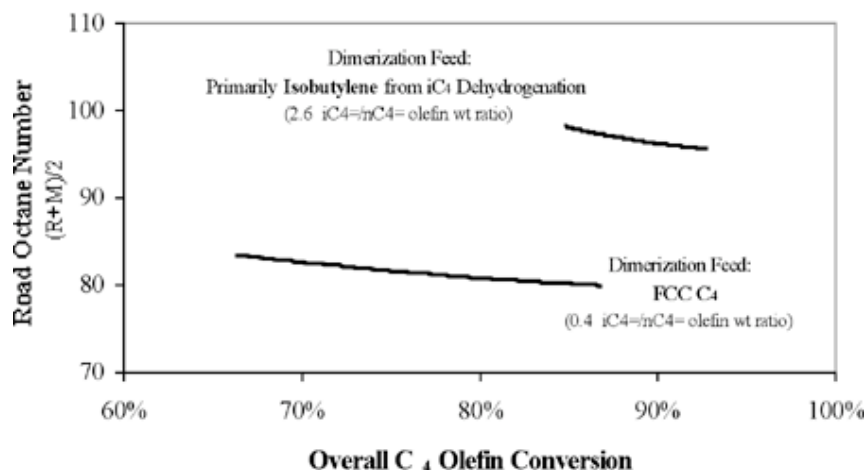


Alkylation vs. Dimerization

Butylene dimerization technologies have received a good deal of attention since California announced that MTBE will be banned from CARB gasoline by the end of 2002. Although licensors have improved catalyst properties and reactor conditions to increase isobutylene dimer selectivity, dimerization still faces the same limitations as past refinery catalytic polymerization processes designed for mixed butylene feeds - low normal butene conversion and a poor octane gasoline product resulting from codimers of isobutylene and normal butene.

Licensors have recently touted the impressive octane benefit of isobutylene dimerization, based on improved selectivity for dimer (C8) products compared to trimers (C12) and tetramers (C16). When a dimerization process is supplied with high purity isobutylene feed, the octane for the saturated and debutanized product stream can exceed 100 RON. However, dimerization technology is not suitable for making gasoline blendstocks from the typical mixed butylene compositions found in FCC C4 fractions. The conversion/octane curves in the graph below are based on experimental data provided by a patent issued to a leading dimerization licensor within the last six months. The difference between the curves for high isobutylene feed content and low isobutylene feed content illustrates the strong negative impact of normal butenes on dimerization reactions:

Dimerization Product Octane Vs. Butylene Conversion for Feeds of Isobutylene and FCC4



To offset the effect of normal butenes and provide an attractive octane product, a refinery dimerization unit is limited to being used in one of two ways:

Dimerization of High Purity Isobutylene Feeds. As the isobutylene/n butene ratio in the dimerization feed stream is increased, higher octane blendstocks are produced. However, most refineries would have to add a costly isobutane dehydrogenation unit to produce enough isobutylene to achieve an effective dimerization feed ratio. Even if a dehydrogenation unit were installed, the refiner would likely need to purchase additional isobutane to support adequate isobutylene production.

0. **Selective Dimerization of Isobutylene** To reduce the negative octane effect from isobutylene/n-butene codimers, some licensors have developed more selective catalysts that they claim will dimerize isobutylene in a mixed butylene feed, while leaving >90% of the normal butenes unreacted. However, the resulting n-butene enriched raffinate must then be converted to gasoline by alkylation. For a grassroots FCC unit, a stand-alone alkylation unit appears to be a far more cost effective downstream solution, when compared to building both a dimerization unit and an alkylation unit to process the dimerization raffinate.

Licensors suggest that existing MTBE units could be retrofitted for dimerization, but there is little commercial experience for performing such a conversion. And while a dimerization retrofit may be a viable option for some MTBE reactor designs, a 30-35% loss of gasoline volume occurs, because methanol is no longer fed to the retrofit unit.

Beyond these shortcomings, dimerization processes have other disadvantages. Some of these are listed below for the various dimerization technologies currently available for license:

0. If a refinery is long on isobutane supply or if isobutane can be purchased cheaply, dimerization is unable to add this volume to the gasoline pool without a dehydrogenation unit, which involves high capital and operating costs.

Depending on local regulations, the olefinic dimerization products may have to be saturated before being added to the gasoline pool. Unfortunately, saturation will often lower dimer octanes and leave a measurable level of olefins in the gasoline product. Since most refineries do not have spare hydrogen supply, capital spending would normally be required to meet the hydrogen demand for the new saturation unit.

Despite recent improvements, dimerization units are likely to yield 10-20% trimers, which contribute to problems meeting T50 and T90 gasoline distillation specifications. It is not yet known whether dimerization, like MTBE production, will generate byproducts that hurt downstream alkylation economics. Some dimerization processes use MTBE as a reaction modifier, which can then be detected in the gasoline pool.

Many dimerization processes use solid catalysts, which will not provide the high level of product consistency expected for a large liquid acid reaction system like that used in sulfuric acid alkylation. Dimerization product quality will suffer due to continual catalyst deactivation and product consistency will be difficult to achieve considering the fluctuating feed composition and contaminant content typical of FCC fractions.

Many dimerization processes involve fixed-bed reactors, which require complex temperature control mechanisms. The difficulty in maintaining uniform operating temperatures will contribute to commercial gasoline properties that do not meet the expectations set by experimental dimerization test results.

Unlike sulfuric acid alkylation, dimerization processes do not produce high octane products from feed combinations of propylene, butylenes, and amylenes from the FCC unit, unless large quantities of isobutylene are available as the primary feed.

The following table below compares the benefits of MTBE production with two options:

- Retrofitting the MTBE unit with dimerization technology and adding a downstream saturation unit to treat the dimerization effluent.
- Expanding the existing alkylation unit that currently alkylates MTBE raffinate.

The data for all three columns assume a typical mixed butylene feed from an

FCC unit.

	Existing MTBE Unit	Retrofit MTBE Unit for	Expand Alkylation Unit
Volume Yield (C5+ Gasoline from Reacted Olefin)	1.25	0.83	1.78
Octane (R+M)/2	110	96	95
Olefin Content Gasoline Blendstock	0 LV%	<2 LV%	0 LV%
Distillation Properties T50 / T90	130°F-132°F	260°F - 355°F	230°F - 275°F

The retrofit dimerization values above assume that a highly selective dimerization catalyst is used to limit the conversion of normal butenes to low octane codimers. The unconverted normal butenes in the dimerization raffinate must be reacted in the existing downstream alkylation unit to form a suitable blendstock for the gasoline pool. The resulting alkylate properties for this raffinate feed stream are not included in the above data.

The dimerization values shown in the table are based on publicly available literature written by leading dimerization technology licensors. Although the alkylation values are supported by commercial experience, STRATCO[®] is not aware of any published data confirming that the above dimerization estimates can be achieved by a refinery dimerization unit.