4.0 MTG, FRACTIONATION, ALKYLATION, HEAVY GASOLINE TREATER

4.1 PROCESS DESCRIPTION

The MTG Unit (Unit 86) dehydrates crude methanol produced in Methanol Synthesis Unit (Unit 84) to produce a hydrocarbon stream containing LPG and gasoline blending components. The hydrocarbon stream produced in the MTG Unit is fractionated in a Fractionation Unit (Unit 87) to recover LPG, a C4/C5 stream to be fed to an alkylation unit, a light gasoline fraction and a heavy gasoline fraction. The light gasoline is added to the gasoline pool and the heavy gasoline is treated to reduce the durene content. Then, the heavy gasoline is also added to the gasoline pool. Single trains are used for all the above units.

4.1.1 Mobil MTG (Unit 86)

This process is licensed by Mobil Oil. It converts methanol into gasoline and lighter products. In the absence of a secrecy agreement with Mobil Oil, a process flow diagram with a material balance is not available. However, unit concepts have been developed by Fluor on the basis of in-house data from other similar projects.

The conversion of methanol to gasoline hydrocarbons is a catalytic process to dehydrate methanol to produce hydrocarbons (44 percent) and Water (56 percent). The hydrocarbons are predominantly in the gasoline boiling range (C_4 to C_{10}) and contain a high percentage of branched paraffins and aromatics.

Crude methanol from the methanol synthesis units is stored in tankage and subsequently fed to the MTG Unit. The storage tank provides the surge capacity to maintain the plant on-stream factor. The methanol feed to MTG is vaporized in a feed-effluent heat exchanger and then the vapors are fed to the DME (Dimethyl ether) reactor. Two DME reactors are provided. The conversion of methanol to gasoline takes place in two stages. In the first stage the methanol is converted to DME and in the second stage the DME is converted to gasoline. The reaction are as follows:

$$2\ CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$$

$$XCH_3\ O\ CH_3 \longrightarrow (2CH_2)_X + XH_2O$$

Small quantities of CO and CO_2 are produced by the process. In addition, trace quantities of organic acids and ketones are also produced.

4.1.1 Mobil MTG (Unit 86) (Continued)

The DME from the DME reactors is fed to the MTG converters. A total of five converters is provided, four on-stream and one on-regeneration. The MTG reactor effluent is cooled and then it is fed to the Fractionation Unit (Unit 87).

The reaction of methanol to produce gasoline is highly exothermic. Approximately 20 percent of the exothermic heat is released in the DME reactors and the remainder is released in the MTG reactors. The heat release in the DME reactor does not create a temperature control problem in that unit. The greater heat release in the MTG reactors requires mixing the feed with partially cooled reactor products to limit the overall temperature rise in the reactor. During the MTG reactions, carbon is deposited on the catalyst. This carbon must be removed periodically. For this reason a spare reactor train was included in the Tri-State design. Regeneration schedules for these reactors must be established to provide a consistent quality of products from the unit.

Product Separation

The effluent from the conversion reactors is cooled in heat exchangers and finally in water coolers to approximately 100°F before entering the product separator. Condensed products enter the horizontal separator drum where three phases are separated. Acidic waste water is removed and routed to the waste water treatment system. The liquid hydrocarbon product is pumped to a storage tank, which will feed the Fractionation Unit (Unit 87).

The major portion of the gas separated from the three phase separator will be recycled to the conversion reactor after necessary compression and preheating. A small portion of the gas which is over the recycle requirement will be chilled to recover propane, butane, and pentane hydrocarbons in the liquid phase, which combined with the main liquid hydrocarbons product are fed to the Fractionation Unit. The residual gas will be used as fuel gas in the plant.

Catalyst Regeneration

Carbon deposition on the DME catalyst is slow. Only infrequent regeneration of this catalyst is required. Regeneration of this catalyst generally follows the procedures for regeneration of the MTG catalyst. The specific details of this regeneration are proprietary. A secrecy agreement is required before the details of the regeneration can be revealed.

4.1.1 Mobil MTG (Unit 86) (Continued)

Coke formation on the conversion reactors catalyst will require regeneration every two weeks. There are five conversion reactors installed for the process. A continuous regeneration schedule with four reactors in operation and one in regeneration will be used to meet this requirement. Zeolite catalyst for regeneration will contain about 30 percent by wt. of cake deposited. A specific regeneration procedure for controlled combustion of the coke using controlled oxygen content of the oxidizing agent (N_2 plus air) and controlled temperature will be practiced according to catalyst vendor's recommendations. Specific details of this regeneration requires secrecy agreement before details can be revealed.

4.1.2 Unit 87 - Gasoline Fractionation

A single distillation train consisting of a deethanizer, depropanizer, depentanizer, and a gasoline splitter will be used to fractionate the liquid hydrocarbon product from the MTG Unit (Unit 86) into separate streams. These streams are: LPG, light gasoline, fuel gas, C_4/C_5's for the HF Alkylation (Unit 88) and heavy gasoline for the heavy gasoline treater (Unit 89). A process flow scheme is attached.

The following process steps are similarly numbered on the attached process flow scheme.

1. Crude gasoline product from MTG Unit will be sent to the deethanizer column, where ethane and lighter hydrocarbons are separated as overhead product.

2. The overhead vapor will be partially condensed and separated in a reflux drum.

3. Condensed liquid hydrocarbons will be sent back to the column as reflux.

4. Condensed water will be removed and sent for waste water treatment.

5. The vapor will flow to the fuel gas header.

6. The bottoms from the Deethanizer will flow to the Depentanizer for removal of pentane.

7. Pentane is an overhead product.

8. The overhead from the Depentanizer is sent to a Depropanizer.

4.1.2 Unit 87 - Gasoline Fractionation (Continued)

9. The overhead stream from the Depropanizer is cooled and collected in a reflux drum.

10. Part of the condensed liquid is used a reflux and the remaining part is collected as LPG- product.

11. The bottoms from Depropanizer contain mixed C_4/C_5's and are sent to HF Alkylation Unit (Unit 88).

12. The bottoms from Depentanizer flow to the Gasoline Splitter.

13. Light gasoline is an overhead product.

14. Heavy gasoline is a bottom product. The bottoms from the Gasoline Splitter are sent to the Heavy Gasoline Treater (Unit 89) for reducing durene content.

4.1.3 Unit 88 - HF Alkylation

The bottoms and stream from the Depropanizer in the MTG Fractionation Unit contains a mixed C_4/C_5 stream. This is the feed to the HF Alkylation Unit. Ordinarily the C_5's would be left in the light gasoline; however, with MTG gasoline, the C_5's must be removed and alkylated. The C_5's cause a volatility problem for the gasoline pool.

Alkylating a C_4/C_5 stream is less common than alkylating a C_4 or a C_3/C_4 stream. The alkylation process is used for combining an isoparaffin with an olefin, or olefin mixtures, to form a highly branched high octane paraffinic product. For example, alkylating isobutane with butene produces isooctanes with an octane rating approaching 100. With amylenes in the feed the octane will be a point or two lower than it would be with butene.

At least two licensors offer the HF Alkylation process. Both Phillips Oil Company and UOP have the technological background to license this process. Details of both processes are proprietary. A licensing agreement is needed to obtain detailed information. The attached flow diagram is a simplified version of the process.

The mixed C_4/C_5 stream is first dried in D-1 to remove the water that is present. Any water present after the acid is introduced into the reactor results in a corrosive environment. With the water removed, the unit can be constructed from carbon steel. The dried hydrocarbon feed is mixed with recycle hydrocarbons and HF acid and fed into

4.1.3 Unit 88 - HF Alkylation (Continued)

reactor R-1. The effluent from the reactor is fed to a settler where the hydrocarbon and acid phases separate. The hydrocarbon lighter phase is fed to the isostripper and the heavy acid phase is split. A portion of the acid phase is recycled back to reactor R-1 and the remainder is fed to the regenerator R-2. The heavy polymer is separated from the acid in the regenerator. The acid phase is recycled back to the reactor. The heavy polymer can be used in the fired reboiler of the isostripper or it can be incinerated elsewhere.

The Isostripper V-1 is the main fractionator for the Alkylation Unit. Reaction product hydrocarbons from reactor R-1 are fed into this unit to recover:

1. Isobutane in the overhead stream
2. Alkylate from the column bottoms
3. A side cut of nC_4/C_5
4. Isobutane recycle from the overhead stream

The overhead product Isobutane is fed to a HF stripper V-2. In this column residual HF is stripped and recycled back to the reactor R-1 thru the isostripper overhead condenser/accumulator system.

4.1.4 Unit 89 - Heavy Gasoline Treater

The heavy bottoms from the gasoline splitter in the Fractionation Unit (Unit 87) contain most of the durene produced in the MTG conversion process. This durene content is above the upper limit for gasoline, and would lead to carburetor problems in cold weather. The durene content is reduced to acceptable levels in this unit.

This process is licensed by Mobil Oil Corporation. Details of the process are not available without secrecy agreements. Even though the unit may require hydrogen, it is not a hydrotreater. A process flow diagram with a material balance is not available. The only work, performed by Fluor, on this unit consisted of ratioing feeds and products to obtain cost information from similar projects.

4.2 FLOW SHEETS

Simplified process flow sheets for Unit 87 - MTG Fractionation and Unit 88 - HF Alkylation are attached. The remaining process flow sheets are proprietary with the process developer.

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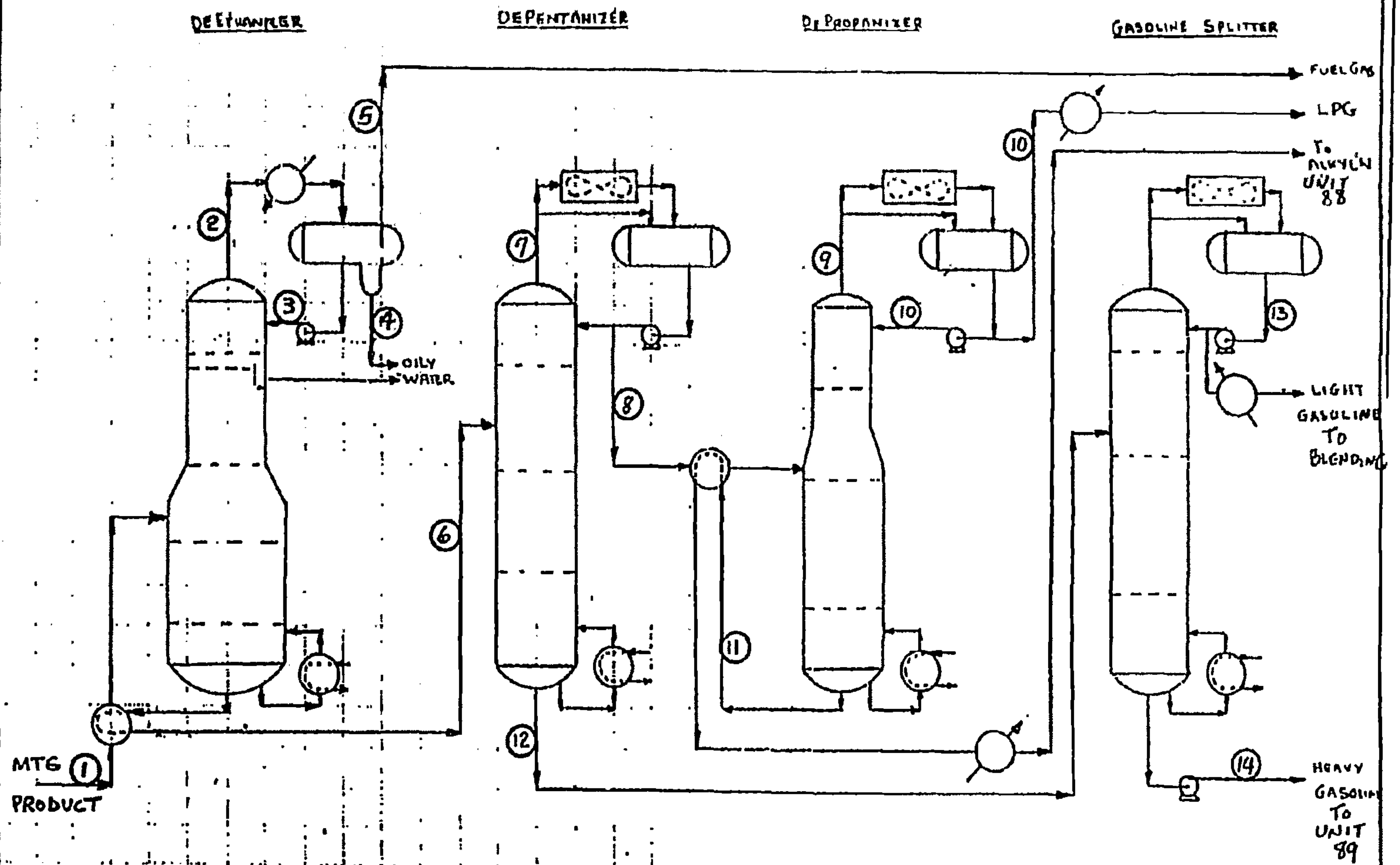

○ REFERS TO NUMBERS IN PROCESS DESCRIPTION

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MTG FRACTIONATION
UNIT 87
TRI-STATE SYNFUELS
835504

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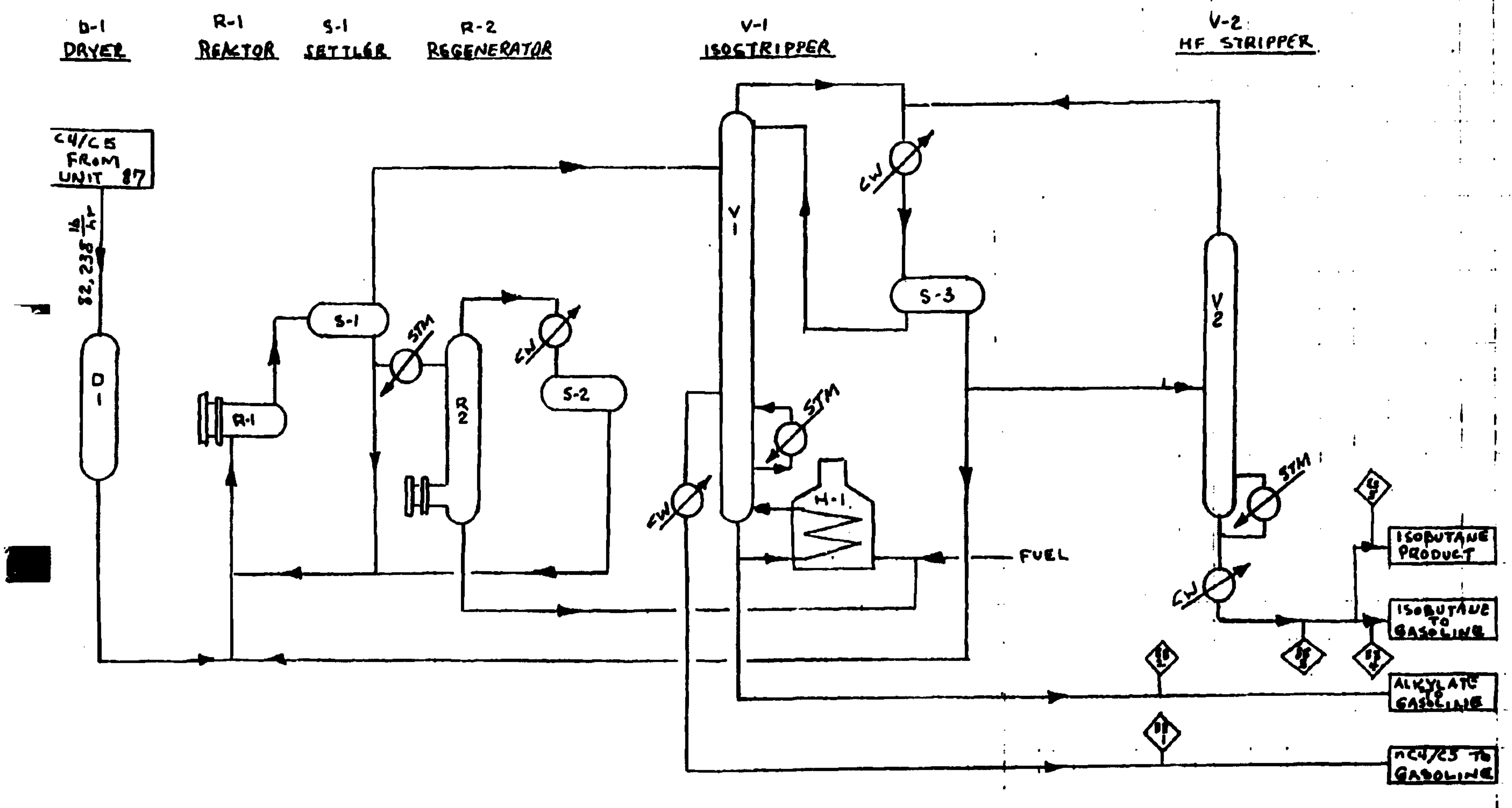

HF ALKYLATION
UNIT 88

TRI-STATE SYNFUELS CO.
835504 5/1/82

4.3 UNIT MATERIAL BALANCE

Stream compositions are proprietary with the licensors involved. Details of the processes cannot be revealed until a licensing agreement is signed.

4.4 ACCOMPLISHMENTS AND DECISIONS

Enough work on these units has been done to assure the required product qualities can be achieved. In addition, enough work has been performed to permit Fluor to develop cost estimates for each unit. These estimates are based on ratios of the Tri-State to feed on similar projects where the design of the units was based on data of adequate details to permit cost estimating.

The quality of the expected gasoline was checked to verify that it meets specs for U.S. unleaded gasoline. The addition of the heavy gasoline treater will reduce the durene content of the gasoline to acceptable levels. Durene has been known to cause icing problems in cold climates. This icing problem disappears when the durene is reduced to less than two percent.

4.5 CURRENT STATUS

For Mobil MTG (Unit 86) the current design has been established on the basis of Fluor in-house data available on the Mobil process for converting methanol to gasoline. On reactivation of the project, licensing agreements should be signed so the process design can be updated based on the latest information from the licensor, Mobil Oil Company.

The current design of the Gasoline Fractionation (Unit 87) should be updated using the composition and quantity of the gasoline product from MTG Unit provided by the process licensors.

The process design of HF Alkylation (Unit 88) was based on Fluor in-house information. The design should be modified on the basis of information provided by the licensor selected for the process.

4.5 Current Status (Continued)

The current design for the heavy gasoline treater (Unit 89) is based on Fluor in-house information. The design for this unit should be a part of the licensing agreement with Mobil. Fluor data for Tri-State should be modified to coincide with Mobil data.

4.6 LICENSOR AND EVALUATIONS

4.6.1 MTG (Unit 86)

Mobil and Lurgi offer the MTG process for licensing. They were both considered for the methanol to gasoline conversion process. Mobil was the preliminary selection as licensor for Tri-State. The Mobil process uses adiabatic reactors, while the Lurgi process uses isothermal reactors. Preliminary discussions were held with Mobil, but no licensing agreement has been completed.

4.6.2 MTG Fractionation (Unit 87)

The design of this unit will be provided by Fluor. Feed compositions must be updated to reflect the latest data from Mobil after licensing arrangements are completed.

4.6.3 HF Alkylation (Unit 88)

Both Phillips Oil Company and UOP have the technical capability to provide the design for this unit. They have a large history of successful units in operation based on their technology. When feed compositions to this unit are known, the licensors should be contacted to obtain data that will permit licensor selection. Data obtained from these licensors previously was based on feeds produced by a Fischer-Tropsch unit. The feeds from the MTG Unit will be different.

4.6.4 Heavy Gasoline Treater (Unit 89)

The design for this unit should be obtained from Mobil on a sole source basis. They are the licensor for the MTG conversion unit and are the only one with detailed information on feed compositions and they have pilot data on the process to reduce the durene content.