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PILOT PLANT CATALYTIC CRACKING STUDIES ON SUMATRA KEROSENE AND PINE ROOT OIL

by

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

Pilot plant catalytic cracking experiments were carried out to produce aviation gasoline from Sumatra kerosene and from pine root oil fractions. Yields of aviation gasoline distillate were as follows:

Charging Stock	Yields
Sumatra Kerosene	25% by vol.
185° end point pine root distillate	70% by vol.
250° end point pine root distillate	50% by vol.
350° end point pine root distillate	35% by vol.

I. INTRODUCTION

The pilot plant, based on a U.O.P. catalytic cracking design, was completed in September 1943. Cracking tests on kerosene fractions from East Indies crudes were carried on until August 1944 by Chem. Eng. Lt., T. KOTANI. In this period several kinds of Japanese acid clays and U.O.P. synthetic catalyst were tested. The U.O.P. catalyst was manufactured by Nippon Gasoline Co. and was thought to be composed of aluminium silicate with zirconium oxide. The U.O.P. catalyst gave slightly higher octane number (about one unit) but was inferior to Japanese natural clays on basis of lower yields, higher olefine content of product, and higher cost of catalyst. The best catalyst was found to be acid clay from near KOMATSU City.

Starting in January of this year, tests on various fractions of pine root oil were carried out by Chem. Eng. Lt. Y. YAMASAKI.

II. DETAILED DESCRIPTION

A detailed flow chart of the pilot plant and operating conditions are shown on Figure 2-(B)5. Catalyst used for these experiments was activated. Japanese acid clay produced near KOMATSU City, ISHIKAWA district. Physical and chemical properties of feed stocks and detailed experimental results are shown in Tables I(B)5, II(B)5, III(B)5, and IV(B)5.

The several feed stocks were as follows:

a) Sumatra light oil; Shipped from YOKKAICHI, Second Fuel Depot.
b) Pine root oil (-250°C), Distilled at OFUNA, column overhead.
c) Pine root (Heavy), Distilled at OFUNA, side cut.
d) Pine root oil (-185°C), Shipped from YOKUYAMA, Third Naval Fuel Depot.
e) Mixed light oil, Mixture of light oils of petroleum origin.
f) Pine root oil (L.O. fraction), Distilled in batch-type still at TSURUMI, Nippon Petroleum Co.

III. CONCLUSION:

On the basis of the above experimental results, it was planned to treat pine root oil commercially according to the scheme outlined in Figure 1(B)5.

In the above scheme catalytic reforming would be carried out in simple units located near the pine root retorts. The catalytic cracking would be carried out in larger more complex units at central refineries. If sufficient catalytic cracking capacity and transportation facilities were available, it would be more desirable catalytically to crack the two fractions separately under op-

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timum conditions for each fraction, to produce satisfactory gasoline with the required volatility. Two catalytic cracking plants for processing kerosene from natural crude have been installed in Japan (at YOKKAICHI, the Second Naval Fuel Depot). Capacity of each plant was 2000 barrels/ day. Process designs were prepared at OFUNA on basis of pilot plant experiments.

It was planned catalytically to crack pine root oil at YOKKAICHI, but this was not accomplished by the end of the war. Some unsuccessful test runs were made on a catalytic unit at TSURUMI. It was also planned to construct some 21 catalytic cracking units, treating 10,20 or 30 kl of charge per day, to handle pine root oil in Japan, out no unit was completed.

Engine and flight tests were made on 40 kl of final catalytic cracked aviation gasoline plus 0.15% lead. Laboratory engine tests at the First Naval Technical Depot showed satisfactory results except for tendency to swell rubber connections. This problem was solved by substituting a better quality rubber. Flight tests in flighter planes made by YOKOSUKA Air Corps showed satisfactory results.

Table I(B)5
DISTILLATION OF CHARGING STOCKS

	Sumatra Light Oil	Pine Root Oil (~250°C)*	(~185°C)**	(Heavy Fract.)
Sp. Gr.	0.822	0.809	0.796	0.896
1st drop°C	81.5	65.0	72.0	122.0
10%	168.0	96.5	100.0	160.5
20%	182.5	110.5	112.0	170.5
30%	192.0	137.5	120.0	180.0
40%	202.5	146.0	128.0	189.0
50%	212.0	157.5	136.0	200.0
60%	223.0	162.0	145.0	217.0
70%	236.5	171.5	152.5	241.0
80%	251.0	181.5	159.0	272.0
90%	271.5	209.0	166.0	348.0
95%		222.0	172.0	
97%			175.5	
E.P.	331.0	238.0	179.5	
A.V.		0.30	0.20	0.60

*Washing of 1% alkali
**Distillation out~185°C

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Table II(B)5
CHARACTERISTICS OF FEED STOCKS

Run No		1	2	Prel.	3	4	5	6	7	8
Date		3.16 0900 3.17 0900	3.17 0900 3.18 0900	3.18 2100 3.19 0900	3.19 1600 3.20 0900	3.20 0900 3.21 0900	3.21 0900 3.22 0900	3.22 0900 3.22 2300	3.23 0900 3.24 0900	3.24 1200 3.25 0500
Run Period (hr)		24	24	12	17	24	24	14	24	17
Charging Stocks		Sumatra L. O.		Pine Root oil (-250°C Cut)			Pine Root oil (-185°C Cut)			Pine root oil (Heavy)
Total Charge (lit)		3560	3540	1550	2810	3110	3290	2120	3380	2830
Charge per hour (lit/hr)		148	148	129	165	130	137	152	141	166
S. V.		5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7
Recycle ratio		6.6	6.6	7.6	5.9	7.5	7.1	6.4	6.9	5.9
Reaction Temp (°C)	1st Reaction Chamb.	449	448	461	454	453	458	448	458	457
	2nd Reaction Chamb.	424	429	436	444	439	441	433	443	455
	3rd Reaction Chamb.	447	437	449	454	452	457	450	460	472
	Mean (°C)	440	438	443	451	448	452	444	454	461
Reaction Press (kg/cm^2)		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Oil Temp. Outlet of furnace tube (°C)		490	483	467	466	470	483	489	481	476
Oil Temp. Inlet of Reaction Vessel (°C)		485	480	459	458	462	477	482	471	476
Flue gas	Amount (m^3/hr)	865	865	865	865	865	865	865	865	865
	Heating Temp. (°C)	547	546	536	546	540	550	556	552	552
	Outlet of furnace tube (°C)	511	507	503	511	515	527	531	523	529
	Pressure (kg/cm^2)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Steam Temp. (°C)		242	286	285	281	278	265	265	274	274
Charging Stock Including Recycle	Sp. Gr. (15°/4°C)	0.857	0.850	0.855	0.856	0.848	0.831	0.831	0.842	0.841
	Ist Drop (°C)	87.5	89.0	72.0	104.0	74.5	84.5	84.5	104.0	82.0
	10 % (°C)	102.0	101.0	165.0	164.0	172.0	177.5	177.5	164.5	174.0
	50 % (°C)	202.0	196.0	213.0	212.5	229.5	223.0	223.0	212.5	224.0
	90 % (°C)	291.0	286.5	295.0	312.0	320.0	290.0	290.0	284.0	294.0
	E. P. (°C)	340.0	329.0	337.0	347.5	356.0	324.5	324.5	317.0	326.0
	U.O.P. Characterization	11.1	11.0	11.2	11.2	11.4	11.3	11.3	11.3	11.4
Flue gas	H_2S %									
	CO_2 %	8.5	7.8	8.7	9.1	8.8	8.7	7.5	9.2	9.3
	O_2 %	6.8	7.6	5.1	6.7	5.8	6.8	8.5	6.5	6.4
	CO %	2.4	2.0	3.9	1.4	2.7	2.2	1.1	1.8	2.1
Yields	Stabilised gas + Pentane (Vol%)	2.6	4.4	9.8	8.3	6.2	6.3	3.5	5.0	4.1
	Aviation Gas (Vol%)	25.0	25.0	73.6	70.3	73.4	70.7	38.8	69.4	34.7
	Kaphtha (Vol%)									
	Kerosene (Vol%)	53.6	55.6		1.4	2.3	30.6	21.2		61.6
	Cracked Gas (wt%)	6.7	6.3	19.6	10.3	6.2	9.1	8.7	8.1	7.6
	Carbon (wt%)	6.2	6.3	9.7	6.9	8.6	8.6	6.6	8.2	6.0

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TABLE II(B)5 cont.
CHARACTERISTICS OF FEED STOCKS

		Run No.	1	2	Prel.	3	4	5	6	7	8	Sum	Stabilized Gas
Properties of Aviation Gasoline		Sp. Gr. (d15°/4°C)	0.752	0.754	0.767	0.769	0.768	0.762	0.785	0.774	0.783	0.761	
	Engler Dist	1st drop (°C)	36.5	39.0	50.0	50.0	46.0	44.0	44.5	54.0	43.0	34.0	
		10 % (°C)	71.5	71.0	80.5	88.0	86.0	77.0	80.0	93.0	82.5	75.0	
		50 % (°C)	113.0	114.5	113.5	112.5	115.0	105.0	104.5	114.5	110.5	111.5	
		90 % (°C)	143.5	140.5	138.0	138.5	142.5	128.5	128.0	137.0	131.0	142.0	
		E. P. (°C)	175.0	169.0	174.5	165.5	176.5	172.0	167.5	173.5	170.0	178.0	
	Octane Value	Plain	75.6	79.0	74.6	74.6	75.0	75.2	77.0	74.8	80.3	75.6	
		Leaded 0.15%	92.7	92.6	90.8	91.0	90.3	90.3	92.2	92.5	93.4	91.7	
	Comp	Unsat (%)	9.0	11.0	9.0	10.5	10.5	11.0	14.0	9.0	17.0	10.0	
		Aromatic (%)	29.9	25.8	30.9	31.3	31.3	32.0	31.0	33.7	41.5	32.4	
		Naphthene (%)	24.3	19.8	22.2	21.3	21.3	20.9	20.5	21.0	14.4	1.1	
		Paraffin (%)	45.8	43.4	37.9	36.9	36.9	36.1	34.5	36.3	27.1	36.5	
		Reid. Vap. Press (kg/cm²)	04.9	04.9	0.39	0.30	0.33	0.36	0.39	0.26	0.38	0.60	
Prop. of Recycle Stocks		Sp. Gr. (d15°/4°C)	0.832	0.831	0.842	0.849	0.846	0.856	0.869	0.867	0.896		
	Engler Dist	1st drop (°C)	83.0	126.0	161.5	182.5	158.0	160.0	156.5	139.0	165.0		
		10 % (°C)	181.0	174.0	184.0	178.0	177.0	176.5	175.	154.0	172.0		
		50 % (°C)	216.0	226.0	211.5	203.0	199.0	200.0	207.0	192.0	199.0		
		90 % (°C)	222.0	263.5	271.5	265.0	259.0	262.0	282.0	277.5	294.0		
		E. P. (°C)	296.0	295.0	310.5	312.0	293.0	294.0	329.5	355.5	355.0		
		U.O.P. Characterization	11.4	11.6	11.3	11.2	11.3	11.1	11.1	10.9	10.8		
Gas Analysis		Sp. Gr. (Air = 1.0)	1.13	1.08	1.05	1.05	1.07	1.07	1.13	1.10	1.09		
		H_2 (%)						11.0		7.7	7.4	10.5	
		CH_4 (%)						30.2		32.8	34.0	30.4	
		C_2H_4 (%)						12.7		20.5	13.6	10.2	
		C_2H_6 (%)						2.9		6.8	4.6	12.2	3.1
		C_3H_6						16.0		9.4	16.7	7.2	31.4
		C_3H_8						2.0		6.4	6.1	9.3	17.0
		C_4H_8						5.0		3.4	2.0	2.1	7.8
		C_4H_{10}						2.3		0.6	3.7	3.7	3.7
		Above C_5						10.3		8.9	5.9	5.4	37.5
		O_2						0.5		0.4	0.6	0.2	
		CO						3.9		1.4	3.3	3.1	
		CO_2						2.3			2.0	2.0	
		N_2						1.9			2.3	3.7	

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Table III(B)5
DISTILLATION OF CHARGING STOCKS

	Mixed Light Oil	Pine Root Oil (L.O. Tract.)
Sp. Gr.	0.820	0.854
1st. drop°C	120.1	122.8
10%	123.5	150.0
20%	175.5	156.0
30%	187.5	163.5
40%	196.5	171.5
50%	207.5	177.5
60%	220.0	185.0
70%	233.5	195.5
80%	249.5	214.5
90%	269.5	245.5
95%	285.0	266.0
97%	295.0	
E.P.	296.0	268.0
Acid Value		0.6
Alkali Value		6.

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Table IV(B)5
CHARACTERISTICS OF PINE ROOT OIL FEED STOCKS

		1	2	Trel	3	4	5	6	7	8(I)	8(II)	9
Run No.		1	2	Trel	3	4	5	6	7	8(I)	8(II)	9
Date		4.25 0900 4.26 0900	4.27 1300 4.28 1000	4.28 2100 4.29 0900	4.29 0900 4.30 0900	4.30 0900 4.30 2400	5.1 1600 5.2 1300	5.4 0900 5.5 0900	5.5 0900 5.6 0900	5.6 1200 5.6 2000	5.6 2000 5.7 0400	5.7 0900 5.8 1000
Run Period (hr)		24	21	12	24	15	21	24	24	8	8	25
Charging Stocks		Mixed light oil		Pine Root Oil (light oil fraction)								
Total Charge (lit)		3400	2950	1560	3550	1730	3130	3450	2800	1050	950	3170
Charge per hour (lit/hr)		142	140	130	148	115	150	144	117	131	119	127
S. V.		5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7
R. R.		5.9	6.0	6.5	5.6	7.5	5.5	5.7	7.3	6.4	7.1	6.7
Reaction Temp (°C)	1st Reaction Chamb	445	455	457	460	459	456	425	415	395	375	332
	2nd Reaction Chamb	440	445	455	657	455	452	425	420	400	380	316
	3rd Reaction Chamb	445	440	445	455	455	460	435	417	395	375	328
	Mean	443	447	452	457	456	456	428	417	397	377	325
Reaction Press (kg/cm²)		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Oil Temp. Outlet of furnace tube (°C)		480	484	470	455	447	444	493	495	505	520	550
Oil Temp. Inlet of Reaction Vessel (°C)		447	468	448	447	428	424	468	467	674	500	505
Flue gas	Amounts (m³/hr)	850	850	350	850	850	850	850	850	850	850	850
	Heating Temp. (°C)	549	545	541	537	504	539	426	390	286	166	68
	Outlet of furnace tube (°C)	513	516	510	508	483	816	407	375	280	164	67
	Pressure (kg/cm²)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Steam Temp. (°C)		202	233	234	242	258	237	190	168	166	157	156
Charging Stock Including Recycle	Sp. Gr. (15°/4°C)	0.854	0.855	0.856	0.858	0.855	0.855	0.852	0.856	0.862	0.862	0.867
	1st drop (°C)	121.6	127.8	145.0	115.0	139.3	135.0	158.0	135.0	156.0	156.0	156.0
	10 % (°C)	160.0	161.5	165.0	167.0	168.0	168.0	172.0	173.0	175.0	175.0	173.0
	50 % (°C)	198.5	197.5	199.0	201.0	205.0	205.0	200.5	203.0	206.5	206.5	202.0
	90 % (°C)	284.0	282.5	287.5	282.0	289.0	286.5	281.0	285.0	285.0	285.0	289.0
Flue gas	CO_2 %	8.5	8.8	9.2	8.0	8.9	9.6	Air only				
	O_2 %	6.4	7.1	6.5	6.5	6.4	7.9					
	CO %	1.6	1.3	1.3	1.6	1.6	1.2					
Yields	Stabilized Gas + Pentane (Vol%)	4.3	2.8	5.2	4.2	4.5	3.8	2.6	4.1	3.3	5.1	5.0
	Aviation Gas (Vol%)	29.1	16.9	46.2	42.6	58.5	54.5	49.0	47.7	39.1	45.7	45.0
	Naphtha (Vol%)	40.3	62.0	35.2	21.1	22.6	21.7	37.7	20.7	21.0	17.9	23.4
	Cracked Gas (wt%)	8.5	8.8	16.0	13.6	15.5	14.8	15.1	17.9	17.1	18.9	17.4
	Carbon (wt%)	6.7	6.1	6.6	7.6	9.9	6.8					

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Table IV(B)5 (Cont.)
CHARACTERISTICS OF PINE ROOT OIL FEED STOCKS

		Run No.	1	2	Prel.	3	4	5	6	7	8(I)	8(II)	9	Sum
Properties of Aviation Gasoline		Sp. Gr. ($d15^{\circ}/4^{\circ}C$)	0.761	0.746	0.784	0.793	0.799	0.798	0.791	0.797	0.799	0.796	0.782	0.786
	Engler Dist	1st drop (°C)	45.5	41.5	46.0	48.5	50.0	50.0	47.0	46.5	49.5	47.5	43.5	45.5
		10 % (°C)	75.5	62.0	82.5	87.0	88.0	89.5	84.5	87.5	89.5	87.0	78.0	76.0
		50 % (°C)	111.0	95.5	111.5	117.0	116.5	120.0	112.5	117.5	120.0	115.0	112.0	115.0
		90 % (°C)	134.0	125.0	147.0	144.0	143.0	154.0	138.5	144.5	146.5	140.0	133.0	149.0
		E. P. (°C)	165.5	150.0	159.0	168.0	161.5	176.5	162.0	162.0	166.0	164.5	168.0	167.5
	O.V.	Plain	79.2	80.0	81.2	80.9	82.0	81.0	81.6	82.6	82.4	82.2	81.3	81.7
		Leaded 0.15%	91.5	91.8	90.5	90.5	91.0	89.6	91.2	91.0	90.8	90.5	88.0	91.2
	Comp	Unsat (%)	10.0	20.5	21.5	19.8	22.0	19.5	19.5	21.0	19.5	22.5	16.5	19.5
		Aromatic (%)	30.6	22.3	25.9	37.8	40.6	39.5	39.4	41.8	40.9	40.6	30.5	40.1
		Naphthene (%)	23.2	27.6	27.9	12.2	19.2	20.6	17.9	13.4	22.1	15.9	18.2	19.0
		Paraffin (%)	36.2	29.6	24.7	30.5	18.2	20.4	23.2	23.8	17.5	21.0	36.8	20.2
	Read Vap. Press (Kg/cm^2)		0.47	0.58	0.37	0.32	0.32	0.47	0.38	0.32	0.29	0.31	0.41	0.60
Prop. of Recycle Stocks		Sp. Gr. ($d15^{\circ}/4^{\circ}C$)	0.841	0.845	0.847	0.873	0.877	0.871	0.890	0.897	0.886	0.886	0.901	
	Engler Dist	1st drop (°C)	157.0	160.5	170.0	144.5	169.5	166.0	181.0	175.5	169.0	169.0	171.0	
		10 % (°C)	180.5	180.5	185.0	179.0	181.0	189.0	205.5	198.0	183.5	183.5	184.5	
		50 % (°C)	208.5	211.0	218.5	209.5	210.0	221.0	249.5	233.0	214.5	214.5	224.0	
		90 % / E.P. (°C)	267.0	266.0	272.5	285.0 / 344.5	294.0	292.5	333.0	300.5	288.5	288.5	306.0	
Gas Analysis		Sp. Gr. (Air = 10)	1.13	1.15	1.13	1.11	1.10	1.14	1.14	1.18			1.14	
		CO_2 (%)	8.0	3.2	3.2	3.2	3.3	2.3	2.6	3.0			2.5	
		O_2 (%)	0.2	1.8	1.0	1.4	0.5	0.6	0.4	0.4			0.4	
		C_nH_{2n} (%)	24.2	31.6	31.4	31.5	29.9	32.1	32.3	28.8			24.2	
		CO (%)	5.2	7.5	7.4	7.5	6.1	2.6	2.5	6.2			3.8	
		C_nH_{2n+2} (%)	50.4	38.5	30.0	34.3	44.0	53.0	51.4	52.8			59.3	
		H_2 (%)	1.39	11.2	16.0	13.6	11.4	9.2	9.7	8.6			9.6	
		N_2 (%)	1.4	5.2	11.0	8.5	5.8	0.2	1.1	0.2			0.3	
		n (%)	2.0	2.0	2.5	2.2	2.6	1.5	1.6	1.0			1.4	

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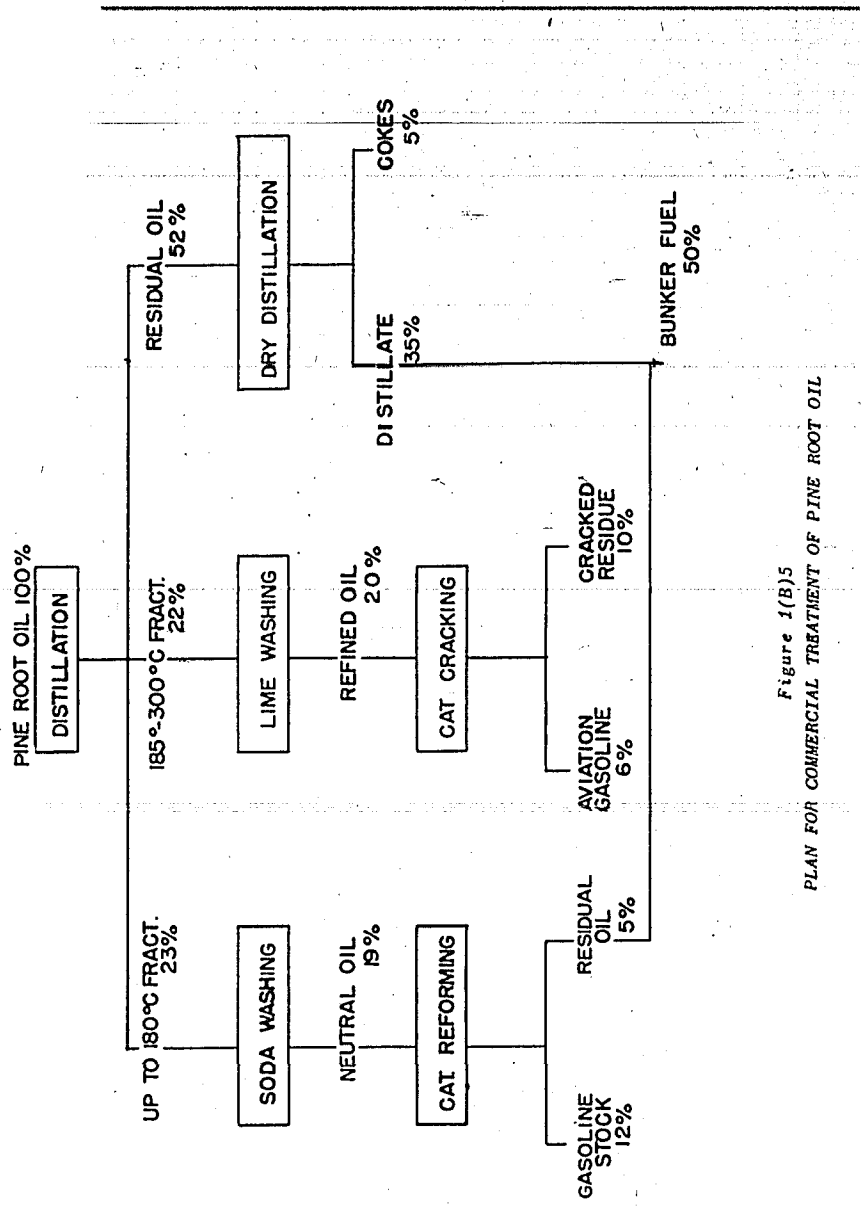

Figure 1(B)5
PLAN FOR COMMERCIAL TREATMENT OF PINE ROOT OIL

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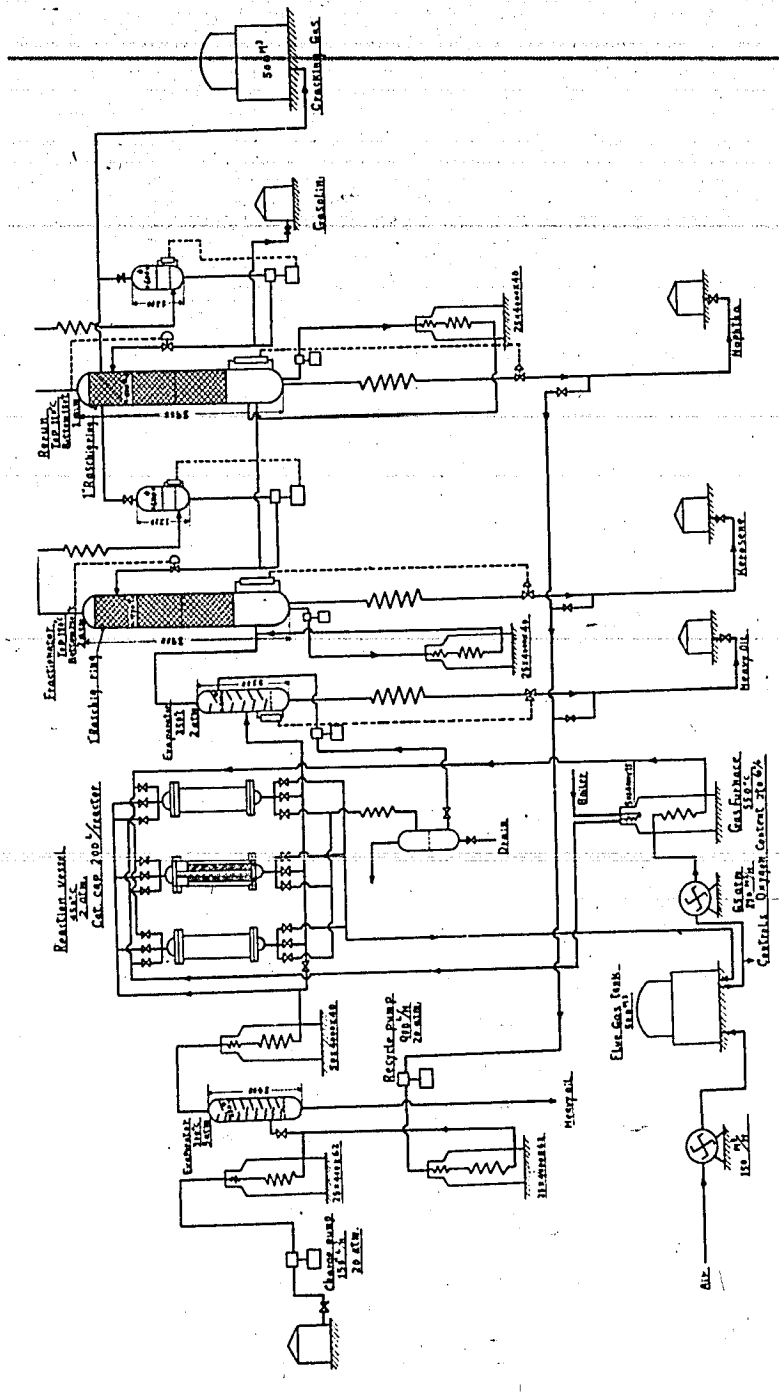

Figure 2(B)5

FLOW CHART OF CATALYTIC CRACKING PILOT PLANT

ENCLOSURE (B)5

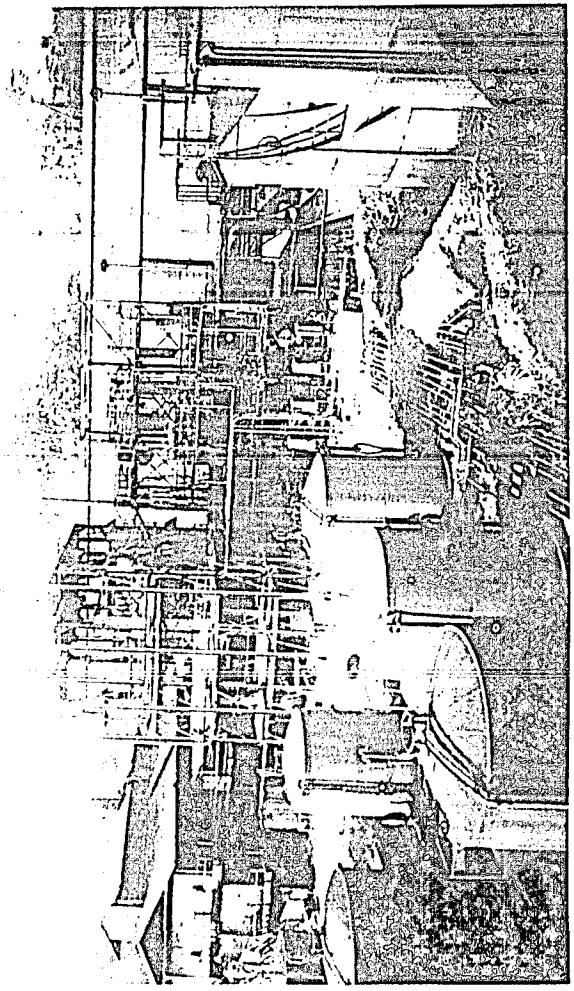

Figure 3(B)5
GENERAL VIEW OF THE CATALYTIC CRACKING PLANT

ENCLOSURE (B)5

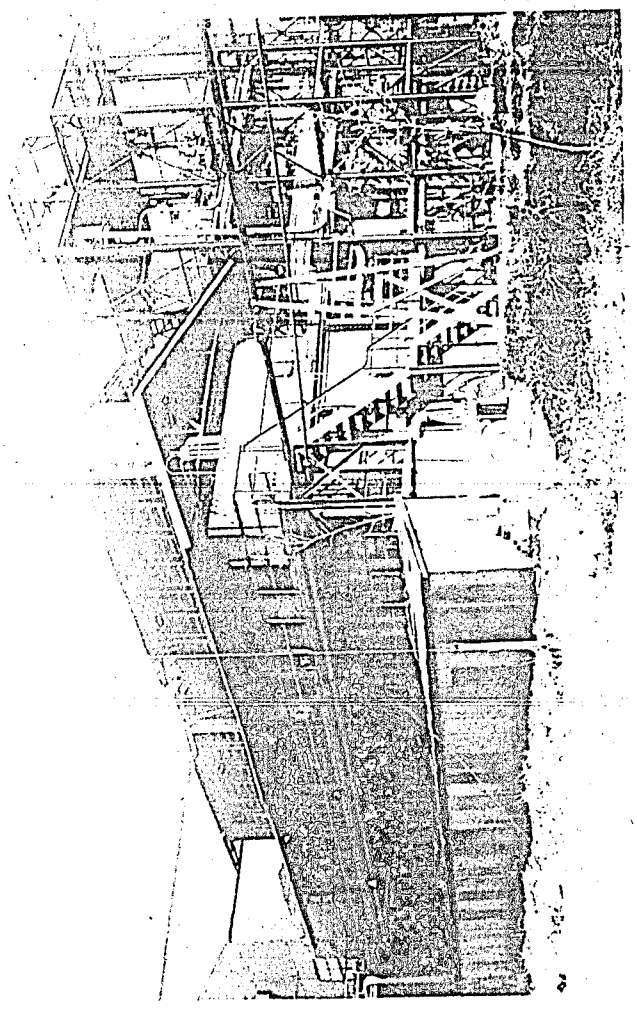

Figure 4(B)5
CLOSE UP VIEW OF THE FURNACE SIDE
OF THE CATALYTIC CRACKING PLANT

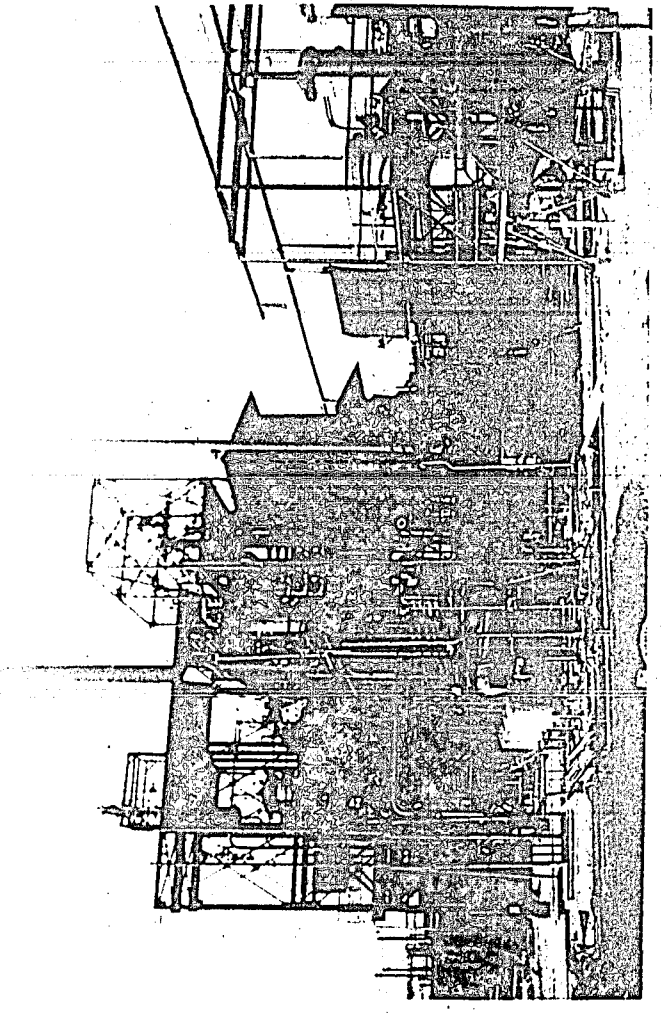

Figure 5(B)5
CLOSE UP VIEW OF THE REACTION CHAMBER
OF THE CATALYTIC CRACKING PLANT