MTBE Process Unit

Supervisory Operating Manual
2.2 Process Description

The MTBE Unit functions to produce MTBE Product for blending into gasoline for octane enhancement as well as increasing the oxygen content as required by the United States Clean Air Act of 1990. The unit may be subdivided into the following sections:

Feed Pretreatment
Primary Reaction
Catalytic Distillation
Methanol Extraction and Recovery

The following is a brief description of the processing scheme as shown on the Process Flow Diagrams (1301-0143-KD-0201&0202). The PFD and the material balance the design case are provided in Section 2.2.1.

A. Feed Pretreatment

In the feed pretreatment section, the C₄ feed from OSBL is washed with water in the Water Wash Column, 43-C-201, to remove catalyst poisons such as nitrogen compounds and metal ions. The wash water enters the column above the top tray, thirty-six, tray of the column under flow control, while the C₄ feed stream enters at the bottom flowing countercurrently to the water. Wastewater leaves the bottom of the column under interface level control and is routed to existing units in the refinery. A coalescer pad located at the top of the column removes any residual droplets of water from the exiting C₄ stream.

B. Primary Reaction

High purity fresh methanol from OSBL combines with methanol recycle from the Methanol Recovery Column, in the Methanol Feed Surge Drums, 43-D-201, and then pumped to the MTBE and TAME unit reaction sections on flow control.
The washed C₄ feed stream mixes with the required amount of methanol feed prior to entering the Primary Reactor. A continuous analyzer located in the C₄ SHU monitors the C₄ stream for isobutene concentration and adjusts the methanol flow rate to maintain the desired methanol-to-isobutene feed ratio.

The mixed feed stream is heated by the MTBE product stream in the CD Reaction Column Bottoms/Feed Exchanger 43-E-201 and further heated, if necessary, to the desired reactor inlet temperature by controlling LP steam required to the Primary Reactor Feed Preheater, 43-E-202. After heating the mixed feed flows to the Primary Reactor where the bulk of the reaction to MTBE occurs. Since the reaction is exothermic, the temperature of the reactor effluent is higher than the temperature of the feed. The maximum reaction temperature is fixed by the bubble point of the reactor effluent at the pressure of the system. Therefore the reaction temperature is effectively controlled by setting the pressure, and thereby the boiling temperature of the system. The bulk of the total reaction approximately ninety percent of the isobutene conversion is accomplished in the Primary Reactor.

As more and more feed is processed through the unit, catalyst activity gradually decreases with time in the reactor due to neutralization of active sites from residual alkaline poisons entering with the feedstocks that are not totally removed in the wash column. This requires raising the overall temperature level of the reaction during the run by increasing the reactor inlet temperature and/or the pressure of the system to maintain a high degree of conversion. As end-of-run approaches, the bulk of reaction tends to shift from the reactor the CD Reaction Column as the catalyst deactivates. When the upper limit of the reaction operating temperature range is attained, the catalyst in the Primary Reactor is dumped and fresh catalyst loaded.
C. Catalytic Distillation

The partially vaporized reactor effluent stream enters the CD Reaction Column 43-C-202 at tray 25. Once in the column, the reaction continues and the MTBE product separates from unreacted C\(_4\)'s. Methanol and C\(_4\)'s form a minimum-boiling azeotrope, so the methanol contained in the column feed up to the azeotrope limit is carried into the tower reaction zone comprised of three catalyst beds. MTBE formed is removed from the reaction zone by distillation, allowing the MTBE reaction to proceed well beyond the limit set by chemical equilibrium. MTBE and methanol also form a minimum-boiling azeotrope whereby methanol is stripped from the MTBE product in the stripping section of the column. Therefore, addition of methanol to the CD Reaction Column must be carefully controlled, otherwise excess methanol will appear in the MTBE product. The MTBE product leaves the CD Reaction Column as the column bottoms. Before the MTBE product is sent to OSBL storage, it is cooled by heating the Primary Reactor feed, mixed with the TAME product, and then cooled in the Product Cooler, 43-E-203.

Control of the CD Reaction Column is similar to a conventional distillation column. The column overhead pressure is controlled by varying the amount of condensed distillate being fed to the Methanol Extraction Column on flow control. The temperature profile in the tower is controlled at a sensitive location, tray 15 by heat input to the reboiler. Reflux is flow controlled and the column bottoms level is controlled by resetting the MTBE product flow rate from the column.

D. Methanol Extraction and Recovery

As stated earlier, methanol forms an azeotrope with C\(_4\)'s and therefore excess methanol up to the azeotrope limit entering with the feed is carried overhead in the CD Reaction Column along with unreacted
C₄'s and lighter components. This excess methanol is recovered by washing the overhead stream with water in the Methanol Extraction Column, 43-C-203. The column has twenty-four trays. Recycle water is fed to the top of the column on flow control while the hydrocarbon stream flows upwardly in a countercurrent pattern. The exiting hydrocarbon stream Raffinate product saturated with water but essentially free of methanol is routed to OSBL under pressure control. The hydrocarbon feed to the extraction column is on flow control reset by the pressure in the overhead line of the CD Reaction Column. The TAME unit has an analogous tower for Methanol Extraction, 43-C-603. Extracted methanol and water exit the bottom of the MTBE and TAME extraction columns and flow to the common Methanol Recovery Column, 43-C-204, under flow control reset by the interface level of hydrocarbon and water phases above the top tray in the respective extraction columns.

The pressure in the Methanol Extraction Column is set by a pressure controller on the raffinate stream. Extracted methanol/water stream is sent to the Methanol Recovery Column for recovery and recycle of methanol and water. There are fifty-five trays in the column which operates at a low pressure just above atmospheric. Reboiling is provided by LP steam. The column overhead pressure is controlled by varying the amount of condensed overhead being fed to the Methanol Feed Surge Drum, 43-D-203, as recycle. The bottoms stream from this column, essentially pure water, preheats the feed to the Methanol Recovery Column and further cools against cooling water in the Recycle Water Cooler, 43-E-207, before being fed to the MTBE and TAME extraction columns on flow control.

A purge stream is withdrawn on flow control and sent to the OSBL wastewater treatment system. When level in the Methanol Column
becomes low, make-up water is added on level control to build back the level. Reboiling is controlled by monitoring and controlling the temperature profile in the column. The temperature control point in the column is on tray 30. The overhead stream, almost pure methanol, is condensed and subcooled in the condenser, 43-E-210, and reflux is on flow control. Net overhead from the column is recycled to the Methanol Feed Surge Drum.