

## PERP Program – New Report Alert

March 2005

Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, *Propylene Refineries (03/04S7)*.

### Introduction

Propylene is a very versatile building block and is the feedstock for a wide range of important monomers, polymers, intermediates, and chemicals. This versatility stems from the unique chemical structure of propylene. Propylene contains both a carbon-carbon double bond and an allylic methyl group (a methyl group adjacent to a double bond) giving chemists, catalyst designers, and engineers two “handles” for carrying out chemical transformations. For instance, using the reactivity of propylene's carbon-carbon double bond allows formation of the following materials:

- Polypropylene via Ziegler Natta olefin polymerization
- Oxo alcohols via hydroformylation chemistry
- Propylene oxide via chlorohydrin chemistry or peroxidation
- Cumene via benzene alkylation
- Methyl methacrylate via acetone cyanohydrin
- Isopropyl alcohol/acetone via hydration/dehydrogenation

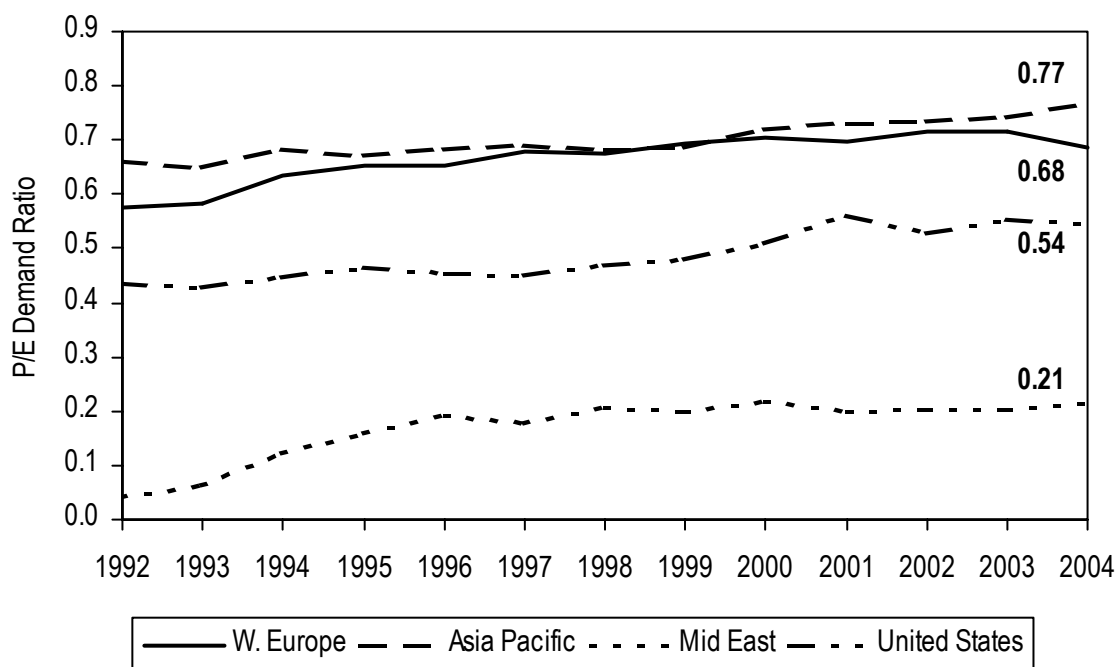
Other important propylene derivatives are based on the unique reactivity of its allylic methyl group:

- Acrylonitrile via ammoxidation chemistry
- Acrolein/acrylic acid via oxidation chemistry
- Allyl chloride/epichlorohydrin via high temperature chlorination/chlorohydrination chemistry

While, as discussed above, there are a number of important propylene derivatives, the derivative that has been and is still driving propylene demand is polypropylene. Polypropylene now consumes 64 percent of the world's propylene production (not including fuel use), up from 17 percent in 1970.

Figure 1 shows the ratio of propylene demand to ethylene demand (P/E) over the 1992-2004 period for various regions. In 1992, the U.S. P/E ratio was 0.43, and in 2004 the P/E ratio is estimated to be 0.54. The same phenomenon is seen in West Europe and Asia Pacific, but to an even greater degree. In Asia Pacific the P/E ratio is very high at 0.77. The Middle East is still heavily ethylene-centric due to the availability of very low cost ethane, and the P/E ratio has stayed relatively flat since 1996.

**Figure 1 Regional P/E Demand Ratio Evolution**

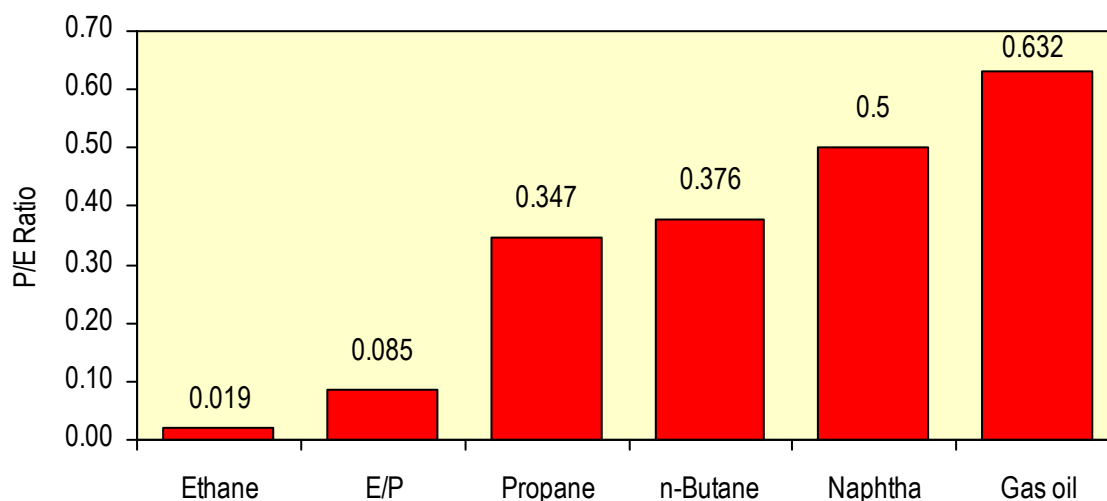


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As propylene growth rate continues to outpace ethylene growth rate, this will continue to put stress on traditional propylene sources, in particular steam crackers. Historically, propylene has been considered a by-product of ethylene production. The amount of propylene coming out of a steam cracker is a function of the cracking feedstock used, as seen in Figure 2. Thus, the amount of propylene able to be produced in steam crackers is essentially fixed by feedstock choices.

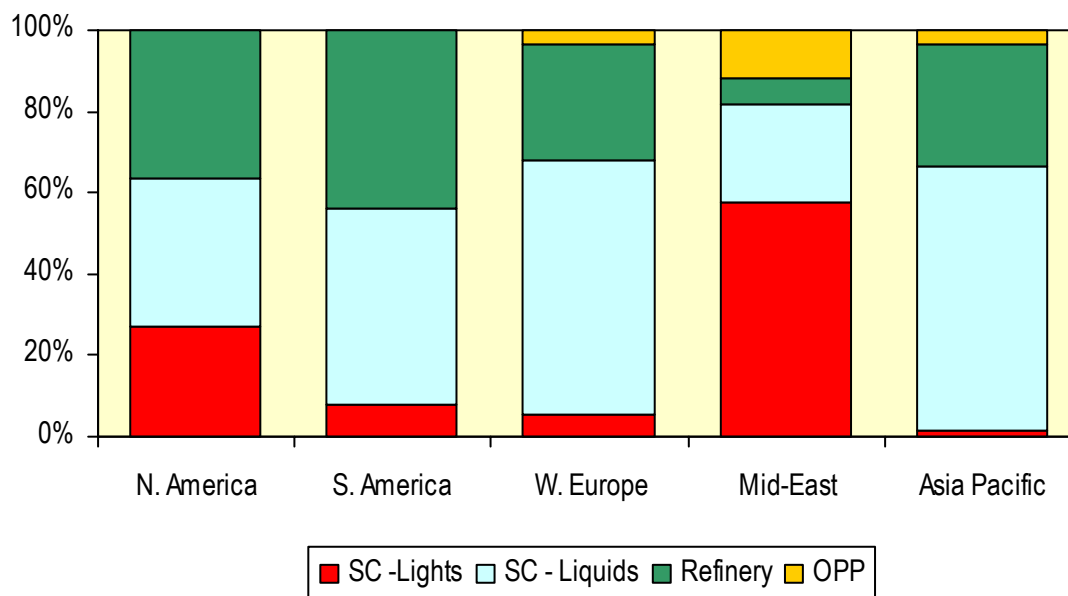
Steam cracker-derived propylene is not able to keep up with propylene demand. To make up this shortfall, refineries capture propylene from fluid catalytic crackers (FCC) and purify it to either chemical grade or polymer grade propylene. Figure 3 shows this breakdown for various regions. FCC units are an important source of incremental propylene in all regions except the Middle East. But it should also be noted that in Western Europe, Middle East and Asia Pacific, other sources of propylene have become necessary. These are the so-called “on purpose propylene” (OPP) technologies and include propane dehydrogenation and olefin metathesis.

**Figure 2**  
**Ton of Propylene per Ton of Ethylene Produced by Different Steam Cracker Feedstocks**



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**Figure 3**  
**Regional Propylene Supply Sources, 2004**



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In the North American, West European, and Asia Pacific regions the P/E ratio is expected to continue to increase over the current high levels. This will put further stress on conventional propylene sources and spur further development and commercialization of OPP technologies for both chemical plants and refineries. This report is aimed at assessing technologies designed for boosting propylene production from refineries.

### **Recovery from Refinery Streams**

Refinery propylene arises primarily from three refinery processes: fluid catalytic cracking (FCC), visbreaking/thermal cracking, and coking. Propylene in all cases is produced as a dilute stream in propane, with the propane/propylene proportions varying considerably depending on the process, feedstock, operating conditions and catalyst. In fluid catalytic cracking, for instance, “refinery propylene” can vary from less than 2 percent to over 6 percent of cracker output on a weight basis; the latter is produced from high severity (gasoline-oriented) operations. The propylene content of the refinery propylene stream can vary from 50 to 75 percent.

In the case of thermal cracking, visbreaking, and coking processes, the propylene yields are lower and the quality often unacceptable other than for refinery fuel. Only in a situation in which there is an associated fluid cat cracker is it possible that recovery of propylene from thermal operations would be considered, but even in these cases it is doubtful.

A refinery having fluid catalytic cracking as its prime propylene source will generate a refinery propylene stream with a propylene concentration of approximately 70 weight percent. Refinery based propylene recovery units can be designed to recover either chemical grade propylene or polymer grade propylene. Propane recovered from the fractionation unit meets LPG specifications and contains approximately 3 weight percent propylene.

### **High Propylene Fluid Catalytic Cracking**

Fluid catalytic cracking (FCC) units typically produce around 3-5 weight percent propylene, depending on feed type, operating conditions, and the nature of the FCC catalyst. This important source of propylene currently accounts for almost 30 percent of the worldwide propylene supply. While propylene is a normal product of the fluid catalytic cracker (FCC) process, conventional FCC operation does not maximize propylene production.

One cost effective way to increase the propylene yield from an FCC unit is the use of specialized catalysts that contain ZSM-5 zeolite. Most units operate with 2 to 5 weight percent of these additives to increase the propylene yield to typically 6-7 weight percent. However, there are an increasing number of refiners that now use as much as 10 weight percent of these additives to obtain

more than 9 weight percent propylene. In Asia Pacific, there is an increasing demand for FCC catalyst technology that will enable refiners to obtain unusually high propylene yields from their existing FCC units.

A new family of catalysts, APEX, has been developed by Davison Catalysts that will allow refiners to take propylene production to a new level. Using proprietary shape-selective zeolite and matrix technologies, APEX catalysts not only produce exceptional yields of propylene in the range of 15-20 weight percent, but also demonstrate low coke make and bottoms cracking activity in the presence of contaminant metals. Propylene yields of more than 20 weight percent are of particular interest to refiners who are considering revamping their FCC units to operate in a “petrochemicals mode.”

Another method to increase propylene production is adding a second reaction zone (up to 20 weight percent). This type of FCC process operates the first reactor at medium severity. This second reactor zone operates at a higher severity using the light naphtha fraction of the feed to maximize propylene production. Meanwhile the gasoline production is about half of the base case and coke production is higher. In addition the concentration of aromatics in the gasoline fraction is higher.

ExxonMobil is working with KBR to offer the MAXOFIN process. This process brings together a high ZSM-5 content additive with improved FCC hardware to produce 18 weight percent propylene yield from vacuum gas oil without resorting to severe operation conditions and high riser steam consumption.

Lummus has developed an enhanced FCC technology that it refers to as Selective Component Cracking (SCC). This process boosts the yield of light olefins by selective injection of naphtha and lighter material into the riser, upstream of the main feed injection nozzles. This system results in a short residence time reaction zone operating at a very high catalyst to oil ratio and high temperature, increasing propylene yields by an additional 2-3 weight percent.

UOP has leveraged its FCC experience and know-how to develop and license a new type of cracking process, PetroFCC, that targets the production of petrochemical feedstocks rather than fuel products. The new process, which utilizes a uniquely designed FCC unit, can produce very high yields of light olefins and aromatics when coupled with an aromatics complex.

Stone and Webster (S&W) have an exclusive agreement with the Research Institute of Petroleum Processing (RIPP) and Sinopec International, both located in the People's Republic of China, with respect to licensing Deep Catalytic Cracking (DCC) technology outside of China. DCC is a catalytic cracking process for producing light olefins ( $C_3$ - $C_5$ ) from heavy feedstocks such as vacuum gas oil.

DCC utilizes fluid catalytic cracking (FCC) principles combined with a proprietary pentasil-shaped, acidic zeolite catalyst, different operating conditions, and other enhancements to achieve its objective. The DCC process results in higher yields for gaseous olefins, especially propylene and butylene, by enhancing secondary cracking reactions, reducing hydrogen transfer reactions, and prolonging contact time between hydrocarbon feed and catalysts. C<sub>3</sub>-C<sub>4</sub> yields are more than double those of conventional FCC units.

### **Olefin Metathesis**

Olefin metathesis, or disproportionation, provides an opportunity to achieve olefin interchangeability. The double bonds of olefins are broken in the reaction, and different olefins are formed using parts of the reactants. The species present, stoichiometry of each species, catalysts employed, and operating temperature will determine which reaction predominates and therefore, which products will form.

Olefin metathesis technology can be incorporated within an FCC facility to boost propylene output. For example, a Lummus version of this technology can be incorporated without having to import ethylene feed. In a typical FCC unit, the three relevant streams for ethylene and propylene production are the Sponge Gas, the C<sub>3</sub> LPG stream and the C<sub>4</sub> Raffinate stream. One approach to producing propylene (and valuable byproduct streams) from these FCC streams consists of:

- Processing the FCC C<sub>2</sub>- Sponge Gas in a Low Pressure Recovery unit (LPR) to recover ethylene which is sent directly to a metathesis unit;
- Processing the C<sub>3</sub> LPG stream from the FCC recovery section in a Propylene Recovery Unit (PRU) to recover the propylene made directly in the FCC unit;
- Processing the FCC C<sub>4</sub> stream in a selective hydrogenation unit followed by an isobutylene removal unit with the n-butenes rich-stream converted to propylene in a metathesis unit.

The LPR and PRU are integrated to maximize product recoveries and minimize utilities.

### **Olefin Interconversion via C<sub>4</sub>/C<sub>5</sub> Cracking**

Propylene via selective C<sub>4</sub>/C<sub>5</sub> cracking technology is generating interest due to the possibility/potential of producing more propylene. Selective C<sub>4</sub>/C<sub>5</sub> cracking technology is similar to metathesis in that low value hydrocarbon streams are converted to higher value olefins. However, the differences between the technologies are many. With selective C<sub>4</sub>/C<sub>5</sub> cracking technologies, C<sub>5</sub> streams can be converted along with the C<sub>4</sub> stream, including isobutene. Normal butenes do not

have to be isomerized. In addition, ethylene is not consumed in the process; in fact, additional ethylene is produced along with the main propylene product.

The chemistry of these technologies is a combination of olefin oligomerization, cracking, disproportionation, and hydrogen transfer.

The catalyst and reaction conditions determine the ultimate distribution of products. In order to maximize olefin production, it is necessary to minimize secondary hydrogen transfer and cyclization reactions, which form paraffins and aromatic compounds.

Kellogg Brown & Root (KBR) is the exclusive licensor for the SUPERFLEX™ technology developed by ARCO Chemical Company, and Lurgi has developed PROPYLUR®. ATOFINA and UOP are also offering a version of this type of technology. None of these processes have been commercialized yet, but all have been pilot-plant tested.

The feed streams for selective C<sub>4</sub>/C<sub>5</sub> cracking can come from many sources. These sources include, but are not limited to, the raw C<sub>4</sub> stream from a steam cracker, a raffinate-1 stream, a raffinate-2 stream, a FCC C<sub>4</sub> stream, and the C<sub>5</sub> stream from cracker pyrolysis gasoline.

## **Economics**

The report presents cost of production estimates for polymer grade propylene via:

- Refinery propylene fractionation
- Deep catalytic cracking
- Low pressure ethylene recovery plus metathesis (Lummus)
- Superflex process (KBR)

## **Commercial**

Steam crackers that use naphtha or heavy liquids feed account for more than 60 percent of global propylene production. Newly commercialized metathesis technology enhances the amount of propylene produced in steam cracking by converting ethylene and butylenes to propylene. Approximately 30 percent is sourced from refinery fluid catalytic crackers (FCCs) or deep catalytic crackers (DCCs), which upgrade atmospheric gas oil into gasoline components. FCCs are a major source of propylene in areas such as the United States where propylene co-production from ethylene plants is lower due to the light cracker feedstocks normally used. The switch to new zeolite FCC catalysts and conversion to DCCs, which produce twice as much propylene as FCCs, are expected to

continue to develop. The growing global supply/demand gap for propylene will be increasingly met by on-purpose production, such as propane dehydrogenation and metathesis.

Other olefins/propylene production routes have been developed, and the licensors are actively promoting their use. These include methanol to olefins (MTO) and production of propylene from C<sub>4</sub>/C<sub>5</sub> olefins.

The report presents supply, demand, and net trade data for the United States, Western Europe, and Asia Pacific, with forecasts to 2015.

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