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THE PROCESS

This section describes the progress and control of the main flow through the equipment, and discusses the methods which operators may use to obtain desired changes in functioning of the unit. Also, there are subsections which describe some of the auxiliary systems and special instrumentation.

It is recommended that the preceding Introduction be studied before reading this or the following sections.

A. PROCESS FLOW

The piping diagrams, the plot plan, and furnace, vessel and special data are in the Appendix. Many of the details given on the drawings are of prime importance and should be studied in conjunction with this subsection of the manual, so as to be informed concerning drains, blinds, bypasses, relief valves, instrumentation (especially the location of the detector elements), stand-by pumps, strainers, vessel internals, utility and auxiliary tie-ins, etc.

These descriptions are brief and will delineate the principal streams only. The Anticipated Operating Conditions and the process flow sheet show the temperatures, pressures, rates, etc., expected at key points in the process.

1. Feed Gas Desulfurizing and Oil-Removal

Natural gas, of the composition indicated in the Material Balance tabulation, will be supplied at the battery limit at sufficient pressure to let-down to 200 psig at KO drum 140-F. The gas is expected to have less than 2 grains of total sulphur per 100 scf (standard cubic feet). Of this, about 0.2 grain per 100 scf will be H₂S and the remainder will be mercaptan sulphur. The feed gas will be saturated with a hydrocarbon oil having a distillation range of about 300 - 470°F.

The flow is from battery limit through line NG-100-6 to PRCV-101 (control valve of PRCa-101) which maintains pressure on the feed gas KO drum 140-F. The flow is metered by FRa-101. Thence through NG-101-6, NG-102-3 and FRRCa-101 (ratio controller actuated by the superheated steam flow to the reformer) to treaters 102-D and 103-D. (Gas for the engine drivers of the compressors and for furnace fuel is taken off through FG-101-4 and FG-102-3, respectively).

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Each treater has two packed zones: (1) a hydrocarbon oil removal zone, and (2) a desulfurization zone. Between beds is a pan and chimney assembly for the purpose of collecting oily condensate and water during steam regeneration. The upper or hydrocarbon oil-removal zone is a 10 ft. layer of granular carbon made from selected carbonaceous raw materials. The lower desulfurization zone is a 10 ft. layer of carbon impregnated with metal oxides. The vessels may be operated in parallel, series, or singly.

The natural gas charge is fed to the upper carbon bed. As the gas passes through the bed, the heavy hydrocarbon constituents are adsorbed. A condition is finally reached where the bed is saturated with heavy hydrocarbon. The vessel is then taken out of service and the carbon is regenerated with superheated steam for a period of 8-16 hours. An overhead condenser, 137-C, and oil separator, 149-F are used during the regeneration procedure (vessel isolated from the process).

Following removal of heavy hydrocarbon components, the feed gas flows to the lower (desulfurization) zone where it is treated for removal of mercaptan sulfur and H_2S . The amount of total sulfur leaving this section is expected to be less than 1 ppm. Regeneration of the desulfurization bed is accomplished by steaming at substantially atmospheric pressure for a period of 8-16 hours after the bed reaches 300°F.

As indicated above, the design of the hydrocarbon-oil and sulfur removal system is based on the use of two vessels, each of which is capable of handling the design amounts of heavy hydrocarbon and sulfur in the feed gas. The design of the piping system, however, permits the vessels to operate in series. The second vessel in the series arrangement serves as a guard. As soon as the packed beds of the first become saturated with heavy hydrocarbons and/or sulfur, the feed gas is switched to the second vessel to permit regeneration of the bed (or beds) in the first vessel. After regeneration, the cycle outlined above is repeated except that the second vessel is placed upstream and the freshly regenerated one serves as the guard. The pressure differentials across the beds may be read during operation or regeneration by use of PdI-101 and/or PdI-102.

2. Raw Synthesis Gas Manufacture

Gas from the treaters flows through NG-111-4 to KO drum 127-F, to the feed gas compressors 108-Ja and 108-Jb (parallel machines each with capacity of 55% of design flow), to an oil separator, through NG-115-3 to the gas preheat coil in the convection section of reformer furnace 101-B. The compressors boost the gas sufficiently to move it on through the synthesis gas formation and purification sections to the syngas compressors. Line NG-112-4 is connected at the compressor suction, to provide gas whenever needed to pressure the shifter effluent and gas purification systems.

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Start-up air (via A-701-3) or saturated 350 psi. steam (HS-110-3) can be put through the gas preheat coil. Line NG-116-3 carries the preheated gas to the junction with SS-110-6 which feeds superheated steam (from another convection coil) through FRCa-101 into the gas stream. The feed-gas ratio - controller FRRCa-101 (reset by steam meter signal) is adjusted so that it maintains a steam/carbon ratio of about 3.9 to 1.0.

The steam-gas mixture is distributed to vertical tubes suspended in the radiant section of the furnace. The stream passes downflow through nickel catalyst with which the tubes are filled. There are four rows, 28 each, totalling 112 parallel catalyst tubes.

The furnace is down-fired with natural gas and purge/flash gas. There are five rows of burners, nine burners in each row. Fuel gas to the burners is regulated by manual pneumatic remote controls MIC-107 through 111. These MIC's will be adjusted by the operator to yield the desired temperature on the combined outlet of process gas and to give balanced combustion conditions within the firebox.

The purge/flash gas in the fuel comes from the synthesis section. This gas is expected to supply about 15% of the fuel for the reformer furnace.

Anticipated temperature to be developed at the outlet of the catalyst tubes at design conditions is 1477°F (TI 1-1, TR 1-1 and TA-101). At these conditions the combined outlet gas is expected to contain about 6.0% unconverted methane on a dry gas basis. The pressure at the outlet of the catalyst tubes is expected to be 220 psig.

The partially reformed gas flows to the inlet of the refractory lined secondary reformer 102-B. A cooled sampling connection is provided on the transfer line to permit laboratory analysis of the effluent gas from the primary reformer

The stream enters the top of the secondary reformer where sufficient air is mixed with the gas to provide the nitrogen required for the ammonia synthesis. The gas, steam and air pass downward through a bed of nickel catalyst. The heat liberated by combustion of part of the gas elevates the temperature to about 1713°F and supplies the energy to complete the reforming and reduce the methane content to approximately 0.2 percent on a dry gas basis.

While the temperature level of the secondary reformer is primarily controlled by the outlet temperature of the primary reformer, and sufficient steam is normally present for the reaction, provision is made for the injection of steam to provide flexibility in operation.

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The combustion air for the secondary reformer is provided by the three-stage, engine-driven compressors 112-Ja and 112-Jb. The machines, their auxiliaries and regulation, are more completely discussed under "Special Equipment" in Section II of this manual. The compressors also serve to supply air to the reformer furnace at startup (for heating catalyst) and to the shift converter when oxidization of the iron catalyst is required, which would only be during a shutdown. The air inlet to line HS-117-3 at the shift converter is kept blinded except when in use.

Air flow to the secondary reformer is metered and regulated by FRCa-102. Excess air from the compressor is released by PICa-101 through the silencer 104-L.

Temperature in the catalyst beds of the secondary reformer are indicated by TI 1-2, TI 1-37 and TI 1-3. These thermowells are located above the bed, in the middle and in the bottom of the bed. The top and bottom impulses are also recorded and provided with high-temperature alarms. Thermowells in this severe service (on 101-B, 102-B and the outlet of the quench drum 102-F) are purged with instrument air to reduce thermocouple deterioration.

Reformed gas effluent leaves the bottom of secondary reformer catalyst bed and immediately enters the quench drum 102-F. The quench drum actually is the bottom part of the secondary reformer but is separately identified for convenience. It is a chamber lined with insulating concrete and provided with water sprays. The sprays cool the gas to 1140°F and simultaneously provide part of the steam required for the reaction with carbon monoxide in the subsequent shift conversion. Flow of water to the sprays is regulated by the temperature controller TRCa-101 for a constant temperature of 1140°F at the process gas inlet to the waste heat boiler 101-C. A continual flow of steam is maintained through the annular space around the spray nozzles for the purpose of protecting the nozzles from the hot gases.

From the quench chamber, the gas flows to the waste heat boiler 101-C where 350 psig saturated steam is generated, while cooling the gas to 750°F. Butterfly valves "A" and "B", operated in opposite directions by TRCa-102, bypass gas at this boiler to regulate the downstream temperature. Valve "A" can be placed on manual remote control by use of MIC-118. A cooled sample point is tapped off the raw synthesis gas line leading to the shift converter 104-D, so that analyses can be made, for comparison with primary outlet.

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A two-inch steam line is provided to permit the addition of more steam if required for the CO-shift, and a four-inch vent to atmosphere is provided for use at startup. The six-inch vent on the shift converter inlet line is for use when oxidizing catalyst in that vessel.

The gas-steam mixture, at 750°F, enters the top of the shift converter. This vessel contains four beds of iron oxide catalyst, each supported on a screen-covered grate, and has three sections: (1) a primary section consisting of two catalyst beds: the first a shallow bed 2' 0" deep, and the other 6' 9" deep; (2) a quench section consisting of a chamber and spray ring which serves to quench the gas effluent from the primary section; and (3) a secondary section consisting of two catalyst beds: the first 8' 9" deep and the second 10' 0" deep. The first bed in the primary section is made shallow in order to minimize replacement costs in the event that it is necessary to remove the top bed because of plugging, damage to catalyst due to mal-operation, catalyst deterioration, or such.

The gas flows downward through the first two catalyst beds of the shift converter. In passage through these beds, the heat of reaction causes the gas temperature to rise to an anticipated 830°F as the CO content of the dry gas is reduced from about 12.0% to a level of 2.1%.

Shifted gas from the primary catalyst section enters the quench section through a centrally located standpipe. In the quench chamber the effluent is cooled by vaporized water and reduces the gas temperature from 830°F to 670-700°F.

After quenching, the shifted gas from the primary catalyst section enters the two-bed secondary catalyst section. In this section the 2.1% CO content of the gas stream is reduced to a level in the order of 1%. This slight conversion results in very little heat of reaction.

A pressure differential indicator, PdI-105, is provided to indicate the pressure drop through the entire shift converter; or, by suitable manipulation of the valving, the pressure drop across the top bed can be determined. Temperature control of the gas leaving the quench chamber is effected by TRCa-103 which throttles the process water to the sprays in the quench chamber. Sample taps permit gas samples to be taken at the outlet of the quench section and after the first bed of the secondary section. Steam distributors are provided in both primary and secondary catalyst sections for use at shutdowns, as will be discussed later.

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Following the two-stage shifting step, the hot gases at 670-700°F are used to: (1) preheat methanator feed inlet gases and (2) provide all the reboiling heat required for the CO₂ removal system. Shift converter effluent, approximately 47% steam and 53% dry gas, flows to the methanator feed heater 103-C in which the effluent is cooled to 615°F in supplying the heat required for preheating the methanator feed stream to 500°F. After this step, process water is sprayed into the line through four sprays to cool the gas stream to its dew point. The water rate is controlled from MIC-101 with the quench water rate indicated on the same instrument. The gas stream temperature attained is recorded on the TR 2-4 and has TA-102 (high)

At a dew point temperature of 334°F, the gas-steam mixture flows through the CO₂ stripper reboiler 102-C. Condensation of steam from the mixture provides all the heat required for reboiling in the CO₂ stripper. From the reboiler, the vapor-liquid stream at 262°F enters the separator drum 106-F for disengagement of liquid from vapor. Hot condensate accumulated in the separator supplies the quench water for the secondary reformer effluent; the shift converter and the shift effluent circuit as described above. It is pumped by the quench pump 102-J, or its spare 102-Ja. In the event of failure of these pumps, signaled by a low flow alarm, a solenoid is actuated to inject boiler feed water as emergency water.

The disengaged vapors leave the shift effluent separator and pass through fan-cooled 129-C where they are dropped to 130°F, condensing most of the remaining water vapor in the stream. This water is removed from the gas in another separator drum, 107-F. The condensate from this vessel and the excess condensate from the first vapor-liquid disengagement are released to the battery limit under level control. Make-up water to the cooling water jacket on the secondary reformer is supplied from this line, also water for caustic mix tank, MEA solution preparation and stripper MEA dilution. A four-inch vent valve is provided to release raw gas from 107-F to atmosphere during start-ups, and to permit operation of the reforming section in the event of difficulty with the purification section.

3. Raw Synthesis Gas Purification

In the purification equipment raw synthesis gas at about 185psig and 130°F is processed for removal of carbon dioxide and carbon monoxide to yield a hydrogen-nitrogen synthesis gas of very high purity (less than 10 ppm of CO plus CO₂). The bulk of the carbon dioxide is removed by absorption using a 20 wt. % aqueous solution of MEA.

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Gas from the raw gas separator 107-F enters the bottom of the CO₂ absorber 101-E. Lean MEA solution, pumped from the CO₂ stripper by pump 103-J, or its spare 103-Ja (turbine driven), is fed to the top tray of the absorber and flows down through the twenty-one trays counter-current to the upflowing gas. The tower will be operated with the MEA level above the gas inlet, controlling the liquid release from the bottom by a signal proportional to the tower differential pressure (affected by the liquid level). Thus LICa-101 functions as a level controller although it actually measures the differential pressure across the tower.

Rich MEA (i. e., carrying the absorbed CO₂) leaving the bottom of the absorber is heated by stripper bottoms in heat exchanger 106-C. This exchanger is composed of two shells arranged in series. The absorber level controller throttles the rich MEA after the heat exchange in the 106-C bundles in order to minimize the gas release in the exchangers. The hot rich MEA then flows to the top of a 25-tray stripping column operating at 7 psig. Reboiler heat is provided by the quenched gas-steam mixture from the shift converter, as described earlier. Carbon dioxide stripped from the MEA passes off overhead through fan-cooled condenser 131-C where water and a little MEA are condensed and accumulate in the CO₂ stripper reflux drum 108-F. The CO₂ escapes through an unvalved atmospheric vent.

Condensate accumulating in the reflux drum is returned to the stripper tower by the reflux pump 104-J (standby 104-Ja) which operates to maintain a constant level in the reflux drum, regulated by LC-104.

There is a tendency for MEA solution to deteriorate with the formation of salts which may result in operational problems such as foaming. In order to eliminate contaminants of this nature and keep the solution reasonably pure, redistillation equipment has been included in the design. A side-stream of MEA will be taken continuously to a steam-heated kettle-type reboiler, 108-C, called the vaporizer. The MEA is vaporized continuously while the input is restricted by the level controller LC-103, thus concentrating the contaminants in the reboiler kettle. Periodically, these contaminants are manually discharged to waste, after neutralizing in the reboiler with caustic delivered by 114-J from caustic tank 138-F.

In addition, a side-stream filter is provided as an accessory to the MEA return line to the stripper. The primary function of this filter is to aid in removal of contaminants which contribute to foaming. It removes solids, degradation products, sludge and other impurities from the system.

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Regenerated MEA solution from the bottom of the stripper passes through the exchanger to the suction of the circulating pump 103-J, or its spare 103-Ja. These pumps return the lean MEA to the top of the absorber via the two-shell cooler 105-C, where the solution is cooled to about 110°F. This completes the MEA circuit. Makeup solution is occasionally pumped from the MEA storage tank 109-F by the pump 105-J, or, more often, condensate is required to replace the water removed in the CO₂. When condensate is required, it is accumulated in the MEA drip sump, from which it can be pumped to the MEA system. Or it may be added to stripper reboiler vapor directly.

Process gas, from which essentially all of the CO₂ will have been removed, passes overhead from the absorber to the knockout drum 129-F. This drum is provided with a demisting pad designed to remove any entrained moisture, which will accumulate in the drum and will be drained to the MEA sump periodically. The drum is provided with a gauge glass and a high warning alarm, LA-110.

The process gas flows to the methanation system from the KO drum. Analyzer-recorder AR-101 monitors the CO₂ content of the gas stream and will be arranged to sound an alarm if the CO₂ content should exceed a pre-set maximum value.

Prior to methanation the gas must be heated to the temperature required for the methanator reaction, 500°F. This is accomplished by heat exchange against methanator effluent in exchanger 126-C followed by exchange against hot shift converter effluent in exchanger 103-C. In the first preheat step, the gas is heated to approximately 350°F by cooling methanator effluent from 625°F to 380°F. In the second step, the gas is heated to 500°F by cooling shift effluent from 670°F to 615°F. Temperature regulation is accomplished by diverting cold process gas around the exchangers through line SG-152-3 under regulation of TRCa-104, which will be set to maintain 500°F at the methanator inlet.

The 500°F process gas enters the methanator 106-D, a vessel containing two beds of a high nickel-base catalyst in 1/4" tablet form. This catalyst is used to induce reaction of CO and CO₂ with hydrogen to form methane and water, accompanied by the evolution of heat. With the inlet temperature at 500°F and a residual CO content of 0.9% in the shift converter effluent, the outlet temperature will be about 625°F; for 1.2% CO content, the anticipated methanator outlet temperature is 700°F.

From the foregoing it is clear that the outlet temperature of the methanator is very sensitive to the quantity of carbon oxides in the gas. Provision is made for injection of cold gas between the beds (manually, using MIC-102) as an aid in temperature control. In addition, if the top or bottom bed

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temperature rises to a pre-set maximum value, the TRA 3-1 or TRA 3-2 will actuate the solenoids VS-101 or VS-106, venting the air signal to the methanator inlet valves, thus causing them to close. Pressure in the line SG-111-10" will rise, of course, when the inlet valves to the methanator close; PIC-105 will release the excess pressure to atmosphere. Alternatively, the methanator inlet valves may be closed by the operator from the main board by use of the pushbutton.

In addition to conversion of residual CO, the methanator serves to convert trace amounts of residual CO₂ to methane and water. It is expected that the total amount of carbon oxides leaving the methanator will be less than 10 ppm.

Connections have been provided at the bottom of the methanator for either flushing out with nitrogen, or for oxidizing the catalyst with air and steam.

4. Compression of Purified Synthesis Gas and Ammonia Synthesis

Purified gas flowing from the methanator is cooled to 380-460°F in passage through the methanator feed/effluent exchanger 126-C and to 100°F in passage through the synthesis gas cooler 127-C. The gas arrives in the synthesis gas compressor suction drum 111-F at about 140 psig pressure. Some of the water formed in the methanation reaction is condensed in the cooling step and accumulates in 111-F, from which it is discharged to blowdown under control of LC-106. This level controller is equipped to sound a high level alarm; a higher float chamber actuates another level alarm, LA-112, and simultaneously shuts down the synthesis gas compressors. A demister pad is provided in the top of the drum to coalesce and knock back any entrained moisture.

The purified gas entering the compressors will be composed of hydrogen and nitrogen in approximately a 3:1 ratio, by volume, and an inert fraction amounting to about 1.7% vol. percent argon, helium and methane. AR-102 is an infra-red analyzer, and records the combined carbon oxides in the gas stream. AR-103 is a thermal conductivity instrument and records the content of hydrogen in the fresh synthesis gas stream, or the converter feed (using a selector switch).

Suction drum 111-F is provided with an automatic release to atmosphere, PRCa-102"B". In normal operation PRCa-102 (split range) controls the pressure on the suction drum by opening or closing PRCV-102"A" in the compressor kickback. However, if the "A" valve is completely closed and 111-F pressure still rises, then PRCV-102"B" opens sufficiently to regulate drum pressure.

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Synthesis gas flows from the suction drum to parallel compressors 109-Ja and 109-Jb. Gas compressed in the first stage cylinder of 109-Ja is cooled to 100°F in the 111-Ca cooler, and enters the first stage discharge drum 112-F from which condensed moisture is ejected. Passing into the second and third stages, it is similarly compressed and cooled, and moisture is removed. The fourth stage discharges through a cooler, joins the parallel stream from 109-Jb, and the combined flow is routed to the ammonia converter at a pressure of about 4700 psig. It joins the synthesis loop at a point where recycle gas is discharged from compressors 110-Ja and Jb.

A block valve between the fourth stage discharge of the syngas compressors and the loop serves to isolate this discharge header from the synthesis system. A silencer is provided in line SG-137A-3 (just upstream of the block valve) to permit discharging gas to atmosphere in the event of difficulty with either the purification system or with the synthesis loop.

The combined fresh and recycle synthesis gas flows through an oil trap 121-F, which is a high pressure vessel with a packed section and having a demisting pad. Any CO₂ in the syngas will form ammonium carbamate and collect as a dust or a cake in the oil trap. Oil and carbamate will be withdrawn periodically through the drain provided, but over a period of time a pressure drop will develop (as indicated by using PI-136) requiring that the synthesis section be stopped for cleaning of this trap.

The ammonia concentration of 6.5 per cent in the recycle gas becomes 5.0 percent when the recycle and fresh syngas are combined. This stream, from the oil trap, is passed through the ammonia-refrigerated chiller 115-C to the secondary separator 122-F where liquid ammonia drops out of the stream at 25°F and is delivered via LC-108 and letdown 133 F to the battery limit. This ammonia removes with it the water of saturation carried by the fresh syngas portion of the flow. This is an essential purifying function for the ammonia synthesis feed since all oxygen compounds, including water vapor, are deleterious to the synthesis catalyst. The gas from the secondary separator, with its ammonia content reduced to about 3.0 percent, is heat exchanged against converter effluent for recovery of refrigeration; it then passes to the inlet of the synthesis converter 105-D.

The synthesis converter consists of a high pressure shell containing a catalyst section and a heat exchanger 116-C. The catalyst section is a cylindrical basket which fits inside the vessel, leaving an annulus between the shell and the basket. There are five catalyst beds, each

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supported on a screen-covered grid. In order to maintain all the catalyst at optimum temperature for maximum yield, provision is made to inject cold feed gas (via MIC's 113 to 117) as quench in the spaces between the beds. Approximately 138 cubic feet of catalyst is contained in the converter. The catalyst zones are arranged so that the top bed contains the smallest quantity of catalyst, to limit the temperature rise before the first quench point. Since the temperature gradient is flatter in succeeding zones, the bed sizes are graduated with the largest at the bottom. Located beneath the catalyst section is the heat exchanger to preheat fresh inlet gas against hot reacted gas from the last catalyst bed.

The normal point of entry for the feed is at the top of the converter, via MICV-105. The gas flows downward between the pressure shell and the wall of the catalyst section; it serves as a cooling medium for the shell and is thus preheated prior to entering the exchanger. The stream enters the exchanger at the bottom of the converter and is preheated against hot effluent by circulating upward around exchanger tubes; thence through a central tube to the top.

For temperature control of the top bed, a portion of the cold feed gas may be introduced to the top directly (by-passing the exchanger). The combined stream flows downward through the catalyst with a rapid temperature rise as the ammonia reaction proceeds. The stream passes through a grid supporting the catalyst, into a space between the bottom of the first and top of the second bed. At this point, the temperature may be reduced and the ammonia content diluted by the injection of some cold feed gas. This quenching arrangement permits control throughout the catalyst beds to obtain optimum temperature for maximum yields. In like manner, the gas flows downward through the other four beds.

In the presence of the iron oxide catalyst, a portion of the hydrogen and nitrogen combines at a temperature of approximately 900°F and a pressure of 4,500-4,600 psig to yield ammonia in a concentration of about 16 percent in the effluent from the last catalyst bed. The hot effluent passes downward through the exchanger (in the converter bottom) giving up heat to the up-flowing fresh feed. From the exchanger, the reacted gas leaves the bottom of the converter at 410°F. It passes through an air cooler and a water cooler, then is cooled to 69°F by exchange against converter feed in 119-C. A major portion of the ammonia liquefies and is removed from the gas in primary separator 123-F. The separated gas, containing 6.5 percent ammonia, passes to the suction of the recirculating compressors for recycle back to the converter.

A portion of this gas is vented as continuous purge to the fuel system to keep the concentration of methane, argon and other inert gases at a low level. These components would otherwise build up in the system, reducing the effective synthesis gas partial pressure and causing lower conversion per pass and lower production capacity. Prior to delivering to the fuel system, the purge gas is chilled in 125-C to 25°F for condensation of ammonia, which joins the primary liquid product.

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Primary liquid product at 69°F and about 4,500 psig is released by LC-109 to approximately 225 psig and flows to chiller 135-C where the temperature is reduced to 37°F. Following combination with liquid ammonia recovered from the purge gas chiller, the stream is delivered to the primary product let-down drum 141-F, regulated by PIC-107. Liquid is delivered by LC-112 to the battery limit. Disengaged let-down gas, after a chilling step to recover small amounts of ammonia, is released to the fuel gas system, along with flashed gas from the secondary letdown 133-F (regulated by PIC-106).

The furnace 103-B is used to heat the converter when activating the catalyst. Also, it is used for heating the gas during startup, to temperatures that will raise the catalyst to a point where the exothermic reaction will begin and become self-sustaining.

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B. AUXILIARY FLOWS

Supplemental systems are required in the unit as adjuncts of the main operation, or to assure proper functioning of the equipment and the process. Below are brief descriptions of some special accessory services; these systems, as well as the usual auxiliaries and utilities, are shown on drawings 63-D1, 63-D2, and 64-D1 through 64-D4, in the Appendix.

1. High Pressure Steam Generation and Distribution

Steam at 350 psig will be available at the battery limit for start-up, make-up and emergency, but normally all the steam required for process within the unit is expected to be produced at the steam drum 101-F as a product of heat recovery from reformer and quench boiler. Steam imported or exported is metered by FR-110. Steam produced from the steam drum is metered by FR-105, which also carries a pressure record. Steam is exported by PC-105, holding pressure in the unit for use as follows.

- a. To satisfy process requirement, chiefly steam to the primary reformer via superheater and FRCa-102 and to 102-F quench sprays via FI-121; also to desulphurizers and oil absorbers for regeneration, to the line between the secondary reformer and the shift converter to provide adjustment of the steam/gas ratio if required, and to the shift converter for operation and regeneration. A superheated steam connection is provided to the desulfurizers.
- b. To MEA vaporizer, and to the fire steam system via PC-103.
- c. To 101-B furnace stack eductor for emergency draft, to the purge eductor at the synthesis section, and through restriction orifices to the stems of the butterflies controlled by TRC-102 on the shifter inlet line.
- d. To the turbine drives. Laterals to the drives are provided with separators.

Treated boiler feed water storage is maintained in tank 147-F (via LC-114) which has LA-125. Condensate from the exhaust condenser and from traps is received in this tank.

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The BFW pumps, 106-J and standby 106-Ja, take suction on this storage and discharge to the steam drum via LC-115 and the preheat coil in the convection section of the reformer. There is a cross-connection between this discharge and the discharge of the circulating pumps, 101-J and Ja, on the steam generation system, also a minimum flow line (with RO) back to the BFW tank. During startup the combustor jacket is supplied from this system; also the quench system is fed if the normal supply of effluent condensate should fail (actuating an alarm and a solenoid valve which operates V-102 in the alternate supply line).

2. Exhaust Steam

The turbine drives exhaust into header ES-101-6. Steam in this line is released as condensate (by PIC-103 holding about 15 psig) through 136-C to the BFW storage 147-F. If pressure tends to drop in this header (no turbines in use, or need for condensate) then PCV-101 feeds in from the fire steam system.

3. Fire Steam

This system has a relief valve and is maintained at about 125 psig by PC-103. It feeds heating coils in MEA tank 109-F, relief valve stack snuffers, space heaters, steam hoses, compressor building snuffers, exhaust system make-up, and snuffing for fireboxes of 101B and 103-B.

4. Refrigeration

An ammonia refrigeration system is provided to serve the chillers in the synthesis section. Ammonia vapors from 115-C low temperature condenser, 121-C primary ammonia flash gas cooler, 135-C primary chiller and from the purge gas cooler 125-C are collected in the refrigerant KO drum 125-F at about 20 psig and 5° F. Compression of these vapors is accomplished by two 55% capacity, single stage, double acting refrigeration compressors operating in parallel. The compressor discharge passes through a separator for oil removal, then is condensed by cooling water in the refrigerant condenser 123-C. The liquid refrigerant is collected in the refrigerant receiver 124-F, from which it flows to the chillers named above. The refrigerant receiver will operate at about 210 psig pressure and 100° F; PIC-108 provides control for the system by recycle of high pressure vapors from the receiver back to the suction drum. In addition a by-pass inside the block valves permits starting or idling each compressor unloaded, and clearance pockets are provided to permit operation at normal and at 90% of normal rates.

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Level alarm and a high level shutdown are provided on the refrigerant flash drum 125-F to protect the compressors; and level controllers are provided on the chillers to provide regulation of the refrigerant to these items.

5. Compressor Cooling Water

A branch, W-188-10, runs from the cool water main, W-100-16, after the main enters the unit at the east battery limit. The branch is equipped with a twin strainer, SP-104, and lies north of the compressor house. Each multi-service compressor has a six-inch and two four-inch laterals, from the eight-inch line. The flow from one lateral is warmed by use in the two turbo-coolers of the engine air supercharger, then is used for cooling the jackets of the syngas cylinders. The other stream is warmed in the engine lube oil cooler, then used in the cylinder jackets of the refrigeration, air and feed gas compressor sections, and in the compressor lube oil cooler.

6. Engine Cooling Water

The supply tank (150-F) for this system is south of the compressor house, and the circuit is as follows. Fill through JW-135-4 to pump 107-J or Ja; thence to twin butterfly valves controlling the split flow (to fan-cooled 110-C and to its bypass). The valves are actuated by a signal to valve "A" (flow to cooler) from THIC-101, which regulates temperature to the engine jackets. Mechanical linkage moves valve "B", in the cooler bypass, when valve "A" moves. A six-inch line runs to the two jacket inlets of each engine, an eight-inch runs from the single outlet to a disengaging pot with vent, overflow, gage glass, drain and condensate make-up line. Eight-inch return lines join and run back (10") to the pumps (circuit complete). There is a recirculating line to the tank from the cooler outlet, and drain lines from the engine inlets back to the tank.

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C. PROCESS PRINCIPLES

This part of the manual outlines the basic reactions, the operating techniques and the effects of changes in conditions, so that the operator may see the various means at his disposal for obtaining efficient operation. Also, the standard discussion on Overpressure Protection at the end of this subsection (insofar as it applies) should be studied.

The process flow sheet (see Appendix) shows the basic design conditions of temperature, pressure, and stream quantities and qualities which have been used to establish the process and determine the sizes and duties of the equipment involved in the operation. These design data, in conjunction with the Anticipated Operating Conditions (Appendix) give an approximation of the values to use at key control points; but it is not expected that these exact conditions will be maintained. The design is reasonably flexible, to permit some adjustment in conditions as experience may dictate.

1. Feed Gas Treaters

The reformer catalyst would be poisoned if exposed to sulfur compounds in the feed gas; also, the gas is saturated with hydrocarbon oil. The feed gas treaters 102-D and 103-D are designed to remove these contaminants, the oil first.

a. Temperature

The treaters operate most efficiently with inlet gas at 60-105°F. It is desirable that the gas be delivered to the unit in that temperature range.

b. Service Period

The treater which is first in line will be operated until one of its beds shows a significant increase in contaminant content, at which time the other treater will take the incoming gas while the spent treater is being regenerated. Or the treaters may be put on a regular regeneration schedule after their capacity is determined in actual operation. It is anticipated that the service period of the hydrocarbon and the sulfur adsorbents will be a week to ten days when operating at design feed rate and analysis.

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c. Inspection of Adsorber Effluents

It is essential that the oil adsorbers (top sections of treaters 102-D and 103-D) be functioning properly. Heavy hydrocarbons would be undesirable in the reformer feed; furthermore, they can impair the efficiency of the activated carbon (desulfurizing material) in the bottoms of the treaters.

Gas samples should be taken frequently (once per shift) during early operations to check for presence of heavier hydrocarbons in the stream at the bottom of the oil adsorber bed. If the analysis begins to show incomplete oil removal, the treater should be taken out of service for regeneration. It is likely that experience will develop a satisfactory operating cycle which will always assure regeneration before the adsorbent is spent, as long as the feed gas is of design, uniform oil content. Also, the sampling schedule can then be made less stringent.

It may prove advisable to regenerate both beds in a treater at the same time, setting the schedule in accordance with the cycle required for the bed which has the shorter service life. However, if sulfur in the feed gas is very low, it frequently will be advantageous to regenerate only the top sections of the treaters.

In like manner the efficacy of the desulfurizing (lower) bed should be checked frequently during early operations, so that the safe service life may be determined and the regeneration frequency established. Sulfur in very minute concentrations (less than 1 ppm) must be observable by the method of testing which is used.

d. Regeneration

Care should be used in the regeneration procedure. The upper bed (oil adsorber) must be steamed sufficiently at about 3000 lbs. per hour to strip practically all oil from the carbon. Superheated steam is most effective in this operation because of its temperature; it is used upflow through the upper bed until there is no further evidence of heavy hydrocarbon removal; high pressure steam may then replace or supplement the superheated steam. Maximum total steam rates to be used in the treater are as follows: 4600 pph SS, or 7650 pph HS in upper bed; 3000 pph SS, or 5500 pph HS in lower bed. When appreciable amounts of SS are used, stay near the SS figures. Restriction orifices have been placed in the HS and SS line to the treaters, so that either flow, alone, will be kept below a rate which might

disturb the beds. Total steam rate can be determined by using FI-118 and FI-119 meters. When near-maximum rates are used (especially after all oil has been removed) the overhead condenser 137-C may become overloaded and large quantities of condensate may accumulate in the overhead separator 149-F, drained by LC-117. During the latter part of the regeneration and steaming period (when little or no oil shows in the separator), the steam may be vented to atmosphere at the treater top. To diminish velocity through the bed, 20 psig pressure must be maintained on the treater during regeneration.

Oily condensate which collects on the pan between the beds must be removed at such a rate that it cannot accumulate and spill into the lower (desulfurizer) bed.

If both sections of the treater are regenerated at the same time, some SS may be used (along with the HS) in the bottom, to keep the stream entering the upper bed at a more elevated temperature. The condensate should be removed from the bottom of the vessel, so that a level of water does not accumulate there.

The condensate formed in, and draining from, the desulfurizer catalyst during regeneration is acidic; facilities have been provided so that refrigeration compressor discharge gas can be metered and injected with the steam during regeneration, to neutralize the condensate. It is anticipated that about 63 pph of ammonia will be required. The pH of condensate should be kept at 7.0 to 7.5.

After regeneration, the treater may be pressured carefully, by introduction of gas through the normal inlet. After pressuring, the vessel should be cooled by putting a small gas flow through it in parallel with the operating treater, while keeping condensate drained. When cool, put the regenerated treater in the second (tail) position.

2. Primary Reformer

After the harmful constituents have been removed, it is desired to pyrolyze the feed gas under conditions which will produce hydrogen in a very economical manner. The following discussion outlines the factors which affect operation, and which therefore should be observed and controlled properly.

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a. Catalyst

The primary reformer catalyst is in the form of 3/4" x 3/4" hollow cylinders which must have uniform loading in the tubes (see Sect. II) so as to assure essentially the same flow rate through each of the 112 tubes. If a tube has abnormal pressure differential, overheating or insufficient reforming may occur there, thus giving improper operation.

Sulfur compounds in the natural gas stream will reduce catalyst activity, but this poisoning is temporary and normal activity may be recovered by stripping the catalyst with sulfur-free gas. The catalyst itself contains some sulfur as it is delivered from the manufacturer; this sulfur is removed during the early phases of unit start-up.

Reforming catalysts that have been activated or placed in operational use are in the reduced state and must not be exposed to oxidizing atmospheres at elevated temperatures except under carefully controlled conditions. During the shutdown of the reforming equipment the catalyst should be kept under a steam atmosphere until the temperature of the catalyst has been reduced to 600°F or less. If the secondary reformer is to be opened, or subjected to an air stream, the catalyst should be carefully oxidized before the steam is shut off. This operation is described under Shutdown Procedure, Section IV.

The catalyst is shipped in the non-pyrophoric, oxidized state. It is pre-shrunk at temperatures higher than those usually encountered in operation and shrinkage in service should be negligible. Wetting of new catalyst does not damage it; however, if water or wet steam should suddenly cool hot catalyst, breakage might occur.

b. Reforming Reactions

The catalysts promote two simultaneous equilibrium reactions in the primary and secondary reformers. These reactions are the steam-methane reaction (higher homologues react in like manner):



and the carbon monoxide shift reaction:



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It would be preferable if these reactions went to completion to give an overall reaction:



but this is not the case and considerable CO occurs in the combustor effluent. Most of this unshifted CO is oxidized to CO₂ in the shift converter, thus increasing hydrogen yield.

c. Reforming Conditions

Temperature - The overall effect of increasing reforming temperature on the effluent gas composition is to reduce the methane and carbon dioxide content, and increase carbon monoxide and hydrogen content. On decreasing reforming temperatures, the effects are reversed.

Pressure - The pressure of the system is so nearly fixed that reforming pressure should be considered invariable. However, increasing pressure has an effect similar to reducing temperatures and reformer designs always represent a compromise in economics.

Steam Rate - Beyond the vital consideration of sufficient steam to prevent coking the catalyst, increasing steam-to-gas ratio will shift both above equilibrium reactions to the right with a net effect of decreased methane and carbon monoxide and increased carbon dioxide and hydrogen in the reformed gas. At the same time, however, utilities consumption will increase. For other than minor deviations, the unit operation is usually most economical at conditions closely approaching design.

Whenever there is any doubt about the true steam-to-gas ratio entering the furnace, the steam rate should be adjusted upward to insure an excess rather than a deficiency until the true ratio can be ascertained.

Should an operating or mechanical accident cause minor coke deposition on the reforming catalyst, the deposit may be removed and the catalyst activity restored by increasing steam-to-gas ratio somewhat above normal for a period of time. If the catalyst coking is considerable, it may be necessary to regenerate the catalyst with steam and air, or to shut down the unit for replacement of the catalyst.

Feed Rate - When the feed gas rate (and companion steam rate) are reduced, the residence time in the catalyst tubes is lengthened, giving more reforming. The effect is similar to that obtained by raising the temperature. It is usually necessary to adjust temperature downward with a major reduction in feed gas rate.

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d. Furnace Operation

In order to obtain the tube outlet temperature required for the primary reforming, a furnace radiant section temperature of about 1775°F will probably be necessary. The firing must be carefully regulated to avoid "cold" banks of tubes and/or local overheating.

The hot flue gases pass down through the box and enter ducts at the floor level. These ducts serve to keep the hot flue gases in efficient contact with the catalyst tubes and to eliminate "dead" spots in the furnace. The draft which pulls the hot gases downward is induced by the reformer furnace fan 115-J, located at the base of the stack. The flue gases are drawn into the ducts and pass into the convection section at around 1750°F. Here heat is given up to the waste heat boiler, to the gas preheater and steam superheater, and to the boiler feed water preheater in the convection or transfer section between the firebox and the stack. The flue gases will leave the convection section at approximately 450°F. The draft is regulated by manual adjustment of the damper, to maintain 0.2 or 0.3 inches (water) draft within the firebox.

Occasional flue gas analyses should be taken; the furnace is designed for 25% excess air. A graph in the Appendix of this manual shows the percent excess air, when the percent CO₂, CO, and O₂ are known. An example of its use is given on the graph.

A steam jet in the stack is arranged to open automatically if power to the draft fan motor is cut off.

Observations of catalyst tube-skin temperatures should be made on a regular schedule, using an optical pyrometer. Hot or brightly-colored spots sometimes indicate voids in the catalyst column, or carbon deposits on the catalyst. The gas burners must be operated to avoid flame impingement on the tubes, as such maloperation would result in early tube failure. A little experience and experimentation will indicate the optimum draft and air register adjustment to provide stable flame patterns and good heat distribution throughout the height of the box.

3. Secondary Reformer

The partially reformed gas enters the 102-B (combustor) top tangentially around the centrally-located air inlet pipe. The swirl of the gas is augmented in passage through fixed blades of a mixer mounted around the air nozzle. Process air from the compressor is fed through the central nozzle, which is a bulbous end on the air pipe and is perforated

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with holes in the lower hemisphere of the bulb. This has the effect of intimately mixing the air and the swirling gas and distributing the heat of combustion over the entire surface of the catalyst bed. The effects of changes in conditions are the same as noted above for the primary reformer.

Maximum efficiency of the overall reforming operation requires that as much reforming as possible be done in this partial-combustion step. Utilization of combustion energy reduces the fuel gas requirement in the reforming furnace. However, the amount of air charged to the secondary reformer is set by the nitrogen requirement, and the degree of reforming will be regulated by variation of primary reformer temperatures, to a large extent.

A water jacket envelops the combustor in order to keep the metal temperatures low on the vessel if leaks develop in the internal lining. Water for the jacket is supplied from the quench system and is limited by a 1/4" restriction orifice.

Close control will be required on the ratio of hydrogen to nitrogen. If it gets very much out of line, difficulties will be encountered at the ammonia converter as will be discussed under the Converter heading below. The analyzer-recorder AR-103 is provided to keep a running check on the synthesis gas to the compressor, or to the gas being circulated through the synthesis loop. This instrument is normally a major reference for operation of the primary and secondary reformers.

Whenever the combustion air flow is altered, temperatures in the secondary reformer should be watched and compensating changes made as necessary. Increasing the air flow will raise the temperature and either a decreased firing rate in the reformer furnace or the addition of steam to the inlet of the secondary reformer should be used to compensate as conditions dictate. When conditions are at an optimum and a change in feed gas flow is necessary, a proportional change (in the same direction) of the air rate will be required to maintain the H_2/N_2 balance.

4. Quench Drum

The quencher is provided with four retractable, solid-cone water sprays served with process water from the quench water pump through a ring header. Each spray reaches into the quench drum through an open valve mounted

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in a surrounding pipe-case, and a packed gland. Steam is fed to the annulus between the spray pipe and the outer case for protection of the sprays. The spray nozzle may be withdrawn past the valve in the outer case; the valve may then be closed and the packing gland can be backed off. The bayonet and tip may then be withdrawn for inspection, and renewal if required.

Quench water at a design rate of about 27 gpm, regulated by TRC-101, is injected into the gas stream issuing from the bed above, to cool it to about 1140°F. This quench supplies a portion of the water required for the subsequent CO-shift reaction. Maximum allowable temperature of the quench outlet is 1200°F.

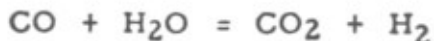
Should the instrument air fail, TRC-101 has been arranged to open (as the safer of the two alternatives) due to the reservoir capacity of the equipment. However, manual control of the quench chamber outlet temperature should then be established quickly as water carry-over to the shifter would damage its catalyst.

5. Quench Boiler

The steam generated in exchanger 101-C is combined with that produced in the reformer waste heat boiler coils. Feed water for 101-C is taken off the discharge of the water circulating pump 101-J which serves this boiler and the reformer steam coils. Splitting of the boiler water stream is effected manually, with F1a-106 and FI-122 to indicate the distribution. Standby pump 101-Ja (turbine driven) kicks on, through FA-105 and VS-105, if circulation fails.

6. Shift Converter

The gas-steam mixture enters the top of the shifter where a large proportion of the CO content will be oxidized in accordance with the following reaction:



This reaction is a reversible one, with "shifting" of the carbon monoxide favored by low temperatures. The rate of reaction, however, is favored by high temperatures.

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The shift catalyst is highly porous and should not be heated to temperatures above 1050°F as fusion may take place and activity for low temperature conversion may be impaired. In addition, the design temperature of the vessel is 850°F and this limitation should not be exceeded. To attain a specified carbon monoxide conversion, the principal operating variables are temperature, steam-to-gas ratio, and flow rate. It is customary to maintain the operating temperature at the design level or lower. With new catalyst, it may be possible to obtain satisfactory conversion at temperatures 25 to 50°F lower than specified by design. The steam/gas ratio is usually maintained constant, while the flow rate is not varied to alter shifter operation, except in very unusual situations.

a. Temperature

If the reaction is already near equilibrium, a decrease in temperature will likely improve conversion, and if it is not near equilibrium a temperature decrease may reduce the shifting. Conversely, if the reaction is near equilibrium, a rise in temperature results in a loss of conversion, and if not near equilibrium a temperature increase will improve conversion.

The conditions selected for the shift converter are based on high temperature for the primary section to take advantage of the higher reaction rate at high CO content in the inlet gas; and comparatively low temperature for the secondary section, to take advantage of favorable equilibrium conditions at low CO concentrations in the gas stream.

b. Steam

Increasing the steam flow results in an increase in CO shift if conversion is already near equilibrium, and a loss of CO₂ if not near equilibrium. Inlet steam-to-dry-gas ratio in the range of about 1.0/1.0 is normal. It is important that at least 20% steam be present in the gas passing over the catalyst when at temperatures above 250°F, otherwise dehydration or change in the structure of the catalyst, with loss of physical strength, may occur.

7. Shifter Catalyst Precautions

Start-up with the new, unreduced catalyst will follow the procedure outlined in Section III of this manual, using hot air for heating the catalyst initially to 225°F to minimize the formation of condensate, then continuing the heating with steam, etc.

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For subsequent start-ups, under no circumstances will air be used for preheating, unless an entirely new charge of catalyst has been installed. After shift catalysts have been exposed to reducing gases (i. e., hydrogen, carbon monoxide) they are pyrophoric and must not be exposed to oxygen (air) except under controlled conditions. Excessive temperatures resulting from too rapid oxidation of the reduced catalyst may cause catalyst and/or vessel damage.

If the catalyst is to be removed from the vessel or if the vessel is to be entered, the general practice is to subject the catalyst to a controlled oxidation procedure to render it non-pyrophoric (see below). It is recommended, however, that oxidation of the catalyst be carried out only when necessary. Even though the procedure is followed carefully, some damage to the catalyst may result. Furthermore, there may be some "dead spots" where the oxidation was inadequate, and some overheating may occur upon exposure to air.

A start-up with reduced catalyst must use steam or a steam-gas mixture as the heating medium, taking all precautions possible to minimize formation of condensate, and keeping any water drained off. Water tends to weaken the binder used in the catalyst manufacture.

When preparing to stop operations or expose reduced shift catalyst, the general procedures are as follows:

- a) If the process gas flow is to be interrupted for only a brief period of time, the shifter may be isolated under process gas pressure, or under a positive steam pressure, keeping any condensate drained out of the vessel.
- b) If the shutdown is to be prolonged but the vessel is not to be entered or exposed at any time to oxygen, isolate it and maintain under a positive pressure with an inert gas or a reducing gas. Desulfurized feed can be used if the shifter is first cooled below 400°F.
- c) If the catalyst is to be inspected by looking into a top man-hole only, it may be cooled with steam to about 250°F. The steam should be purged out at this point with nitrogen or carbon dioxide and the vessel thus cooled further if desired. While maintaining a slight positive bleed of nitrogen or carbon dioxide (CO₂ is best, because heavier) open the man-hole for inspection. Only a slight flow of inert gas is required to limit air diffusion. Inspectors should wear air masks.

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d) Should it be necessary for a man to enter the shifter, he should be equipped with an air or oxygen mask and a suitable harness so that if oxygen supply fails he may be pulled from the vessel. However, the Safety Department of the plant should pass on the advisability of allowing a man to enter a vessel of unoxidized catalyst.

e) If inspection reveals that only the top portion of catalyst should be removed, due to solids collection or catalyst breakage, and it is desired to avoid oxidation of catalyst, an industrial vacuum outfit can be used to pull the desired portion of the used catalyst out of the reactor while maintaining the bleed of inert gas. The discharged catalyst should be dumped into steel drums and wet down, if necessary, to prevent development of high temperatures.

f) If it is desired to oxidize only the top portion of the top shift converter bed, it would probably be well to establish a small flow of CO₂ or steam to the quench chamber and allow this inert cushion to protect and insulate the beds below the steam/air injection point. The unreduced beds should, of course, be protected with inert gas when steaming is discontinued.

g) If the used catalyst is to be removed from the shifter and there are no plans for salvaging it, it may be unloaded without oxidation. However, the use of this procedure is left to the discretion of the plant supervision. If this procedure is used, the catalyst is permitted to flow into steel drums and wetted to prevent rapid oxidation.

h) If it is desired to oxidize all the catalyst, before unloading or opening the shifter, the following procedure may be used. Prior to initiation of oxidation, the converter bed temperatures should be adjusted to about 550°F and the process gas should be flushed out. The vessel should be isolated and lined up to the oxidation vent. A flow of regeneration steam through FI-120 should be established at about 5000 pph and 3 or 4 mol % air added, say 300 # per hour. The temperature rise during oxidation probably will not exceed 150°F as long as the concentration of air in the steam does not exceed 3 to 4 mol percent. (The temperature should not be allowed to exceed 850°F; if it should rise to that point, air injection should be discontinued until the temperature is again under control). When the oxygen content of the noncondensable gas at the exit of the shifter exceeds 15 mol percent, raise the air content to 6% for two hours. If there is no increase in the bed temperatures, increase the air content to 8%-- and so forth in

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two-percent increments until 15% air is reached. If there is no further evidence of oxidation, the steam may be slowly reduced and the air content of the steam-air mixture can be increased to a maximum of 75% during cooling of the catalyst to assure complete oxidation. When the temperature of the catalyst bed has decreased to about 250°F the steam supply may be shut off. The air is stopped when the vessel is cool.

When carrying out procedures below normal operating pressures, do not exceed design velocities through the beds. Sudden pressuring and depressuring, and changes in rates of flow should be avoided, to obviate "heaving" the beds. At all times, and particularly when hot, the catalyst should be protected from contact with liquid water. Temperatures of the catalyst bed should not be changed at a rate greater than 150°/hr.

8. Shifter Effluent Quencher

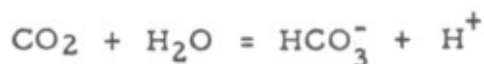
Shift converter effluent flows to the methanator feed heater 103-C, then is cooled by a quench water spray which cools the gas to its dew-point. The temperature should be easy to maintain reasonably well, as long as a small excess of quench water is used. High temperatures should be avoided on the stripper reboiler; it is for this reason that the quench is provided. Excessive temperatures tend to shorten the life of the reboiler bundle.

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9. Carbon Dioxide Removal System

The cooled raw synthesis gas, containing about 18% CO₂, is fed to the bottom of the CO₂ absorber. The carbon dioxide contained in the gas stream is removed by absorption in aqueous monoethanolamine solution at relatively high pressure and low temperature. The carbon dioxide so absorbed is subsequently stripped from the MEA solution at higher temperatures and low pressure.

MEA solution is basic (alkaline) and will rapidly react with the hydrogen ion in acidic solution (such as CO₂ in water). Hence, the presence of MEA is very effective in promoting solution of CO₂ in water in the absorber, by moving the following reaction to the right.



The CO₂ may then be removed by bringing the charged (rich) solution to a boil in the stripper. The release of the gas is accelerated and made more complete by the steam-stripping action in the stripper system (at low pressure). The stripped (lean) solution is thus reactivated, ready for another pass through the absorber. Below are discussions of the factors influencing efficiency and control of the CO₂ removal system.

a. Absorbent Characteristics

In the initial phase of CO₂ absorption (at the MEA inlet to the top of the absorber) the solution must be lean enough to reduce the CO₂ content of the purified gas stream to the desired point. The CO₂ content of the purified gas is expected to be in the range 250-500 ppm. High CO₂ content in the lean solution will retard CO₂ absorption; in addition, the corrosive tendency of the solution is increased by the presence of excess carbon dioxide. Normally, poor solution regeneration is responsible for the presence of excess CO₂ in the lean solution, and the more probable causes of poor regeneration are insufficient CO₂ stripper reboiler heat, or solution contamination. The most desirable regeneration situation is to furnish adequate stripping vapor to the stripper tower so that essentially all of the CO₂ is removed from the solution before it drops into the reboiler. Low carbon dioxide concentration in the reboiler will give a low reboiler corrosion rate. The residual CO₂ in the lean solution is expected to be less than 2.5 cu. ft. per gallon.

Ample absorbent must be circulated to remove a given quantity of CO₂ without approaching saturation of the solution. High CO₂ concentrations make the rich solution more corrosive. This condition is aggravated as the

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rich solution proceeds through heat exchange to higher temperature, with pressure reduction at the same time. It is for this reason that the absorber level control throttles valve is located downstream of the MEA exchanger. It is anticipated that the CO₂ loading will be 5.0 to 6.0 scf per gallon of rich 20 wt. % MEA solution.

Concentration of MEA in the lean solution may be varied to suit unit requirements; the range is usually 17 to 22%. At close to absorption limits, the lower the solution strength, the greater must be the circulation rate to accomplish equal purification of the process gas stream. Since the heat input to the stripper is relatively invariable, the absorbent circulation rate must be kept approximately proportional to the synthesis gas rate. This limits the range of the circulation rate that may be used and requires that the MEA concentration be kept within the approximate limits indicated above.

Assuming a constant circulation rate, a constant gas rate to the absorber and a constant level (differential) in the absorber, the level in the stripper bottom should be almost a constant, except for water loss overhead with the CO₂. Most of this water is condensed and returned as reflux, entering the stripper on the top tray with the rich MEA. However, there is a slow but constant loss of water to the CO₂ stream leaving 108-F reflux drum. This water will be made up by addition of steam condensate through FI-124 to the vaporizer return line to the stripper.

b. Operating Conditions

Changes in process gas rate, especially increases, require proportional changes in absorbent rate and perhaps cooling water rate on 105-C cooler. When an increase in process gas rate is anticipated, it is wise to increase circulation rate a small amount, prior to each small gas rate change. During and following changes in flow rates, the purified gas from the absorber should be watched carefully to avoid low-grade purification. Considerable time may elapse before conditions reach a firm equilibrium again.

In general, absorption is favored by low temperatures and high pressure. These factors are subject to very little variation because of the limitations of design and equipment. At reduced rates there may be a little flexibility in temperature control. However, for consistency, the absorber MEA inlet temperature should be kept fairly close to the design 110°F. Previous experience seems to indicate little increase in absorption efficiency at temperatures below 110°F, while at temperatures above 117°F absorption tends to drip off quite rapidly.

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Another factor influencing the efficiency of absorption is the contact time of the process gas with the MEA. To increase the contact time, the absorber is designed for partially flooded operation. The level control for the absorber is not of the displacement type but uses a differential pressure cell and actually measures and will maintain a given differential across the whole absorber. Increasing the set differential pressure (at a constant gas rate) increases the hold-up of MEA in the absorber, and thus the contact time with the gas. This usually gives improvement in absorption. However, if the differential pressure is increased by an increase in gas rate, the LIC will compensate to return the differential to the original value, and the net result will be a reduction in absorber MEA hold-up and a higher stripper level. In normal practice the MEA holdup (the setting of LICa-101) will be just a little more than the minimum required to give satisfactory CO₂ absorption.

If it is desired to circulate the absorbent when there is a major change, or no gas flow through the absorber tower, it is usually necessary to regulate the LIC manually to maintain a level in the stripper gauge glass, returning the control to automatic after the normal gas flow is re-established.

The maximum liquid level to be carried in the stripper is one foot below the reboiler return. However, a normal mid-glass level should ordinarily be maintained; volume above the mid-glass level acts as a surge capacity to avoid submerging the reboiler return line in the event of a drop in level in the CO₂ absorber, while continued operation at an abnormally low stripper level may accelerate wear on the MEA circulating pumps.

c. Absorbent Contamination

Various undersirable contaminants tend to accumulate in the working MEA solution; these must be removed, as they tend to cause foaming, corrosion or loss of absorptive capacity. The contaminants are generally in the form of suspended solids, non-volatile acids, heat-stable salts and high-boiling MEA degradation products.

Two equipment items are included in the MEA circuit expressly to remove contaminants. The first is a slip-stream strainer, 101-L, which is a shell containing cotton filter bags. Some of the most troublesome cases of foaming are caused by minute quantities of surface-active agents; these may be removed by use of the filter. It also serves to collect suspended solids, such as pipe scale, iron oxides, sand, etc., all of which may contribute to foaming problems. The solids must be removed by opening the

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filter and cleaning the bags periodically. When putting the filter on the line, the bypass should be pinched to give about 2 psi drop through the filter. The bags should be cleaned at about 10 psi differential.

The second solution-cleaning item is the MEA vaporizer 108-C, an adjunct of the stripper tower. This item is a sidestream redistillation apparatus and is usually operated in a semi-continuous manner. Generally speaking, most of the contaminants found in used MEA solution are either high-boiling or non-volatile. Proper use of the vaporizer will remove almost all of the fouling materials. These may include very fine suspended solids, inorganic salts and high-boiling amine conversion products.

A sidestream of lean absorbent is taken by gravity flow on vaporizer level control, so that its tubes are kept submerged. The vaporizer uses 350 psig steam which is pressure-reduced through PC 104 to a maximum of 100 psig. The steam rate will be manually set at 1400 pph, as indicated on FI-123. Given constant stripper conditions, which is normally the case, a constant steam rate will induce a constant flow of MEA to the vaporizer. The level control will maintain a constant level in the vaporizer as the MEA is boiled off. When first put into operation, the temperature of the vapors leaving the vaporizer will be about the same as those leaving the stripper reboiler. However, as high-boiling contaminants accumulate in the vaporizer, the exit vapor temperature will tend to rise. When the vaporizer outlet temperature reaches about 290°F, the accumulated contaminants are ready for removal. Operating the vaporizer above 300°F is not recommended, as such temperatures can cause redistillation of contaminants, thus returning them to the circulating MEA solution.

The length of each vaporizer operating cycle depends on the condition of the MEA solution and on the steam rate. When the absorbent is in good condition, build-up of contaminants will be slow. If the steam rate is low, the MEA rate through the vaporizer will be low and the accumulation of contaminants will be slow. The vaporizer is designed to turn over the absorbent inventory in two or three days. Some operators keep the vaporizer in nearly continuous operation, while others feel that the circulating solution may be kept in order by operating the vaporizer as little as two days per month. Chemical analyses of the lean circulating solution and its behavior (i. e., absorptivity, and foaming tendencies) will ultimately establish the operating requirements for the vaporizer.

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A caustic injection line to the vaporizer is provided to neutralize acids and release MEA inactivated as monoethanolammonium oxalate and formate. When about ready to isolate and dump the vaporizer, shut off the MEA inlet, add 5 or 10 gallons of 10% caustic solution to the vaporizer and boil until the vapor outlet temperature stabilizes, but do not exceed the 300°F vapor outlet limit. The steam may then be shut off, the vaporizer isolated and drained, and then be filled, flushed and drained, using a mildly alkaline water. A gallon or two of 10% caustic solution should be put in the vaporizer after the flushing. Lean absorbent may be fed again if another cycle is to be started, or the vaporizer may be left isolated awaiting the next requirement. It is recommended that the alkali used be a low-salt caustic to reduce the possibility of chloride attack on the vaporizer internals.

Proper use of the above contaminant removal facilities should prevent foaming difficulties. However, if foam appears it may be helpful to use an antifoam agent to minimize MEA losses and permit continuation of operations while measures are taken to eliminate the contaminants. The most commonly used anti-foam agents are long-chain aliphatic alcohols, silicones and phosphate esters. Experimentation may be necessary to determine the best agent, as a product that works well for one plant may be ineffective in another. Antifoam agents are manufactured by Jefferson Chemical, Union Carbide, Du Pont, Dow and others. Literature on foaming problems and MEA solution control may also be obtained from the above sources.

A recently devised test for corrosive quality of MEA solutions is as follows:

- (1) Make a 10 wt. % copper sulphate solution.
- (2) Add a standard amount of solution (experience will dictate quantity) to an 8 oz. sample of MEA solution.
- (3) If the MEA is
non-corrosive, it turns dark navy blue
slightly corrosive (oxalic acid), it turns light green
very corrosive (glycine & high MW compounds), it turns grass green.

There are a number of corrosion inhibiting additives which may be used to supplement the clean-up equipment provided.

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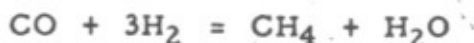
10. Methanator

Process gas, containing only traces of CO₂ and around 1% CO, flows from the top of the absorber to the overhead knockout drum. Entrained moisture will be removed in the demisting pad; thus preventing damage to the hot methanator catalyst.

If on/off LC-105 does not remove the liquid from the KO drum, then LA-110 will sound off. Provided the situation cannot be quickly corrected and carryover results, the inlets to the methanator should be closed - thus venting the process gas stream via PIC-105 until the difficulty is overcome. The pushbutton on the board will close the inlet valves.

Entrainment in the absorber overhead may be due to high submergence in the tower, or high absorbent rate.

The objective of methanation is to complete the removal of the carbon oxides from the synthesis gas, since they are harmful to the ammonia synthesis catalyst. Removal of the oxides is accomplished by their conversion to methane, which is inert in the ammonia reactor. The methanation reactions are as follows:



Both reactions are exothermic (actually, the CO₂ is first reduced to CO, then to methane) and will, at normal operating conditions, give about 625°F methanator outlet temperature.

The catalyst volume, at design rates, is equivalent to a space velocity of 3000 volumes of gas per hour per volume of catalyst. Lower gas rates will tend to improve the methanation, other factors being equal.

The methanator will be operated at as low an inlet temperature as will achieve the desired gas purification. It is expected that the total amount of carbon oxides in the gas stream leaving the methanator will normally be less than 10 ppm, as indicated on AR-102. If the shift converter and the CO₂ absorption system are operating properly, the methanator outlet temperature should run between 600 and 700°F. The methanator has temperature recorder and alarm TRA-3 - 1 for the outlet of the upper bed. This alarm, which will activate the solenoids VS-101 and VS-106 and divert the methanator feed to the vent, should be set to prevent temperature higher than 750°F. A similar alarm, TRA-3 - 2, operates on the bottom of the lower bed. Catalyst bed temperature should never exceed 800°F.

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Some degree of control over the reactor outlet temperature may be achieved by use of the MIC-102, which permits the injection of cold gas between the beds as quench. There is nearly 2 1/2 times as much catalyst in the lower bed as in the upper, thus the conversion and, accordingly, the temperature rise through the upper bed is somewhat limited. Addition of quench between the beds reduces the temperature, while the net carbon oxides content of the total gas stream entering the lower bed is reduced by whatever degree conversion was accomplished in the upper bed. If the inlet gas contain 1.0 percent CO, there will be about 130°F temperature rise in the upper bed, assuming 500°F inlet gas temperature.

Loading and activation procedures are discussed in Sects. II and III of this manual. Once the catalyst has been placed in operation or reduced it should not be exposed to air or to oxidizing atmospheres. In a plant shut-down where methanator entry is not anticipated, it should always be blocked in under an atmosphere of hydrogen or nitrogen. For removal of catalyst an oxidation procedure as described in Section IV should be followed.

Under certain conditions, carbon monoxide and nickel may react to form nickel carbonyl, $\text{Ni}(\text{CO})_4$, which is highly toxic, and is a gas at temperatures over 110°F. Whenever men are going to enter or open the methanator, stringent precautions should be taken to assure that carbonyls are not present. (Iron carbonyls may be formed in the shift converter; however, the procedures anticipated for starting and shutting down this item will preclude their formation)

The most likely time for nickel carbonyl formation is during start-up or shutdown, since these procedures involve the temperature range favorable for carbonyl formation. A few simple precautions will suffice.

Shutting down: The catalyst should never be permitted to cool down to ambient temperature in the presence of CO. When the process gas contains CO, the methanator should be flushed with a CO-free gas before the temperature drops to 200-400°F. At moderate pressure and when the CO concentration is low, temperatures in excess of 200°F will prevent carbonyl formation, while 400°F should be considered the safe limit at high pressure and/or high CO concentrations.

Starting up: The pressure on the methanator should be kept low, when heating up on process gas, until the bed temperatures are above 200°F.

11. Ammonia Synthesis System

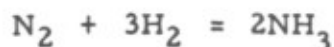
After cooling, compression and removal of oil and carbamate,

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the purified synthesis gas is fed to the synthesis system: Following are discussions of factors affecting operation of this system.

a. Conditions Influencing the Converter Reaction

The synthesis reaction, which is induced by the catalyst, may be illustrated by the following equation.



The equilibrium point for this reaction is such that, at the proposed operating conditions, the ammonia content of the reactor effluent will be about 17.5%. The unconverted gases are recycled back through the reactor to get the ultimate production. It will be noted that one molecule of nitrogen plus three of hydrogen produce two molecules of ammonia (not four).

Temperature: The effect of a change in temperature on the ammonia synthesis reaction is a double one, as it affects both equilibrium percentage and reaction rate. As the synthesis reaction is exothermic, a rise in temperature lowers the equilibrium percentage of ammonia and at the same time accelerates the reaction. This roughly means that under conditions far from equilibrium, temperature rise will lead to higher conversion, while on the other hand, for a synthesis system giving a conversion near the equilibrium percentage a rise in temperature will lead to a lower conversion. Efficiency always varies directly with temperature when catalyst deterioration is not taken into account. Conversion efficiency is defined as the ratio of the actual percent NH_3 in the converted gas to that theoretically possible under the conditions in question.

Pressure: As the synthesis of ammonia involves a decrease in volume (decrease in the number of molecules), the equilibrium percentage of ammonia will increase with pressure. At the same time the reaction rate is accelerated by increasing the pressure; hence the conversion will improve with higher pressure.

Space Velocity: At higher process gas rates (higher space velocity in the converter) the synthesis reaction has less time to operate and does not produce as high concentration of ammonia in the converter effluent as is produced when the gas is moving through more slowly. However, the reduction in yield is far less than proportional to the percent increase in space velocity. The increased production of ammonia, due to the greater amount of gas put through the reaction zone, more than offsets the tendency toward decreased production due to less complete reaction (less residence time). Therefore, at normal or less than normal throughputs, an increase in gas rate to the

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converter (other conditions unchanged) will give increased production.

The usual method of changing space velocity is by altering the recycle (circulation) rate. With more circulation (if available) the temperatures will tend to drop in the converter beds, due to less conversion per pass; pressure will tend to drop because of more total production of ammonia.

less ammonia *less ammonia*
Hydrogen/Nitrogen Ratio: The fresh synthesis gas feed (excluding recycle) to the synthesis section should usually have a hydrogen to nitrogen ratio of about 3 to 1. This is the case because the combining of hydrogen with nitrogen to form ammonia is in the ratio of 3 to 1. However, it should be recognized that the hydrogen to nitrogen ratio within the ammonia converter can be other than 3 to 1. It has been found that maximum conversion percentage is obtained at a 2.5 to 1 ratio of hydrogen to nitrogen in the converter. The ratio in the fresh gas feed may be altered slightly from 3 to 1 to obtain the optimum of 2.5 to 1 in the combined gas feed to the converter.

Inert Gases: A continuous bleed of gas will be maintained from the recycle compressor suction header to the fuel gas system. This purge stream is required to control the concentration of methane and other inert gases which would otherwise build up in the synthesis circuit, resulting in lower conversion and reduced production capacity.

Synthesis Gas Rate: Increasing the synthesis gas rate, alone, produces more ammonia and has these effects upon the conditions discussed above:

- (1) The system pressure will increase.
- (2) The catalyst bed temperature will increase.
- (3) The inert gas content will rise.
- (4) The $H_2:N_2$ ratio may change.

Conversely, decreasing the synthesis gas rate will have the reverse effects.

Under normal operating conditions, the synthesis gas rate is determined by production requirements. An increase in gas feed to the synthesis section usually will be obtained by more production of gas from the fore end of the plant.

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b. Control of Synthesis Operation

The synthesis system essentially rides on the line from the discharge of the synthesis gas compressor fourth stage. Gas (H_2 and N_2 , mixture 3:1) is consumed as determined by the operating conditions, catalyst activity, and resultant capacity of the synthesis loop. The gas from the compressor keeps replacing the removed or converted gas. If excess synthesis gas is available, the pressure on the converter increases to the limit of the compressor controls, and then raw synthesis gas is vented before the first stage of compression. If there is insufficient gas, the loop pressure drops until the production of ammonia is reduced and comes in balance with the gas available.

There are several variables, one or more of which may be changed to alter synthesis loop operation. The more important controlling variables are listed below -

- Synthesis gas rate
- Circulation rate
- Purge rate
- Converter bed temperatures
- Converter feed chill-temperature
- Hydrogen/nitrogen ratio
- Purity of feed gas

It will be noted that system pressure is not listed as a variable which is available for control. The pressure frequently changes as a result of the manipulation of other conditions, but it is rare that a change would be made for the sole purpose of raising the pressure, to the exclusion of all other effects. The system is usually so operated that the pressure remains reasonably well below limits, while minimizing the purge rate and while maintaining converter temperatures low enough to assure long catalyst life. Lower pressures usually indicate good operation, provided feed and purge rates are normal and the converter temperatures are satisfactory.

Following are the factors affecting each of the synthesis loop conditions that the operators watch, to detect changes or abnormalities in the process. If these factors are known, it is easier for an operator to explain a change in operating conditions. He can then manipulate one or more variables to make necessary corrections.

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More NH₃ Prod. = more pressure.

Converter Pressure: The main factors which individually or collectively contribute to an increase in the synthesis loop pressures are:

- (1) An increase in the synthesis gas rate. ↑
- (2) A decrease in converter temperature. *more recycle
more S.G.
less S.G.* ↑
- (3) A change in gas composition away from the optimum 2.5:1 ? ratio of hydrogen to nitrogen.
- (4) An increase in the ammonia content of the circulating gas. ↑
- (5) An increase in the inert gas (fixed gas) content of the circulating gas. ↓
- (6) A decrease in the circulation gas rate. ↓
- (7) Poisoning of the catalyst due to impure synthesis gas.
- (8) Aging of the catalyst.

Conversely, a decrease in the pressure is caused by the reverse of the actions above.

Catalyst Temperature: - The main factors which individually or collectively contribute to an increase in the catalyst temperatures are:

- (1) An increase in the synthesis gas rate. ↑
- (2) A decrease in the circulation rate. ↓
- (3) A closer approach to the optimum 2.5:1 hydrogen to nitrogen ratio.
- (4) A decrease in the ammonia content of the circulating gas. ↑
- (5) An increase in converter system pressure.
- (6) A reduction in the cold gas by-pass (quench) rate to the converter. ↑

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- (7) A decrease in the inert content of the circulating gas.
- (8) An increase in catalyst activity, following a temporary poisoning due to impure synthesis gas.

Conversely, the factors causing a decrease in the catalyst temperatures are the reverse of those mentioned above.

The best temperature for steady operation is the lowest temperature which will give the maximum yield of ammonia product, yet high enough to provide stability in case of pressure surges. Excessive temperatures will age the catalyst and cause rapid reduction in catalyst activity.

Hydrogen-to-Nitrogen Ratio: The main factors which individually or collectively contribute to a change in the $H_2:N_2$ ratio of the circulating gas are:

- (1) A change in the composition of the synthesis gas from the reforming and purification systems.
- (2) A change in the synthesis gas rate.
- (3) A change in the ammonia content of the circulating gas.
- (4) A change in the inert (fixed) gas content of the circulating gas.

The hydrogen-nitrogen composition of the gas to converter is controlled to maintain about 2.5:1 ratio. A rapid change of ratio will cause a rapid temperature change.

Ammonia Content of the Circulating Gas: The factors which individually or collectively contribute to a change in the ammonia content of the circulating gas are:

- (1) A change in cooling in the converter effluent coolers 117-C, 118-C and 119-C.
- (2) Overloading, or a change in cooling in the chiller 115-C.

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- (3) An excessively high level in the primary separator, 123-F or secondary separator, 122-F.

It is anticipated that the ammonia concentration of 6.5% in the recycle gas will become 5.0% when the recycle and fresh feed gases are combined. After chilling in 115-C, it is expected that the ammonia concentration in the combined gas stream entering the converter will be 3.0%.

Inert Gas Content of Circulating Gas: The principal constituents which contribute to the inert content of the circulating gas are argon and methane. These gases tend to build up and raise pressure in the system, thus reducing the effective synthesis gas partial pressure. This is reflected in lower conversion per pass. The inert concentration in the system is controlled by withdrawing a stream of purge gas overhead from the primary separator. Design is based on a fixed gas concentration of 17%. However, it may be found by experience that at higher concentrations overall ammonia production can be increased, by conserving hydrogen which would otherwise be lost in the purge gas.

From the preceding discussion of the ammonia synthesis operation it can be seen that the efficiency is affected by the controllable variables listed at the beginning of this item "b". All of these factors are interdependent and a change in one will have an effect on the others. Consequently, good operation will be a combination of operating experience and a recognition of the factors affecting the operation of the system. Thus if a drastic change in one of the operating conditions occurs, experience will dictate what steps should be taken to compensate for the change, so that the system will remain in good control. Any changes should be made slowly when possible, so as to avoid major disturbances.

c. Converter Catalyst Characteristics

Catalyst Activation: The synthesis catalyst is made from fused iron oxides containing potassium, calcium and aluminum oxides as stabilizers and promoters, and is charged to the ammonia converter in an unreduced state. The catalyst must be activated before production of ammonia will take place. The activation requires reduction of the iron oxide to practically pure element iron.

The reduction takes place during a period when hydrogen is passed over the unreduced catalyst at progressively higher pressures and

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temperatures. The hydrogen combines with the oxygen from the iron oxide and forms water. The water is removed (as much as possible) before the gas is recycled over the catalyst. The amount of water produced during the activation period is a good indication of the progress of the catalyst reduction. At the start of the reduction period, a small amount of water is formed and as reduction of the catalyst progresses, water formation increases. The reduction of the catalyst is aided by fairly high temperatures and controlled pressures. The water formation will reach a peak and then gradually taper off near the end of the reduction period.

The reduction temperature should always be kept below that at which the catalyst is going to operate, so as to avoid deactivation due to (1) high concentrations of water vapor in the circulating gas, or (2) excessive heat. Too low temperature will cause catalyst reduction to move slowly; if temperatures drop low enough, reduction will stop.

The effect of pressure and/or pressure - change during catalyst reduction can be critical. If each catalyst bed is not activated uniformly as reduction moves downward, an increase in pressure may cause channeling. That is, the more reduced catalyst areas will promote the reaction of hydrogen and nitrogen to form ammonia in local sections of the bed. This reaction gives off heat and will cause catalyst bed temperatures to become higher and difficult to control in these localized areas. The pressure during catalyst reduction should be maintained at a point where reduction is symmetrical and temperatures in a horizontal section of the bed do not spread beyond a small range. Increasing the pressure will promote ammonia formation; lowering the pressure will retard ammonia formation.

The catalyst can be reduced at fairly low gas rates; however, the higher the velocities through the catalyst the shorter will be the reduction period, and channeling through the beds may diminish at higher rates.

Synthesis gas is recycled through the converter during catalyst reduction. When the reaction has started, it is very important that the circulating gas be cooled as much as possible (without risking the danger of freezing water in the equipment) to condense and remove the water vapor from the gas before recharging to the converter. Otherwise, gas with a high concentration of water vapor would enter the catalyst beds which are already reduced. Water vapor will cause deterioration or poisoning of the reduced catalyst. As soon as ammonia synthesis has started, the ammonia produced will lower the freezing point and permit water removal from the gas stream at lower temperatures.

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Careful control of conditions during catalyst activation will result in uniform reduction, which will promote longer catalyst service.

Reduction of the synthesis catalyst will be accomplished during the initial startup of the plant. The recommended procedure, to be used as a guide, is described in Section III.

Catalyst Thermal Resistance: Even when operated on pure synthesis gas, ammonia catalysts do not retain their activity indefinitely. Some data indicate that when pure gas is being used, temperatures below 1022 °F (550 °C) do not affect the catalyst, whereas higher temperatures will harm the catalyst. These data also show that catalyst which has suffered slightly from excessive temperatures may show a loss of activity when tried out at 752 °F (400 °C), whereas the activity at 932 °F (500 °C) may be unchanged. It should, however, be emphasized that no definite temperature limit exists below which the catalyst is unaffected. At a fixed temperature level, but under more severe conditions of pressure and space velocity, the deterioration of the catalyst should be expected to develop more rapidly.

Degradation of the catalyst will first be apparent in reduced efficiency during operation at lower temperatures, higher pressures and/or higher gas rates. It has been observed that the more the catalyst activity has declined from the initial value, the more prolonged or severe will be the treatment required to produce further injury.

Catalyst Poisons: Compounds which (when present in the synthesis gas) are capable of reducing catalyst activity and/or life, are called poisons. Such substances normally form more or less stable compounds with the active materials of the catalyst. There are permanent poisons which cause lasting irreversible lowering of catalyst activity. They form stable surface compounds with active parts of the catalyst. Other poisons may cause only temporary decreases in activity; the initial effectiveness is restored in a relatively short time after removal of the poisonous compound from the gas.

The most important group of poisons of ammonia synthesis catalyst are oxygen compounds. These cannot be classified as temporary poisons; neither are they permanent poisons. When an oxygen compound such as carbon monoxide is present in small quantities in the synthesis gas, some active areas of the catalyst combine with oxygen thus

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reducing catalyst activity. When the oxygen compound is removed from the synthesis gas, the catalyst again is fully reduced, but all the regenerated centers do not revert completely to the initial state or regain their initial activity. So the oxygen compounds cause a strong temporary and a small permanent decline in catalyst activity. The usual oxygen compounds which poison the catalyst are water vapor, carbon monoxide, carbon dioxide, and molecular oxygen. Other significant poisons are hydrogen sulfide (permanent) and oil spray deposits, which are not real poisons as this term is used here, but which are capable of lowering the activity of the catalyst by clogging the surface.

Catalyst Mechanical Strength: The synthesis catalyst is mechanically strong; however, the operator should not expose it to excessive abuse. Mal-operation may cause very rapid temperature fluctuations, resulting in catalyst breakage. During the reduction period any fast temperature changes should be carefully avoided; during this interval the catalyst is thought to be particularly sensitive to mechanical crushing and quick temperature variation.

Catalyst Stabilization: Reduced iron catalyst is highly pyrophoric. The term stabilization applies to treatment by which the catalyst is rendered non-pyrophoric in such a way that it is possible to revivify it without any appreciable loss in activity.

The catalyst must be stabilized (oxidized) before opening the converter for maintenance work, inspection, or catalyst change. The oxidation is done primarily for safety reasons. Or it may be for the purpose of saving the catalyst for further use. Stabilization procedure is discussed in Section IV.

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D. SPECIAL INSTRUMENTATION

In subsection C, above, there was discussion of the effects of changes in the principal process variables. Instrumentation has been provided for regulation of these conditions. Data on controls and other instruments are given in the final specifications book and on the process piping/instrument flow diagrams in the Appendix. An instrument symbol list is included. Operators should be familiar with the actions which the various control valves will take in case of air failure - so as to visualize the steps which must be taken at such a time.

A few instruments, of somewhat special nature, are described briefly below.

1. Feed Gas Flow Controller

FRRCa-101 measures and controls the feed gas to the unit. When its "ratio" feature is in operation, the flow controller derives its setting from the air signal which is representative of the process steam flow. Thus, if a steam failure occurs, the indicated steam flow will fall off, but as it diminishes it will also reduce the feed gas rate proportionally, thereby greatly minimizing the likelihood of coking the reformer catalyst. The steam/gas ratio may be altered by use of the ratio adjustment provided.

An air switch is provided which will permit operation of the gas feed controller without dependence on FRRCa-101. This will permit instrument maintenance work on the steam flow controller without disturbing the feed gas rate. However, it must be realized that when the master controller is isolated, the safety features provided by the FRRC system are nullified; therefore the instruments should be returned to automatic ratio control as soon as feasible.

2. Air-Purged Thermowells

Thermowells for reformer tubes, combined reformer outlet, combustor catalyst beds and the quench boiler inlet are all provided with air purge to avoid reduction of the thermocouple junctions by hydrogen seepage through the thermowell walls. Dry instrument air is fed to the bottom of each thermowell through a stainless steel tube and passes up and out through a connection in the thermocouple head. A combination filter and orifice in the air line union limits the air flow. A bubbler may be attached to the purge-exhaust connection, so that the rate of purge may be observed.

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3. Twin-Valved Controllers

There are several controllers, each of which regulates a pair of valves, instead of a single CV. The two valves are marked "A" and "B" for such a controller. In some cases the valves move simultaneously, in opposite directions, with a change in air signal; TRCV's 102 A & B on the quench boiler 101-C are such valves.

Other controllers are split-range, so that the "A" valve moves through its full stroke as the air signal changes through a part of its range, and the "B" valve moves during the latter part of the signal range. Such valve pairs are used to give alternate flows when the "A" valve (normal control) does not handle the situation. Example: PRCV's 102 A & B on the syngas compressor kickback and suction KO vent, to control suction pressure.

4. Pressure Reducers for MEA Blanket Gas

NG-131-3/4 brings gas to the MEA storage tank, where the pressure is reduced in two stages by PCV 103 and PCV 102, to provide blanket gas for the tank at a pressure of about five inches of water.

5. Gas Analyzers

Three analyzers are provided for this unit. Two are of the type which directs a beam of infra-red light through a continuous sample of the process stream and records the concentration of one component (or group) in the stream. AR-101 is calibrated for CO₂ and will serve the methanator inlet; A-101 will sound if CO₂ content is too high. AR-102 is calibrated to indicate total carbon oxides (CO + CO₂) at the synthesis gas compressor suction drum.

AR-103 is a thermal conductivity instrument, and indicates the concentration of hydrogen in the sample. This analyzer is arranged to service two sample sources: (1) the fresh-feed to the synthesis loop, sampled at the syngas compressor suction drum, and (2) the mixture of fresh feed and recycle, sampled at the converter inlet. The analyzer will record the hydrogen content of one stream until the sample source is switched manually.

Detailed instruction manuals have been provided by the vendors for installation, calibration and operation of these instruments. It is essential that these instructions be followed faithfully by qualified personnel.

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6. Purge-to-Fuel-Gas Flow Controller

Stable primary reformer furnace outlet temperature may depend to a large extent upon a fuel gas of constant quality. The fuel contains purge gas from the ammonia synthesis reactor. This purge is of much lower heating value than the natural gas used for the bulk of the furnace heating, and will be of sufficient volume to provide about 15% of the heat required at the reformer furnace. This purge gas flow may be quite erratic at times when the synthesis section operation is unsteady. Regulator FRCa-104 has been provided to vent the excess over its set-flow of purge gas to the burners. The controller should be set so that the purge will exceed that flow most of the time.

Purge is released from the synthesis section through the bypass of PICV-102 on the purge gas separator. In case of excessive loop pressure, PICV-102 opens.

7. Methanator Temperature Controllers

Cold synthesis gas of specified carbon-oxides content flows from the CO₂ absorber toward the methanator. Enroute the gas is heated to 500°F in passage through 126-C and 103-C exchangers. Some of the cold gas may be by-passed around the exchangers for temperature control; this flow is regulated by TRCV-104. The butterfly valve SP-105 may be throttled, if necessary, to create a pressure differential sufficient for effective temperature control.

When either methanator bed temperature alarm functions, the solenoid valves 101 and 106 close the methanator inlets. These solenoids (like the others on this unit) must be manually repositioned before the inlets can be re-opened.