

# Enhanced Olefin Reduction

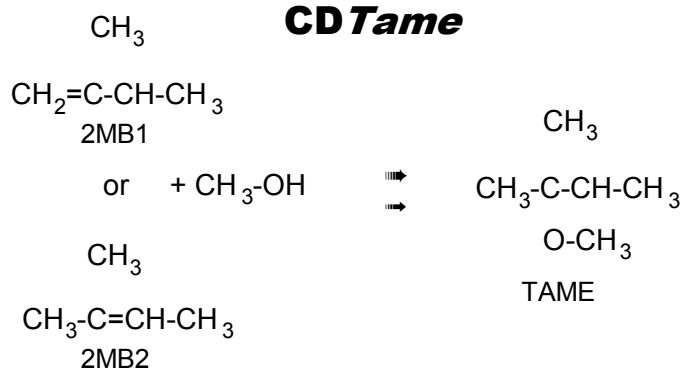
## CDTECH

### Introduction

Simple hydrogenation of C<sub>5</sub> olefins produces a mixture of isopentane and normal pentane which is high in vapor pressure and low in octane, hence not very attractive for gasoline blending. Conversion of C<sub>5</sub> olefins to TAME is a good way to convert a problem into an asset. The TAME product has

Figure 1

### Isoamylenes Etherification



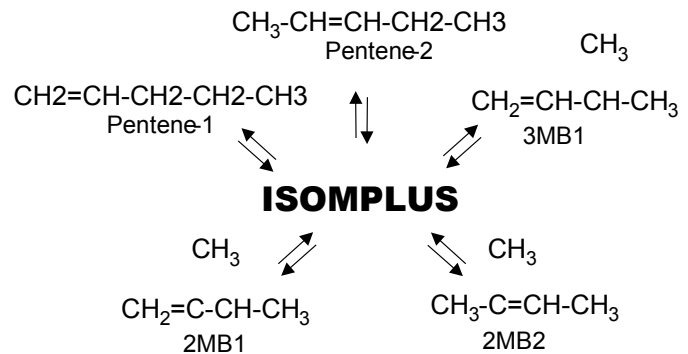
high octane and low vapor pressure as well as contained oxygen. The other option is to alkylate the C<sub>5</sub> olefins. This route produces greater volume but with higher vapor pressure and lower octane value. The TAME route also achieves lower capital and operating cost than alkylation.

### Production of TAME from C<sub>5</sub> Olefins

Reactive Isoamylenes can be converted to TAME by etherification with methanol. The reactive isoamylenes include 2-methyl butene-1 and 2-methyl butene-2. These reactions are shown in Figure 1. The other C<sub>5</sub> olefins can be converted to reactive isoamylenes through skeletal isomerization. The reaction of pentene-1, cis/trans pentene-2 and 3-methyl butene-1 to reactive isoamylenes are shown in Figure 2.

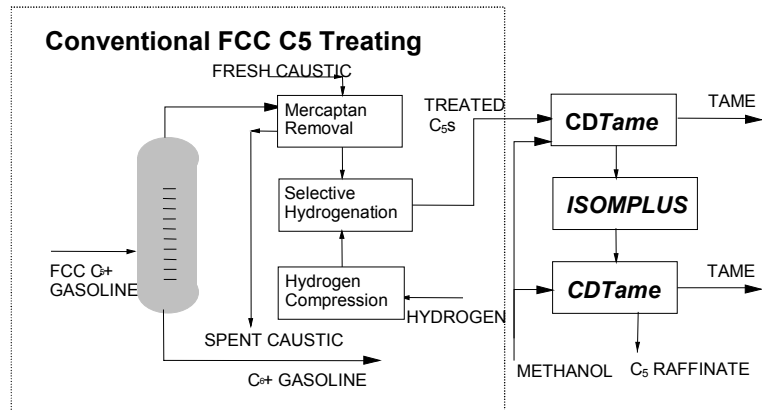
Figure 2

### Olefin Skeletal Isomerization



A simplified flow diagram for the production of TAME from FCC gasoline is presented in Figure 3. The FCC gasoline (light catalytic naphtha) is fractionated in a distillation column to separate the C<sub>5</sub> fraction from the C<sub>6</sub>+ fraction.

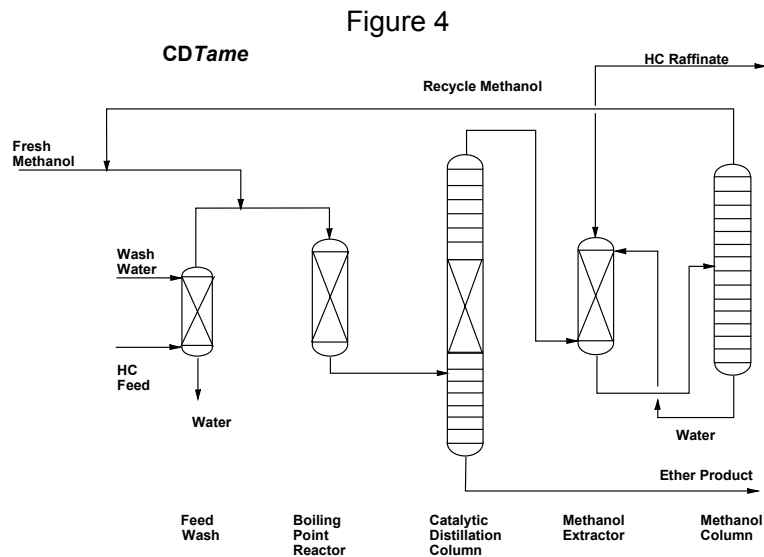
### Refinery TAME Production



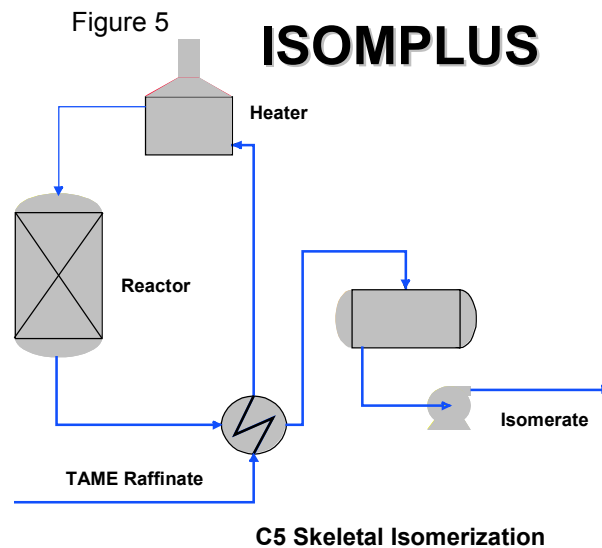
The C<sub>5</sub> stream usually contains over 1% of diolefins. The diolefins are very reactive and readily form oligomers. These oligomers cause problems in TAME manufacture by fouling the etherification catalyst and by producing yellowish foul smelling TAME product. It is necessary to reduce the diolefin concentration to less than 100 ppm to minimize the problems. Therefore, selective hydrogenation of the diolefins in the C<sub>5</sub> stream is required. Conventional practice is to hydrogenate the diolefins over palladium catalyst in a separate fixed bed reactor.

The C<sub>5</sub> olefin stream usually contains enough mercaptans to keep the palladium catalyst from performing at its capacity. This is because the sulfur compounds are more strongly adsorbed on the catalyst than the other components. Therefore, the mercaptans are normally removed upstream of the selective hydrogenation step. The conventional method of removing the mercaptans involves contact with a caustic stream and subsequent contact with oxygen. The refinery must deal with the fresh caustic make-up as well as dispose of the spent caustic waste stream. In addition the residual oxygen dissolved in the treated hydrocarbon stream must be removed since it will degrade the polymeric substrate in the TAME etherification catalyst thus decreasing the catalyst life.

After mercaptan and diolefin removal, the next step would be etherification of the existing reactive isoamylenes with methanol. This step has been commercialized using the CD*Tame*<sup>®</sup> technology from CDTECH (Figure 4). Conversions of reactive isoamylenes exceeding 90% have been achieved.



The remaining C<sub>5</sub> olefins represent additional potential olefins via skeletal isomerization. The ISOMPLUS<sup>®</sup> technology is available from CDTECH/Lyondell for this purpose (Figure 5). Conversion of normal pentenes exceeding 65% at greater than 95% selectivity to reactive isoamylenes have been demonstrated. The zeolytic catalyst developed for this process provides a very simple process scheme with low capital and operating costs. No diluents or catalyst activation agents are required. The process is characterized by long catalyst operating cycle length and low byproduct yield.



Etherification of the reactive isoamylenes resulting from skeletal isomerization is best achieved by use of a second TAME unit. This unit will be smaller and have fewer equipment items than the first TAME unit. This approach actually saves capital and operating cost relative to a single TAME unit with recycle from the skeletal isomerization step. The combination of skeletal isomerization with a second TAME unit can increase TAME by as much as 70% over that from a TAME unit only.

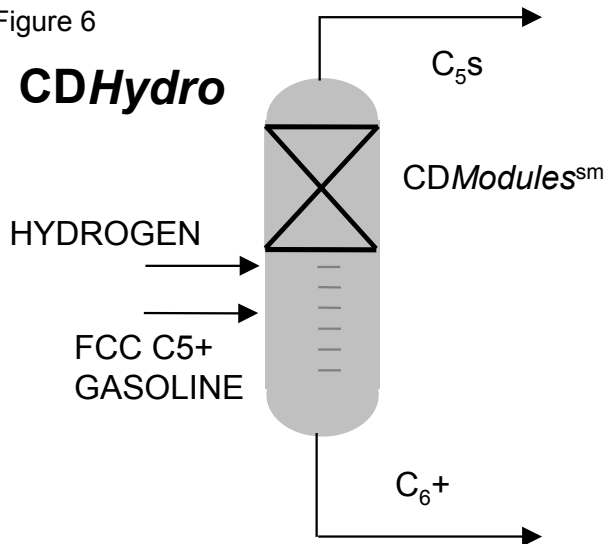
The estimated capital costs for each of the units to process 10,000 BPD of C<sub>5</sub>'s are:

Unit	\$(million)
Depentanizer	3.9
Mercaptan Removal	1.3
Selective Hydrogenation	3.9
Hydrogen Compressor	0.3
TAME/ISOM/TAME	<u>21.0</u>
Total	30.4

### CDHydro®

CDHydro technology combines distillation and selective hydrogenation and was developed for the removal of diolefins from C<sub>3</sub>, C<sub>4</sub> and C<sub>5</sub> streams. This technology utilizes palladium catalyst which has been placed in the rectification section of a distillation column (Figure 6). The catalyst is contained in a proprietary structured packing (CDModule<sup>SM</sup>) which has fractionation capabilities similar to conventional trays. Hydrogen and hydrocarbon feed containing diolefins are introduced in the distillation column below the catalyst section.

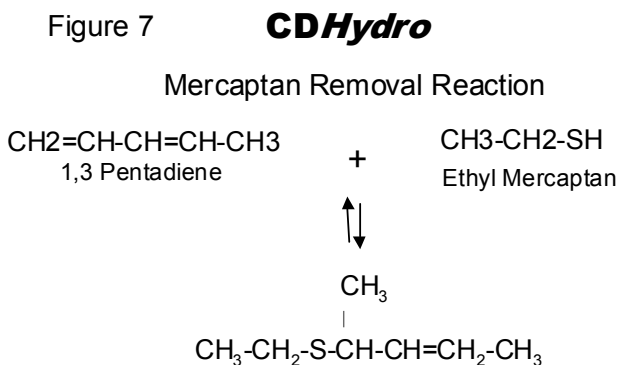
Figure 6



Incorporating catalyst in the fractionation column provides several advantages in the areas of mercaptan effect, catalyst fouling resistance, selective hydrogenation performance and capital/operating cost.

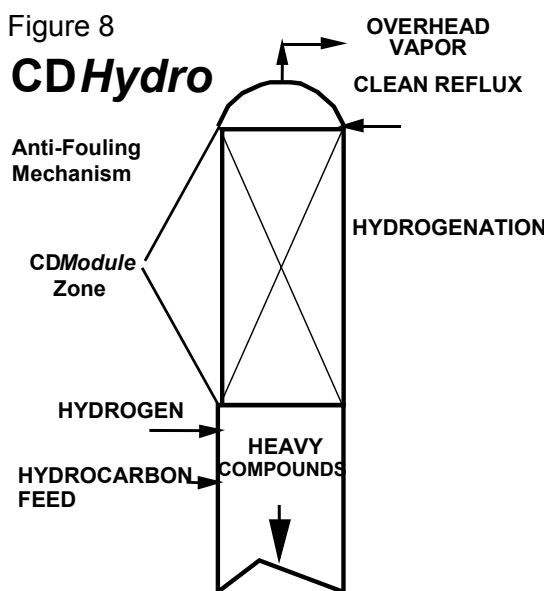
## Mercaptan Effect

When the mercaptans are adsorbed onto the catalyst at the bottom of the *CDModule* bed a reaction occurs as shown in Figure 7. The mercaptans such as ethyl mercaptan react with diolefins to produce sulfides, which have much higher boiling points than the surrounding hydrocarbons. As a result the sulfides are quickly fractionated to the bottom of the distillation column and exit with the  $C_6+$  product. Since the  $C_6+$  fraction already contains similar sulfide compounds a new problem is not created. The mercaptan-diolefin reaction goes to completion in a very small portion at the bottom of the catalyst zone. The selective hydrogenation of diolefins occurs above this zone and proceeds to very high conversion at high selectivity. Overhead  $C_5$  streams containing less than 10 ppm of diolefins and less than 1 ppm of mercaptans have been produced.



## Catalyst Fouling Resistance

Fouling typically causes a gradual loss of catalyst activity and the need for regeneration/replacement. It results from heavy compounds which settle on the catalyst and form a solid phase. This solid phase eventually builds up and blocks the pores preventing access to the catalyst sites. Normally the heavy materials are removed by a hot hydrogen strip but there is usually residual material which is not removed. As the residual material accumulates the catalyst activity eventually cannot be restored to the desired level. At this point it becomes necessary to replace the catalyst with a new load. The heavy materials which cause the fouling can be contained in the feed or be formed in the reactor due to oligomerization.



Oligomers result when diolefins join to form dimers, trimers or higher molecular weight compounds. In a conventional fixed bed process with reactor recycle the oligomers and feed heavy materials are continuously circulated over the catalyst increasing the exposure to foulants.

For *CDHydro* the catalyst fouling situation is very different. The heavies in the feed are fractionated out of the light hydrocarbons before they enter the *CDModule* zone (Figure 8). The oligomers that form have much higher boiling points than the surrounding hydrocarbons and are quickly fractionated away from the *CDModule* zone before they sufficiently increase in size to cause problems with the catalyst. In addition, the *CDModule* zone is continuously washed with a reflux stream of clean, hydrogenated hydrocarbons. As a result the *CDHydro* process has virtually eliminated the conventional catalyst fouling mechanism.

### **Selective Hydrogenation Performance**

Conventional processes normally require multiple reactor stages to reduce diolefins to a low ppm level. The extra reactor stages can add considerably to the capital cost of the selective hydrogenation unit.

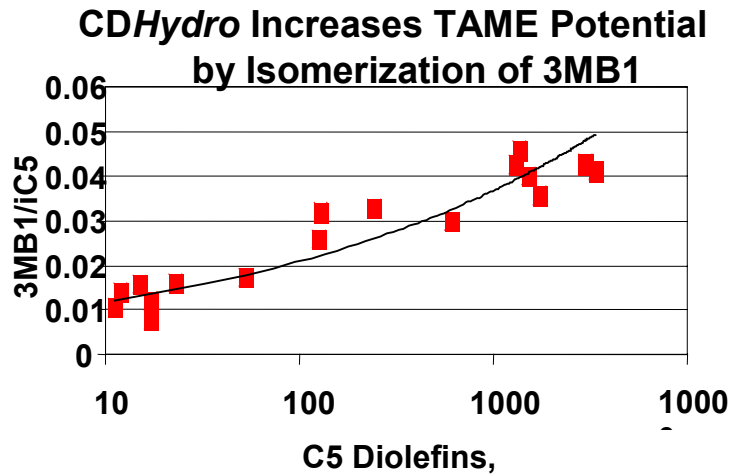
Olefin yield is related to the production of olefins from the hydrogenation of diolefins less the loss of olefins from hydrogenation to paraffins. There is no significant normal pentane production except where there is essentially complete hydrogenation of diolefins. At this point the olefin yield is over 100% because all of the dienes have been converted to olefins and none of the olefins have been converted to paraffins. Once the diolefin conversion is complete and the olefins are the only species adsorbed on the catalyst, there is detectable conversion of olefins to paraffins. This will lower the olefins yield. *CDHydro* does not require additional separate reactor stages to achieve high diolefin conversion levels.

### **Isomerization**

3-methyl butene-1 is a non reactive isoamylenes and cannot be etherified in the TAME unit. It can be isomerized to reactive isoamylenes using hydrogen and palladium catalyst. The diolefin concentration must be reduced to very low levels before much 3-methyl butene-1 can be converted. This reaction occurs in conventional processes but requires multiple stages to get significant conversion.

Since CDHydro is able to produce very low diolefin levels without additional separate stages the 3-methyl butene-1 can very easily be isomerized to essentially equilibrium levels (Figure 9). In typical operation the 3-methyl butene-1 will be reduced to less than 2% of the isoamylenes without significant loss of C5 olefins.

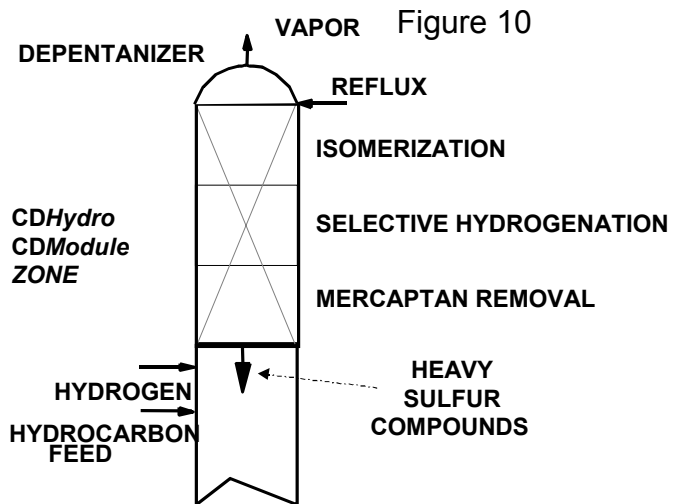
Figure 9



Thus the TAME potential can be maximized through proper choice of selective hydrogenation /isomerization goals. Pentene-1 is also isomerized to pentene-2 at the same time. This improves the blending value of the C<sub>5</sub> stream because pentene-2 has higher octane and lower vapor pressure than pentene-1.

### Multi-operation Process

In summary, the CDHydro process combines several process operations into a single unit operation (Figure 10). Distillation separates the feed into two fractions and removes heavy catalyst foulants from the feed. It also prevents the fouling of catalyst by removing oligomers from the catalyst bed. Mercaptans are converted to sulfides and low temperature equilibrium conversion of olefin isomers is achieved.

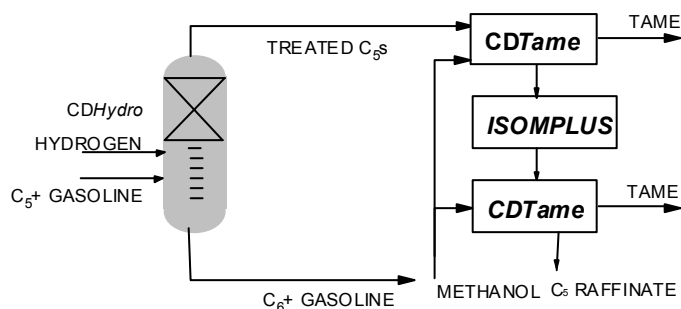


## Capital/Operating Cost

The modified flow diagram for TAME production utilizing *CDHydro* is shown in Figure 11.

Figure 11

### Optimized Refinery TAME Production



The estimated capital cost for each of the units in the modified TAME production scheme is:

Unit	\$(million)	
	<i>CDHydro</i>	Conventional
Conventional Depentanizer	-	3.9
<i>CDHydro</i> Depentanizer	4.3	-
Mercaptan Removal	0.0	1.3
Selective Hydrogenation	0.0	3.9
Hydrogen Compressor	0.0	0.3
TAME/ISOM/TAME	<u>21.0</u>	<u>21.0</u>
Total	25.3	30.4

The cost of the depentanizer is increased slightly to incorporate the hydrogen feed line, hydrogen controller and vent stream condenser. *CDHydro* eliminates the need for a mercaptan treatment step. In addition the selective hydrogenation function has been incorporated into the *CDHydro* depentanizer, so there is no requirement for a separate unit. Hydrogen pressure required for this *CDHydro* process is compatible with most refinery hydrogen systems; consequently, a separate hydrogen compressor is not needed.

Power requirements for the conventional selective hydrogenation feed pump, recycle pump, cooling media and hydrogen compressor have been eliminated. Raw material cost for make-up caustic in the mercaptan removal step has been eliminated along with the cost

for disposing of the waste spent caustic stream. These factors all serve to reduce the operating cost of producing TAME.

### **Conclusions**

TAME production is cost effectively enhanced through the combination of technologies. The use of *CDHydro* technology can reduce the capital cost of the C<sub>5</sub> feed preparation by more than 50%. TAME potential of a refinery C<sub>5</sub> stream can be expanded by as much as 70% with the use of ISOMPLUS technology. These approaches can improve the attractiveness of TAME production while also providing lower RVP gasoline with reduced ozone emissions potential.