Table VI. Aged High Temperature Properties of Carboxy Rubbers and Some Commercial Elastomers

	Aged 8 Hours °F.			
	...	300	...	400
	Test Temperature, °F.			
Polymer	300	300	400	400
BD-MMA-MAA, 3% MAA (Table IV, E)				
Tensile, p.s.i.	1330	590	870	190
Elongation, %	300	100	260	10
BD-MMA-MAA, % MAA (Table IV, C)				
Tensile, p.s.i.	1300	1050	910	280
Elongation, %	420	230	330	50
BD-MMA (Table V, A)				
Tensile, p.s.i.	1490	950	960	380
Elongation, %	470	360	500	70
SBR [a]				
Tensile, p.s.i.	890	270	260	170
Elongation, %	180	30	100	60
Hevea [b]				
Tensile, p.s.i.	1530	690	500	125
Elongation, %	400	440	500	80
Cohrlastic HT655 [c]				
Tensile, p.s.i.	560	510	360	330
Elongation, %	500	490	340	240
Viton A [d]				
Tensile, p.s.i.	...	...	220	210
Elongation, %	...	...	60	70
Butyl [e]				
Tensile, p.s.i.	1140	850	790	360
Elongation, %	260	180	150	90

[a] Stock 2405 (*9*). [b] Stock 2404 (*9*). [c] Stock 5065 (*9*). [d] Stock 104A-410 (*5*). [e] Stock 8787 (*9*).

tures from 400° to 550° F. Studies on some of these modifications and further compounding of the butadiene-methyl methacrylate copolymer are in progress.

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Component Analysis of Naphtha Fractions of Three Venezuelan Crudes

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Quality and quantity data on petroleum fractions boiling up to 210° F. were needed in isolating high yields of high octane number isopentane, isohexanes, and isoheptanes in virgin naphthas for inclusion in aviation gasoline. As part of the over-all program, a complete analysis was made of the naphthas from three Venezuelan crudes boiling up to 210° F.

The project consisted of fractionating each 310° F. final boiling point naphtha into the C_5, C_6, C_7, and C_8 fractions. The C_6 and C_7 fractions were refractionated into 2% cuts, and infrared and ultraviolet techniques applied to determine their compositions. Low temperature distillation methods were used to determine those compounds boiling below normal pentane.

To adhere as closely as possible to plant operations, no treatment affecting the composition of the sample was made prior to distillation or to the small cuts prior to analysis. Distillations were carried out under conditions designed to simulate those in the units and no attempt was made to isolate pure compounds.

Refractive index and specific gravity measurements were made on each cut as aids in the analyses. At the time the work was done gas chromatography was not available at these laboratories. Since then, several units have been acquired, and future analyses will utilize this technique. The work was repeated on a less extensive scale using gas chromatography; the results were essentially the same. One interesting development, however, was the identification of hydrocarbons not suspected.

MATERIALS AND EQUIPMENT

Distillation. Three distillation units were used in this work. Podbielniak Hyd Robot low temperature fractional distillation units were used to analyze the naphthas for those compounds boiling below normal pentane. This equipment is conventional, commercially available, and adequately covered in the literature (*10-14*).

The initial separations of the samples into broad isomer cuts were made in a Fenske-type distillation column (*5*), of a semi-automatic nature having a nominal capacity of 1 to 5 liters. The apparatus consists of a still pot, packed column, still head, receiver, and temperature measuring devices. The column is a vacuum-jacketed glass tube with an inside diameter of 25 mm. and with a packed section 1.5 meters long. The packing is 3/32-inch stainless steel Fenske-type helices supported by a 12-mesh stainless steel conical screen 80 mm. from the bottom of the column. The still head is of the total reflux-intermittent take-off-liquid dividing type. It consists of a reflux chamber, condenser, and product cooler. A solenoid-actuated plunger controlled by a Flexopulse timer of variable setting is used to control liquid product removal and thus control reflux ratio (*1,6*). Copper-constantan thermocouples and an L&N manually operated portable potentiometer are used to measure overhead vapor temperatures. The still pot is heated by a Variaccontrolled Glas-Col heating mantle adjusted manually to hold a certain pressure drop.

Column efficiency is high, approximately 80 theoretical plates, when held at total reflux for 6 hours at a boil-up rate of 1300 ml. per hour. The column has an operating holdup of 125 ml. at a pressure drop of 7 mm. of mercury. The column was tested using a mixture of methylcyclohexane and 2,2,4-trimethylpentane (*4*).

The final distillations were carried out in a column with a nominal capacity of 0.1 to 1.0 liter. This column is much more efficient than the Fenske, though differing only in the fractionating section. The column is made up of two parts: a Podbielniak Heli-Grid packed inner tube and an outer Podbielniak vacuum jacket, both of the type normally used in low temperature fractionation. The Heli-Grid packed tube has an inside diameter of 13 mm. with a packed section 915 mm. long. The top and bottom of this column were modified to have the still put outside the standard vacuum jacket and thus permit the use of various size pots. The smaller diameter tubing just above and below the packed section was removed, eliminating all constrictions along the length of the column, and glass tubing of the required length and size was then attached to the top and bottom of the column and standard ball joints were added. A glass support was added having the same general outline as a standard 100-ml. Podbielniak still pot. This support was attached only at the bottom, eliminating the need for expansion joints in the lower part of the column. These modifications permit easy changing of still pots and the use of conventional still heads and pots.

The column has 100 theoretical plates at a boil-up rate of 150 ml. per hour, an operating pressure drop of 4 mm. of mercury, and an operating holdup of 21 ml. These conditions are at total reflux using a test mixture of 2,2,4-trimethylpentane–methylcyclohexane (*15*).

Spectrographic. For infrared measurements, the Beckman Model IR-2 was used (*17*). This instrument, equipped with sodium chloride optics, is capable of scanning spectra over the range 2 to 15 microns with a wave length reproducibility of 0.01 micron. The measurements were made with an automatic recorder. To minimize error, the instrument is housed in a

Table I. Slit Widths and Wave Lengths of Absorption Peaks and Base Line Points for Compounds in 90° to 214° F. Boiling Range

Compound	Slit Width, MM.	Wave Length, Microns Peak	Base Line	
n-Pentane	0.850	13.74	13.30	14.10
Cyclopentane	0.459	11.24	10.80	11.60
2,2-Dimethylbutane	0.208	8.28	7.80	8.50
2,3-Dimethylbutane	0.241	8.92	8.50	9.20
2-Methylpentane	0.850	13.56	13.30	14.10
3-Methylpentane	0.366	10.56	10.00	10.80
n-Hexane	0.850	13.82	13.30	14.10
Methylcyclopentane	0.366	10.30	10.00	10.80
2,2-Dimethylpentane	0.850	13.54	13.30	14.10
2,4-Dimethylpentane	0.595	12.38	12.10	12.60
Cyclohexane	0.495	11.64	11.34	11.86
2,2,3-Trimethylbutane	0.271	9.27	8.90	9.50
3,3-Dimethylpentane	0.314	10.05	9.50	10.36
1,1-Dimethylcyclopentane	0.216	7.62	7.51	7.70
2,3-Dimethylpentane	0.232	8.97	8.36	9.20
2-Methylhexane	0.232	8.59	8.36	9.20
cis-1,3-Dimethylcyclopentane	0.232	8.75	8.36	9.20
trans-1,2-Dimethylcyclopentane	0.224	7.83	7.60	8.30
trans-1,3-Dimethylcyclopentane	0.325	10.52	9.42	10.50
3-Methylhexane	0.850	13.59	13.30	14.10
3-Ethylpentane	0.430	11.16	10.75	11.40
n-Heptane	0.850	13.87	13.30	14.10
2,2,4-Trimethylpentane	0.224	8.08	7.60	8.30
cis-1,2-Dimethylcyclopentane	0.325	9.69	9.42	10.10
Methylcyclohexane	0.508	11.89	11.35	12.10

Table II. Infrared Analysis of Synthetic Blends in the Boiling Range 95° to 209.2° F.

	Blend 1			Blend 2			Blend 3			Blend 4			Blend 5			Blend 6			Blend 7		
	Given, vol. %	Found, vol. %	Dev.	Given, vol. %	Found, vol. %	Dev.	Given, vol. %	Found, vol. %	Dev.	Given, vol. %	Found, vol. %	Dev.	Given, vol. %	Found, vol. %	Dev.	Given, vol. %	Found, vol. %	Dev.	Given, vol. %	Found, vol. %	Dev.
n-Pentane	5.7	6.1	+0.4	13.1	13.4	+0.3	9.8	8.7	1.1												
Cyclopentane	14.3	13.9	– 0.4	18.3	18.8	+0.5	19.6	18.9	0.7												
2,2-Dimethylbutane	5.7	6.0	+0.3	5.5	4.9	– 0.6	3.9	4.4	+0.5												
2,3-Dimethylbutane	11.4	12.7	+1.3	7.4	7.4	0.0	7.8	8.7	+0.9												
2-Methylpentane	42.8	42.9	+0.1	28.7	29.2	+0.5	39.2	40.0	+0.8	33.3	32.7	0.6	29.7	29.5	0.2						
3-Methylpentane	14.3	13.4	– 0.9	8.6	8.2	0.4	9.8	9.5	– 0.3	33.3	33.0	– 0.3	29.7	29.4	– 0.3						
n-Hexane	5.7	5.0	– 0.7	7.0	6.4	– 0.6	9.8	9.8	0.0	33.4	34.3	+0.9	29.8	30.5	+0.7						
Methylcyclopentane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0												
Benzene				11.4	11.7[a]	+0.3							10.8	10.6[a]	– 0.2						
2,2-Dimethylpentane																					
2,4-Dimethylpentane																0.8	1.5	+0.7			
Cyclohexane																18.5	20.2	+1.7			
3,3-Dimethylpentane																10.6	11.8	+1.2	14.6	14.8	+0.2
1,1-Dimethylcyclopentane																10.5	7.5	3.0	15.0	12.6	– 2.4
2,3-Dimethylpentane																11.3	12.0	+0.7	16.2	17.3	+1.1
2-Methylhexane																9.2	8.5	– 0.7	3.8	4.4	+0.6
cis-1,3-Dimethylcyclopentane																10.1	10.4	+0.3	0.4	0.0	– 0.4
trans-1,2-Dimethylcyclopentane																9.7	3.9	5.8	3.9	0.0	– 3.9
trans-1,3-Dimethylcyclopentane																9.8	9.1	– 0.7	2.5	1.7	0.8
3-Methylhexane																9.5	15.1	+5.6	12.8	13.5	+0.7
3-Ethylpentane																			14.8	17.1	+2.3
n-Heptane																			16.0	18.6	+2.6

[a] Determined by ultraviolet analysis.

Table III. Analysis of Low-Boiling Hydrocarbons by Low-Temperature Fractionation

	Liquid Vol. %				
	La Rosa medium	Bachaquero		Tia Juana medium	
Naphtha	whole N.D.	Deb. dry gas	Deb. naphtha	Deb. dry gas	Deb. naphtha
Methane	. . .	7.0	. . .	0.6	. . .
Ethane	0.1	8.3	. . .	8.1	. . .
Propane	0.7	24.9	. . .	33.2	. . .
Isobutane	0.9	19.8	. . .	19.8	. . .
n-Butane	3.9	39.5	. . .	36.8	1.9
Isopentane	4.4	0.5	3.4	1.5	4.6
n-Pentane	4.2	. . .	4.3	. . .	5.0
Higher than *n*-pentane	85.8	. . .	92.3	. . .	88.5
	100.0	100.0	100.0	100.0	100.0
310° F. naphtha, vol. %	100.0	10.9	89.1	11.8	88.2
Crude vol. %	11.4	0.6	4.9	1.8	13.4

Table IV. Infrared Analysis of Total Pentane Fractions from Fenske Distillation

Naphtha		La Rosa Medium	Bachaquero	Tia Juana Medium
Naphtha, vol. %		6.00	6.00	9.50
Crude vol. %		0.68	0.33	1.44
Temperature range, °F.		82.0-96.8	82.0-97.2	81.0-105.2
Sp. gr. 20/4		0.630	0.622	0.626
Compound	B.P., °F.	Volume %		
Isopentane	82.2	37.6	51.2	43.4
n-Pentane	96.9	59.5	46.6	54.2
Cyclopentane	120.7	2.9	2.2	2.4

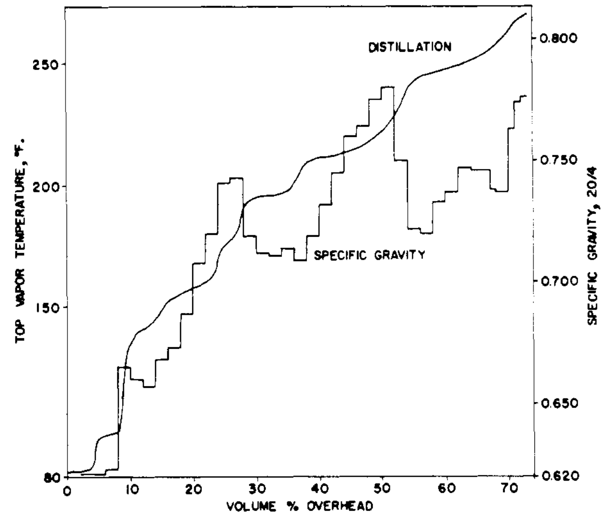

Figure 1. La Rosa normal distillate

constant-temperature, constant-humidity room. An absorption cell, equipped with sodium chloride windows, having a light path of 0.1 mm. was used.

Ultraviolet measurements were made on a manually operated Beckman quartz spectrometer, Model DU (*16*), in the near-ultraviolet region using a hydrogen discharge tube as the light source. The instrument is equipped with a photomultiplier attachment permitting the use of very narrow slit widths. It is capable of measuring absorbances with an accuracy of better than 1%, and wave length settings are reproducible to 0.1 mμ in the 250-mμ region. The absorption cells are of all-quartz construction with a 1-cm. light path.

Miscellaneous. Specific gravity measurements were made with a Fisher-Davison gravitometer (*7*), a direct reading instrument capable of determining specific gravities of liquids with an accuracy of ±0.001.

Refractive indices were measured in a Bausch and Lomb Abbe type refractometer with an accuracy to ±0.0001.

All specific gravity and refractive index measurements were carried out in a room in which the temperature is held at 21° ±1° C. (68° to 72° F.).

EXPERIMENTAL

Fractional Distillation. The naphtha fractions of three Venezuelan crudes were investigated. The sample of La Rosa naphtha was obtained from a visbreaking unit, in which a whole naphtha with a final boiling point of 310° F. was topped prior to visbreaking the heavier fractions. Bachaquero and Tia Juana medium naphthas, also with 310° F. final boiling points, were cut from the whole crudes in a laboratory batch still of approximately 15-plate efficiency at total reflux. The gas fractions (butane and lighter) from the Bachaquero and Tia Juana crudes were collected separately in a debutanization operation and analyzed in Podbielniak low temperature distillation units. Small samples of each naphtha, whole naphtha in the case of La Rosa and debutanized naphtha in the case of Bachaquero and Tia Juana, were also charged to the Hyd-Robot low tem-

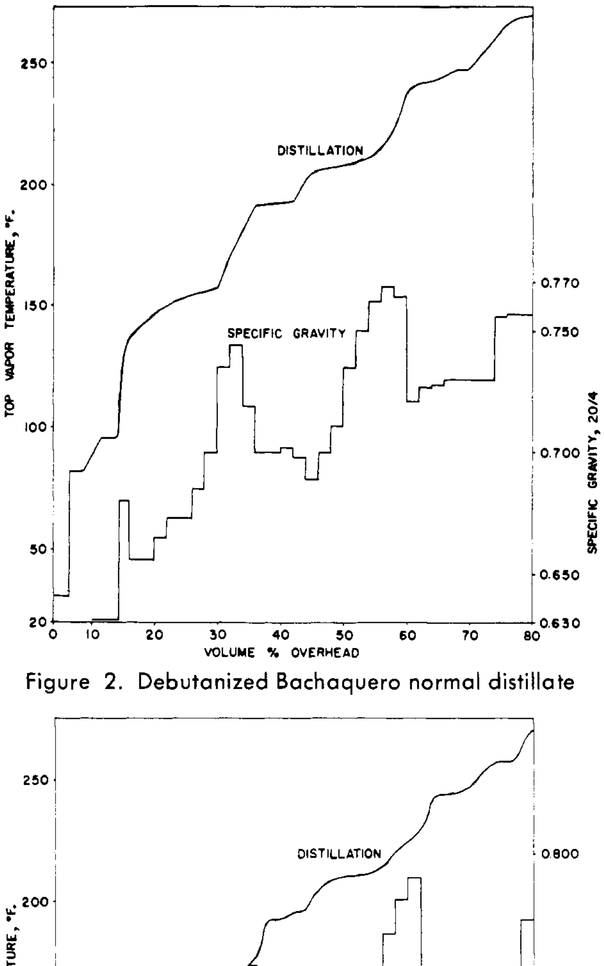

Figure 2. Debutanized Bachaquero normal distillate

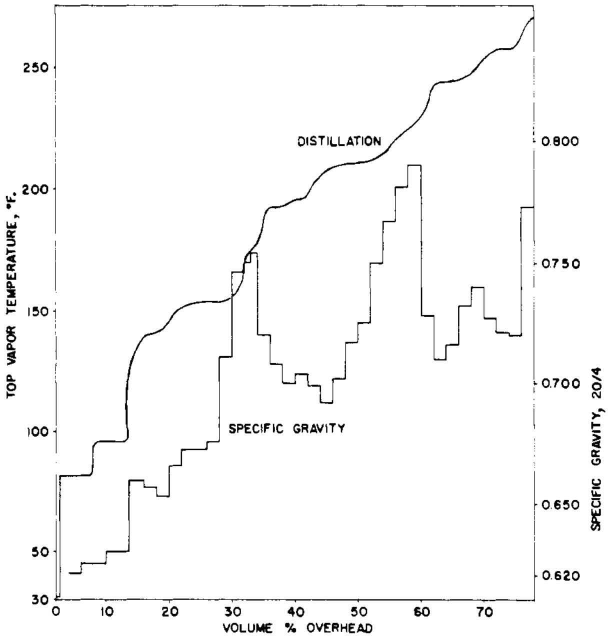

Figure 3. Debutanized Tia Juana normal distillate

Table V. Composition of Fractions from La Rosa Medium Naphtha in the Boiling Range 96.8° to 180.4° F.

Vol. % of fraction on 310° F. whole naphtha 18.0
Vol. % of fraction on crude 2.1

Cut Nos.		1	2	3-4	5-8	9-11	12-17	18-21	22-34	35-40	Bottoms[a]
Cut temp., °F.		97.2	119.2	137.6	138.0	143.0	145.6	148.8	155.6	166.0	. . .
Cut vol., %		2.25	2.25	4.50	9.00	6.75	13.50	9.00	29.25	13.50	10.0
Cumul. vol., %		2.25	4.50	9.00	18.00	24.75	38.25	47.25	76.50	90.00	100.0
Compound	B.P., °F.										
Isopentane	82.2	4.8									
n-Pentane	96.9	90.8	44.6	2.5							
Cyclopentane	120.7	4.4	43.3	23.1	3.7						
2,2-Dimethylbutane	121.5		12.1	5.2	0.8						
2,3-Dimethylbutane	136.4		0.0	20.4	12.9	6.6	2.9	0.5			
2-Methylpentane	140.5			48.8	71.8	58.3	35.3	11.4	1.3		
3-Methylpentane	145.9				10.8	34.8	43.7	24.1	5.1		
n-Hexane	155.7					0.3	16.7	59.0	78.3	26.2	
Methylcyclopentane	161.3							1.8	9.3	57.8	
2,2-Dimethylpentane	174.6									0.7	
2,4-Dimethylpentane	176.9									3.7	
Cyclohexane	177.3									1.2	
Benzene	176.2						1.4	3.2	6.0	10.4	
Compounds boiling above 155.7° F.											100.0

[a] Bottoms added to 180.4° to 216.0° F. fraction.

perature units for analysis of *n*-pentane and lower boiling compounds. Equivalent samples were charged to the Fenske column, but the low boiling compounds were taken overhead as a total gas fraction, and the volume was measured with a wet-test meter. This volume was then converted to liquid volume on the Podbielniak analyses.

In the initial fractionation of each naphtha, 4 liters of sample were charged to the Fenske column and 2% cuts were taken overhead. Prior to each distillation, the column was preflooded and held under total reflux for 2 hours before product was taken overhead. The column was operated at a 10 to 1 reflux ratio and a boil-up rate of 1300 ml. per hour. Each cut was weighed to obtain material balance, the specific gravity determined, and the cuts were combined into the C_6, C_7, C_8, and bottoms fractions. The boiling ranges selected for these blends of major fractions were made sufficiently wide to provide enough bottoms for the subsequent distillations.

The C_6 and C_7 fractions of each naphtha were then fractionated in the Heli-Grid packed column into 2% cuts, ranging from 10 to 16 ml. each, depending upon the size of the charge. Each cut was weighed; the specific gravity and refractive index were measured, and later the individual components were determined by infrared and ultraviolet methods. This column was operated in essentially the same manner as the Fenske column, in that it was preflooded and then held under total reflux for 2 hours before taking product over. Reflux ratios of 10 to 1 and a boil-up rate of 150 ml. per hour were held throughout these distillations.

In each of these Heli-Grid distillations 60 to 80% (by volume) of the charge was taken overhead. The bottoms were then blended into the next higher boiling Fenske fraction, and this in turn was fractionated into 2% cuts to 60 to 80% (by volume) overhead.

A special narrow boiling fraction of La Rosa naphtha (172° to 190° F.), obtained from the distillation of whole naphtha in a column of about 15 theoretical plates run at 20 to 1 reflux ratio, was also analyzed by high efficiency fractionation and infrared and ultraviolet spectrographic techniques. The distil-

Table VI. Composition of fractions from La Rosa Medium Naphtha in the Boiling Range 160.0° to 216.0° F.

Vol. % of fraction on 310° F. whole naphtha 24.0
Vol. % of fraction on crude 2.7

Cut Nos.		1	2-3	4-5	6-10	11-25	26-29	30-32	Bottoms
Cut temp., °F.		174.0	175.2	186.0	194.4	199.0	208.4	209.2	. . .
Cut vol. %		2.0	4.0	4.0	10.0	30.0	8.0	6.0	36.0
Cumul. vol. %		2.0	6.0	10.0	20.0	50.0	58.0	64.0	100.0
Compound	B.P., °F.								
Benzene	176.2	2.7							
Methylcyclopentane	161.3	5.7							
2,2-Dimethylpentane	174.6	6.1	3.7	3.1					
2,4-Dimethylpentane	176.9	36.8	17.3	10.1	2.6				
Cyclohexane	177.3	42.0	76.6	55.0	17.1				
2,2,3-Trimethylbutane	177.6	6.7	2.3	0.4	0.4				
3,3-Dimethylpentane	186.9		0.1	3.5	1.4	0.2			
1,1-Dimethylcyclopentane	190.1			3.8	4.5	0.3			
2,3-Dimethylpentane	193.6			6.7	14.9	9.4	0.5		
2-Methylhexane	194.1			7.6	28.3	23.0	3.2		
cis-1,3-Dimethylcyclopentane	195.4			0.5	5.8	7.3	4.5		
trans-1,2-Dimethylcyclopentane	197.4			0.0	4.1	10.6	7.0		
trans-1,3-Dimethylcyclopentane	197.4			2.3	3.4	7.1	1.3		
3-Methylhexane	197.5			7.0	16.9	37.0	25.9	1.0	
3-Ethylpentane	200.2				0.5	3.1	7.3	0.4	
n-Heptane	209.2				0.1	2.0	46.5	79.7	
2,2,4-Trimethylpentane	210.6						0.0	0.3	
cis-1,2-Dimethylcyclopentane	211.1						0.0	2.8	
Methylcyclohexane	213.6						3.8	15.8	
Compounds boiling above 200.2° F.									100.0

Table VII. Composition of fractions from Bachaquero naphtha in the Boiling Range 97.2° to 173.6° F.

Vol. % of fraction on 310° F. whole naphtha 10.3
Vol. % of fraction on crude 0.6

Cut Nos.		1-2	3-4	5-8	9-16	17-22	23-35	Bottoms[a]
Cut temp., °F.		102.8	121.0	136.8	142.0	147.6	156.0	. . .
Cut vol. %		4.0	4.0	8.0	16.0	12.0	26.0	30.0
Cumul. vol. %		4.0	8.0	16.0	32.0	44.0	70.0	100.0
Compound	B.P., °F.							
Isopentane	82.2	9.9						
n-Pentane	96.9	86.5	40.6	9.5				
Cyclopentane	120.7	3.6	44.8	24.5	5.7			
2,2-Dimethylbutane	121.5		13.5	8.1	1.5			
2,3-Dimethylbutane	136.4		1.1	22.7	15.5	6.3		
2-Methylpentane	140.5			35.2	63.3	42.5	10.0	
3-Methylpentane	145.9				14.0	44.4	21.7	
n-Hexane	155.7					6.1	58.8	
Methylcyclopentane	161.3					0.0	5.1	
Benzene	176.2					0.7	4.4	
Compounds boiling above 145.9° F.								100.0

[a] Bottoms added to 173.6° to 211.0° F. fraction.

Table VIII. Composition of Fractions from Bachaquero Naphtha in the Boiling Range 153.0° to 210.3° F.

Vol. % of fraction on 310° F. whole naphtha 18.3
Vol. % of fraction on crude 1.0

Cut Nos.		1-10	11-18	19-24	25-35	36-42	43-46	Bottoms
Cut temp., °F.		167.2	178.0	194.0	196.8	201.2	210.3	. . .
Cut vol. %		20.0	16.0	12.0	22.0	14.0	8.0	8.0
Cumul. vol. %		20.0	36.0	48.0	70.0	84.0	92.0	100.0
Compound	B.P., °F.							
n-Hexane	155.7	41.0	1.3					
Benzene	176.2	8.0	1.1					
Methylcyclopentane	161.3	45.2	12.8					
2,2-Dimethylpentane	174.6	0.6	3.7	0.2				
2,4-Dimethylpentane	176.9	3.7	14.4	5.5				
Cyclohexane	177.3	1.5	64.4	25.2				
2,2,3-Trimethylbutane	177.6		2.3	0.4				
3,3-Dimethylpentane	186.9			3.4	0.3			
1,1-Dimethylcyclopentane	190.1			7.7	2.7			
2,3-Dimethylpentane	193.6			15.9	17.0	5.3		
2-Methylhexane	194.1			16.3	24.2	9.8	0.4	
cis-1,3-Dimethylcyclopentane	195.4			8.2	13.4	10.2	2.1	
trans-1,2-Dimethylcyclopentane	197.4			3.0	11.0	19.9	4.8	
trans-1,3-Dimethylcyclopentane	197.4			1.5	4.9	7.9	0.4	
3-Methylhexane	197.5			12.2	24.3	37.0	10.7	
3-Ethylpentane	200.2			0.5	1.8	7.0	6.1	
n-Heptane	209.2				0.4	2.9	67.4	
2,2,4-Trimethylpentane	210.6						0.5	
cis-1,2-Dimethylcyclopentane	211.1						1.6	
Methylcyclohexane	213.6						6.0	
Compounds boiling above 200° F.								100.0

lation curves, specific gravities, and refractive indices are shown in Figure 10. From this analysis, the leaded aviation blending octane number and the leaded supercharge blending index of the fraction were calculated. At the same time, engine tests were run on the whole fraction to test the validity of using this method for estimating aviation octane blending values.

Spectrographic. Infrared was used to determine the paraffin and naphthene compounds present in each 2% cut, while ultraviolet was used to determine aromatics—in this case only benzene, because the investigation was limited to the analysis of compounds boiling up to 214° F. The only exception to this was in the analysis of the final cut from the distillation of the 172 to 190° F. La Rosa fraction prepared on a low efficiency column; here, toluene was also found.

The base line method of analysis (*8*) was used to obtain the infrared absorbances of the paraffins and naphthenes present in each cut. In this procedure, the absorption curve of each compound is obtained with respect to the radiant energy background. The absorbances are determined by measuring the height of the peaks using total extinction as the reference line. The base line is obtained by drawing a line through two predetermined points on either side of the peak to be determined. These points are located on the radiant energy line, and the base line drawn corresponds to the radiant energy background. The distances from total extinction to the point of maximum absorption, I, and from total extinction to the base line, I_0, are measured and the absorbance calculated from the equation:

$$\text{Absorbance} = \log_{10} I_0/I$$

The approximate positions of the base line points and absorption peaks were obtained from the literature (*2*). However, the exact location of these points (Table I) was established by

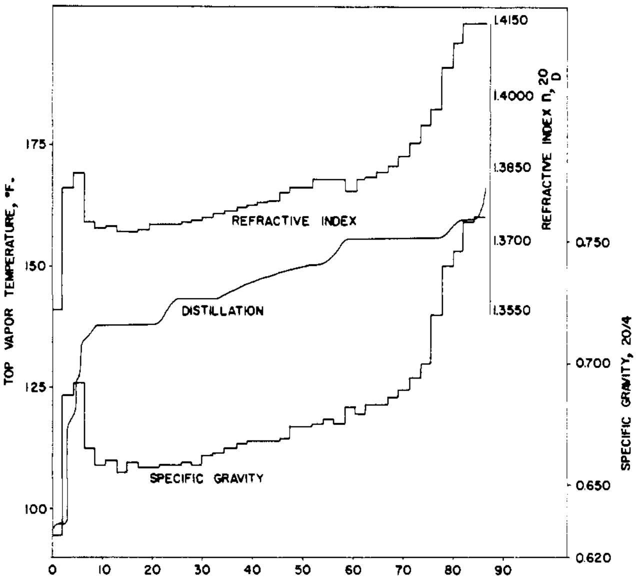

Figure 4. La Rosa normal distillate isohexane fraction

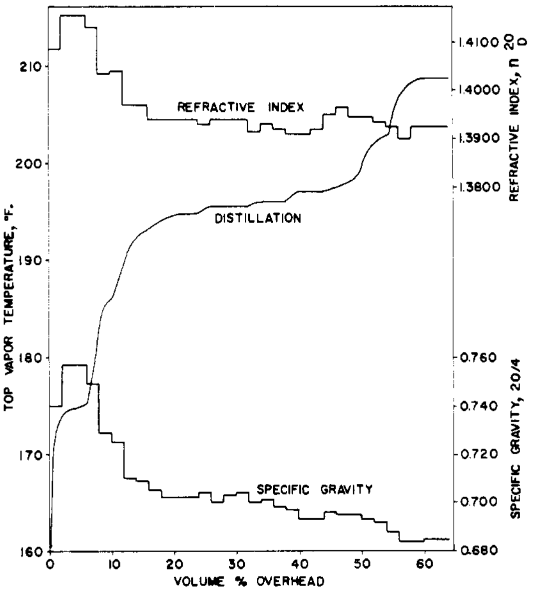

Figure 5. La Rosa normal distillate isoheptane fraction

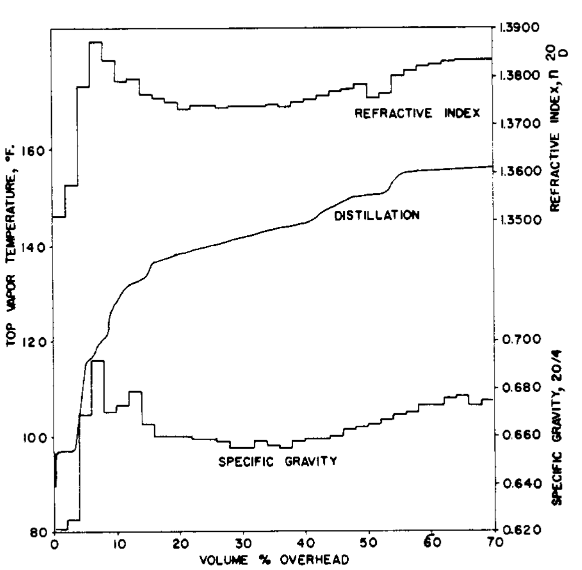

Figure 6. Bachaquero normal distillate isohexane fraction

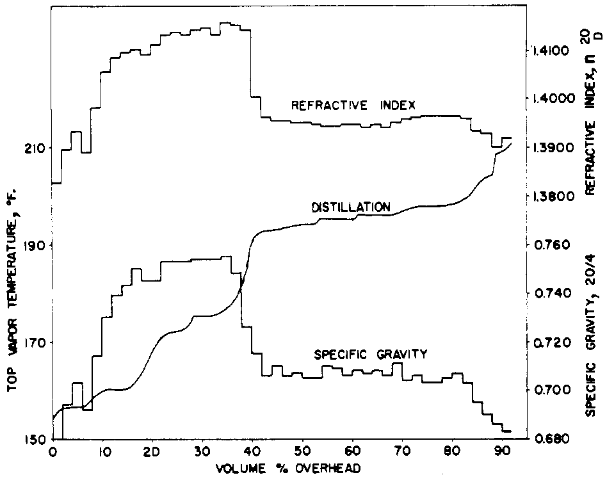

Figure 7. Bachaquero normal distillate isopheptane fraction

scanning pure compounds from the National Bureau of Standards, A.P.I. Project 46. In this procedure, the instrument was also calibrated for those compounds investigated. Calibration data were obtained on each compound by scanning through a major peak and calculating the absorbance using the base line method. This procedure was then repeated at major absorption peaks of those compounds boiling just above and below the compound in the absorption cell. Thus, the absorbances of each compound were determined at the absorption peaks of the interfering compounds. From these absorbances, correction coefficients were calculated which were applied in the analysis of the individual cuts. No corrections were made for the presence of benzene in the infrared analyses because benzene offered negligible interference at the wave lengths used.

Benzene was determined in the ultraviolet region, using the specific extinction coefficient technique. Pure benzene obtained from the National Bureau of Standards, A.P.I. Project 46, was dissolved in spectroscopic grade iso-octane (2,2,4-trimethylpentane) and the absorbance determined at 248.6 mμ. The benzene was diluted with iso-octane until an absorbance of 0.3 to 0.6 was obtained. The specific extinction coefficient was then calculated from the formula:

$$K = \frac{\text{absorbance}}{cl}$$

where K = specific extinction coefficient in liters per gram-centimeter
c = concentration of benzene in grams per liter
l = length of light path in centimeters

Each cut from 130° to 180° F. was analyzed for benzene and the concentration determined from the absorbance and the specific extinction coefficient. The same general procedure was used to determine toluene in the bottoms from the distillation of the special La Rosa naphtha fraction. In this case, however, the bottoms (5.0 volume % of charge) had to be percolated through silica gel prior to the infrared analysis of paraffins and naphthenes because of serious interference with the determination of *n*-heptane.

CALCULATIONS

To determine the concentration of each pure hydrocarbon in each cut by infrared, a series of simultaneous equations is needed. Many methods are available for the solution of a system of simultaneous equations but become time-consuming when dealing with sets of equations of an order higher than four (*3*).

To facilitate the solution of the large numbers of sets of equations, an IBM card program calculator was used. The "inverse" matrix for each set of simultaneous equations was obtained quickly and accurately from the absorbances determined during instrument calibration.

The procedure in obtaining the final matrix is simple (*9*). The absorbances of the pure compounds, for which calibration data were obtained, are arranged in matrix form according to increasing boiling points of the compounds with the major coefficients occurring as the diagonal elements. This information is then punched on IBM cards and inverse matrices are calculated.

A total of 18 inverse matrices were calculated ranging from four to ten unknowns. The ranges included:

1. *n*-Pentane–2,3-dimethylbutane
2. Cyclopentane–2-methylpentane
3. 2,3-Dimethylbutane–*n*-hexane
4. 2-Methylpentane–methylcyclopentane
5. *n*-Pentane–2-methylpentane
6. Cyclopentane–3-methylpentane
7. 2,3-Dimethylbutane–methylcyclopentane
8. *n*-hexane–cyclohexane
9. Methylcyclopentane–2,2,3-trimethylbutane
10. 2,2-Dimethylpentane–3,3-dimethylpentane
11. 2,4-Dimethylpentane–1,1-dimethylcyclopentane
12. *trans*-1,2-Dimethylcyclopentane–*n*-heptane
13. 2-Methylhexane–*n*-heptane
14. *n*-Pentane–methylcyclopentane
15. Cyclohexane–3-methylhexane
16. 2,4-Dimethylpentane–3-methylhexane
17. 3,3-Dimethylpentane–*n*-heptane
18. 2-Methylhexane–methylcyclohexane

The accuracy of the calibrations and the "inverse" matrices was determined by analyzing synthetic mixtures prepared from National Bureau of Standards pure hydrocarbons. The synthetic mixtures prepared contained the same compounds present in certain key fractions analyzed. The fractions selected covered the entire range of compounds analyzed. These analyses, shown in Table II, indicate that the deviation from the true composition was generally less than ±1% and only rarely exceeded ±2.5%. The largest deviation is with *trans*-1,2-dimethylcyclopentane, which suffers from interference with

Table IX. Composition of Fractions from Tia Juana Medium Naphtha in the Boiling Range 105.2° to 175.2° F.

Vol. % of fraction on 310° F. whole naphtha 17.2
Vol. % of fraction on crude 1.6

Compound	B.P., °F.	1	2–3	4–10	11–18	19–20	21–30	Bottoms[a]
Cut Nos.		1	2–3	4–10	11–18	19–20	21–30	Bottoms[a]
Cut temp., °F.		120.0	136.8	140.8	144.0	147.2	156.0	. . .
Cut vol. %		2.0	4.0	14.0	16.0	4.0	20.0	40.0
Cumul. vol. %		2.0	6.0	20.0	36.0	40.0	60.0	100.0
n-Pentane	96.9	30.9	1.4					
Cyclopentane	120.7	52.7	36.3	2.8				
2,2-Dimethylbutane	121.5	16.4	11.6	1.9				
2,3-Dimethylbutane	136.4	0.0	19.4	13.7	3.4	0.6		
2-Methylpentane	140.5		31.3	78.7	53.3	23.7	2.5	
3-Methylpentane	145.9			2.9	43.0	68.0	17.6	
n-Hexane	155.7				0.3	7.0	75.8	
Methylcyclopentane	161.3					0.0	0.0	
Benzene	176.2					0.7	4.1	
Compounds boiling above 140.5° F.								100.0

[a] Bottoms added to 175.2° to 214.8° F. fraction.

Table X. Composition of Fractions from Tia Juana Medium Naphtha in the Boiling Range 155.2° to 214.8° F.

Vol. % of fraction on 310° F. whole naphtha 25.4
Vol. % of fraction on crude 3.85

Compound	B.P., °F.	1–10	11–12	13–15	16–18	19–31	32–40	Bottoms
Cut Nos.		1–10	11–12	13–15	16–18	19–31	32–40	Bottoms
Cut temp., °F.		159.2	169.6	176.4	190.8	198.3	211.2	. . .
Cut vol. %		20.0	4.0	6.0	6.0	28.0	18.0	20.0
Cumul. vol. %		20.0	24.0	30.0	36.0	62.0	80.0	100.0
n-Hexane	155.7	63.8	2.0	0.1				
Benzene	176.2	7.6	11.8	0.4				
Methylcyclopentane	161.3	26.4	47.7	2.5				
2,2-Dimethylpentane	174.6	0.2	4.6	2.7				
2,4-Dimethylpentane	176.9	2.0	10.3	20.7	7.2			
Cyclohexane	177.3		23.6	70.0	36.6			
2,2,3-Trimethylbutane	177.6			3.6	1.1			
3,3-Dimethylpentane	186.9				4.2	0.3		
1,1-Dimethylcyclopentane	190.1				6.4	0.9		
2,3-Dimethylpentane	193.6				12.1	11.0		
2-Methylhexane	194.1				18.4	27.4	0.4	
cis-1,3-Dimethylcyclopentane	195.4				2.5	7.7	0.3	
trans-1,2-Dimethylcyclopentane	197.4				0.6	8.4	0.8	
trans-1,3-Dimethylcyclopentane	197.4				0.6	3.3	0.2	
3-Methylhexane	197.5				10.3	36.4	4.0	
3-Ethylpentane	200.2					2.7	1.5	
n-Heptane	209.2					1.9	82.7	
2,2,4-Trimethylpentane	210.6						0.3	
cis-1,2-Dimethylcyclopentane	211.1						1.5	
Methylcyclohexane	213.6						8.3	
Compounds boiling above 200.2° F.								100.0

closely boiling isomers. The mean deviation of these data is ±0.8%.

The effect of benzene upon the absorbances of other hydrocarbons was determined by analyzing synthetic blends containing known amounts of benzene. These analyses were carried out, completely ignoring the presence of benzene. Benzene has a negligible effect, if any, at the wave lengths used to determine the other components in the blends. The investigation of the effects of benzene was limited to those compounds boiling below 176° F. because it did not occur in higher boiling fractions. In addition, the concentration was limited to 10 to 11% because this was about the maximum amount encountered in any one fraction. These results are shown in blends 2 and 5.

Limits of 99.0 to 104.0% were set on all analyses, before normalizing. If the total of any analysis was outside these limits, the analysis was repeated. All results were normalized to 100.0%, except in the analysis of the bottom cut of the special fraction of the La Rosa naphtha in which toluene was found. In this case, the results were normalized to 98.2%, because the cut contained 1.8% toluene.

RESULTS

The analyses of the light hydrocarbons, *n*-pentane and lighter, as obtained by low temperature fractionation are shown in Table III. As the La Rosa sample was obtained from the naphtha separator of a refinery unit, some of the lighter components were lost to the refinery gas handling facilities. Methane is absent and the ethane to isopentane concentrations are undoubtedly low. Bachaquero and Tia Juana naphthas, however, were obtained by crude fractionation in laboratory equipment, and it was possible to recover all the light components present in the crude samples.

The Fenske distillation curves and specific gravity results are shown in Figures 1 to 3. The analyses of the C_5 fractions from the Fenske distillations are given in Table IV.

The C_6 and C_7 fractions prepared from appropriate Fenske cuts of each naphtha were refractionated into 2% cuts in the Heli-Grid packed column. The distillation curves, specific gravity, and refractive index measurements are shown in Figures 4 to 9. Each 2% cut was analyzed separately by infrared spectrophotometry and the results grouped where similarity in composition occurred (Tables V to X).

All the possible isomers of the paraffins, C_5 and C_6 naphthenes and aromatics, except for 2,2-dimethylpropane (neopentane), boiling up to 214° F. were identified in each of the naphthas. The detailed composition of each naphtha is shown in Table XI. This table is limited to those compounds boiling up to 200.2° F. (3-ethylpentane) because the distillations were not carried far enough to isolate the higher boiling compounds completely.

Comparing the three naphthas by compound type, the highest octane quality can be expected from Bachaquero because of the higher naphthene content. Tia Juana is the most paraffinic of the three naphthas, so it might have the poorest octane quality. However, comparing the normal paraffins to the corresponding branched isomers, La Rosa has a generally higher proportion of normal paraffins and consequently the lowest octane quality of the three naphthas.

A comparison of the individual branched paraffin isomers in the hexane boiling range shows the highest octane quality may be expected from Bachaquero because of the proportionately lower concentration of low octane methylpentanes. In this respect, Tia Juana and La Rosa naphthas are almost identical and would have essentially the same octane quality.

Table XI. Composition of Venezuelan Naphthas

Naphtha	La Rosa Medium	Bachaquero	Tia Juana Medium
Analysis Range °F., initial B.P. to	209°	210°	211°
Sp. gr. 20/4, debutanized naphtha	0.701	0.735	0.720
Crude gravity, °API	25.4	15.9	26.7
Crude, vol. %	11.4	5.5	15.2

Compound	B.P., °F.	Volume per cents					
		Naphtha	Crude	Naphtha	Crude	Naphtha	Crude
Methane		. . .	. . .	0.76	0.042	0.07	0.011
Ethane		0.09	0.010	0.90	0.050	0.96	0.146
Propane		0.70	0.080	2.71	0.149	3.92	0.596
Isobutane		0.93	0.106	2.16	0.119	2.34	0.356
n-Butane		3.94	0.449	4.31	0.237	6.01	0.914
Isopentane	82.2	4.39	0.500	2.79	0.153	4.26	0.648
n-Pentane	96.9	4.16	0.474	3.35	0.184	4.66	0.708
Cyclopentane	120.7	0.61	0.070	0.83	0.046	0.69	0.105
2,2-Dimethylbutane	121.5	0.12	0.013	0.21	0.012	0.18	0.028
2,3-Dimethylbutane	136.4	0.60	0.068	0.75	0.041	0.56	0.085
2-Methylpentane	140.5	3.75	0.428	3.03	0.167	3.84	0.583
3-Methylpentane	145.9	2.58	0.294	1.95	0.107	2.33	0.354
n-Hexane	155.7	6.80	0.776	3.88	0.213	5.91	0.899
Methylcyclopentane	161.3	2.17	0.247	2.21	0.122	1.86	0.283
2,2-Dimethylpentane	174.6	0.11	0.013	0.15	0.008	0.10	0.015
Benzene	176.2	0.74	0.084	0.51	0.028	0.66	0.100
2,4-Dimethylpentane	176.9	0.60	0.068	0.68	0.037	0.63	0.096
Cyclohexane	177.3	1.91	0.217	2.47	0.136	1.67	0.254
2,2,3-Trimethylbutane	177.6	0.07	0.008	0.08	0.004	0.07	0.011
3,3-Dimethylpentane	186.9	0.09	0.010	0.09	0.005	0.08	0.012
1,1-Dimethylcyclopentane	190.1	0.16	0.019	0.28	0.015	0.16	0.024
2,3-Dimethylpentane	193.6	1.11	0.125	1.17	0.064	0.91	0.138
2-Methylhexane	194.1	2.47	0.278	1.59	0.087	2.11	0.323
cis-1,3-Dimethylcyclopentane	195.4	0.76	0.085	1.01	0.055	0.56	0.085
trans-1,2-Dimethylcyclopentane	197.4	1.00	0.112	1.09	0.060	0.60	0.091
trans-1,3-Dimethylcyclopentane	197.4	0.64	0.072	0.44	0.024	0.24	0.036
3-Methylhexane	197.5	3.64	0.410	2.35	0.128	2.74	0.416
3-Ethylpentane	200.2	0.38	0.043	0.35	0.019	0.25	0.038
Paraffins boiling above	200.2	2.19	0.247	1.08	0.059	3.93	0.593
Naphthenes boiling above	200.2	0.34	0.038	0.11	0.006	0.45	0.068
Total		47.05	5.344	43.29	2.377	52.75	8.016

A similar comparison of the isoheptane–*n*-heptane proportion in the three naphthas was not possible because the distillations were not carried out far enough to isolate all of the *n*-heptane present. However, among the heptane paraffin isomers, both La Rosa and Tia Juana show a general deficiency in high octane components when compared to Bachaquero. Comparing the relative concentrations of naphthenes shows La Rosa to be essentially equal to Tia Juana. Both, however, are lower than Bachaquero, pointing out the superior octane quality of Bachaquero naphtha.

Octane Determinations. The analyses of the individual cuts not only supply yield data, but provide a means by which product octane quality can be estimated from available octane blending values of pure hydrocarbons.

To test the validity of these calculations, a special La Rosa Naphtha cut was tested for supercharge blending index and analyzed by fractional distillation and infrared and ultraviolet spectroscopy. Figure 10 shows the distillation curve as well as the specific gravities and refractive indices of the 2% cuts. Engine testing of this special cut shows a supercharge blending index which agreed within one index number with the calculated value. Local experience with such normal naphtha fractions has shown a good correlation of (1) blending values in alkylate-isopentane mixture and (2) blending values calculated from compound analysis based on individual compound values. These latter values had been obtained in blends with anti-knock reference fuels or other base stocks differing from commercial stocks used here.

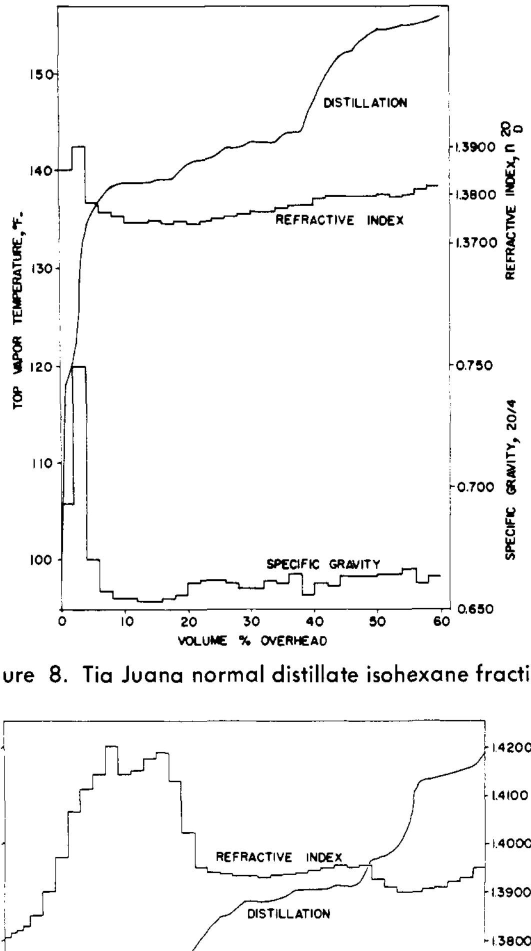

Figure 8. Tia Juana normal distillate isohexane fraction

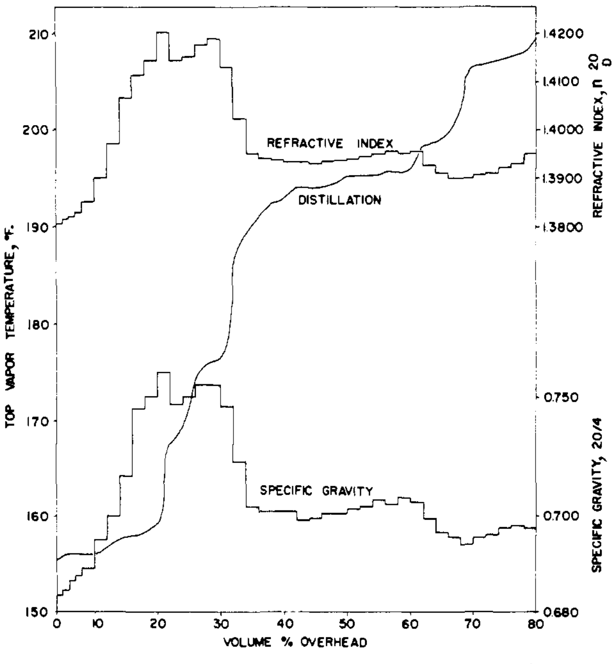

Figure 9. Tia Juana normal distillate isoheptane fraction

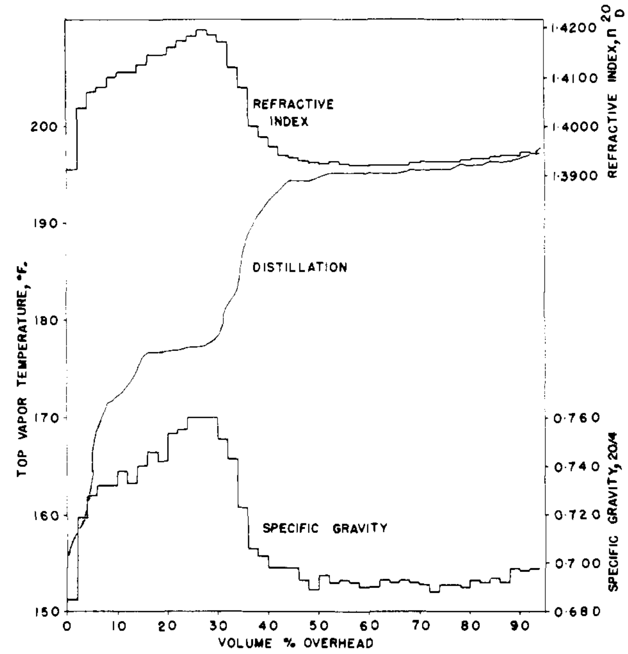

Figure 10. La Rosa normal distillate true boiling still cuts 11 to 22 (172° to 190° F.)

Thus, other calculated blending values would be equally valid and this method could be used in lieu of engine testing involving extensive sample preparation and time.

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