

X. ISOMERIZATION OF NORMAL BUTANE

The isomerization of normal butane is carried out using aluminium chloride catalyst activated with HCl. This is the only plant in Germany for the isomerization of butane. The process, as used in Germany, is similar to one variation used in the United States. A simplified flow diagram of the process is attached as Fig. XXIII and a photograph of the three isomerization reactors is shown in Fig. XXIV.

Each reaction vessel consists of a 1 metre diameter cylindrical vessel having a cone bottom. The straight section of the reactor is approximately 6 m. in length. Liquid normal butane of 95-96% purity is first dried by washing with 96% sulphuric acid. The dried feed is pumped under 18 atms. pressure through a preheater where it is heated to 95°C and then mixed with 100-150 cu.m. of recycle HCl gas for 1.6 cu.m. of liquid feed to give a 10% concentration of HCl in the reactor charge. The charge enters the base of the reactor near the cone, flows upward through a 2 m. depth of Raschig rings, then through a 1 m. bed of lump aluminium chloride occupying a volume of approximately 700 litres. Above the aluminium chloride, the material passes through an empty zone of 1-1/2 m. in height to prevent aluminium chloride carry-over. The effluent from the top of the reactor is cooled to 25°C by indirect water cooling, and passes to a receiver from which some sludge is removed. The hydrocarbon-HCl mixture from the receiver is pumped through a preheater where the temperature is raised to 60°C and introduced near the top of a HCl stripping tower. The bottom temperature of the stripping tower is maintained at about 118°C to remove the butanes and any propane formed so that propane does not build up in the recycle HCl stream. Reflux is supplied to the top of the column by means of a water-cooled condenser in the ratio of 2.5 parts of reflux to one of overhead product. The recycle gas contains 80% HCl, 15% propane, and 5% isobutane. Make-up HCl is added to this recycle stream and it is mixed with the feed to the reactor.

The catalyst employed in the process is technical aluminium chloride containing a small amount of ferric chloride as an impurity. The ferric chloride is said to be essential for the reaction. The conversion of normal butane to isobutane per pass is 25-30% with an ultimate yield of 95-97%. Each reactor produces 250-300 kgs. of isobutane per hour. The consumption of aluminium chloride is 1% by weight of the isobutane produced. The consumption of HCl is 0.1 - 0.3% by weight of the isobutane produced.

According to the personnel interrogated, ordinary carbon steel is used in the construction of the reactor. It was reported that no corrosion trouble had been encountered with the use of carbon steel, although this appears very unlikely since the aluminium chloride sludge has been found to be very corrosive in a similar type unit. Difficulty was encountered, however, with deposition of aluminium chloride in the cooler at the outlet of the reactor. Apparently no effort was made to remedy this trouble.

This process has not reached the stage of development obtained elsewhere and it is doubtful whether anything new is to be learned from the Germans in the field of isomerization using aluminium chloride. The isomerization of pentane and hexane has not progressed beyond the laboratory stage.

XI. SYNTHETIC LUBRICATING OIL MANUFACTURE - LEUNA

Information on this subject was secured at Leuna by inspection of the plant and by interviews with the following I.G. personnel (May 8 -15, 1945)

- Dr. Giessen - in charge of organic chemicals manufacture.
- Dr. Gericke - in charge of operation of the lubricating oil plant and some smaller chemical plants.
- Dr. Zorn - in charge of lubricating oil research for the past 15 years.

SUMMARY OF PROCESS:

Ethylene of 95% purity is obtained by thermal cracking of ethane in admixture with oxygen. The ethylene is polymerized batchwise in the presence of a special aluminum chloride catalyst. The polymerized oil is separated from the aluminum chloride complex, steam distilled to remove light ends, and given a final clay treatment before use.

The plant was designed for the production of 200 B/CD (850 metric tons/month) finished lubricating oil from 1630 MCF/D (60°F - 760 mm.) of ethane. Actual production in continuous operation was about 85% of this figure. Yield of finished lube oil from original ethane was about 48.5 weight per cent.

PROCESS DETAILS:

The overall material balance for the plant is given in Fig. XXV based on 170 B/CD (700 T/Mo) lubricating oil production. Details of processes are given in Figs. XXVI - XXIX; based on design stream day operation where available.

1) Thermal Cracking of Ethane

The ethane cracking equipment consists of four parallel units, each with an ethane charge capacity of 617 MCF/D. Ethane (three volumes) and oxygen (one volume) are preheated separately at atmospheric pressure in gas-fired tubular heaters to 1100 - 1200°F and 750°F, respectively. The heaters are constructed of Sicromal (8-12% Cr). The hot gases are mixed during passage through a refractory assembly ("tulip") in the bottom of the subsequent ethane cracking furnace. The mixture passes upward through the cracking chamber, which is filled with 1-1/4" dia. ceramic spheres. Cracking conditions are approximately 1616°F and 300-400 mm. mercury absolute pressure. The cracked gases are quenched by a water cooled heat exchanger and then by direct injection of water. Vacuum is held on the cracking furnace by a water sealed vacuum pump which discharges the cooled gases to the next stage of the process.

It is interesting to note that the design capacity of four cracking furnaces is 2470 MCF/D ethane, producing 4,200 MCF/D water-free cracked gas; actual requirement (once through) for the 200 B/D lubricating oil production is 1,825 MCF/D, indicating a 75% stream time efficiency. The factor determining stream time efficiency is coking of the lower section of the ethane

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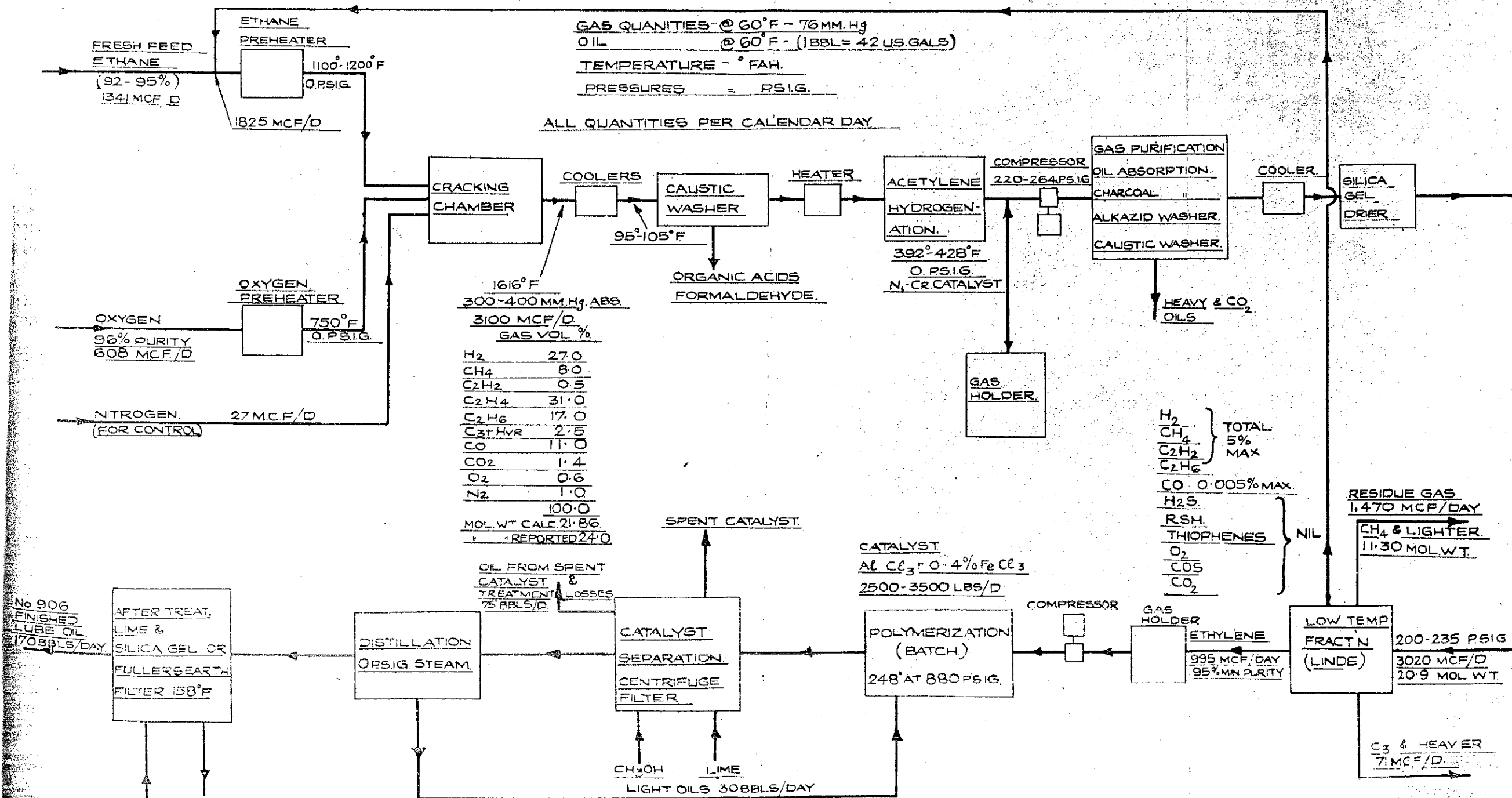


FIGURE XXV

SCHEMATIC FLOW DIAGRAM. LUBE OIL MANUFACTURE FROM ETHANE CRACKING IG AMMONAKWERK MERSEBURG. LEUNA.

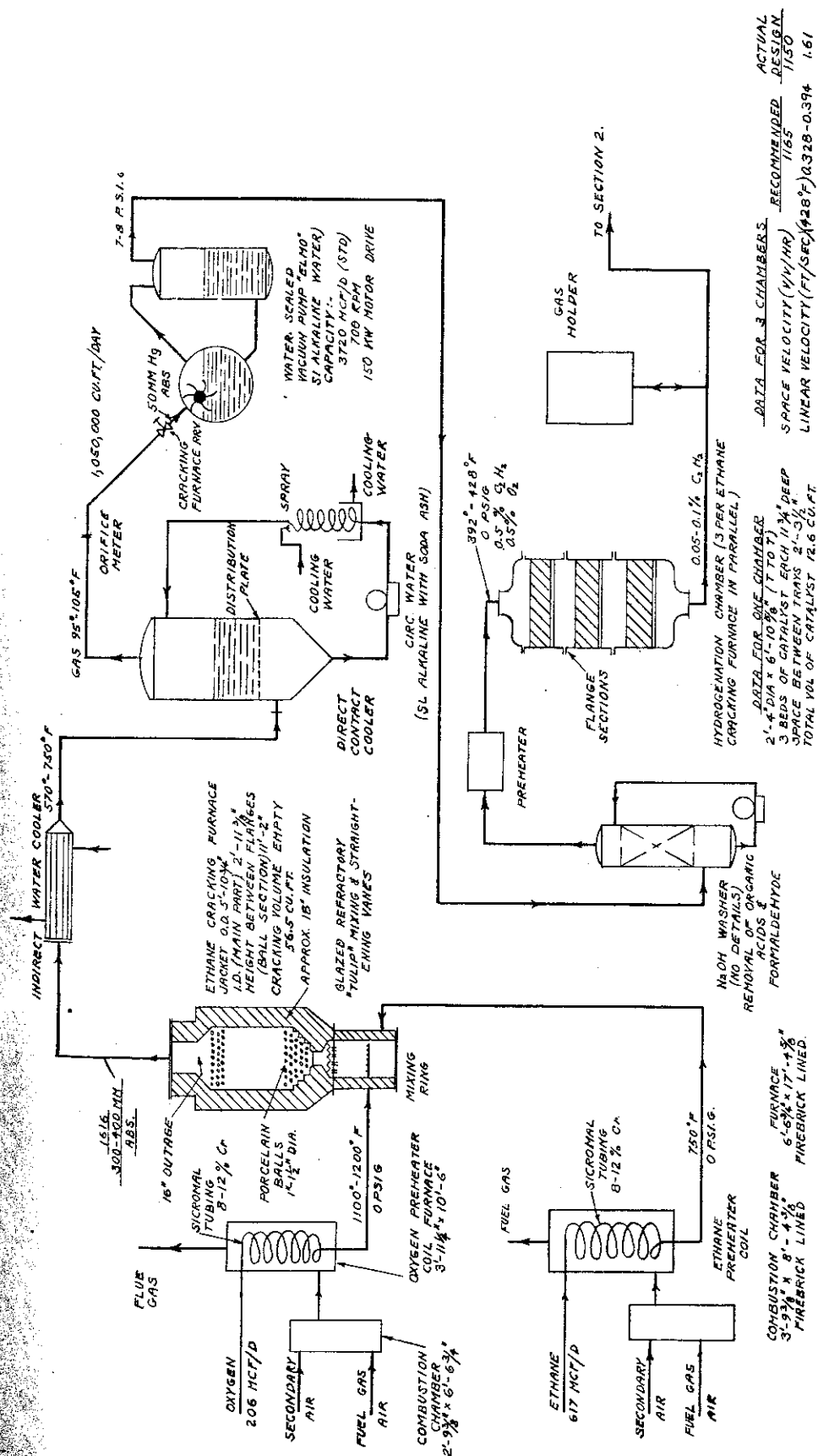


FIGURE XXVI - FLOW DIAGRAM SECTION I. LEUNA WORKS, LUBRICATING OIL FROM ETHYLENE. ETHANE CRACKING. DESIGN DATA FOR ONE UNIT FOUR UNITS PARALLEL.

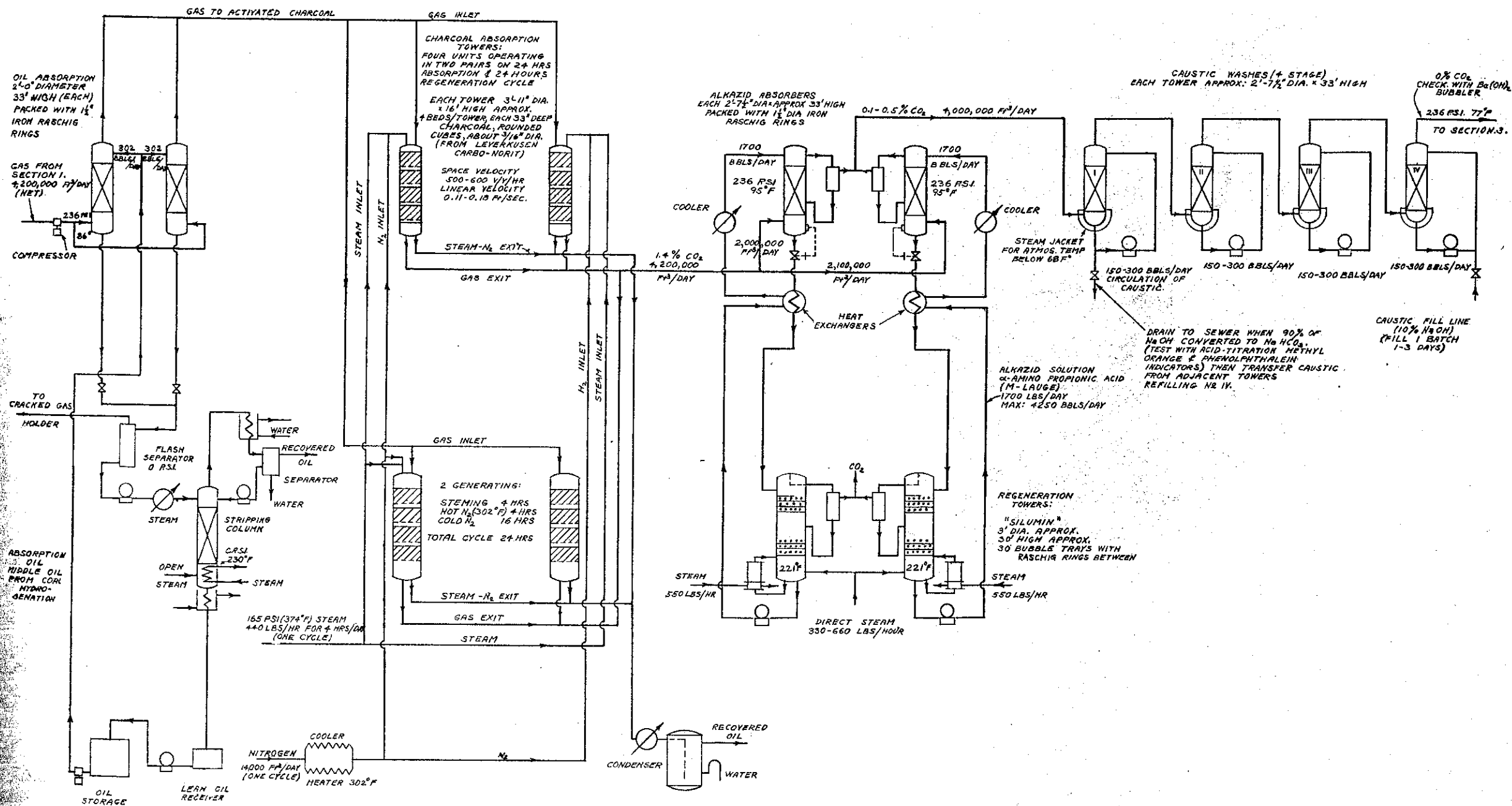


FIGURE XXVII.- LEUNA WORKS FLOW DIAGRAM-LUBRICATING OIL FROM ETHYLENE (SECTION 2) ETHYLENE PURIFICATION.

cracking furnace where oxidation occurs. A small amount of nitrogen (up to 2% of the ethane) is added to the ethane cracking furnace as a control of cracking.

The products of cracking are next washed with caustic soda in order to remove organic acids and formaldehyde.

2) Acetylene removal:

Acetylene is removed by hydrogenation over a nickel-chromium catalyst at a temperature of about 400°F, atmospheric pressure and a gas space velocity of 1,165 volumes gas (at standard condition)/volume catalyst/hour. Linear velocity was stated to be 0.33 - 0.39 ft/sec. but vessel dimensions indicated a greater linear velocity at the above space velocity. The hydrogen required for hydrogenation is already present in the cracked gas. Any oxygen present in this gas is hydrogenated to water.

After hydrogenation, the four gas streams are combined in one gas holder. From this point the gas is compressed to 220-264 psig. and undergoes four further purification processes at this pressure.

3) Oil Absorption:

The gas is passed counter-current to a middle oil (from coal hydrogenation) for absorption of benzene and higher hydrocarbons. The rich oil is stripped with steam in the usual way.

4) Activated Charcoal Absorption:

The gas is next passed through towers containing activated charcoal (rounded cubical pellets 13/64" diameter from Carbo-Norit Union, Leverkusen) in order to remove the last traces of benzene. These towers are operated on a 24-hour absorption/24-hour regeneration cycle. Regeneration is accomplished by steaming at 374°F followed by drying and cooling with nitrogen. The effectiveness of the absorption is checked by cooling a gas sample down to -76°F and noting whether there is any condensation.

5) Alkazid Washer:

The bulk of the CO₂ is removed by counter-current washing with an alkazid solution ("M-lauge", α-amino propionic acid). The alkazid solution is regenerated by heating and steam stripping at atmospheric pressure. The exit gas contains 0.1 to 0.5% carbon dioxide.

6) Caustic Washer:

Four counter-current towers in series are used, each circulating individually. The last tower in the series is filled with new 10% caustic soda (50 Be); and the caustic solution is transferred stepwise to the preceding tower in the system. The caustic in the first tower is dumped when 90% of the available sodium hydroxide has been converted to the bicarbonate. The caustic soda is not regenerated.

To ensure complete removal of carbon dioxide, a sample of exit gas is continuously bubbled through a barium hydroxide solution.

7) Linde Low Temperature Fractionation:

This plant was designed by the Linde Company for the separation of the washed gas into four fractions. The gas is dried over silica gel, precooled and fed into the first tower under pressure. The first tower produces methane and permanent gases as overhead product and ethylene and heavier as bottoms product. Reflux is secured by a methane compression refrigeration cycle. The overhead product is put to fuel gas.

The bottoms from the first tower expand into the second tower at about 7 psig. This tower yields ethylene and ethane overhead and propylene and heavier hydrocarbons are passed from the kettle to fuel gas. Reflux is provided by expanding ethylene directly into the top of the tower.

The ethylene + ethane overhead fraction passes to the third tower, which gives ethylene as an overhead product and ethane as a bottoms product. Reflux is provided in the same manner as in the second tower. The ethylene is compressed to 1200-1500 psi for storage and the ethane fraction is recycled to the ethane cracking furnace. This recycle constitutes about 26.5% of the total feed to the furnace.

Reboil heat is supplied indirectly to all three towers by relatively warm ethylene from the discharge of the ethylene refrigeration compressors. The general heat exchange arrangement is shown in the attached flow sheet, Fig. XXVIII.

The three towers are copper lined and all equipment inside the towers is made of copper. The three towers and part of the heat exchanger system are enclosed in an insulated box. Two parallel plants are used for this fractionation at full load.

8) Polymerization of Ethylene to Lubricating Oil:

The reaction is carried out in batch autoclaves. The Leuna plant has ten reactors, four of 400 cu.ft. capacity each and six of 290 cu.ft. capacity each. A batch can be run through a reactor in 12-14 hours.

The procedure for polymerizing a batch of ethylene comprises the following steps:

(a) A slurry is made in the reactor by mixing aluminium chloride (5-7% by weight on the finished lubricating oil) with light oil from the process. This slurry occupies 15-25% of the volume of the reactor and is kept in suspension by the mixer at the bottom of the autoclave. The aluminium chloride contains 4-6% ferric chloride.

(b) The reactor is purged of air with ethylene and then closed in.

(c) Ethylene is added to give 440 psi pressure.

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(d) The autoclave is heated to 158°F by circulation of hot water in the jacket. Reaction immediately sets in, the temperature rises to about 356°F and the pressure to about 515 psi. The compound thus formed represents the catalyst for the subsequent polymerization of ethylene.

(e) The reaction is quenched at the above maximum point by circulating cold water in the jacket. This procedure, from the first addition of ethylene, requires about fifteen minutes.

(f) When the temperature is reduced to 230°- 248°F., ethylene (at 882 psi) is introduced and the temperature is held constant in this range by jacket cooling. The polymerization causes a pressure drop in the reactor until the reactor is liquid full. At this point the temperature at the top and bottom of the autoclave are the same and the pressure in the autoclave is the same as the ethylene line pressure.

(g) When the autoclave is liquid full, the ethylene supply line is closed, the pressure on the reactor is vented down by gas release at the top of the reactor (to be described later), and the contents are ready for further processing.

The above procedure refers to the preparation of an oil to a final viscosity at 220 S.S.U. at 210°F (6° Engler at 100°C). To produce an oil of viscosity 105 S.S.U. at 210°F. (3° Engler at 100°C), the polymerization temperature is controlled at 356°F. The yield of oil from ethylene is reduced at the higher temperature.

The first Leuna autoclaves were made from steel containing 12-16% Cr and the oil manufactured was of the desired high viscosity. Subsequently more reactors were added, and these were manufactured from ordinary carbon steel. With a 95% purity ethylene from Leuna, these latter reactors gave a low viscosity oil (3-4° Engler) for 3 to 4 months, but subsequently gave a high viscosity oil. The plant at Schkopau (see following section), operating on a higher-purity ethylene, had no difficulty making a high viscosity oil in carbon steel reactors from the first. Gericke believes that, from this and other evidence, a high-purity ethylene is essential and that impurities in the ethylene, as well as reactor wall material, may influence polymerization. No corrosion difficulties have been experienced at Leuna as long as the equipment is kept absolutely dry.

Catalyst Separation and Disposal:

The contents of a reactor are pressured into a batch separation vessel. If the oil and catalyst complex layers do not readily separate, a small amount of methanol is added. The total mixture then passes through a scraper-type (schal) centrifuge, in which the heavier complex is continuously scraped from the outer drum and retained for further processing. The oil then pass through a DeLaval centrifuge for further catalyst separation. The optimum temperature for catalyst separation is about 194°F.

The oil, still containing a small amount of complex, next goes into an autoclave in which methanol (2% on oil) and lime dust are added. This treatment breaks down the catalyst complex and neutralises the acid formed. The