

## **Focus on Profit:**

# **C<sub>4</sub> Processing Options to Upgrade Steam Cracker and FCC Streams**

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## **INTRODUCTION**

The future of our industry will be shaped by product flexibility, low capital investment and energy efficiency of larger capacity plants. Steam cracker and FCC unit owners are striving to increase the value of their orphaned C<sub>4</sub> streams. ABB Lummus Global offers a full range of technologies to process these C<sub>4</sub> streams into value-added products. New innovative technologies expand the processing choices, including ethylene/butene metathesis for propylene production, C<sub>4</sub> self-metathesis that produces ethylene, propylene and hexene-1 and catalytic distillation/hydrogenation for C<sub>4</sub> diene removal and hydroisomerization.

This paper reviews the commercially proven C<sub>4</sub> processing technologies in the ABB Lummus Global portfolio, discusses how they work, their advantages, and the applications that provide the best fit.

Sources of C<sub>4</sub>'s typically include:

- Steam Cracker C<sub>4</sub>'s
- FCC Unit C<sub>4</sub>'s
- Natural Gas Liquids

The typical C<sub>4</sub> stream compositions and flow rates from a 600 kta steam cracker and a 50,000 BPD FCC Unit are shown in the following Table 1. The compositions are quite dissimilar, which requires a different processing strategy for each one.

Table 1

*wt% of C<sub>4</sub> stream*

	<b><u>600 kta Steam Cracker</u></b>	<b><u>50,000 BPD FCC Unit</u></b>
Butadiene	50	--
Isobutylene	25	15
n-Butenes	15	37
Butanes	10	48
<b>TOTAL, mta</b>	<b>240,000</b>	<b>360,000</b>

Products from these C<sub>4</sub> feeds can include:

- Propylene (via metathesis of butenes with ethylene)
- Hexene-1 (via self-metathesis of butenes)
- MTBE (or ETBE)
- Butadiene
- Isobutane
- Isobutylene
- Raffinate for Alkylation
- C<sub>4</sub> LPG
- Maleic Anhydride

The portfolio of C<sub>4</sub> processing steps offered by ABB Lummus Global is:

<b><u>C<sub>4</sub> Processing Step</u></b>	<b><u>Technology(s)</u></b>
Metathesis - C <sub>2</sub> <sup>-</sup> + C <sub>4</sub> <sup>-</sup> - C <sub>4</sub> s	Olefins Conversion (OCT) (ABB Lummus Global)
Selective Hydrogenation	CDHydro <sup>®</sup> ; BASF
Total Hydrogenation	ABB Lummus Global
Dehydrogenation	CATOFIN <sup>®</sup> ; CATADIENE <sup>®</sup> (ABB Lummus Global)
Etherification	CDMtbe <sup>®</sup> , CDEtbe <sup>®</sup>
MTBE Decomposition - Isobutylene	CDIB <sup>®</sup>
Selective Hydrogenation/Etherification	CDEtherol <sup>®</sup>
Butadiene Extraction	BASF
Skeletal Olefin Isomerization	ISOMPLUS <sup>®</sup> (Lyondell/CDTECH)
Paraffin Isomerization	ABB Lummus Global
Maleic Anhydride	ALMA (ABB Lummus Global/Lonza)

The entire ABB Lummus Global technology portfolio is depicted in Figures 1 and 2.

The entire CDTECH<sup>1</sup> technology portfolio is depicted in Figure 3.

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<sup>1</sup> CDTECH<sup>®</sup> is a partnership between ABB Lummus Global and Chemical Research and Licensing, a CRI subsidiary. CDMtbe<sup>®</sup>, CDEtbe<sup>®</sup>, CDEtherol<sup>®</sup>, CDHydro<sup>®</sup>, CDIB<sup>®</sup> and ISOMPLUS<sup>®</sup> are all processes developed and commercialized by CDTECH.

## **C<sub>4</sub> PROCESSING TECHNOLOGIES**

### ***Metathesis – Olefins Conversion Technology***

The Olefins Conversion Technology (OCT) from ABB Lummus Global reacts n-butenes with ethylene to produce polymer grade propylene. This technology, which has been in commercial operation since 1985, gives the olefin producer added flexibility to balance ethylene and propylene production depending on market conditions.

Two chemical reactions take place in the single fixed-bed reactor (Figure 4): propylene is formed by the metathesis of ethylene and butene-2; and butene-1 is isomerized to butene-2 as butene-2 is consumed in the metathesis reaction.

This technology can be used with a variety of C<sub>4</sub> streams including the mixed C<sub>4</sub>'s produced in steam cracking, raffinate C<sub>4</sub>'s from MTBE or butadiene extraction, and C<sub>4</sub>'s produced in FCC units. The ethylene stream can vary from dilute ethylene typical from an FCC, to polymer-grade ethylene. All paraffins in the feed pass through the system as inerts. This feed flexibility allows the producer to take advantage of many lower-valued feed stocks.

Figure 5 is a simple process flow diagram of the Lummus OCT process. Fresh C<sub>4</sub>'s plus C<sub>4</sub> recycle are mixed with ethylene and sent through a guard bed to remove trace impurities from the mixed feed. The feed is heated prior to entering the vapor phase reactor where equilibrium reaction takes place. The per-pass conversion of butylene is greater than 60% with overall selectivity to propylene exceeding 90%. The reactor is regenerated on a regular basis.

Reactor effluent is sent to the ethylene recovery tower where unreacted ethylene is recovered and recycled to the reactor. The C<sub>2</sub> tower bottoms are processed in the C<sub>3</sub> tower to produce propylene product and a C<sub>4</sub> recycle stream. Purge streams remove non-reactive light material and C<sub>4</sub>'s and heavier materials.

In their November 30, 2001 Monomers Market Report, Chemical Market Associates, Inc. (CMAI) evaluated the relative capital investment required to produce propylene from various technologies. They range from the capital-intensive route of FCC units and steam crackers to the low cost of a propylene/propane splitter. As shown in Figure 6, metathesis is the lowest capital cost route to produce propylene.

The OCT from ABB Lummus Global can also be utilized in butenes “self-metathesis” mode to produce ethylene, propylene and hexene-1. This does not use ethylene as feed to the reactor system. A semi-works self-metathesis unit is under construction at Sinopec’s Tianjin ethylene plant, and will be started up in early 2003.

### ***Selective Hydrogenation***

ABB Lummus Global offers two selective hydrogenation processes that can be used to convert butadiene to normal butenes. The choice depends on project-specific parameters such as butadiene content, and whether the project is a retrofit or a grassroots design.

#### ➤ CDHydro<sup>®</sup> Process

This is a technology developed by CDTECH in which hydrogenation and distillation take place in single unit operation. It has various applications for C<sub>3</sub>, C<sub>4</sub> and C<sub>5</sub> processing. Applications for C<sub>4</sub>’s include feeds with high or low butadiene concentration, and involve debutanizer and butene splitter designs. Catalytic distillation has several inherent advantages over conventional fixed bed processes:

1. By incorporating hydrogenation in the distillation column, all of the equipment normally associated with a fixed-bed Selective Hydrogenation Unit is eliminated. This results in lower capital cost.
2. The catalyst operates at essentially constant temperature in a turbulent flow regime. This leads to higher selectivity and improved product yields.

3. Mercaptan compounds react with diolefins, forming heavy olefinic sulfides that exit in the bottoms. The distillate is sulfur-free.
4. The heat of reaction is used to displace a portion of the reboiler duty. This reduces energy costs.
5. Dimers, gums and sulfides are much heavier than the surrounding components. These materials are easily separated down and away from the catalyst zone. In addition, clean reflux flows over the catalyst zone “washing” the catalyst beds. These characteristics lead to more stable operation and improved catalyst life.

➤ BASF Selop

This is a fixed bed technology developed for steam cracker C<sub>4</sub> feeds with high butadiene concentration. Process conditions are mild, and all equipment is constructed of carbon steel. It was originally commercialized by BASF in Antwerp in 1993.

In the Selective Hydrogenation Unit, butadiene in the C<sub>4</sub> feed stream is hydrogenated to butenes. By appropriate choice of the process conditions and catalyst, a C<sub>4</sub> effluent with maximum butene-1 or maximum butene-2 can be achieved. The extent of reaction is such that the treated C<sub>4</sub> stream exiting the unit contains a butadiene level of 10 ppmw. Yield loss to n-butane will vary with the residual butadiene content and is low.

Selective hydrogenation to achieve a low residual level of butadiene is performed in a two-stage reactor system. The reactor feed temperature and butadiene concentrations are controlled by a recycle of the product from the reactors.

Hydrogen is fed to the reaction loop under flow control. Optimization of the hydrogen flow is achieved by setting the hydrogen feed rate proportional to the C<sub>4</sub>

feed flow and correcting for the changes in the butadiene content in both the C<sub>4</sub> feed and the reactor outlet streams.

### ***Total C<sub>4</sub> Hydrogenation***

ABB Lummus Global offers its own fixed bed hydrogenation technology for total saturation of steam cracker C<sub>4</sub>'s for pyrolysis feed, LPG, or n-butane feed applications.

This well-proven technology offers a unique system for self-balancing reaction heat removal and a low recycle rate. Changes in heat release due to changes in feed composition or flow rate cause a corresponding change in vapor generated. Since condensed vapors are totally recycled, the system adjusts to the new conditions by automatically changing the recycle quantity.

This design approach results in lower catalyst requirement, long cycle times between regeneration, and a catalyst life of 5 years or longer.

### ***Butane Dehydrogenation***

ABB Lummus Global is the licensor of CATOFIN<sup>®</sup> and CATADIENE<sup>®</sup> technologies. CATOFIN converts isobutane to isobutylene while CATADIENE converts n-butane to butadiene. These mature technologies have been utilized in industry for decades, with improvements being made continuously. Eight CATOFIN process units are providing isobutylene feedstock for production of 110,000 BPSD of MTBE.

Single train capability of up to 900,000 MTA of isobutylene affords the producer lower investment economy of scale, low operating costs, and an environmentally sound design. Figure 9 is a flow sheet for isobutylene production.

The CATOFIN process uses fixed-bed reactors with a catalyst that has been selected to optimize the complex relationship among conversion, selectivity and energy consumption. The overall selectivity of isobutane to isobutylene via the

CATOFIN process is greater than 90%. The entire reactor sequence is computer controlled and requires no operator input. On-stream efficiencies of 98+%, excluding biannual turnarounds of 2-3 weeks, are routinely achieved.

CATOFIN dehydrogenation is a continuous process, with cyclic reactor operation. During the hydrocarbon processing step, fresh feed and recycle feed (from an MTBE synthesis unit or C<sub>3</sub> splitter bottoms) are vaporized by exchange with various process streams and then raised to reaction temperature in the charge heater. The reactor effluent is routed through a high-pressure steam generator, feed-effluent exchanger, and trim cooler to the compressor.

The compressor discharge is cooled, dried and routed to the low temperature recovery section to reject light ends. The low temperature section off-gas, which is a hydrogen-rich gas, can be sent to a Pressure Swing Adsorption (PSA) Unit to purify the hydrogen. Recovered liquids from the low temperature recovery section, along with the effluent flash drum liquid, are fed to distillation facilities and/or an MTBE synthesis unit for product recovery.

### ***Etherification***

The CDMtbe<sup>®</sup> and CDEtbe<sup>®</sup> (Figure 10) technologies licensed by CDTECH convert isobutylene to MTBE and ETBE using methanol and ethanol respectively. These catalytic distillation processes have design options for 99.9% conversion. CDTECH etherification technology continues to capture the majority of projects for these products.

The patented CDMtbe process is based on a two-step reactor design, consisting of a boiling point fixed bed reactor followed by final conversion in a catalytic distillation column. The process utilizes an acidic ion exchange resin catalyst in both its fixed bed and proprietary catalytic distillation structures.

The unique catalytic distillation column combines reaction and fractionation in a single unit operation. Conversion of isobutylene in excess of fixed bed equilibrium

limitations is achieved simply and economically. By using distillation to separate the product from the reactants, the equilibrium limitation is eliminated and higher conversion of isobutylene is attained. Catalytic distillation also takes advantage of the improved kinetics through increased temperature without penalizing equilibrium conversion.

In September 2001, CDTECH and Snamprogetti announced a global agreement to combine and market their expertise in the conversion of MTBE units to iso-octene/iso-octane production. This is in response to Owners who want to exit the MTBE market in response to the potential elimination of MTBE from gasoline pools.

### ***MTBE Decomposition***

Isobutylene purity in excess of 99.9% can be produced from MTBE using the CDTECH CDIB<sup>®</sup> technology (Figure 11). This fixed bed process uses a proprietary acidic catalyst to decompose commercial grade MTBE feed to high purity isobutylene and commercial grade methanol. The decomposition reaction takes place in the vapor phase.

Commercial MTBE feedstock is first fractionated to remove light ends and heavies. The high purity MTBE is fed to the decomposition reactor where MTBE is converted to isobutylene and methanol. Heat of reaction is supplied by medium pressure steam. Methanol is extracted from the reactor effluent in a water wash. Fractionation of the aqueous stream recovers wash water, MTBE for recycle and methanol. The water-washed reactor effluent is fractionated to remove heavies (including MTBE for recycle) and light ends, leaving high purity isobutylene product.

The CDIB technology can be provided as a stand-alone unit or coupled with a CDMtbe unit to provide an efficiently integrated unit. This technology is being operated in several plants worldwide.

## ***Selective Hydrogenation/Etherification***

CDEtherol<sup>®</sup> technology offered by CDTECH processes C4 streams from refinery units to produce MTBE. The technology, can accomplish selective hydrogenation of low butadiene concentration streams, etherification, and butene-1/butene-2 isomerization. This technology offers economies in production of ethers and in alkylation, as well as improved alkylate quality from the isomerization of butene-1 to butene-2.

This patented process is based on a two-step reactor design, consisting of an ETHEROL trifunctional catalyst reactor followed by final conversion in a catalytic distillation column. The process utilizes a proprietary trifunctional catalyst in its fixed bed reactor and acidic ion exchange catalyst in its proprietary catalytic distillation structures.

## ***Butadiene Extraction***

BASF's butadiene extraction process uses non-corrosive n-methyl pyrrolidone (NMP) as the extractive distillation solvent. The unit is comprised of the following sections: Extractive Distillation; Degassing; Distillation; Solvent Regeneration; Chemical Injection System and Waste Water Stripping.

The evaporated crude C<sub>4</sub> stream enters the first column, the main-washer, at the bottom of the tower. NMP, in a counter-current flow, washes the more soluble butadiene and the acetylenes out of the C<sub>4</sub>-cut. This solution is pumped to the top of the rectifier. The acetylenes are removed in the after-washer column, where they are dissolved in NMP at the bottom. The top product of the after-washer is the crude butadiene. This stream will finally be distilled to meet product specifications.

This mature technology offers advantages in feedstock flexibility, energy efficiency, safety, and simplified plant operations.

### ***C<sub>4</sub> Olefin Skeletal Isomerization***

CDTECH and Lyondell Petrochemical Co, offers the ISOMPLUS<sup>®</sup> fixed bed skeletal olefin isomerization technology (Figure 12) for conversion of n-butenes into isobutylene.

A zeolite catalyst specifically developed for this service provides near-equilibrium conversion of normal butenes to isobutylene at high selectivity and long process run lengths. A simple process scheme results in low capital and operating costs.

Hydrocarbon feed containing normal butenes, such as MTBE unit raffinate, is evaporated and superheated prior to entering the skeletal isomerization reactor. The hydrocarbon stream does not require steam or other diluents, or the addition of catalyst activation agents to promote the reaction. The hot vapor passes through a fixed bed reactor where up to 44% of the contained normal butenes are converted to isobutylene at approximately 90% selectivity. Reactor effluent is cooled and compressed to a heavy end column where C<sub>5+</sub> is separated by fractionation.

The butene Isomerate is suitable for feed to an MTBE unit. When an ISOMPLUS unit is operated in a recycle mode with a high conversion MTBE unit, production of MTBE can be significantly increased.

### ***Paraffin Isomerization***

ABB Lummus Global offers its own isomerization technology for efficient conversion of n-butane to isobutane. A main application is in field butane-based MTBE plants where isobutane is produced as feedstock for the dehydrogenation unit. The technology is also used in refineries to produce isobutane feedstock for alkylation units.

The process technology combines high per-pass conversion and selectivity to achieve high product yields (ca. 98.5 wt% on a C<sub>4</sub> basis). High catalyst activity and stability at low hydrogen flow rates minimize required reactor volumes and can allow

the elimination of hydrogen recycle facilities. Capital cost is further minimized by including commercially proven proprietary fractionation hardware to reduce the size of the deisobutanizer product recovery tower.

This process, which utilizes an AKZO/TOTAL catalyst, has been utilized in many projects representing more than two million MTA of isobutane production. The first plant came on stream in 1995 as part of an ABB technology package of ISOM/CATOFIN/CDMtbe to produce MTBE.

### ***Maleic Anhydride - ALMA***

The ALMA process produces high purity, superior quality maleic anhydride from n-butane. Jointly developed and licensed by ABB and Lonza SpA, the ALMA process combines the unique features of a fluid-bed reactor with that of a non-aqueous recovery system. This modern processing combination results in savings in capital investment and a product that surpasses the rigorous performance specifications of various end-use markets.

The exothermic heat of reaction is removed by generating saturated high pressure steam, which is combined with the steam produced in the off-gas incinerator and superheated. A portion of the steam can be used to drive the air compressor, with excess exported or used to generate electric power. This results in greater energy efficiency for the process.

## **C<sub>4</sub>'s PROCESSING OPTIONS**

### ***Steam Cracker C<sub>4</sub>'s Processing Options***

Steam crackers have the greatest number of C<sub>4</sub> processing options due to several factors:

- The high butadiene content in the crude C<sub>4</sub>'s
- The option of saturating the C<sub>4</sub>'s and recycling to pyrolysis, and

- The availability of ethylene for metathesis with mixed n-butenes or butene-2 to produce propylene
- Self-metathesis for ethylene, propylene and comonomer hexene-1

As seen in Figure 14, crude C<sub>4</sub>'s from a cracker can be treated in many ways. The most attractive C<sub>4</sub> processing alternative is ABB Lummus Global's Olefins Conversion Technology (OCT) that converts ethylene plus butene-2 or mixed n-butenes to produce propylene. OCT combined with a steam cracker can significantly vary the propylene-to-ethylene product ratio and improve overall plant economics.

Typical steam crackers with liquid feedstocks operate with a propylene-to-ethylene ratio range of 0.45 to 0.65 depending upon cracking severity. The mixed C<sub>4</sub> product stream contains butadiene, butylenes and butanes. Butylenes can be reacted with ethylene via metathesis to increase the propylene-to-ethylene ratio. If butadiene is not required as a product, it can be selectively hydrogenated to butenes to provide additional butylene feed for metathesis. The steam cracker/OCT combination can result in propylene-to-ethylene ratios exceeding 1.1 as determined by the quantity of butylenes that are available for conversion in the OCT unit (Figure 15).

The BASF Fina Petrochemicals steam cracker in Port Arthur, Texas produces over 950,000 metric tons per annum (MTA) ethylene and over 544,000 MTA propylene. An OCT unit is under construction that will add more than 300,000 MTA additional propylene, increasing the propylene-to-ethylene ratio (P/E) from 0.57 to 1.0.

The ethylene-butene metathesis is also being used by Shanghai SECCO Petrochemical, the joint venture of BP (50%), Sinopec (30%) and Sinopec Shanghai Petrochemical (20%), which is building a 900,000 MTA ethylene plant at Caojing, China. The overall P/E ratio is 0.65, as some butadiene is recovered as product.

Table 2 illustrates three operating scenarios. Case 1 recovers C<sub>4</sub>s as a mixed C<sub>4</sub> product. This is typical of an operation where butadiene is a desired product for recovery. Case 2 hydrogenates and recycles the C<sub>4</sub>s to cracking. The naphtha feed requirement is reduced. This operating scenario has become more popular in recent years as butadiene demand has not kept pace with ethylene growth rates. However,

this option reduces the quantity of hydrogen available for product sales. A more economic variation of Case 2 is to selectively hydrogenate the butadiene to butylenes to produce metathesis feed. This is shown in Case 3. The propylene/ethylene product ratio increases from 0.55 for Cases 1 and 2 to 0.94 for Case 3. This option requires more naphtha feed but 73% of the incremental naphtha feed is converted to propylene via metathesis. The IRR improves by 3 – 5% depending upon product price scenarios.

**Table 2**  
**Material Balance Comparison**

Case	1	2	3	
Case Description	Stand-alone Steam Cracker Exported C <sub>4</sub> s	Stand-alone Steam Cracker No Exported C <sub>4</sub> s	Steam Cracker integrated with an OCT Unit	
<b>Feedstock, kta</b>				
Naphtha Feed	2088	1810	2213	+403*
<b>Products, kta</b>				
Methane Fuel Gas	389	393	437	
PG Ethylene	760	760	760	
PG Propylene	418	418	713	+295*
Mixed C <sub>4</sub> s	263	0	0	
Pygas	196	181	235	
Fuel Oil	60	56	66	
Acid Gas	<u>2</u>	<u>2</u>	<u>2</u>	
<b>Total</b>	<b>2088</b>	<b>1810</b>	<b>2213</b>	

\* 73% of incremental naphtha converted to propylene

In addition to maximizing the propylene-to-ethylene (P/E) ratio of a steam cracker, OCT can also be utilized to optimize steam cracker complexes operating in the conventional P/E range.

Table 3 illustrates different naphtha steam cracker options that produce an overall P/E ratio of 0.65. In Case 4, the P/E ratio is controlled by the cracking severity; the 0.65 P/E ratio represents a typical low severity operation on naphtha feed. In Case 5, the severity is increased and the OCT unit is added to react butylenes and ethylene to attain the same 0.65 ratio. A range of values are shown in Case 5 to reflect the

results depending upon whether butadiene is recovered as product or selectively hydrogenated to produce more OCT unit feed. Addition of the OCT unit results in a lower cost complex with lower specific energy consumption that in turn results in improved gross and net margins for the steam cracker/OCT combination.

**Table 3**

	<u>Case 4</u>	<u>Case 5</u>
<b>Feedstock</b>	<b>Naphtha</b>	<b>Naphtha</b>
<b>Naphtha Severity</b>	<b>Low</b>	<b>High</b>
<b>P/E</b>	<b>0.65</b>	<b>0.65</b>
<b>Naphtha Feedrate</b>	<b>Base</b>	<b>2 - 5% lower</b>
<b>C<sub>3</sub> from OCT</b>	<b>--</b>	<b>15 - 28%</b>
<b>TIC</b>	<b>Base</b>	<b>5 - 8% reduction</b>
<b>Gross Margin</b>	<b>Base</b>	<b>&lt;1 - 3% improvement</b>
<b>Net Margin</b>	<b>Base</b>	<b>2 - 6% improvement</b>
<b>Energy</b>	<b>Base</b>	<b>8 - 9% lower</b>
<b>BD</b>	<b>Base</b>	<b>17% less</b>
<b>Benzene</b>	<b>Base</b>	<b>25 - 50% more</b>
<b>Pygas</b>	<b>Base</b>	<b>&lt;2 - 12% less</b>

Since the OCT unit produces propylene, the steam cracker can operate at higher cracking severity while maintaining the same overall P/E ratio. The higher cracking severity processes less feed and produces less by-products, resulting in a smaller ethylene plant. Since the ethylene plant is the major cost and energy component, the overall result is that the steam cracker/OCT unit combination outperforms the low severity steam cracker. The addition of the OCT unit to the steam cracker improves capital and operating expenses as compared to larger plants operating in the traditional low severity range.

In addition to the advantages discussed for grassroots complexes, the OCT unit can also be used as an effective debottlenecking tool. It can be applied to plants currently operating at low severity and looking to increase capacity without sacrificing P/E ratio or for plants operating at high severity and looking to debottleneck for higher capacities and P/E ratios.

The crude C<sub>4</sub>'s can be totally hydrogenated to C<sub>4</sub> LPG using ABB Lummus Global technology. BASF Butadiene Extraction can produce butadiene for those applications where there is an attractive market.

BASF selective hydrogenation technology can be used to convert butadiene to normal butenes. CDMtbe or CDEtbe can be used for etherification. Alternatively, CDEtherol can generally be used in lieu of separate selective hydrogenation and etherification steps to process raffinates from butadiene extraction.

To enhance MTBE or ETBE production, ISOMPLUS technology can be used.

If pure isobutylene is required, CD/B MTBE cracking technology can be used.

### ***FCC C<sub>4</sub>'s Processing Options***

In current market conditions, FCC unit profitability is significantly enhanced by the increased flexibility to operate at higher propylene production rates and recoveries. It is currently feasible to double or triple FCC propylene yields by utilizing combinations of customized catalysts, higher severity operation, enhanced FCC design features and improved recovery facilities.

Selective Component Cracking (SCC) is Lummus' maximum olefins catalytic cracking process. In this high olefin production mode the yield of gasoline decreases but the octane number increases. As the yield of propylene increases, the ethylene yield also increases. Ethylene recovery followed by butylene/ethylene metathesis to propylene can improve overall FCC plant economics (Figure 16).

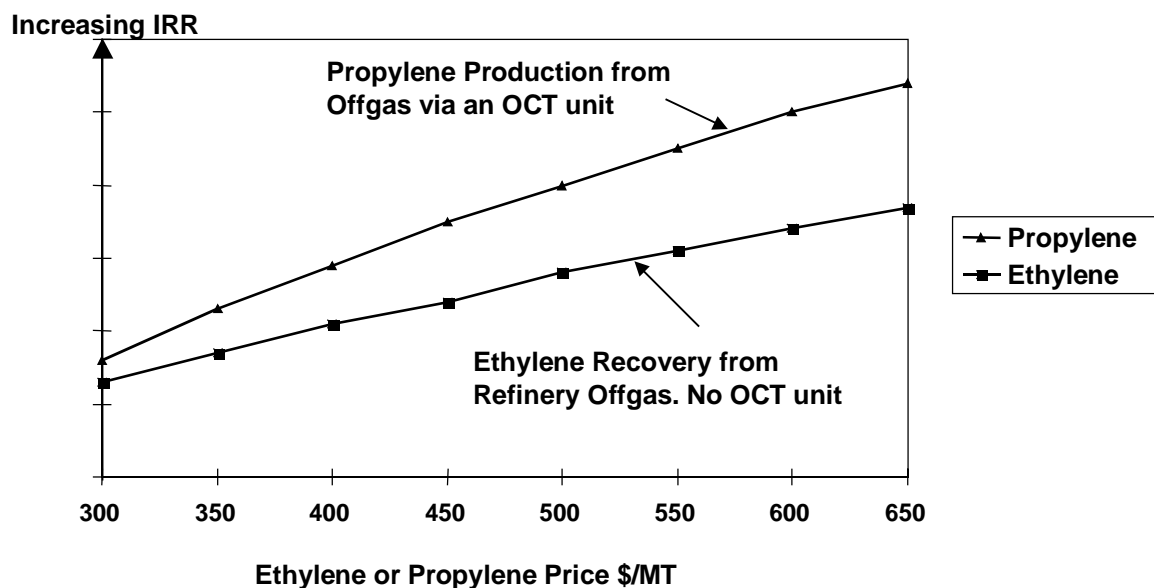
ABB Lummus Global has a patented low cost low-pressure-recovery (LPR) flow scheme for ethylene recovery in cat cracking units that does not sacrifice reliability, flexibility or safety. In this process, typically greater than 95% of the ethylene is recovered from the FCC off gas stream that is normally used as fuel gas.

Adding the LPR unit results in simple payouts typically less than two years, with excellent returns over the historical range of ethylene prices. LPR upgrades ethylene

in FCC offgas from fuel value to product value. Most refineries with operating FCCs have the infrastructure in place for handling propylene product but not ethylene product. So the LPR process can also be used to recover ethylene for further processing via metathesis with refinery C<sub>4</sub>s to maximize propylene. The LPR/OCT combination further improves the economics over the LPR unit alone.

The Figure below illustrates the IRR over a range of product values for ethylene recovery only and propylene production via LPR/OCT. Adding the OCT to the LPR unit increases IRR 10 to 20% even after considering that historically propylene price ranges 0.8 to 0.85 of ethylene price. This is because the major feed in producing propylene is butylene, which is significantly lower in price than either ethylene or propylene. The OCT unit combined with FCC maximizes high propylene production flexibility.

## Refinery Offgas Olefin Recovery Effect of Propylene and Ethylene Prices on IRR



Typical FCC processing options are depicted in Figure 17. If ethylene is not recovered, C<sub>4</sub> self-metathesis can produce propylene and comonomer hexene-1. FCC C<sub>4</sub>'s can be processed to MTBE plus butadiene-free raffinate for alkylation. MTBE production can be enhanced by skeletal isomerization of normal butylenes. Butene-1 can be produced from normal butylenes.

*CDHydro* technology is used to selectively hydrogenate butadiene in the C<sub>4</sub> feed to normal butenes. *CDMtbe* or *CDEtbe* etherification technology produces MTBE or ETBE. Alternatively, *CDEtherol* can be used to accomplish selective hydrogenation and etherification within a single process unit (dashed box).

ISOMPLUS technology can greatly increase MTBE production beyond the amount based on the isobutylene content of the FCC C<sub>4</sub>'s.

ALMA maleic anhydride technology offers an additional option to produce these high value-added products.

### ***Natural Gas Liquids Processing Options***

Saturated C<sub>4</sub>'s from natural gas liquids can be processed into isobutane, isobutylene, MTBE (or ETBE), or butadiene, as depicted in Figure 18.

Using the paraffin isomerization technology from ABB Lummus Global, C<sub>4</sub> LPG or n-butane can be isomerized to isobutane. Isobutane is dehydrogenated to isobutylene using CATOFIN<sup>®</sup> technology. The isobutylene can be etherified with methanol or ethanol using *CD Mtbe*<sup>®</sup> or *CDEtbe*<sup>®</sup> technology to supply the markets for MTBE and ETBE. In situations where butadiene shortfall exists, CATADIENE<sup>®</sup> can be used to produce butadiene.

## **SUMMARY**

Product flexibility, low capital investment and energy efficiency of larger capacity plants will shape the future of the olefins industry. The choice of C<sub>4</sub> processing technology requires optimization for the individual site requirements to maximize return on investment.

The ABB Lummus Global C<sub>4</sub> processing portfolio offers a full range of commercialized technologies for upgrading of low value C<sub>4</sub> streams from Steam Crackers, FCC Units and Natural Gas Liquids to produce propylene, butene-1, butadiene, isobutylene, MTBE and hexene-1. We have built this broad base of processes through research and development, co-venturing process development and executing license agreements with industry leaders.

For further information please contact us on ABB Lummus Global's website at [www.abb.com/lummus](http://www.abb.com/lummus).

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Lummus Claims Recovery Package Cuts Costs, Raises Coproduct Value  
Chemical Week February 27, 2002  
Stephen J. Stanley, interviewed by Andrew Wood Chemical Week

Capital Investment for Propylene Production  
CMAI November 2001

Metathesis: Refinery and Ethylene Plant Applications  
The 1<sup>st</sup> Asian Petrochemicals Technology Conference, Taipei, May 22-23, 2001  
Steven I. Kantorowicz and Ronald M. Venner ABB Lummus Global

Innovative Technologies for Capacity Expansion and Product  
Flexibility of Steam Crackers  
The 11<sup>th</sup> Ethylene Conference, Maoming, PRC November 20-23, 2000  
Steven I. Kantorowicz ABB Lummus Global

JV Builds World's Largest Single Train Olefins Plant  
Oil & Gas Journal September 20, 1999  
Thi Chang Oil & Gas Journal

Low Pressure Recovery of Olefins from Refinery Offgases  
Lummus 8<sup>th</sup> Ethylene Seminar  
Frank D. McCarthy and Aivars E. Krumins

Olefins Conversion Technology  
Lummus 9<sup>th</sup> Ethylene Technology Seminar  
S.M. Edwards

Propylene Options  
EEPC HSE Conference 2000  
Aivars E. Krumins

Ethylene  
Kirk-Othmer Encyclopedia of Chemical Technology 4<sup>th</sup> Edition  
K.M. Sundaram, E.F. Olszewski and M.M. Shreehan

Figure 1  
**ABB Lummus Global Technology Portfolio**

*Chemical/Petrochemical/Polymer Processes*

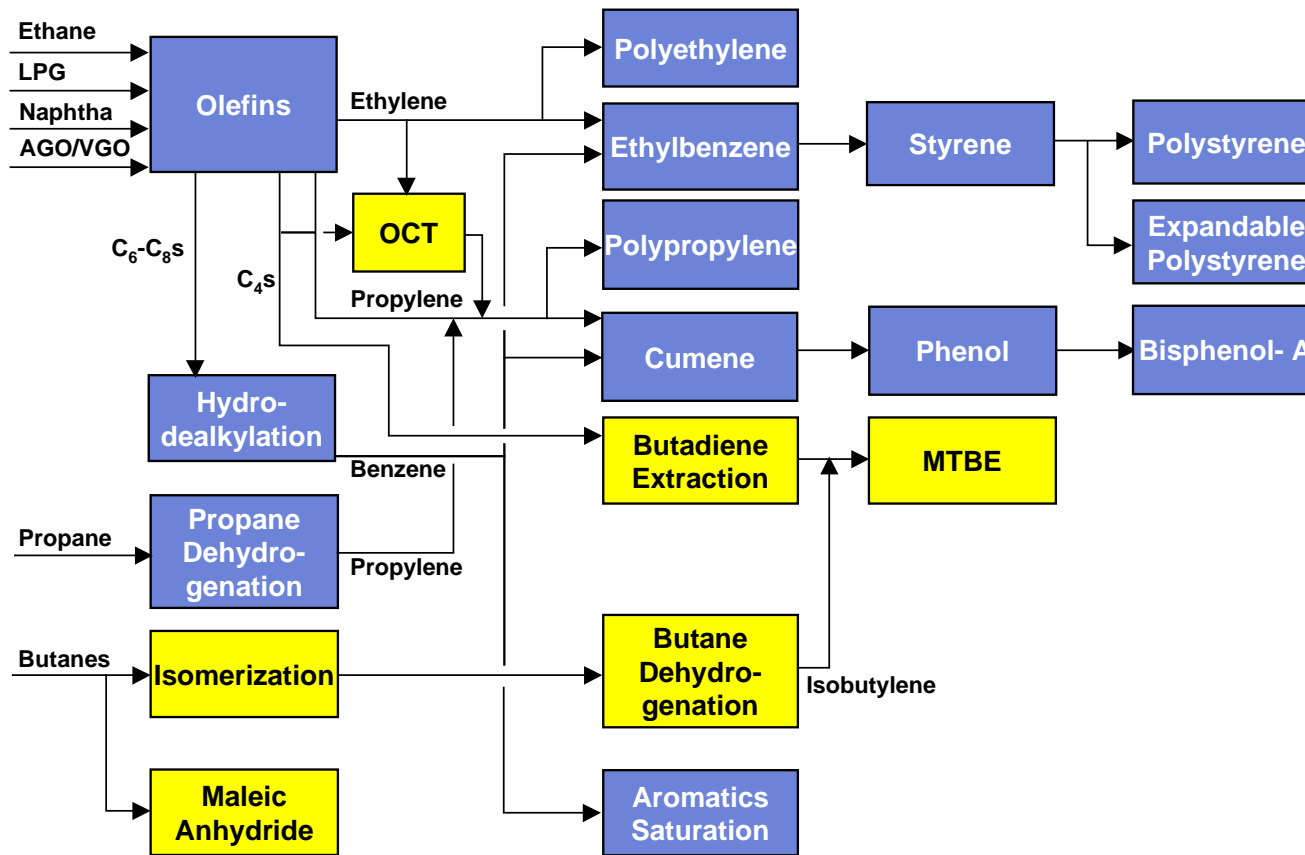


Figure 2  
**ABB Lummus Global Technology Portfolio**  
*Refining Processes*

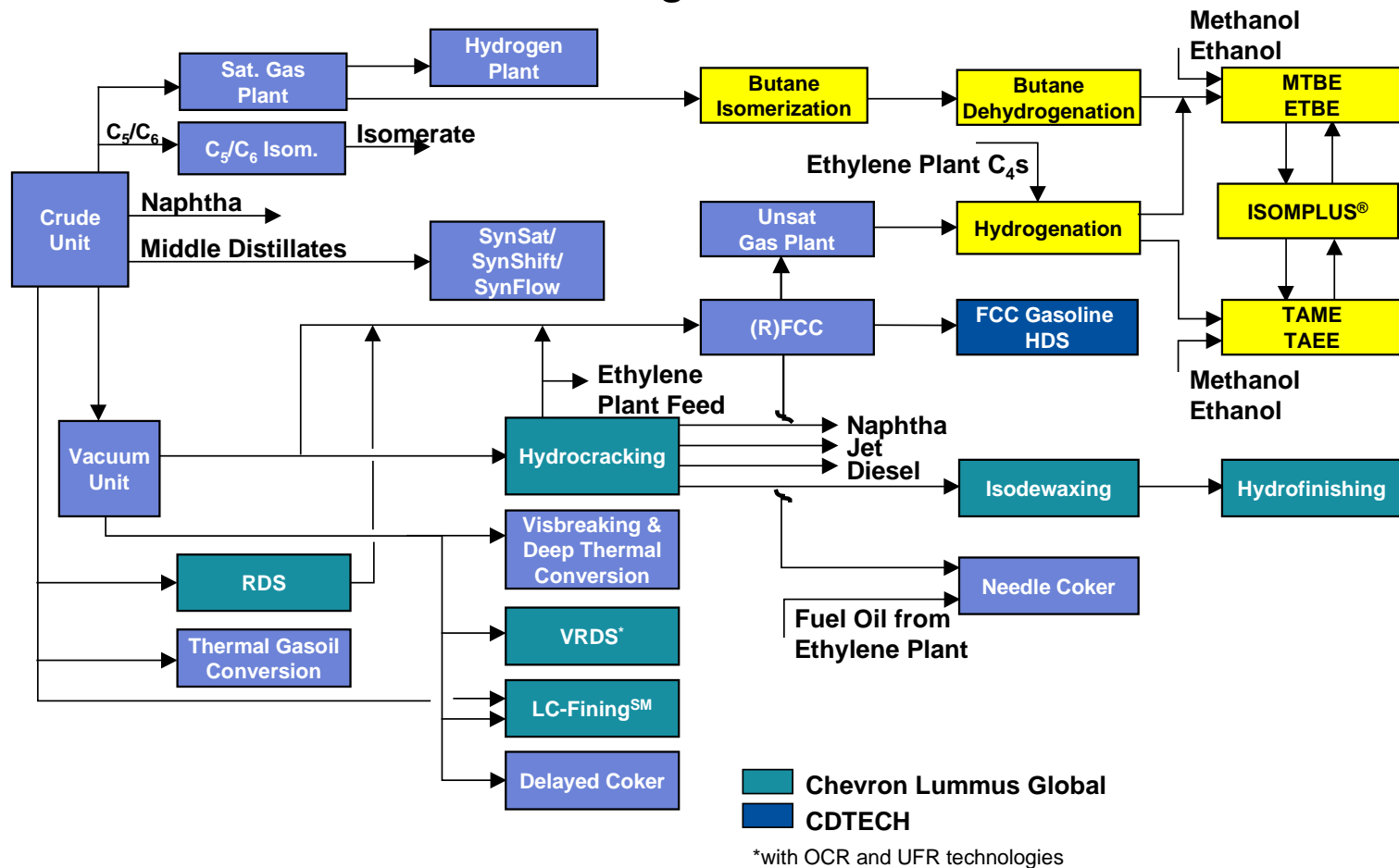


Figure 3

# CDTECH Technology Portfolio

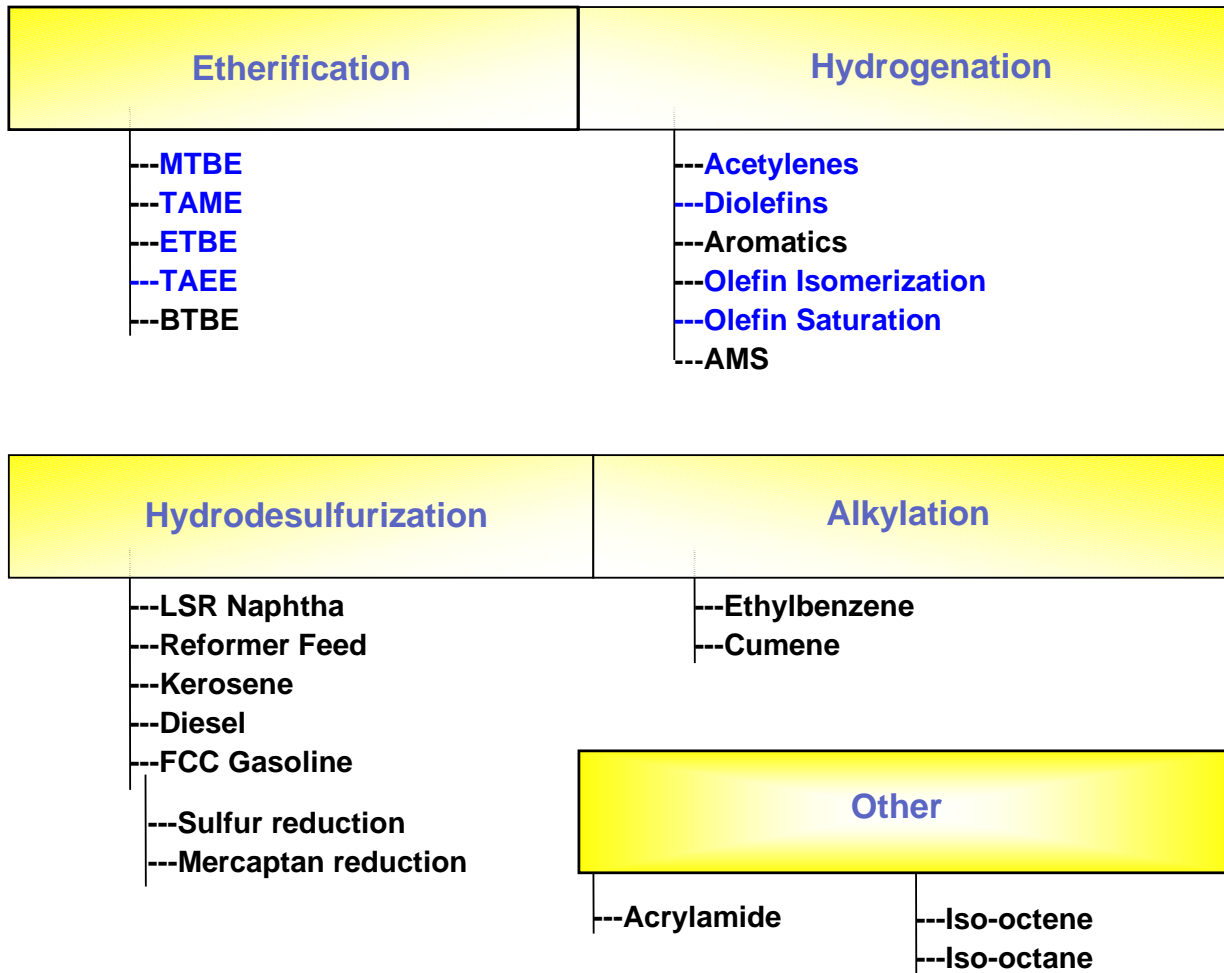
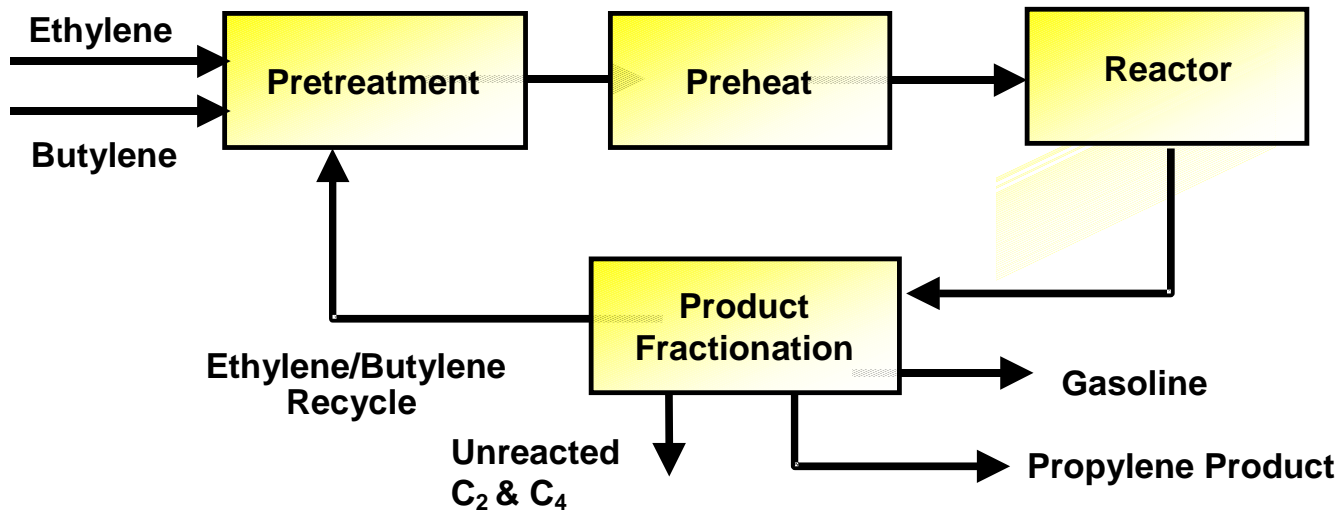
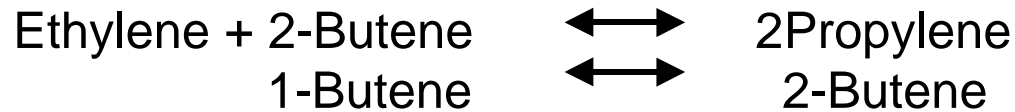


Figure 4

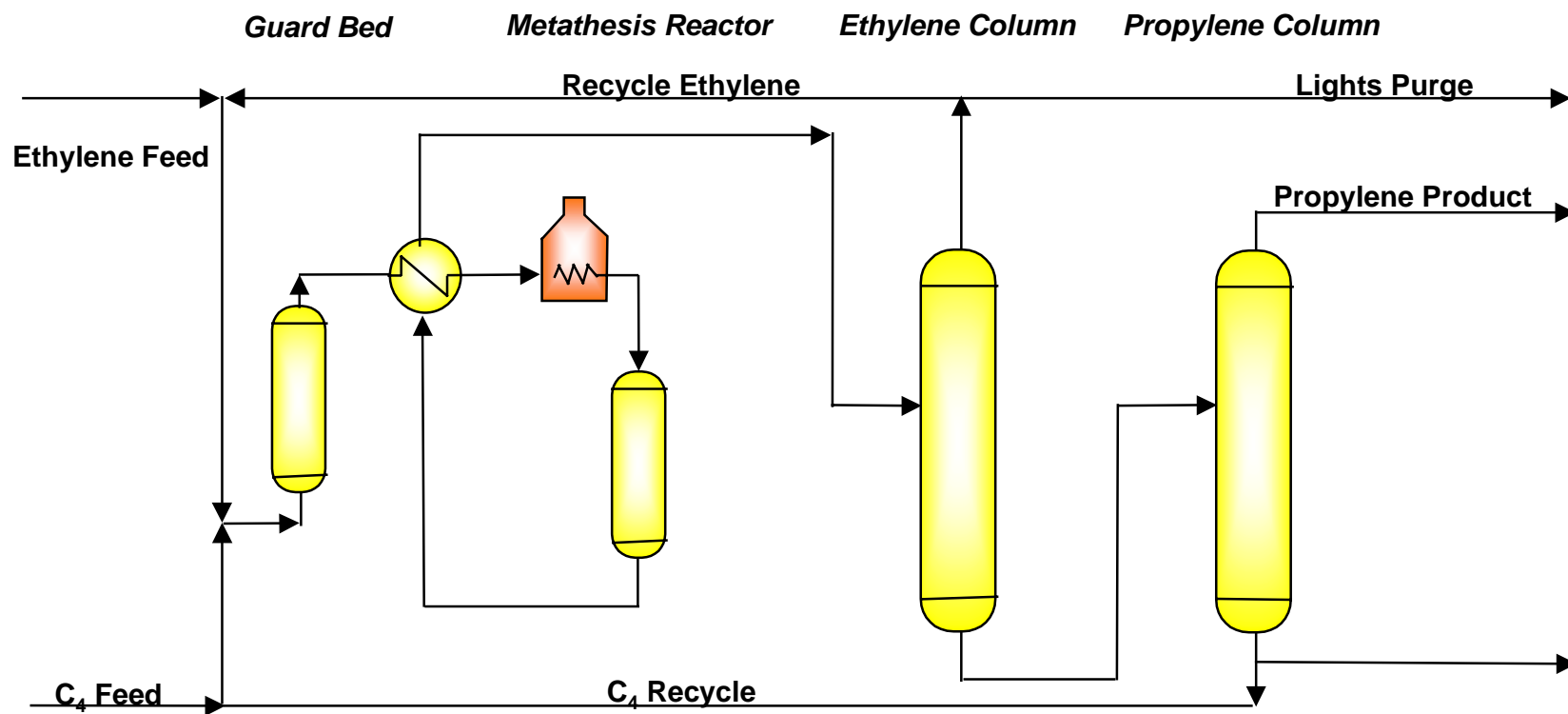
# Olefins Conversion Technology (OCT)

*Propylene from ethylene and butene*



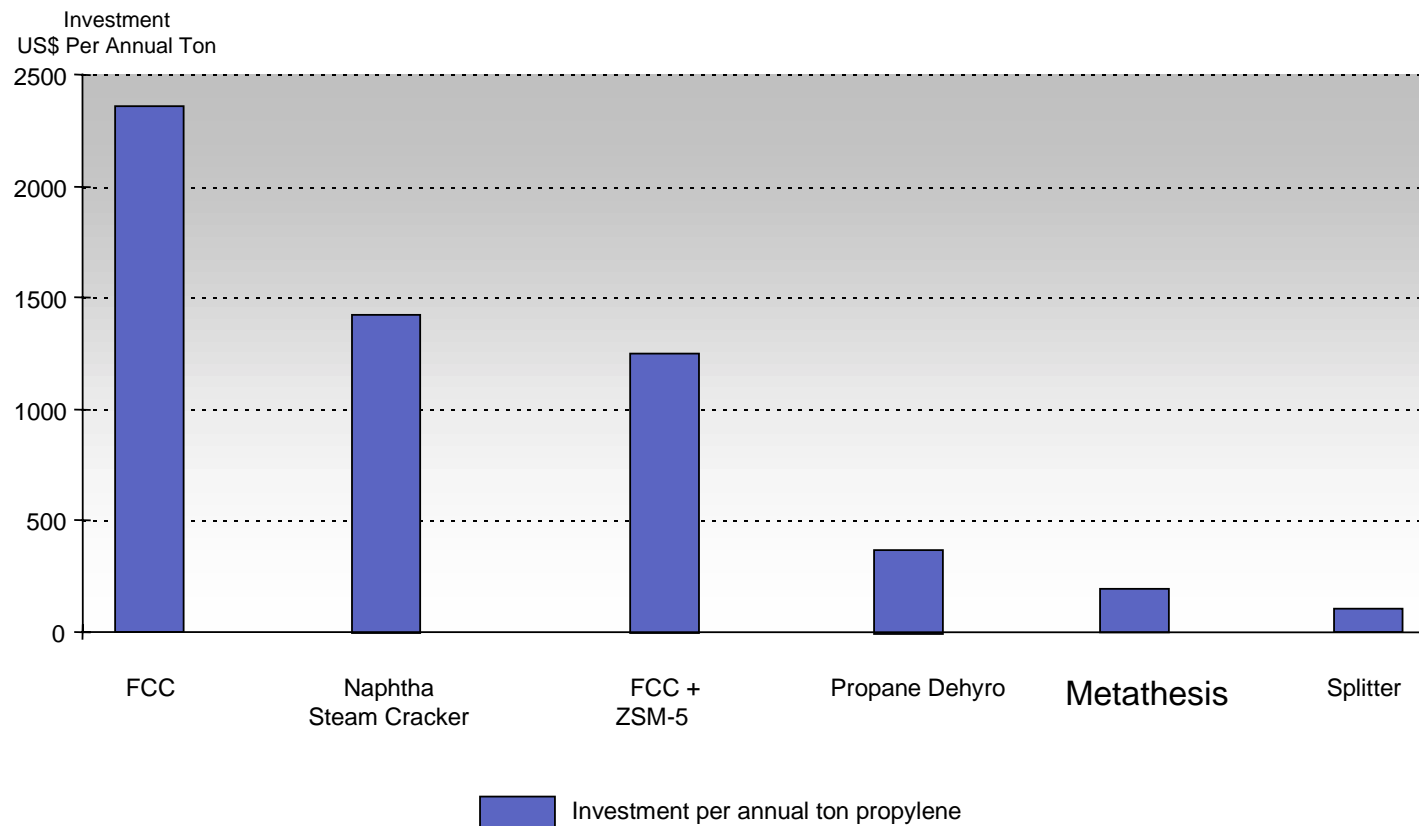
**Low capital route  
to propylene**

Figure 5  
**OCT - Process Flow Schematic**



***No Superfractionators Required***

Figure 6  
**Relative Capital Investment for Propylene Production**



Ref: CMAI Nov. 30, 2001

Figure 7  
**CDHydro<sup>®</sup> Tower**

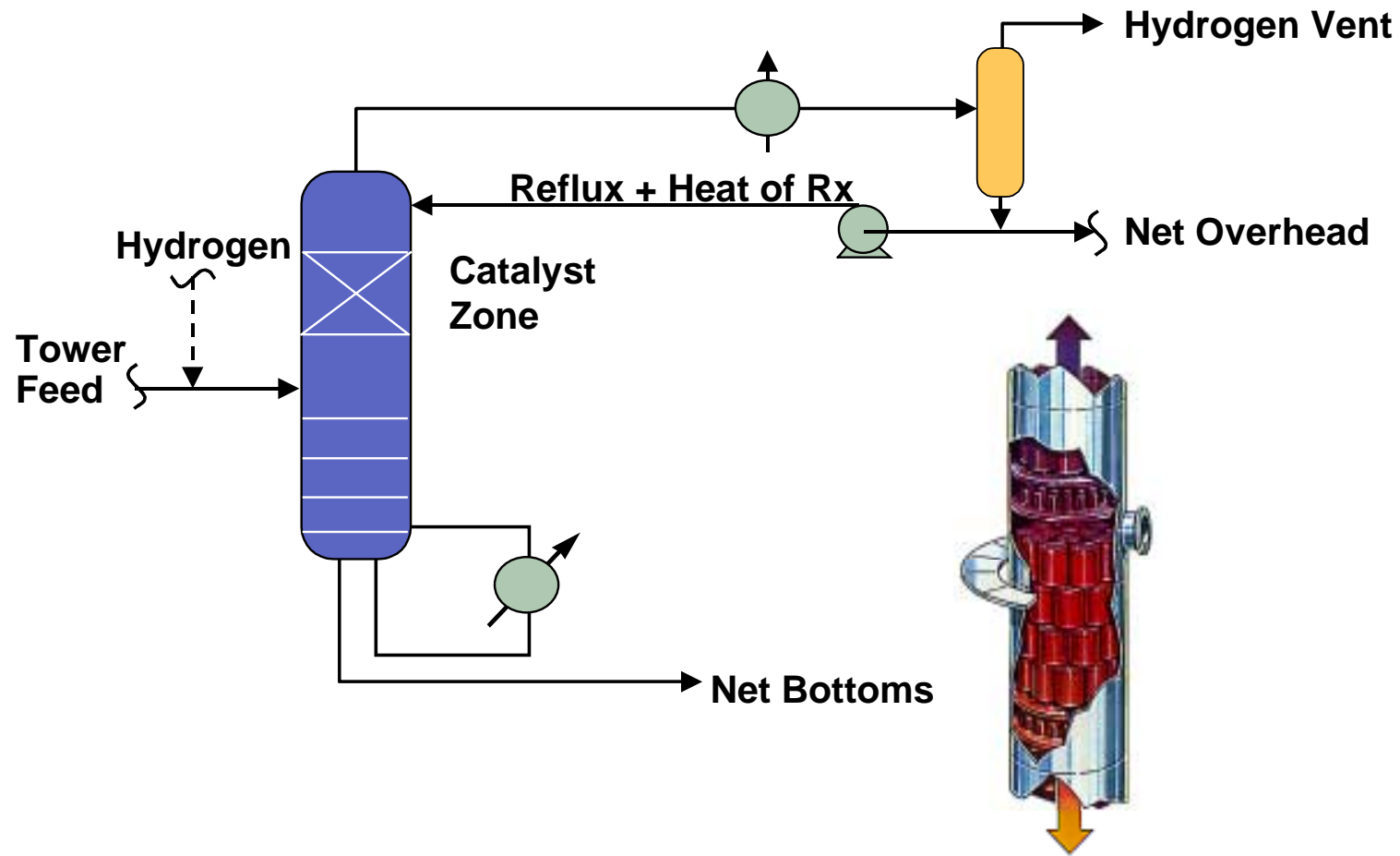
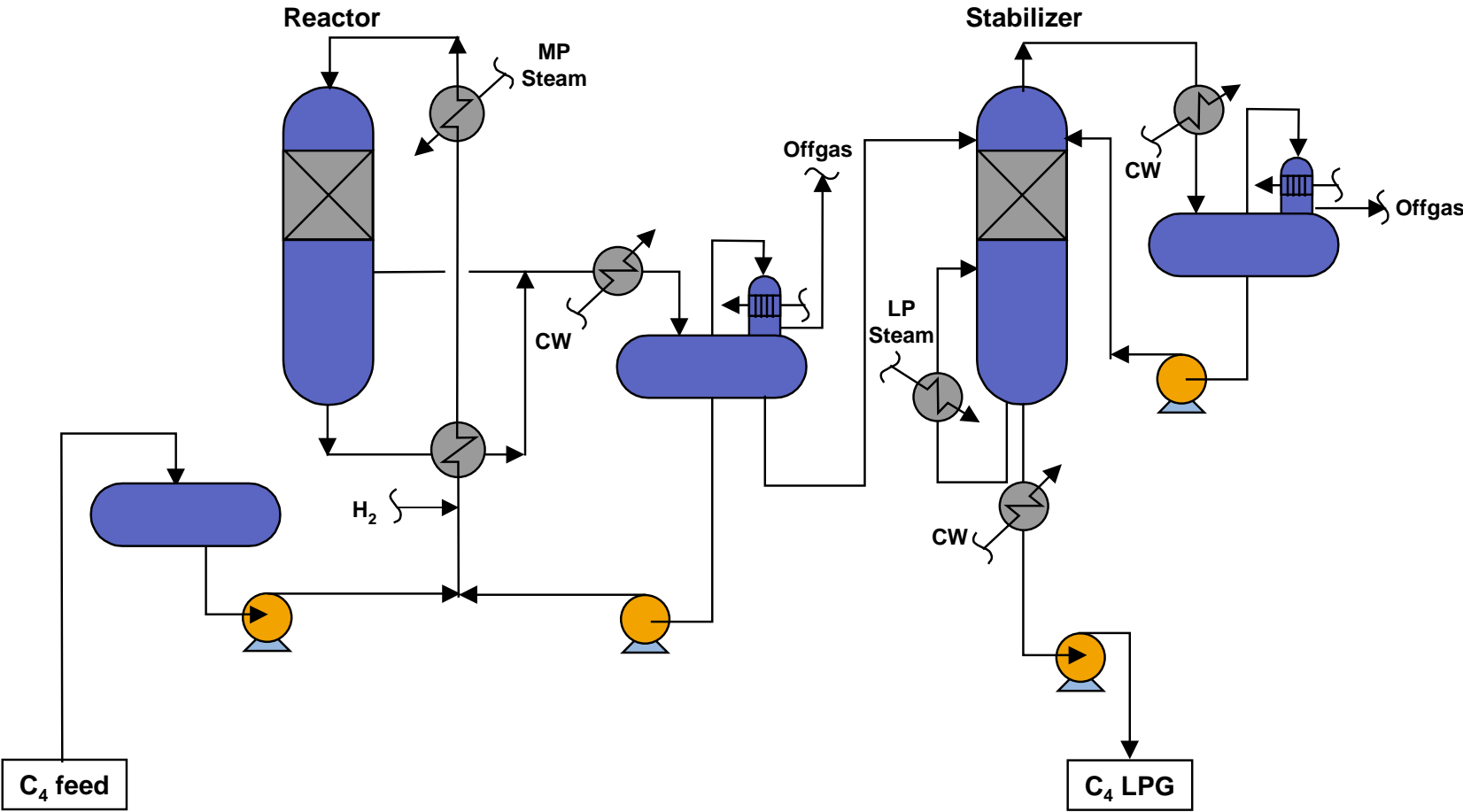


Figure 8  
**Total C<sub>4</sub> Hydrogenation**



# Figure 9 CATOFIN® Dehydrogenation Processing Scheme

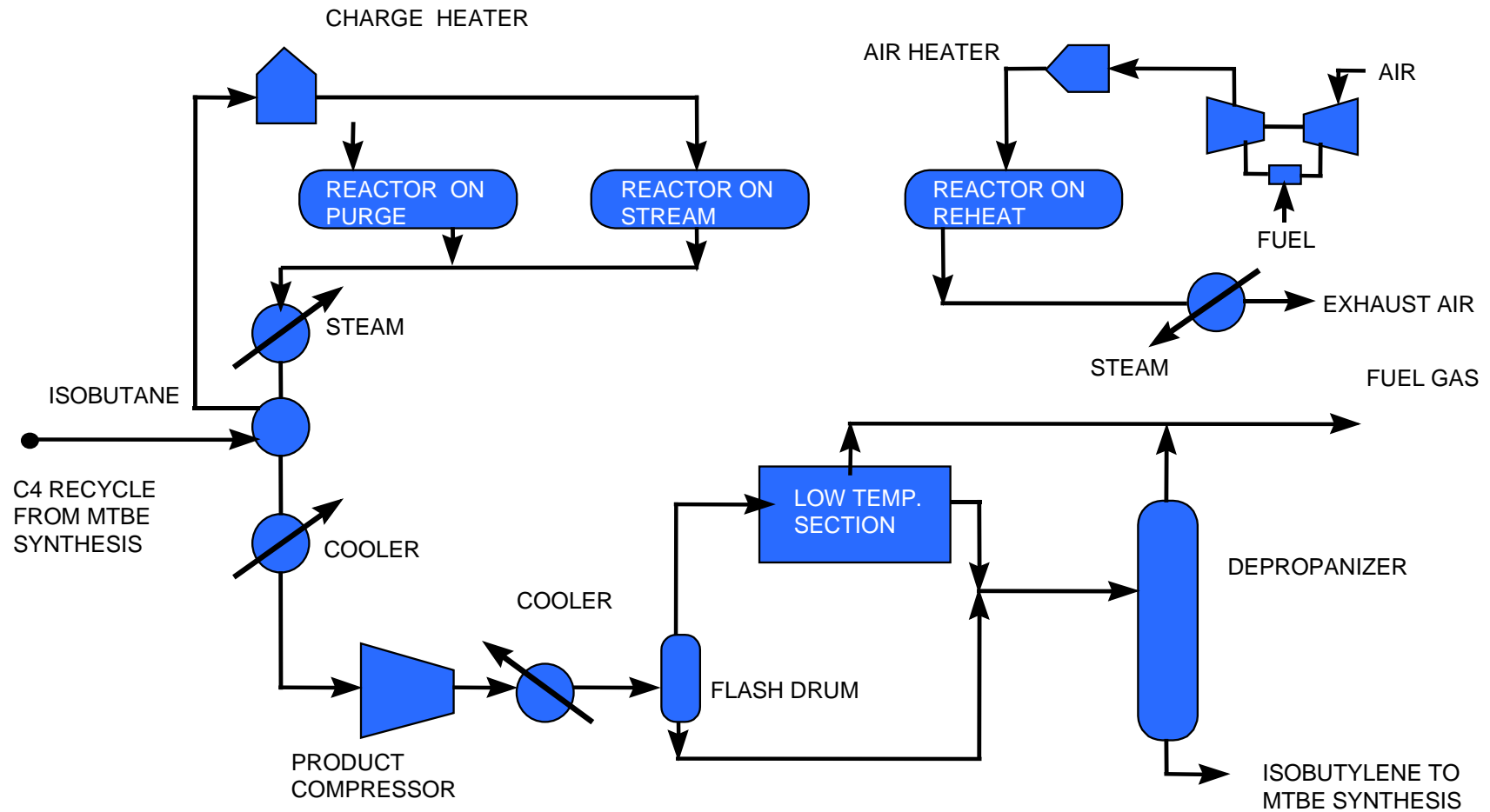


Figure 10  
**CDTECH Ethers Process**  
**MTBE or ETBE**

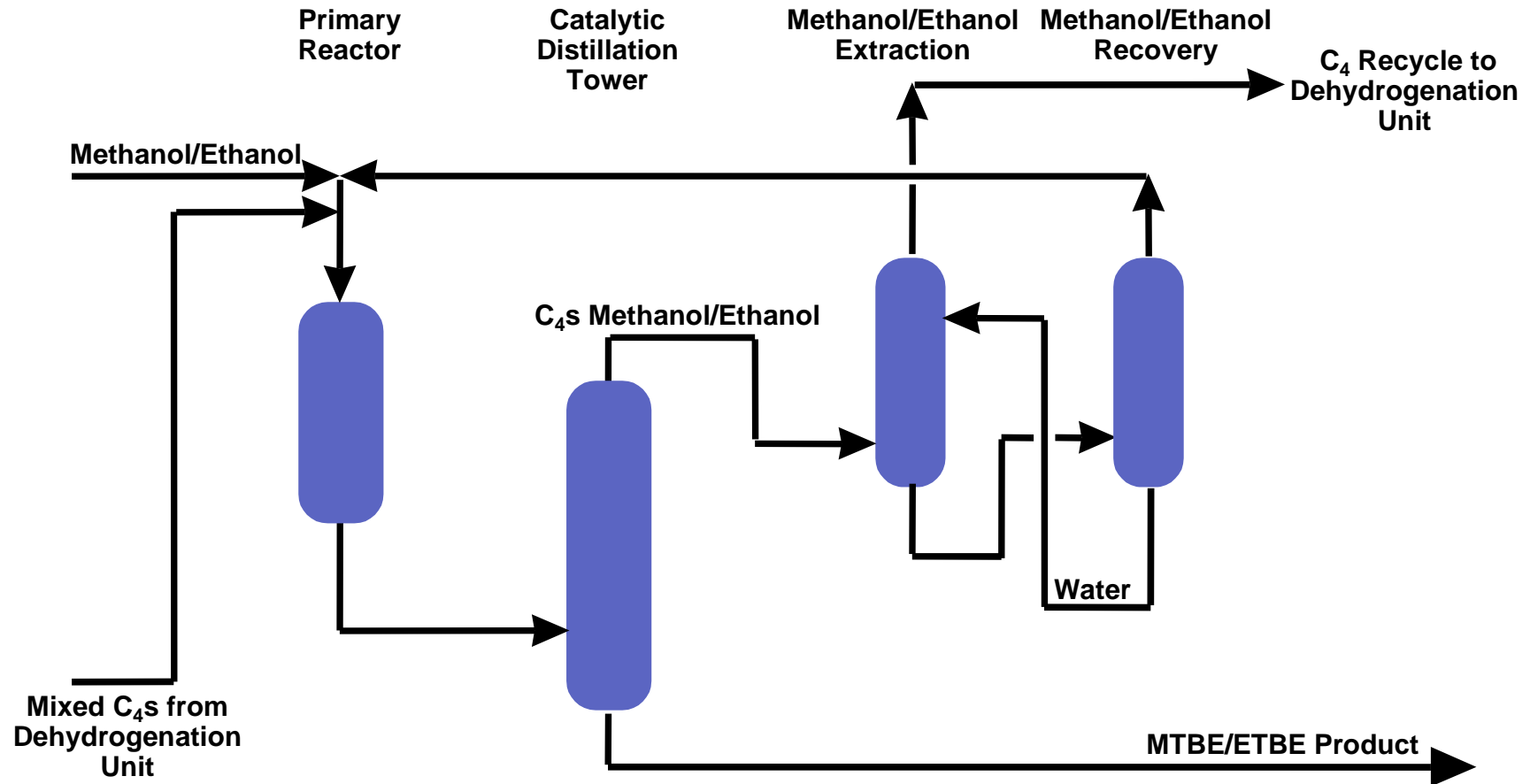


Figure 11  
**CDTECH - CDIB**  
**Isobutylene Unit Integrated With MTBE Unit**

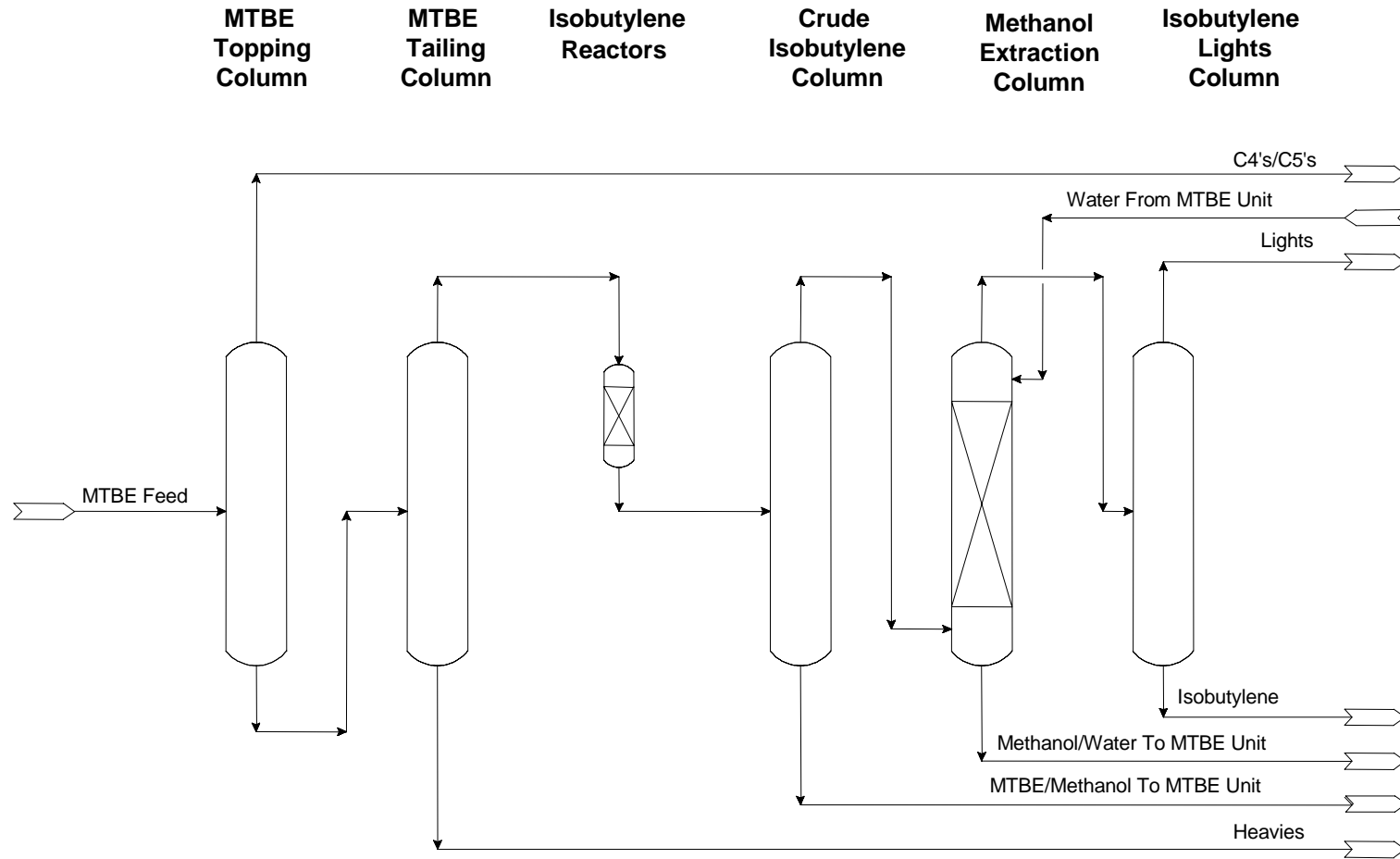


Figure 12  
**ISOMPLUS<sup>®</sup>**  
**C<sub>4</sub> Skeletal Isomerization Process**

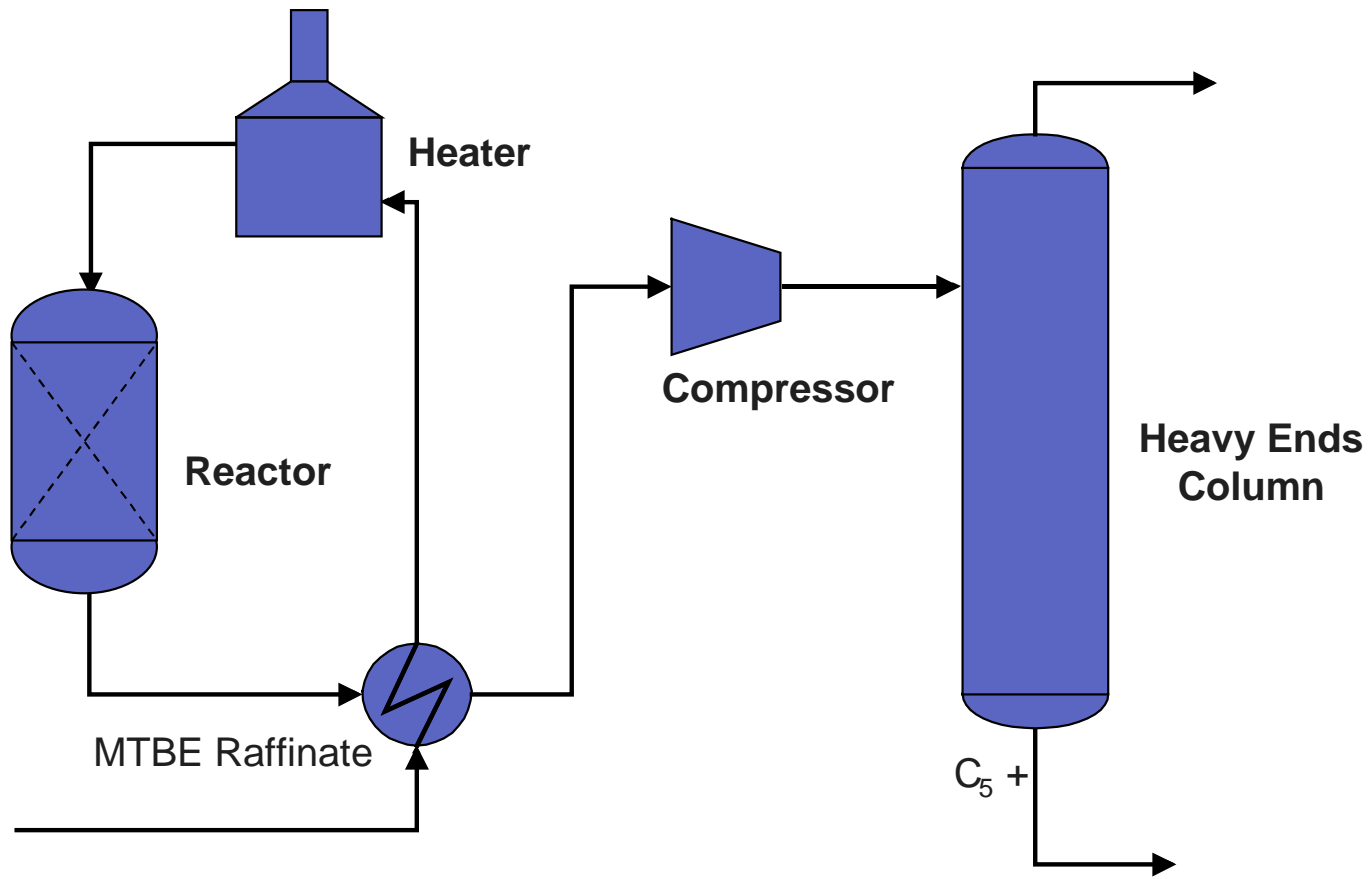


Figure 13  
**Maleic Anhydride**

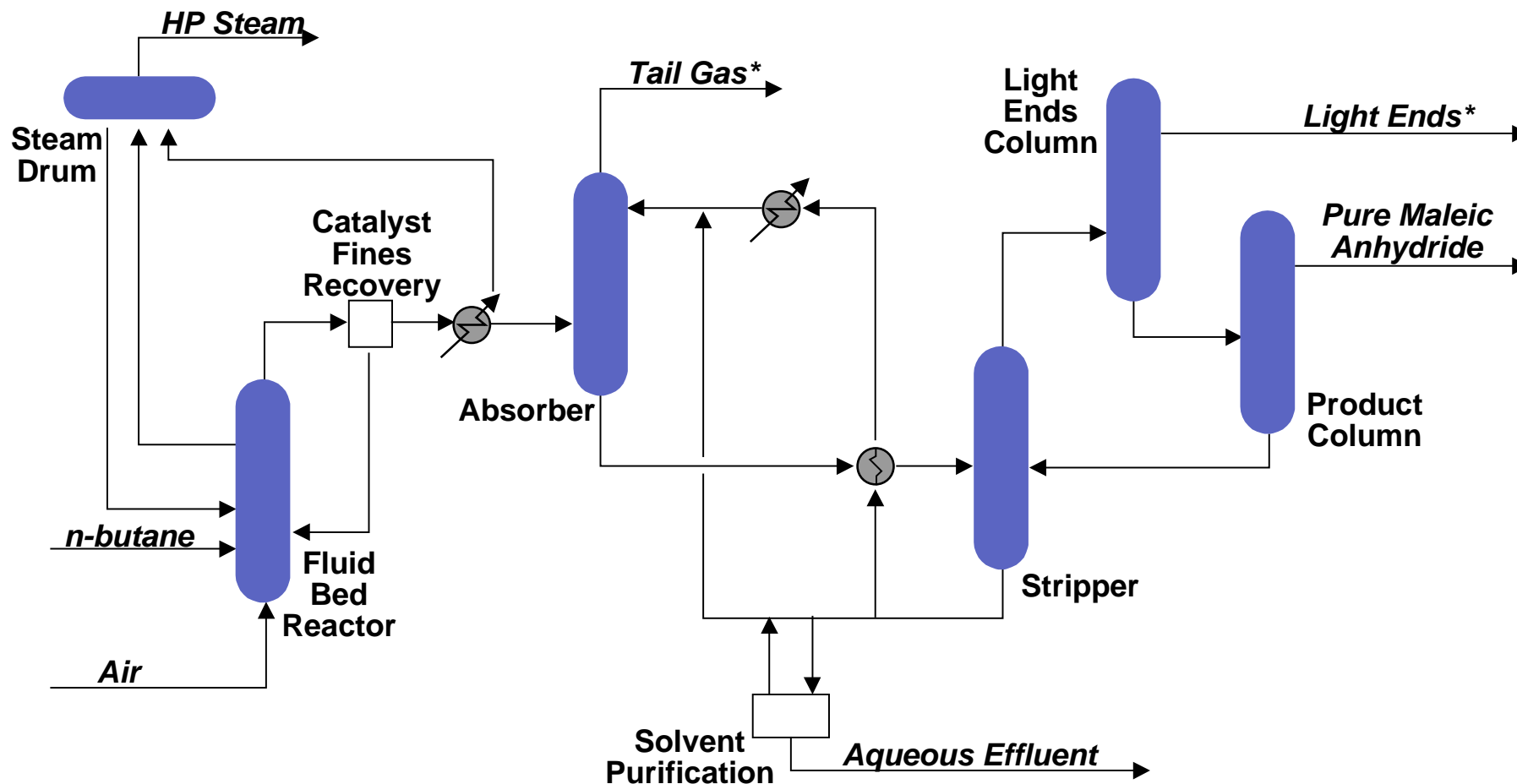


Figure 14  
**Steam Cracker Ethylene & C<sub>4</sub>s Processing Scheme**

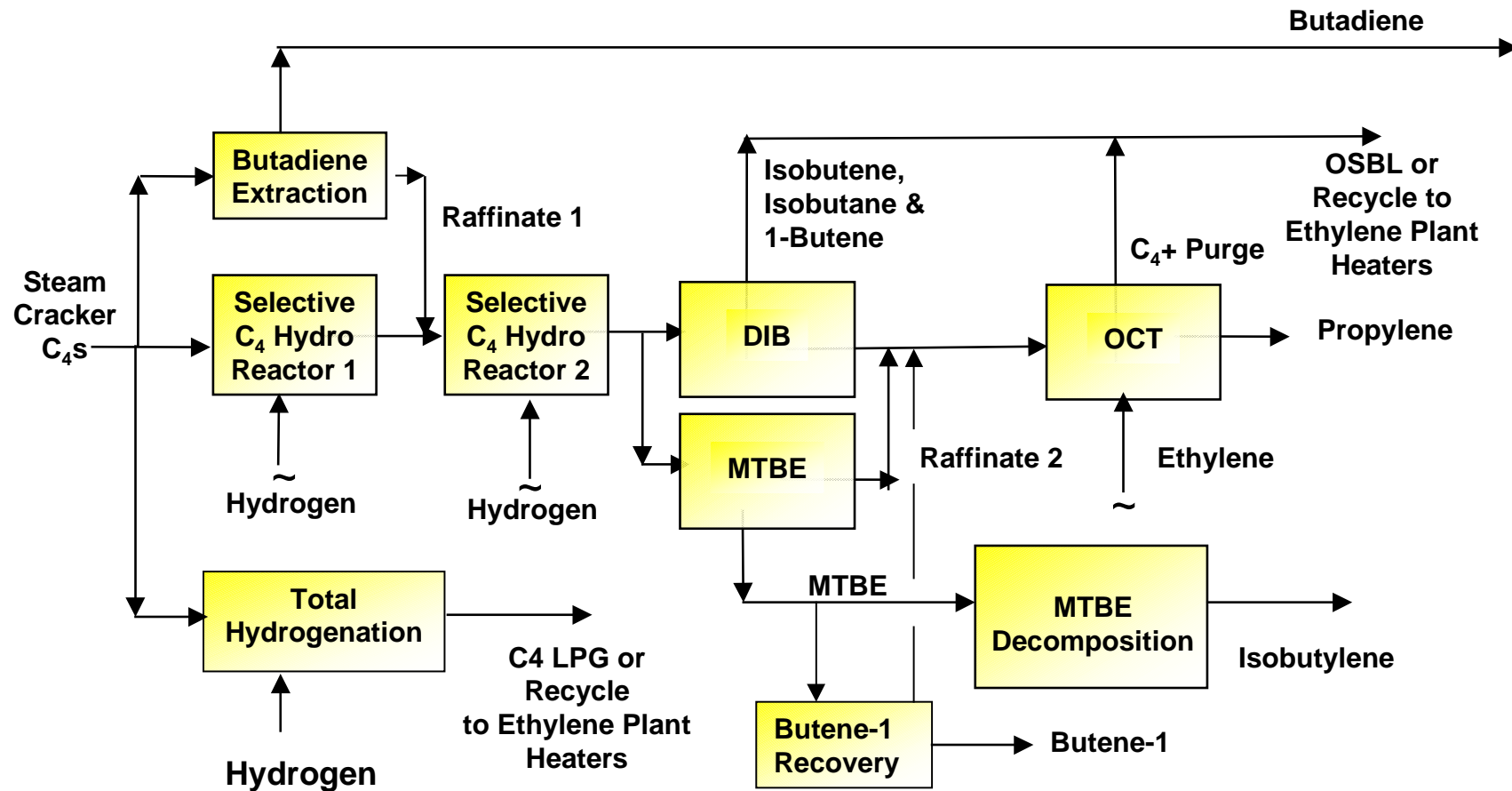
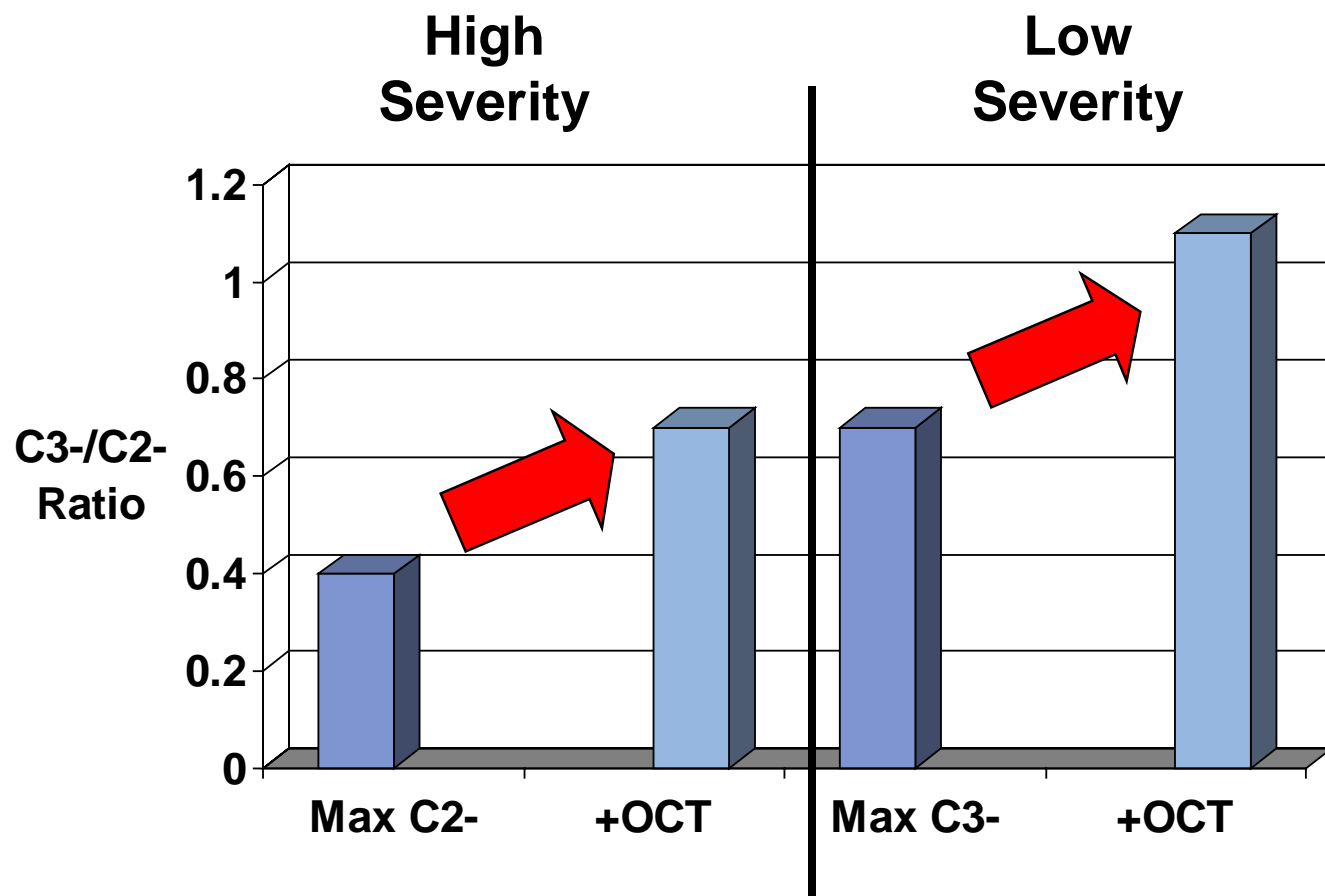


Figure 15

# Steam cracker OCT results



***OCT enhances P/E product flexibility for all crackers***

Figure 16  
**FCC Propylene**  
*OCT Results*

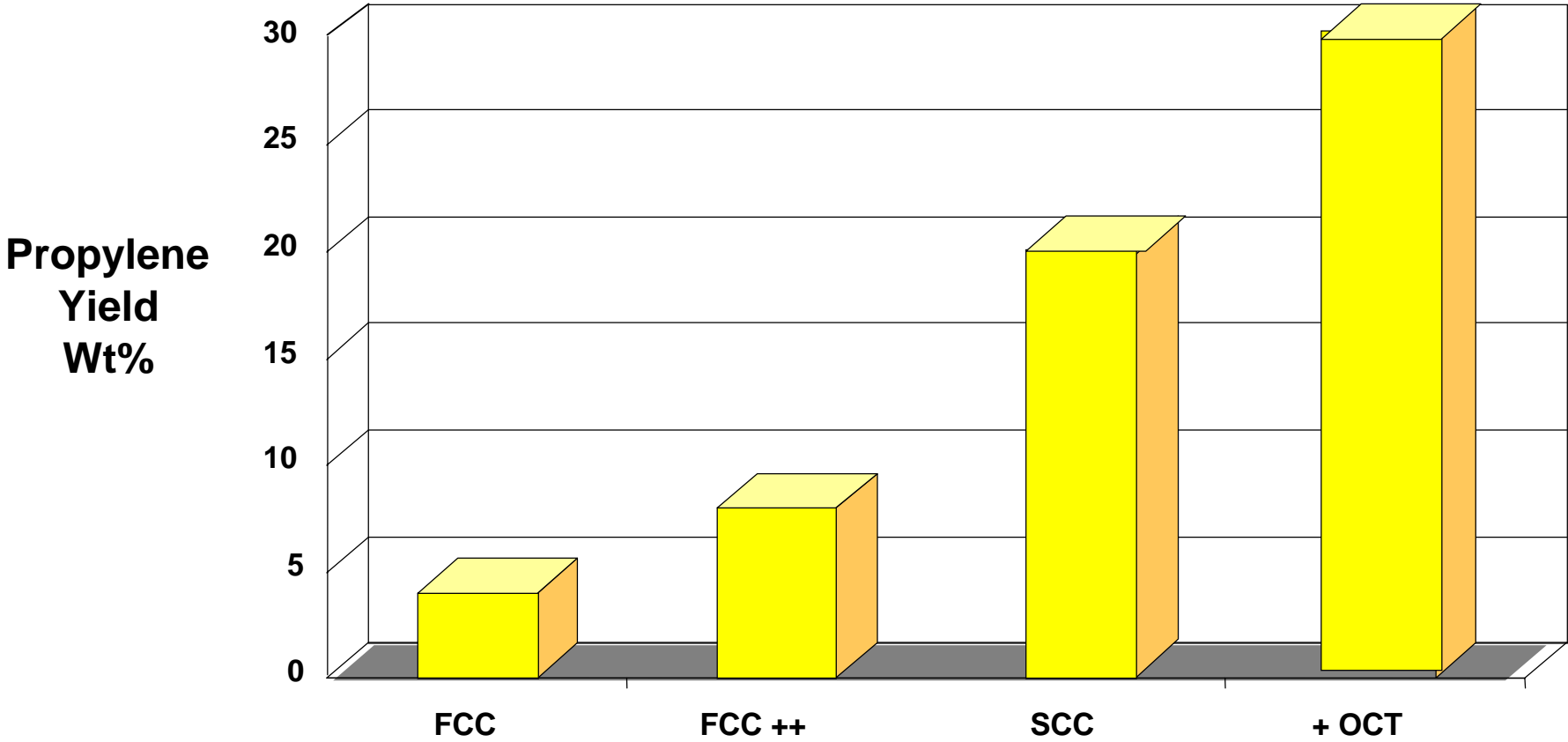


Figure 17

# FCC C<sub>4</sub>s & FCC Off Gas Processing Scheme

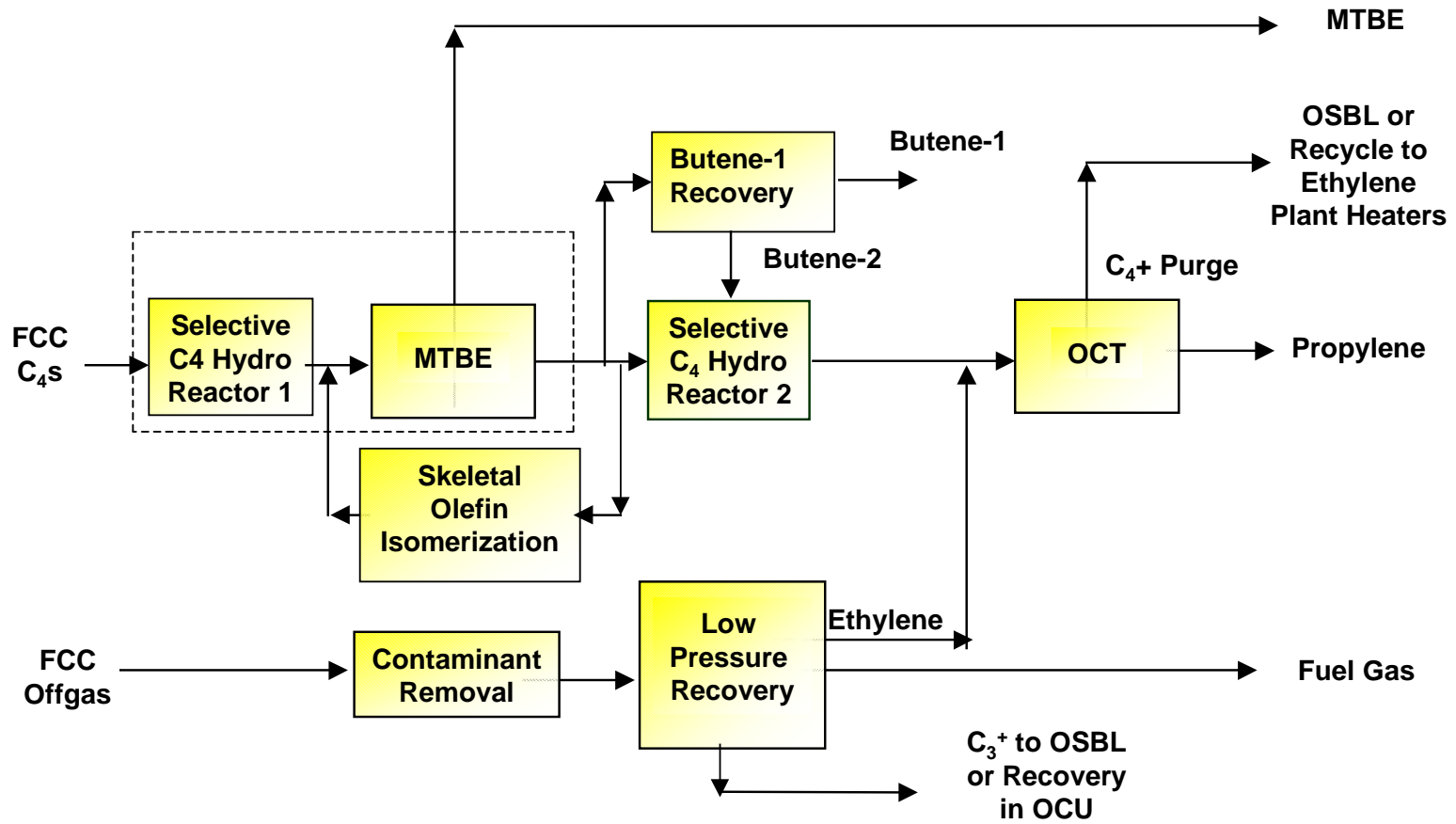


Figure 18  
**Natural Gas Liquids Processing Scheme**

