PART II - METHANOL DISTILLATION.

Process description.

Fig. 5 gives a flow diagram of the methanol distillation system. Raw methanol from the synthesis system is expanded into the raw product storage tank which operates at 12 - 15 atm. Dissolved gases are thereby released and are vented. The liquid flows through a second expansion valve which reduces the pressure to 6 - 8 atm., is preheated and introduced into the 1st rectification column. In this column the dimethylether is distilled

off, condensed, and sent to a storage tank, 98% pure dimethylether is obtained and is used for making dimethyl sulfate and dimethyl aniline.

The bottoms, free of methylether, are sent to a 2nd rectification unit. In this unit "V" methanol (Vorlauf methanol), consisting of 95% methanol and 5% methyl isobutyl ether, methylal, methyl formiate, etc., is separated and goes to a "V" methanol storage tank. The bottoms are cooled and introduced into settling and intermediate storage tanks. In the line going to these tanks a 1% solution of potassium permanganate in water is added to the stream in the amount of 0.3% of the product flow. The purpose of this addition is to oxidize any organic compounds and decompose the iron carbonyl contained in the product. The temperature at the mixing point should not exceed 30°C. otherwise oxidation of methanol takes place.

The liquid is allowed to stand in the intermediate storage tanks for at least 8 hours and preferably 24 hours for settling to take place. The clear liquor is decanted and conducted to the 3rd rectification unit. The sludge settled on the bottom of the intermediate storage tanks goes to a filter press. The filtrate is also sent to the 3rd rectification unit and the filter cake is discarded. The side stream of the 3rd rectification column is the pure product and goes to the product measuring tank where it is analyzed for purity. If it meets the specifications it is sent to the final product storage. A portion of the reflux is sent to the "V" methanol storage tank. The total production of "V" methanol from the 2nd and 3rd rectification units amounts to 3 - 10% of the crude methanol. This product is injected into the isobutyl alcohol synthesis system or used as fuel.

The bottoms from the 3rd rectification column are sent to a residue storage tank and from there are fed into the reboiler of the 4th rectification column which operates in a batchwise manner. The first overhead from the 4th rectification column is pure methanol and is sent to the product measuring tank. After a certain time the purity of the overhead is such that it must be sent to the raw methanol storage tank. Finally, when ethyl methyl ketones, di-isobutyl ketones, diisopropyl alcohol and mostly isobutyl alcohol begin to boil off, the overhead is sent to the higher alcohols storage tank. This product is used in the isobutyl plant. The residue in the reboiler, which is mainly water, is discarded.

The elaborate methanol distillation system described above is considered necessary at Oppau in order to obtain a product pure enough for formaldehyde manufacture.

Description of equipment

The following tabulation presents the principle information on the various rectification columns:

Rectification Column No:	1	2	3	4
Diameter	Top Sect. 0.6m. Bot.Sect. 1.0m.	1.5m.	2.9m.	1.5m.
Height	8.5m.	22.5m.	23.6m.	22.5 m.
Material of construction: column	steel	steel	steel	steel
Bubble caps	-	cast iron	cast iron	cast iron
Type of plates:	Bamag sieve type	Bubble caps	Bubble caps	Bubble caps
Number of plates:	Top Sect.23 Bot.Sect.21	70	70	70
Distance between plates	-	30 cm.	-	-
Feed injection point from bottom:	8th, 12th and 18th plates	16th, 20th and 28th plates normally 20th	17th, 21st and 27th plates normally 21st	16th, 20th and 28th
Side stream take off point from bottom:	-	-	52nd, 56th and 60th plates normally 60th	31st, 37th and 41st plates

The above information was given from memory by Dr. E. Haarer and since the detailed drawings for this equipment could not be located, the accuracy of this information cannot be vouched for.

Operating data, Yields and Utilities

The distillation system as described is said to be suitable to handle normally 160 to 190 tons of crude methanol per day, with a maximum of 240 tons per day.

The following tabulation presents the principal operating data for the various distillation columns:

Rectification column No.:	1	2	3	4
Operating pressure (absolute):	6 to 8 atm.	1 atm.	1 atm.	1 atm.
Temp. at the bottom of the column:	110° C..	68 to 70° C.	89 to 90° C.	72 to 100° C.
Temp. at the top of the column:	30 to 35° C.	62° C.	64° C.	46 to 98° C.
Ratio of reflux to distillate:	10:1	6:1	-	3:1 to 1:1
Ratio of reflux to side stream:	-	-	2.5:1	-

As the operation of the 4th rectification column is batchwise, operating conditions at the beginning and end of the cycle are given.

The above information was also given from memory by Dr. E. Haarer and its accuracy cannot be vouched for.

One ton of raw methanol furnishes the following products:

Pure methanol ..... 780 to 830 kg.
"V" methanol ..... 30 to 100 kg.
Dimethylether ..... 20 kg.
Higher alcohols ..... 0.2 to 0.3 kg.

The yield of pure methanol, based on the methanol content of raw methanol fed to the system, is approximately 89%.

In the methanol distillation system the following utilities are required per ton of pure methanol produced:

Electricity	17.0 kwh.
Steam	2.7 tons
Cooling water	163.0 cu.m.
Operating labor	0.7 man hours

Analytical methods

The distilled methanol is subjected to the following chemical tests:

1. Sulfuric acid test - To 5 c.c. of methanol cooled to under 5°C. is added 5 c.c. of pure concentrated H_2SO_4. The resulting mixture is shaken and its temperature should not exceed 5°C. A dark coloration of the mixture indicates the presence of traces of olefines, which are very poisonous to formaldehyde catalyst. A slight coloration is acceptable. If the solution remains white, the product is of excellent quality.

2. Boiling point test - An entire sample of methanol must distill off without a temperature increase of more than 0.3 to 0.4° C.

3. Potassium permanganate test - 1.3 c.c. of 0.1% $KMnO_4$ solution in water are added to 100 c.c. of the product. The mixture must be placed in a water bath and maintained at 17 to 18° C. The color should change from violet to brown in not less than 20 minutes. A longer period indicates a better product, while a shorter period indicates that an insufficient amount of $KMnO_4$ has been added in the process.

4. Test for iron - 10 c.c. of 25% NH_4OH and 10 c.c. of 30% H_2O_2 are added to 100 c.c. of methanol. The mixture is boiled with a reflux cooler for 30 minutes. The flocculent iron compound is filtered out, dissolved in hydrochloric acid, and a standard colorimetric test for iron is applied. Traces of iron in the product indicate that an insufficient amount of $KMnO_4$ has been added in the process for breaking up the iron carbonyl.

5. Bromine number - This test is applied to the raw methanol. To 100 c.c. of product, the bromine solution is slowly added until a yellow coloration identical to the standard solution is obtained. The number of c.c. of bromine solution added is the bromine number.

The bromine solution is prepared by adding 4.2 c.c. of concentrated bromine to 1000 c.c. of 50% acetic acid and the resulting mixture well shaken.

The standard solution is prepared by adding 0.05 gr. of potassium dichromate to 1 liter of water.