PART I - METHANOL SYNTHESIS SYSTEM

General:

The methanol production technique at Oppau is based on experience gained in the manufacture of ammonia and isobutyl alcohol. The first isobutyl unit at Oppau was attached to the ammonia plant, use being made of certain ammonia plant equipment and building facilities.

Methanol, which is used at Oppau for the production of formaldehyde, was formerly received from the I.G. Plant at Leuna. Later, as the demand for formaldehyde increased, a new isobutyl plant was constructed at Oppau and the isobutyl plant, connected with the ammonia plant, was converted to methanol production.

At present there are two complete methanol synthesis loops in operation at the ammonia plant, each having a capacity of 90 to 100 tons per day, and the new isobutyl plant is shut down because of an insufficient supply of gas.

According to the interrogated personnel the modern methanol plants built elsewhere in Germany by I.G. Farbenindustrie are very similar in construction and layout to the new isobutyl plant at Oppau. However, a different catalyst is used and the space velocity for methanol synthesis is about 3 times that for isobutyl synthesis.

Methanol is produced from hydrogen and carbon monoxide, in the presence of a suitable catalyst according to the following reaction:

$$2\ H_2 + CO \rightarrow CH_3OH$$

The following undesirable side reaction, giving small amounts of dimethyl ether also takes place:

$$2\ CH_3OH \rightarrow (CH_3)_2O + H_2O$$

If the temperature of the catalyst is allowed to rise above about 400°C. the following highly exothermic reaction takes place with further increase in temperature:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

The raw material used for methanol synthesis at Oppau is a water gas of approximately the following composition:

52.5% H_2, 41% CO, 5% CO_2, and 1.5% N_2

Sulfur is removed from this gas by passing it through activated carbon at low pressure. A portion of the gas is sent through a low pressure CO conversion system to adjust the ratio of H_2 to CO to the proper proportion and the combined gas is then compressed to 25 to 27 atm., and scrubbed with water for the removal of CO_2. This is followed by a final compression to about 260 atm. after which it is sent to the synthesis system as fresh make-up gas.

Process Description

Fig. 1 gives the flow diagram of a methanol synthesis loop. Although the equipment is generally designed for a maximum pressure of 325 atm., the usual operating pressure at Oppau is 250 to 260 atm.

The fresh make up gas has the following approximate composition:

68.0% H_2
29.0% CO Ratio $\frac{H_2}{CO}$ = 2.2 to 2.4
0.5% CO_2
2.1% N_2 Maximum sulfur content, 1 to 2 mg/cu.m. of gas
0.2% CH_4

This gas is passed through a vessel containing activated carbon which removes catalyst poisons such as carbon oxysulfide and iron carbonyl. The removal of these impurities takes place at room temperature, and it is necessary to inject into the gas stream about 0.5 gm. of ammonia per 1 cu.m. of gas, as well as oxygen in slightly over the stoichiometric amount for oxidizing the sulfur contained in the gas. The purified gas is introduced into the synthesis loop at the suction side of the circulator.

Starting at this point the flow of gas is as follows: The gas leaving the circulator passes through an oil trap, where lubricating oil is removed, and is then conducted to the interchanger. In this vessel the gas is heated by the gas leaving the converter and, after passing through the starting heater, enters the converter. A portion of the cold gas by-passes the interchanger and is injected between the catalyst beds in the converter for temperature control. The gas leaving the converter passes through the interchanger where it is cooled by the incoming gas and then goes to a double pipe water cooler in which the product is condensed. The product is removed from the gas stream in the product separator following the water cooler and the non-condensed gases are returned to the suction of the circulator. A constant bleed is maintained after the product separator to control inert gas concentration in the loop.

Condensate removed from the product separator containing methanol, water, dimethylether, higher alcohols and impurities is known as "raw methanol" and is sent to the distillation system.

Description of Equipment.

One complete synthesis loop consists of the following equipment:

2 Activated carbon vessels - suitable for either 2 or 3 synthesis loops. One is operated and one is spare. These vessels are vertical towers 800 mm. I.D. x 8 m. high and each contains 4 meters of activated carbon (M Khole) packing. The packing is 7 to 10 mm. in size. See section on catalyst for preparation of activated carbon.

1 Circulator - At Oppau several of the old vertical-type steam driven circulators, originally installed for ammonia production, are used. The new plants are equipped with more modern machines. For instance, at the Waldenburg plant where 3 methanol loops were erected for a total production of 300 tons per day, 3 electrically driven circulators each having a capacity of 100,000 to 110,000 cu. m. per hr. NTP, were installed. They are constant speed units and operate at 122 R.P.M.

1 Oil Trap - Oppau uses standard vertical cylindrical vessels. The newer methanol plants are using cylindrical vessels 600 mm. I.D. x 6 m. long, installed at a small angle from the horizontal in order to provide a large disengaging surface.

1 Product separator - Oppau uses standard vertical cylindrical vessels. Newer plants have inclined vessels, similar to the oil traps, and are 800 mm. I.D. x 6 m. long.

1 Water cooler - Horizontal double-pipe unit consisting of 4 rows in parallel, 10 pipes high. The inside pipes, 45 mm. I.D. x 8 m. long, carry the high pressure gas while water is circulated counter-currently in the outside pipes which have an I.D. of 120 mm. The total surface of 1 unit is approximately 260 sq. m. The inside pipes are made of N5 steel (3% Cr, 0.25% Mo, 0.1% C). It was found that severe corrosion took place at the inlets to the cooler and pieces approximately 1 ft. long of N8 steel (3% Cr, 0.5% Mo, 0.5% Wo) were welded to the N5 pipes at the inlet ends.

1 Interchanger - (Fig.2) This unit is of the shell and tube type. The shell is a steel forging made of S2 carbon steel (Siemens Martin steel with 0.2% C, having 40 to 45 Kg/sq. mm. tensil strength and 26% elongation), 800 mm. I.D. x 12 M. long. It has a 10 mm. thick liner of N5 (3% Cr, 0.25% Mo, 0.1% C) or N8 (3% Cr, 0.5% Mo, 0.5% Wo) special steel protected by a 2 mm. thick brass (63% Cu, 37% Zn) liner. The two heads are also protected with 2 mm. thick brass plates. The tube bundle consists of 757 copper manganese alloy (Cu + 1.5% Mn) tubes, 8 mm. I.D. x 14 mm. O.D. x 10.34 m. long, rolled and silver soldered into copper manganese tube sheets. The total surface is 265 sq. m. There are 57 baffles each with circular holes 51 mm. dia. giving a total gas passage area of 285 sq. cm. The tube bundle is surrounded by a 2 mm thick copper manganese plate on the outside of which a 125 mm. thick

kieselguhr brick lining is installed, held in place by a 2 mm. thick brass shell. The tube bundle has funnel-shaped heads at each end made of copper manganese, the lower funnel being bolted to the bottom head of the vessel while the upper funnel is provided with a stuffing box which permits the tube bundle to expand. To prevent gas from by-passing the tube bundle, 5 asbestos packing rings are provided along its length as well as stuffing boxes at each end.

1 Converter - (Fig. 3). The shell is a steel forging 800 mm. I.D. x 12 m. long. The inside linings of the converter, similar to those of the interchanger, are indicated on Fig. 4. For installing the 10 mm. thick special steel liner the forging is heated with steam to a temperature of 250°C. and then the liner is inserted. The method used for inserting the 2 mm. thick brass liner is indicated on Fig. 4. The bulged portion of the liner is pressed against the shell with a jack and the whole liner is then hammered.

The present methanol converters in use at Oppau have old type catalyst baskets. Gas is introduced into the bottom of the converter and rises through a central tube in which a heating element is inserted. The gas then flows downward through the basket, which is completely filled with catalyst. Inserted into the catalyst mass are five equally spaced perforated pipe rings, made of N8 or copper manganese alloy, through which cooling gas is introduced. This converter is charged with approximately 2.6 to 2.7 cu. m. of catalyst, having a specific gravity of 1.4 to 1.5, and is said to have a capacity of 90 to 100 tons per day at 260 atm. pressure.

The newer type converters, such as were installed in the Hydebreck plant, have 6 catalyst beds. The cooling gas is introduced under each of the five top beds, the general arrangement being indicated on Fig. 4. The catalyst grate is made of N8 steel and is covered with a copper manganese screen, having 3 mm. openings, on which the catalyst rests. Four 3 point thermocouple leads are installed for measuring the temperatures in the converter. This type converter is charged with approximately 3 cu. m. of catalyst having a specific gravity of 1.4 to 1.5 and is said to have a normal capacity of 110 tons of raw methanol per day with a possible maximum of 150 tons per day at 300 atm. pressure.

Miscellaneous: In the more recent installations the starting heater is in a separate vessel as indicated on Fig. 1. The heating element consists of 40 mm. wide x 7 mm. thick copper bands wound around porcelain insulated pipes. Transformers for the starting heaters can be regulated to furnish from 80 to 400 KVA at 16 to 20 volts.

In recently built plants the shells of the high pressure vessels are of the wrapped or wound construction as described by Norman W. Krase in FIAT Final Report No. 611 dated December 12, 1945, entitled:

"Design and construction of high pressure compressors and reaction equipment". When built in this manner the special steel liner is 25 mm. thick and serves as a mandrel for the windings.

Piping in the synthesis loop, carrying hot gases, is made of N8 steel.

Another interesting feature in the newer plants is the provision made for the expansion of the interconnecting hot piping. Both the interchanger and the starting heater are supported by 10 cm. diameter rolls and can move as the hot piping interconnecting them expands. This arrangement obviates the necessity of long expansion bends.

Operating Data, Yields and Utilities.

a. Operating Conditions

A typical analysis of gas at the inlet of the converter is as follows: 18.4% CO, 67.2% H_2, 0.7% CO_2, 0.6% CH_4 and 13.1% inert gases. Plant experience has indicated that the percent CO in the gas entering the converters must be less than 20% in order to prevent the formation of appreciable quantities of higher alcohols.

The maximum operating temperature in the catalyst bed is between 360 and 390°C. The normal pressure drop across the converter with a new catalyst charge is 12 to 14 atm. After about 6 months of operation this pressure drop increases to about 20 atm. It was pointed out by the operating personnel that it is very important to maintain a constant pressure drop across the converter, as a sudden variation of even a few atmospheres increases the amount of undesirable components in the raw methanol. As the catalyst gets older in order to maintain a desired production rate, the pressure drop is increased very gradually by regulating the by-pass valve across the circulator.

The raw methanol leaving the synthesis loop has the following approximate composition: 1 to 2% $(CH_3)_2O$, 6 to 8% H_2O, 90% CH_3OH and 0.8 to 1.0% higher alcohols and ketones. The following information on the composition and properties of raw methanol was obtained from operating data for the Waldenburg plant:

Appearance	clear and colorless
Specific weight at 20°C	0.821
Water per cent	10 to 13
Dimethylether	10 to 12 c.c./500 c.c.
Free acid	2 to 5
Saponification number	5 to 8
Bromine number	2 to 3

According to the operators the bromine number of the raw methanol should be as low as possible. A high number indicates the presence

of unsaturated alcohols and ketones. The upper limit is from 5 to 7. Good quality product should have 3 and excellent product 1.

b. Material quantities.

Approximately 3000 cu. m. of fresh feed are required per ton of raw methanol. The circulation rate is about 8 times the make-up or approximately 100,000 cu. m. per hour. The average bleed from a loop is about 15% of the fresh feed or 450 cu. m. per ton of raw methanol.

c. Production capacity and yields.

A synthesis loop as described above, with the new type converter, is said to have a normal capacity of 110 tons of raw methanol per day. The conversion per pass is between 12 and 16% of the amount of CO fed to the converter. The yield of methanol contained in the raw product based on the CO fed into the system is approximately 72%. This yield based on the H_2 fed into the system is approximately 62%.

d. Utilities.

It is estimated that, under normal operating conditions one methanol synthesis loop as installed at Oppau, producing 100 tons of raw methanol per day, requires the following utilities per ton of raw methanol:

Electricity	25 kwh.
Steam	0.3 tons
Cooling water	130 cu. m.
Operating labor	1.54 man hours.

Catalysts.

The activated carbon (M Kohle) used for the removal of sulfur compounds and iron carbonyl from the fresh feed is prepared in the following manner: Ruhr anthracite 1 to 10 mm. in size is used as raw material. 400 liters of this material are charged into a special brick-lined furnace and the charge is ignited. Air, water gas and enough steam for temperature control are introduced into the bottom of the furnace. A temperature of 920°C, (not to exceed 950°C) is maintained for 3 hours. During this time the bulk density of the raw material, which at the start is 700 gm/liter, increases to 900 gm/liter and then decreases to 550 gm/liter which should be the density of the final product. The resulting product is screened and the 7 to 10 mm. material is used for the activated carbon vessels.

The catalyst used for methanol synthesis is a zinc chromate having the following composition before reduction: 26 to 30% Cr_2O_3, 59 to 64% ZnO, 1 to 1.5% graphite and 9 to 10% H_2O.

This catalyst is prepared at the I.G. plant at Leuna as follows: 100 kg. of zinc oxide in fine powdered form are mixed with 240 liters of water to form a suspension. Then 50 kg. of chromic oxide are added. According to Leuna this addition should be very rapid as the zinc chromate mixture has thixotropic properties and a non-homogeneous product may result, giving a poor quality catalyst. Approximately 150 liters of the water is then removed in a press. The material is dried in a shelf dryer with air at 110°C, pulverised in a mill, mixed with graphite, and then tabletted. The finished product is in the form of small cylinders 10 mm. diameter x 10 mm. high.

At present a new and simpler method is employed at Oppau for the preparation of this material: 100 kg. of pure powdered zinc oxide and 40 kg. of pure crystalline chromic oxide are mixed in a stainless steel (18-8) mixer and 40 liters of water are added, as well as 2 kg. of graphite. The temperature must not exceed 30°C. when graphite is added, otherwise lumps are formed. From the mixer the material is sent to the pelleting machine. The specific gravity of the pellets is 1.7 to 1.75. The catalyst made according to this method has not yet been employed on a large scale.

The normal catalyst life was said to be from 6 months to 1 year. On removal of a spent charge about 60 to 70% is found to be pulverized. A change of catalyst is made when the pressure drop across the converter reaches approximately 20 atm. and the spent catalyst is pneumatically removed from the converter. New catalyst should be carefully charged to avoid breakage.

A new catalyst charge is reduced in the following manner: The synthesis loop is purged with nitrogen and a pressure of 2 to 3 atm. of nitrogen is applied. The circulator is started at about 1/3 of the normal rate (30,000 cu. m. per hour), and fresh gas is slowly fed to the system. The temperature is slowly raised by means of the starting heater to 100 to 110°C, and the pressure to 260 atm. These conditions are maintained for 30 to 48 hours, during which time water separated in the product drum is measured. In the next 24 to 36 hours the temperature in the converter is raised until the entire catalyst bed is at a temperature of 250°C. At this stage the temperature can be raised to the normal operating temperature in 2 to 3 hours.