ADVANCES IN PROCESS TECHNOLOGY THROUGH CATALYTIC DISTILLATION

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Background

The first catalytic distillation process using heterogeneous catalyst came onstream in 1981. This plant was started up by Charter Oil at its Houston, Texas refinery. Since then, CDTECH has licensed its catalytic distillation technologies more than a hundred (100) times for various applications. There are now in excess of seventy (70) operating CDTECH units. Some major operating unit highlights are:

- 60 operating ethers units (including 2 ETBE and 10 TAME)
- 10 operating selective hydrogenation units
- 2 operating ethyl benzene units

The applications for Catalytic Distillation have expanded since 1981. Ethers - MTBE, ETBE, TAME, as can be seen from above, have been the backbone of CDTECH's technology portfolio. Now; however, technology for Selective Hydrogenation within a catalytic distillation environment, CD*Hydro*®, is achieving commercial success. For the nine operating CD*Hydro* units, there are four major areas of application:

- in C4/C5s, Butadiene and/or Pentadiene selective hydrogenation (8 units)
- in C6s, Hexadiene selective hydrogenation (1 unit)
- in aromatics, with benzene saturation (1 unit)

Some of the reasons that catalytic distillation has proven to be commercially attractive are;

- lower capital cost
- higher conversion
- longer catalyst life

Capital costs are reduced by combining catalytic reaction with distillation within the same piece of equipment, often reducing the need for a separate reactor. An example of this would be the selective hydrogenation of butadiene which can be combined within an existing MTBE unit Debutanizer saving the cost of a separate selective hydrogenation reactor and associated equipment

For some equilibrium limited reactions, using catalytic distillation enables conversions well in excess of fixed-bed equilibrium limitations. An example of this is MTBE production. With CDTECH's process, isobutylene conversions in excess of 99.9% are achievable with one fixed bed reaction step and one distillation step compared to 96-97% for a fixed bed process using two reactors.

Removal of heavies by distillation can result in a cleaner environment for catalyst operation. An example of this is CD*Hydro* technology, where the typical catalyst life reduction by oligomer fouling is minimized by distillation. The constant washing of the catalyst by reflux and the distillation of heavies on formation results in long catalyst life.

In the following sections, a number of recently, or soon to be, commercialized catalytic distillation applications are described.

- Butadiene selective hydrogenation combined within an MTBE unit
- Pentadiene selective hydrogenation
- C4 acetylene conversion
- Benzene saturation

*Combined CD*Mtbe *& CD*Hydro

Selective hydrogenation of C4's has always been of wide interest from refiners. When treating refinery and petrochemical C4 streams, selective hydrogenation increases normal butenes available for alkylation, reduces acid consumption in alkylation units, and improves the quality of HF alkylate.

The use of selective hydrogenation in the refinery is being driven by increased FCC unit severity and the new FCC catalyst formulations which are being used to increase the production of olefins for alkylation and ethers production. Diolefin levels are concurrently increased, resulting in increased acid consumption in alkylation units and increased acid regeneration costs.

Traditionally, fixed bed processes using palladium on alumina catalysts have been used to hydrogenate the diolefins in a C4 stream to mono-olefins. With fixed bed processes, the reaction is carried out in the liquid phase or in mixed phase. Hydrogen concentration and reaction conditions are controlled so that over hydrogenation of the mono-olefins to paraffins is largely prevented.

In 1994 a new process was commercialized for selective hydrogenation in a distillation column, utilizing special catalyst-containing packing in the reaction zone. Termed CD*Hydro*, the process offers the major advantage of combining reaction and distillation, thereby saving significantly on capital cost.

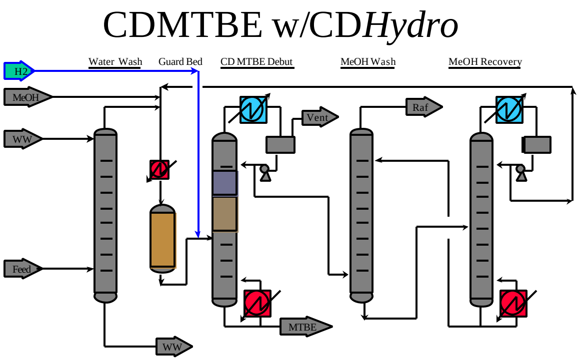

Figure 1

The economic impact of adding CD*Hydro* to an MTBE unit (figure1) will be demonstrated by the following example: an existing CD*Mtbe* unit with a 10,000 bpd raffinate product containing 0.5wt% butadiene feeding a sulfuric acid alkylation unit. CD*Hydro* is to be retrofitted within the CD column and this will result in a reduction of the residual butadiene to less than 100 ppmw.

Trays are removed from the column and replaced by CD*Hydro* bed supports and some vapor/liquid redistributors. CD*Hydro* catalyst contained within a distillation packing will be loaded into the column and a hydrogen line will be provided. Due to the additional lights in the system there will be non-condensibles in the CD column overhead system. Two cases are considered for the vent system; 1) once-through hydrogen - vent to FCC gas plant for gas recovery, 2) recycle blower - vent gases recycled except for a small purge to stop build up. Case 1 offers the simplest system, but case 2 offers lower hydrogen costs.

Low cost and short payback makes CD*Hydro* addition to an existing MTBE unit economically attractive in the present refinery economic climate particularly in comparison to an equivalent fixed bed selective hydrogenation unit. Case 1 and Case 2 are similar in payback, but the differences are in initial cost and hydrogen consumption. For case 2, the hydrogen consumption is significantly reduced, but at the cost of additional equipment (recycle blower); however, the payback on this item alone is 1 year offering long term operating cost savings. At refineries with

Table I - Comparison of Hydrogenation Options

	Fixed Bed SHU	CD*Hydro*: once through H2	CD*Hydro*: recycle H2
Initial Cost (plant modifications, engineering, initial catalyst cost)	$3,500,000	$900,000	$1,100,000
Net Annual Savings (acid savings less H2, catalyst lease, license fees)	$1,400,000	$900,000	$1,100,000
Payback (months)	30	12	12

Basis:

CD*Mtbe* unit; 10,000 bpd of raffinate, (0.5wt% butadiene reduced to less than 100 ppmw in product)

Hydrogen cost = 3 $/MSCF,

Acid consumption 13.4 lb/lb butadiene (from Stratco)

Acid regeneration cost=$75/ton

little or no capacity in the Wet gas compressor this option is more attractive as this will limit the C4 losses to vent gas.

The economics and hence viability of alkylation pretreatment are very site specific. The most significant factors are alkylation acid type and acid regeneration costs. The above example covers H_2SO_4 alkylation, the most common alkylation process; however, for HF alkylation economics, CD*Hydro* is also attractive particularly due to the isomerization of Butene-1 to Butene-2 which increases the alkylate octane by a couple of numbers. Maximizing Butene-2 has also been demonstrated using CD*Hydro* at higher hydrogen rates. This favors the use of a recycle blower to reduce hydrogen consumption.

Acid regeneration cost is the most significant element in H_2SO_4 alkylation. The effect of this cost on net annual savings is significant. The payback for CD*Hydro* addition (CASE 2) at $30/ton (estimated in-situ regeneration cost) is about 4 years. For $125/ton (estimated ex-situ regeneration cost on US West coast), it is 6 months.

CDTECH is now in a position to offer the most economic technical and commercial solution for Alkylation pretreatment based on your site-specific criteria.

Penatadiene Selective Hydrogenation

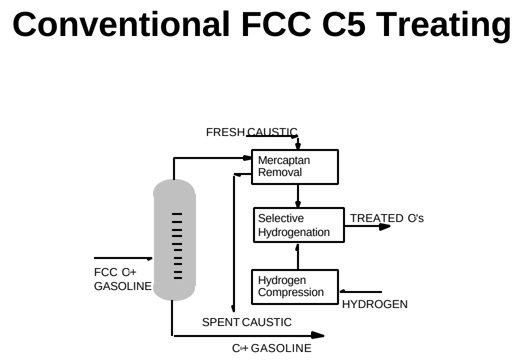
Conventional FCC C5 Treating

Figure 2

For TAME production, the removal of pentadienes to a low level is typically required. The diolefins can cause fouling within the TAME unit, resulting in reduced the life of the catalyst and other operating difficulties. The TAME product can also be discolored and odorous.

Selective hydrogenation of the diolefins to olefins is required in the FCC C_5 cut to prevent these problems. However, selective hydrogenation catalysts such as palladium are normally sensitive to the presence of mercaptans in the C_5 cut (typically 20 to 500 ppm). The conventional treatment would require mercaptan removal upstream of the selective hydrogenation unit such as extractive treatment with caustic (figure 2). Unfortunately, such treatment normally leaves trace quantities of oxygen in the C_5 cut which can cause deterioration of etherification catalyst or high acid consumption in the alkylation unit. In addition, the waste caustic from this unit is another polluting effluent and can be expensive to treat prior to disposal.

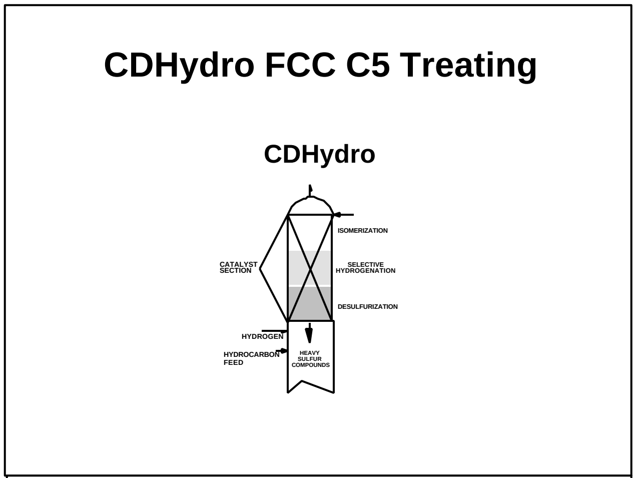

Figure 3

CD*Hydro* operates at pressures significantly lower than conventional fixed bed reactors. As a result, compression of hydrogen is normally not required. Mercaptans react with diolefins to form olefinic sulfides in the bottom of the catalyst zone (figure 3). These compounds have higher boiling points than the C_5 fraction and are easily fractionated to the bottom product. The olefinic sulfides are thermally stable unlike disulfides from caustic sweetening and therefore do not decompose in the reboiler to cause other problems. The overhead stream is desulfurized without the use of caustic and essentially all sulfur leaves the column with the bottom product. In the middle section of the catalyst hydrogen reacts with C_5 diolefins to selectively produce olefins. The overhead stream is low in diolefins and mercaptans and is better as feedstock to either TAME or alkylation units. In the upper section, double bond isomerization occurs once the pentadiene concentration has been reduced.

Use of CD*Hydro* in the depentanizer reduces capital cost via elimination of:

1. A separate hydrogenation unit
2. A caustic treating unit
3. Hydrogen compression

Additional benefits of selective hydrogenation are reduction of RVP, increased octane of the C_5 cut and increased TAME product potential. The double bond isomerization accompanying the selective isomerization is responsible for all three effects. Moving the double bond from the alpha to the beta position on the molecule converts 3-methyl butene-1 to 2-methyl butene-2 or 2-methyl butene-1 and converts pentene-1 to cis or trans pentene-2. In both cases the beta position molecule has lower vapor pressure and higher octane than the alpha position molecule.

C4 Acetylene Conversion

There are generally four options for handling C4 Acetylenes in Butadiene extraction:

1. Secondary extraction of acetylenes or two stage stripping to produce an acetylenes rich extract.
2. Partial conversion of the acetylenes in a feed hydrotreater followed by secondary extraction of acetylenes or two stage stripping to produce an acetylenes rich extract which is then recycled to the feed.
3. High conversion of the acetylenes in a feed hydrotreater. The residual acetylenes are then distilled from the Butadiene product.

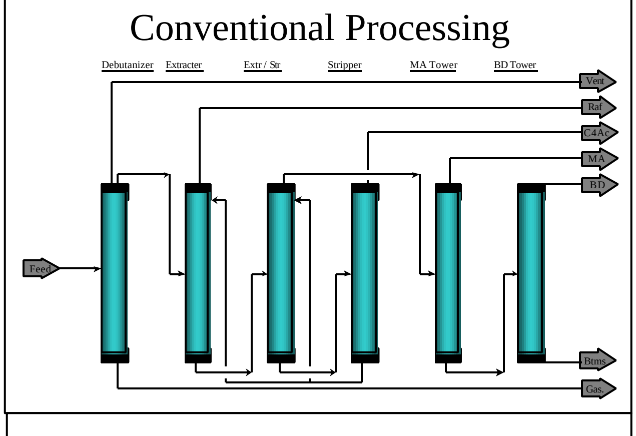

Figure 4

4. “Complete” hydrogenation of acetylenes before feeding to the extraction unit.

The conventional butadiene extraction process (Figure 4) produces three byproduct streams in addition to the butadiene product and the raffinate; lights (including methyl acetylene), heavies which includes 1,2 butadiene and C5’s and an acetylenics concentrate. The latter stream the biggest source of butadiene loss. Most plant operate with 2 pounds of butadiene diluent for every pound of acetylenes. This stream is often flared, fueled or otherwise downgraded.

Direct hydrogenation of the concentrate can be used to recover the value of this acetylenics concentrate. It is rarely practiced due to short catalyst life. This does however, yield a gain in butadiene.

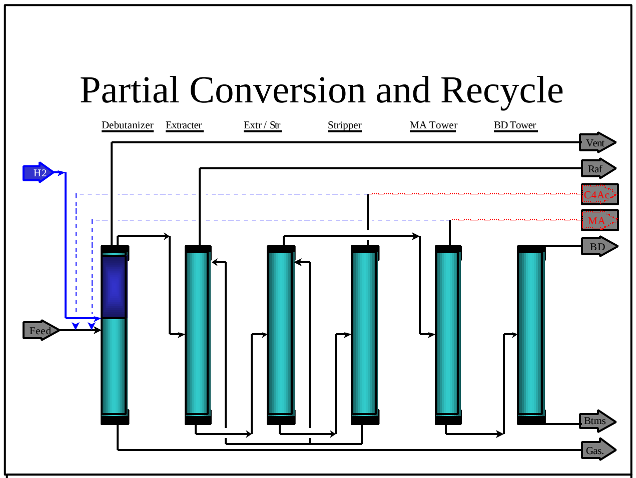

Figure 5

Catalytic distillation packing in the Debutanizer (Figure 5) can be used to partially hydrogenate the feed and the recycle acetylenes.

Published data on fixed bed reactors indicate 40% conversion of vinyl acetylene without reaction losses of butadiene but no conversion of ethyl acetylene or 1,2 butadiene. Even with an acetylenics recycle to feed ratio of 1:10, the butadiene losses in the acetylenics purge is 2.5%. The unique conditions in the Debutanizer allow partial conversion of the Ethyl Acetylene and 1,2 butadiene using conventional catalyst. This eliminates purge losses, reduces the recycle rate to feed ratio to 1:50 with no conversion of butadiene to butenes. This new option can also provide pretreatment to off-load a fixed bed hydrogenation unit and extend the catalyst cycle length.

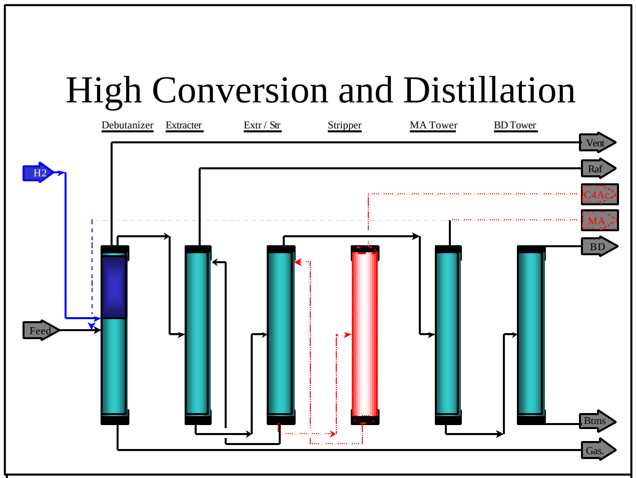

Figure 6

The third alternative is high conversion of the acetylenes in the feed before extraction (figure 6). The residual acetylenes (ca 200 ppm) are then distilled from the product via the post fractionators. This can considerably reduce the complexity and cost of the extraction unit. The fourth alternative is complete conversion of the acetylenes in the feed (less than 10 ppm) before extraction

Table II – C4 Acetylene Hydrogenation Comparison

	Double Extraction	**Conventional Fixed Bed**	**Novel Fixed Bed**	**CDHydro** **Partial Conversion**	**CDHydro** **High Conversion**	**CDHydro** **“Complete” Conversion**
BD Losses	3 lb BD per lb Ac = 6% to fuel	EA not converted ∴2% to fuel	Green Oil Purge => 1%	no loss of BD Ac to butenes	3% BD + Ac to butenes	8% BD + Ac to butenes
Capacity Impact	Base	10% recycle	Eliminates Ac extraction and MA tower	2% recycle Reduced load Ac extraction	Eliminates Ac extraction	Eliminates Ac extraction and MA tower
Net Annual Benefit*	Base	$3,200,000	$2,600,000	$5,000,000	$4,100,000	$2,800,000
Basis:		Improved product yields (product values below) less catalyst cost, capital cost allowance (@20%), license fee				
fuel ($/lb)	$0.03					
butene ($/lb)	$0.13					
BD ($/lb)	$0.18					

A process using a fixed bed reactor using a novel reactor has been used for complete hydrogenation of acetylenes. The capital and operating costs (Table II) largely offset the high butadiene yield.

The CD*Hydro* process is flexible. It can be operated between maximum butadiene recovery to maximum feed clean-up as economic conditions require.

Benzene

In the typical refinery benzene comes from several sources however, the benzene from the reformer usually represents 50-80% of the total. FCC gasoline is only a minor contributor to benzene in the gasoline pool. As a result the reformate is the natural place to focus benzene reduction. A new CD*Hydro* application for the hydrogenation of benzene in reformate has been commercialized. Texaco is operating this unit at its Bakersfield refinery to produce CARB gasoline with low benzene content. This option can be installed at about 30% less capital cost than a conventional reformate splitter followed by a fixed bed benzene hydrogenation unit.

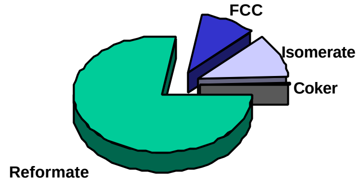

Figure 7

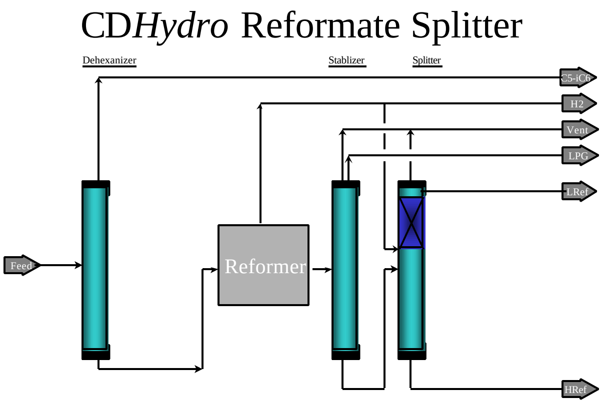

Figure 8

Conclusion

Catalytic distillation offers many technology advantages for a growing list of process applications. CD*Hydro*, selective hydrogenation in a catalytic distillation environment, has been commercialized in four major areas of processing. The advantages over conventional fixed bed technology include: lower capital cost, lower operating cost and improved product quality.

CDTECH's catalytic distillation technology has been in use for 17 years with over seventy plants operating worldwide.