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The changing dynamics of olefin supply/demand

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1. Introduction

Ethylene and propylene are the two key building blocks of the petrochemical industry. However, ethylene has always reigned supreme, and consequently the industry evolved around steam cracking technology designed to maximize production of ethylene, with propylene and the other building blocks, butadiene and the aromatics, only coming along as by-products. But, as key propylene derivatives have grown rapidly over the last 10 years and are likely to continue doing so, a vexing dilemma is facing the industry: propylene is booming on the demand side, but on the supply side it is relegated to by-product status with its fortunes linked to the vagaries of the ethylene supply/demand situation. Thus, this raises the question of how the industry will address this imbalance and ensure adequate propylene supplies into the future.

2. The changing demand ratio of ethylene and propylene

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 chemical structure of propylene. Like ethylene, propylene contains a carbon–carbon double bond, but unlike ethylene, propylene also contains 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, exploiting the reactivity of propylene's carbon–carbon double bond allows formation of the following materials:

- polypropylene via Ziegler Natta 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.

While 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/chlorohydrin chemistry.

But what derivative is driving the very strong growth of propylene? Fig. 1 illustrates the global demand breakdown for propylene in 1970 and in 2004. In 1970, the key derivatives all compose about the same size share, anywhere from 11 to 18% of total demand with no one derivative standing out too much. However, currently the situation is much different. Polypropylene now consumes 64% of the world's propylene production (not including fuel use) and is clearly the driver for propylene demand.

Fig. 2 illustrates the astounding growth of polypropylene since the mid-1980s. This growth was stimulated by the advent of very high-productivity polypropylene catalysts and the relatively low cost of propylene. As seen in the figure, Asia is expected to be the dominant region with respect to polypropylene demand in the future.

The very strong growth of polypropylene is forcing a structural change in propylene's supply pattern. Fig. 3 compares the regional demand ratio for ethylene and propylene over the 1992–2004 timeframe. While the overall demand for ethylene is greater than propylene over this timeframe, the rate of growth for propylene has outpaced

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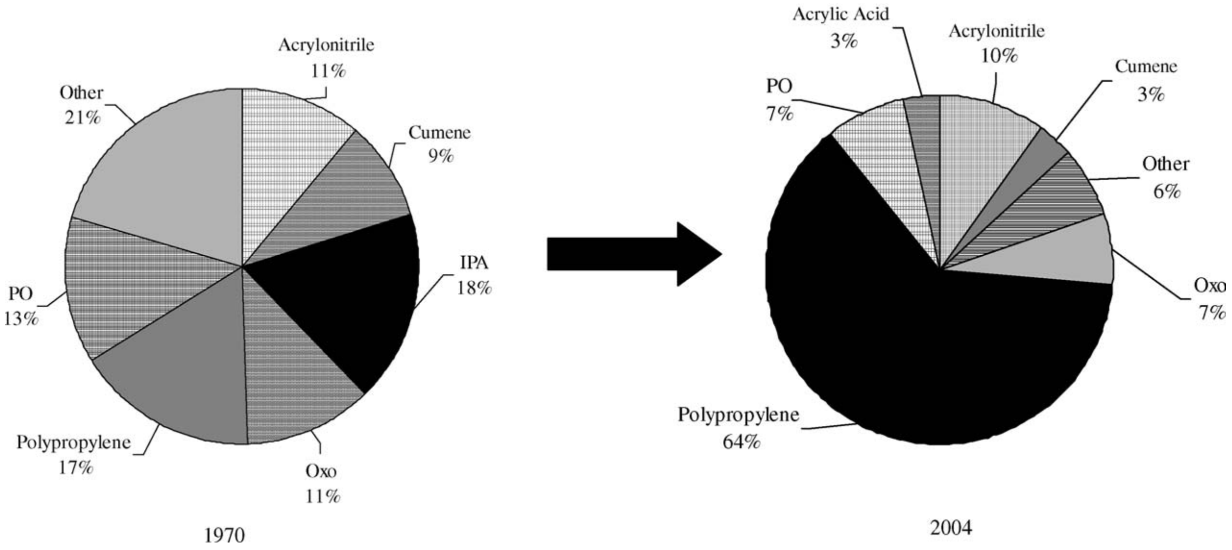

Fig. 1. Global propylene demand pattern, 1970–2004.

ethylene's growth rate. For instance, in the U.S., the P/E demand ratio has increased from 0.43 in 1992 to 0.54 in 2004. The same phenomenon is seen in West Europe and Asia Pacific, but to an even greater degree. In Asia Pacific, the P/E demand ratio is a very high 0.77. The Middle East is still heavily ethylene-centric due to the availability of very low cost ethane with the P/E ratio staying relatively flat since 1996.

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. For example, if ethane is the feedstock, only 0.019 t of propylene are produced for every ton of ethylene made. As feedstocks get heavier, propylene output increases as shown in Fig. 4. Thus, the amount of propylene able to be produced in steam crackers is fixed (with some limited amount of flexibility based on operating severity and the ability to change feeds from gas to liquids that some crackers have).

To make-up this shortfall, refineries are able to capture propylene from fluid catalytic crackers (FCC) and purify refinery grade propylene to either chemical grade or polymer grade propylene. Fig. 5 shows the breakdown of propylene sources on a regional basis. In all regions, refineries are an important source of propylene, but especially so in the U.S. as steam cracking feeds in the U.S. are relatively light and produce lesser amounts of propylene than those regions using liquid feedstocks. Fortunately, the large installed FCC capacity base in the U.S. allows the propylene supply gap to be bridged relatively easily. But it should also be noted that other sources of propylene have also become necessary. These are the so-called "on purpose propylene" technol-

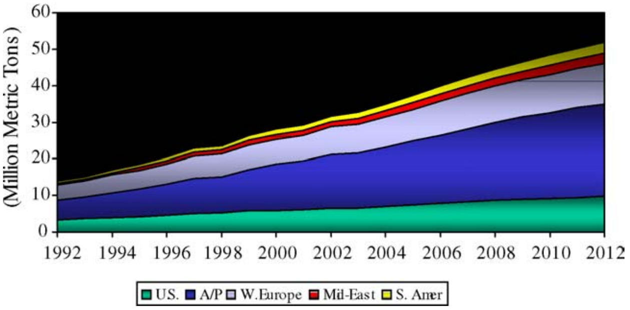

Fig. 2. Regional polypropylene demand.

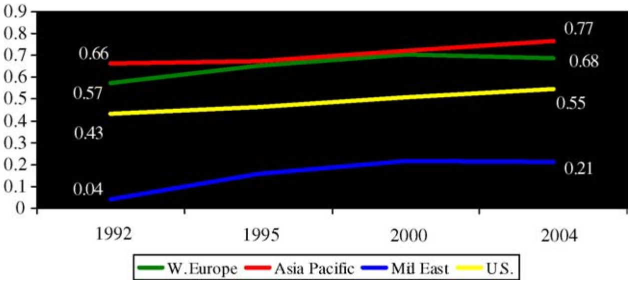

Fig. 3. Regional propylene/ethylene demand ratio growth, 1992–2004.

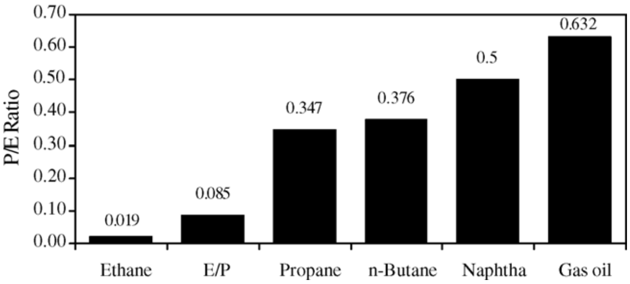

Fig. 4. Ton of propylene per ton of ethylene for various cracker feeds.

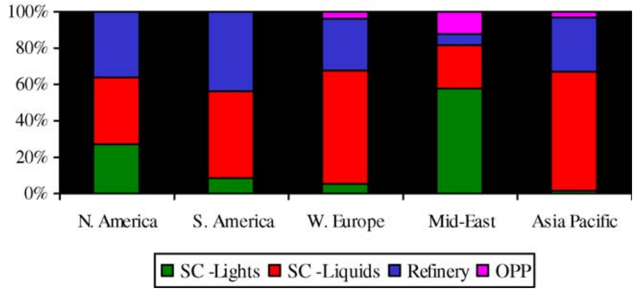

Fig. 5. Regional propylene supply sources, 2004.

ogies and include propane dehydrogenation, olefin metathesis and other emerging processes.

What does the future look like with regards to propylene supply? Fig. 6 gives Nexant ChemSystems' forecast of incremental ethylene and propylene demand from 2004 to 2012 by region on a relative basis. The incremental P/E demand ratios are also shown for each region. In the North American, West European and Asia Pacific regions, the P/E demand 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 plans for propylene-boosting technologies for petrochemical plants, refineries and stand-alone units. This paper will focus on those technologies geared for increasing propylene yields from steam crackers and FCC units.

3. On-purpose propylene technologies

The impending propylene supply/demand gap has stimulated technology developers to improve or tweak conventional technologies to increase the amount of propylene from them or develop whole new ways to make propylene ‘‘on-purpose’’.

3.1. 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.

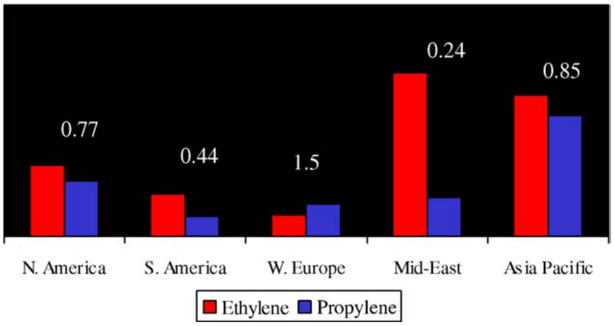

Fig. 6. Regional P/E ratios of incremental ethylene and propylene demand, 2004–2012.

In order to make propylene, this technology combines ethylene and butylenes from the naphtha crackers C_4 stream. This process also has the option of dimerizing ethylene into 2-butene or using *n*-butenes from C_4 fractions, followed by the metathesis reaction between ethylene and 2-butene to yield propylene.

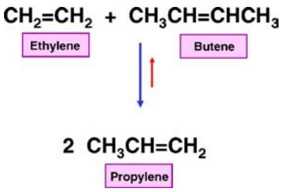

ABB Lummus Global purchased Phillips' Olefins Conversion Technology (OCT, also known as Triolefins) in 1997. BASF and Fina are operating a plant using this technology as an addition to their joint venture liquids steam cracker at Port Arthur, TX. With the addition of the OCT, the nameplate capacity of the cracker is 1.8 billion pounds (816,000 metric tons) per year ethylene and 1.95 billion pounds (885,000 metric tons) per year propylene. OCT has also been implanted at Mitsui Chemicals olefins plant in Osaka, Japan. Lummus has announced several other OCT contract awards. Axens is also licensing metathesis technology. The IFP-CPC Meta-4 process was jointly developed by Institut Français du Pétrole (IFP) and Chinese Petroleum Corporation (CPC) of Taiwan. A demonstration pilot plant using this metathesis technology was operated from April 1988 to September 1990.

Lummus has also developed ways olefin metathesis technology can be incorporated within an FCC facility to boost propylene output.

3.2. C_4/C_5 olefin interconversion

Propylene via selective C_4/C_5 cracking technology is generating interest due to the possibility/potential of producing more propylene. Selective C_4/C_5 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_4/C_5 cracking technologies, C_5 streams can be converted along with the C_4 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.

This type of process has been described by several companies in recent years. Mobil Technology has developed a process marketed as MOI^{SM}—Mobil Olefin Interconversion technology. Kellogg Brown & Root (KBR) is the exclusive licensor for the SUPERFLEX^{TM} 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 first commercial SUPERFLEX^{TM} unit for SASOL, South Africa, is scheduled to startup in late 2005 making 550 million pounds of propylene.

As with metathesis, there are various situations for the application of these technologies for increasing propylene production. The feed to the unit can come from a naphtha cracker or from an FCC unit. The selective C_4/C_5 cracking unit can be stand-alone, add-on, or fully integrated. For a stand-alone unit, the product from the reactor is fed to a separation section for propylene and possibly ethylene recovery. For an integrated unit, the product from the reactor would be fed to the steam cracker's recovery section. The exact feed point would depend on the capacity of the columns and the separation scheme of a particular plant. The distillation columns for the cracker would have to be larger, but the recovery columns for the olefin interconversion unit would be eliminated. In this report, the technology will be described as an enhancement to FCC units.

The chemistry of these technologies is a combination of olefin oligomerization, cracking, and disproportionation. These reactions are summarized below using a notation prescribed by Mobil:

$$C_{x=} + C_{y=} \rightarrow C_{x+y=} \quad \text{(oligomerization)}$$

$$C_{x+y=} \rightarrow C_{x=} + C_{y=} \quad \text{(cracking)}$$

$$C_{x=} + C_{y=} \rightleftharpoons C_{u=} + C_{v=} \quad \text{(disproportionation)}$$

$$\begin{aligned} C_{u=} + C_{v=} \rightarrow {} & \text{cyclo-olefins, paraffins, naphthenes,} \\ & \text{aromatics(hydrogentransfer)} \end{aligned}$$

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.

The process characteristics of the selective C_4/C_5 cracking technologies reviewed are summarized in Table 1.

The feed streams for selective C_4/C_5 cracking can come from many sources. These sources include, but are not limited to, the raw C_4 stream from a steam cracker, a raffinate-1 stream, a raffinate-2 stream, a FCC C_4 stream, and the C_5 stream from cracker pyrolysis gasoline. The only pretreatment recommended is the selective hydrogenation of all dienes. Although dienes can be fed to the process, selectivity to propylene is enhanced if the dienes are first converted to olefins. That makes selective hydrogenation economically desirable if the dienes content is high in the feed. All other components can be fed to the process.

3.3. FCC catalyst additives

Another effective way to increase the propylene yield from an FCC unit is the use of specialized catalyst additives that contain ZSM-5 zeolite. These FCC catalyst additives were first introduced by Davison Catalysts in 1984 and function by converting gasoline range olefins produced by the primary FCC catalyst and converting these olefins to propylene and butylenes. More than a one-third of the world's FCC units utilize ZSM-5 additives either continuously or intermittently (to take advantage of favorable economics in the propylene market). Most units operate with 2–5 wt% of these additives to increase the propylene yield to typically 6–7 wt%. However, there are an increasing number of refiners that now use as much as 10 wt% of these additives to obtain more than 9 wt% propylene.

Table 2 shows typical yields from an FCC unit with and without ZSM-5 additives.

As seen in the table, increased propylene yields come at the price of decreased gasoline production. This is the trade-off that refiners have to grapple with in order to maximize their operating profits.

Recently, Davison introduced a new high performance ZSM-5 additive called OlefinsUltra^{TM}. The intrinsic activity of this additive exceeds even that of previous versions and it is claimed to provide the highest activity per pound of any commercially proven ZSM-5 additive. Davison has also developed a new family of catalysts, APEX. Using proprietary shape-selective zeolite and matrix technologies, APEX catalysts produce very high yields of propylene with low coke make.

3.4. FCC process and catalyst modifications

Deep catalytic cracking (DCC) process developed by the Research Institute of Petroleum Processing (RIPP) and

Table 1
Selective C_4/C_5 cracking technology process characteristics

	MOI	SUPERFLEX^{TM}	PROPYLUR	AtoFina/U
Reaction temperature	>1000 °F	900–1300 °F	>/=930 °F	500–600 °C
Catalyst	ZSM-5	Zeolite	Zeolite	Zeolite
Reaction pressure	15–30 psig	1–2 bars	1.3–2 bars	1–5 bars
Reactor system	Fluid bed	Riser	Fixed bed	Fixed bed
Catalyst regeneration	Continuous, fluid bed	Continuous	Cycle	Cycle
Feed pretreatment	Selective hydrogenation of dienes	Selective hydrogenation of dienes	N/A	N/A

Table 2
FCC product slate with and without ZSM-5 additive comparison

	Conventional FCC (wt%)	Conventional FCC + ZSM-5 (wt%)
Total C_2–	2.1	2.1
Propylene	5.9	9.9
LPG (excluding propylene)	12.8	16.2
C_5 + gasoline	51.6	45.6
LCO + HCO	22.0	20.6
Coke	5.6	5.6

Table 3
DCC product slate and olefin yields

	DCC Type I	DCC Type II	FCC
Yields[a] (wt%)			
C_2–	11.9	3.6	3.5
C_3–C_4	42.2	34.5	17.6
C_5 + Naphtha	26.6	41.0	54.8
Light cycle oil (LCO)	6.6	9.8	10.2
Decanted oil (DO)	6.1	5.8	9.3
Coke	6.0	4.3	4.3
Loss	0.6	1.0	0.3
Total	100.0	100.0	100.0
Olefins (wt% on feed)[a]			
Ethylene	6.1	1.8	0.8
Propylene	21.0	14.3	4.9
Isobutylene	5.1	6.1	1.9
Total butylenes	14.3	14.7	8.1
Isoamylene	–	6.8	–
Total amylenes	–	9.8	–

[a] Feedstock: waxy Chinese VGO (pilot plant data).

Sinopec International, utilizes fluid catalytic cracking principles combined with a proprietary catalyst, different operating conditions, and other enhancements to achieve its objective of producing light olefins from vacuum gas oil (VGO). DCC, licensed exclusively by Stone and Webster outside of China, operation is similar to FCC in the way the catalyst is handled and regenerated. The main fractionator and recovery section have a similar configuration, with adjustments made for the different product slate.

There are two distinct operation modes for DCC. Type I is for maximum propylene production and Type II is for reduced severity and produces less propylene. It also maximizes iso-olefins production. Type II is more suitable for FCCU revamps. Each operation mode utilizes a different catalyst and operates with different reaction conditions. Table 3 shows the cracking yields from the two types in comparison to typical FCC yields.

When compared to FCC, the gas and light olefins yield (C_2– and C_3–C_4) is significantly higher for both DCC modes, Types I and II. More amylenes are produced with Type II at the expense of ethylene and propylene production. Compared with steam cracking (SC), DCC produces significantly less ethylene and significantly more propylene. The DCC process is more suitable for propylene and/or butylenes production than for ethylene production.

UOP has leveraged its FCC experience and know-how to develop and license a new type of cracking process. The PetroFCC process 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. The PetroFCC process is capable of producing a product slate of 35 lv (liquid volume)% propylene, 12 lv% ethylene, 20 lv% butylenes, and 20 lv% of benzene and *para*-xylene. This is a substantial increase in the yield of petrochemicals compared to a conventional FCC unit.

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 wt% propylene yield from vacuum gas oil without resorting to severe operation conditions and high riser steam consumption.