Question 30: What process parameters can affect alkylate T90? What are the critical variables you monitor in both sulfuric and HF units? Discuss processing schemes, feed impacts and operating variables.

Randy Peterson (STRATCO)

The type of feed is very significant for T90. Amylenes make alkylate with higher T90 in both sulfuric and HF units. Propylene generally makes lower T90 than butylene in HF units. However, with sulfuric-catalyzed technologies, propylene can increase T90 as discussed below. Diene contaminants (butadiene and pentadiene) also raise T90 for both catalysts since they form heavier alkylate. Selective hydrogenation units that remove dienes are therefore helpful in reducing T90.

In sulfuric alkylation, propylene reacted with butylene and especially amylene in the same reactor will lead to higher T90s than if they were alkylated separately. This is due to side reactions that produce heavier alkylate. Therefore, segregated feed systems where different olefins are fed to specific acid stages are beneficial. Normal olefins have lower T-90 and End Points relative to isoolefins. Thus, MTBE/TAME raffinate has lower T-90s than mixed butylenes/mixed amylenes.

For a given feed type in sulfuric alkylation, I/O ratio is the most critical process variable. The lower the I/O, the higher the T90. Low acid strengths also increase T90 so acid staging should be designed to minimize the fraction of alkylate produced at the lowest acid strength. For HF alkylation, low I/O ratio is also the most significant variable causing increased T90. Acid strengths above 90-92 wt% increase EP and T90 due to the higher activity of the catalyst and tendency for polymerization. Low acid strengths (below 87 wt%) also tend to increase T90 due to increased side reactions and increased acid carryover in the iso recycle. Excessive internal acid regeneration can raise EP/T90 as well.

Higher reactor feed nozzle ?P and/or increased reaction zone mixing reduce T90 for both catalyst types.

John Clower (Chevron)

Alkylate T-90 can be affected by a number of different schemes, feeds, and operating variables within a Sulfuric Acid Alkylation plant. An increase in T90 signifies heavier, lower octane product, normally a result of polymer formation.

The critical operating variable to monitor for alkylate T90 is the isomer to olefin ratio. Polymerization becomes a favorable reaction at I:O ratios of less than 5:1. At these ratios, olefins can react with other olefins in the acid continuous emulsion. At Chevron we monitor alkylate endpoint to track polymerization as a check for reaction conditions.

Increased contactor temperatures can also increase polymerization, but likely would not increase T90 as the polymer would not be a large percentage of the total alkylate product.

Olefin feed segregation is one means of controlling alkylate quality and acid spending strengths. Segregation of C3 olefins allows for their operation at higher acid strength contactors. At Chevron we segregate C3/C4 olefins to high acid strength contactors and C4/C5 olefins to low acid strength contactors.

C3 olefins tend to make conjunct polymers at low acid strengths and will also form polymers with C5 olefins at low strengths. If a plant feeds less than 10% C5 olefins, an increase in that percentage will result in increased T90.

Greg Harbison (Marathon Petroleum)

Reaction temperature and isobutane to olefin (I/O) ratio are two of the most important variables we monitor for alkylate quality. Acid to hydrocarbon ratio is also an important variable and is routinely monitored for our UOP units which have a pumped acid design. For COP Units, this is not a variable that can be changed.

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