Copy 1

FIAT FINAL REPORT NO. 423

SYNTHETIC LUBRICATING OIL MANUFACTURE, RHENANIA-OSSAG MINERALOWERKE A. G. HARBURG REFINERY

JOINT INTELLIGENCE OBJECTIVES AGENCY
WASHINGTON, D. C.

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (U.S.)
Office of the Director of Intelligence

FIAT FINAL REPORT NO. 423 14 NOVEMBER 1945

SYNTHETIC LUBRICATING OIL MANUFACTURE RHENANIA-OSSAG MINERALÖLWERKE A.G. HARBURG REFINERY.

BY

MR. J.G. ALLEN

Joint Intelligence Objectives Agency

FIELD INFORMATION AGENCY, TECHNICAL

10 p. fold. diags.

TABLE OF CONTENTS.

Drawings.

Personnel of Team:

Mr. J. G. Allen (U.S.).

SYNTHETIC LUBRICATING OIL MANUFACTURE
RHENANIA-OSSAG MINERALÖLWERKE A.G.
HARBURG REFINERY.

Introduction.

This report is based on the interrogation of Dr.Karl Zerbe, Research Director, and Alois Becker, Assistant Chief Engineer of Rhenania, at the Shell House, Hamburg, on the 11 October 1945, by Mr. J. G. Allen (U.S.).

Summary of Information.

The interrogation was based on flow sheets of the synthetic lube oil plant at Harburg. These flow sheets and the detailed report which follows cover the design and operation of this plant in its three parts:

1) Wax cracking for olefin manufacture;
2) Polymerization of olefins and disposal of used aluminum chloride;
3) Finishing of raw polymer into lubricating oil.

The Harburg plant had a capacity of 700 T/Mo. lube oil production with a yield of about 54 weight percent of the paraffin wax charged. It is of especial interest in that it operated on wax from natural petroleum refining.

The plant was dismantled late in the war for re-erection on the Harz mountains. The equipment was shipped in two boats, and was last heard of at Magdeburg, on the Elbe River.

Description of Process.

Details are shown in the attached flow sheets. It should be noted that these are primarily design flow sheets, and are not exactly consistent with one another on throughput volumes. The data on yields, as shown on the sheets, may not be exactly consistent with later operating data.

Wax Cracking.

In Figures 1 and 2 are shown the equipment and flow for wax cracking. The use of natural waxes from the manufacture of oils such as spindle oil and heavy machine oil distillate is recommended. These have an average molecular weight of about 500. With heavier waxes, such as wax from cylinder oil, there is difficulty in vaporization in the cracking furnace. It is important that the wax used be deoiled to less than 5 percent oil content. Otherwise, coking in the cracking furnace and the evaporators takes place.

The wax first receives direct heat exchange in the bottom of the dephlegmator tower, and combines with the recycle there before it reaches the furnace coil. The furnace is divided into two sections: (1) a vaporizer, using convection and radiant heating, and (2) a cracking section, where three parallel coils with radiant heating are used. Intermediate is the first evaporator in which any non-vaporized oil drops out and in which four dry bubble trays serve as a mist extractor to prevent unvaporized oil particles from entering the second section of the furnace.

The division of the flow into the cracking section coils is accomplished by orifices set in the lines. All attempts to use regulating valves for this job were unsuccessful. The injection of steam before the cracking coil controls the cracking time which is normally about 6 to 7 seconds. The degree of cracking is checked by the determination of the bromine number of the cracked distillate product. This value is normally about 120, using the method of McIlheny.

The cracked product from the furnace is immediately quenched with water (condensate) and is then separated in the usual manner into gas, cracked distillate, recycle cracking stock and residuum.

Yields shown on the design flow sheet (Figure 1) compared with actual yields given below. Maximum capacity of the plant was stated to be 60 tons of charge per day.

	Weight Per Cent Yields.	
	From Flow Sheet.	Actual.
Gas and Loss	24	30-35
Cracked Distillate	55	60-65
Residuum	21	10
	100	100

Polymerization (Figure 3).

For polymerization, the cracked distillate, average molecular weight 290-300, boiling range approximately 40° to 300°, is used. The process is carried out batchwise in 10-ton lots. The distillate is circulated with continuous addition of a thick aluminum chloride slurry and with controlled temperature depending on the type of oil required. The following variations in operating temperature were noted:

20°C. gives a thick cylinder oil; requires longer polymerization time and gives lower yields.

40°C. usually used for the required aviation oil blending component. Gives a viscosity of about 12°E/50° and 5.5°E/100°C.

60°C. gives oil with a viscosity of about 4°E/50°C.

A minimum circulation rate of about 20 times the charge volume per hour gives sufficient mixing without the use of the stirrer in the reactor.

For the regular oil (5.5°E/100°C), a period of 3 to 4 hours is required to add the previously calculated amount of aluminum chloride. Following this addition, the oil is circulated about 2 hours more or until the bromine number decreases to 0. The use of the auxiliary agitators for ~~this latter circulation frees the primary agitators for~~ another fresh batch polymerization.

Following the polymerization, the oil and aluminum chloride were originally separated in a centrifuge, but

this system was replaced by settling in "tubs" at 30-40°C. for about 12 hours. The raw polymer is separated for further refining in the next step. The sludge is drawn off and decomposed by the addition of warm water, and the "sludge oil" recovered is further polymerized in subsequent batches. No recovery of aluminum chloride is attempted.

It is essential that the sludge oil be absolutely dry to avoid subsequent corrosion difficulties, and more elaborate plans were laid for sludge-oil drying in the relocated plant than were actually used at Harburg.

The polymerization plant, as shown, is considered capable of charging 40 tons/day distillate and yielding 36 tons/day (90% yield) of raw polymer.

Contact Refining (Figure 4).

The raw polymer is mixed with about 4% of clay and enough lime to neutralize its acidity (Note: flow sheet shows 4% lime and 1% clay). This mixture is heated to about 250°C. in a pipe still to decompose aluminum and chlorine complexes still remaining in the oil. A minimum of about 200°C., together with some soaking time, is required for this decomposition. The HCl is then vented from the oil to cut down the corrosion in subsequent distillation steps where steam is present.

The oil is then stripped of its light components by atmospheric and vacuum fractionation. The oil from the atmospheric distillation is filtered through Sweetland filters to remove the clay and lime. The latter residue from the filters contains about 40% oil which is recovered by extraction with gasoline.

The finished oil from the vacuum distillation was used as a blending component for aviation lubricating oil.

Yields from the contact refining and atmospheric distillation were as follows (based on raw polymer charged):-

	Wt.%
Gasoline, 70 Oct. No., Motor Method	5
Gas Oil (Diesel fuel) 40 Cetane No.	15
Lube Oil	80
	100

Vacuum distillation further reduced the lube oil yield to about 60%, based on the raw polymer charged to the contact refining step.

Capacity of this section of the plant was 50 T/D raw polymer.

Summary of Yields.	T/D	Weight % Yields based on Wax Charge.	Ultimate.
Charge to Wax Cracking	60	100.0	100.0
Yields from Wax Cracking.			
Gas and Loss	18	30.0	30.0
Cracked Distillate	36	60.0	
Residuum	6	10.0	10.0
	60	100.0	
Yields from Polymerization			
Raw Polymer (90% of distillate)	32.4	54.0	
Loss	3.6	6.0	6.0
	36.0	60.0	
Yields from Contact Refining & Finishing.			
Gasoline, Gas Oil (Diesel Fuel) (40% of Raw Polymer, principally Gas Oil)	13.0	21.6	21.6
Finished Lube Oil (60% of Raw Polymer)	19.4	32.4	32.4
		54.0	100.0

Operating Efficiency of Unit.

The unit was stated to have a normal operating time of 300 days per year or an efficiency of 82 per cent. The normal length of run was 28-30 days, and the principal cause of the shut-down was coking of the evaporators and the tube coil. This major difficulty is tied in with the amount of oil in the wax.

Special precautions in keeping up the operating efficiency were observed in the design of injection nozzles, one of which could be cleaned during operation, and in the design of the heat exchangers on the feed line to the contact-refining furnace which could be segregated and cleaned individually of lime and clay deposits.

Comments on Synthetic Lube Oil Manufacture (by Dr. Zerbe).

1. Fischer-Tropsch wax is the ideal material for this operation. It contains n-paraffins and gives alpha- and beta-olefins on cracking which polymerize into the best lubricating oil. No distinction is made between alpha- and beta-olefins for this purpose. One plant run was made by Rhenania on Fischer-Tropsch wax from "gatsch" furnished by Ruhrchemie. This gave an oil of 120 V.I., compared with 100-105 normally produced from natural wax. Difficulty was experienced in deoiling the "gatsch". It was necessary to use a two-stage extraction with benzol-acetone, using 300-400 per cent of solvent each time and a temperature of -30°C.

2. Natural waxes contain iso-paraffins and tend to give gamma-olefins which polymerize into poorer lubricating oils. Wax from brown coal tar processing is intermediate in value between Fischer-Tropsch wax and natural petroleum wax as a feed stock for lube oil manufacture.

3. The synthetic lube oil normally produced by Rhenania has an average molecular weight of about 300.

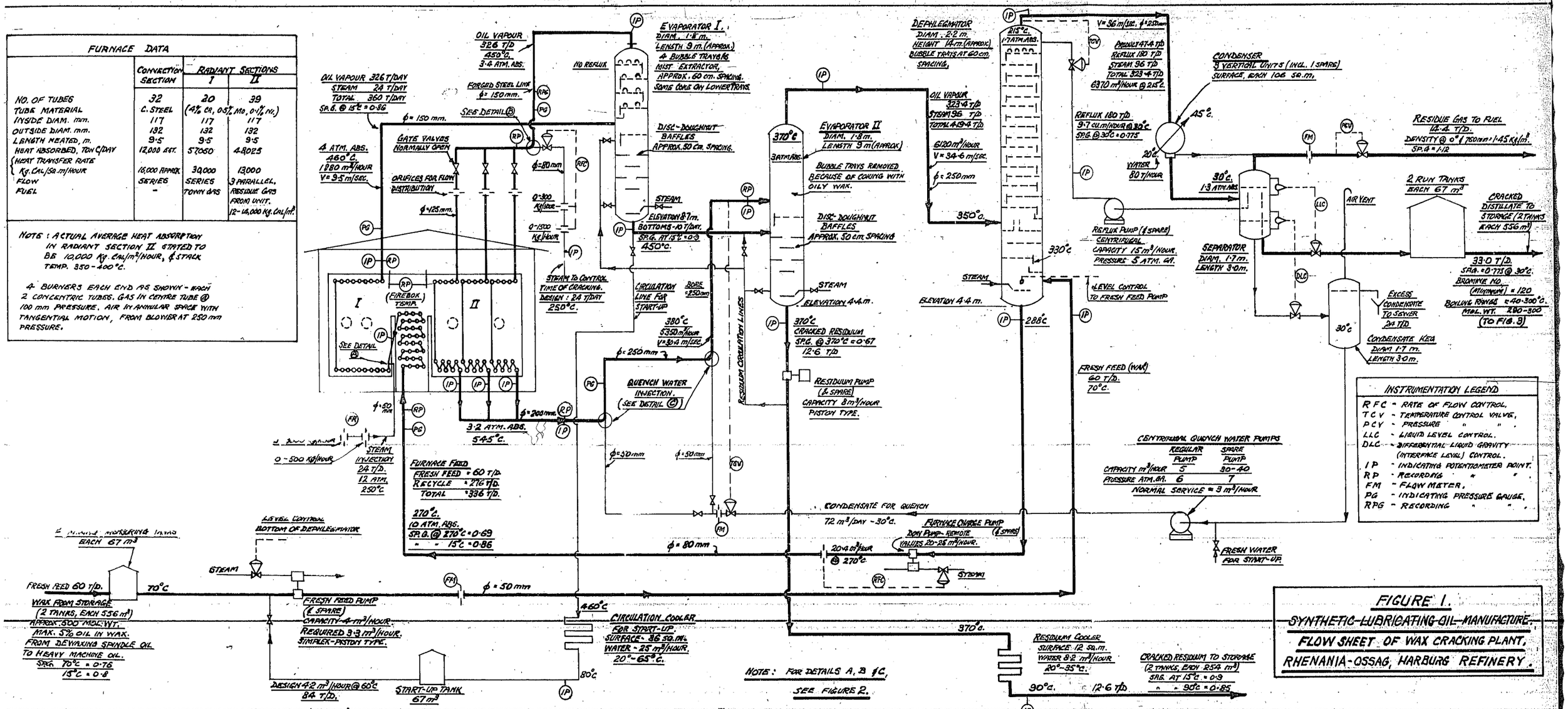
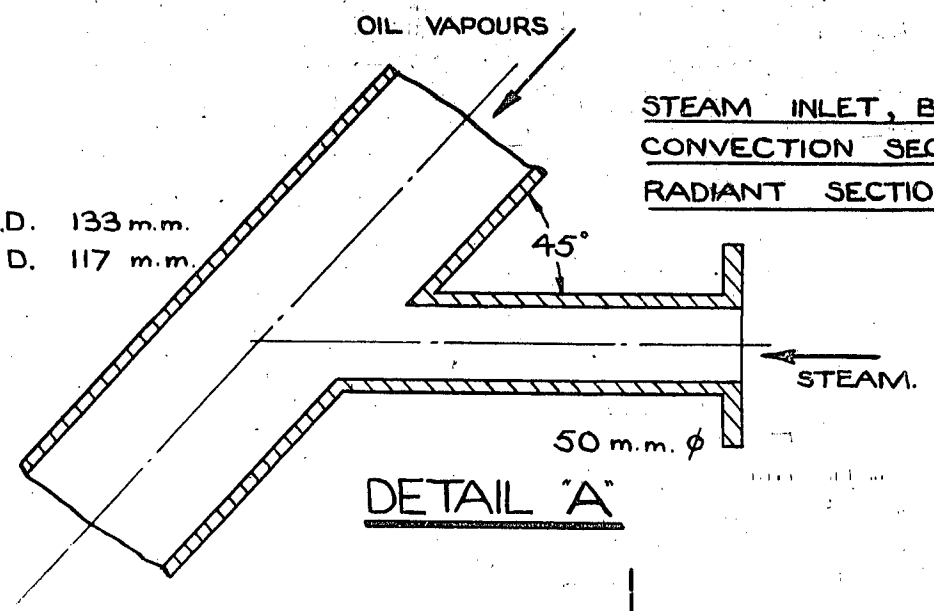


FIGURE 1.

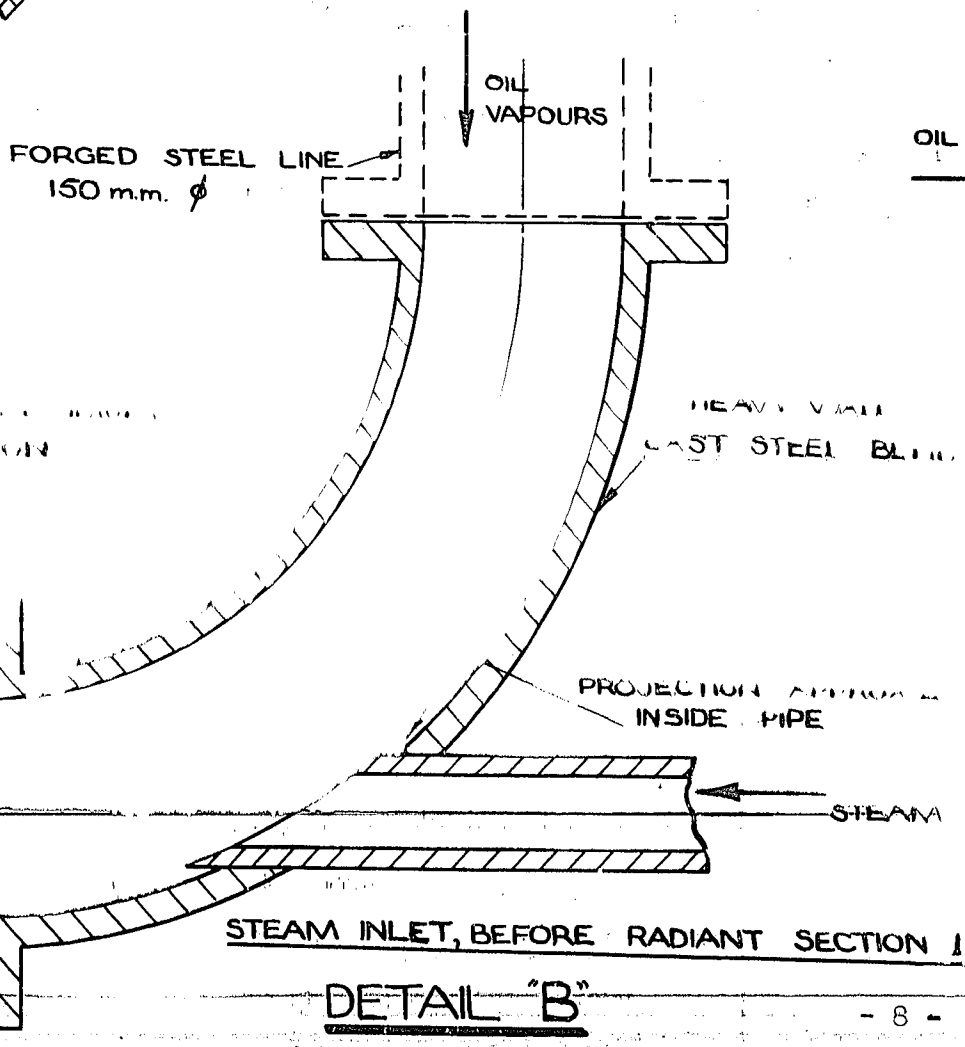
SYNTHETIC-LUBRICATING-OIL-MANUFACTURE.

FLOW SHEET OF WAX CRACKING PLANT, RHENANIA-OSSAG, HARBURG REFINERY.



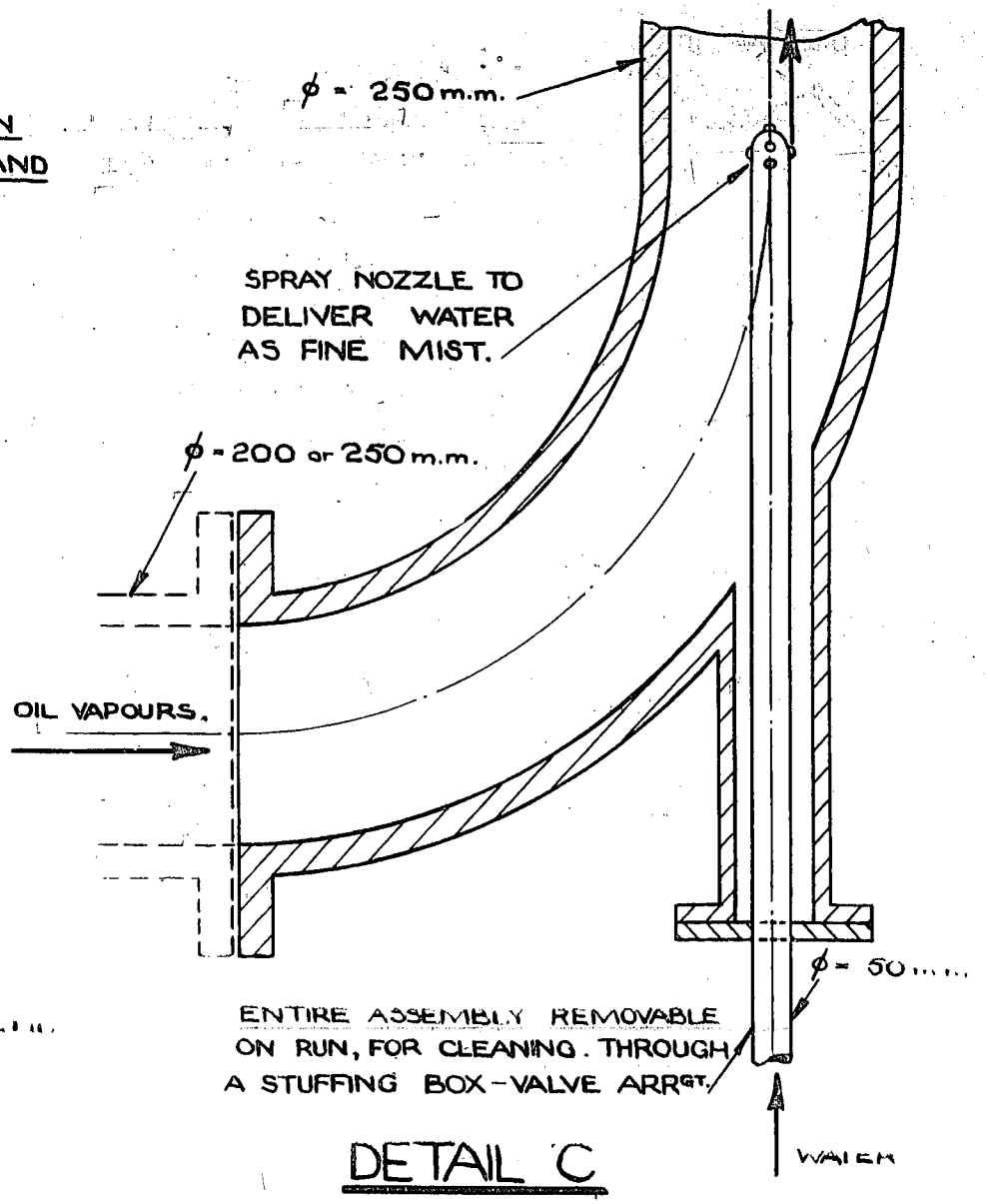
STEAM INLET, BETWEEN CONVECTION SECTION AND RADIANT SECTION I

DETAIL "A"



STEAM INLET, BEFORE RADIANT SECTION II

DETAIL "B"



DETAIL C

QUENCH WATER INLET IN TRANSFER LINE

FIGURE. 2.

SYNTHETIC LUBRICATION OIL MANUFACTURE

DETAILS OF INJECTION FITTINGS.

WAX CRACKING PLANT

RHENANIA - OSSAG, HAMBURG REFINERY

Note:- LOCATION OF FITTING SHOWN ON FIG. 1.

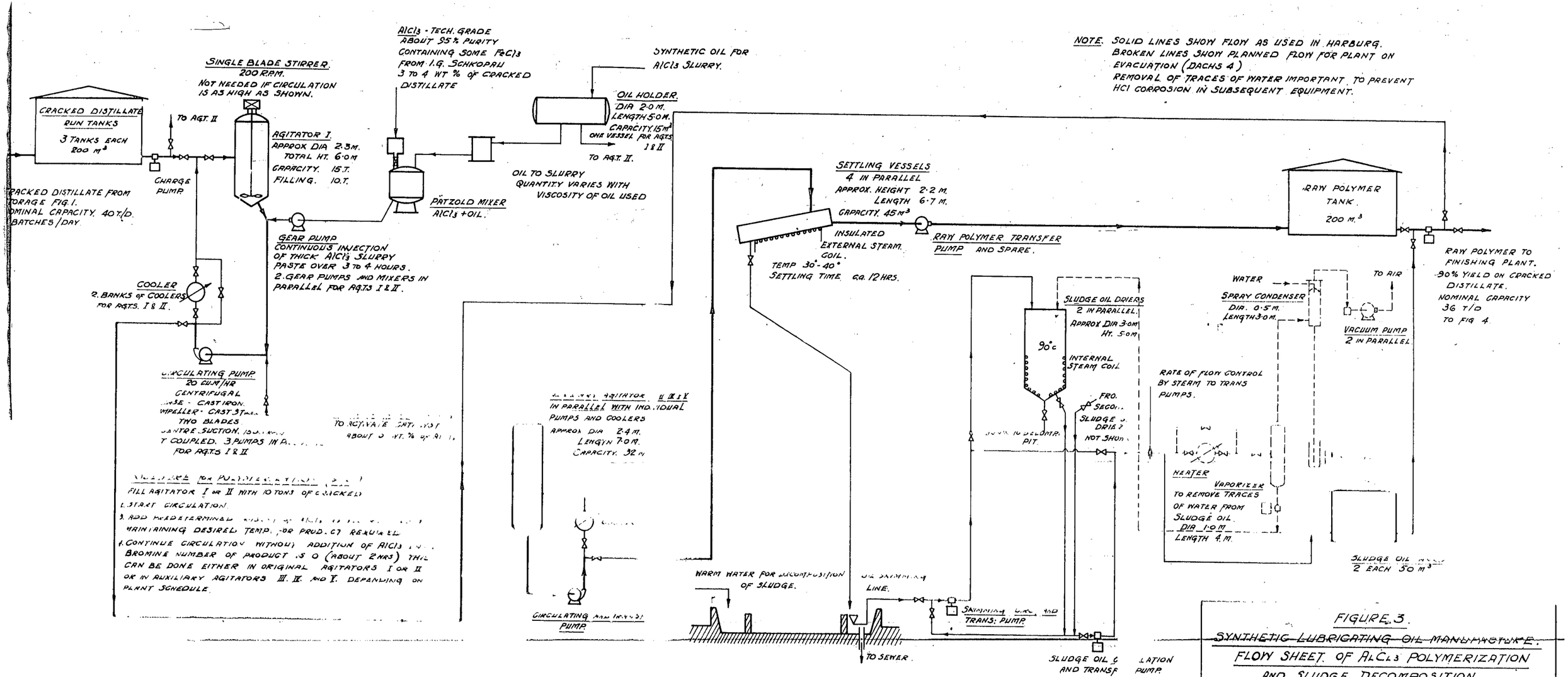
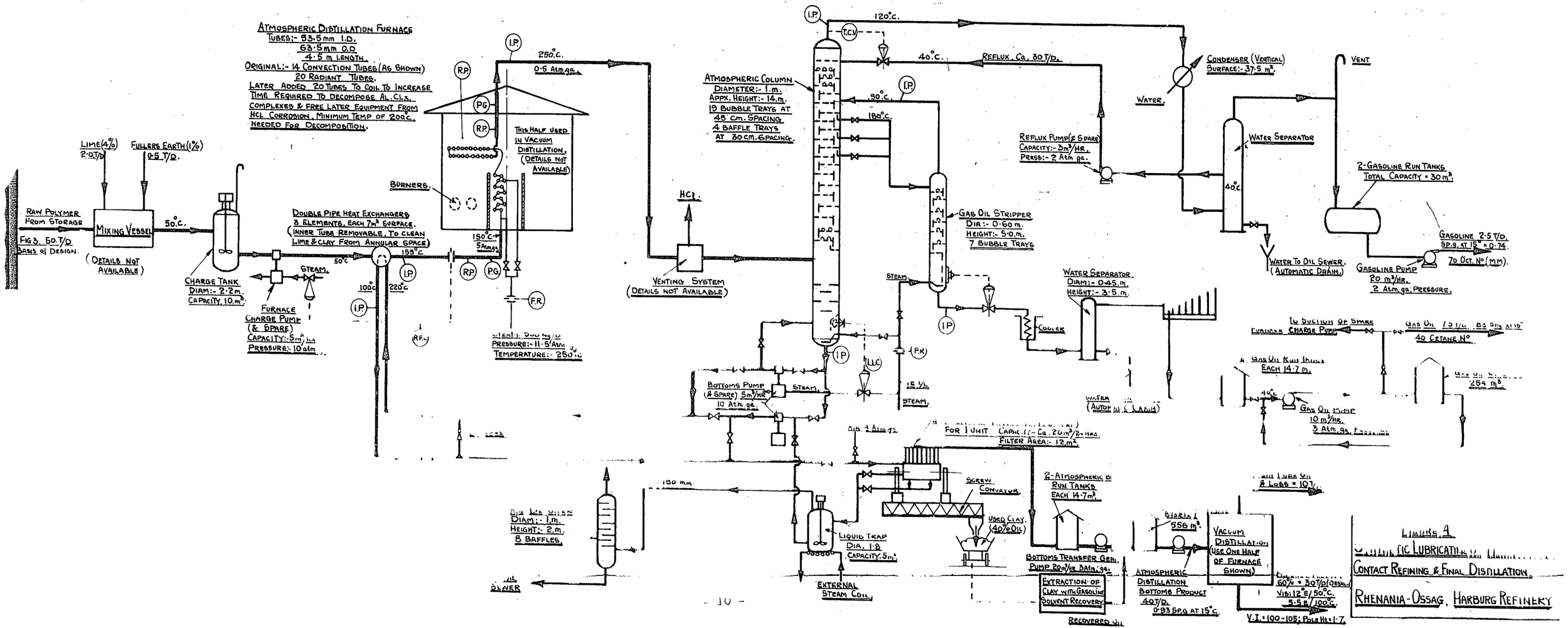


FIGURE 3.

SYNTHETIC LUBRICATING OIL MANUFACTURE.

FLOW SHEET OF $AlCl_3$ POLYMERIZATION AND SLUDGE DECOMPOSITION.

RHENANIA-OSSAG. HARBURG REFINERY.


ATMOSPHERIC DISTILLATION FURNACE
TUBES:- 53.5mm I.D.
63.5mm O.D
4.5 m LENGTH.
ORIGINAL:- 14 CONVECTION TUBES (AS SHOWN)
20 RADIANT TUBES.
LATER ADDED 20 TUBES TO COIL TO INCREASE TIME REQUIRED TO DECOMPOSE Al.Cl.3. COMPLEXED & FREE LATER EQUIPMENT FROM HCl CORROSION. MINIMUM TEMP OF 200C. NEEDED FOR DECOMPOSITION.
LIME (4%) 2·0 T/D
FULLERS EARTH (1%) 0·5 T/D.
RAW POLYMER FROM STORAGE
FIG 3. 50 T/D BASIS of DESIGN.
MIXING VESSEL
(DETAILS NOT AVAILABLE)
50°C.
CHARGE TANK DIAM:- 2·2m. CAPACITY 10.m3.
FURNACE CHARGE PUMP (& SPARE) CAPACITY:- 5m3/hr PRESSURE:- 10 atm
STEAM.
DOUBLE PIPE HEAT EXCHANGERS 3 ELEMENTS, EACH 7m2 SURFACE. (INNER TUBE REMOVABLE, TO CLEAN LIME & CLAY FROM ANNULAR SPACE)
50°C
155°C
100°C
220°C
I.P.
R.P.
P.G.
F.R.
BURNERS.
THIS HALF USED IN VACUUM DISTILLATION, (DETAILS NOT AVAILABLE)
250°C.
0·5 Atm ga.
150°C
5 Atm ga.
HEAT: 300 m/J/D
PRESSURE:- 11·5 Atm
TEMPERATURE:- 250°C
VENTING SYSTEM (DETAILS NOT AVAILABLE)
HCl.
ATMOSPHERIC COLUMN DIAMETER:- 1.m. APPX. HEIGHT:- 14.m. 19 BUBBLE TRAYS AT 45 cm. SPACING. 4 BAFFLE TRAYS AT 30 cm. SPACING.
T.C.V.
120°C.
40°C.
REFLUX. Ca. 30 T/D.
80°C.
180°C.
GAS OIL STRIPPER DIA:- 0·60 m. HEIGHT:- 5·0 m. 7 BUBBLE TRAYS
REFLUX PUMP (& SPARE) CAPACITY:- 3m3/HR. PRESS:- 2 Atm ga.
CONDENSER (VERTICAL) SURFACE:- 37·5 m2
WATER
VENT
WATER SEPARATOR
40°C
WATER TO OIL SEWER. (AUTOMATIC DRAIN.)
2-GASOLINE RUN TANKS TOTAL CAPACITY = 30 m3.
GASOLINE 2·5 T/D. SP.G. AT 15° = 0·74
GASOLINE PUMP 20 m3/HR. 2 Atm ga. PRESSURE.
TO OCT. N° (MM).
WATER SEPARATOR DIAM:- 0·45 m. HEIGHT:- 3·5 m.
COOLER
STEAM
BOTTOMS PUMP (& SPARE) 5m3/HR 10 Atm ga.
15 V/L
LLC
WATER (AUTOMATIC DRAIN)
TO SUCTION OF SPARE FURNACE CHARGE PUMP
GAS OIL 1·2 T/D. SP.G. AT 15° 40 CETANE N°
4 GAS OIL RUN TANKS EACH 14·7 m3
264 m3
GAS OIL PUMP 10 m3/HR. 3 Atm ga. PRESSURE
FOR 1 UNIT CAPACITY:- Ca. 20m3/24 HRS.
FILTER AREA:- 12.m2
SCREW CONVEYOR
USED CLAY (40% OIL)
2-ATMOSPHERIC DI RUN TANKS EACH 14·7m3
150 mm
DIA LIQUID WASH DIAM:- 1.m. HEIGHT:- 2.m. 8 BAFFLES
LIQUID TRAP DIA. 1·8 CAPACITY 5m3
EXTERNAL STEAM COIL
BOTTOMS TRANSFER GEAR PUMP 20m3/hr 3 Atm ga.
EXTRACTION OF CLAY WITH GASOLINE SOLVENT RECOVERY
RECOVERED OIL
ATMOSPHERIC DISTILLATION BOTTOMS PRODUCT 40 T/D. 0·93 SP.G. AT 15°C
VACUUM DISTILLATION (USE ONE HALF OF FURNACE SHOWN)
556 m3
60% = 30 T/D (APPROX)
VIS 12°E/50°C.
5·5 E/100°C.
V.I. 100-105; POUR Pt +1·7
LUBES A
CONTACT REFINING & FINAL DISTILLATION.
RHENANIA-OSSAG, HARBURG REFINERY