

## **Olefin Transformation - A Means to Ease Your MTBE Woes**

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### **Introduction**

The oxygen mandate by government regulatory agencies was the cornerstone in their mission for the production of cleaner burning gasoline. As a result, the oxygenated fuels industry expanded swiftly over the last decade as a means to achieve the targeted levels of oxygen content and to supply an octane enhancement ingredient for gasoline. MTBE was the overwhelming choice of many refiners to satisfy the oxygen content specification. In addition, environmental regulators worldwide reduced the maximum acceptable RVP specification for gasoline, limiting the refiner's ability to blend significant quantities of C<sub>4</sub>s into gasoline. The production of MTBE was an economical alternative. By reacting high vapor pressure isobutylene with methanol to produce MTBE, a low value C<sub>4</sub> became a value-added product with high-octane value and low vapor pressure characteristics that added to the overall volume of the gasoline pool.

Ironically, the state government regulatory agency that initiated the drive towards the production of oxygenates is now mandating the removal of MTBE from gasoline. Momentum is currently building towards the elimination of MTBE from gasoline. With the potential for the MTBE market to diminish as swiftly as it developed, MTBE producers are left scrambling to find alternative C<sub>4</sub> processing options.

Finding a profitable, alternative use for isobutylene previously targeted for MTBE production is facility-specific and dependent upon existing processing strategies within the facility as well as the availability of other potential feed materials. One possible derivative that is not usually associated with C<sub>4</sub> processing is propylene, which is mainly used for polypropylene production. Demand for propylene is consumer driven, unlike MTBE, which was superficially built on the shifting foundation of environmental regulations. Polypropylene continues to make inroads into the large volume polyethylene market as an economical alternative for plastic products. Given this inroad, propylene

demand is expected to grow by 5.5% over the next several years and exceed ethylene demand by approximately 1%.

A recent trend in many refineries with FCC units is downstream integration for propylene supply to polypropylene units. Currently, approximately 70% of worldwide propylene production are from ethylene plants with most of the balance from FCC off-gases. A small percentage of propylene is produced via propane dehydrogenation or ethylene/butene metathesis. The addition of new ethylene plant capacity will not satisfy demand for propylene since substantially more ethylene is produced per unit of feed than propylene. Alternative methods will be required to meet this demand.

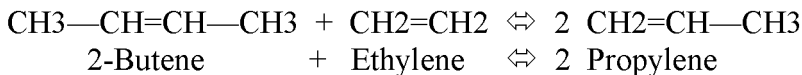
### **Propylene Production through Olefins Conversion**

ABB Lummus Global's (Lummus') portfolio of technologies contains a unique combination of commercially proven processes that offer the capability to produce propylene from the isobutylene. The keystone of this combination is Olefins Conversion Technology (OCT), which utilizes metathesis (disproportionation) for the interconversion of light olefins. Metathesis is an equilibrium reaction between two olefins where the double bond of each olefin is broken to form intermediate reactants. These intermediates recombine to form new olefin products. Some disproportionation reactions utilizing C<sub>4</sub> olefins are:

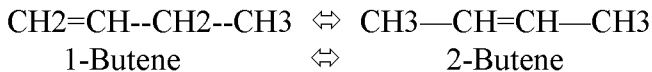
- 1-butene with itself to form ethylene and 3-hexene;
- 1-butene and 2-butene to form propylene and 2-pentene;
- 2-butene and ethylene to form propylene.

This discussion will concentrate on the third reaction shown above.

The butene/ethylene metathesis to propylene consists of the following reaction:



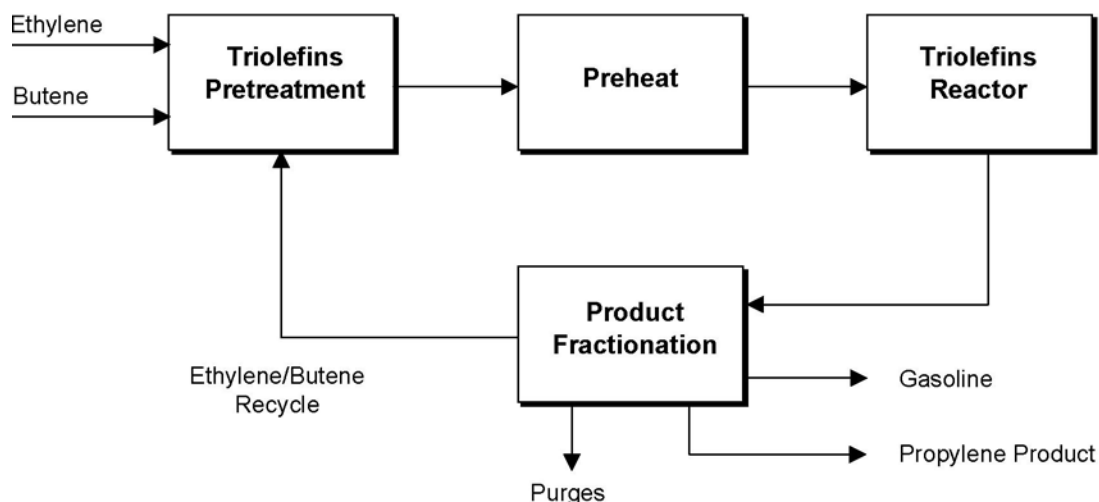
In addition, an isomerization reaction also occurs in the system.



These are vapor phase reactions occurring in a fixed bed reactor under essentially isothermal conditions. Equilibrium metathesis conversion ranges from 65 to 70% of the butenes with propylene selectivity ranging from 90 to 98%. Optimal conditions are achieved by adjusting the temperature, pressure, and ethylene-to-butene ratio for various design considerations. Essentially two thirds of the propylene is produced from low value butenes and when coupled with low capital cost results in excellent economics for the production of propylene.

A simple block flow diagram for OCT is shown in Figure 1. Recycle ethylene and butene are combined with fresh ethylene and butene and pretreated to remove catalyst poisons. The pretreater effluent is vaporized and superheated by cross exchange with the hot reactor effluent. In the reactor, catalyst promotes the reaction of 2-butene and ethylene to propylene and simultaneously isomerizes 1-butene to 2-butene. The product from the reactor is cooled and sent to the fractionation section to recover polymer grade propylene product and ethylene and butene for recycle. Light reaction by-products are purged from the system while heavy reaction by-products are removed as a slipstream and can be mixed in the gasoline pool. This process can be integrated with existing facilities to increase operating efficiency and reduce capital expenditure.

**Figure 1      Olefins Conversion Technology**  
**Ethylene + Butene ----- ► Propylene**



Phillips Petroleum Company originally developed Olefins Conversion Technology. In 1997, Lummus acquired OCT with exclusive rights to license OCT for C<sub>2</sub> to C<sub>5</sub> olefins. This proven, low capital cost approach has been demonstrated on a commercial scale with various metathesis applications.

The original unit was developed for Shawinigan Chemicals Ltd. of Canada to perform the reverse reaction of producing ethylene and butenes from propylene. The unit operated successfully from 1965 to 1972 until it was shutdown for economic reasons. Phillips Petroleum Company designed another OCT application to produce neohexane and isobutylene from ethylene and diisobutylene using the same metathesis catalyst. Lummus designed a unit to convert ethylene to propylene by combining the dimerization of ethylene to butene with the metathesis of ethylene and butene. This unit was put into operation at Lyondell Petrochemical Company (Equistar) in June of 1985 and Lummus expanded the unit's capacity in 1992.

Two recent awards are currently in the engineering phase. The first unit will combine OCT with Lummus' patented, low pressure FCC Off-gas Recovery System within an existing refinery in Europe. Ethylene recovered from FCC off-gas will be reacted with n-butenes currently feeding an alkylation unit. The second unit will be fully integrated with a grassroots steam cracker for BASF-Fina.

### Ethylene Feedstock for the OCT Unit

Three common sources for ethylene feedstock are:

1. Steam cracker ethylene product,
2. FCC off-gas,
3. Vents from polyethylene units.

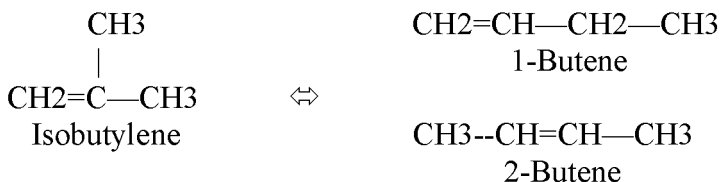
Polymer grade ethylene is the cleanest ethylene feedstock available for OCT. It requires minimal pretreatment for trace components such as carbon dioxide while other sources of ethylene typically require more rigorous pretreatment. Though polymer grade ethylene costs more than other types, capital expenditure is lower because no investment is required for recovery and purification.

FCC off-gas is an inexpensive source of ethylene since this stream is usually valued at fuel gas cost. Pretreatment, fractionation and refrigeration are necessary for recovery of the ethylene product; however, an FCC off-gas recovery system typically has an attractive internal rate of return.

Another source of ethylene is the high and low-pressure polyethylene unit vents. This source may not normally provide the quantity of ethylene necessary; consequently, other sources of ethylene would supplement any shortfall. These vents must be treated to remove water and oxygen. A compressor is usually required to boost these streams to a reasonable processing pressure.

### Isobutylene Conversion to Normal Butenes

With MTBE phase-out, alternative isobutylene uses will be necessary. For the production of propylene with the OCT process, isobutylene reacts with itself and normal butenes to produce isoamylenes and some ethylene and propylene. While isobutylene does react with n-butenes to produce some propylene, overall propylene production decreases since isobutylene's reaction with n-butenes significantly reduces the n-butenes available to react with ethylene to produce propylene. To enhance the production of propylene, it is necessary to convert the isobutylene to n-butenes.

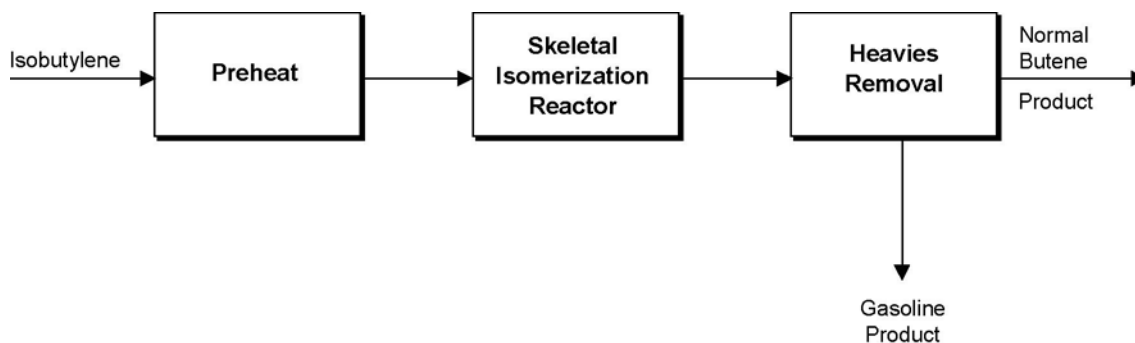


A skeletal isomerization process was developed to convert isobutylene to normal butenes. The process reaction is equilibrium limited and conversion of isobutylene to n-butenes is approximately 62% with selectivity to n-butenes of approximately 90%.

Figure 2 depicts the flow scheme for the skeletal isomerization process. Isobutylene rich feed is totally vaporized and superheated prior to entering the fixed bed isomerization reactor where isobutylene is converted to near-equilibrium yield of n-butenes. The isomerization reaction is slightly exothermic. Product from the reactor is cooled and sent to a heavies column for removal of C<sub>5</sub> and heavier by-products. These heavy compounds have good octane value and can be blended into the gasoline pool. The overhead of the heavies column can be processed in a butene splitter for separation of the unreacted isobutylene.

## Figure 2 - Skeletal Isomerization Technology

Isobutylene -----► Normal Butenes



### Hydroisomerization of 1-Butene to 2-Butene

While it is possible to feed a mixed olefin stream to the skeletal isomerization unit, there are advantages to increasing the concentration of isobutylene in the feed by removing normal C<sub>4</sub> olefins.

1. The reaction is equilibrium limited; therefore, reducing the normal C<sub>4</sub> olefins in the feed increases the conversion of isobutylene.

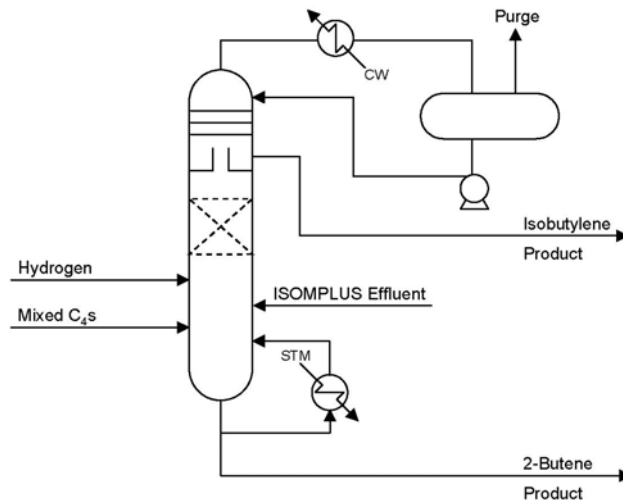
2. The size and ultimately the cost of the skeletal isomerization unit are reduced since the capital and operating costs directly correlate to the gross throughput of the unit.

Catalytic Distillation (CD) combines fractionation and reaction in a single unit operation. One commercial application of CDTECH's *CDHydro*<sup>®</sup> technology combines hydroisomerization with distillation. This CD application has unique advantages when applied at typical operating conditions used for the separation of C<sub>4</sub>s. These unique advantages include:

- . The production of an isobutylene overhead product with a low 1-butene content;
- . The increased production of 2-butene from the isomerization of 1-butene.

Additional 2-butene is separated to the bottom of the CD column as it is created, which allows the reaction of 1-butene to 2-butene to go beyond the limit of single stage equilibrium. Figure 3 shows the basic CD column as applied to this application. Mixed C<sub>4</sub>s feed the CD column along with effluent from the skeletal isomerization unit. A small amount of hydrogen is required to promote the isomerization reaction. The catalyst section of the column contains catalyst enclosed in a proprietary structured distillation packing. Isobutylene rich overhead product is sent to the skeletal isomerization unit. The bottoms product is rich in 2-butene and lean in isobutylene making it an ideal feed for the OCT unit. A small purge of hydrogen and non-condensable by-products formed in the skeletal isomerization unit is removed overhead.

**Figure 3 - *CDHydro*<sup>®</sup> Technology**  
**Application: Hydroisomerization 1-Butene-»2-Butene**



Depending on the butadiene content of the mixed C<sub>4</sub> stream, it may be advantageous to have a fixed bed reactor upstream of the CD column. This reactor serves two purposes to:

1. Saturate high concentrations of butadiene;
2. Perform bulk hydroisomerization.

Increasing the concentration of 2-butene feeding the CD column reduces the amount created in the rectification section. 2-butene is a heavy component in the separation of C<sub>4</sub>s; consequently, less work is required to separate the C<sub>4</sub>s.

The initial *CDHydro* process license was for a butene splitter application at Shell's Norco, LA refinery. The unit successfully started up in February of 1994. Unlike traditional fixed-bed technologies, catalyst fouling is not the primary factor that determines run length in the *CDHydro* process since fouling is essentially eliminated. Fouling is minimized by the following inherent characteristics of the *CDHydro* process:

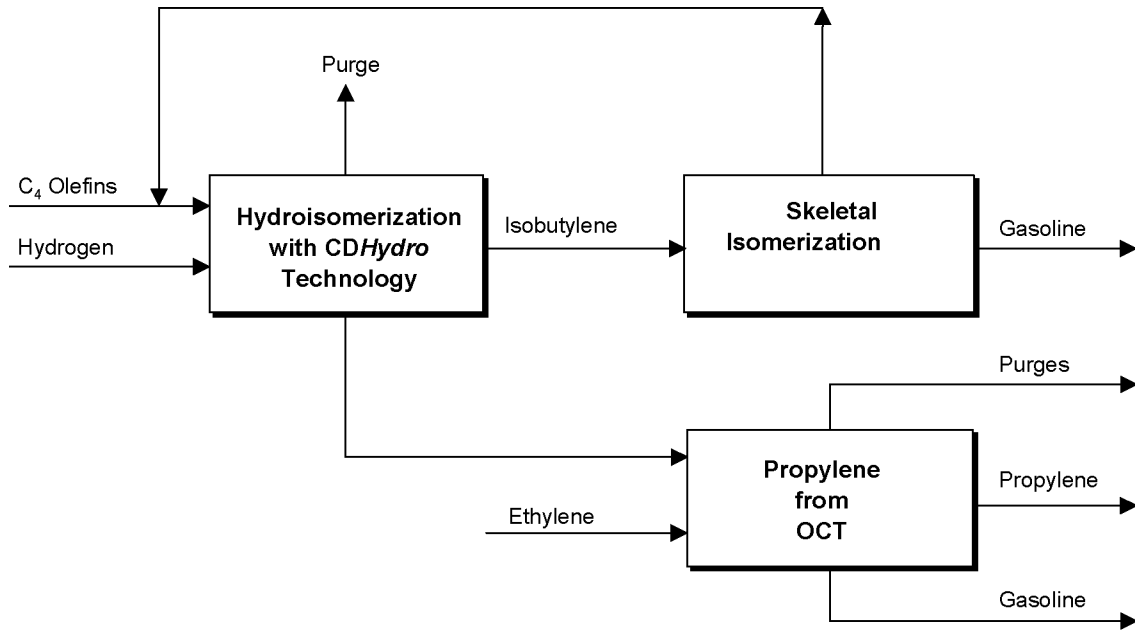
- Any heavy fouling material contained in the feed separates down and away from the catalyst zone;
- Any oligomer material formed is much heavier than the surrounding compounds and immediately separates from the catalyst zone before fouling polymers have sufficient time to form; and
- Clean reflux continuously washes heavy compounds from the catalyst.

*CDHydro* technology has fourteen commercial operating units for various hydrogenation applications with over 350,000 operating hours. None of these units has had a detectable loss of catalyst activity.

### **Integrated Processes For Propylene Production from Isobutylene**

Figure 4 is a block flow diagram showing the production of propylene from the combination of process technologies described above. Mixed C<sub>4</sub>s, essentially free of butadiene, are fed to the *CDHydro* butene splitter to separate isobutylene from normal butenes. The hydroisomerization of 1-butene to 2-butene results in the production of an isobutylene rich overhead stream and a bottoms stream rich in 2-butene. The isobutylene stream is ideal feed for the skeletal isomerization of isobutylene to normal butenes and the bottoms product is perfect for propylene production via metathesis. Since skeletal isomerization of isobutylene is equilibrium limited, the effluent from the skeletal isomerization process is returned to the *CDHydro* butene splitter. This flow scheme is well suited to both refinery and steam cracker facilities. As mentioned earlier, ethylene feed can be provided from an accessible source of high purity ethylene or by recovery from low value by-product streams.

**Figure 4 Propylene Production from C<sub>4</sub> Olefins**



For the refiner, this process provides the following potential advantages:

- A means to meet lower vapor pressure specifications for the gasoline pool;
- Assistance to off-load the alkylation unit.

On the horizon, refiners will be confronted with requirements for reduced RVP and olefin content specifications for gasoline. These requirements will force refiners to reduce the amount of C<sub>5</sub>s blended into the gasoline pool. C<sub>4</sub> olefins could be backed out of the alkylation unit and C<sub>5</sub> olefins substituted, thereby reducing the overall vapor pressure of the gasoline pool as well as the olefins content.

## **Conclusion**

As mentioned in the introduction, alternative process options for isobutylene are dependent on many site-specific factors. For certain facilities, propylene production may offer the following advantages:

- A means for increasing operating margins;
- A solution to problems created by MTBE phase-out;
- An option to meet more restrictive RVP and olefin content specifications.

In many cases, transforming olefins to produce propylene may not be the first opportunity that comes to mind for isobutylene; however, it is an opportunity that should not be overlooked.

## **References**

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

Refinery 2000: Increase Propylene Recovery from an FCC Unit – R. M. Venner - 1998 De Witt Petrochemical Review

Olefins Conversion Technology - S. M. Edwards – 1998 ABB Lummus Global 9<sup>th</sup> Ethylene Technology Seminar.

Triolefins – Break the Propylene Barrier – E. F. Olszewski – CMAI 1998 World Petrochemical Conference

Alternate Routes to Enhanced Propylene Production – S. J. Stanley, H. Schmitz, M.M. Shreehan – 1998 ABB Lummus Global 9<sup>th</sup> Ethylene Technology Seminar

Ethylene 2000 – A. E. Krumins – 1997 – De Witt Technology Conference