ENCLOSURE (B) 16

PART IV

STUDIES ON HYDROCRACKING OF OMONOGAWA GAS OIL

by

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SUMMARY

This study was made to investigate the production of aviation gasoline by hydrocracking Omonogawa gas oil. It was found that the fraction boiling between 160-220°C was the best feed stock for preparing high octane aviation gasoline.

INTRODUCTION

A. History of Project

Although Omonogawa gas oil had characteristics similar to Oha gas oil, yet upon hydrocracking under similar conditions a poorer quality of gasoline was obtained (see Table XXX(B)16). The conditions selected for these tests were optimum from the standpoint of yield, and catalyst No. 6 which was the best known for hydrocracking of mineral oils, was used. In view of these results, further work was centered on determining whether gasoline of higher quality could be made by hydrocracking special cuts from Omonogawa gas oil.

B. Key Research Personnel Working on Project

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II. DETAILED DESCRIPTION

A. Raw Materials

An Omonogawa gas oil, boiling range of 125-298°C, was fractionated into 18 narrow boiling cuts. Properties of the gas oil and each of these cuts are given in Table XXXI(B)16 and Figure 5(B)16.

B. Test Apparatus

These experiments were made in the 1-lit/hr continuous hydrocracking unit #3. A flow chart of this unit is given in Figure 4(B)16.

One liter of used catalyst, No. 6, was packed in the preheater and one liter of new catalyst, No. 6, was paced in the reaction chamber. Afte the apparatus was examined for leakage at 300 kg/cm², the pressure was reduced to 200 kg/cm^2, heating was started, and H_2 circulated at the rate of 1 m^3/hr. After temperature in the reaction chamber reached 300°C, oil was charged into the preheater by the high pressure feed pump at the rate of 1 lit/hr and mixed with hydrogen. In the preheater the mixture was ~~heated to 300°C by electric heaters, and introduced into the reaction~~ chamber maintained at 430°C. From the reaction chamber the mixture of hydrocracked products and gas passed through the condenser and into the high pressure separator. The gas and liquid products were separated under full pressure, the liquid being withdrawn to the low pressure separator and sent to storage. The gas from the high pressure separator was reduced to normal pressure, flow rate measured in the gas meter and then discharged to the air.

Oil was flashed into the low pressure separator intermittently (every 30 mins) and drawn off from the bottom.

The product oil was distilled to yield an aviation cut with 150°C endpoint and a residual oil.

A summary of reaction conditions follows:

Reaction pressure	200 kg/cm^2
Temperature of preheater	300°C
Temperature of reaction chamber	430°C
H_2 charged	1 m^3/hr
Oil charged	1 lit/hr
S.V. of oil	1.0
Catalyst	NiO.MoO$_3$.Active clay (1:3:3)

C. Yield and Properties of Products

Yields and properties of products are summarized in Tables XXXII(B)16, XXXIII(B)16, and XXXIV(B)16. In these runs there was generally a 5-20% loss of oil product in gas due to intermittent operation of the low pressure separator. Properties of aviation gasoline ~~obtained in these runs~~ are given in Table XXXV(B)16 and Figure 6(B)16.

On the aviation gasolines from gas oil samples No. 1, 2, 3, and 4 the 50% points were 121, 121.5, 128, and 112°C, but in the case of samples No. 5-18 it was 90-105°C. These results indicated that it was more difficult to hydrogenate the lighter boiling gas oil cuts.

Yield of aviation gasoline was best for samples No. 10-14, with the exception of samples No. 1-4 which had large amounts of material boiling up to 150°C in raw material maximum octane number was indicated for samples No. 5-9. Properties of topped oil are given in Table XXXVI(B)16. The content of aromatic hydrocarbons in the topped oil decreased and the content of paraffinic hydrocarbons increased as compared with the feed stocks.

III. CONCLUSIONS

On the basis of these experiments it was concluded that the fraction of Omonogawa gas oil boiling in the range 160-220°C was the optimum hydrocracking charge for production of high octane aviation gasoline.

In comparing the hydrocracking of Oha and Omonogawa gas oil, for a given boiling range cut these oils have similar compositions and the reaction on hydrocracking is the same.

The total Oha gas oil, however, gave a better yield of high octane gasoline since it had a narrower boiling range than the Omonogawa gas oil, and a higher content of the optimum 160-220°C components.

ENCLOSURE (B)16

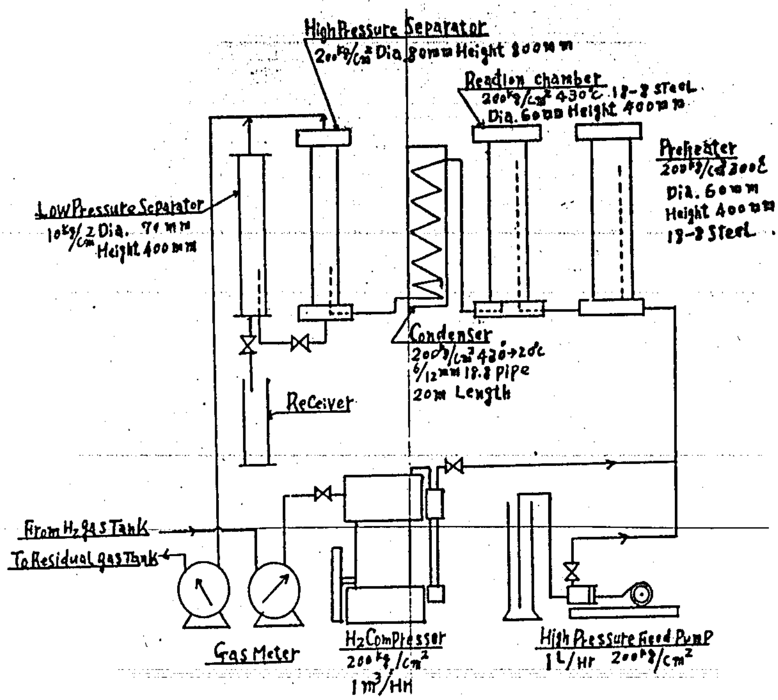

Figure 4(B)16

FLOW CHART OF THE APPARATUS

ENCLOSURE (B)16

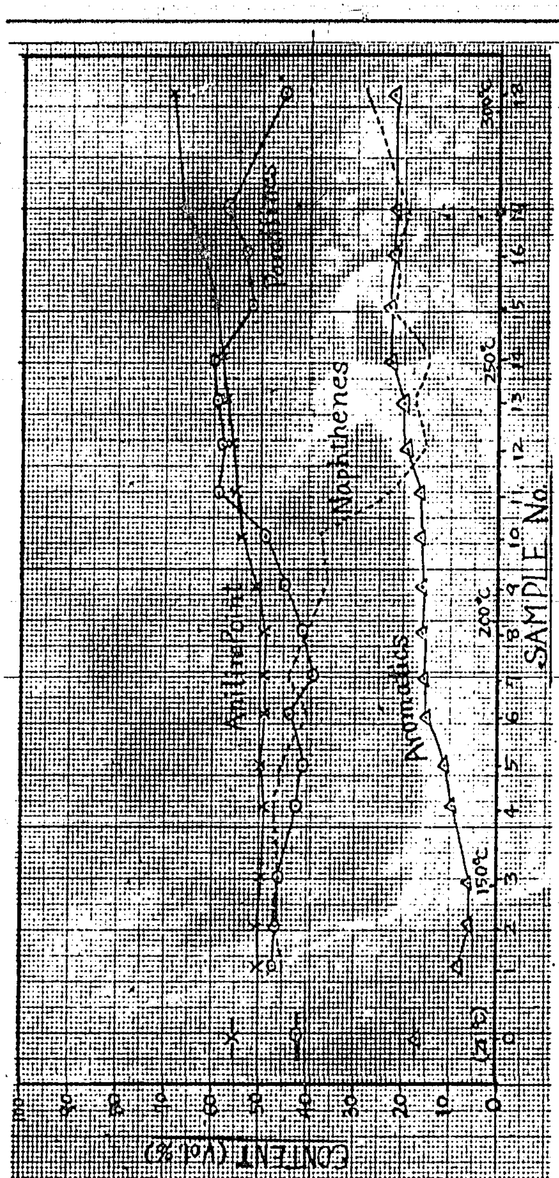

Figure 5(B)16
PROPERTIES OF RAW MATERIALS

ENCLOSURE (B)16

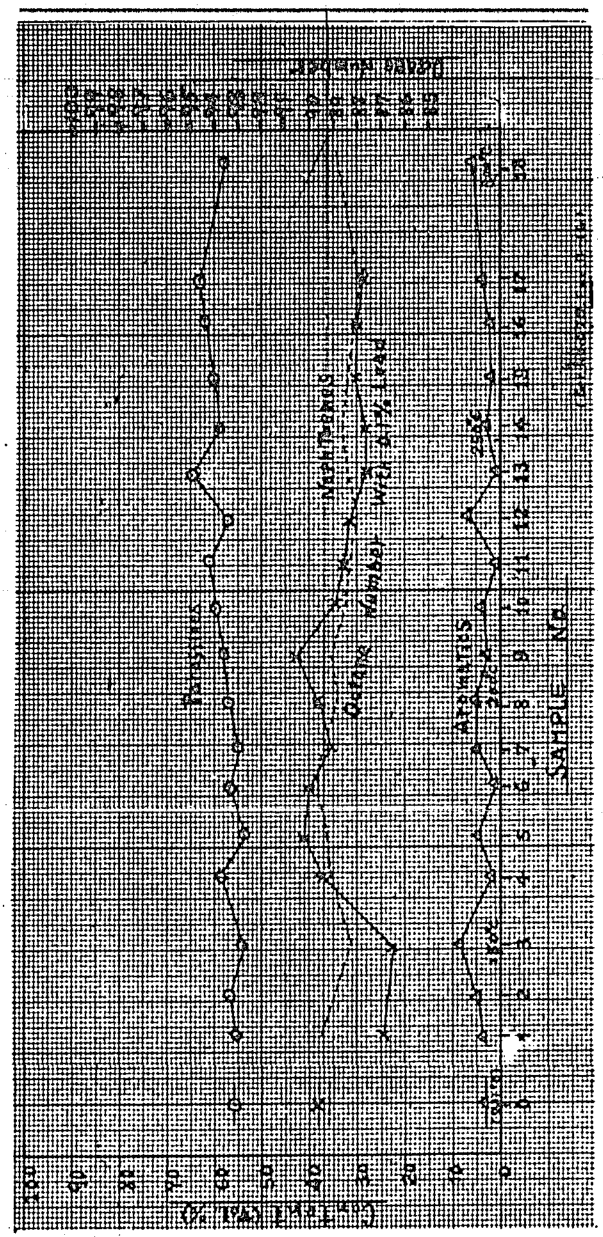

Figure 6(B)16
PROPERTIES OF AVIATION GASOLINE

ENCLOSURE (B)16

Table XXXII(B)16
YIELD AND H_2 CONSUMPTION

Run No.	Sample No.	Density of Sample (d_4^{20})	Density of Product (d_4^{20})	Run Period (hr)	Oil Charged (l/hr)	Product (l/hr)	Yield (vol. %)	H_2 Charged (ml/hr)	Residual Gas (m^3/hr)	H_2 Consumption (wt. %)
1	0	0.8229	0.7663	4.5	1.2	1.1	93.8	1.7		
2	1	0.7685	0.7379	3.0	1.2	0.8	67.3	1.1	0.8	2.5
3	2	0.7766	0.7501	3.5	1.0	0.7	68.3	1.1	0.8	4.0
4	3	0.7858	0.7404	4.0	1.0	0.9	86.5	1.3	1.3	1.5
5	4	0.7967	0.7407	3.0	1.0	0.8	79.1	1.3	1.0	3.5
6	5	0.8056	0.7677	3.0	1.0	0.9	94.5	1.5	0.6	9.9
7	6	0.8127	0.7481	3.5	1.0	0.8	83.3	1.3	0.4	9.3
8	7	0.8220	0.7511	5.0	0.9	0.7	74.4	1.4	0.7	9.1
9	8	0.8301	0.7476	4.0	1.1	1.0	91.0	1.2	0.8	4.2
10	9	0.8348	0.7550	3.5	1.0	0.7	70.0	1.1	0.8	3.1
11	10	0.8370	0.7423	4.0	1.0	0.7	74.4	1.4	0.7	7.5
12	11	0.8412	0.7413	3.5	1.1	1.0	90.6	1.1	0.7	5.1
13	12	0.8455	0.7440	4.5	0.9	0.7	75.6	1.0	0.8	
14	13	0.8487	0.7393	3.0	0.9	0.8	88.9	1.1	0.7	5.1
15	14	0.8543	0.7648	5.5	1.0	1.0	97.8	1.1	0.7	4.2
16	15	0.8570	0.7570	4.5	1.0	0.9	93.7	1.1	0.9	2.3
17	16	0.8611	0.7632	2.0	1.1	1.0	90.2	1.1	0.7	3.8
18	17	0.8685		2.0	1.0	1.1	104.9	1.1	0.6	4.8
19	18	0.8724		3.0	0.9	1.0	104.2	1.1	0.7	4.7

Table XXX(B)16
COMPARISON OF HYDROCRACKING OF OHA AND OMANOGAWA GAS OIL

			Oha	Omanogawa
Boiling range of gas oil			150-250	125-298
Density of gas oil			0.832	0.823
Reaction Conditions	Catalyst		NiO.MoO$_3$.active clay	NiO.MoO$_3$.active clay
	H_2 pressure (kg/cm^2)		200	200
	Temperature		420	420
Gasoline Fraction	Yield (vol. %)		70	43.6
	Density d_4^{20}		00.7118	0.7107
	Distillation	I.B.P. (°C)	29.3	31.0
		10% (°C)	53.5	55.0
		50% (°C)	97.0	97.0
		90% (°C)	141.5	142.5
		F.B.P. (°C)	165.5	164.5
Octane Number	Clear		74.0	70.3
	With 0-1% lead		91.7	89.0

Table XXXI(B)16
PROPERTIES OF RAW MATERIALS

		Sample No. 0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Mean B.P. (°C)		211.0	133.4	141.1	151.1	164.2	172.6	182.3	189.6	198.6	207.2	216.9	225.5	234.1	243.2	251.6	261.6	271.4	280.4	303
d_4^{20}		0.8229	0.7685	0.7766	0.7858	0.7967	0.8056	0.8127	0.8220	0.8301	0.8345	0.8370	0.8412	0.8455	0.8482	0.8543	0.8570	0.8611	0.8685	0.8724
n_D^{20}		1.4869	1.4266	1.4304	1.4355	1.4408	1.4460	1.4490	1.4540	1.4581	1.4615	1.4620	1.4660	1.4690	1.4726	1.4768	1.4775	1.4798	1.4775	1.4852
Fractional Distillation	I.B.P.	124.5	99.0	122.0	140.5	149.0	158.0	170.0	177.5	189.5	199.0	210.0	218.0	228.0	237.0	246.0	257.0	266.5	276.5	284.5
	10%	149.5	117.5	129.0	143.5	153.5	163.5	173.5	183.0	193.0	202.5	211.5	220.5	230.0	239.5	245.5	259.0	267.5	277.5	296.5
	20%	161.5	123.0	131.0	144.0	155.0	164.5	175.0	184.0	194.0	203.0	213.0	222.0	230.5	240.0	249.0	259.5	268.5	278.5	298.5
	30%	174.0	126.0	133.5	145.0	155.5	165.5	176.5	185.0	195.0	204.0	213.5	222.5	231.0	241.0	249.5	259.5	269.0	279.0	300.5
	40%	201.5	127.5	136.0	147.0	167.5	167.0	178.0	186.5	196.0	204.5	214.0	223.5	232.0	241.5	250.0	260.0	270.0	279.2	301.2
	50%	219.5	131.5	138.0	148.5	159.5	168.5	179.0	187.5	197.0	205.5	215.5	224.0	232.5	242.0	250.5	260.5	270.5	279.5	302.0
	60%	233.0	136.5	141.5	150.0	161.6	170.5	180.5	189.0	198.0	206.5	216.0	225.0	233.0	243.0	251.0	261.5	271.5	280.0	302.5
	70%	244.5	140.0	144.5	152.5	163.5	172.0	182.5	190.5	199.5	208.0	217.5	226.0	234.5	243.5	252.0	262.0	272.5	281.0	304.5
	80%	255.0	143.5	147.5	156.0	166.5	175.0	184.5	192.5	201.5	210.0	219.0	228.0	236.0	245.0	253.0	263.0	274.5	282.0	308.5
	90%	269.5	151.0	156.0	162.0	172.0	179.0	189.5	197.0	205.0	213.0	222.0	230.5	238.0	247.5	255.0	265.0	274.5	283.5	312.5
	F.B.P.	298.0	173.0	174.0	174.0	213.0	215.5	215.5	213.5	217.0	224.0	233.5	241.5	250.5	255.5	263.0	271.5	282.5	288.0	324.5
Constitute Analysis H.C.	Unsat. (%)	1.0	0.0	0.0	0.0	0.5	0.0	1.0	0.5	0.5	1.0	0.0	0.0	0.5	1.0	0.5	0.0	0.5	0.0	1.0
	Arom. (%)	16.8	8.0	6.0	6.0	10.0	15.6	11.8	15.9	16.7	16.2	17.0	17.0	19.9	20.7	23.6	23.7	22.9	22.0	23.0
	Naph. (%)	40.5	44.8	47.0	47.6	47.1	40.4	45.9	44.4	40.5	36.9	33.2	23.5	21.2	18.7	15.9	23.9	22.7	20.2	29.9
	Para. (%)	41.7	47.2	47.0	46.4	42.4	44.0	41.3	39.2	41.3	45.9	49.8	59.2	58.4	59.6	60.0	52.4	53.9	57.8	46.1
Aniline Point	(°C)	55.6	49.8	50.6	49.8	49.8	49.6	49.6	49.4	49.4	51.2	54.2	55.3	57.2	58.6	58.8	60.2	62.8	67.8	69.2
	Sat. H.C. (°C)	68.2	58.2	59.8	61.2	61.2	63.2	62.2	63.6	65.8	68.6	71.0	73.4	75.3	78.4	79.6	80.0	83.2	86.2	89.3

ENCLOSURE (B)16

Table XXXIII(B)16
PROPERTIES OF OIL PRODUCT

		Sample Number																		
		0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
d_4^{20}		0.7663	0.7379	0.7501	0.7404	0.7407	0.7677	0.7481	0.7611	0.7476	0.7550	0.7423	0.7413	0.7440	0.7343	0.7648	0.7570	0.7632		
Distillation	I.B.P.	60.0	55.0	56.0	48.0	44.0	56.0	50.5	57.5	45.5	52.0	48.5	49.5	51.0	48.0	54.0	66.0	56.0	63.0	61.0
	10%	92.0	91.2	80.0	80.5	72.8	97.0	78.0	88.5	72.8	82.2	69.0	72.5	76.5	72.0	83.0	86.0	84.0	93.0	98.0
	20%	108.0	104.2	99.0	104.0	88.2	117.0	96.0	109.5	88.5	100.3	83.5	87.0	90.0	84.8	100.5	101.0	101.0	115.0	118.0
	30%	123.5	113.0	112.0	119.0	101.0	140.0	113.5	127.5	105.2	118.0	97.0	101.0	103.0	97.0	117.0	110.0	118.0	131.59	148.0
	40%	132.3	118.8	119.5	127.5	126.0	157.7	131.5	143.5	123.0	131.5	109.0	113.0	115.0	107.0	138.0	128.0	133.0	159.0	172.5
	50%	142.7	123.0	125.0	133.7	138.8	160.5	148.7	158.0	140.0	151.0	122.0	131.5	132.6	122.0	172.0	148.2	156.0	181.0	218.0
	60%	160.0	126.5	129.0	138.5	144.5	164.0	161.0	169.0	162.0	176.0	140.0	150.0	152.0	142.0	212.0	170.0	193.0	255.5	282.0
	70%	182.0	131.0	132.3	143.2	150.0	168.2	165.0	177.0	180.5	192.0	163.0	142.0	182.0	166.5	233.0	224.0	254.0	280.0	299.0
	80%	217.0	134.0	139.0	148.5	156.0	175.0	177.0	185.0	190.0	200.8	201.5	215.0	216.0	220.0	251.0	269.0	272.0	285.0	305.0
	90%	251.0	144.0	156.2	155.5	164.0	182.8	183.0	192.0	199.0	209.0	214.0	226.0	233.0	242.0	258.0	268.0	279.0	296.0	312.0
	F.B.P.	282.0	180.7	166.5	178.4	181.0	235.1	204.2	218.5	219.5	229.0	232.5	237.0	248.8	254.0	276.5	278.5	285.0	299.0	329.0
Aniline point of Product		55.2	58.4	57.6	59.0	59.6	56.4	59.2	59.6	60.0	61.0	60.8	61.8	62.0	62.0	64.6	65.0	65.0		
Constitution (H.C.)	Unsat.	3.2	0.5		2.1	1.8	0.8	0.6	0.0	0.6	2.0	4.2	1.8	2.2	2.3	1.7	3.5	2.0	1.8	0.8
	Arom.	4.7	4.7		9.0	1.6	6.5	2.3	5.9	5.0	1.5	2.1	3.2	7.0	0.9	2.5	3.3	2.2	7.8	10.0
	Naph.	38.7	39.0		34.7	39.7	44.6	44.9	41.9	40.7	36.5	37.6	37.1	33.5	33.1	35.4	28.1	27.5	28.4	31.5
	Para.	53.4	55.8		54.2	56.9	51.9	47.8	52.2	53.7	60.0	56.1	57.9	57.3	63.7	60.4	65.1	68.3	67.0	57.7

Table XXXIV(B)16
ANALYSIS OF RESIDUAL GASES

Run No.	CO_2	C_nH_{2n}	CO	C_nH_{2n+2}	H_2	n
1	0	0.2	0	2.0	96.4	1.2
2	0.2	0.6	0.4	3.9	94.4	1.0
3	0.2	0.2	0	6.4	92.7	0.7
4	0	0.2	0	4.9	94.5	1.6
5	0	0.4	0.6	5.9	91.8	1.3
6	0	0.4	0	12.9	86.3	1.3
7	0	0.1	0	9.3	89.6	1.4
8	0	1.0	0.2	7.1	90.5	1.5
9	0	0.8	0	6.6	92.6	1.2
10	0	0.2	0	2.7	97.1	1.8
11	0	0.2	0	4.9	94.0	1.6
12	0	0.6	0.4	4.9	92.4	2.0
13	0					
14	0	0.2	0.1	3.9	95.7	2.5
15	0	0	0.3	4.9	94.4	1.0
16	0	0.2	0.2	6.0	93.0	1.3
17	0	0.4	0	5.0	94.2	1.8
18	0	0.4	0	4.3	94.3	2.3
19	0	0.2	0	5.7	93.2	2.5

Table XXXV(B)16
PROPERTIES OF AVIATION GASOLINE

	Sample Number																		
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Yield (vol. %) of oil product	54	95	93	86	70	39	51	45	55	50	64	60	58.5	63	64	52	49	36.3	33
d_4^{20}	0.7394	0.7412	0.7363	0.7418	0.7285	0.7186	0.7122	0.7169	0.7070	0.7084	0.7127	0.7182	0.7109	0.7133	0.7198	0.7149	0.7162	0.7178	0.7140
Fractional Distillation I.B.P.	58.0	62.0	55.5	57.5	46.5	43.0	41.0	52.5	44.0	41.5	41.5	49.0	45.5	49.0	47.5	50.5	48.5	50.0	48.5
10%	82.0	86.0	82.5	81.0	68.0	62.5	61.5	69.5	64.5	62.0	61.0	67.0	65.0	69.0	67.0	69.0	68.0	70.0	68.0
20%	92.2	105.0	95.0	101.0	79.5	72.0	70.0	76.5	74.5	72.5	70.5	76.5	72.5	79.0	76.5	78.0	77.5	80.0	79.0
30%	102.0	113.0	109.5	112.0	90.5	79.5	78.5	83.5	83.5	80.5	98.5	84.5	81.0	88.0	85.0	86.0	85.5	89.0	88.0
40%	110.0	117.5	117.0	121.0	101.5	86.5	86.0	89.5	90.0	87.0	85.0	90.5	87.5	94.0	91.5	93.0	94.0	97.0	96.5
50%	115.0	121.0	121.5	128.0	112.0	90.5	93.5	95.5	96.0	93.0	93.0	97.0	94.0	100.0	98.0	99.0	101.0	103.0	104.0
60%	120.5	124.5	125.5	132.5	122.5	104.0	102.5	101.5	101.5	99.0	99.5	103.5	100.0	107.0	105.0	105.0	107.5	109.0	111.0
70%	126.5	128.2	126.5	133.0	131.0	115.5	111.0	107.5	107.5	106.0	106.5	110.5	107.5	114.0	112.0	111.5	114.5	115.5	119.0
80%	135.0	133.2	134.0	140.0	137.5	127.0	129.0	116.5	115.0	115.0	114.0	117.5	111.0	121.5	120.0	119.0	123.5	123.0	128.0
90%	141.7	139.0	140.5	144.0	145.0	142.0	149.0	131.5	128.0	125.0	125.0	131.5	126.0	135.5	133.0	133.0	138.5	137.5	139.5
97%	152.0	148.0	151.0	149.0	152.5	155.0	164.0	153.5	158.0	158.0	138.0	145.0	141.0	156.0	151.5	155.0	151.0	156.5	162.0
F.B.P.	175.0	154.0	160.5	157.0	161.0	161.5	169.5	169.5	163.5	161.5	151.0	167.0	152.5	163.0	166.0	166.0	163.5	169.0	168.0
Aniline Point		57.4	52.0	58.2	58.6	56.4	58.0	57.2	58.8	58.4	59.4	59.4	58.6	58.6	58.6	58.6	58.8	58.8	58.4
Constitution (H.C.) Unsat.	2.5	0.5	0.5	2.5	2.5	2.0	1.0	0.0	1.0	1.0	1.0	3.0	3.0	0.5	2.0	2.5	2.5	0.5	2.5
Arom.	3.9	4.9	5.9	9.7	2.3	5.6	1.9	6.0	5.9	3.9	5.0	1.9	7.7	0.9	3.9	2.9	2.9	4.9	6.8
Naph.	37.4	38.4	36.1	32.7	36.1	37.5	39.4	38.2	35.3	36.7	33.9	33.2	31.5	33.5	34.5	33.4	32.1	30.9	34.1
Para.	56.2	56.2	57.5	55.1	59.1	54.9	57.7	55.8	57.8	58.4	60.1	61.4	57.8	65.1	59.6	61.2	62.5	63.7	58.6
Values Unleaded	66.7	66.2		65.5	68.3		70.8	69.4	69.3	70.9	68.7	66.9	66.9	66.4	67.5	66.5	65.1	65.7	
Leaded 0.1%	89.7	87.2		86.7	89.7	90.5	90.2	89.4	89.8	90.7	89.1	88.7	88.4	87.7	89.8	88.2	88.1	87.8	

Table XXXVI(B)16
PROPERTIES OF RESIDUAL OIL

	Sample Number																		
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
d_4^{20}	0.8107	0.7872	0.7783	0.7792	0.7826	0.7952	0.7886	0.7964	0.8010	0.8033	0.8059	0.8058	0.8032	0.8176	0.8148	0.8118	0.8179	0.8203	0.8314
Fractional Distillation I.B.P. (°C)	156.5	154.0		149.0	150.5	151.5	157.5	159.0	167.0	166.5	174.5	172.5	159.0		172.0	161.0	161.5	165.5	168.0
10%	167.0	157.0		153.0	153.0	158.0	162.5	169.5	175.0	178.5	187.5	189.55	181.5	191.5	202.0	192.5	195.5	202.5	208.0
50%	[illegible]	164.0		157.0	158.0	155.8	171.0	180.0	186.5	195.5	202.5	211.0	214.5	226.0	238.5	246.5	258.0	269.5	298.0
90%	[illegible]	211.0		169.0	169.0	182.0	183.0	193.0	200.5	208.0	217.5	225.5	233.5	143.0	254.0	262.0	272.5	281.0	317.0
F.B.P.	[illegible]	260.0		192.5	187.5	247.5	201.0	213.0	216.5	222.0	232.0	240.0	248.5	258.0	266.0	272.5	285.0	299.5	339.0
Aniline Point Crude Residue	55.5	61.0	59.2	59.0	60.6	57.8	61.6	61.8	63.8	64.8	65.8	67.8	68.2	70.0	70.0	72.8	73.2	74.8	74.4
Sat. H.C.	60.6	62.6		61.2	61.4	61.5	62.4	63.2	64.2	68.8	67.7	69.8	71.2	70.4	71.0	77.2	78.2	81.8	83.4
Constitution (H.C.) Unsat.	[illegible]	0.5		0.0	0.0	0.0	0.2	0.0	0.0	0.0	1.0	0.0	0.8	4.0	1.2	4.5	1.5	0.0	0.0
Arom.	5.7	0.4		4.6	1.0	10.4	2.7	5.8	4.0	2.0	5.9	5.2	5.9	0.7	0.0	3.8	8.8	12.0	11.6
Naph.	[illegible]	[illegible]		47.0	48.1	49.2	50.6	44.9	47.3	49.3	44.3	42.9	36.6	32.4	37.0	22.4	23.1	5.5	30.2
Para.		[illegible]		48.4	50.9	40.4	46.7	49.3	48.7	48.7	48.8	51.9	56.7	62.9	61.8	69.3	66.6	72.5	58.2