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Report Abstract

Propylene
PERP06/07-3

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1 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 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. Thus, there are many more propylene derivatives than ethylene derivatives. But clearly, it has been the tremendous growth of polypropylene over the last 15 years or so that has been really driving propylene demand. In fact, the growth rate of propylene has outpaced the growth rate of ethylene over this period. This in turn has put stress on the conventional supply sources of propylene.

The conventional routes to propylene are as a by-product of olefins production (steam cracking) or recovery from refinery processes (fluid catalytic cracking). However, petrochemical producers are finding it hard to source propylene for new projects, as many ethylene projects, especially in the Middle East are based on cracking ethane or ethane/propane and produce relatively low amounts of propylene and refiners would rather use refinery propylene in their gasoline streams. New sources have emerged that have been designated “on-purpose propylene plants”. These technologies include propane dehydrogenation (PDH), olefins conversion (e.g. metathesis), high-severity fluid catalytic cracking (FCC) and methanol-to-propylene (MTP).

This new report assesses the technology and economics of propylene production by both conventional and on-purpose means.

2 CONVENTIONAL TECHNOLOGIES

2.1 Steam Cracking

Propylene is the primary ethylene co-product from a steam cracker. A summary of the propylene yields (relative to feed) and to ethylene yield is given in Table 1 for representative feedstocks.

Table 1 Propylene Yield from Representative Cracker Feedstocks

	wt % Based on Feed	P/E Weight Ratio
Natural Gas Liquids		
Ethane	1.5	0.019
Propane	14.0	0.294
<i>n</i> -Butane	16.4	0.364
Light Naphtha	15.7	0.421
Gas Oil	15.6	0.632

The ratio of co-products to ethylene can be varied by the degree of cracking severity, which is a function of operating conditions. Lower severity yields less ethylene and relatively more co-products (e.g. propylene). However, since the driving force is normally ethylene maximization (the co-product market balance coming from the alternative sources of supply), the normal condition is moderately high severity cracking (i.e. maximizing the ethylene production). This is especially true when cracking ethane since there is no significant amount of co-products. However, short-term optimization of ethylene cost, instances of high co-product value, particularly propylene, may dictate lowering the severity (and maximizing olefin production).

Propane and butane provide the largest increase in propylene yields as cracking severity is lowered. The yield of propylene (relative to feed) for heavy liquids changes less dramatically from low to high severity cracking conditions.

2.2 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 two percent of the feed to over 6 percent on a weight basis; the latter is produced for high severity (gasoline oriented) operations. The propylene content of the C₃ 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 C₃ stream with a propylene concentration of approximately 70 weight percent. Refinery based propylene recovery units can be designed to recover either chemical grade propylene (92 weight percent purity) or polymer grade (99+ weight percent). Propane recovered from the unit meets LPG specifications and contains approximately three weight percent propylene.

3 ON-PURPOSE PROPYLENE TECHNOLOGIES

3.1 Propane Dehydrogenation

Propane dehydrogenation technology is a derivative of light paraffin dehydrogenation. The origin of some of the technologies discussed had been isobutane dehydrogenation. However, the current generation systems are an adaptation from butadiene production units. The OleflexTM process was conceived and commercialized as a propylene technology.

Propane dehydrogenation is attractive in situations where low value propane is available or sufficient propylene is unavailable from steam crackers or refineries, and a local market exists for propylene derivatives. Propane dehydrogenation produces a single product (propylene) from a single feed (propane) so it provides a relatively simple project opportunity for on-purpose propylene production or for propylene derivative producers looking to back-integrate.

There are currently ten propane dehydrogenation plants in operation and they make up nearly three percent of the world's propylene supply.

3.2 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 catalyst bed temperature will determine which reaction predominates and therefore, which products will form.

Propylene production in a traditional naphtha cracker is affected by the severity of the cracker operation. Decreasing severity increases propylene yield, at the same time decreasing ethylene yield and increasing production of C₄s. When both ethylene and propylene are in high demand, propylene production is often sacrificed. The addition of a metathesis unit increases propylene production at all cracker severities. For example, at high cracker severity, the propylene to ethylene (P/E) ratio can be as high as 0.7, a ratio typical for low severity cracker operation without an added metathesis unit. At low cracker severity, the P/E ratio can exceed 1.0. In addition, the C₄ cut, which may not have high value, is eliminated.

There are various situations for the application of metathesis for increasing propylene production. The feed to the unit can come from a naphtha cracker or from an FCC unit. The metathesis unit can be standalone, add-on, or fully integrated with a steam cracker. For a standalone unit or an add-on, the product from the metathesis reactor is fed to a separation section for propylene recovery. No propane/propylene splitter is needed as no propane is produced. For a fully integrated unit, the product from the metathesis reactor would be fed to the first column in the steam cracker's recovery section. The distillation columns for the cracker would have to be larger, but the columns for the metathesis unit would be eliminated.

Lummus has been the leading supplier of olefin metathesis technology and since 1997 have licensed 24 metathesis units.

3.3 High Severity Fluid Catalytic Cracking

Fluid catalytic cracking (FCC) is the workhorse of most refineries, used to convert heavy fuel oil distillates into lighter components, primarily gasoline. Although most FCC research has focused on increasing efficiency and gasoline conversion, recently there has been interest in using this technology to produce light olefins instead by increasing reaction severity via riser temperatures, adding shape selective catalyst additives and by installing a propylene recovery unit. Many companies now market or have developed FCC-type processes for this purpose, including:

- Stone & Webster – Deep Catalytic Cracking (DCC) and Catalytic Pyrolysis Process (CPP)
- KFUPM/Japan Petroleum Energy Center/Saudi Aramco – High Severity FCC (HS-FCC)
- Indian Oil Company/Lummus – INDMAX
- ExxonMobil/KBR – MAXOFIN
- Fortum Oy – NexCC
- UOP - PetroFCC

Central to these processes are modifications to different zeolite catalyst formulations accompanied by innovation in the FCC hardware, and some changes in the operating parameters.

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 and this percentage will continue to increase as the percentage of propylene supplied from steam crackers decreases as a result of an increase in ethane-based cracking. While propylene is a normal product of the fluid catalytic cracker (FCC) process, conventional FCC operation does not maximize propylene production. In the next few years, operators of FCC units will look increasingly to the petrochemicals market to boost their revenues by taking advantage of economic opportunities that arise in the propylene market.

3.4 Methanol to Propylene (MTP)/Methanol to Olefins (MTO)

The availability of low cost mega-scale methanol along with the rise in ethylene and propylene costs from conventional routes makes these processes viable. Low cost (advantaged) gas regions generally support ethane cracking rather than heavy liquids cracking, hence such regions have ample supply of ethylene, but insufficient propylene supply. The MTO and MTP technologies allow the development of C₃ based petrochemicals in the low cost gas or coal-rich areas without resorting to subsiding propane or naphtha.

Lurgi claims that a 5,000 metric ton per day methanol plant could produce 474 thousand metric tons per year of propylene along with C₄⁺ hydrocarbons and some minor amounts of ethylene with their technology.

A UOP/Hydro MTO process unit combined with an olefin cracking unit (OCP) can produce 650 thousand metric tons per year of propylene along with 350 thousand metric tons per year of ethylene from 2.6 million metric tons per year (7,170 metric ton per day) of methanol.

3.5 Selective Olefin Cracking

Propylene via selective C₄/C₅ cracking technology is generating interest due to the possibility/potential of producing more propylene. Selective C₄/C₅ 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 C₄/C₅ cracking technologies, C₅ streams can be converted along with the C₄ 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.

Companies offering selective olefin cracking are ExxonMobil, KBR and UOP/Total.

4 EMERGING ON-PURPOSE TECHNOLOGIES

New on-purpose propylene technologies are continuing to be developed. The following technologies are described in the report:

- SINOPEC Olefins Catalytic Cracking (OCC) Process
- SINOPEC Catalytic Pyrolysis (CPP) Process
- ExxonMobil Propylene Catalytic Cracking (PCC) Process
- Asahi Kasei Chemicals Omega Process
- Total Petrochemical/UOP Olefin Cracking Process

5 ECONOMICS

Cost of production economics for the following processes/cases are contained in the report:

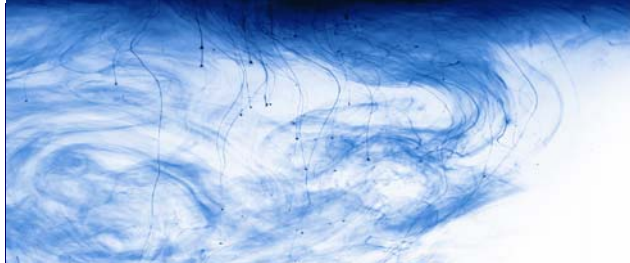
- Refinery Propylene Fractionation
- Propane Dehydrogenation
- Deep Catalytic Cracking (DCC)
- Catalytic Pyrolysis Process (CPP)
- Superflex Process (2 cases: light cracker naphtha and pyrolysis C₄'s feedstocks)
- Methanol to Propylene (MTP)
- Methanol to Olefins (MTO)
- MTO coupled with Olefins Cracking Process
- Metathesis (stand alone case)
- Metathesis (naphtha cracker plus metathesis/exported butadiene)
- Metathesis (naphtha cracker with mixed C₄s to metathesis)
- Metathesis (integrated with a FCC unit)

Cost of production economics for the following sensitivities are also provided in the report:

- Propane dehydrogenation using propane with Middle East discount
- MTP and MTO using natural gas at stranded gas pricing
- Metathesis cases with high propylene/ethylene price ratio

6 COMMERCIAL ANALYSIS

Regional capacities and supply/demand/trade outlook to 2012 are also provided in this report.



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