Luena Works - April 24, 1942.

Calculations for the Separation of Butane and Butylene by Azeotropic Distillation

The calculations are based on the separation of the mixture containing 25% olefins of which 40% are alpha and 60% beta butylene.

An azeotropic mixture of 50% by volume of butane and 50% by volume of methylamine boiled at 6.8°F. in the presence of methylamine. Constant boiling mixtures of alpha and beta butylene which contain equal amounts by volume of methylamine remain as bottoms. The azeotrope with beta butylene boils at 14°F., that with alpha butylene at 10.4°F. The liquid mixtures of hydrocarbon and amine form a single phase over the entire region of concentration.

According to the German patent #559437 of September 19, 1932, a distillate containing 4.5 parts of butylene, 28.5 parts of butane and 42 parts of ammonia results from the distillation of a mixture consisting of 18 parts of butylene, 27 parts of butane and 55 parts of ammonia at 133°F. and 82 psi. The reflux consists of 13.5 parts of butylene, 0.5 parts of butane and 13 parts of ammonia. When the distillate is cooled to about 81°F., two layers are formed. The lower layer consists of 1 part of butylene, 2 parts of butane and 38 parts of ammonia, whereas the upper layer consists of 3.5 parts of butylene, 25 parts of butane and 4 parts of ammonia. The ammoniacal layer exclusively is used as reflux. According to the patent the use for further quantities of ammonia as additional reflux is advantageous.

Figure 1 shows the boiling curve of a mixture of butane, butylene and methylamine. Distillation was carried out in a Podbielniak column at a pressure of 270 mm. Hg.

Figure 2 shows the diagram of the distillation unit in which the distillation was carried out with methylamine as auxiliary agent. It can be seen that for each kilogram of butane distilled one kilogram of methylamine must be distilled. From the boiling points of the azeotropes it can be calculated that the ratio of the vapor pressures is 1:1.2. If it is assumed that this ratio can be retained at the operating pressure of the column, a minimum reflux ratio of 1:7.5 is calculated. Without making assumptions for the degree of purity of the product and the number of theoretical plates necessary, the practical reflux ratio can be estimated as 1:9. This means that a quantity equal to 10 times the overhead product must be evaporated in the still. At a column head temperature of about 194°F., which corresponds to a pressure of 191 psia., 3,960 B. t. u. are necessary per pound of butane in the charge to the still.

No assumptions for the energy requirement for the separation of hydrocarbons from amines can be made since details of the process are not available.

Assuming that the permissible effective gas velocity in the column is 4.7" per second, a column diameter of 0.15 sq. ft. must be provided per pound of butane distilled overhead per hour.

Working according to the instructions of the German patent #559437, a continuously operated column would operate at a pressure of 294 psi. and a column head temperature of 104°F. Under such conditions the energy required for separation would amount to 173 B. t. u. for the hydrocarbons and 828 B. t. u. for the ammonia, making a total of 1,001 B. t. u. Separation of the hydro-

carbon mixture from ammonia by washing with water and concentration of the ammonia from the solution so obtained would require an additional energy of 649 B. t. u. Assuming that the permissible vapor velocity is 5.5" per second a cross-section of 0.03 sq. ft. must be allowed per pound of butane recovered as overhead product per hour. It must be emphasized that the calculations are based on the assumption that no additional reflux of ammonia is used.

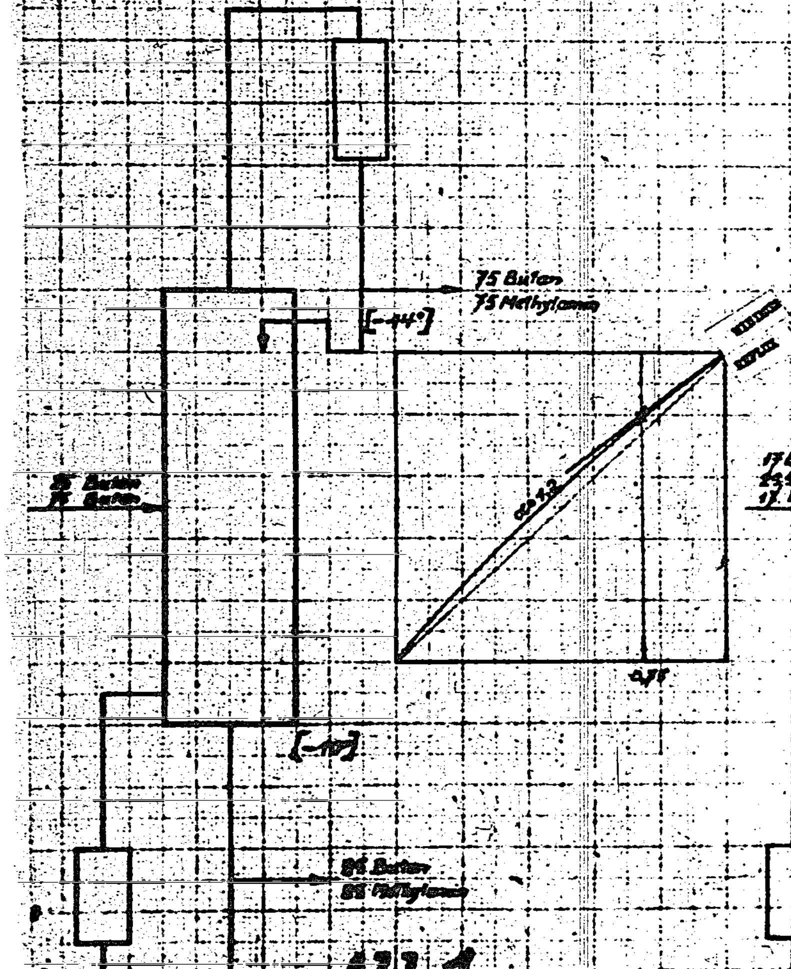

Abb. 1.

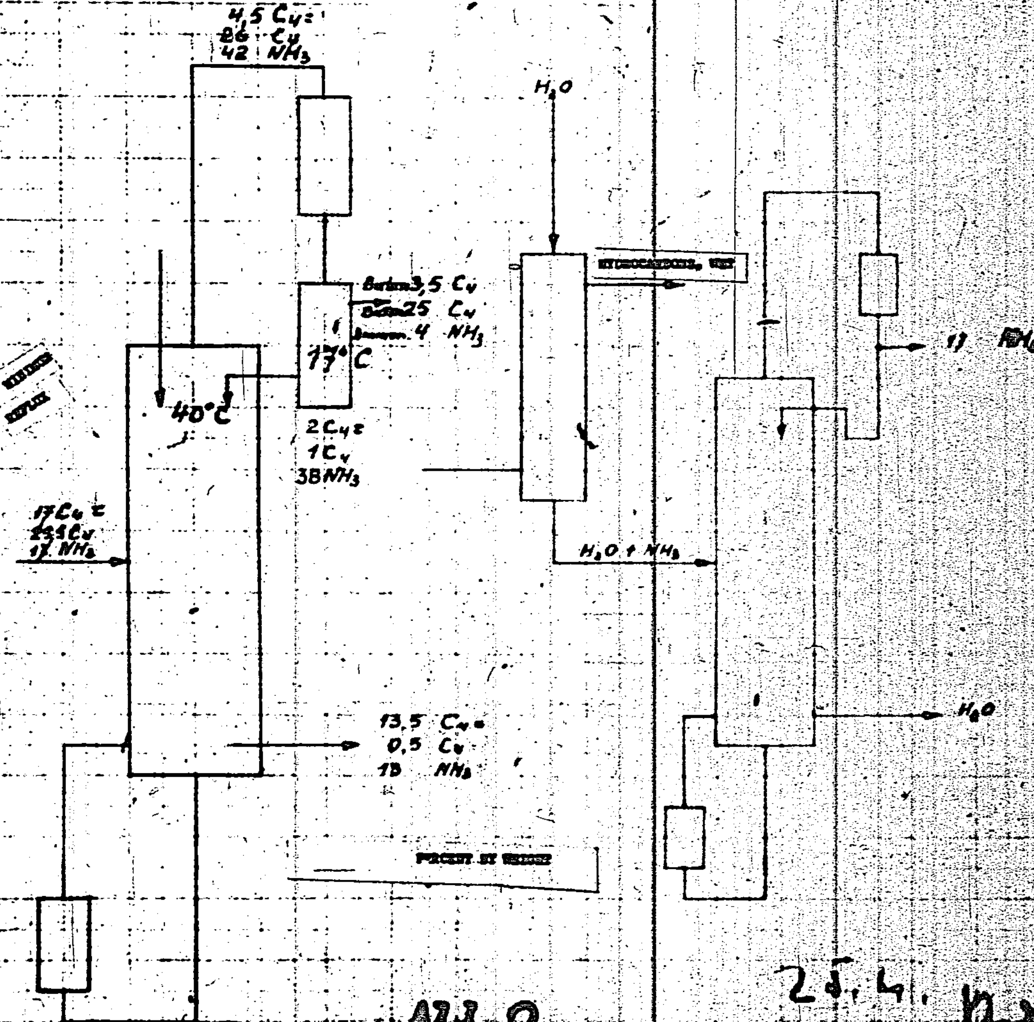

Abb. 2.

25.4.

DISTILLATION CURVE

DISTILLATION OF A BUTANE-BUTYLENE-METHYLAMINE MIXTURE (C_4:amine ab. 1:2)

OVER A PODBIELNIAK COLUMN