BASE CASE I 3.4 PROCESS DESCRIPTIONS

The discussions below follow the block flow diagram (BFD) or the process flow diagram (PFD) as noted. These diagrams are placed at the end of the discussion. Detailed compositions and flows of the numbered streams are found on the material balance sheets in Appendix A.

3.4.1 <u>General</u> (BFD ZO-GEM-6894)

Sized coal is received from the offsite Coal Handling Unit 128 (see Sub-Section 3.5) and is gasified in Coal Pressure Gasification Unit 101. The raw gas generated is partially converted in Raw Gas Shift Unit 102 to meet Methanol Synthesis Unit 110 requirements, and is cooled in Raw Gas Cooling Unit 103 and Shifted Gas Cooling Unit 104 before flowing to Gas Purification Unit 105. This unit removes the H2S, CO2 and naphtha from the raw gas. The purified gas (synthesis gas), is compressed and fed into Methanol Synthesis Unit 110. The crude methanol is used as feed to Methanol Conversion Unit 150, which converts the methanol into gasoline. Stabilized gasoline is recovered in Fractionation Unit 152. Additional gasoline is produced in HF Alkylation Unit 153 by alkylating the olefins recovered in Unit 152. C3 LPG and mixed butanes are also recovered in the alkylation unit. The naphtha recovered within Gas Purification Unit 105 is upgraded in Naphtha Hydrotreating Unit 151.

The gasoline product is produced from stabilized gasoline, hydrotreated naphtha, alkylate and a portion of the mixed butanes in the offsite Gasoline Blending Unit 154. (See Sub-Section 3.5.)

The purge gas of Methanol Synthesis Unit 110, containing mainly the methane of the synthesis gas, is sent to the SNG upgrading train. This train consists of Methanation Unit 112, where unreacted CO and H₂ and higher hydrocarbons are converted to additional methane, CO₂ Removal Unit 113 for upgrading the methane to SNG quality, and SNG Drying Unit 114.

The hydrogen necessary for hydrotreating is produced in H₂ Recovery Unit 111 by absorption from a side stream of the purge gas from Methanol Synthesis Unit 110. The offgas of Unit 111 is recompressed to the SNG upgrading train pressure.

The H₂S contained in the Gasification Unit 105 offgas is converted in Sulphur Recovery Unit 106 to sulphur.

The gas liquors condensed in Units 101, 103, 104 and 105 are pumped to Gas Liquor Separation Unit 107, where dusty tar and oil are recovered. The gas liquor is processed further in Phenol Recovery Unit 108 and Ammonia Recovery Unit 109.

Sulphur and anhydrous ammonia are saleable products. Dusty tar, oil and phenols are not further upgraded, but are used as fuel.

3.4.2 Gasification Unit 101 (PFD ZO-GEM-6895 and 6896)

Purpose of the Unit is to convert coal into raw synthesis gas.

Technology Used

As defined in the scope of the study, the Lurgi Coal Pressure Gasification Process is used. This is a partial oxidation process by addition of oxygen and steam in the Lurgi countercurrent moving bed pressure gasifier.

Coal Handling Inside the Gasification Building

The well-sized coal is transported from Coal Handling Unit 128 to the top of the gasifiers by two-100 percent capacity inclined belt conveyors. During normal operation, each belt conveyor operates at 50 percent capacity and feeds two horizontal conveyors which run between two rows of gasifiers. Two spare horizontal conveyors are provided.

Coal is fed from the horizontal conveyors to the coal bunkers, 101-Y-01, by means of mobile automatic stations, each of which consists of a tripper and a reversible belt. Four stations have been provided with two stations normally operating.

All coal handling in the gasification building is controlled from a central control room.

Process Description

Gasification (PFD ZO-GEM-6895)

The well-sized coal is charged from the coal bunkers, 101-Y-01, into the gasifiers via automatically operated coal locks, 101-D-02. The bed of coal is gasified in countercurrent flow with the gasification agent. While travelling from the top to the bottom of the gasifier, the coal is dried, devolatilized and gasified.

The gasification agent is a mixture of oxygen and steam which is introduced into the bottom of the gasifier through a rotating grate. The ash is removed by this grate and discharged via the semi-automatic Ash Lock 101-D-03 and flows to Ash Handling Unit 129.

The steam addition moderates the gasifier temperature to below the ash liquefaction point. The partial combustion of the coal with the oxygen supplies the heat necessary for the gasification reactions.

The hot raw gas leaving the gasifier is cooled and scrubbed in Wash Cooler 101-E-01 with recycled gas liquor. By this operation the crude gas is saturated with steam and the dust and the heavy tars are removed. Before leaving the unit, further cooling takes place in Waste Heat Boiler 101-E-01 where 100 psig steam is produced.

The dusty gas liquor leaving the wash cooler and the waste heat boiler is sent to Gas Liquor Separation Unit 107.

Lock_Gas_Recompression_Section_of_Unit_101 (PFD ZO-GEM-6896)

When the coal locks are depressured, raw gas is released. The portion which is released down to about 70 psig is fed to the last stage of Lock Gas Recompressor 101-C-41 after passing through Venturi Scrubber 101-D-41. The portion which is released down to atmospheric pressure is fed to the first stage of this recompressor via Lock Gas Holder 101-F-41.

The small quantity escaping during the charging operation of the coal locks, 101-D-02, is not recompressed due to the presence of air and is exhausted by Coal Lock Suction Fan 101-C-01 through Venturi Scrubber 101-F-05 to the atmosphere.

The lock gas recompressor also compresses the Gas Purification Unit 105 recompression gas and the main compressor syngas losses of Methanol Synthesis Unit 110 (Base Case I only).

3.4.3 Raw Gas Shift Unit 102 (PFD ZO-GEM-6897)

Purpose of the Unit is to increase the $\rm H_2/CO$ ratio of the raw synthesis gas to meet the requirements for methanol conversion. Only a sidestream of the raw gas has to be converted.

The exothermic shift reaction is as follows:

$$CO + H_2O \longrightarrow CO_2 + H_2$$
.

No additional steam is required for the reaction, since sufficient steam is contained in the raw gas.

In addition to the conversion of CO, most of the unsaturated hydrocarbons, higher phenols, HCN and organic sulfur are hydrogenated and the tar is hydrocracked into oil and naphtha.

Technology Used

For CO conversion in the raw gas generated in the Lurgi gasifier, Lurgi has developed a technology using commercial catalysts.

Process Description

The water content of the raw gas from Gasification Unit 101 is adjusted by cooling in the 50 psig Waste Steam Generator 102-E-04. In Separator 102-F-01, the condensed gas liquor is separated from the raw gas. The condensed gas liquor then flows to Gas Liquor Separation Unit 107 via Raw Gas Cooling Unit 103.

In Heat Exchangers 102-E-01, 02 and 03, the raw gas is heated to reaction temperature by heat exchange against the shifted gas. The raw gas then flows to Prereactor 102-D-01, which serves primarily as a guard bed trapping polymerized hydrocarbons and dust. The prereactor can be bypassed and regenerated when the pressure drop across the catalyst bed becomes excessive.

The partially shifted gas from the prereactor flows to Reactors 102-D-02 and 03 for further conversion. The shifted gas from 102-D-03 is cooled in Exchangers 102-E-01 and 02 against the raw feed gas and then flows to Shifted Gas Cooling Unit 104.

Provisions have been made to periodically regenerate the catalyst using steam and air.

3.4.4 Raw Gas Cooling Unit 103 (PFD ZO-GEM-6898)

Purpose of the Unit is to cool the raw synthesis gas coming from the gasifiers to a temperature as low as possible using cooling water, thereby reducing the downstream refrigeration requirements for gas purification.

Within the dictated temperature limitations, heat is recovered by the production of LP steam.

During cooling the raw gas, gas liquor, containing tar, oil, phenols and ammonia, is condensed.

Technology Used

The technology used has been developed by Lurgi for the special requirements of the Lurgi Coal Gasification Process.

Process Description

The raw gas is first cooled in the 50 psig Steam Generator 103-E-01. It is then cooled in the 20 psig Steam Generator 103-E-102. To further reduce the raw gas temperature, it is cooled by air in 103-E-03 and by cooling water in 103-E-04. To prevent the formation of ammonium carbonate, which could plug the tubes, gas liquor is injected into 103-E-04.

The gas liquor condensed in these steam generators and Trim Cooler 102-E-04 flows to Tarry Gas Liquor Tank 103-F-04. Part of the gas liquor is recycled to Wash Cooler 101-E-01 in Unit 101; the balance is sent to Gas Liquor Separation Unit 107.

3.4.5 Shifted Gas Cooling Unit 104 (PFD ZO-GEM-6899)

Purpose of the Unit is to cool the hot shifted gas to a temperature as low as possible using cooling water, thereby reducing the refrigeration requirements for gas purification. (See Paragraph 3.4.4).

Technology Used

The technology used has been developed by Lurgi for the special requirements of the Lurgi Coal Gasification Process.

Process Description

The shifted gas is first cooled in the 100 psig Steam Generator 104-E-01. The shifted gas is then cooled in the 20 psig Steam Generator 104-E-02. To further reduce the shifted gas temperature, it is cooled by air in 104-E-03 and by cooling water in 104-E-04. To prevent the formation of ammonium carbonates, which could plug the tubes, gas liquor is injected into 104-E-04.

After 104-E-04, the shifted gas is compressed by Booster Compressor 104-C-01 in order to overcome the pressure drop of Raw Gas Shift Unit 102. The compressed shifted gas is then cooled by 104-E-05 and combined with the cooled raw gas from Unit 103.

The gas liquor from the coolers and steam generators flows to Gas Liquor Separation Unit 107.

3.4.6 Gas Purification Unit 105 (PFD ZO-GEM-6900)

Purpose of the Unit is to remove the sulfur compounds and carbon dioxide from the raw gas to the desired levels required by the methanol conversion unit. Naphtha, hydrogen cyanide and water are also removed.

Technology Used

The selected Lurgi Rectisol Process purifies the raw gas by physical absorption using cold methanol as the absorption agent. The Rectisol process is currently in successful commercial operation. The application of this process is most economic at a high partial pressure of CO₂ in the feed gas.

Although a high selectivity of sulphur removal can be achieved to meet the requirements of the Claus sulphur recovery process, the non-selective route has been chosen using the Stretford sulphur recovery process. The Rectisol/Stretford combination is believed to be the most economic system for a low sulphur coal, based on previous studies for commercial-sized SNG plants.

The Naphtha and Methanol Recovery Section (NMR) of the Rectisol process has been developed to meet special requirements of the Lurgi Coal Gasification Process.

Process Description

The Refrigeration Unit 141 maintains the two temperature levels of -45°F and 32°F required for gas purification.

Absorber Section

The feed gas is cooled sequentially in 105-E-01 with synthesis gas, in 105-E-02 with + 32°F refrigerant, in 105-E-03 with synthesis gas and flash gases and in 105-E-04 with -45°F refrigerant. The feed gas, after cooling, enters the prewash section of Absorber 105-D-01 where it is washed with a small quantity of methanol to remove the naphtha, HCN, and water. The main section of the absorber consists of a low and a middle section, with an intermediate chilling loop, where the gas is scrubbed with flash regenerated methanol to remove the bulk of sulphur compounds and carbon dioxide. From the main section the gas flows to the fine wash section in the top of the absorber. In the fine wash section, the gas is scrubbed with hot regenerated methanol to remove the remaining sulphur compounds and carbon dioxide to the specified level for methanol synthesis. The gas then exits the unit by heat exchange with the feed gas, and the syngas flows to Methanol Synthesis Unit 110.

Regeneration Section

The rich methanol leaving the bottom of Absorber 105-D-01 is now regenerated in Flash Regenerator 105-D-02. The laden methanol is flashed in several steps down to a slight vacuum, where dissolved gases are released. Gas from the first flash stage is sent to Lock Gas Compressor 101-C-41 to recover the bulk of the co-absorbed CH₄, CO, and H₂. The other flash gases are sent to Sulphur Recovery Unit 106.

A portion of the bottoms of the flash regenerator becomes the semi-lean solution used in the middle section of the absorber, while the remainder is further regenerated in Hot Regenerator 105-D-03 by a steam heated reboiler. The fully regenerated methanol (lean methanol) is used in the top section of Absorber 105-D-01. The offgas leaving the hot regenerator is combined with the above described flash gases and sent to Sulphur Recovery Unit 106.

Naphtha and Methanol Recovery Section

The methanol from the prewash section of Absorber 105-D-01 is flashed in Prewash Flash Column 101-D-04 before it is sent to the naphtha and methanol recovery section, which is shown as a block on the PFD.

This block consists of: (1) Mixer-Settler Extractor for recovering of naphtha, (2) Azeotrope Tower for fine recovery of naphtha, and (3) Methanol Water Tower for recovering of the prewash methanol.

The extraction agent is boiler feed water, which is recovered from the bottom of the methanol water tower and sent to Waste Water Treatment Unit 135.

The recovered naphtha, which contains all of the organic sulphur compounds and about 50% of the HCN contained in the raw gas is sent to Naphtha Hydrotreating Unit 151.

The remaining 50% of the HCN will leave the NMR section as a HCN offgas which is recycled by the Lock Gas Compressor 101-C-41 to Raw Gas Shift Unit 102 for conversion to ammonia.

3.4.7 Sulphur Recovery Unit 106 (PFD ZO-GEM-6901)

Purpose of the Unit is to recover the sulphur from the various acid gases of the plant complex. The sulphur is recovered as elemental sulphur with a purity of 99.5%.

Technology Used

The Stretford Process which was developed by the British Gas Corp. is used to generate salable, solid sulphur from low concentration $\rm H_2S$ gases. (These gases are not suited for the Claus process).

The Stretford Process is an absorption process using a sodium carbonate solution with additives.

The overall chemical reaction including absorption and regeneration is written as:

$$2 \text{ H}_2\text{S} + \text{O}_2 \longrightarrow 2 \text{ H}_2\text{O} + 2 \text{ S}$$

Process Description

The feed gas is contacted countercurrently in Absorption Column 106-D-01 by the circulating Stretford solution. The H_2S -free gas exits the top of the absorber and goes to Unit 122 to be incinerated. It contains less than 10 ppm of H_2S . None of the COS in the feed gas, however, is absorbed.

The rich Stretford solution enters Reaction Chamber 106-D-02 which provides the time necessary for the completion of the chemical reaction. Then, the rich Stretford solution flows by gravity to Oxidizer 106-D-03, where it is contacted with air. In 106-D-03, the Stretford solution is oxidized for reuse, and the sulphur particles float to the top of the liquid as a froth.

The regenerated Stretford solution overflows from the oxidizer into Solution Pump Tank 106-F-01, and, after cooling, it is recycled back to the absorber.

The sulphur froth from the oxidizer flows by gravity to Pump Tank 106-F-02, from which it is pumped to Sulphur Vacuum Filter 106-F-03. From there it flows by gravity to Sulphur Melter 106-E-02 and on to Melted Sulphur Accumulator 106-F-04.

3.4.8 Gas Liquor Separation Unit 107 (PFD ZO-GEM-6902)

Purpose of the Unit is to separate by gravity the dusty tar, oil and co-absorbed gases from the various gas liquor streams.

Technology Used

The technology used has been developed by Lurgi for the special requirements of the Lurgi Coal Gasification Process.

Process Description

Dusty Gas Liquor

The dusty gas liquor coming from the waste heat boiler in Unit 101 and from 103-F-04 in Unit 103 is cooled in 107-E-01 and mixed with the cooled gas liquor from Units 103 and 104. The mixture then flows into Tar Separator 107-F-01 via Expansion Vessel 107-F-02. In the tar separator, tar is settled out in the conical bottom section and pumped to Tank 107-F-10.

The gas liquor leaving 107-F-01 flows by gravity to Oil Separator 107-F-04. The oil separated in 107-F-04 flows by gravity to Oil Tank 107-F-08. The gas liquor flows by gravity to Surge Tank 107-F-07.

Oily Gas Liquor

The oily gas liquor coming from Heat Exchangers 104-E-01 and 02 of Shifted Gas Cooling Unit 104 is cooled and then mixed with the gas liquor coming from Gas Purification Unit 105. This combined stream flows by gravity, via Expansion Vessel 107-F-03, into Separator 107-F-05, where the separated oil flows by gravity to Oil Tank 107-F-08.

<u>Gas</u> <u>Liquor</u>

The gas liquor leaving Separator 107-F-05 flows by gravity to Final Separator 107-F-06, where it is combined with the gas liquor from Surge Tank 107-F-07.

The gas liquor separated in 107-F-06 flows by gravity to Final Surge Tank 107-F-09, and from there, it is pumped to Phenol Recovery Unit 108 for further treating. The oil recovered in 107-F-06 flows by gravity to Oil Tank 107-F-08.

Tar and Oil

The tar is burned in Boiler Unit 122. The oil is fuel for Superheaters 123 and 124. The various expansion gases are scrubbed in Ammonia Scrubber 107-D-01 for ammonia recovery and then sent to Sulphur Recovery Unit 106.

3.4.9 Phenol Recovery Unit 108 (PFD ZO-GEM-6903)

<u>Purpose of the Unit</u> is to recover phenolic components from the gas liquor.

Technology Used

For the removal of phenols, the Lurgi Phenosolvan Process is provided. It is a solvent extraction process using di-isopropyl ether as the solvent. The Phenosolvan Process has been commercially used in syngas and towngas plants based on Lurgi Pressure Coal Gasification and is under consideration for the proposed U.S. SNG plants.

Process Description

The gas liquor coming from Gas Liquor Separation Unit 107 flows to Sand Filters 108-F-02, where any remaining solids are removed. The filters are backwashed with cleaned gas liquor and the mud liquor from the filters is returned to Unit 107. From the sand filters, the cleaned gas liquor flows to Saturation Column 108-D-01, where it is saturated with CO2 in order to increase the efficiency of extraction.

The saturated gas liquor flows by gravity to the multi-stage, mixer settler type extractor, 108-D-02, to be divided into a phenolic-solvent phase and a dephenolized-gas-liquor phase.

The dephenolized gas liquor flows to Raffinate Settler 108-F-06 for the purpose of recovering the remaining solvent. From there the gas liquor is pumped to Ammonia Recovery Unit 109.

The phenolic-solvent phase from the extractor flows, via Extract Settler 108-F-07, to Extract Receiver 108-F-08. It then is pumped, via Partial-Feed Evaporator 108-E-02, into Solvent Regenerator 108-D-04. In the overhead of this column, the bulk of the solvent is recovered and pumped back to Extractor 108-D-02. The bottom product is a phenol-solvent mixture which is pumped into Phenol Tower 108-D-05, where the remaining solvent is stripped out using live steam.

The overhead solvent-water mixture of 108-D-05 is returned to Extract Settler 108-F-07. The bottom product of phenols is pumped to Main Boiler Unit 122 to be burned.

A small portion of the phenols is recycled, partly for recovering solvent from the offgases in Vent Scrubber 108-D-06 and partly for recovering solvent from Unit 109 offgases in Phenol Solvent Scrubber 108-D-03. In the upper part of the phenol solvent scrubber, these offgases are scrubbed by waste water for phenol recovery, before being sent to Sulphur Recovery Unit 106.

3.4.10 Ammonia Recovery Unit 109 (PFD ZO-GEM-6904)

Purpose of the Unit is to recover the ammonia from the gas liquor before final treatment for use as cooling water make-up.

Technology Used

The technology used has been jointly developed by Chemie Linz and Lurgi, mainly for the purpose of removing ammonia from the Lurgi gasifier gas liquor. The product is a salable ammonia of either agriculture or chemical grade.

Ammonia recovery in the Chemie Linz/Lurgi Process is accomplished by the use of stripping and scrubbing techniques without the addition of chemicals or solvents.

Process Description

After heating, the gas liquor enters Deacidifier 109-D-01, where the remaining gases and phenosolvan solvent are stripped out by reboiler steam. The gases leaving the stripper are scrubbed with cooled waste water under elevated pressure to remove ammonia. The stripped gases are sent back to Phenol Recovery Unit 108. The gas liquor containing the ammonia leaves the bottom of the deacidifier and is pumped after cooling to Total Stripper 109-D-02, where all the ammonia and the remaining gases are stripped out by reboiler steam under atmospheric pressure.

The bottom product of the total stripper is the clean gas liquor containing less than 100 ppm free ammonia. It is sent after cooling to Waste Water Treatment Unit 135 for final treating.

The overhead vapors from the total stripper are partially condensed in the bottom of Acid Gas Scrubber 109-D-03 in order to increase the ammonia concentration. The condensate is refluxed back to the total stripper.

In Acid Gas Scrubber 109-D-03, the vapors are scrubbed by a recycled aqueous ammonia solution from the process. The heats of reaction and condensation are removed by cooled pump-arounds. The bottom stream of the acid gas scrubber, which contains free ammonia and ammonium salts, is pumped by 109-G-05 to Ammonia Stripper 109-D-04. The bottoms of the ammonia stripper, containing a highly concentrated stoichiometric ammonium salt solution, is recycled back to 109-D-01. The stripped ammonia from the ammonia stripper overhead flows to the acid gas scrubber for recovery.

The ammonia vapor flowing overhead from Acid Gas Scrubber 109-D-03 is condensed and dried by compressing and cooling in the Ammonia Liquefying and Drying (ALD) Section before being sent to storage.

A small liquid stream containing water and organic substances is removed in the ALD Section and sent to the main waste water stream.

3.4.11 Methanol Synthesis Unit 110 (PFD ZO-GEM-6905)

Purpose of the Unit is to produce methanol from the purified synthesis gas.

Technology Used

For the production of methanol, the Lurgi Low Pressure Methanol Synthesis Process has been selected. This process offers maximum safe operation due to its highly developed reactor design and has wide commercial usage.

The (H_2 + CO) conversion is 85.2 mol. %.

Process Description

The synthesis gas is compressed, Syngas Compressor 110-C-01, to about 1100 psig and mixed with the recycle gas stream. The Recycle Gas Compressor 110-C-02 compresses the mixture to overcome the pressure losses of the recycle loop. This loop consists of Heat Exchanger 110-E-03 (heating syngas/recycle gas against methanol/recycle gas), Reactor 110-D-01. Condensers 110-E-04 and 05, and KO Drum 110-F-01, in which the unconverted gas is separated for recycling.

The high pressure methanol liquid is expanded into Expansion Vessel 110-F-03 for degassing; the methanol is sent to Methanol Conversion Unit 150.

The expansion gas of 110-F-03 is recompressed in H_2 Recovery Unit 111 and sent to Methanation Unit 112.

To eliminate the concentration of inerts in the recycle gas, a portion of the recycle gas is purged continuously and fed to Methanation Unit 112.

3.4.12 H₂ Recovery Unit 111 (PFD ZO-GEM-6908)

Purpose of the Unit is to recover hydrogen for hydrotreating the gasifier naphtha. The hydrogen source is a slip stream from the methanol unit purge gas.

Technology Used

Because of the relatively high ${\rm CO}_2$ content of the feedgas, the Pressure Swing Process of Union Carbide Corp. is used.

Process Description

The main equipment of the unit are four parallel pressure-swing absorbers, 111-D-01; one is in operation and three are in regeneration. During operation, essentially all of the non-hydrogen components and a portion of the hydrogen are absorbed. The remaining hydrogen leaves the absorber at a purity of over 98%.

Regeneration is by pressure reduction in 3-stages with the final pressure being nearly atmospheric. The regeneration cycle is controlled automatically by motor values. An absorption/regeneration cycle requires several minutes.

The desorbed gases, called pressure-swing offgases, are recompressed by Compressor 111-C-01 back into the methanol unit purge gas stream before being changed to Methanation Unit 112. Gas Holder 111-F-01 on the suction side of the compressor, is necessary for buffering the non-static, pressure-swing off gas flow from the regenerating absorbers. Compressor 111-C-01 also recompresses the expansion gas from Unit 110.

3.4.13 Methanation Unit 112 (PFD ZO-GEM-6906)

Purpose of the Unit is the production of SNG meeting the specifications for compatibility with existing pipeline gases. In addition, the CO content must be lowered to less than 0.1%.

The principal reactions in methanation are described by the following equations:

$$CO_2 + 4 H_2 \longrightarrow CH_4 + 2 H_2O$$
 exothermic $CO + 3 H_2 \longrightarrow CH_4 + H_2O$ exothermic $CO + H_2O \longrightarrow CO_2 + H_2$

Other minor reactions include the hydrogenation of ethylene to ethane and the cracking of ethane to methane.

Technology Used

The Lurgi Methanation Process is used. This process is the first process developed for the methanation of high CO concentration gases, and has been included in the proposed commercial U.S. SNG plants.

Process Description

The feed gas is made up of the purge and expansion gases from Methanol Synthesis Unit 110.

The methanation unit consists of two down-flow, fixed-bed reactors in series. The feed gas is heated in 112-E-06 and 03 against the second reactor, 112-D-02, product. Steam is injected in the feed gas and the gas is also diluted with a portion of the methanated gas from the first reactor, 112-D-01. The dilution gas is compressed by Recycle Compressor 112-C-01, after having been cooled in 112-E-01 and 02. MP steam is generated in 112-E-01.

The net reactor effluent from the first reactor flows to the second, or clean-up, reactor in which final methanation takes place. The clean-up reactor effluent is heat exchanged against the feed and cooled in Exchangers 112-E-04 and 05.

Process water condensed from the reactor effluent stream is collected and routed to BFW Preparation Unit 131.

The methanated gas leaves the unit for further treating in CO_2 Removal Unit 113.

3.4.14 CO₂ Removal Unit 113 (PFD ZO-GEM-6907)

Purpose of the Unit is to lower the $\rm CO_2$ content in the SNG to about 0.5%, thereby improving its quality.

Technology Used

The Amine Guard Process of Union Carbide Corp. uses a monoethanol amine solution as the absorbant. This process offers better economics than a conventionally designed MEA wash system and provides complete protection against corrosion. A MEA process was chosen because the specified low final CO₂ content does not allow the use of a hot potassium carbonate process and the partial pressure of CO₂ in the feed gas is too low for economical use of a physical absorption process, such as Rectisol.

Process Description

The Methanation Unit 112 product gas and the offgases of Fractionation Unit 152 are charged to Absorber 113-D-01 in which the CO₂ is washed out by counter-current flow with lean MEA solution. In the top of the absorber, the gas is scrubbed with a small flow of BFW to recover trace amounts of MEA. The purified gas then flows to SNG Drying Unit 114.

The absorber bottoms product (rich MEA solution) is expanded after heat exchange in 113-E-01 into MEA Regenerator 113-D-02, where the CO₂ and other co-absorbed compounds are stripped from the MEA solution. The steam in the regenerator overhead is condensed in Condensers 113-E-04 and 05, and the remaining offgases are sent to Boiler Unit 122 for incineration. The steam condensate is refluxed to the top of the regenerator. The lean solution from the bottom of the regenerator is pumped back to the Absorber 113-D-01, after being cooled in 113-E-01, 02 and 03.

The offgases of Fractionation Unit 152 are compressed to the SNG pressure by Light Gas Compressor 113-C-01. After compression, the gas is cooled and the heavier hydrocarbons, which condense, are returned to Unit 152.

3.4.15 SNG Drying Unit 114 (PFD ZO-GEM-6907)

Purpose of the Unit is to dry the wet SNG to a water content of 4 lb/MMSCF before its introduction into the SNG pipeline system.

Technology Used

The TEG Wash Process, a commercial process for drying natural gas, is used.

Process Description

The drying agent is a mixture of triethylene glycol (TEG) and other ethylene glycols.

The SNG is contacted countercurrently in Water Absorber 114-D-01 with lean TEG. The water-rich TEG flows from the absorber to TEG Regenerator 114-D-02, which is heated by fuel gas. The steam stripped from the TEG is discharged to the atmosphere. The small reflux stream required is condensed within the vent tube by air cooling.

The regenerated TEG is stored in 114-F-01, where it is cooled by the rich TEG, before being pumped into the top of Water Absorber 114-D-01.

3.4.16 Methanol Conversion Unit 150 (PFD ZO-GEM-6915)

Purpose of the Unit is to dehydrate crude methanol to LPG and gasoline hydrocarbons which can be marketed directly without further processing.

Technology Used

Mobil has demonstrated a simple catalytic process to dehydrate methanol to the stoichiometric yield of hydrocarbons (44%) and water (56%).

This development has been reported under ERDA Contract No. E(49-18)-1773, and in references cited. The hydrocarbons are predominately in the gasoline boiling range (C_4 to C_{10}), and the gasoline is chemically conventional consisting of highly branched paraffins (51%), highly branched olefins (13%), naphthenes (8%) and aromatics (28%). Its unleaded research octane number (RON) ranges from 90 to 100. Essentially, no hydrocarbons larger than C_{10} and no oxygenates are produced.

Small amounts of CO, CO₂ and coke and trace amounts of formic acid and acetone in the water product are formed as by-products. After fourteen days on stream, enough coke accumulates on the catalyst to require regeneration. The catalyst is regenerated by coke combustion in a controlled manner to limit the maximum temperature to 900°F. Since the catalyst converts other oxygenates and is tolerant to water, crude methanol without any purification can be charged directly, thereby simplifying the methanol synthesis.

From laboratory investigations, the reaction path from methanol to hydrocarbons appears to be reasonably well represented by:

2 CH₃OH
$$\xrightarrow{-\text{H}_2\text{O}}$$
 CH₃OCH₃ $\xrightarrow{-\text{H}_2\text{O}}$ = = paraffins aromatics cycloparaffins

alcohol ether olefin

The reaction is highly exothermic with the heat of reaction being about 740 Btu/lb of methanol. Therefore, the principal problem in designing a reactor system is heat removal. In the fixed bed reactor system, this problem is minimized by dividing the above overall reaction (and reactor system) into two steps. In the first, methanol is partially dehydrogenated to form an equilibrium mixture of methanol, dimethyl ether and water. About 20% of the heat of reaction is released in this first step without any recycle for temperature control. In the second step, where hydrocarbon conversion takes place, a large recycle gas stream (from 6/1 to 9/1 ratio) is used to limit the temperature rise across the bed to about 125°F.

While other systems, such as quenched reactor, tubular heat exchange reactor, or fluidized bed reactor could be designed, the fixed bed, gas recycle system has been well demonstrated and is readily scaleable to higher throughputs.

The commercial process design conditions, yields and catalyst properties used in this study are shown in Tables 3.4.1, 3.4.2 and 3.4.3, respectively. These data were developed from ERDA Contract No. E(49-18)-1773 and represent the best estimate at this time of a commercial fixed bed operation.

TABLE 3.4.1

PROCESS DESIGN CONDITIONS FOR FIXED BED METHANOL CONVERSION UNIT 150

Nominal Operating Conditions I.

Feed Composition (See Material Balance Stream 37.)

18,360.3 lb. mol/hr. Methanol 1,382.4 lb. mol/hr. Water 42.5 lb. mol/hr. Others

19,785.2 lb. mol/hr. (52,585 B/SD)

Base Yields (See following Table 3.4.2.)*

Reactor Conditions

First Reactors (DME)

Pressure, Inlet Temperature, Inlet Temperature, Outlet Space Velocity

Catalyst Estimated Ultimate Catalyst Life

6 lb. fresh feed/hr/lb. catalyst Mobil first stage catalyst

1 vear

315 psig

566^OF

768^OF

Second Reactors (M-Gasoline)

Pressure, Inlet Temperature, Inlet Temperature, Outlet Space Velocity

Molar Recycle Ratio Catalyst Estimated On-Stream Time Before Regeneration Estimated Ultimate Catalyst Life

300 psig 625^OF 752°F 1.84 lb. fresh feed/hr/lb. catalyst

7.5/1 (based on fresh feed) Mobil second stage catalyst

14 days

1 year

Regeneration Conditions II.

Aged Catalyst Coke Level (Second Reactors) 30 wt. % on catalyst (Controlled oxygen content and controlled maximum temperature procedure similar to conventional petroleum naphtha pretreater/reformer regeneration is employed.)

TABLE 3.4.1 (continued)

III. Metallurgy

The basic metallurgy for the Methanol Conversion Unit 150 is carbon steel. Reactors have a 304SS internal liner over 3" of refractory to minimize the effects of any possible temperature excursions. The high pressure separator, 150-F-01 in process flow diagram ZO-GEM-6915, has a PVC lining to protect against the acid water (pH=3.5). The tubes of Exchangers 150-E-01, 06 and 07 are 316SS to protect from acid water corrosion. In addition, the shell of Exchanger 150-E-01 is carbon steel with 316SS lining. The acid water lines are PVC lined.

* Yields are the average over 14 days of operation before catalyst regeneration. Although yield shifts are significant during the 14 days (see Reference 2), the 5-reactor system, Unit 150 design basis, minimizes the yield shift effects.

TABLE 3.4.2

METHANOL CONVERSION UNIT 150 BASE FEED AND PRODUCT COMPOSITION (Basis: 100 Lb-Mole Methanol in Feed)

Component Names	Feed	Product
Galac (a.g. CH	.000	.128
Coke (as CH _{0.8})	.000	.129
Acetone	.000	,163
Formic Acid	100.000	.000
Methanol	.000	.000
Dimethylether Water	7.529	106.951
Carbon Monoxide	.000	.017
Carbon Dioxide	.000	.053
	.000	.040
Hydrogen Methane	.000	.746
	.000	.193
Ethane	.000	.018
Ethene	.000	1.474
Propane	.000	.064
Propene	.000	.665
N-Butane I-Butane	.000	2.155
Butenes	.000	.270
N-Pentane	.000	.268
I-Pentanes	.000	2.353
Pentenes	.000	.435
Cyclopentane	.000	.047
Methylcyclopentane	.000	.214
N-Hexane	.000	.113
I-Hexanes	.000	1.991
Hexenes	.000	.297
Methylcyclohexane	.000	.062
N-Heptane	.000	.026
I-Heptanes	.000	.786
Heptenes	.000	.292
1,3-Dicyclopentane, cis	.000	.233
I-Octanes	.000	.228
Octenes	.000	.301
N-Propylcyclopentane	.000	.299
N-Nonane	.000	.015
I-Nonanes	.000	.084
Nonenes	.000	.116
N-Butylcyclopentane	.000	.071
I-Decanes	.000	.024
Decenes	.000	.045
Benzene	.000	.280
Toluene	.000	.070
Ethylbenzene	.000	.876
m- + p-Xylenes	.000	.240
o-Xvlene	.000	.818
1.2.4-Trimethylbenzene	.000	.034
1,3,5-Trimethylbenzene	.000	.004

TABLE 3.4.2 (continued)

Component Names	<u>Feed</u>	Product
p-Ethyltoluene I-Propylbenzene 1,2,4,5-Tetramethylbenzene 1,2,3,5-Tetramethylbenzene 1,2,3,4-Tetramethylbenzene p-Diethylbenzene Penta-Methylbenzene 2-Methylnaphthalene Total Lb-Mole Weight (lbs)	.000 .000 .000 .000 .000 .000 .000 107.529 3,339.846	.292 .014 .436 .063 .023 .198 .068 .017 124.832 3,339.846

TABLE 3.4.3

METHANOL CONVERSION UNIT 150 CATALYST PROPERTIES

	Mobil Catalysts	
	First Stage	Second Stage
Туре	Extrudate	Extrudate
Geometry	1/16" x 3/16"	1/16" x 3/16"
Bulk Density	35 lb/cu ft	36 lb/cu ft
Crush Strength	50 lb/in	33 lb/in
Cost	*	*

^{*} Since Mobil has no specific commercial experience in making the second stage catalyst in the amounts required for a major syn fuels industry, an accurate cost cannot be given at this time. We are sure, however, that its cost will contribute only a minor portion to the total gasoline cost and, therefore, its addition at a later time will not alter any current economic evaluation study conclusions.

Process Description

Depressured crude methanol, pumped (150-G-01) to reaction pressure and vaporized in Heat Exchangers 150-E-01 and 02, flows to DME Reactor 150-D-01, where it is catalytically converted to an equilibrium mixture of methanol, dimethylether and water. Inlet operating conditions are 315 psig and 566°F.

The equilibrium mixture then flows to the M-Gasoline reactors (150-D-02), of which five are operating and one is undergoing regeneration. A gas recycle stream from Separator 150-F-01, after compression (150-C-01) and heat exchanged (150-E-04 and 05) against the reactor effluent, is fed along with the equilibrium mixture into the M-Gasoline reactors. The recycle stream controls the temperature rise. Its temperature is maintained to give a reactor inlet temperature of 625°F.

Cooling of Reactor 150-D-02 effluent occurs as follows: (1) Steam Generator 150-E-03, (2) the recycle stream and methanol feed heat exchangers, (3) BFW Heat Exchanger 150-E-06 and (4) Air Trim Cooler 150-E-07. Separator 150-F-01 operating conditions are 248 psig and 155°F. The purge gas flow is limited to that only required for control. The liquid hydrocarbon product is pumped (150-G-02) to Unit 152. A small amount, five gpm, of hydrocarbon product is recycled from the separator to the inlet of BFW Exchanger 150-E-06 for durene crystallization control.

Regeneration of the M-Gasoline reactors takes place about once every 14 days. After a reactor is taken off line, it is depressured and purged with nitrogen until there is less than about 1 to 5 vol. % of hydrocarbons present. Then the reactor is pressured to about 150 psig with nitrogen flow through Recycle Compressor 150-C-02. The temperature is maintained at 650°F by use of Furnace 150-B-01. Air is introduced slowly until oxygen content reaches about 1 vol. %. The maximum catalyst bed temperature is maintained at less than 850°F. When the oxygen content in the recycle gas becomes higher than 0.1 vol. %, the inlet temperature is slowly raised while maintaining a maximum temperature of 900°F in the bed. The hot spent regeneration gas is cooled by heat exchange with the fresh regeneration gas (150-E-08) and Fan Cooler 150-E-09. Condensed water is removed via Drum 150-F-02.

3.4.17 Naphtha Hydrotreating Unit 151 (PFD ZO-GEM-6908)

Purpose of the Unit is to obtain a clean, odor free, stable material from the raw gasifier naphtha for gasoline pool blending. Reaction conditions chosen will substantially saturate the raw naphtha olefins with little aromatic-ring hydrogenation, thereby reducing the octane rating as little as possible.

Technology Used

Hydrotreating is a versatile process in which the quality of a wide variety of petroleum materials can be improved with the proper choice of catalyst and operating conditions. It is used commercially to remove impurities such as sulfur, nitrogen and oxygen, to saturate olefinic double-bonds and to improve the odor, color, stability and burning characteristics. Generally, catalysts and conditions employed result in as little as possible carbonbond cracking. Pressures range from 200 to 1,000 psig, and temperatures from 400 to 750°F. Typical liquid hourly space velocities are from 1 to 10 volume of oil per hour per volume of catalyst. Hydrogen-rich gas recycle may or may not be used depending upon the severity of operation. Since hydrogenation reactions are exothermic, multi-bed reactors with a hydrogen recycle quench are used to control reactor temperatures when the hydrogen consumption is large. A large number of catalysts have been developed. Various colbalt-molybdena catalysts with alumina supports; however, account for the bulk of the applications. This catalyst is oxygen regenerable, and quite rugged in nature. Commercial processes are licensed by BP Trading, IFP, Exxon, Gulf, Shell, Union Oil and Standard Oil (Indiana).

Process Description

The raw naphtha is pumped (151-G-01) to reactor pressure, heat exchanged with the reactor effluent in Exchanger 151-E-01, heated to reactor temperature in Fired Heater 151-B-01, and charged to Reactor 151-D-01. A portion of the hydrogen feed is mixed and heated with the naphtha; the remainder is used as a cold quench for temperature control in the multibed reactor. The reactor effluent is further cooled (151-E-02 and 03) before flushing in Separator 151-F-01. A small BFW flushing stream is added before 151-E-01.

The hydrogen-rich vapor passes first through an amine tower for hydrogen sulfide control, and then split into recycle and purge gas streams. The purge gas is incinerated in Boiler Unit 122. After compressing (151-C-01), the recycle and hydrogen make-up are combined before separating into the hydrogen feed and quench streams.

The separator liquid product is charged to Stabilizer 151-D-05. The light gas/hydrogen sulfide overhead products are sent to Sulfur Recovery Unit 106. Condensed Accumulator 151-F-03 liquids are refluxed. Cooled (151-E-06 and 07) stabilized naphtha is sent to offsite Blending Unit 154. A small sour water stream is also obtained from Separator 151-F-01.

Regeneration systems are provided for Reactor 151-D-01 and the rich amine solution from Absorber 151-D-02.

3.4.18 Fractionation Unit 152 (PFD ZO-GEM-6916)

Purpose of the Unit is to obtain a low C2 concentration alkylate unit charge and a stabilized gasoline for pool blending.

Process Description

The high pressure condensate (stream 58) from the SNG train is flashed in Drum 150-F-01. The depressured liquid and the hydrocarbon product from Unit 150 are fed to Deethanizer 152-D-01. The ethane-rich tower overhead and the flash drum vapors are sent to Unit 113 in the SNG train. The deethanizer bottoms after being cooled in Deethanizer Side Reboiler 152-E-02 is fed to Stabilizer 152-D-02. Products are cooled alkylation feed (overhead) and stabilized gasoline (bottoms). Both towers employ steam reboilers (152-E-01 and 05).

3.4.19 Alkylation Unit 153 (PFD ZO-GEM-6916)

Purpose of the Unit is to increase the gasoline yield by the reaction between iso-butane and butene/propene and to yield commercial grade propane and butane liquified petroleum gases.

Technology Used

Alkylation, in petroleum refiring, normally means the reaction of butene and/or projene with iso-butane to produce a higher molecular weight iso-paraffin. For example:

$$C_4H_{10} + C_4H_8 \longrightarrow C_8H_{18}$$

i-Butane n-Butene i-Octane

Alkylation can occur without catalysts, but commercially, acid catalysts are used with sulfuric acid and hydrogen flouride being the two most important. Unlike the simple reaction above, a mixture of isomers is obtained. In addition, polymerization occurs, and "sludge" is yielded requiring catalyst regeneration. Alkylation, highly exothermic, liberates 600 to 700 Btu/lb of iso-butane. Commercial processes are licensed by Phillips Petroleum, UOP Process and Stretford Engineering.

Process Description

The iso-butane/olefin fresh feed is first mixed with the cooled HF acid/iso-butane recycle streams (153-E-16), and then, this mixture is charged to the combined Reactor/Settler 153-D-01. The reactor effluent - inert hydrocarbons, excess iso-butane and alkylate - after heating (153-E-01 and 02) is fed to Deisobutanizer 153-D-02. Products are a C3/i-C4 overhead, mixed-butanes side-cut and alkylate bottoms. The overhead mixture, after condensing in Condensers 153-E-08 and 09, is pumped (153-G-01) into Depropanizer 153-D-03 for separation into the C3 LPG product and excess iso-butane recycle.

The hydrogen fluoride is recycled from Reactor/Settler 153-D-01. A continuous slip stream from the acid recycle is purified in a conventional HF rerun unit (not shown).

Not shown on the simplified process flow diagram are a HF stripper in the C_3 LPG stream and caustic washes in the product streams to remove all traces of acid.

The capacities of the principal process units have been summarized below in conventional flow rates:

	Input Output	1 1,755 MMSCF 742 MMSCF 53.3 M Bb1 25.7 M Bb1 - - (750 Bb1/SD alkylate) 148 MMSCF
rate	ty,	1 (750
[flow	-Capaci	MT coa MMSCF MMSCF MMSCF M Bbl M Bbl M Bbl M Bbl
tiona	In	22.8 331 1,062 742 52.6 1.3 25.7 25.7 213
been summarized below in conventional flow rates	Лате	Gasification Raw Gas Shift Gas Purification 1 Methanol Synthesis Methanol Conversion Naphtha Hydrotreating Fractionation Alkylation SNG Train
peen sum	Unit No.	101 102 105 110 150 151 151 153

































