Ammonia/Methanol Plant Startup

Automated startup of the gasification unit reduced many of the hazards involved, lowered the number of personnel required, and permitted faster startup of the reactors.

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Precise and carefully observed safety procedures were an essential part of the startup and operation of Veba-Chemie's ammonia/methanol plant in Gelsenkirchen, West Germany. This article describes the commissioning and pre-commissioning of the oxygen turbo-compressor, as well as the safety systems involved in the gasification section, which uses 940 lb./sq. in. gauge oxygen.

The complete plant can simultaneously produce 1,250 ton/day of ammonia and 450 ton/day methanol. As illustrated in Figure 1, the complex consists of air separation, Shell gasification, Rectisol H_2S removal, high temperature CO shift conversion, Rectisol CO_2 removal, liquid nitrogen scrubbing, ammonia synthesis, a refrigeration unit, insulated tank farm, methanol synthesis, and methanol distillation.

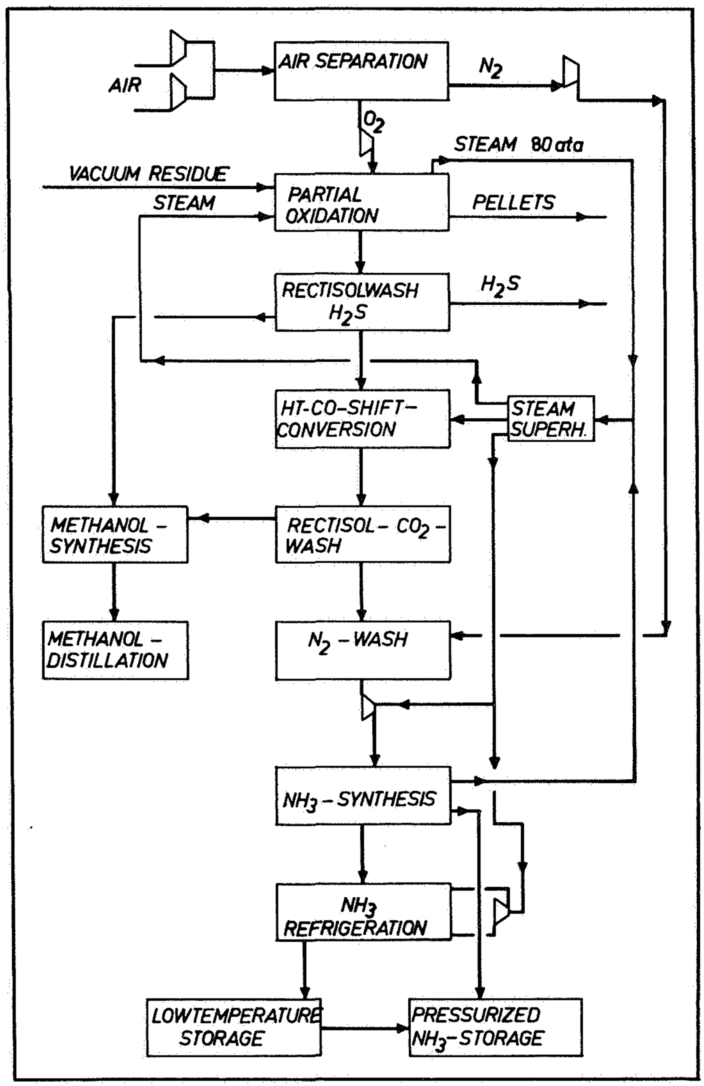

Figure 1. Flow diagram of Veba-Chemie's ammonia/methanol plant.

The plant is sufficiently flexible to increase methanol synthesis to 600 ton/day at the expense of the ammonia synthesis. Similarly, the ammonia output can be increased to 1,400 ton/day. Tank farm capacity of 25,000 ton NH_3 is available to cope with downtime in ammonia synthesis. Tankage of equivalent capacity is provided for methanol.

The following units were created for this complex:

1. Air separation for 1,400 ton/day oxygen and over 1,500 ton/day nitrogen. Messer-Griesheim, who supplied the turnkey cold box had thus far built plants for maximum 75% oxygen production.
2. Oxygen turbo-compressors with 940 lb./sq.in. gauge discharge pressure, from Demag. In the past oxygen turbo-compressors were operated at a maximum of 700 lb./sq.in. gauge.
3. Shell gasification with 50% increase in capacity and with a newly developed four coil waste heat boiler. The process pressure was raised from 630 lb./sq.in. gauge in the past to 840. A new design for the reactors and waste heat boilers was used, including new materials of construction. An automatic system was developed for safe and accurate startup. Figure 2 is a photograph of the unit.
4. The synthesis gas downstream CO_2 removal must have a CO_2 and methanol purity of 0.1 parts/million because of the downstream nitrogen scrubbing unit, which is equipped with plate type exchangers.
5. The nitrogen scrubbing unit by Linde is a new development in refrigeration recovery by expansion of the nitrogen to its partial pressure. Operation is above the critical nitrogen pressure.

The ammonia/methanol complex uses the advantages of an infrastructure, integrated with the overall Veba plant, as shown in Figure 3.

Feedstock from refinery within the complex

A refinery within the works supplies 3 million bbl./yr. of residue from a visbreaker and vacuum distillation to the gasification and pelletizing unit.

There is a connection to an oxygen system for import and export. High pressure steam (for startup or partial load operation), and electric power, are supplied from a nearby power plant, to which the pellets from the gasification unit are sent.

The H_2S from the Rectisol wash is converted to elemental sulfur in a Claus kiln.

Ammonia synthesis gas can be sent to other ammonia plants operated by the company via pipeline or tank trucks for further processing.

From the units just listed, the oxygen compressor and the oxygen consuming part of the gasification unit had to be handled with utmost accuracy and care.

Before the plant was commissioned in 1972-73, the

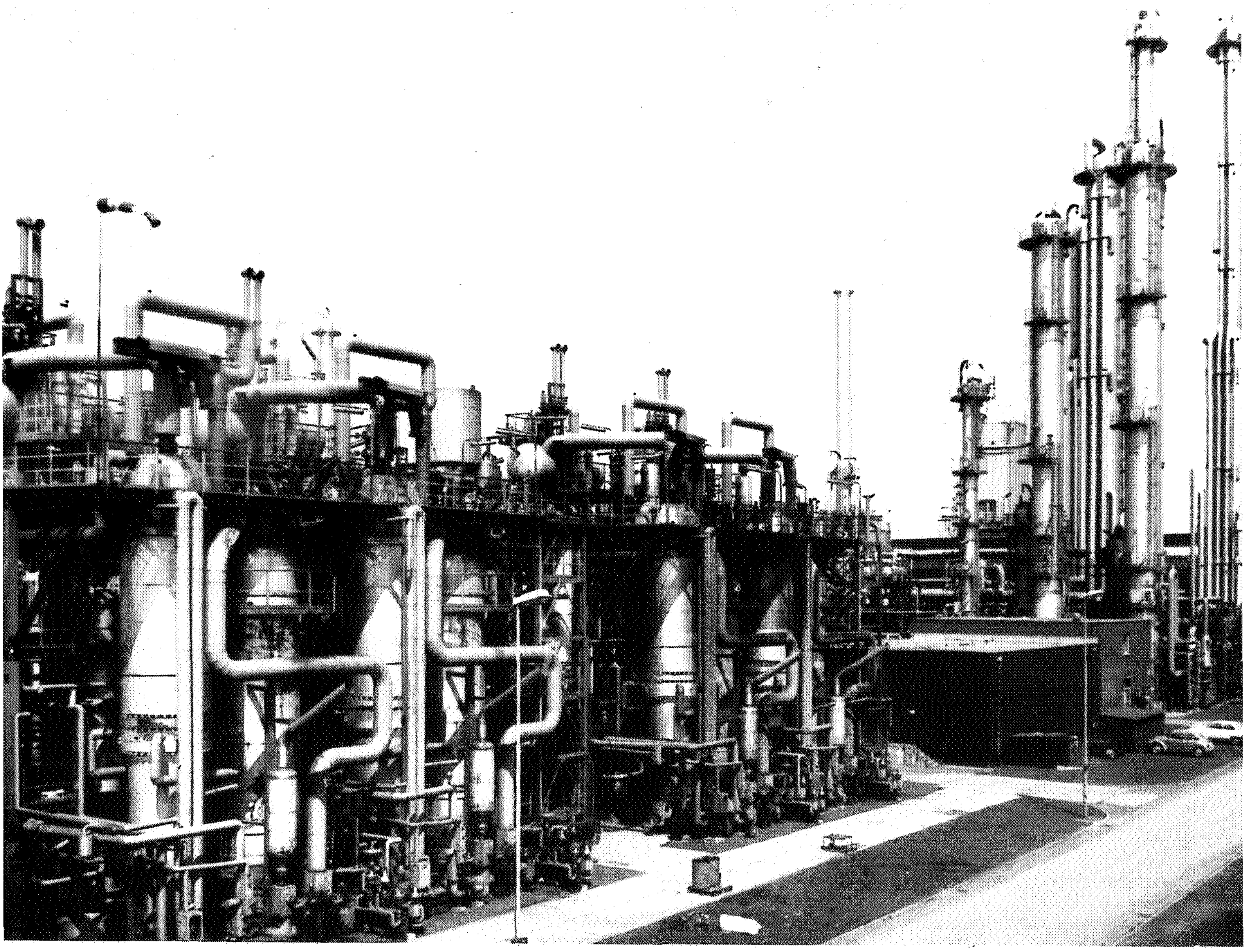

Figure 2. The partial gasification unit and the Rectisol scrubbing unit.

company had no experience with the operation of oxygen turbocompressors at pressures above 840 lb./sq. in. Therefore, extraordinary efforts were made to make sure of an absolutely clean system both up- and downstream of the compressor and in the compressor itself.

In the 32 in., 600 ft. long pipe upstream of the oxygen compressor, residual amounts of oil were removed manually by treating with trichlorethylene. Cleanliness was checked by ultraviolet light.

The stainless steel oxygen pipeline between compressor and gasification was:

1. Cleaned with a commercial detergent.
2. Treated with 1.5% fluoric acid at 120°F.
3. Rinsed with BFW (boiler feed water)
4. Treated with 0.3% citric acid.
5. Rinsed with NH_3-doted BFW (pH = 9.5).
6. Dried with N_2 (dew point = −284°F.).

All parts of the oxygen compressor that could be removed—such as coolers, internal recirculation piping, valves, and filters—were cleaned with trichlorethylene and remounted by workers in white suits with oil-free tools.

Fire protection built into compressor

The compressor is equipped with an emergency system that is activated in case of fire. In this case, the fire valve upstream of the compressor closes, and oxygen is expanded from the fourth, sixth, eighth, and tenth compression stages.

To monitor a potential outburst of fire there are eight two-out-of-three temperature cutouts, and eight temperature-sensitive fusion cones which melt at a critical temperature and initiate a pressure drop in an auxiliary

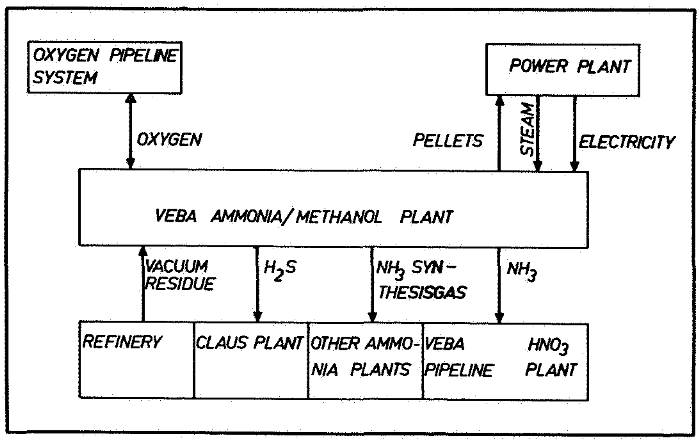

Figure 3. How the ammonia/methanol unit is integrated within the total processing complex.

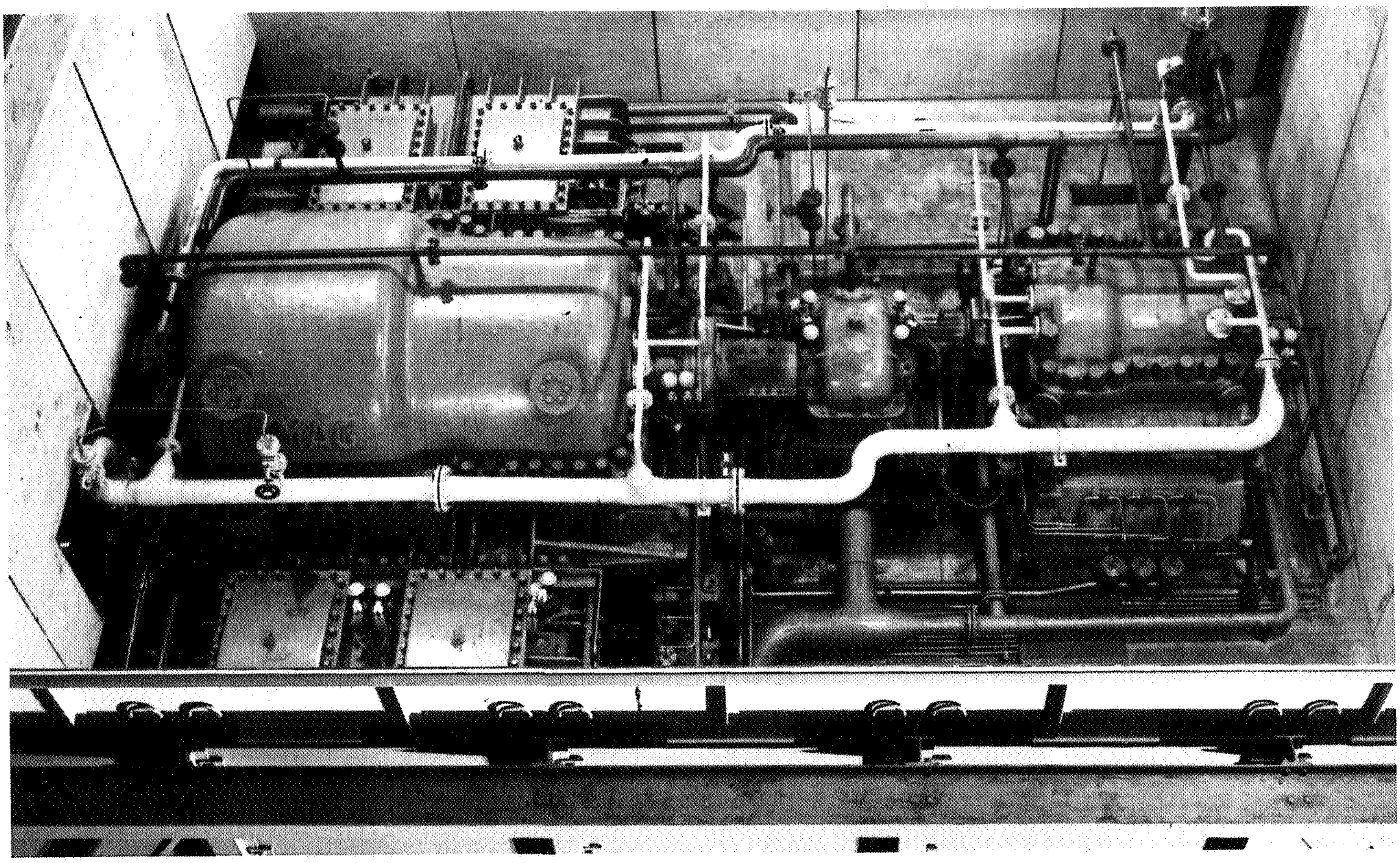

Figure 4. The oxygen compressor.

nitrogen system, which finally leads also to the emergency cutout.

In addition, the compressor can be shut down by two axial displacement, four vibration monitors, a four-fold rise in the pressure difference in the seal-gas system, the pressure upstream of the compressor, and a failure in the oil system. The entire compressor is surrounded by an explosion-proof cage, which must not be entered during operation.

Commissioning of the oxygen compressor, Figure 4, involved the following operations:

1. In the beginning, the test runs were performed with nitrogen from the air separation unit. First, all routine tests were performed including the operation at the surge limit. Also, several types of bearings were tested, the best proving to be the segmental bearings.

2. The next stage was to run the compressor with a N_2/CO_2 mixture. During the determination of the surge limit, pressures up to 1,315 lb./sq.in. gauge were reached. All shutdown cases were simulated.

3. After these tests, the compressor was shut down and flooded for some hours with oxygen, purged with nitrogen, and then restarted. Within six to seven hours, the nitrogen was replaced by oxygen at a pressure of about 630 lb./sq.in. gauge. Then the pressure was raised to 940 lb./sq.in. gauge and the compressor operated under these conditions 48 hours. After this successful test run, the compressor was shut down for bearing inspection.

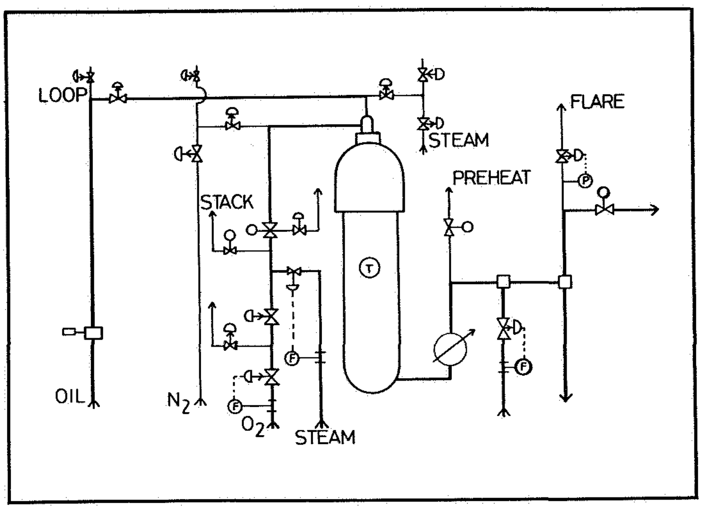

Figure 5. Flow diagram of the gasification reactor system.

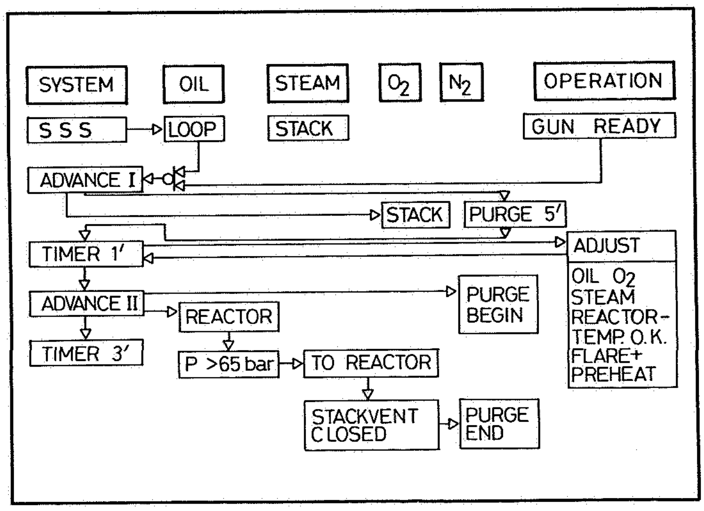

Figure 6. Automatic startup safety system.

Based on our experiences, we recommend, first, that extremely clean seal gas be used. We use air from the air separator upstream of our expansion turbines. Second, any oxygen compressor that has been shut down for a considerable period of time should be restarted according to the procedure described above.

In case the air separator also has to be started, the restart of the compressor can begin with air from the oxygen line of the air separation unit in the early phase of startup. Then, with improving conditions in the air separator, the air gradually changes to pure oxygen.

Safety system

The 1,400 ton/day of oxygen, at more than 840 lb./sq.in. gauge, has to be handled in the gasification unit with extreme care. In smaller gasification units a safety system is already installed to protect against excess oxygen in the reactor during operation. For the Veba-Chemie Type 1,000 Shell reactors, a more elaborate safety system was developed.

The system monitors the operational data during both startup and operation. During startup, it also initiates the subsequent moves of the specific valves depending upon the status of the startup procedure. This provides the advantages of greater safety, good accuracy, fewer personnel, and a faster startup.

The essential features of the system are described below. Figure 5 shows the arrangement of oil, oxygen, and steam lines. Oil flows through a jet where it is atomized to a fine spray. Oxygen and superheated steam enter the reactor tangentially. Where the oil and the O_2/steam mixture meet, the reaction begins.

The criteria that trigger the safety system exist in the startup safety system (SSS), and in the operating safety system (OSS). For the SSS the criteria are: emergency cutout, oil pump power dip, and oxygen valves incorrect. For the OSS the criteria are the same with the addition of high/low oil pressure, high/low oxygen flow, and low steam flow.

When a gasification reactor must be started, the mode is first switched onto the SSS, as shown in Figure 6.

The oil pump can then be started manually and the oil recirculated to the tank. Steam flow to the startup silencer can be adjusted to normal rate. After the gun has been reported to be installed, Advance Button No. 1 is pressed. This opens the oxygen line to the startup silencer and adjusts the oxygen flow. Simultaneously, from a high pressure vessel, nitrogen purges the reactor in five minutes. A timer then gives one minute to adjust the oil, O_2, and steam flow, to check the temperature of the preheated reactor, to open the flare valve, and to close the preheat valve.

After this, with all conditions correct, the signal, "Press Advance Button 2," appears. Once this button is pressed, oil flows to the reactor, and simultaneously the nitrogen purge starts again to prevent oil vapors flowing back into the oxygen/steam line.

As soon as the oil pressure upstream of the reactor exceeds 910 lb./sq.in. gauge, the steam/oxygen mixture is admitted to the reactor. The nitrogen purge ends with the steam/oxygen stack vent completely closed. Also, with the pressing of Advance Button No. 2, a timer is started, as seen in Figure 7.

Within three minutes, the following conditions have to be correct: gas pressure must be higher than 70 lb./sq.in. gauge, quench water must flow, and the stack valve for steam/O_2 must be closed.

After these three minutes, the automatic check begins and it lasts for 30 seconds. If one condition is not correct, the reactor is shut down. Otherwise, the signal appears: "Normalize Temperatures and Pressures."

When that is completed, the operator checks the oil pressure, O_2 flow, and steam flow. If these are correct, the mode is switched from the SSS to the OSS. From this time forward, the complete monitoring system is activated.

In case of a shutdown, first the oxygen is cut off, as seen in Figure 8. Steam goes to the stack, and oil is recirculated. After automatic nitrogen purge of the reactor, the train can be depressurized. Meanwhile, the oil line is purged with steam. When the reactor pressure is less than 70 lb./sq.in. gauge, the nitrogen purge continues for three minutes. Then the gun can be removed. After changing the gun, the reactor system can be restarted. #

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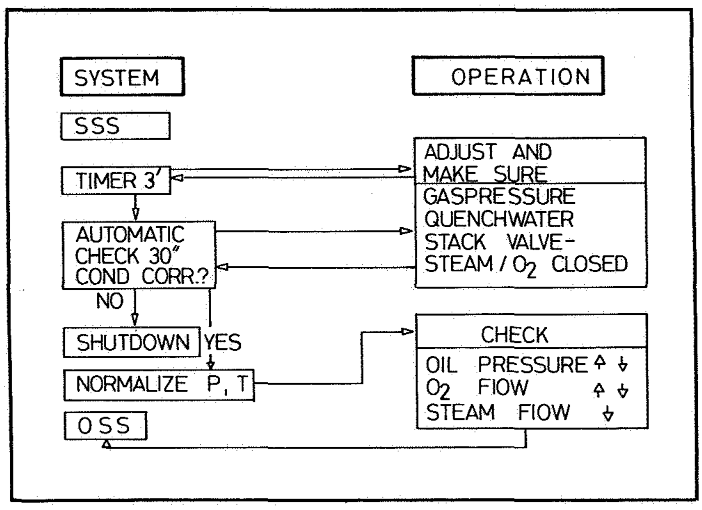

Figure 7. Startup safety check.

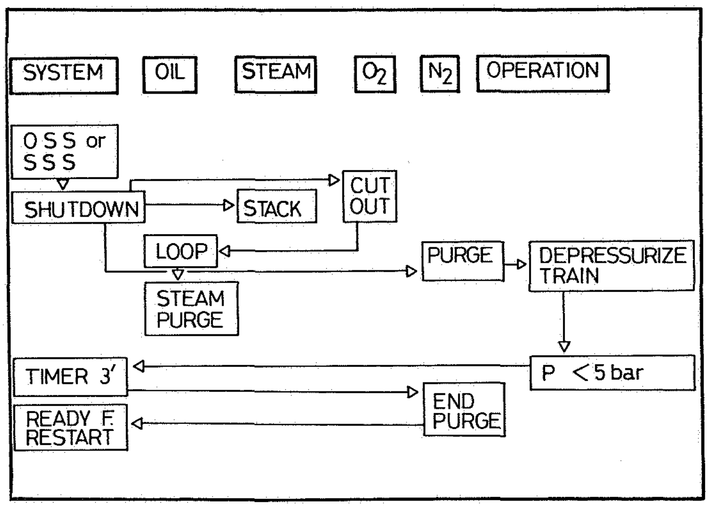

Figure 8. Automatic shutdown.

DISCUSSION

O. J. QUARTULLI, M. W. Kellogg Co.: I notice that the reliability of individual pieces of equipment of various unit operations is quite high. Collectively, what was the stream efficiency of this plant?
BUTZERT: Well, since this is some kind of prototype of plant, I wanted to know how reliable is each of those units and to failure of which units the plant had to close down for so and so much production time. So these percentages counting reliabilities of each unit are independent. In order to calculate the overall reliability you have to add always the difference of each reliability to hundred percent of all units. Subtracting this sum from one hundred you receive the overall onstream efficiency, about 90%.
QUARTULLI: How many gasifiers did you provide in the design and were all of them in operation at design capacity?
BUTZERT: We have four gasifiers in parallel, each making one million standard cubic meters per day carbon monoxide and hydrogen. We are taking the gas load of about three reactors for ammonia production and of one reactor for methanol production.
QUARTULLI: In the course of your discussion on emergency measures no mention was made of failure of flow of boiler feedwater to the steam generators downstream of the gasifiers. What measures are taken for protection of equipment against boiler feedwater failure? Is there an automatic shutdown of the unit?
BUTZERT: Yes that's correct and that I am asked very often, and I can state that we did not have any trouble with the waste heat boiler, I assume you mean that in the gasification units. We didn't have any erosion. We have a small but tolerable H_2S corrosion on the apex. But that is in allowable rate.
Q. What happens if there is no water going to the steam generator.
BUTZERT: Well you have to shut down the plant of course.
Q. But I mean, what emergency measure do you have? Is there an automatic shutdown?
BUTZERT: No that is to be made from the control room.
QUARTULLI: Does the condensed water downstream of the high temperature shift converter contain excessive amounts of methanol carried over from the Rectisol unit. Also, does this condensate contain any ammonia which might have been produced in the shift converter? How do you handle this effluent stream?
BUTZERT: This water contains silicium oxide and carbon dioxide and that is all because the H_2S is removed in advance in the H_2S removal unit. We find ammonia from neutralizing the circulation water, but no methanol.
QUARTULLI: Does the process water condensed downstream of the gasifiers contain excessive amounts of HCN? If so, what treating steps are necessary for disposal of this stream?
BUTZERT: It contains bigger amounts HCN and therefore we have installed a HCN stripper.
MAX APPL, BASF, Germany: Mr. Butzert, one question with respect to reliability of operation of your gasifiers. You said you have installed four gasifiers. My question is how often you have to shut down those gasifiers during the year in order to change your oil guns?
BUTZERT: First, we have to change the gun every 1,500 hours and when we do that, we raise the load of the remaining 3 reactors to an entire of 330%, so we lose a 70% production from those entire 400% gastification load through this hour which we need for changing the gun. Second, we have to inspect the burner noses every 3000 hours or we have to replace them every six thousand hours. I think that answers your question.
APPL, BASF, Germany: Yes, but I am thinking that your concept is a mixed plant for making ammonia and methanol. If I think only in terms of making a big ammonia plant, so you would in your concept be limited to use a least three or four gasifiers. Apart from maximum capacity for one gasifier, the proper reason in your case is that you have to change burners every 1500 hours and you can't run a centrifugal compressor below 75% without recycle operation due to suction problems. I personally think that it should be better to have a higher capacity for the gasification units. We are operating also a partial oxidation plant and we think it feasible in our Texaco type, to achieve a production of 1000 metric tons of ammonia with one generator. And we have developed our type of oil burner, so that we are able now to run that burner for one year without interruption in the Texaco gasification.
BUTZERT: Our four reactors can run on a load of 70%, but also on 110%, so the range is running between 280 and 440%. And so we can arrange for this inspection this higher load, and make our short shutdown of only one reactor.
APPL: And a second point I wanted to discuss, concerns the waste heat boiler route, which you have chosen. There is another route, the quench type version. We, in our company operate both versions—in one plant we are making synthesis gas for Oxosynthesis and are producing hydrogen and CO. This plant is equivalent to about 1200 metric tons of ammonia. The other one is a real ammonia plant which produces about 500 metric tons per day. For the ammonia plant, we have chosen the quench type version and for the syngas plant we have taken the waste heat boiler type.

But in doing merely ammonia, we think that the quench type is being the simpler and the more economic one, quenching and making shift conversion and after shift conversion to remove H_2S first and then CO_2 by a rectisol washing unit. We feel it is simpler because in the other case you have first to install a waste heat boiler and then to go down to a temperature level of about minus 30 degree centigrade, for the first rectosol washing, then to go up with temperature again and to bring in the steam for shift conversion which means that you need a cooler-saturizer system which is fairly elaborate, and then after shift conversion go again down to about minus 60 degree for CO_2 removal, second step of the rectisol washing unit.

Q. Was your decision to choose your route influenced by the fact that you are producing methanol, too?

BUTZERT: Exactly what I wanted to say because the methanol contact is on the copper basis so you must not have any H_2S in this synthesis gas, and since you have to have a mixture containing between 20% and 30% carbon monoxide and the remaining hydrogen, you have to have two trains, one from the H_2S removal unit and one from the carbon dioxide removal unit. And so you have to put the high temperature CO-shift conversion between those rectisol units. And that answers also the question about the design of the gasification type.

APPL, BASF, Germany: And the final question is soot recycle. You are feeding your soot to your power plant. Have you never tried or thought about a recycle within the plant as we actually do in our Texaco plant?

BUTZERT: Yes, now presently we make pellets which contain about 20% of carbon and the remaining is 10% water and 70% oil. But we are now going to make some experiments in recycling since we are planning to build our plant on the northern seacoast with about 50% soot recycle.

APPL, BASF, Germany: In our Texaco gasification—just to explain to the gentlemen here who are not so familiar with that system—we recycle the soot in the following way: We make water scrubbing, and after water scrubbing we extract the soot from water with naphtha. The naphtha containing the soot is separated from the water layer, and the clear water is fed back again to the process. The soot-naphtha is mixed with fresh oil and fed to a distillation column where the naphtha is recovered and the soot oil mixture from the bottom of the column is then used for gasification in the gas generator again. This system works perfectly, nowhere any accumulation of soot. We have practially 100% soot recycle with no problems and have operated this way since more than seven years.

Q. In the design of the plant, was any thought given to pumping liquid oxygen up to pressure then vaporizing, rather than vaporizing first then compressing?

BUTZERT: Yes, in the beginning we were afraid of utilizing the turbo compressor with a discharge pressure of 67 bars, and so we calculated that alternatively, but it showed out that it wouldn't be economical. And so we went for the route to vaporize the oxygen and bring it to the turbo compressor.

Q. Can you tell us something about your experience with the refractory lining of the reactor, especially from the ash of the fuel line that you use?

BUTZERT: Yes, our fuel oil contains about 150 ppm vanadium, 60-80 ppm nickel and about the same amount of iron. In former refractory linings which consisted of silimanite, there was a really extensive slag building. We installed a 99.5% alumina refractory lining and it has proven that there is almost no slag been built.

Q. Could you give us your opinion on the relative capital costs in your plant, your feeding vaccum resid to make ammonia, in comparison with a gas based conventional plant?

BUTZERT: Well, in West Germany there are different conditions than here in the U.S. and I want rely on the remark of Dr. Appl last afternoon that in Germany there is the trend to bring some premium for utilizing high sulfur containing oil. So you have to make the calculation from a different point of view. And so I would prefer not to answer directly to your question.

APPL, BASF, Germany: May I answer your question relating to the investment. We personally feel that investment for partial oxidation plant, properly designed with one or two generators, is about 40% higher than a normal gas steam reforming plant. The energy consumption in terms of btus, is 20% higher than for a gas reforming plant.

I guess that will answer your question. The difference in price necessary between gas and oil feed, should be somewhat more than about 30 dollars per short ton, in order to overcome those differences. Depends a little on your philosophy with return of investment and depreciation.