

CHAPTER V.

CYCLE OF FILLING AND DISCHARGING A
SYNTHESIS CONVERTER.

When filling a converter, a large or small catalyst container is put on top of such a converter in which air has been replaced by CO_2 by introducing this gas at the bottom and further by putting a special frame on top of the oven and blowing CO_2 from cylinders through this frame. The catalyst, saturated with CO_2 , is then dropped from the container into the oven, which has to be done carefully in order to get an even distribution of catalyst over the converter cross section. During the filling procedure a small stream of CO_2 is blown continuously through the frame on top of the oven.

After the converter has been filled, the oven is closed. As the top cover is concave, leaving an atmosphere of air above the catalyst, nitrogen or CO_2 is blown under this cover over the catalyst to replace this air.

Filling and closing a converter takes about 5 hours.

The converter is then heated up by blowing 18 atm. steam into the water-circulating system. This takes about 2 - 3 hours and is continued until a steam pressure of 5 atm. is reached. Then synthesis gas - preferably gas from a first-stage converter - is passed over the catalyst in order to determine whether or not reaction will start, which is shown by the CO_2 recorder. If so, then no further heating is done. If not, heating is continued while synthesis gas is passing through, until reaction starts. This is generally the case when a steam pressure of 5 - 6 atm. is reached.

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The initial gas rate is 600 - 700 m³/h, which is raised gradually to 1400 m³/h. When starting on gas from a first-stage converter, after about two - three days the switch-over to fresh gas is made or the new converter is left in the second stage for more than half of its lifetime, as in this case the catalyst will be more protected, mainly from sulphur. Figures given were about 2500 hours in the second stage and the rest of its lifetime in the first stage.

It is also possible to start a converter on fresh gas; however, in that case the initial gas rate should not be over 600 m³/h, which furthermore should be very slowly increased. This quantity is limited by the capacity of the steam back-pressure regulator.

Conversion in either stage is controlled by the CO₂ content, as fresh gas entering the first stage has a practically constant percentage of CO₂ (about 13.4 % at Holten). When working on a 75 % contraction in the first stage, gas leaving this stage would contain about 55 % CO₂. At 57 % contraction, which is normal, the CO₂ content would be about 35 - 36 %. 57 % contraction means a conversion of CO of about 70 %.

Normally operation is as follows. After starting, as explained above, with a gas rate of 600 - 700 m³/hour, which is increased gradually, a fixed gas rate of about 1200 to 1300 m³/h is maintained. By controlling the steam pressure the temperature is regulated in such a way as to obtain a certain conversion of CO. By gradually raising the temperature up to, say, 200°C, this CO conversion is practically kept constant. Further increase in temperature is not advantageous owing to increasing methane formation. Therefore, once a certain maximum temperature has been reached the gas quantity

would have to be gradually reduced in order to maintain the same CO conversion. 2

However, in actual practice the catalyst is regenerated before this maximum is reached, e.g. after about 1000 hours' operation, by which time the operating temperature has been increased to about 195°C. After this regeneration (hydrogenation) which will be explained below, it is possible to obtain again the same CO conversion as before with the same gas rate, but at a lower temperature, for instance 190°C. Again this temperature is gradually increased to about 200°C in order to maintain the same CO conversion. This will then take about 800 hours, at about which point the catalyst will be regenerated a second time. Soon after this second hydrogenation it will be necessary gradually to reduce the gas rate, maintaining the temperature at a maximum of 203 - 205°C. The gas rate is then lowered very slowly to a minimum of about 800 m³/hour over a relatively long period of time, during which one or two more regenerations will be carried out. If the CO conversion at this final gas rate and a temperature of 203 - 205°C drops below 55 - 60 % in the first stage, usually such converter is taken off the line.

Graph N° 1 in annex E shows the actual variation of gas rate, contraction and "Leistung" with the time during the entire lifetime of two catalyst fillings. During this period 4 regenerations were carried out. It is interesting to see that the "Leistung" before the first regeneration was exactly the same for the two converters. After this regeneration one converter showed a slightly better "Leistung" than the other one. One will furthermore notice the drop in operating temperature after each regeneration.

We were told that both these converters were kept for more than the usual length of time in the first stage.

The hydrogen to be used for these hydrogenations or regenerations should be free from CO as much as possible, i.e. should contain less than, say, 0.1 % CO. The CO₂ content should preferably not be higher than 1 to 2 %. This hydrogen is kept in circulation at a rate of about 1500 m³ per hour per converter. It passes the converters in the same direction as synthesis gas, i.e. from top to bottom, is then cooled down to separate any liquid products and returned by a blower to the converter.

Part of this circulation gas is continuously blown off in order not to increase the methane content above a certain percentage and fresh hydrogen continuously supplied to the cycle at a rate of 300 - 400 m³/h for two converters. Analyses for methane before and after the converter show whether the regeneration (hydrogenation) is finished.

After a catalyst is taken off the line it is once more hydrogenated to lower the wax content before transporting it to the catalyst plant. In the beginning Holten used pure hydrogen for this latter hydrogenation also, but lately they have started using synthesis gas with the additional purpose of trying to kill the catalyst at higher temperatures and furthermore because synthesis gas is cheaper. As synthesis gas usually gas from the first stage is taken, but fresh gas can also be used for this purpose. When hydrogenating with pure hydrogen no increase in temperature is noticed. However, with synthesis gas the catalyst is still active enough to give a rise in temperature. The steam pressure

is then kept at about 19 atm. The time for this last dewaxing step is about 24 hours.

When starting to use synthesis gas instead of hydrogen for dewaxing, Holten apparently did not have any more pure Co-Th catalysts in operation. We were told, however, that with Co-Th catalyst they would prefer to use hydrogen mixed with some synthesis gas, as dewaxing of this catalyst is more difficult than of catalysts containing Mg.

The latter dewaxing and the regenerations mentioned above with pure hydrogen during the period of actual operation are carried out in order to free the catalyst as much as possible from accumulated paraffin, which is cracked at the normal operation temperature in the presence of hydrogen. In the case of normal hydrogenation with pure hydrogen about 3000 kg total products, of which about 1500 kg consists of CH_4 , are obtained per converter. When dewaxing with synthesis gas just after taking a converter off the line, very probably more CH_4 and more total products are formed, firstly because this cracking is carried out at higher temperatures and secondly because CH_4 will be formed not only from the paraffin itself, but also from the CO of the synthesis gas. When using pure hydrogen for the last hydrogenation it is necessary to heat the catalyst with steam. An endeavour was made to preheat the hydrogen to 350°C , but this did not help at all.

In future Holten may apply extraction with certain gasoline fractions instead of regeneration with hydrogen. They consider extraction to be a better method of removing paraffin from the catalyst, but the best method of doing this, and what gasoline fractions should be used, has still to be investigated. It is

realized, however, that in this case no Cobalt carbides, if formed during the synthesis operation, can be reduced, as is done apparently when regenerating with hydrogen.

After this last treatment with synthesis gas at higher temperatures is finished, the steam pressure is released very quickly to atmospheric or somewhat higher pressure, which will cool down the converter. Then a few preparations have to be made before the converter can be discharged, during which time the converter will cool down somewhat more. The gases within the converter are replaced by nitrogen or CO_2 . An almost horizontal chain scraper is connected to the bottom part of the converter and an almost vertical bucket conveyor fitted in such a way that the catalyst, after leaving the first conveyor, is picked up and dropped into a catalyst container (see Annex A, figure 10). Then the two bottom plates, on which the catalyst rests, are opened, which can be done from the outside.

In general the catalyst runs easily out of the converter. When most catalyst has been transported via the two conveyors into the catalyst container, the oven is further cleaned by poking and, if necessary, air blowing. In case the catalyst should not run out freely, the converter is completely closed again and again treated with synthesis gas at higher temperatures, as described above.

Air in the catalyst container should be entirely replaced by CO_2 before starting to fill it with spent catalyst. CO_2 is also blown over the conveyor during transport of the catalyst from converter to container. After being filled, the container is closed and brought to the catalyst plant.

Generally, spent catalyst is not stored; this is not on account of the catalyst itself, but only to

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limit the number of containers in circulation.

This catalyst still contains paraffin, viz.

when using Co-Th catalysts	15 - 35 %
for mixed catalysts	8 - 20 %.

An endeavour was made at the time to remove this paraffin from the catalyst in situ, which means in the converter itself, with steam. This did not meet with success, as a temperature of about 400°C is necessary and Ruhrbenzin's synthesis plant is not equipped for preheating the steam to this temperature. Therefore, steaming to remove paraffin was worked out separately and, when found to be possible, carried out ~~in the catalyst plant before starting the dissolving,~~ etc., procedure. Since using catalysts containing Mg, steaming of spent catalyst is not necessary any longer, as such catalysts usually do not contain more than 20 % paraffin, which remains in the Kieselguhr during the dissolving procedure. The catalyst is, therefore, now dropped from the containers into barrels, which are emptied directly into the dissolving tanks. All spent catalyst is tested on its paraffin content (this analysis takes about one hour), because steaming is still carried out when the paraffin content is over 25 %.

This steaming not only lowers the paraffin content of the catalyst, but also helps to kill the activity of the catalyst, as spent catalyst is of pyrophorous nature. Formerly all spent catalyst, even if the paraffin content was not too high, was entirely de-activated, losing thereby its pyrophorous nature. This latter treatment could be done with either steam or steam + air or air alone.

With Th catalyst one has to be very careful not to exceed certain temperatures when oxidizing the

catalyst with air, as otherwise part of the thorium will become insoluble in nitric acid. Such temperatures are, when measured with a thermometer in the catalyst, 150 - 190°C. The actual catalyst temperature may be then as high as 400 - 500°C. Therefore, in such cases, oxidation - that is killing the activity - should be carried out slowly or by small additions of air or oxygen to nitrogen. Cobalt itself is not sensitive to these temperatures, although when going to still higher temperatures one apparently passes a range in which Cobalt can also be harmed.

It is also possible to oxidize with steam, in which cases the temperature may be considerably higher without affecting the dissolving properties of the thorium. However, this is more expensive and more difficult from a mechanical point of view. Nevertheless, when de-activating Th catalyst, Holten think that steam is to be preferred, as in that case it is not necessary to control the temperatures very closely.

The amount of gas which is circulated when oxidizing with air is 300 m³/h. When working with steam 1 - 1.5 tons per hour is required. Duration: 10 - 12 hours per oven charge when using air; 18 - 20 hours per oven charge when using steam.

An endeavour will be made to oxidize the spent catalyst, while still in the converter, by introducing small quantities of oxygen to steam.

Holten are installing new equipment for transporting the spent catalyst - which now no longer consists of pure Co-Th catalyst and, therefore, does not contain too much paraffin - directly from the converter to the dissolving tanks. In this case the spent catalyst will be dropped into a vessel of about 2 m³, into which

$\text{Co}(\text{NO}_3)_2$ solution also runs, equipped with a stirrer which mixes the spent catalyst vigorously with the nitrate solution and from which a pump takes suction, pumping this solution directly into the dissolving tanks, at the same time recirculating part of the liquid back into this vessel. This would save much time and labour if found to be a success.

Ruhrchemie's catalyst plant is able to rework about 6 - 8 converter charges per day. Ruhrbenzin's own consumption is not more than half an oven charge per day; therefore, it is considered to be a small plant and most of the spent catalyst they rework comes from their licensees.

There are apparently 3 catalyst plants at present in Germany, viz. one at Holten, one at Ruhland and one at Lützkendorf. Outside Germany this Fischer process is applied, for instance, by Kuhlmann, who also have their own catalyst plant.