

# MTBE Units Expansion/Conversion

## CDTECH

### Introduction

Gasoline standards throughout the world are continuing to move toward cleaner burning gasoline. This includes mandating limits on aromatics, benzene, sulfur, RVP and distillation characteristics. All of these changes must be met while maintaining or increasing gasoline octane. Some of the possible blendstocks that fulfill the above requirements are isomerate, alkylate, oxygenates and iso-octane.

While isomerate offers some octane boost, it is substantially less than the boost derived from alkylate, oxygenates and iso-octane.

Conventional alkylation units all use sulfuric or hydrofluoric acid as catalyst, which are highly corrosive and toxic, and would raise significant environmental concern. In addition, alkylate is normally not a commercially available commodity but rather a captive stream used in the refinery.

Methyl-Tert-Butyl-Ether (MTBE) became the single most widely used oxygenate in RFG, primarily for its superior blending characteristics and economics compared to ethanol, its main rival in the oxygenate market. However, concern was raised over the wide use of MTBE, especially in California, where MTBE was detected in some water wells. With pressure from the regulators to reduce or eliminate the use of MTBE as a blending component in gasoline, refiners may be forced to use alternative blendstocks.

Catalytic Distillation technology enhances production of MTBE. CDTECH's *CDMtbe*<sup>®</sup> technology can be used for design of new units as well as expanding existing units.

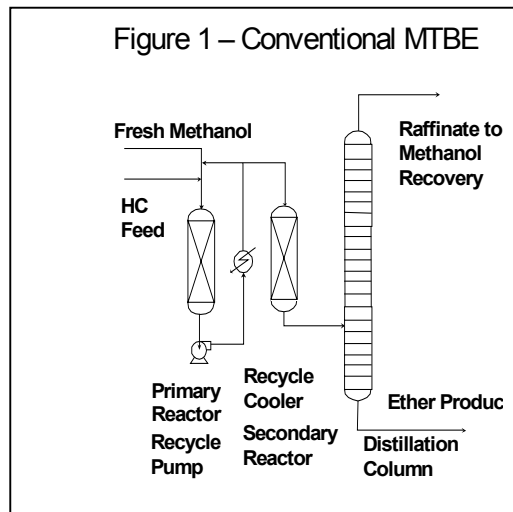
Iso-OctAne is the high octane C<sub>8</sub> product, rich in iso-octane, resulting from selective dimerization of isobutene using CDTECH/Snamprogetti's *CD/soether*<sup>SM</sup> technology.

Installation of a new *CDIsoether* unit or revamping an existing MTBE unit using *CDIsoether* technology offers an economic solution to producing superior C<sub>8</sub> blendstock.

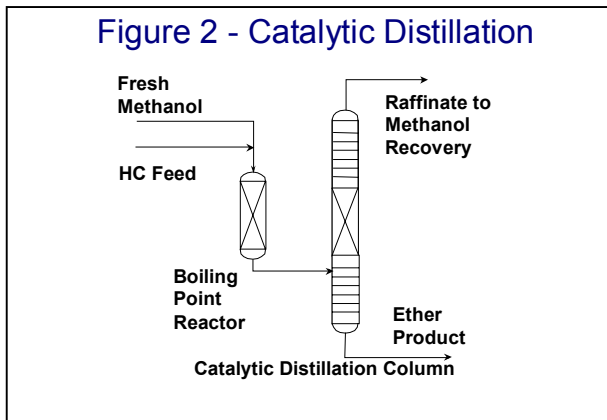
### **CDMtbe Technology**

Prior to 1981 all MTBE was produced using conventional fixed bed reactors. The reaction of isobutylene with methanol over a strong acid ion exchange catalyst produces an equilibrium mixture of MTBE. The reaction is exothermic and increasing temperature pushes equilibrium back towards the reactants, isobutylene and methanol. Conventional technology utilizes two fixed bed reactors to accomplish the reaction (Figure1).

The first bed is operated with a large recycle of cooled reactor effluent to limit the reaction temperature rise by dilution. This step produces most of the conversion (90%) and operates far enough from equilibrium so that the reaction rate is limited by kinetics rather than equilibrium. The net effluent of the first reactor is cooled and fed to the second reactor without any diluent. Here, the reaction proceeds at much lower rate at close to equilibrium conditions. With the use of excess methanol, a typical isobutylene conversion of 96% is achieved. Recent catalysts with higher activity have achieved 97% conversion.



The problem with fixed bed reactors is that the catalyst eventually loses activity and conversion levels fall accordingly. The catalyst continually loses activity due to thermal degradation but the major culprit is usually catalyst poison in the C4 feedstock. Some designs try to delay the conversion loss with a large excess of catalyst resulting in very big reactors. Still the conversion will fall and MTBE production will suffer until the catalyst is replaced. The improvement to conventional technology is CDMtbe® (Figure 2).

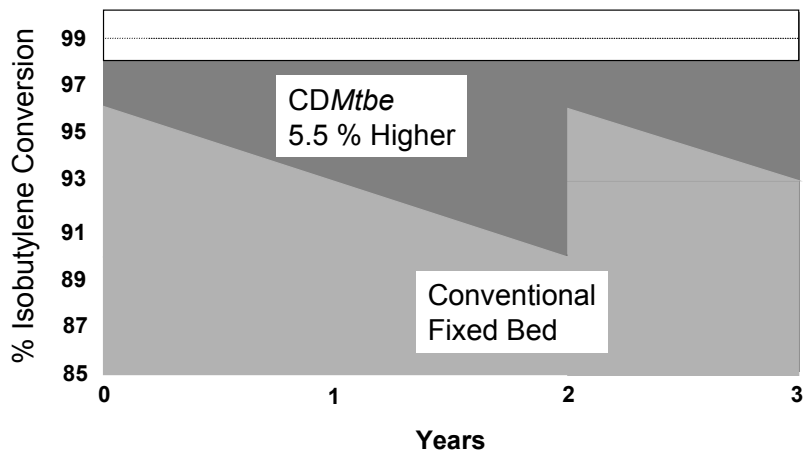


A fixed bed reactor is still used for the bulk conversion of isobutylene, However the version used by CDTECH is a boiling point reactor. It operates at lower pressure so that when the heat of reaction heats the reaction mix up to the desired temperature, the additional reaction heat is absorbed by partially vaporizing the liquid mix. This method provides precise temperature control and does not waste the heat of reaction by rejecting it to cooling water. A recycle stream and recycle cooler are not required and the resulting reactor size is reduced since diluent is not required for refinery FCC feedstocks. The two phase reactor product is discharged to the fractionation column where the heat of reaction contributes to the heat load required by the distillation.

The alternative to the conventional second fixed bed reactor is catalytic distillation (CD). The catalyst is contained in *CDModules*<sup>SM</sup> which promote simultaneous reaction and distillation. Due to its higher boiling point MTBE is easily separated from the isobutylene and methanol. As a result the equilibrium reaction is shifted to higher conversion. Higher reaction rates can be achieved because higher temperature is possible at the reduced MTBE concentration. The heat of reaction also contributes to the distillation heat load. A typical isobutylene overall conversion of 98% is demonstrated on FCC feedstocks. As the catalyst in the

boiling point reactor loses activity, the conversion of isobutylene is gradually moved to the catalytic distillation column. High overall conversion has been demonstrated continuously over the three year life of the *CDModules* (Figure 3). The difference in net MTBE production over the three year period can be as much as 5.5%.

Figure 3 - More MTBE from CD



Addition of a catalytic distillation column is an economical means to increase the capacity of an existing conventional MTBE unit. The two existing fixed bed reactors can be arranged in parallel and a CD Column added to handle the effluent from both reactors. In this arrangement, it is possible to essentially double the capacity of the existing unit. The remaining equipment can be debottlenecked or parallel equipment added to meet the desired capacity.

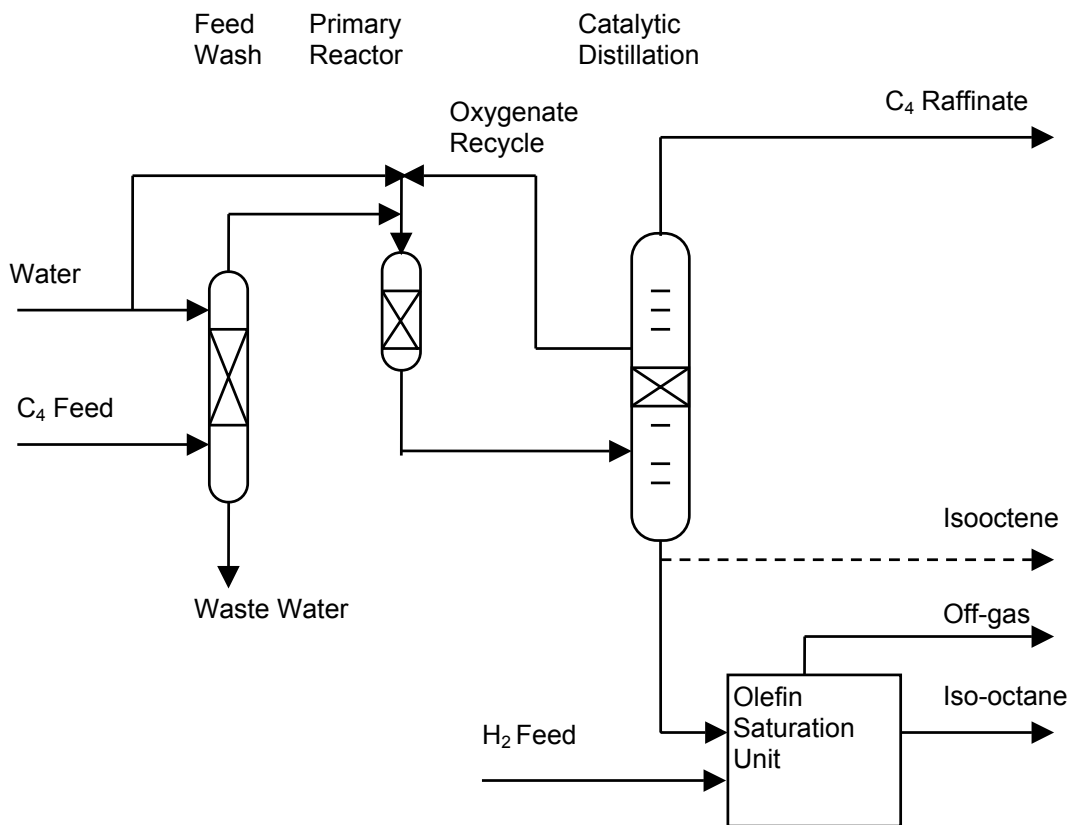
### The *CDIsoether*<sup>SM</sup> Technology

Iso-octane (2,2,4-trimethyl-pentane) is the reference compound for the measurement of octane and, by definition, has a clear RON and clear MON of 100. Iso-OctAne refers to a product very rich in iso-octane (or similar tri-methyl-

pentanes), produced by selective isobutylene dimerization followed by olefin saturation using CD/*soether* process. Although this dimerization technology has been known since before World War II, Snamprogetti was the first company to revise this reaction and to substantially improve selectivity to the desired dimer products. The work, begun in 1994, was previously presented at NPRA Annual Meetings<sup>1,2</sup>. In the second half of 2000, Catalytic Distillation Technologies (CDTECH) and Snamprogetti agreed to combine and market their expertise in isobutylene dimerization technologies. The features offered by the combined technologies have allowed further optimization of capital cost, isobutylene conversion and selectivity to high-octane gasoline blendstock for refinery, petrochemical and chemical-based units. The combined technology, called CD/*soether*, provides the most flexible and cost-effective solution to revamp existing MTBE plants to Iso-OctEne/Iso-OctAne production.

A typical flow scheme for the CD/*soether* unit can be represented as follows:

**Figure 1: Flow Scheme**



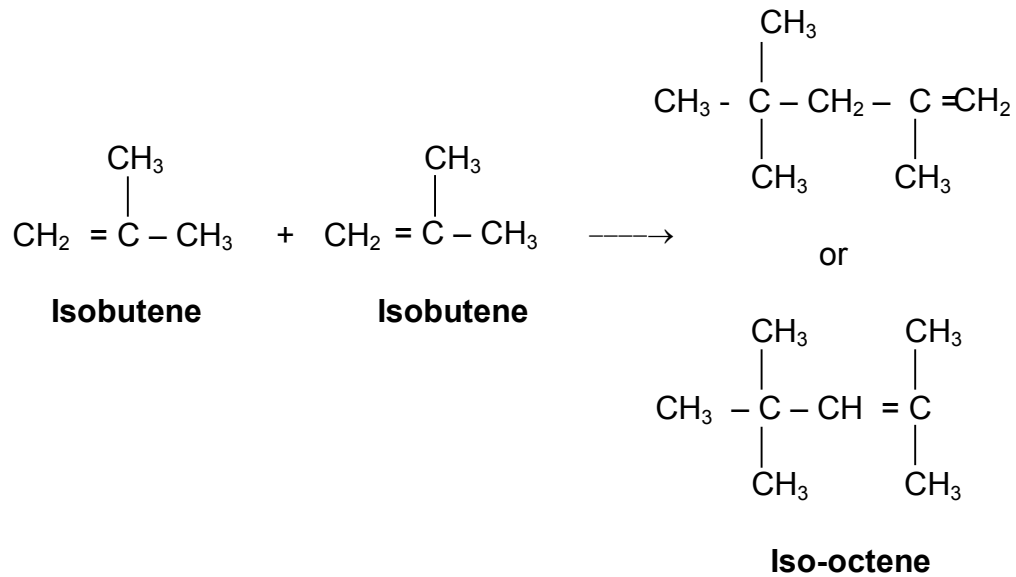
Isobutylene is dimerized on an acid resin catalyst into a diisobutylenes-rich, Isooctene fraction (Iso-OctEne product). Optionally, isobutylene can be partially etherified into MTBE, or ETBE, and partially dimerized into Isooctene. The Iso-OctEne product can be then hydrogenated into an iso-octane-rich alkylate (Iso-OctAne product). The dimerization process can be used in any existing MTBE (or ETBE) plant, irrespective of the C<sub>4</sub> stream source (FCC, isobutane dehydrogenation, or steam cracking).

The *CD/soether* technology uses an oxygenate selector, which moderates the resin acidity to overcome some typical drawbacks of prior technologies, typically arising from difficult temperature control. Without good temperature control, excessive formation of heavier oligomers (trimers, tetramers) could occur resulting in poor distillation characteristics of the product.

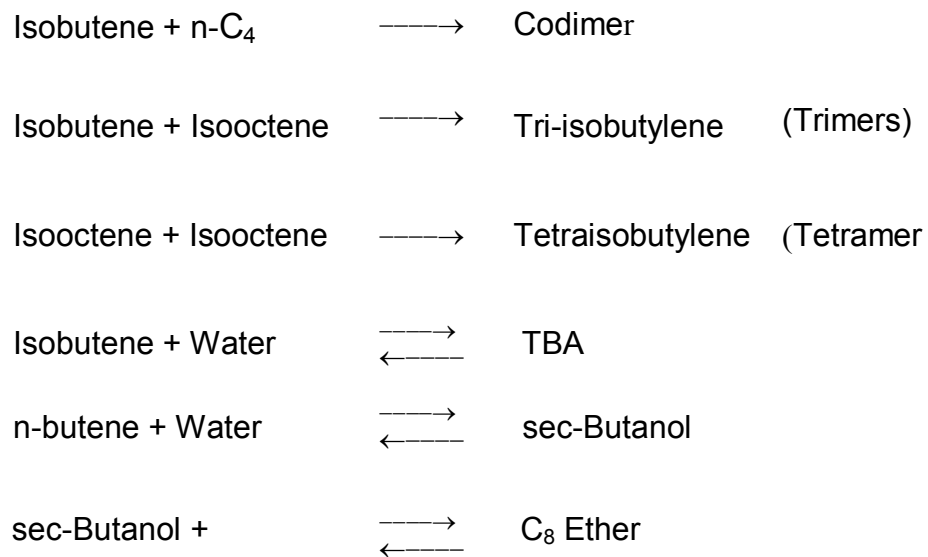
Different selectors can be used to control the product quality. Tert-butyl-alcohol (TBA) and Methyl-tert-butyl-ether (MTBE) are two well-studied components (water or methanol will have the same effect since they equilibrate with TBA or MTBE). It may be advantageous to use either selector depending on the specific requirement. MTBE is more tuned to cases that require to have the flexibility to produce either MTBE or Iso-OctEne, while TBA is more tailored for a market where MTBE has been banned. In particular cases, a mixture of the two selectors can be used.

The main reaction in the Iso-OctEne synthesis is the dimerization of isobutylene to 2,4,4-trimethyl-1-pentene (DIB). Side reaction include co-dimer (trimethyl-pentenes, dimethyl-hexenes) production as well as trimers (C<sub>8</sub>) and tetramers (C<sub>12</sub>) due to isobutylene reacting with n-olefins and further oligomerization respectively. In the olefin saturation unit, the C<sub>8</sub> and C<sub>12</sub> olefins are hydrogenated to respective paraffins. The following Reactions represent the process chemistry in a TBA selected *CD/soether* process for the Iso-OctEne synthesis:

Main Reaction:



Side Reactions:



## Reactor Options

CDTECH and Snamprogetti bring their vast experience base in MTBE production, and offer a variety of reactor systems in order to optimise revamping or grass root construction:

- *Boiling point fixed-bed reactors (BPR)*: Temperature is controlled without heat removing systems. Excellent option for existing MTBE unit with BPR; lowest capital cost revamps.
- *Catalytic distillation towers (CD)*: Excellent finishing reactor to achieve high selectivity and high isobutylene conversion without additional capital investment.
- *Water-cooled tubular reactors (WCTR)*: Excellent temperature control, especially for highly concentrated isobutylene C<sub>4</sub> feedstocks, as it gives very high conversion per pass without requiring any recycle.

The proper combination of these different reactors allows achievement of various conversion targets with high selectivity and without recycle. According to the specific situation and the specific C<sub>4</sub> feedstock processed, an optimum solution can be developed.

Hydrogenation is carried out in a typical trickle-bed reactor. Depending upon the nature of the C<sub>4</sub> feedstock treated and the level of contaminants contained, different hydrogenation catalysts can be employed: nickel-based for very clean feedstocks, palladium based for low to medium content of contaminants or Ni-Mo catalysts for highly contaminated feedstocks. Iso-OctAne product with very low olefin content (< 1%) can be achieved in all cases.

## Product Quality

Operating under optimal conditions, trimers content is limited at about 5-15 wt %, while tetramers are present at the level of only a few thousand ppm. Heavier oligomers are not produced at detectable levels. Extensive blending studies have shown that no particular difference is observed between the blending properties (octane and distillation curve parameters) of an Iso-OctAne stream containing 10% or less of trimers, and one containing 15% trimers, provided that the tetramers content is below 10,000 ppm.

The Iso-OctAne and Iso-OctEne product RON and MON are higher than those of the normal alkylate produced by commercially available alkylation technologies as shown in the following table:

**Table 1: Product Properties**

|                | Iso-OctAne product | Iso-OctEne product | Normal Alkylate | MTBE  |
|----------------|--------------------|--------------------|-----------------|-------|
| Blending RON * | 97 – 103           | 112 – 115          | 97 - 99         | 116   |
| Blending MON * | 94 - 98            | 93 – 96            | 90 - 92         | 100   |
| RVP (psi)      | 1.7                | 1.5                | 4.5             | 8.0   |
| Sp. Gravity    | 0.702              | 0.728              | 0.697           | 0.745 |

\* Base Gasoline RON = 95.0; MON =85.0

RVP of Iso-OctEne/ Iso-OctAne are much lower than that of normal alkylate and MTBE. This lowers the potential RVP of the gasoline pool, which permits more butane, isopentane or even more ethanol, to be blended into the gasoline pool.

In those areas where olefins are not severely limited, Iso-OctEne can be blended directly into the gasoline pool or sold on the market as a high octane and low RVP blending component.

### **CASE STUDY : Iso-Octene Production In Existing Refinery MTBE Unit**

The case study is based on a C<sub>4</sub> feedstock from an FCC unit with 15% Isobutylene concentration feeding the existing MTBE unit at a rate of 10,000 BPSD. It assumes that the MTBE plant is US-based and adopts a typical CDTECH MTBE unit configuration. TBA is used as the selectorator and the revamp is designed in order to minimize changes to existing equipment and piping.

Reaction conditions can range from 40 to 170°F at 5 to 20 barg. This process utilizes an acidic ion exchange catalyst in the boiling point fixed-bed reactor similar to the MTBE process. TBA and sec-butanol (SBA) are formed from the reaction of water with isobutylene and n-butenes respectively. C<sub>8</sub> ether is formed as by-product from the reaction of butenes with butanols.

The C<sub>4</sub> feedstock is mixed with make-up water and oxygenate recycle and heated before entering the boiling point reactor, in which, by design, the liquid is heated to its boiling point by the heat of reaction and a limited amount of vaporization takes place. Reactor effluent flows to the Iso-OctEne purification section where the unreacted C<sub>4</sub> hydrocarbons distill overhead. The purification of the Iso-OctEne product from the oxygenate is accomplished in existing fractionation equipment after some minor modifications. The pure Iso-OctEne product can be rundown to storage or fed to a hydrogenation unit for saturation to Iso-OctAne. The selectorator oxygenate stream is recycled back to the reactor. A methanol recovery section is not required.

#### **Two major revamping options are available:**

- *Option 1* - Use existing Boiling Point Reactor to achieve a conversion per pass of 80-85% at dimers selectivities of 90+%. No CD Modules are used.
- *Option 2* – Same as option 1 but employ the CD Tower as finishing reactor. This option can be used to achieve greater than 97% isobutylene conversion with dimer selectivity of 87+%.

For option 1, the revamp requires only minor changes to existing equipment and piping; the only new equipment required is to upgrade the existing CD Tower reboiler. Option 2 will employ proprietary *CDModules* to further optimize process performance. Either option can be used as an effective solution depending on the refinery's requirements.

### **Material Balance for Case Study**

The overall material balance for the cases are shown in the following table:

Table 2: Material Balance

|                 |      | <u>MTBE Case</u> | <u>Revamp Option 1</u> | <u>Revamp Option 2</u> |
|-----------------|------|------------------|------------------------|------------------------|
| C4 feed rate    | Lb/h | 86208            | 86208                  | 86208                  |
| Methanol        | Lb/h | 7225             | 0                      | 0                      |
| Water feed      | Lb/h | 20               | 82                     | 82                     |
| C4 Raffinate    | Lb/h | 73583            | 74115                  | 69720                  |
| MTBE            | Lb/h | 19870            | 0                      | 0                      |
| Iso-OctEne      | Lb/h | 0                | 12175                  | 16570                  |
| Iso-OctAne      | Lb/h | 0                | 0                      | 0                      |
| Fuel Gas        | Lb/h | 0                | 0                      | 0                      |
| Product Octane: |      |                  |                        |                        |
| RON             |      | 116              | 114                    | 113                    |
| MON             |      | 100              | 94                     | 93                     |
| (R+M)/2         |      | 108              | 104                    | 103                    |

### **Economic Comparison for Case Study**

The economics for MTBE unit conversion are dependent on a number of factors including gasoline price, feedstock value, and regulatory environment. Depending on the processing options available within the refinery, the economics may be different than presented here. For this paper, we look at the economics of an MTBE conversion to Iso-OctEne production based on approximate feed and product prices in November 2001. The values are derived from those published in October and November issues of Oxy-Fuel News from Hart Publication. They are summarised in the following table. Utility costs, based on information from one plant location have been used for the economic analysis and are as follows.

Table 3: Feed and Product prices

|                         |               | <u>Nov 2001</u> |
|-------------------------|---------------|-----------------|
| FCC C <sub>4</sub> feed | \$/bbl        | 17.96           |
| Methanol                | \$/bbl        | 13.23           |
| Water                   | \$/M gal      | 4.9             |
| C4 Raffinate            | \$/bbl        | 17.96           |
| MTBE                    | \$/bbl        | 32.46           |
| Fuel Gas                | \$/lb         | 1.0             |
| Iso-OctEne              | \$/bbl        | 26.65           |
| Regular Gasoline        | \$/bbl        | 22.74           |
| Octane Premium          | \$/octane-bbl | 0.23            |

Table 4: Utility Costs

|                |          |       |
|----------------|----------|-------|
| 600 psig steam | \$/M lb  | 2.85  |
| Cooling Water  | \$/M gal | 0.10  |
| Electricity    | \$/kW H  | 0.022 |

The simple payout for the revamp options of the MTBE unit is summarised in the following table. Option 2 with catalytic distillation offers better payoff than option 1. The value for the Iso-OctEne product is \$26.65/ bbl based on the Nov 2001 gasoline prices.

Table 5: Economic Summary

|                                |         | Option 1 | Option 2 |
|--------------------------------|---------|----------|----------|
| Incremental Investment cost    | MM US\$ | 1.37     | 1.49     |
| Average Annual Operating costs | MM US\$ | 0.68     | 0.79     |
| Net Profit                     | MM US\$ | 1.04     | 1.41     |
| After Tax Profit               | MM US\$ | 0.62     | 0.84     |
| Simple Payout                  | Years   | 2.2      | 1.8      |

## Experience

The CD/*soether* technology has been fully proven in different combinations of reactors, selectivators and feedstocks using:

- Bench scale reactors
- Once-through pilot reactor
- Closed-loop process demonstration unit (PDU) located at the Snamprogetti Research Laboratories in Milan.
- Commercial large scale MTBE reactors.

Five industrial runs have been carried out worldwide processing the most relevant C<sub>4</sub> feedstocks and producing more than 5,000 tons of Iso-OctEne/Iso-OctAne, thus allowing a full characterization of the products.

## **Conclusions**

The *CD/soether* technology can be used to process C<sub>4</sub> feedstocks from a wide variety of sources similar to those processed in MTBE units, i.e. FCC, steam cracker, or dehydrogenated isobutanes from field butanes. The technology is highly flexible giving the client an option to continue producing MTBE even after the revamp. It also enables the refiner to achieve isobutylene conversion and selectivity to meet overall plant economics.

CDTECH's and Snamprogetti's knowledge and unparalleled commercial experience in production of MTBE and Iso-OctEne provide the most economical and proven for technologies for octane enhancement. Our technology portfolio provides the refiner with flexibility for expanding existing MTBE units as well as converting MTBE units to Iso-OctEne production. Both products are high quality gasoline blendstock with low vapor pressure and high octane number.

## **References**

1. Trotta, Roberto; Di Girolamo, Marco; Pescarollo, Ermanno; Marchionna, Mario and Hyland, Michael J.; " High Octane Alkylate from field butanes- The Snamprogetti ISOETHER process" NPRA Annual Meeting 1997 – AM-97-54.
2. Trotta, Roberto; Marchionna, Mario; Di Girolamo, Marco; Pescarollo, Ermanno and Hyland, Michael J.; " How to make alkylate without an acid alkylation unit" NPRA Annual Meeting 1998 – AM-98-51.