

Catalytic

Distillation

Technologies

Selective Hydrogenation of MTBE/ETBE C₄ Raffinates



Technology Profile

Overview The CDHydro catalytic distillation technology processes C₄ streams from refineries or steam crackers within an MTBE/ETBE debutanizer to produce a raffinate with a high butylenes content that is essentially free of butadiene. After methanol recovery, the treated C₄ raffinate can be used for butene-1 production or alkylation feed. The CDHydro process is one of a family of process technologies developed and commercialized by Catalytic Distillation Technologies (CDTECH) for license to the petroleum refining and petrochemical industries. CDTECH is a partnership between Lummus Technology, a CB&I company, and Chemical Research & Licensing, a CRI company.

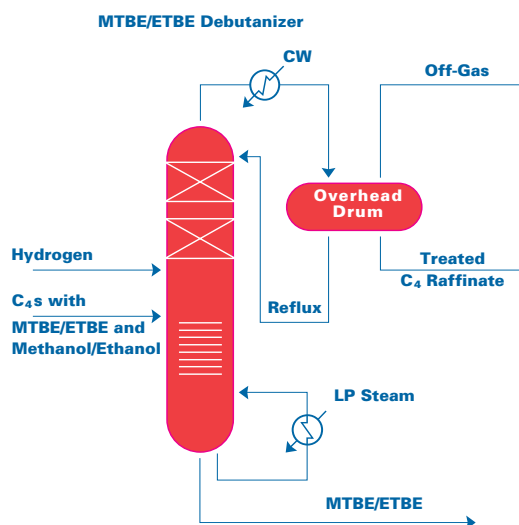
Selective Hydrogenation-General The patented CDHydro process achieves selective hydrogenation of butadiene to normal butenes in a catalytic distillation column. Selective hydrogenation increases butenes available for alkylation or isomerization, reduces acid consumption in alkylation units, and greatly improves the quality of HF alkylate. The process uses commercially available catalyst in its proprietary catalytic distillation structures (CDModules™).

The C₄ stream is combined with hydrogen below the reaction zone in the MTBE/ETBE debutanizer. Treated C₄ raffinate is taken overhead. The washing action of the reflux minimizes oligomer formation, flushing heavy compounds from the catalyst and promoting long catalyst life. Excess hydrogen and lights are vented from the overhead drum. The catalyst is sulfur tolerant. Feed sulfur compounds react with diolefins to form heavy compounds which exit in the tower bottoms with the MTBE/ETBE product. The distillate product is essentially mercaptan-sulfur-free.

The unique catalytic distillation column combines reaction and fractionation in a single unit operation. This constant pressure boiling system assures precise temperature control in the catalyst zone. Low reaction temperature and isothermal operation enhance selectivity and minimize yield losses to paraffins. Isomerization of butene-1 to butene-2 can be maximized to improve HF alkylate quality, or minimized for increased butene-1 recovery. Reaction heat is fully utilized.

Capital costs are considerably lower than conventional hydrotreaters since the single column design eliminates costs associated with fixed-bed systems. The CDHydro process would typically be installed in a conventional or catalytic MTBE/ETBE debutanizer, either as a retrofit or in a new column.

CDHydro Process Flow Diagram

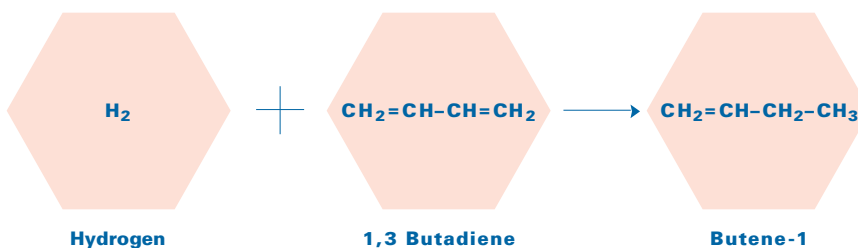
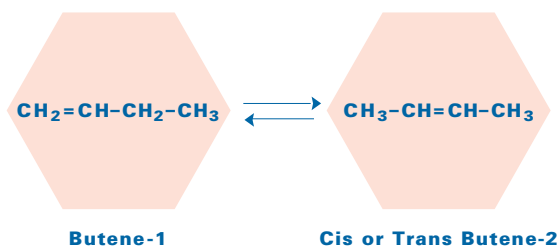


Advantages**CDHydro process offers:**

- Low capital cost
- Low catalyst requirements
- Low operating cost
- High product yield (low paraffin make)
- No polymer recycle across catalyst
- Use of reaction heat
- Sulfur tolerant catalyst
- Essentially mercaptan-sulfur-free distillate product
- Flexible butene-1/butene-2 ratio
- Retrofit to existing C₄ columns
- All carbon steel construction

CDTECH's catalytic distillation offers:

- Improved kinetics
- High conversion
- Low capital cost
- Low utilities
- Long catalyst life with sustained high conversion
- Reduced plot area

Selective Hydrogenation of MTBE/ETBE C₄ Raffinates**Process Chemistry****Selective Hydrogenation****Isomerization****Typical Overall Material Balance**

Feeds	HF Alkylation Application	H₂ SO₄ Alkylation Application
	LB/HR	LB/HR
C ₄ Feed	100,000 <small>(Butadiene 1 wt. %)</small>	100,000 <small>(Butadiene 1 wt. %)</small>
Hydrogen (100 % basis)	60	40
Products		
Treated C ₄ raffinate	80,080	80,180
MTBE/ETBE	19,620	19,620
Off-gas	360	240

Typical C₄ Product Composition

(will depend on feed composition and client requirements)

Residual Butadiene	< 10 ppm	< 500 ppm
Paraffin make (n-butane)	< 1 %	< 1 %
Butene-1/Butene-2 ratio	0.05 – 0.1	0.2 – 1.0
Sulfur	< 1 ppm	< 1 ppm

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