogen I	10.3	982			32	55	13
II	8.2	(982 est.)			17	51	32

Total	46.2		4.9	1.3	7.7	20.1	12.2

The accuracy of the molecular weights given, which were determined by vapor-pressure osmometry in benzene, is subject to the degree of intermolecular association exhibited in the fractions. For very polar molecules such as strong acids or bases, this association could be considerable. Along with the estimation of the apparent integrated absorption intensities, this determination is the largest source of possible error in the analysis of compound types by infrared spectroscopy. The results in Table 5 show that carboxylic acids and phenols are found only in the acid concentrates. Carbazoles (pyrrolic N-H) and amides, however, are found in all three major nonhydrocarbon fractions. The appearance of the same compound type in several fractions is presumably explained by differences in acidity or basicity which are caused by the hydrocarbon portion of the molecule. Multifunctionality could also be a factor in the distribution of compound types.

Major differences occur between the four acid subfractions. Acid subfraction I is relatively concentrated in nitrogen acids, subfraction II in phenols, and subfractions III and IV in carboxylic acids. The separations greatly facilitate infrared analysis because the high concentration of compound types results in a higher intensity of the infrared absorption bands. In addition, the separations provide fractions which are amenable to further studies such as the determination of the chemical properties and reactivity of the compound types present.

The base fractions contain substantial quantities of amides. Predictably, more amides, which are weak bases, appeared in the weak base fractions I and II than in the strong base fraction III. The neutral nitrogen compounds are largely carbazole and amide types. This, again, is expected because both types are generally nonreactive nitrogen compounds.

In order to analyze the base subfractions beyond the capabilities of infrared spectroscopy, the three fractions were titrated for basic nitrogen to determine the average strength of the bases and the amount of titratable nitrogen present. The results are given in Table 6.

TABLE 6. - Potentiometric titration of bases

Fraction	Strong bases		Very weak bases		Bases titratable ^(a) Wt. %
	HNP ^(b) (mv)	Wt. % N	HNP (mv)	Wt. % N	
Bases I			483	1.12	68
II			429	1.42	91
III	231	1.65	466	0.16	123

(a) Assuming monofunctionality and using molecular weights from Table 5.

(b) Half-neutralization potential.

The first two base fractions contain only very weak bases. These bases titrate with an HNP roughly equivalent to amides (11). Base fraction I was shown to contain 67 percent amides by IR, and thus it is likely that essentially all of the titratable nitrogen in this fraction is of the amide type. Base fraction II contains 55 percent amides (by IR analysis) and 36 percent titratable nitrogen types other than amides. This type(s) is a stronger base than the amides because of the lower HNP exhibited in this fraction than in bases I. A further indication that the unidentified bases are stronger than amides is that bases II have been defined as being stronger than bases I by the separation procedure. Bases III, which comprise over 70 percent of the total bases, contain large quantities of strong bases; essentially no weak bases are present in this fraction. An HNP of 231 could result from alkyl pyridines or quinolines (11). Strong nitrogen bases that have been found in crude oils have been predominantly of the pyridine type.

A tentative identification of condensed benzologs of pyridine has been made in this P.R. Spring bitumen by fluorescence spectroscopy. An accountability of over 100 percent could result from an inaccurate molecular weight determination caused by polar base association. Further, multifunctionality (more than one nitrogen per molecule) would cause an artificially high accountability. Of the total 1.00 percent nitrogen present in the P.R. Spring bitumen, .11 percent is found as carbazoles, .31 percent as amides, .15 percent as strong bases, and .43 percent unidentified.

A group-type analysis of the saturated hydrocarbons was obtained using a modification of the mass spectral method originally proposed by Hood and O'Neal. This method allows the determination of saturated hydrocarbons according to number of rings. Table 7 lists the results of this analysis. The data show that over 60 percent of the saturates are 2- and 3-ring compounds.

TABLE 7. - Group-type analysis of P.R. Spring saturated hydrocarbons

Number of rings	Wt. percent of saturates
0	7.1
1	12.3
2	29.4
3	31.5
4	14.1
5	4.4
6	1.3
Monoaromatics	0

Group-type analysis of aromatic hydrocarbons was not obtainable because of the wide molecular-weight ranges represented within a given series of compounds. The characterization of a bitumen sample with a discrete boiling range would allow group-type analysis of aromatics. The distillation and subsequent characterization of distillates and the residue were, however, beyond the scope of the present work.

CONCLUSIONS

A preliminary characterization of a Utah tar sand bitumen has been made using methods developed for high-boiling petroleum fractions. The characterization includes information about the major compound types. This information can be compared with similar data for other tar sands bitumens and, more importantly, can be correlated with data from petroleum samples for which refining characteristics are known. Examination of the P.R. Spring bitumen showed that it differed significantly from representative petroleum residues, principally in its high non-hydrocarbon content. Compositional information is important because of the effects that composition has on the recovery and processing of the bitumen.

ACKNOWLEDGMENT

The work reported in this paper was performed under a cooperative agreement between the Bureau of Mines, U.S. Dept. of the Interior, and the University of Wyoming.

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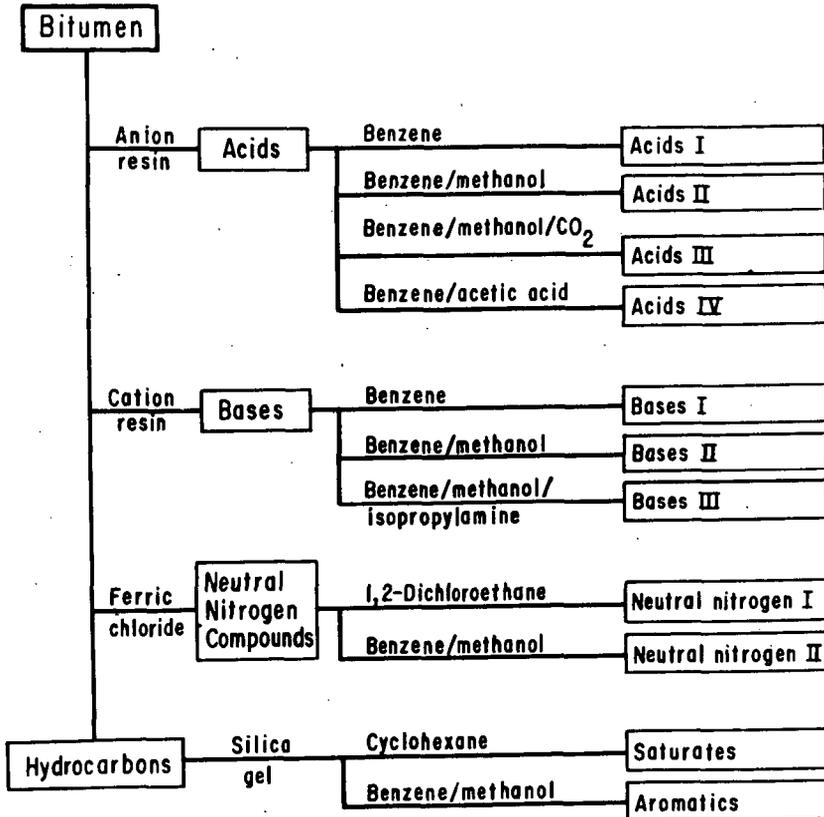


FIGURE 1. - SEPARATION SCHEME