University of Petroleum and Energy Studies

Technologies for Propylene Maximization

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Submitted By:

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Certificate

This is to certify that the project report on "Technologies for propylene Maximization" submitted to the university of Petroleum and Energy Studies, done by Mr. Rahul Shamra, in partial fulfillment of the requirement for the award of degree of bachelor of technology in applied petroleum Engineering (academic session 2003-2007) is a bonafide work carried out by him under my supervision and guidance. This work has not been submitted anywhere else for any other degree or diploma.

T. Chandrasekhar
8/5/07

Date

Mr.T. Chandrashekhar

Introduction

To understand the topic at hand, "The Technologies used for Propylene maximization," first of all we need to answer the question, what is propylene? Propylene - also known as propene - is one of the major building blocks of the petrochemical industry. To give a more definitive answer from a chemistry point of view, we have, Propylene, also known by its IUPAC name propene, is an organic compound having the chemical formula C3H6. It is the second simplest member of the alkene class of hydrocarbons, ethylene (ethene) being the simplest. At room temperature and pressure, propylene is a gas. It is colorless, highly flammable, and has an odor similar to garlic. (This smell is added to make it easily detectable, pure propylene, like most simple hydrocarbons, has no natural scent.)

Now that we know what propylene is, we need to understand why is it so important? The answer comes to us in the fact that propylene is used to make further useful chemicals. The materials that are derived from propylene include: polypropylene; acrylonitrile (which is converted to acrylic fibers and coatings); propylene oxide (which then goes into polyurethane resins and other chemicals); oxo alcohols (which are used in PVC plasticisers and coatings); cumene (which is ultimately used to make epoxy resins and polycarbonate); and isopropyl alcohol (which is used as a solvent).

As a result, propylene is a key component of countless end use products. Examples include automobile headlights, taillights, disk brake pads and bumpers; carpets; CDs and optical disks; clear film food wrap; eyeglasses; flexible foams used in bedding and furniture; rigid foam insulation; impact-resistant and bullet-proof windows; molded plastic goods such as buckets, food containers, kitchen utensils and wastebaskets; nitrile rubber hoses, seals and gaskets; paints and protective coatings; grocery bags; synthetic fibers for blankets, sweaters, socks and fleeces; water cooler bottles; and wood products such as plywood, oriented strand board and laminates.

The main use of propylene though is as a monomer, mostly for the production of polypropylene. More than 60% of the world's production of propylene is used to make polypropylene. Since its invention in 1954, polypropylene has grown into one of the most widely- used and versatile products of the petrochemical industry. Propylene has a similar calorific value to propane but a lower mass of combustion products so a higher flame temperature. Propylene also has approximately twice the vapor pressure of propane at room temperature and pressure

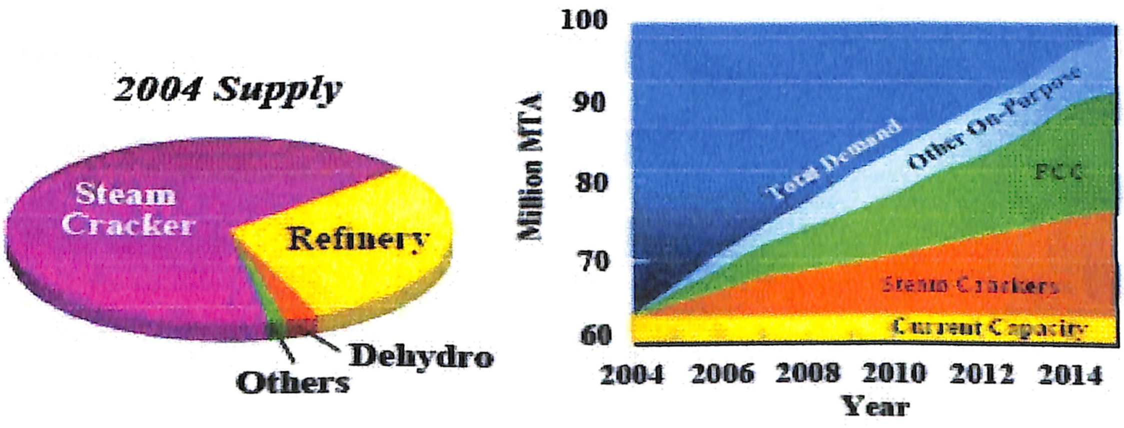
What is the best way to produce propylene? Approximately two-thirds of the current production of propylene is supplied from thermal steam cracking of liquid feedstock's (primarily naphtha). Figure 1 shows that the balance is supplied mostly from refinery FCC units that have installed propylene recovery facilities or from the dehydrogenation of propane. These routes to propylene were selected because each producer at some point determined that this was the best way to produce the products they desired for their particular opportunity. This does not mean that the producers that selected a different route got it wrong but instead it demonstrates that there is no single answer as to which way is universally the best. There are many different opportunities available, which is one reason why various companies have developed a broad portfolio of propylene producing technologies

There are more options available today than ever before for the production of propylene. Perhaps most importantly, all these alternatives are needed to fill the growing gap between propylene demand and supply from conventional sources. Each of these routes can offer competitive economics in certain situations. Understanding which is best suited for a particular application is a critical step towards selecting the right project.

Figure 1

Propylene Supply and Demand

Polymer Grade & Chemical Grade



Source: CMAI

GLOBAL SUPPLY AND DEMAND

The global demand for propylene derivatives

1) The global demand for propylene derivatives (propylene conversion) is expected to rise at an average annual rate of 5.4% from the 2002 level of 56.2 million tons to 77.1 million tons in 2008, topping the rise in demand for ethylene derivatives.

2) The average annual rate of demand growth for this period is expected to be 6.1% in Asia, 5.4% in North America and 3.3% in Western Europe. Demand from **India** alone is expected to rise at a **brisk 9.7%.**

Global demand for propylene derivatives (propylene production)

	Global Total	Asia							Western Europe	North America	Middle East
		Total	South Korea	Taiwan	China	ASEAN	India	Japan			
Demand 2002	56.2	20.4	1.7	1.0	8.3	2.7	1.6	4.6	14.4	13.9	1.3
Demand 2008	77.1	29.0	2.1	1.3	13.7	3.4	2.8	5.3	17.5	19.1	2.2
Increase 02-08	20.9	8.7	0.3	0.3	5.4	0.7	1.2	0.7	3.1	5.2	0.9
Growth rate 02-08	5.4%	6.1%	2.8%	4.1%	8.7%	5.3%	9.7%	2.4%	3.3%	5.4%	9.1%

Unit: Million Tons

The Supply and demand balance for propylene and propylene derivatives

1) The growth in supply of propylene derivative products in India is not keeping pace with the growth in demand. As such, the negative demand-supply balance (excess imports over exports) for propylene derivative products in India is expected to increase **to 1.4 million tons in 2008.**

2) The import position of propylene derivatives for the Asian region is expected to expand to 4.6 million tons.

Global supply and demand balance for propylene derivatives and propylene (propylene conversion)

(Unit: million tons)

		Global Total	Asia							Western Europe	North America	Middle East
			Total	South Korea	Taiwan	China	ASEAN	India	Japan			
2002	Production	55.9	19.3	3.0	1.2	5.6	3.2	1.4	5.0	14.7	15.4	1.4
	Demand	56.2	20.4	1.7	1.0	8.3	2.7	1.6	4.6	14.4	13.9	1.3
	Balance	-0.3	-1.0	1.3	0.2	-2.8	0.5	-0.2	0.4	0.3	1.5	0.1
2008	Production	71.3	24.4	3.3	1.7	8.3	4.1	1.4	5.6	16.1	19.6	3.0
	Demand	77.1	29.0	2.1	1.3	13.7	3.4	2.8	5.3	17.5	19.1	2.2
	Balance	-5.8	-4.6	1.2	0.3	-5.4	0.7	-1.4	0.4	-1.4	0.5	0.8

COMMERCIALLY AVAILABLE ROUTES TO PROPYLENE

The routes currently available for producing propylene can be categorized into the following five groups:

- Steam Cracking
- Fluid Catalytic Cracking
- Propane Dehydrogenation
- Natural Gas or Methanol to Olefins
- Olefin Conversion

STEAM CRACKING

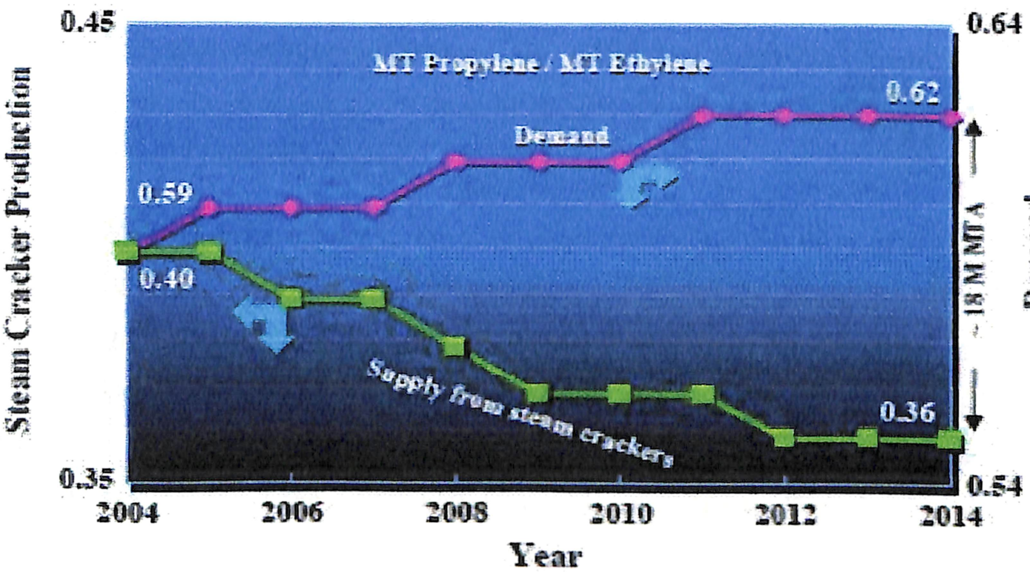
It is widely recognized that naphtha steam crackers are the largest current source of propylene. The yield of propylene from a naphtha cracker is about 15 wt-% of the naphtha feedstock while the yield of ethylene is about twice the propylene yield. Thus, the propylene/ethylene product ratio for a naphtha cracker is approximately 0.5. Because ethylene has historically averaged a higher market price than propylene, ethylene producers have primarily built naphtha crackers to meet their ethylene demands and recovered propylene as a co-product.

Ethylene producers try to maximize their profitability and competitiveness by utilizing cost advantaged feedstocks and by taking advantage of economies of scale by building larger units. The availability of ethane at stranded gas prices Globally has attracted a large build-up of ethane-based steam cracker capacity over the next few years, 24 new steam crackers are in the pipeline across the globe. Ethane-based crackers produce very little propylene such that it is generally uneconomical to recover the propylene as a product. Consequently, this build-up of ethane-based crackers will result in less propylene production per ton of ethylene produced. Figure 2 shows that currently there are 0.40 tons of propylene produced by steam crackers for every ton of ethylene. As a result of the build-up of ethane-based crackers, the propylene production rate from steam crackers is anticipated to fall to 0.36 tons of propylene per ton of ethylene by 2014. Over the same time period, the demand for propylene is expected to increase relative to the demand for ethylene (from 0.59 tons of propylene per ton of ethylene today to 0.62 tons of propylene per ton of ethylene in 2014). These market dynamics, if proven true, will result in a growing gap between propylene demand and propylene supplied from ethane based steam crackers. But fortunately for India, it does not employ ethane based steam crackers (only two in use by IPCL). In the Indian scenario natural gas being scarce and expensive, naphtha crackers have come up in a big way. They have been discussed below.

Figure 2

$C_3^=/C_2^=$ Ratios

Worldwide



Data Source: CMAI 2005

<u>Steam Cracking</u>

Naphtha → Ethylene + Propylene

2 : 1

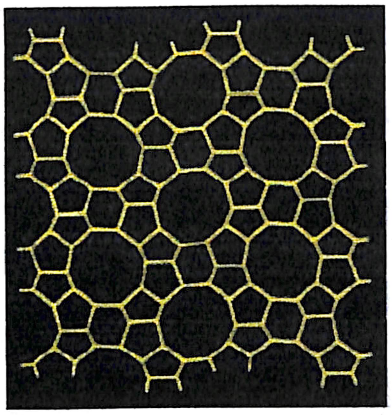
Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing commonly olefins, including ethylene and propylene.

In steam cracking, a gaseous or liquid hydrocarbon feed like Naphtha is diluted with steam and then briefly heated in a furnace (obviously without the presence of oxygen). Typically, the reaction temperature is very hot —around 850°C—but the reaction is only allowed to take place very briefly. In modern cracking furnaces, the residence time is even reduced to milliseconds (resulting in gas velocities reaching speeds beyond the speed of sound) in order to improve the yield of desired products. After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line exchanger.

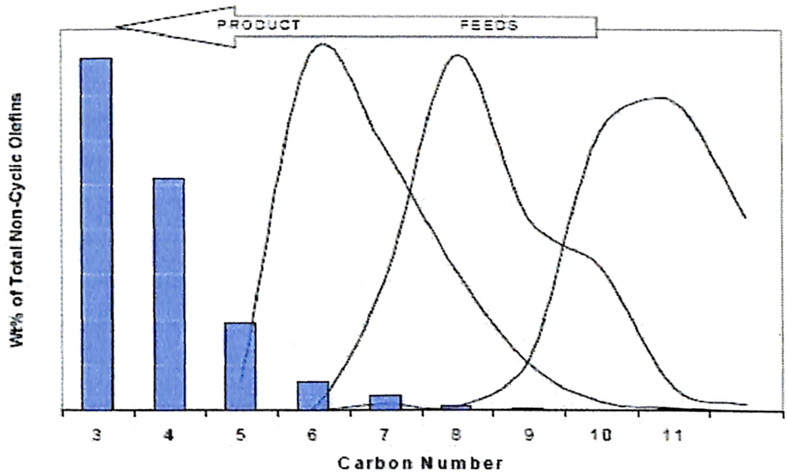
The products produced in the reaction depend on the composition of the feed, the hydrocarbon to steam ratio and on the cracking temperature & furnace residence time. Light hydrocarbon feeds (such as ethane, LPGs or light naphthas) give product streams rich in the lighter alkenes, including ethylene, propylene, and butadiene. Heavier hydrocarbon (full range & heavy naphthas as well as other refinery products) feeds give some of these, but also give products rich in aromatic hydrocarbons and hydrocarbons suitable for inclusion in gasoline or fuel oil. The higher cracking temperature (also referred to as severity) favours the production of ethene and benzene, whereas lower severity produces relatively higher amounts of propene, C4-hydrocarbons and liquid products.

The process also results in the slow deposition of coke, a form of carbon, on the reactor walls. This degrades the efficiency of the reactor, so reaction conditions are designed to minimize this. Nonetheless, a steam cracking furnace can usually only run for a few months at a time between de-cokings. Decokes require the furnace to be isolated from the process and then a flow of steam or a steam/air mixture is passed through the furnace coils at 950 -1050 C . This converts the hard solid carbon layer to Carbon Monoxide and Carbon Dioxide. Once this reaction is complete, the furnace can be returned to service.

Figure 2a
Reaction Equilibration in Catalytic Naphtha Cracking



<u>ZSM-5</u>
3D(10x10x10)
5.3 x 5.6 Å, 5.1 x 5.5 Å



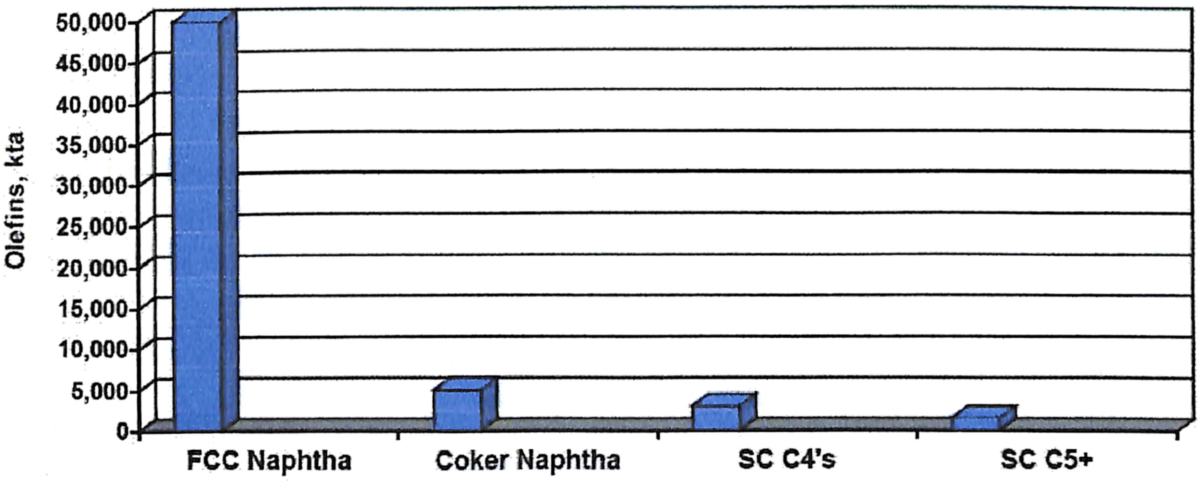
Feedstock Considerations

Modern polypropylene units require about 300 thousand metric tons per year (300 kta) of propylene per train. Production of such large volumes of propylene from olefinic naphtha and C4 cracking requires large volumes of olefinic feedstock. Such large quantities of olefinic feedstock molecules can be obtained from FCC's (cat naphtha), Cokers (Coker naphtha), and steam crackers (C4's and pyrolysis gasoline). But by far, the largest source of olefinic feedstock molecules is cat naphtha from FCC, with steam crackers lagging far behind.

Olfine yields from different feedstocks

Products	Yield (wt %)			
	Ethane	Propane	Ethane/Propane (60:40)	Naptha
Ethylene	84.0	43.7	67.9	30.1
Propylene	1.0	15.2	6.7	15.6
Others	15	41.1	25.4	54.3

Figure 2b
Olefin Feedstock Potential



Apart from the above a hypothetical integration procedure can be preformed on the naphtha cracker and a process known as metathesis, described later, to give significantly higher yields of propylene as can be seen from the table below.

Integrated Metathesis

Products	Naphtha Cracker	Naphtha Cracker plus Methathesis
Ethylene (kmta)	1,000	850
Propylene (kmta)	500	920
Butylene (kmta)	300	-
Olefin Value* ($MM/yr)	855	885
Investment ($MM)	1,000	1080

Ethylene = $500/ton, Propylene = $500/ton, Butylene = $350/ton

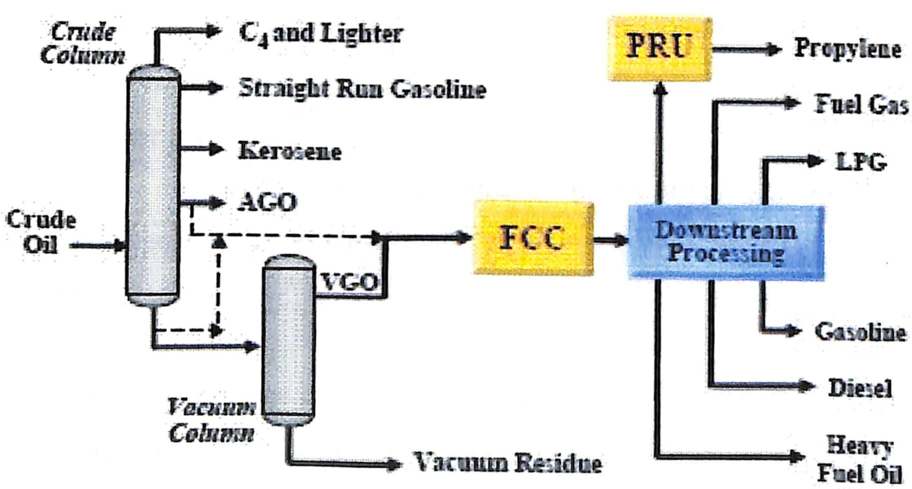
FLUID CATALYTIC CRACKING

The second largest source of propylene supplied for petrochemical applications is from fluid catalytic cracking (FCC) units. The primary function of the FCC unit has typically been to produce gasoline but a significant amount of propylene is produced as a co-product. Conventional refineries utilize propylene for motor fuel production through the use of alkylation or catalytic condensation processes. Some refineries have installed a propylene recovery unit (PRU) to obtain higher values for their propylene by producing polymer-grade or chemical-grade propylene.

This is especially prevalent in locations in close proximity to petrochemical plants, such as in North America, Western Europe, and Northeast Asia. FCC units are expected to fill much of the propylene supply/demand gap but there are logistic and strategic issues that inhibit some refineries from recovering the full propylene potential from their FCC units.

Figure 3

Propylene from Refineries



Propylene Recovery Units

Conventional FCC technology yields approximately 4 to 7 wt-% propylene and about 1 or 2 wt-% ethylene. It is often uneconomical to recover the ethylene from conventional FCC units, especially in smaller units. Propylene, however, can be recovered by adding a PRU. A PRU generally consists of a three-column fractionation train followed by driers and treaters to remove contaminants in order to produce high purity polymer-grade propylene. The PRU fractionation train includes a depropanizer column to separate the C4 and heavier hydrocarbons from the C3 - material and a deethanizer column to separate the C2 - material from the C3 material. These two columns typically contain about 40 trays and use conventional reboiler and condensing systems.

The separation of propane from propylene is more difficult and requires about 180 trays to achieve 99.5% or higher polymer-grade purity. If conventional fractionation trays are used, this column consists of two vessels due to the height required. Substantial savings in capital and operating costs can be achieved by utilizing high capacity MD™ trays and High Flux™ tubing (a UOP product) with a heat-pumped C3 splitter design. A heat-pumped fractionating column uses the heat from the overhead vapors to reboil the bottoms liquid instead of a conventional overhead condenser and bottoms reboiler system. The savings are achieved because:

A single column can be used for the C3 splitter instead of two columns due to the low tray spacing requirements for the MD trays

A smaller diameter is required due to the high liquid loading available with the MD trays

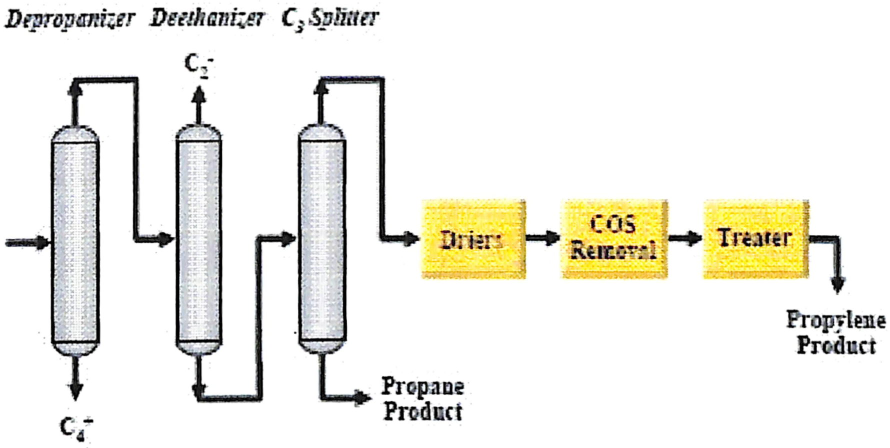
A reduction in the number and size of exchanger shells is achieved by using High Flux tubing

A lower overall pressure drop which requires a smaller compressor with less horsepower and thereby reduced utility requirements.

The savings and performance of C_3 splitter design has been proven in more than 120 applications using MD trays, and more than 80 applications using High Flux tubes.

Figure 4

UOP Propylene Recovery Unit



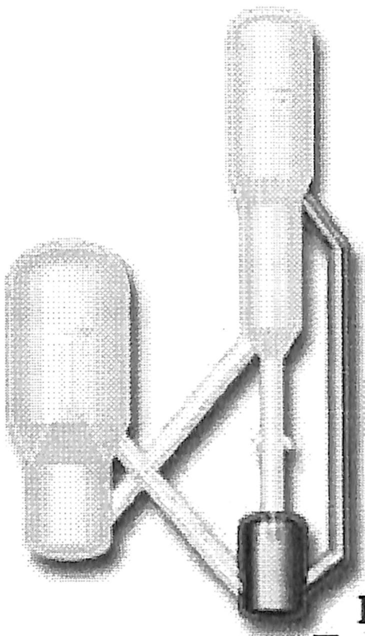
High Severity FCC

One of the first changes refiners typically make to increase the propylene yield and selectivity from their FCC unit is the use of specially formulated FCC catalysts and/or shape-selective catalyst additives. These catalysts and additives increase the yield of propylene and other light olefins at the expense of gasoline and distillate products. Propylene yields can be further increased by adjusting the reaction severity via the riser outlet temperature. Taken together, these modifications can result in propylene yields that approach 10 wt-%.

In addition, mechanical equipment such as the RxCatTM technology can be used to enhance catalytic cracking while minimizing non-selective thermal cracking. RxCat decouples the catalyst circulation from the unit's heat balance. This allows operation with higher catalystto- oil ratios up the reactor riser, which provides higher conversion and increased flexibility.1 Figure 5 shows the FCC reaction section with RxCat technology. The addition of RxCat enables the FCC to produce propylene yields well beyond 10 wt-%. The ultimate propylene yield in these revamp applications is usually constrained by limitations in the downstream equipment or recovery unit(s).

Figure 5

FCC Unit with RxCat Technology



PetroFC Technology (or Deep Catalytic Cracking)

The PetroFCC process targets the production of petrochemical feedstock's utilizing a uniquely designed FCC unit, producing very high yields of light olefins and aromatics (via the gasoline range material) when coupled with an aromatics complex. Demand for light olefins as petrochemical feedstock's--especially for propylene--is expected to continue to increase in the foreseeable future. Additional propylene produced from the increase in steam cracker ethylene production is expected to be insufficient to meet this demand, and propylene from other sources will be required. The FCC process is highly flexible and can help to fill the propylene "gap."

Although principally designed to produce gasoline, the FCC unit is frequently operated to produce distillates or LPG. When in LPG mode, the FCC unit produces enhanced yields of petrochemical feedstock's. With the PetroFCC process, substantially greater quantities of light olefins and petrochemical feedstock's are produced while minimizing or eliminating the yield of gasoline and heavier liquid fuels.

The PetroFCC process achieves much higher light olefin yields than a conventional FCC process. RxCat technology is used in the PetroFCC to provide the benefits of enhanced catalytic cracking which delivers increased propylene yields and reduced dry gas make. Another benefit of the PetroFCC technology is the flexibility it provides the operator with regards to catalyst and additive selection. The PetroFCC operator is able to select catalyst and additives from a variety of commercially available sources to help them best meet their processing and product objectives. A PetroFCC unit can achieve propylene yields of 22 wt- % and ethylene yields of 6 wt-%.

The catalyst section of the PetroFCC process incorporates UOP's RxCat technology, the use of shape selective zeolite additive with a selected standard FCC catalyst as the balance and optimized operating conditions to enhance light olefin production. The PetroFCC catalyst has the following essential features.

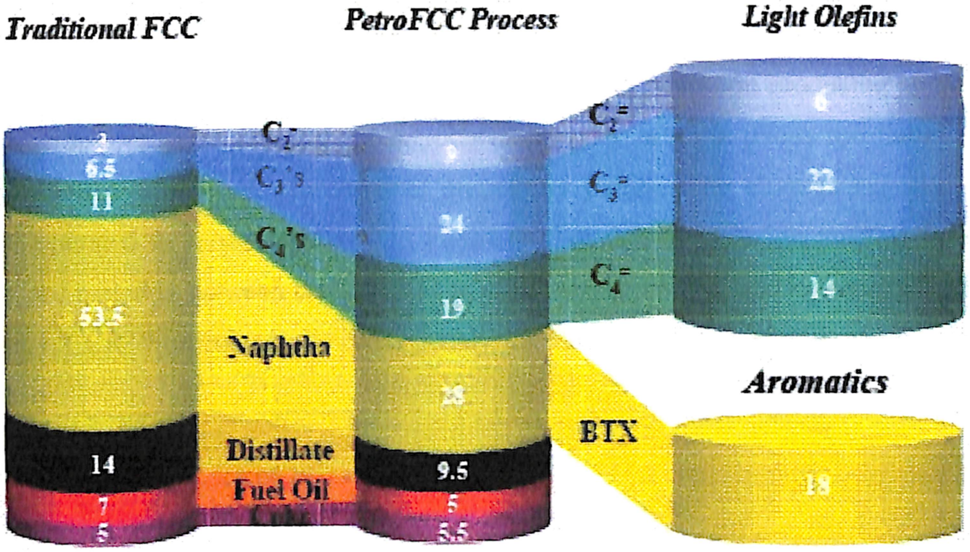
- High degree of hydrothermal stability
- Low hydrogen transfer activity
- Good coke selectivity

The PetroFCC catalyst formulation is carefully designed to optimize the formation of carbonium ions. This is because olefins tend to form carbonium ions more easily than paraffin's. Hence given the right carbonium ion "environment" following the primary cracking, the olefins tend to rearrange while paraffin's are relatively less reactive. The overall flow scheme of PetroFCC process is similar to that of conventional FCC. As the PetroFCC process generates much larger quantities of gaseous product, its reactor has a larger diameter to prevent catalyst carry over. The operating conditions of PetroFCC process are more severe than those of conventional FCC. However, the reaction temperature of PetroFCC is much lower than that of stream cracking.

Figure 6

Typical PetroFCC Process Unit Yield, wt-%

(VGO Feed)



Although the quantities of naphtha and distillate are reduced, the concentration of aromatics in the naphtha increases with use of the PetroFCC process, so that yields of about 18 wt-% aromatics (benzene, toluene, xylenes) are possible. In addition to the increased propylene yield, the C4 olefin yield is also increased which offers refiners the opportunity to increase the production of high quality motor fuel alkylate. Alternately, the C4 - C8 olefinic cuts can be converted in the Olefin Cracking unit to yield even more ethylene and propylene. Olefin Cracking will be discussed a bit later in this Report.

NOTE: while it is to be noted that the PetroFCC technology and the Deep Catalytic Cracking technology are essentially the same type of technology, they have been patented by different companies. The DCC technology was developed by the Research institute of petroleum Processing (RIPP) of china, while the PetroFCC belongs to UOP.

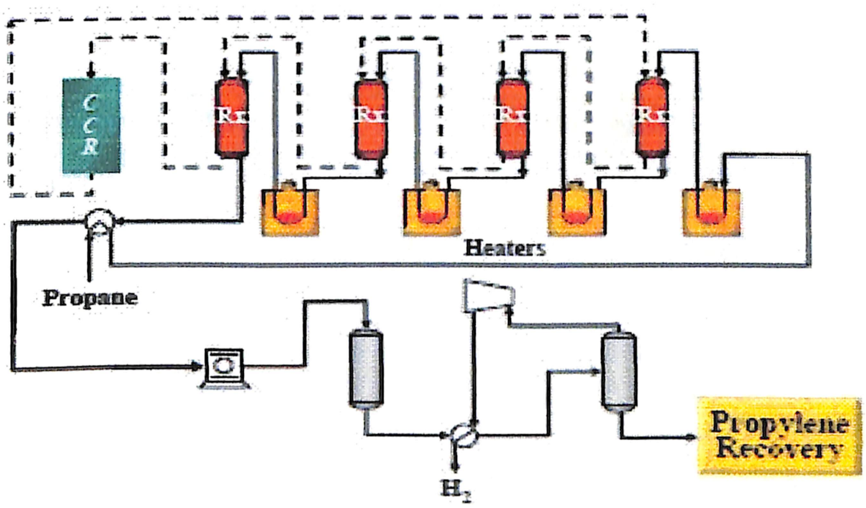
Propane Dehydrogenation (PDH)

Oleflex Process

Since 1990, propane dehydrogenation has been providing a growing source of propylene or petrochemical applications. There are currently eight plants in operation producing approximately 2.5% of the worldwide propylene supplied for petrochemicals. Six of these plants use the Oleflex™ process licensed by UOP. The Oleflex process uses proprietary platinum on alumina catalyst. Four adiabatic reactors are operated in series as shown in Figure 7. The dehydrogenation reaction is endothermic so interheaters are included between each reactor to maintain the desired reactor temperatures. The Oleflex process uses a CCR™ regenerator to continuously regenerate the catalyst and maintain high conversion and selectivity.

Figure 7

C_3 Oleflex Process



The yield of propylene from propane feedstock is over 85 wt-% with the Oleflex process. The amount of ethylene produced is very small, such that it is usually not recovered. The ethylene together with the other reactor byproducts is typically used to supplement the fuel consumption for a propane dehydrogenation unit. This means that propylene is the only product produced from a propane dehydrogenation unit unless there is a local demand for the hydrogen produced by the dehydrogenation reaction.

CATOFIN Process

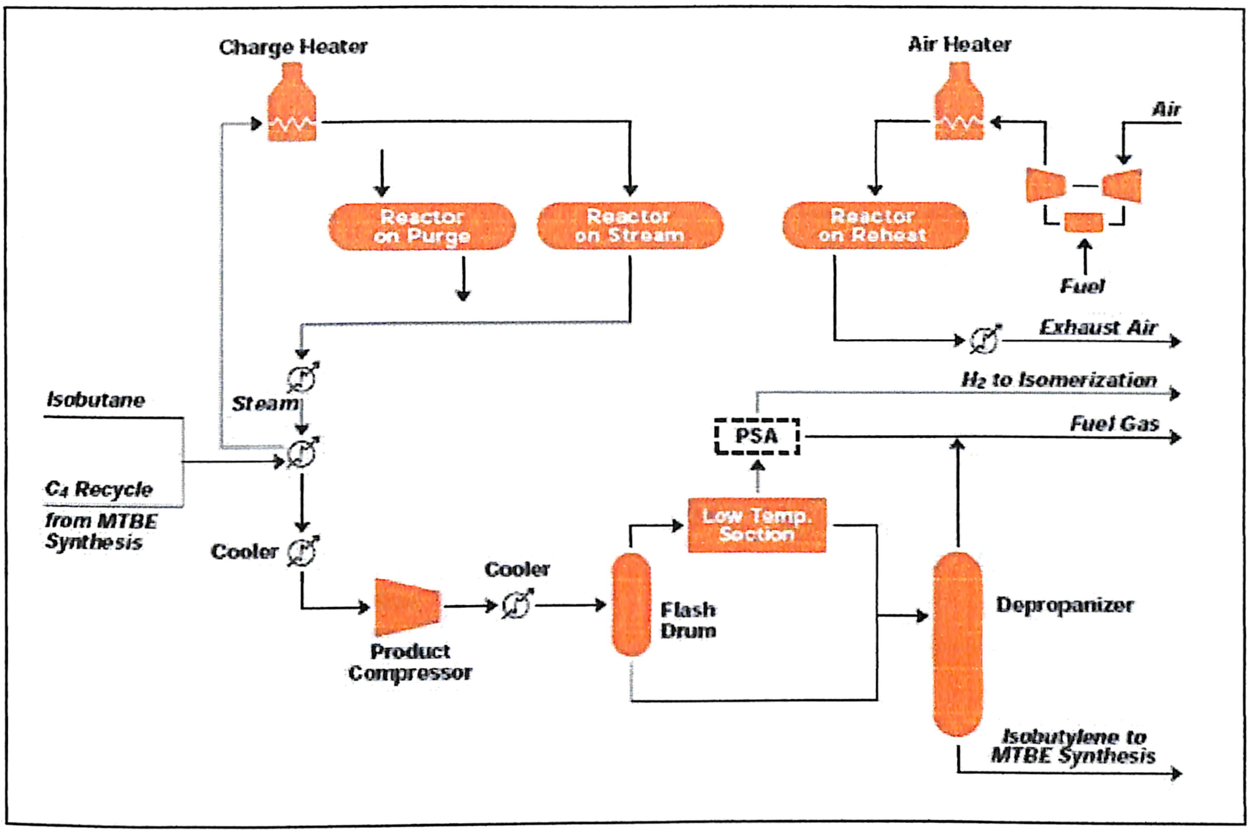
The CATOFIN dehydrogenation process is a reliable, proven route for the production of isobutylene, propylene or anylenes from isobutane, propane or isopentanes respectively. ABB has exclusive worldwide licensing rights to the technology. Eight CATOFIN process units are providing isobutylene feedstock for production of 110,000 BPSD of MTBE. Two CATOFIN units have been licensed to produce 675,000 MTA of propylene The CATOFIN process uses fixed-bed reactors with a catalyst that has been selected to optimize the complex relationship among conversion, selectivity and energy consumption. The overall selectivity of isobutane to isobutylene via the CATOFIN process is greater than 90 mol percent; the selectivity of propane to propylene is greater than 86 mol percent; and the selectivity of isopentanes to anylenes is approximately 75 mol percent. On-stream efficiencies of 98+ percent, excluding biannual turnarounds of 2-3 weeks, are routinely achieved.

Process Features	Client Benefits
High per pass conversion (48-53%) and high catalyst selectivity	Lower investment and operating costs
Single train capability up to 900.000 MTA of isobutylene or 450.000 MTA of propylene or 300,000 MTA of amylenes	Economy of scale
No catalyst losses	Environmentally sound design
No hydrogen recirculation or dilution steam	Lower investment and operating costs

Feeds	Products
Isobutane (99% purity)	*LB/LB of Feed* Isobutylene .876 Hydrogen .023 Fuel Gas .088 Other .013
Propane (98% purity)	*LB/LB of Feed* Propylene (99.5% purity) .847 Hydrogen .027 Fuel Gas .096 C_4+ Reject .007 Other .023
Isopentane	Values available upon request

CATOFIN dehydrogenation is a continuous process, with cyclic reactor operation. During the hydrocarbon processing step, fresh feed and recycle feed (from an MTBE synthesis unit or C3 splitter bottoms) are vaporized by exchange with various process streams and then raised to reaction temperature in the charge heater. The reactor effluent is routed through a high pressure steam generator, feed-effluent exchanger, and trim cooler to the compressor. The compressor discharge is cooled, dried and routed to the low temperature recovery section to reject light ends. The low temperature section off gas, which is a hydrogen-rich gas, can be sent to a Pressure Swing Adsorption Unit (PSA) to purify the hydrogen.

Recovered liquids from the low temperature recovery section, along with the effluent flash drum liquid, are fed to distillation facilities and/or an MTBE synthesis unit for product recovery. Ancillary equipment is required for the reheat/ regeneration steps that are necessary to prepare the off-line reactors for their next reaction phase. The entire reactor sequence is computer controlled and requires no operator input for the cyclic operation.



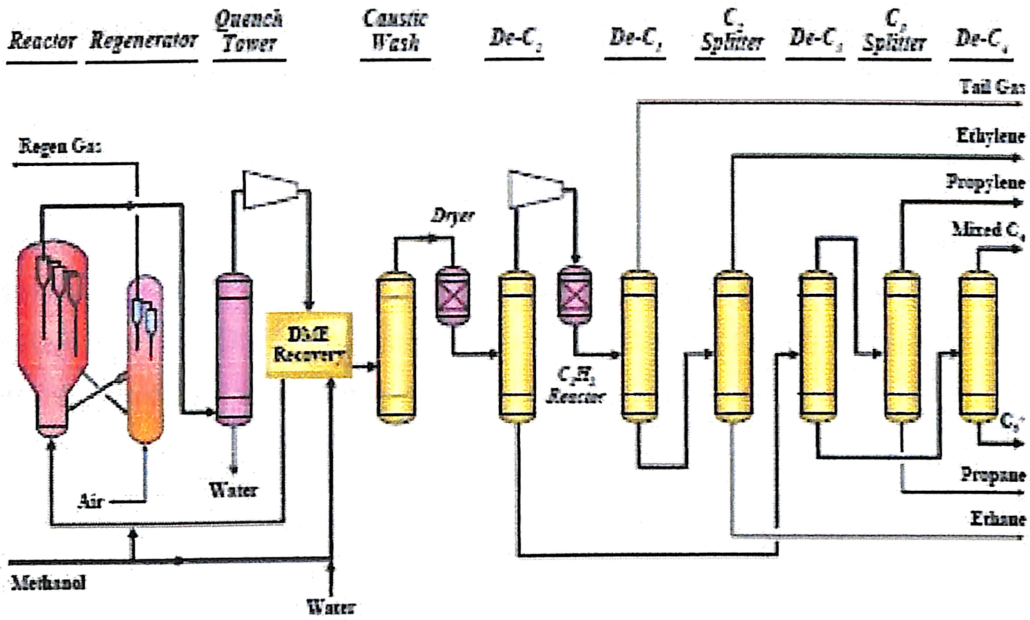
The diagram shown is for the production of isobutylene. For propylene production, the depropanizer is replaced by a deethanizer, and a C3 splitter is provided for product recovery. A deoiler is also included to reject a small amount of C4s and heavier material.

METHANOL TO OLEFINS (MTO)

There are two types of methanol-to-olefins processes available. The first is the MTO process, which produces propylene and ethylene with minimal or no C5+ co-product. The second is a "methanol-to-propylene (MTP)" process, which produces propylene and gasoline.

Figure 8

UOP/HYDRO MTO Process



The MTO process was developed for the selective production of ethylene and propylene from either crude or refined methanol. MTO combines well proven FCC and naphtha cracker technologies with a proprietary new catalyst from UOP. The catalyst used in the process is based on a silicoalumino phosphate, SAPO-34. The technology has been extensively demonstrated in a demo plant by Norsk Hydro and more than ten years of development have been completed. The MTO process converts methanol to ethylene and propylene at close to 80% carbon selectivity in a fluidized bed reactor. The carbon selectivity approaches 90% if butenes are also accounted for as part of the product slate.

MTP/MTO

Methanol → Ethylene + Propylene

1 : 2

Methanol to Propylene

$$3\ CH_3OH \rightarrow CH_3CH{=}CH_2\ +\ 3\ H_2O$$

The MTO reaction is exothermic. Carbon or coke accumulates on the catalyst and must be removed to maintain catalyst activity. The coke is removed by combustion with air in a catalyst regenerator system. Other co-products include very small amounts of C1-C4 paraffin's, hydrogen, CO and CO2, as well as ppm levels of heavier oxygenates that are removed to ensure that the product olefins meet polymer-grade specifications. The MTO process offers the greatest flexibility of any propylene producing technology. The ratio of propylene/ethylene product can range from less than 0.8 to more than 1.3. When combined with the Olefin Cracking process (to be discussed later) to convert the heavier olefins, the overall yields of ethylene plus propylene increase to about 85 to 90 % and propylene/ethylene product ratios of more than 1.5 are achievable.

OLEFIN CONVERSION

Olefin conversion technologies produce light olefins from other olefins. There are two main types of olefin conversion technologies available: metathesis and olefin cracking. Metathesis processes produce propylene by reacting ethylene with 2-butenes. Olefin cracking processes produce ethylene and propylene by cracking heavier olefinic feedstock's (typically C4 to C8 range). Olefin conversion processes are often combined or integrated with the other olefin producing technologies mentioned above to provide higher light olefin production with a shift towards maximizing propylene production.

Metathesis

Metathesis technology has been available for many years but only recently has it gained much attention because of high propylene values in some geographic regions. In general, metathesis can be economical when propylene is valued equal to or higher than ethylene.2 Metathesis economics are extremely sensitive to the ratio of propylene to ethylene (P/E) price and at P/E ratios below 1.0, it provides low profitability and can be uneconomical to operate due to relatively high cash costs of production.

Overview

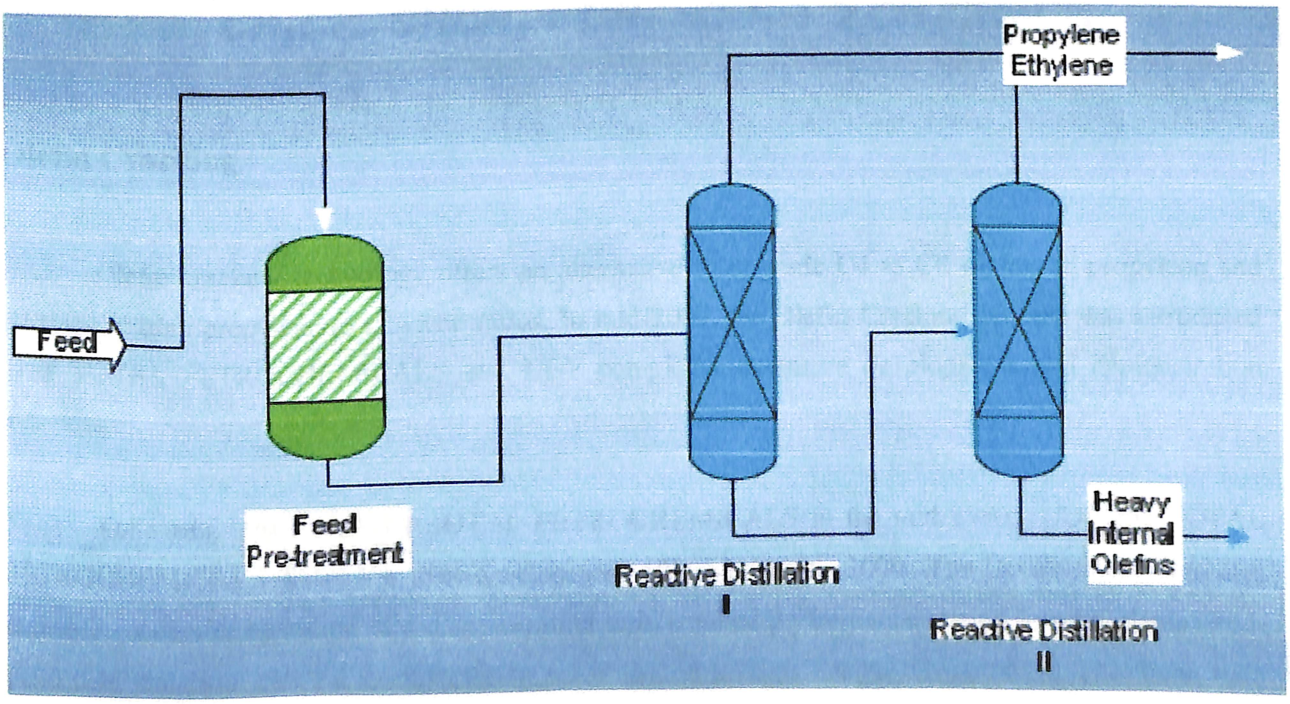
Multiple-Phase Metathesis (MPM) process converts ethylene plant, refinery and other chemical synthesis olefin by-products to propylene and even more valuable higher olefins via a patented reactive distillation process.

Feedstock

The primary feedstock's to MPM process are C4 and C5 raffinates, including C4 Raffinate II and Raffinate III. Other potential feedstock's may be olefinic or partially olefinic Fischer-Tropsch streams.

Process

Treated feedstock is introduced into a reactive distillation unit. Depending on the desired conversion to propylene or desired higher olefins composition, the bottoms of the reactive distillation unit may be sent to additional one or two reactive distillation units. Propylene and some ethylene in the overhead products may be separated and sent to propylene/ethylene recovery, while the heavier components are recycled.



Product

The process produces at least a bi-modal product distribution: light and heavy. Light products consist primarily of propylene with a small amount of ethylene. The heavy products are higher linear internal olefins in a bell-shaped distribution of both odd and even carbon numbers approximately 4-5 carbon numbers wide. For example, the heavy product may be in the range C10-C14 with an average carbon number 11.8. Other possible product ranges are C6-C10 and C15-C18. If desired, a tri-modal or tetra-modal product distribution is possible: C3/2, C6-C10, C10-C14 and C15-C18, with the C6-C10, C10-C14 and C15-C18 products each in a bell-shaped distribution.

Metathesis

Butene + Ethylene → 2 Propylene

Metathesis

$$CH_3CH{=}CHCH_3 + CH_2{=}CH_2 \rightarrow 2\,CH_3CH{=}CH_2$$

Olefin Cracking

Olefin cracking technology offers an alternative to upgrade C4 to C8 olefins to propylene and ethylene at high propylene to ethylene ratios. In mid-2003, the Olefin Cracking process was introduced after TOTAL PETROCHEMICALS and UOP completed extensive development and demonstration activities.

Following initial work by TOTAL PETROCHEMICALS in the mid 1990s, UOP and TOTAL PETROCHEMICALS formed a joint-development alliance in late 2000. The development activities included successful operation of a demonstration unit, catalyst performance testing in pilot plants, feed-yield determination, catalyst manufacturing scale-up and process design development. The demo unit, started in 1998 at an industrial facility associated with TOTAL PETROCHEMICALS in Antwerp, Belgium, processes commercial feedstock's from operating plants. The demo unit includes feed pretreatment, a reactor section, catalyst regeneration facilities, and internal recycle capabilities.

The Olefin Cracking process features fixed-bed reactors operating at temperatures between 500 and 600 °C and pressures between 1 to 5 bars gauge. The process utilizes a proprietary zeolitic catalyst from UOP and provides high yields of propylene at propylene/ethylene product ratios of about 4.0. The catalyst minimizes the reactor size and operating costs by operating at high space velocities and high conversions and selectivities without requiring an inert diluent stream. A swing reactor system is used for catalyst regeneration. The layout of the product separation facilities is dependent on how the olefin cracking unit is integrated with other processing plants such as a naphtha cracker, an FCC or an MTO unit.

Figure 9

ATOFINA/UOP Olefin Cracking Process

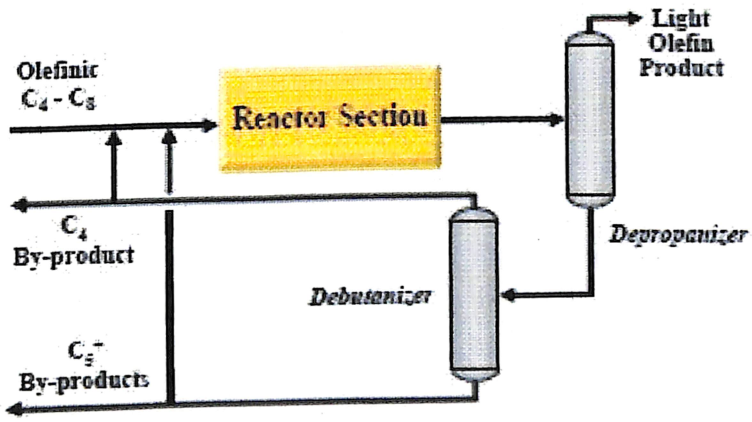


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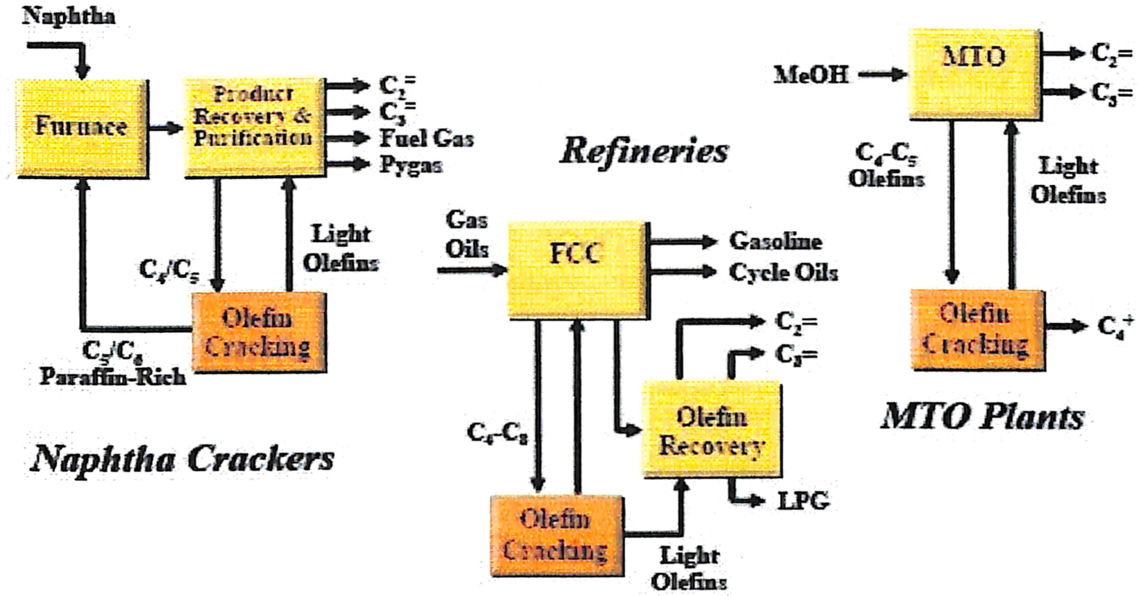
Figure 10

Olefin Cracking Applications



COMPARISONS OF PROPYLENE PRODUCTION ROUTES

Several factors must be considered when selecting a propylene production route. Process economics are always an important factor but each of the aforementioned alternatives offer attractive economics under specific conditions. It is extremely rare that more than one or two of these alternatives may be suitable for a particular project. Therefore, it is important to understand the key factors that help determine which alternatives provide the best fit for a particular project. The key factors to consider include:

- Feedstock availability, cost and flexibility
- Propylene yield and co-products disposition
- Propylene capacity
- Capital costs
- Fit with existing production assets
- Refinery/petrochemical integration strategy or gas production/petrochemical Integration strategy

Identifying the feedstock's that are available can greatly help narrow the choices of the various routes. In particular, if a certain feedstock is available at an advantaged price it may indicate that a particular route offers the greatest opportunity. Some pricing may be seasonal or impacted by other market factors such as crude oil or natural gas prices so producers may wish to diversify their cost structure for propylene production. Feedstock compositions may also change over time, so flexibility to handle various feedstock's or feedstock compositions may be important in some situations.

Propylene yield is a key factor because this dictates how much feedstock is required. In some cases, the amounts of co-products can outweigh the amount of propylene production so the disposition of the co-products can have a huge influence on the overall project economics and structure. In cases where there are little or no co-products, the project complexity may be much simpler and the project can be less sensitive to factors outside of the propylene value and feedstock cost.

The propylene capacity, capital costs, and fit with existing production assets can help identify which alternatives may be attractive for a particular opportunity. If there is a desire to expand existing facilities then certain alternatives may fit better than others which may be better suited for new grass-roots projects. Finally, a refinery/petrochemical integration strategy or gas production/petrochemical integration strategy may dictate that a particular route to propylene is attractive. For example, a refiner like Reliance Petroleum Ltd. may wish to diversify into petrochemicals production to achieve higher added value to products, especially when refining margins are tight. Alternatively, a gas producer or country with large natural gas reserves may prefer to invest in downstream petrochemical production to monetize natural gas assets, reduce imports and create more jobs. Some of these key factors are compared between each of the alternative routes to propylene below.

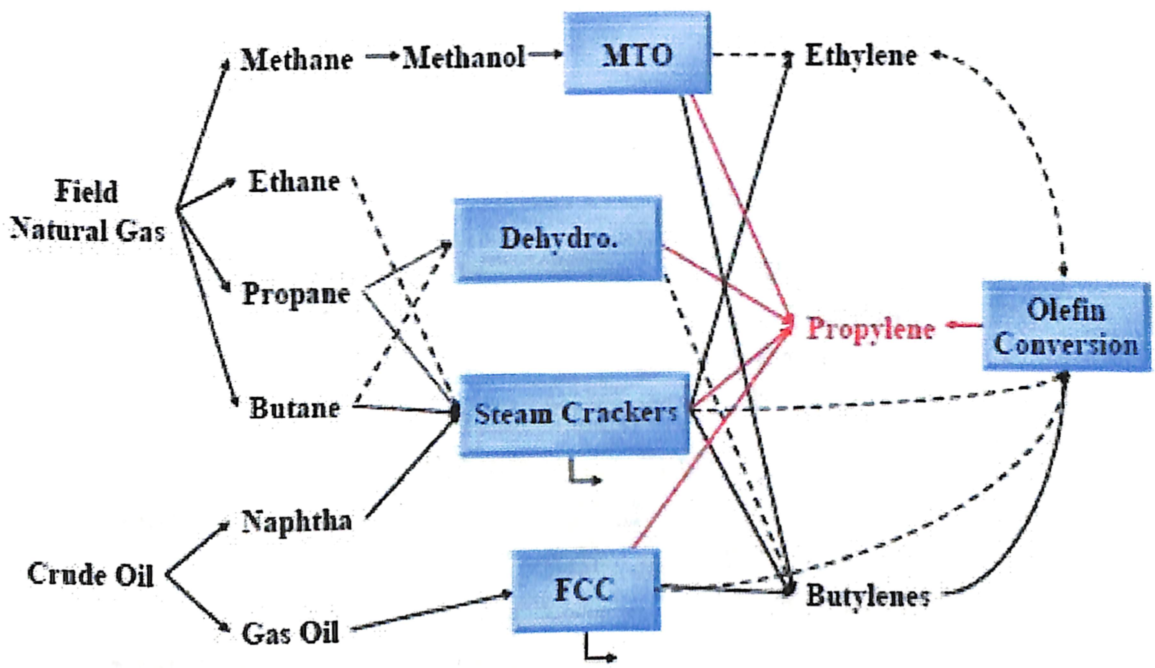
FEEDSTOCKS

The most significant component of the costs of production is the cost of raw materials. The ability to effectively utilize a secure source of low-cost feedstock is perhaps the most important factor in competitiveness. The various routes to propylene start with either natural gas or crude oil as shown in Figure 11. Crude oil is widely traded throughout the world so there is relatively little geographical differentiation between crude oil and crude oil derived feedstock prices. Crude oil prices have historically ranged from $10 per barrel to more than $60 per barrel now-a-days. Near the low end of this range crude oil derived feedstock's such as naphtha for steam crackers or gas oil for FCC units, are available at low-cost but of course the opposite is true near the upper end of this range (as in recent times). The attractiveness of alternatives that use crude oil derived feedstock's depends on expectations for long-term crude oil prices relative to natural gas based feedstock's.

Natural gas is much more costly to transport than liquids so geographically there are large differences in pricing of natural gas and some natural gas liquids (NGL). Propane and butanes (LPG) can be shipped at moderate costs so there is less geographical differentiation for LPG prices compared to prices for methane and ethane. The net-back values (equivalent to the price at the export destination less the costs associated with shipping, storage, and import) for propane and butanes can offer attractive feedstock pricing for dehydrogenation purposes.

Figure 11

Feedstocks for Commercially Available Routes to Propylene



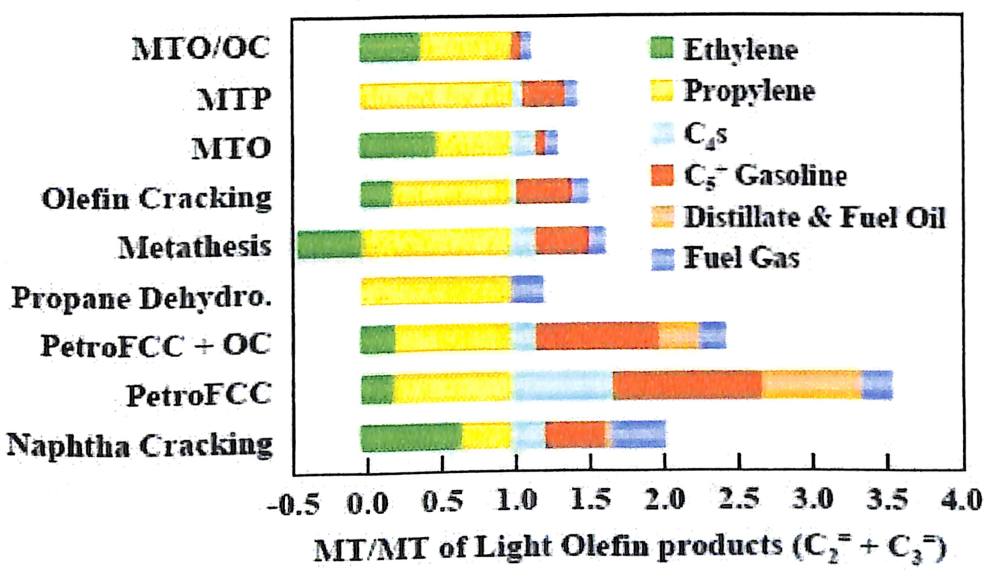
Some areas of the world have abundant supplies of natural gas but have very limited local demand for its use. In these regions the natural gas is referred to as "stranded" and the alternatives to monetize the gas require large investments and costly shipping (such as liquefied natural gas (LNG)). In these locations, although the end market value of the natural gas may be high, the net-back value where the gas is produced is typically less than $1.00 per million Btu. This offers opportunities to access low-cost natural gas for other applications such as propylene production via methanol combined with methanol-to-olefins.

PROPYLENE YIELD AND CO-PRODUCTS

Each of the alternatives produces a different mix of products. When comparing alternatives with different product mixes it helps to compare them relative to the amount of light olefins (propylene and ethylene) produced because propylene and ethylene offer similar market values and most propylene producers are also ethylene producers.

Figure 12

Co-product Production



Naphtha Cracking

Naphtha cracking produces around 0.67 tons of ethylene and 0.33 tons of propylene for every ton of light olefin produced. In addition there are about 0.7 tons of C4 + byproducts that must be marketed to achieve good economics. Although not very selective towards propylene, naphtha cracking remains the largest source of propylene production and the primary benchmark for competitiveness.

FCC and PetroFCC Technology

Conventional FCC units typically produce as much as 18 tons of C4+ products for every ton of light olefin produced (with very little ethylene). In this case, propylene is a relatively small byproduct for FCC. PetroFCC technology, on the other hand, produces only 2.4 tons of C4 + products for every ton of light olefin produced, which clearly shifts its focus from motor fuels production to high value petrochemicals production. In addition to the high yields of propylene, ethylene, and BTX, PetroFCC technology also yields substantially higher amounts of C4 and C5 olefins. These fractions can be charged to an Olefin Cracking unit to further increase the yields of ethylene and propylene. The combination of olefin cracking with PetroFCC technology reduces the amount of C4 + products to about 1.3 tons per ton of light olefin produced.

Propane Dehydrogenation

Propane dehydrogenation is a true on-purpose propylene producer with essentially no co products. The small amount of fuel gas produced by the minor non-selective reactions is used within the Oleflex complex to supplement the fuel gas requirements so no other products need to be marketed. The single feed, single product feature of propane dehydrogenation is one of the most attractive aspects of this option, especially for propylene derivative producers looking to back-integrate for a secure cost effective source of propylene.

Olefin Cracking

Olefin cracking produces about 0.2 tons of ethylene and 0.8 tons of propylene for every ton of light olefin produced. The amount of co-product largely depends on the composition of the feedstock's since non-olefins are unreacted. When integrated into an ethylene plant (steam cracker) the C4 + co-product is well suited for recycle to the furnaces to further enhance the light olefin yields. This allows naphtha crackers to reduce the amounts of C4 + co-products and achieve higher yields of light olefins.

MTO

MTO offers very high selectivity to light olefins with only about 0.2 tons of C4 + co-products per ton of light olefins. One of the unique features of MTO is its broad flexibility to adjust the ratio of propylene to ethylene production. This offers opportunity to adjust the MTO product mix as the ratio of the propylene/ethylene market price changes and thereby maximize profitability.

In situations where it is desirable to avoid marketing C4 + co-products, The Olefin Cracking process can be integrated with the MTO process to increase light olefin yields and effectively eliminate the C4 + co-product. In this case the very small amounts of residual C4 + hydrocarbons can be used to supplement the fuel requirements for the MTO complex and the product marketing is completely focused on the light olefin or olefin derivative products.

PROPYLENE CAPACITY

The various alternatives for propylene production do not all fit within the same range of propylene capacity so the amount of propylene desired is also an important consideration. Some of the alternatives offer opportunities for revamp applications to increase capacity or modify the product mix. Other alternatives offer opportunities to integrate new units into existing facilities for increased propylene production. Still other alternatives are applicable for complete new unit capacity additions.

If a relatively small amount of additional propylene is required then a revamp of an existing facility is usually best. Revamps generally require smaller capital investments because they require incremental expansion of existing facilities. This allows revamps to be economical at smaller incremental capacities. However, there are limitations on how much more propylene can be produced by modifying existing facilities. At some point the cost for revamping can approach or even exceed the cost for new construction as bottlenecks of revamping existing facilities are exceeded.

Revamp alternatives include adding a PRU in a refinery, modifying the FCC unit to increase propylene production, converting an FCC unit to more closely resemble a High Severity FCC or PetroFCC unit, or adding additional furnaces to a steam cracking unit.

In situations in which it is not feasible to revamp existing facilities to achieve the desired propylene capacity or if a different feedstock or product mix is desired (i.e. higher propylene/ethylene product ratio, less C4 + product) it may be best to consider integrating a new unit into existing facilities. This would include adding an olefin conversion unit or an MTO unit to an existing ethylene plant. These projects require higher capital than simple revamps but much less capital than required for complete new unit additions. In general, these projects would typically require incremental propylene capacity expansion of at least 100 kMTA to justify the higher capital. As with the revamps, there are limitations on how much capacity can be achieved using existing facilities integrated with new unit additions, so for capacity increases beyond 300 kMTA it may be more practical to build new "grass roots" units.

New "grass roots" units require the highest capital investments but offer the most flexibility and state-of-the-art performance. In general, a capacity of at least 250 kMTA propylene is required to achieve close to world-class economic performance. Grass roots projects could include a new naphtha cracker, High Severity FCC or PetroFCC unit, PDH unit, MTO unit, or olefin conversion unit.

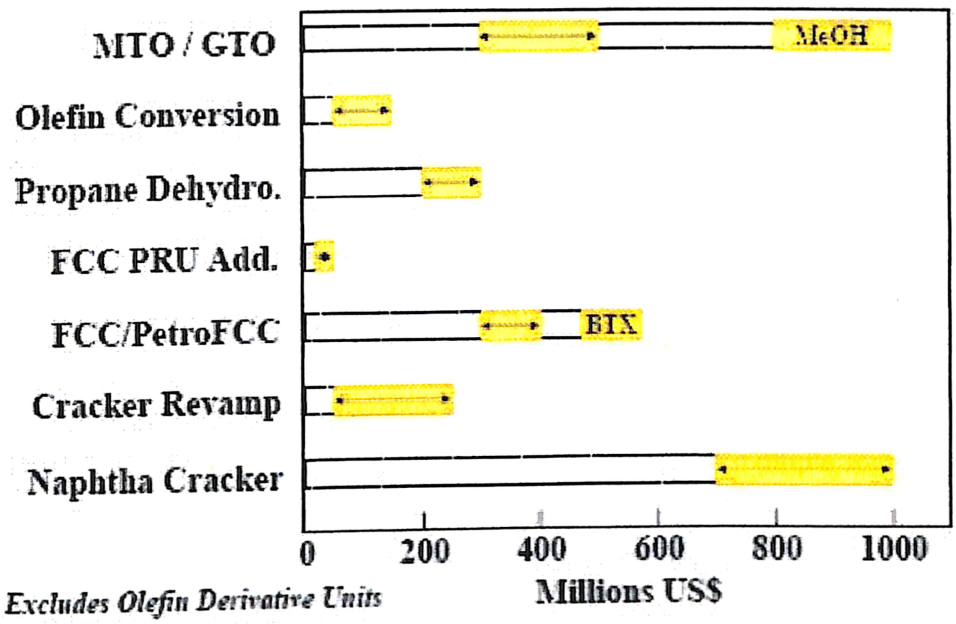
CAPITAL INVESTMENTS

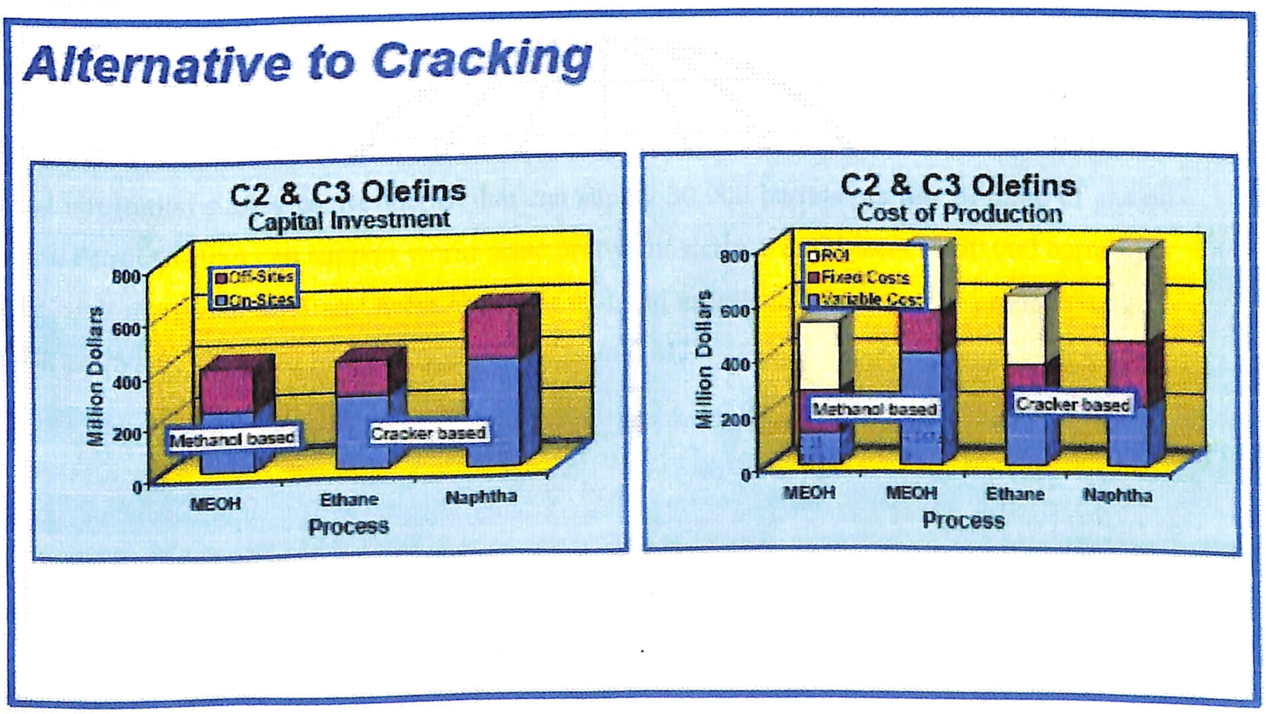
The range of capital investments for a propylene project can vary from around $50 million for a small revamp or addition of the PRU or olefin conversion unit up to $1 billion for a world-scale grass-roots naphtha cracker or gas-to-olefin plant (syngas/methanol units plus MTO unit). Often the propylene projects are combined with downstream propylene derivative projects so the overall investments can be even greater. In considering such projects, one must consider the abilities to raise the equity needed and secure the project financing. Larger projects may require forming a joint venture for implementation so the complexity of projects needs to be carefully considered and compared against a company's strategic plans and objectives.

Figure 13

Capital Investment Ranges

For Typical Project Sizes and Scope





Applications for Propylene Production Routes

The many alternatives available for propylene production offer a wide variety of opportunities but determining the right route to propylene can be confusing. There are certain factors that apply to each alternative that can narrow the choices and help determine which one is best for a particular project.

PRU & FCC Additives

Propylene recovery units offer opportunities for refiners with an FCC unit to obtain higher values for propylene instead of using it for conversion to motor-fuel blendstocks. FCC catalyst additives can be used to increase the production of propylene such that FCC, or High Severity FCC units can support propylene derivative projects. The proximity to propylene or propylene derivatives markets is a key factor because in some cases it may be necessary to pool propylene production from multiple sources to supply enough propylene to support a world-scale propylene derivative project.

PetroFCC Technology

The PetroFCC process shifts fluid catalytic cracking from a motor fuel production platform to a platform for generating base petrochemicals from gas oils. The PetroFCC process is ideal for refinery and petrochemical integration strategies. Refineries that can supply 30,000 barrels per day or more of gas oil feedstock for a PetroFCC unit can support world-scale propylene derivative projects. A 50,000 barrels per day PetroFCC unit integrated with an Olefin Cracking unit and aromatics complex can produce roughly 700,000 MTA propylene, 200,000 MTA ethylene and 250,000 MTA BTX.

PROPANE DEHYDROGENATION

PDH offers opportunities for simple back-integration for propylene derivative producers looking for a secure, economical source of propylene. PDH produces a single product (propylene) so there is no need to market any co-products unless there is a local need for hydrogen, which can easily be recovered from an Oleflex unit.

The key for any PDH project is the propylene-propane price differential. About $200/MT is the minimum long-term average price differential required between propylene and propane in order to achieve good economics with an Oleflex complex. It is not true that PDH is only feasible when tied to discounted propane. In fact, most of the PDH plants that have been installed are located where propylene is needed as opposed to where "cheap" propane is located.

PDH offers three specific advantages to propylene derivative producers.3 First, a PDH plant makes a single product, propylene. A company specifically interested in producing propylene derivatives may not want to produce ethylene or C4 + co-products that are made from naphtha crackers, or gasoline and fuels from refineries. PDH focuses an investment specifically on propylene capacity. Second, production costs for a PDH plant are tied to the cost of propane.

Propane prices are not tied directly to naphtha prices or the propylene market; therefore, PDH allows large propylene derivative producers to diversify the overall cost structure of their feedstock. Finally, some of the best locations for propylene derivative plants do not have good access to byproduct propylene. Given the high cost of shipping and storing propylene, PDH is generally more cost-effective than buying propylene for these locations, if propane is available.

PDH requires a relatively low capital investment compared to other grass-roots alternatives for producing similar amounts of propylene. Good economies of scale are achieved with unit capacities of 250,000 MTA or larger. Oleflex process offers experience and reliability with six commercial units in operation. Over 1.25 million MTA of propylene capacity has come on-stream using the Oleflex process since 1990 and the on-stream Oleflex process capacity is expected to double over the next few years.

MTO

MTO is part of a two-step process, which converts natural gas to methanol followed by the conversion of methanol to light olefins. MTO projects are driven by the desire to monetize stranded gas and the market demands for ethylene and propylene and their derivatives. Stranded natural gas prices are generally independent of crude oil and naphtha market prices so MTO provides another means for olefin derivative producers to diversify the cost structure for their feedstocks. MTO can provide much lower costs of production and higher returns on investment than naphtha crackers especially now when crude oil market prices are above $50 per barrel.

MTO can also provide much lower costs of production and higher returns on investment than ethane crackers using ethane or natural gas liquids extracted from natural gas at prices above $3 per million Btu. MTO projects are tied to mega-scale methanol projects for two reasons. First, the amount of methanol required for an MTO project is consistent with the methanol production from today's latest world-scale methanol projects (5,000 to 7,500 t/d methanol). Second, the costs of methanol production from a mega-scale methanol unit are low enough to support alternative uses for methanol such as fuel applications or MTO.

MTO plants can be located near or integrated with the methanol plant or they can be located separately with the methanol plant located near the gas source and the MTO plant located near the olefin markets or olefin derivative plants. In either case the methanol plant is located with access to otherwise stranded natural gas (typically valued at less than $1 per million Btu). If there is local demand for a portion of the light olefins or their derivatives, then it can be desirable to locate the MTO unit at the same location as the methanol unit. If all of the light olefins or their derivatives are to be exported, then it may be preferable to ship methanol to an MTO unit that is located near the olefin or olefin derivative markets.

OLEFIN CONVERSION

Olefin conversion technologies offer opportunities for upgrading low-value heavier olefins to light olefins via either metathesis or olefin cracking. These technologies favor high yields of propylene so they are especially well suited for projects looking to maximize propylene production. Olefin conversion units integrate with other olefin production and recovery facilities such as ethylene plants (steam crackers), refinery FCC units, or MTO units.

Methathesis units are generally economical when propylene is valued higher than ethylene Feedstocks for metathesis include Raffinate-1 or Raffinate-2 that have been processed to maximize the 2-butene content and ethylene. Approximately 0.42 tons of ethylene are consumed per ton of propylene produced. Metathesis integration results in a reduction in net ethylene production so it requires the availability of excess ethylene. Isobutylene is unconverted in metathesis (isobutylene in the feed is undesirable) and the technology is unsuitable for converting C5-C8 olefins to propylene.

The Olefin Cracking process was developed to utilize low value byproduct streams containing C4 to C8 olefins from steam crackers, fluid catalytic cracking (FCC) refineries, and/or methanol-to-olefins (MTO) plants.5 When combined with steam crackers, the process allows the steam cracker to expand capacity and achieve higher propylene/ethylene production ratios. For FCC refineries, the technology utilizes FCC byproduct streams to increase propylene and ethylene production while reducing the olefin content of gasoline blending streams with little or no loss of octane. For MTO complexes, the technology increases the yield of light olefins for a given amount of methanol feedstock and reduces or eliminates the C4 + byproduct streams. (Refer to Figure 10 for an overview how Olefin Cracking can integrate with these other processes)

The Olefin Cracking process is generally economical when propylene to ethylene price ratio is between 0.8 to 1.2. Approximately 0.25 tons of ethylene are produced per ton of propylene produced. Olefin cracking integration results in an increase in net ethylene production. Alternately, ethylene production can be maintained constant by reducing cracker severity and/or reducing the steam cracker naphtha consumption. Olefin cracking feedstock's can include Raffinate-1, Raffinate-2 and/or C5, C6, C7, or C8 olefins from naphtha crackers, FCC, cokers, or MTO. The feedstock's can be pooled together from various sources to achieve good economies of scale while reducing the amounts of C5 olefins that are blended into gasoline. The C4-C8 purge streams from olefin cracking can be recycled to cracker furnaces to further supplement olefin production

The Indian Perspective

The employment of the latest and best technology helps not only in improving cost efficiencies but also in producing products meeting consumer expectations. Production of good quality propylene requires control over processes used to manufacture them. There are many ways of producing propylene. The best technologies available for the production of propylene have their own pros & cons. The selection out of these technologies depends upon the requirement of the individual and various factors ranging from feed availability to capital investment. In India, the scope of research into newer technologies has been limited to areas involving lesser risks and returns.

While IPCL has been involved in fine-tuning the imported processes (Steam crackers setup in 1960s) and developing indigenous catalysts (so as to lower process costs), RIL has been involved significantly in developing new applications to produce its propylene in Indian context (which increases demand for propylene). The existing petrochemical complexes are at this time using Steam crackers, as their main technology for the production of propylene. Some of the companies using this type of technology include Haldia petrochemicals Ltd. (HPL) and IPCL. While companies like Reliance Industries Ltd. (RIL), have used a modified FCC unit discussed above for production of propylene as well as crackers.

RIL commissioned its first propylene plant with a capacity of 0.35 mtpa in October 1996 at Hazira. This was followed by the commissioning of two lines of 0.2 mtpa each at Jamnagar in April 1999. The third line at Jamnagar of 0.2 mtpa was commissioned in December 1999. The new reliance petrochemicals plant coming up at Jamnagar will be using a steam cracker to maximize propylene/ethylene production. RIL is amongst top ten global producers of petrochemicals globally. RIL's polymers and polyester business is integrated with its cracker facility at Hazira, as well as its refinery at Jamnagar. It produces olefins—ethylene, propylene, and butadiene—with installed capacities of 0.750 mtpa, 0.365 mtpa, and 0.225 mtpa, respectively. RIL's present polymer manufacturing capacity includes 1.15 mtpa of Polypropylene.

New Projects

With propylene capacities of 1.58 mtpa, India also accounts for only 2% of the world propylene capacity. But this is set to change with various new plants coming up and the older plants been revamped. In the recent past, the GoI has taken various steps to enhance competitiveness of the industry by reducing customs and excise duties, and introducing value-added tax (VAT) to replace sales tax. The GoI has also agreed to establish several special economic zones (SEZ) and chemical parks across the country. As a result, the GoI expects the petrochemicals industry to attract investments of around US$18 billion over the period 2006-10.

RPL is investing Rs. 270 billion in setting up a refinery at Jamnagar with a capacity to process 580 kilo barrels of crude oil per stream day (KBPSD), and 0.9 mtpa plant for polypropylene. The plant is proposed to be set up in a SEZ at Jamnagar being set up by RFL. The expansion project is expected to be complete by end-2008, and will increase the refinery's throughput to 60 million mtpa, making it the world's largest refining unit. The Polypropylene expansion will raise Reliance's total capacity to 2.7 mtpa, and reinforce the company's position as one of the leading Polypropylene producers.

IOC is planning to invest Rs. 121 billion towards setting up a fully integrated petrochemicals complex at Panipat, Haryana. The complex will have installed capacities of 0.86 mtpa of ethylene, 0.575 mtpa of propylene, and 0.6 mtpa of Polypropylene. IOC is also setting up a petrochemical complex at Paradip, Orissa. The project is expected to be commissioned by September 2009. IOC plans to build a 15 mtpa refinery at Paradip, which will be integrated with a downstream petrochemical complex with production capacities of 0.68 mtpa of Polypropylene and 0.6 mtpa of styrene.

Conclusion

The Indian petrochemicals players are not known for their adventurous attitudes i.e. be safe and secure, go in for what is tried and tested, also a large amount of the technologies discussed about are not feasible in India due to the low availability of natural gas as feedstock. Along with this the propylene demand in India at this time is not very high. There is already a high surplus in the Asian market causing a lot of project cancellations. But the Indian propylene market demand is growing at an astonishing 20% per annum. Indian companies would concentrate on technologies that would not be bogged down by this problem. Namely the DCC and the steam crackers. While these technologies can produce propylene for the future demand rise, they can also produce other important chemicals like gasoline and ethylene until that future arrives.

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