MAXIMIZATION OF PROPYLENE

A PROJECT REPORT

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Submitted by

AJIT PRATAP AGNIHOTRI
ROLL No. R080205002

Under the Guidance of

Dr. R.P. BADONI
DISTINGUISHED PROFESSOR, COE, UPES

COLLEGE OF ENGINEERING

UNIVERSITY OF PETROLEUM AND ENERGY STUDIES, DEHRADUN
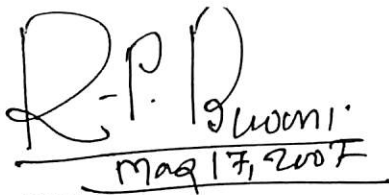
MAY, 2007

UNIVERSITY OF PETROLEUM & ENERGY STUDIES

CERTIFICATE

This is to certify that the project work entitled on **"Maximization of Propylene"** submitted by **Ajit Pratap Agnihotri** in partial fulfillment of the requirement for the award of degree of Masters of Technology (Refining and Petrochemical Engineering), at College of Engineering, University of Petroleum & Energy Studies, Dehradun is a record of the work carried out by him under my supervision and guidance.

To the best of my knowledge, the contents of this project work did not form a basis of award of any previous degree or published material by any one else.

May 17, 2007

Dr. R P Badoni
Distinguished Professor
College of Engineering
UPES, Dehradun

17·05·07

Dr. B.P. Pandey
Dean
College of Engineering
UPES, Dehradun

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It is my pleasure to express my gratitude to those who have helped and encouraged me in various ways in carrying out this Project work.

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I also like to thank faculty members of COE, UPES and the Librarian to let me have access to sizeable and valuable data, inputs and latest trends with respect to Propylene production techniques.

I am also very grateful to all my friends who were very helpful to me.

Date: 17-05-07

AJIT PRATAP AGNIHOTRI

Place:

<u>PREFACE</u>

It gives me immense pleasure to present my dissertation work on **"MAXIZATION OF PROPYLENE"** before all individuals, groups' institutions and corporations which are related to Petrochemicals Industry.

The Petrochemicals Industry is growing at a very fast pace and is making its presence felt in all spheres of living ways. Propylene is major source of various petrochemicals products.

This Dissertation is divided into three chapters.

First Chapter provides information of commercially available routes to Propylene.

Second Chapter concentrates on comparisons of Propylene production routes.

Third Chapter focuses out look on the Propylene maximization.

I hope this work will be beneficial to all students, individuals, groups, institutions and corporations related to Petrochemicals Industry.

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ABSTRACT

Propylene is one of the most important basic organic products, and the annual growth rates for propylene exceeds that of ethylene as a result of the huge growth in the propylene derivatives. Propylene, a light olefin, is like ethylene one of the most important feed stocks for the petrochemical industry.

Most of the propylene consumed in the production of petrochemicals is produced as a by- product of ethylene production. Expected capacity additions in the ethylene industry over the next few years will result in less propylene production per ton of ethylene from conventional ethylene plants as a result of shifts towards lighter cracker feed stocks. Over this same period the demand for propylene is growing slightly faster than ethylene demand.

The propylene production is projected to come from a number of sources, both refinery and petrochemical-complex based. On the refining side, increased propylene production from FCC units is expected to be a major contributor. It is expected that this FCC production will come from revamps of existing FCC units as well as an increasing petrochemical focus in new FCC units installed to meet transportation fuel market demands. On the petrochemical side, there are more alternative routes to propylene available than ever before. These alternatives include propane dehydrogenation, methanol-to-olefins, and olefin conversion including metathesis and olefin cracking processes.Each of these alternatives can offer competitive economics in certain situations.

This report provides an overview of the projected propylene supply situation as well as an update from UOP on the latest developments in these technologies, a comparison of these alternatives and a discussion on key factors that would recommend one processing route over another.

Introduction

1. What is propylene?

Propylene, also known by its IUPAC name propene, is an organic compound having the chemical formula C_3H_6. 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, odorless (mercaptan, a hydrocarbon with an odor similar to garlic is sometimes added to propylene to make it easily detectable), and highly flammable. It is found in coal gas and can be synthesized by cracking petroleum. Propylene is a major commodity in the petrochemicals industry. The main use of propylene is as a monomer, mostly for the production of polypropylene. Propylene is also used as a fuel gas for various industrial processes. It has a similar calorific value to propane, but a lower mass of combustion products, so it has a higher flame temperature. Propylene also has approximately twice the vapour pressure of propane at room temperature and pressure.

2. 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 feedstocks (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 UOP has 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

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growing gap between propylene demand and supply from conventional sources (Figure *i*). 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.

Fig i

Propylene Supply and Demand
Polymer Grade & Chemical Grade
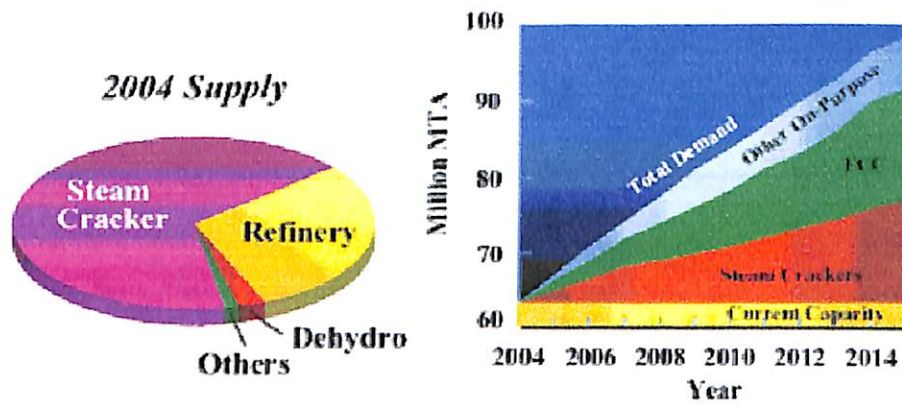
CHAPTER 1

COMMERCIALLY AVAILABLE

ROUTES TO PROPYLENE

1. 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

Currently, 30% of the world's propylene is supplied by refinery FCC operations and the remaining is co-produced from ethylene Steam Cracking of naphtha or other feed stocks. In 2005, global demand for propylene reached about 67 million tons and its annual demand growth is expected to increase by 4.8% during 2005-2010. As global demand for propylene continues to grow, opportunities for new production routes continue to emerge. Practically there are several options to increase FCC Propylene yield. These options include the use of high-selective FCC catalysts, zsm-5 additives, high severity operation (higher reaction temp.), reprocessing of FCC naphtha, and emerging propylene-oriented FCC processes.

The naphtha steam cracking process-the main propylene source with about 70 % share in the primary production, produces about twice as much ethylene as propylene. Propane Dehydrogenation could give a high yield of propylene, but the feed stock is only cost effective in some limited areas, making the process expensive and limiting the production of propylene. The other route for producing propylene is metathesis of ethylene and butylenes, which will consume same highly valuable ethylene as main feedstock.

CONVENTIONAL TECHNOLOGIES:

1.1. Steam Cracking

1.2. Fluid Catalytic Cracking

1.3. Propane Dehydrogenation

1.1. 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 has attracted a large build-up of ethane-based steam cracker capacity over the next few years. 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 1.1 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 in2014).

$C_3^=/C_2^=$ Ratios
Worldwide
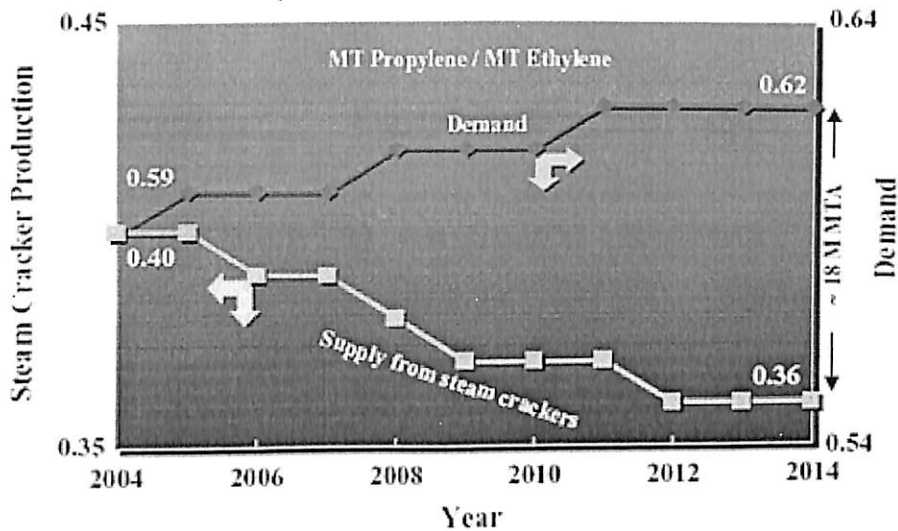
Fig 1.1

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 the lighter alkenes (or commonly olefins), including ethene (or ethylene) and propene (or propylene).

In steam cracking, a gaseous or liquid hydrocarbon feed like Naphtha, LPG or Ethane 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. The process also results in the slow deposition of coke, a form of carbon, on the reactor walls. This degrades the effectiveness 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-coking.

Steam cracking is a type of thermal cracking. It is the most important process for the production of olefins like Ethylene, Propylene and Butadiene. All three are

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produced in various ratios by the cracking of feed stock such as Ethane, LPG and Naphtha.

$$\text{Naphtha} \xrightarrow{\text{Steam cracking}} C2 + C3 + C4$$

$$\text{Ethane} \xrightarrow{\text{steam cracking}} \text{Ethylene + Propylene + others}$$
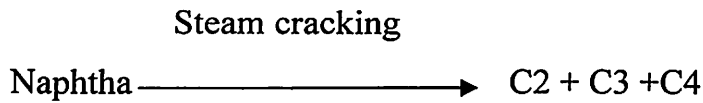
Auraiya gas cracker (GAIL PATA) used ethane as a feed stock.

In the steam cracking operation steam helps as a diluent to reduce the partial pressure of hydrocarbon. Reduction in pressure increases the cracking constituently more light ends are formed and further steams can oxidize the carbon deposited in tubes.

> Steam cracking is a high temperature process.
> Short residence times taken by steam cracking process.

Process Conditions:

Steam cracking depends upon the following factors:

- Type of compounds present in the feed.

- Hydrocarbon to steam ratio.

- Furnace residence time.

- Partial pressure.

- High/low severity operation.

Naphtha cracker plant:
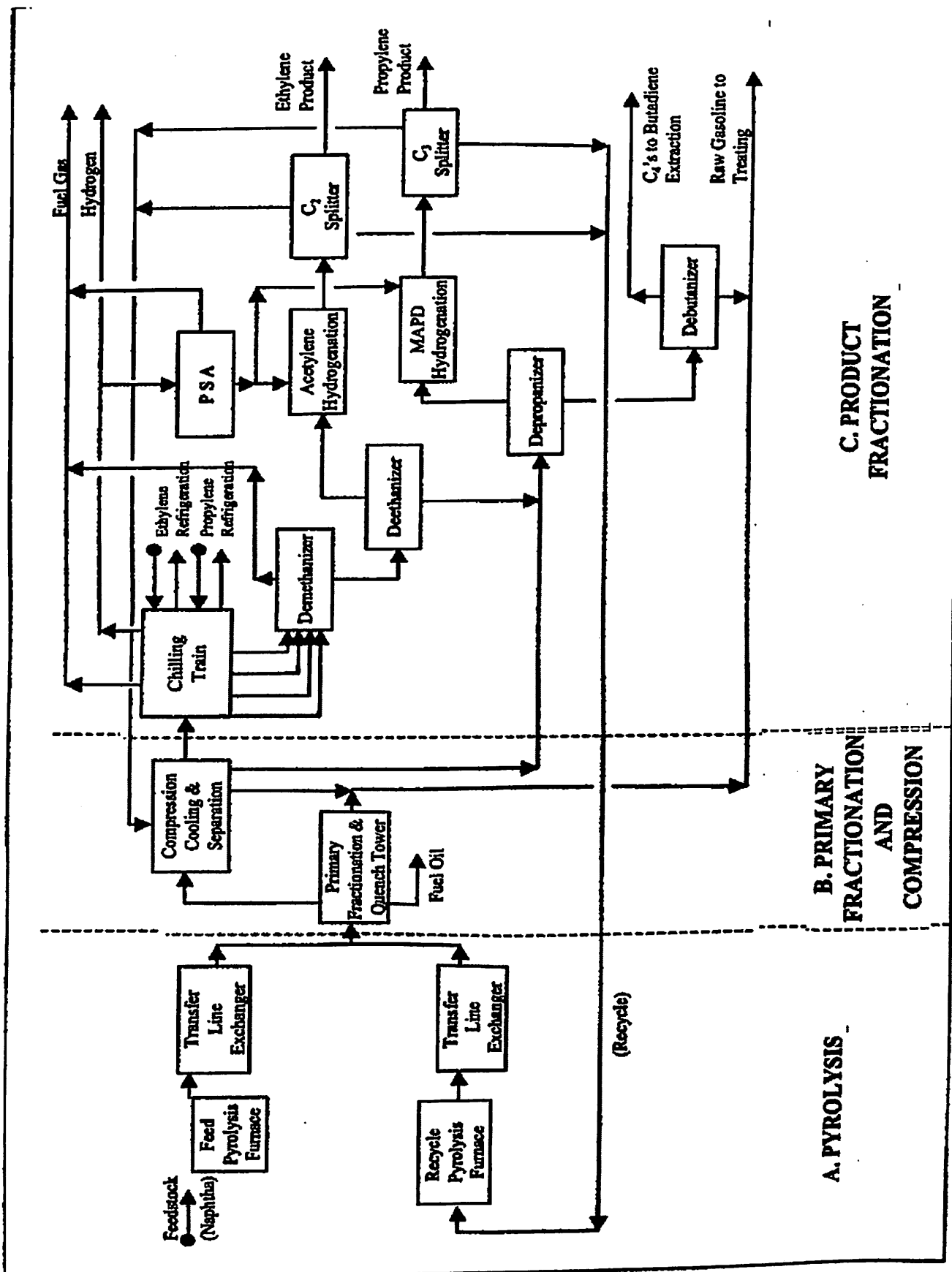
Fig 1.2

Variables:-

- Feed stock –Naphtha

- Outlet temperature – 820 deg.

- Pressure – atm+

- High steam diluent's rate.

- Residence time - .35sec.

The plant comprises of two major sections:-

Hot section: Comprises the cracking furnace. Effluent heat exchangers and steam dilution generation. It also comprises separation section of quenching, gas compression and gas drying.

Cold section: Comprises of chilling rain and hydrogen separation, series of distillation columns eg. De methanizser, De-ethanizer, Ethylene Fractionator, De-propanizer, Propylene Fractionator, and De-butaneizer.

Naphtha cracking is done in short residence time.
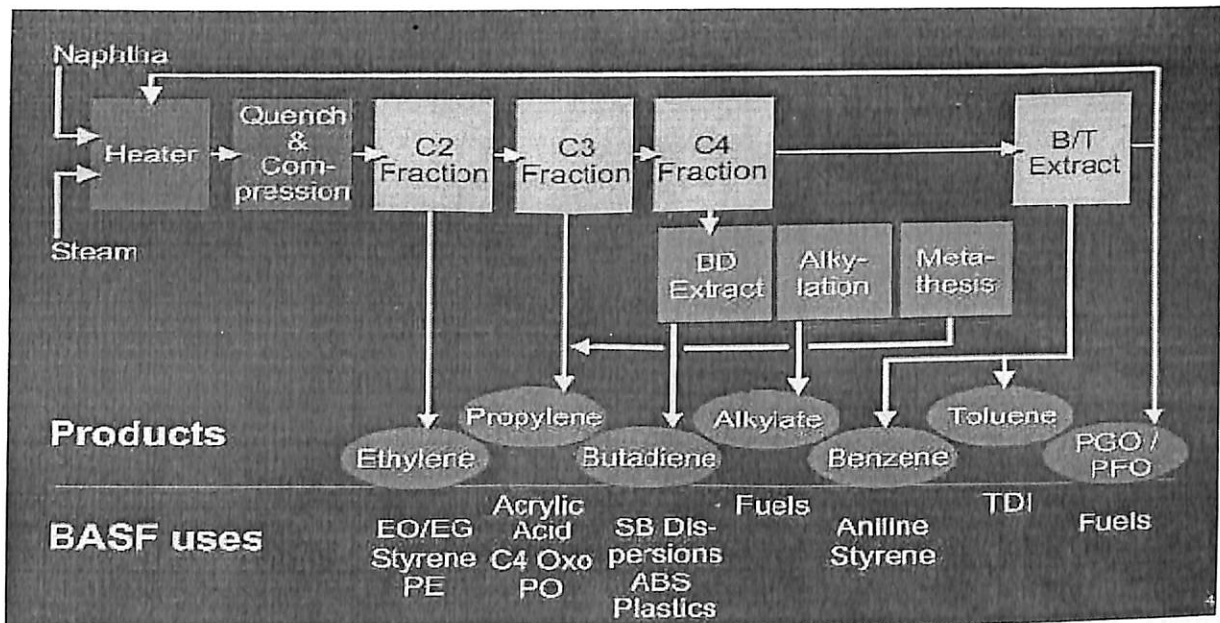
Fig 1.3

This process represents the first significant advance in olefins technology and offers a near petrochemical alternative route. This process is commercially very efficient because it takes short residence time.

1.2. 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.

Propylene from Refineries

Fig 1.4

FCC Hardware-

1. Riser
2. Reactor
3. Regenerator
4. Cyclone

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Process variables:

Feed   Vacuum gas oil (VGO)

Catalyst   USY ZSM-5 catalyst

Typical operating conditions

Reactor temperature   500-550 ^{0}C

Reactor pressure   15-25 PSI

Regenerator temperature   650-700 ^{o}C

Regenerator pressure   28 PSI

Propylene Recovery Units

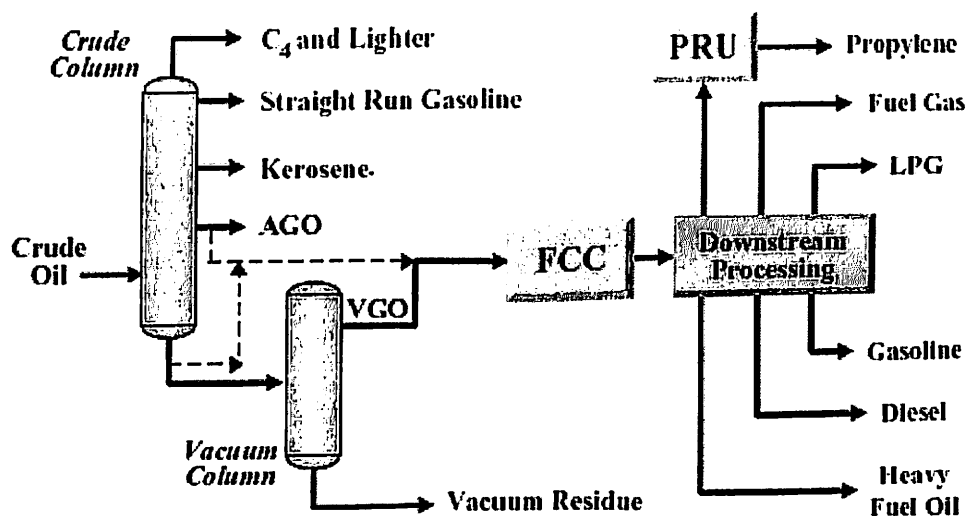Conventional FCC technology yields approximately 4 to 7 wt-% propylene and about 1 or 2 wt-% ethylene. It is often uneconomical to recover the ethylene from conventional FCC units, especially in smaller units. Propylene, however, can be recovered by adding a PRU. A UOP PRU generally consists of a three-column fractionation train followed by driers and treaters to remove contaminants in order to produce high purity polymer-grade propylene. The PRU ractionation 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 UOP's high capacity MD trays and High Flux tubing 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:

1. 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

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

3 .A reduction in the number and size of exchanger shells is achieved by using High Flux tubing and a lower overall pressure drop which requires a smaller compressor with less horsepower and thereby reduced utility requirements.

The savings and performance of UOP's C3 splitter design has been proven in more than 120 applications using MD trays and more than 80 applications using High Flux tube.

UOP Propylene Recovery Unit

Depropanizer   Deethanizer   C₃ Splitter
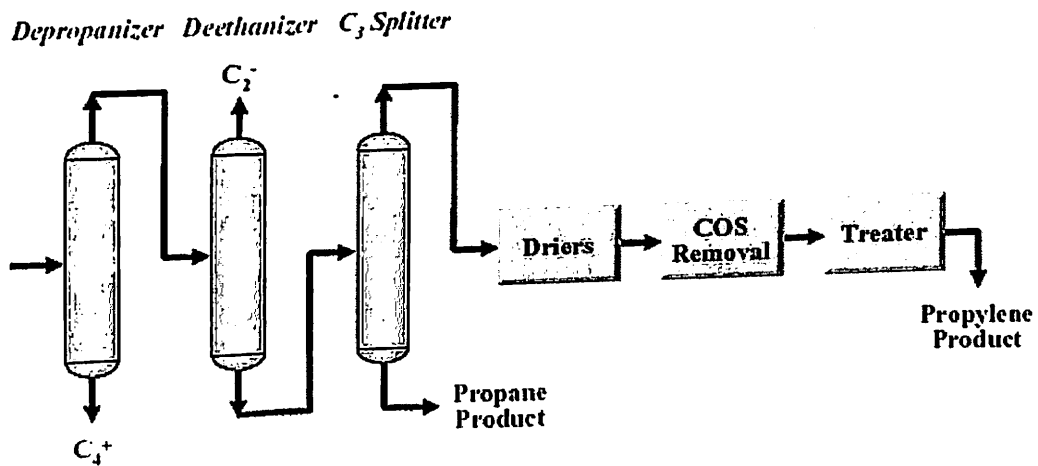
Fig 1.5

1.3. PROPANE DEHYDROGENATION (PDH)

Propane dehydrogenation has been providing a growing source of propylene for 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 1.6. 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.

C_3 Oleflex Process
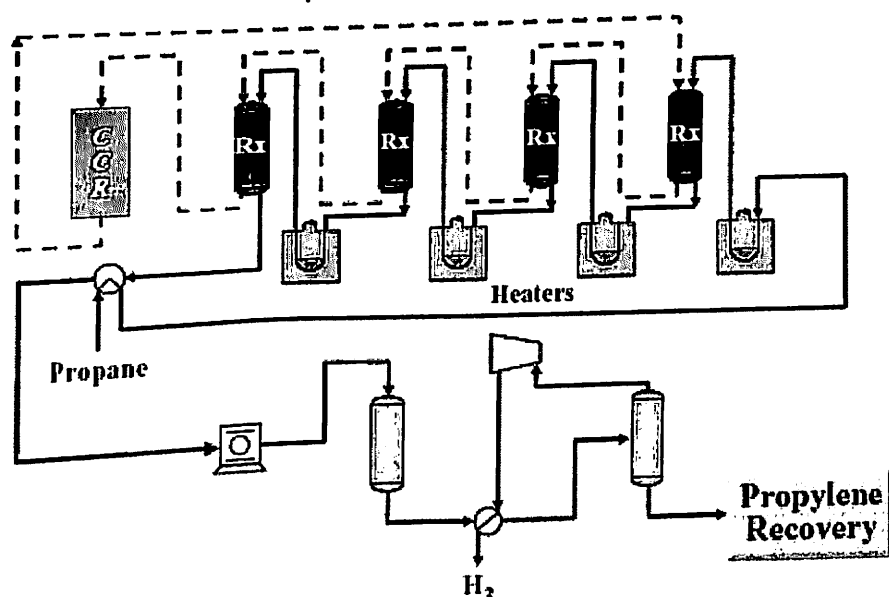
Fig 1.6

The yield of propylene from propane feedstock is over 85 wt-% with the Oleflex process. 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.

A typical method for dehydrogenation of propane to propylene is shown in Figure 1.6. In this process, propane is sent to a reactor section where dehydrogenation occurs over a

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catalyst. Catalyst activity is maintained by continuous regeneration. The effluent from the reactor is compressed and sent to cryogenic separation to remove hydrogen, which is recovered and recycled. The olefin product, which contains propylene, unreacted propane, and some byproducts, is fed to a selective hydrogenation process to remove dienes and acetylenes. During selective hydrogenation, dienes and acetylenes are converted to mono-olefins (ethylene and propylene). If hydrogenation is not selective, they are converted to paraffins (ethane or propane). The propylene/propane stream is finally sent to a C3 splitter to separate propane (which is recycled to the reactors) and propylene product. The yield of propylene is about 85 percent by weight.

PROPANE DEHYDROGENATION FLOW DIAGRAM
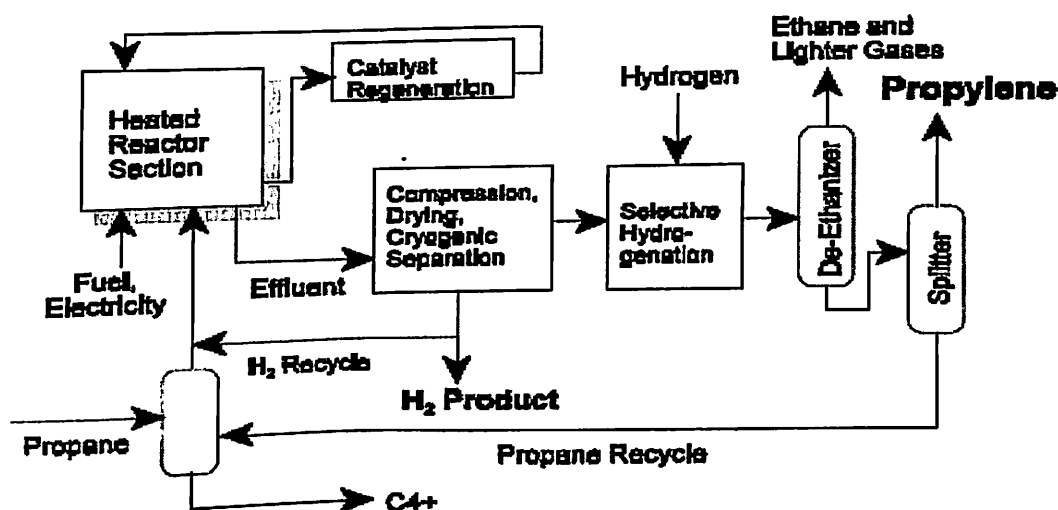
Fig 1.7

Key Energy and Environmental Facts - Propylene Manufacture/Dehydrogenation			
Energy	Emissions	Effluents	Wastes/Byproducts
Net Energy Exporter: Net Steam Export: 497 Btu/lb	Largest source - fugitive emissions (C4 and C5 compounds)	Largest source - process water	Hydrogen, light gases

Table 1.1

CURRENT TECNOLOGIES:

1.4. Methanol to Propylene

1.5. Olefin Conversion:
          1.5. (A) OCC
          1.5. (B) Olefin Metathesis

1.6. High-Severity FCC

1.4. METHANOL TO PROPYLENE (MTP)

There are two types of methanol-to-olefins processes available. The first is the UOP/HYDRO 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.

Lurgi is in the unique position to license the MTP technology also combined with the other proprietary Lurgi technologies such as Mega Syn and Mega Methanol to realize full production cost savings for the benefit of the client.

Technology

Lurgi Methanol to Propylene technology is based on the efficient combination of two main features:

■ Fixed-bed reactor system selected as the most suitable reaction system from a technological and economic point of view regarding this specific task.

■ Highly-selective and stable zeolite-based fixed-bed catalyst commercially manufactured.

Methanol even at lower grade than grade AA is catalytically converted to hydrocarbons, predominantly propylene. Propylene is the single main product as shown in the flow diagram. There is no ethylene product. Gasoline, LPG, fuel gas and water are by-products. Methanol fed to the MTP plant is first converted to DME and water in a DME pre-reactor. Using a highly active and selective catalyst, thermodynamic equilibrium is achieved, resulting in the methanol/water/DME mixture at appropriate operating conditions.

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MEHANOL TO PROPYLENE PRODUCTION
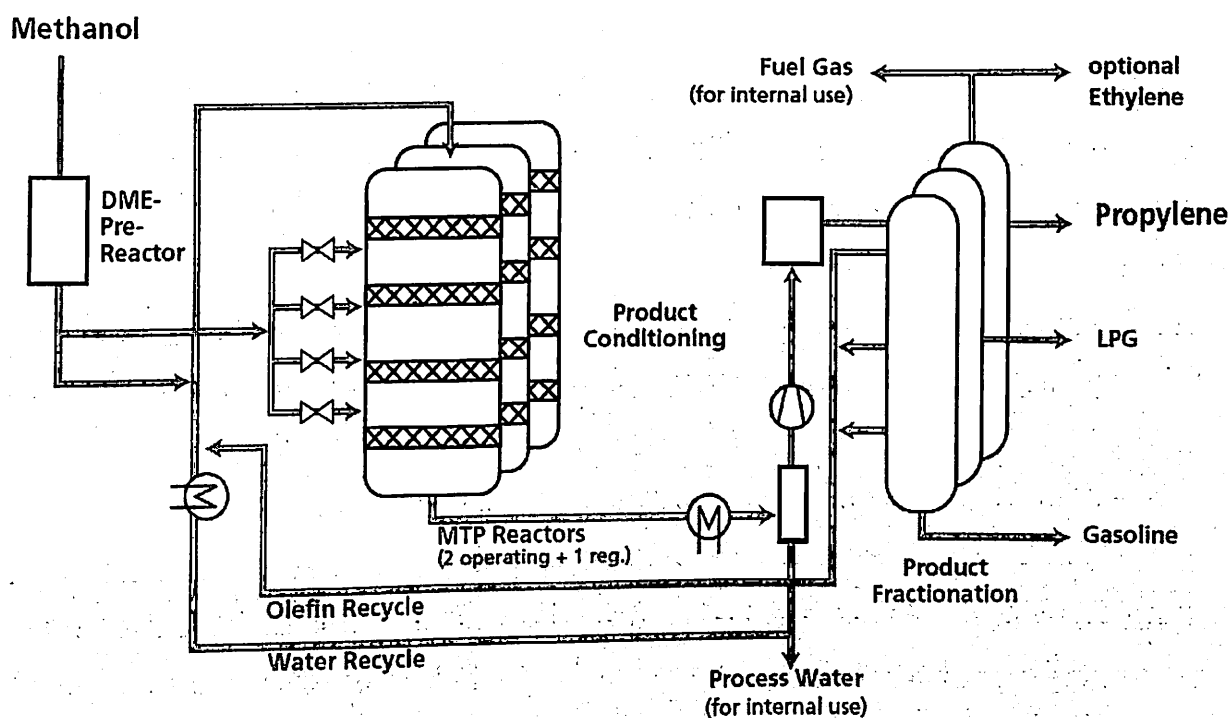
Fig 1.8

MTP PROCESS

Olefin recycle and steam made from water recycle are added to this mixture before it enters the first MTP reactor of the multi-stage adiabatic reactor system. The methanol/DME conversion rate exceeds 99%, with propylene as the essential compound. Additional reaction proceeds in the downstream reactor stages. Aiming at similar reaction conditions and maximum propylene yield, process parameters are controlled by feeding

Minor streams of fresh feed between the stages. The product mixture leaving the reactor system is cooled. It consists of product gas, organic liquid and water, which have to be separated.

After product gas compression, traces of water, CO2 and DME are removed and the gas is further processed yielding chemical- grade propylene with a typical purity of more than 97%. Several olefin-containing streams as indicated in the flow diagram are recycled to boost the propylene yield. To avoid accumulation of inert materials in the loop, a small Purge is required for light-ends and the C4/C5 cut.

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The excess water resulting from the methanol conversion is also purged. It can be used as raw water or for irrigation after inexpensive standard treatment. It can even be processed to potable water. Occurrence of coke formed on the active catalyst surfaces is a crucial feature and inherent in catalytic conversion of olefins due to inevitable side reactions. Cause and amount of coke formation have a decisive impact on the combination of the reactor system and the catalyst selection. Due to the necessary semi-continuous operation, one or two reactor systems are in operation while the other or the third one is in regeneration or on stand-by mode (not shown in the flow diagram).

After a cycle of approx. 500 – 600 hours of operation, the catalyst has to be regenerated by burning the coke with a nitrogen/air mixture. The regeneration is carried out at temperatures similar to the reaction itself; hence the catalyst particles do not experience any unusual temperature stress during the in-situ catalyst regeneration procedure.

In cooperation with Stat oil and Borealis, Lurgi is currently operating a demonstration unit for the new Methanol-To-Propylene (MTP) technology at the Stat oil methanol plant at Tjeldber-godden in Norway. The Demo Unit has been operating for over 3000 hours since start-up in early 2002.

The reactors are fixed-bed type, and are loaded with a tailor made proprietary zeolite catalyst. The operating conditions of the MTP reactors in the Demo Unit in terms of bed height, linear gas velocities, pressure drop and adiabatic temperature profile are identical to their proposed commercial counterpart, which will facilitate the risk-minimized scale-up to commercially sized reactors. The demonstration unit is also equipped with a simplified separation facility in order to produce real recycle streams.

Results of the Demo Unit operation confirm previous expectations that the cycle length exceeds the values measured in smaller lab-scale unit, right now typical cycle lengths of more than 600 hours are obtained. The propylene yields are within the expectations and prove the high selectivity of the catalyst towards propylene.

Advantages of our Technology

	Advantages	Major effects
Feed , Product		
■ Methanol, the only feedstock	■ Chemical base product ■ Availability worldwide ■ Reasonable price in case of using Lurgi Mega-Methanol technology, especially for stranded/flared gas utilization ■ Independence of petroleum impacts	■ Significant reduction of investment Requirement, simple logistic.
■ Propylene production only	■ Handling and/or downstream processing polymers of one main Product, no ethylene.	
Reactor system, Catalyst		
■ Catalytic fixed-bed reactors	■ Ease of scale-up compared to fluidized-bed.	■ Low investment cost.
■ Defined residence time	■ Maximum propylene selectivity, low propane yield, limited by-product formation.	■ Simplified product upgrading. ■ Reduction of operating cost.
■ Low coking tendency of catalyst	■ Extended cycle time minimized number of regenerations, long catalyst lifetime.	
■ In situ-regeneration at	■ No mechanical and thermal stress on the Catalyst, no attrition.	

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mildest controlled Conditions		
■ Complete separation of operation and regeneration services	■ Breakthrough of regeneration gas compounds excluded.	20

Table 1.2

The UOP/HYDRO MTO process (Figure 18) was jointly developed by UOP and Norsk Hydro 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 silicoaluminophosphate, 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.

CATALYSTS

For the MTO process, two types of catalysts are used:

- Micro porous zeolite catalyst ZSM-5
- Shape selective molecular sieve Silicoaluminophosphate catalyst SAPO-34.

Recently the trend has shifted towards using SAPO-34 rather than ZSM-5 as it shows higher selectivity for light olefins i.e., ethene & propene as compared to ZSM-5. At 100% methanol conversion, ZSM-5 showed 23-40% selectivity for lower olefins in fixed bed reactor whereas SAPO-34 showed 60-70% selectivity in fluidized bed reactor.

ZSM-5 Catalyst:

It has a channel structure with pore openings defined by 8-rings of oxygen atoms.
Factors Affecting Product Selectivity:

- Acidity
- Structural Geometry
- Active Site Distribution

ZSM-5 is one of the most versatile catalysts ever found. It is mainly used for hydrocarbon interconversion, meta-xylene to Para-xylene, for example. ZSM-5 is a zeolite with high silica to alumina ratio. The Substitution of an aluminum ion (charge 3+) for a silicon ion (charge 4+) requires the additional presence of a proton. This additional proton gives the zeolite a high level of acidity, which causes its activity. ZSM-5 is a highly porous material and throughout its structure it has an intersecting two-dimensional pore structure. ZSM-5 has two types of pores, both formed by 10-membered oxygen rings. The first of these pores is straight and elliptical in cross-section; the second pores intersect the straight pores at right angles, in a zigzag pattern and are circular in cross section.
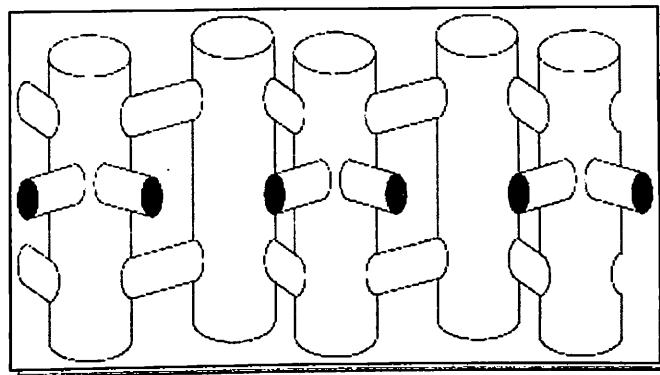
Fig.1.9 **Schematic figure of the pore structure of ZSM-5**

This unique two-dimensional pore structure allows a molecule to move from one point in the catalyst to any where else in the particle. The large openings are the elliptical, straight pores in ZSM-5. For the MTG process it is the pores created by these 10-oxygen rings, along with the zig-zag pores intersecting them that are essential to the formation of products that are desirable components of gasoline. An 8-oxygen ring zeolite will not produce molecules with 6 or more carbons, molecules of this size will not fit into the small pores of these zeolites. The large pores of a 12-oxygen ring zeolite produce large amounts of C-11 and C-12 compounds, which are undesirable products for gasoline.

Cation exchange of the catalyst enhances its selectivity properties as in the case of The-modified ZSM-34. With use of ZSM-5 catalyst, the ethane-to propene ratio obtained is always less than unity. Also it is found to be more selective towards production of aromatics (high octane gasoline). Thus, ZSM-5 is a preferred catalyst for the MTG (methanol to gasoline) route rather than MTO (methanol to olefin) route.

SAPO -34 Catalysts:

It has a cage like structure. The nano cages are of 1.0 nm by 0.7 nm diameter and interconnected through 8-ring windows of ca.0.38 nm in diameter.

Factors Enhancing Product Selectivity:

- Cage like framework
- Low acid density on internal and external surface

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- Fast crystallization techniques adopted in recent years
- Enhancement of shape selective effect by deposition of coke
- Good thermal stability
- Excellent mechanical properties and abrasion resistance

Synthesis and Characteristics of Sapo-34 Catalyst:

1) *Low cost synthesis method:*

Synthesis with triethylamine as templating agent and using dual-template technology to control the crystal size of molecular sieve reduces the cost of production by 20% as compared to catalyst preparation with TEAOH (tetraethyl hydroxylamine) template, which is an expensive reagent.

2) *Better catalyst preparation procedures:*

The small pore limitations of SAPO molecular sieves result in a rather high ethene selectivity. However it is for the same reason that it is difficult to apply conventional modification methods such as ion-exchange & impregnation to change the properties of the catalyst.

Modification in the synthesis of the molecular sieves seems to be critical for improvement of catalytic performance. Remarkable results were obtained using Ni-SAPO-34 on which an ethene selectivity of 88% was found at 450 °C with 100% methanol conversion & without coke formation. This catalyst is not easy to reproduce because the selectivity is very sensitive to those properties, which depend on the preparation procedure. Inui & Kung reported a reliable procedure for the synthesis of Ni-SAPO-34, and investigated the factors involved in its preparation.

The authors point out that

- Order of mixing of the starting materials is important to obtain a homogeneous gel mixture.
- The sequence of addition of seed crystals, milling for a time, treatment with ultrasonic waves and application of rapid crystallization method seem necessary to obtain a satisfactory catalyst.

The latest modification of synthesis method is that of nano-functionalization as the internet information given below reveals:

Nanofunctionalization of catalysts for methanol-to-olefin chemistry: A family of nanostructured catalysts for methanol-to-olefin (MTO) chemistry is developed by ship-in-a-bottle fictionalisation of the silico-aluminophosphate HSAPO-34. The CHA topology of this catalyst is characterized by nano-cages of 1.0 nm by 0.7 nm diameter that is interconnected through 8-ring windows of ca. 0.38nmin diameter. We recently reported that catalysts active for the conversion of methanol to olefins require methylbenzene molecules in the nano-cages, and these function as part of the active sites. Ethylene selectivity in MTO catalysis is related to the number of methyl groups on benzene rings trapped in the nanocages. We have developed procedures to either functionalize the methylbenzenes in place or to synthesize other species in the nano-cages, by ship-in-a-bottle routes that modify the catalyst by creating steric constraints in the cages or altering acidity. Catalysts with improved properties have been obtained.

Acid Properties:
A linear relationship between internal acid density & the selectivity to ethylene was observed. Thus, one may expect to obtain more selective formation of ethylene by controlling acid density bto less than 0.4 μmol /m^2. Addition of metals in SAPO-34 molecular sieve enhances light olefin selectivity and suppresses alkane formation.

Role of Ni:
For most samples of SAPO-34, Ni is incorporated into the framework in the tetrahedral & octahedral coordination state. Increasing the content oh Ni gradually increases the selectivity to lower olefins by affecting acid properties of catalyst under

real reaction conditions. The assumed reason was due to the low density of acid sites of higher acidic strength and to the presence of only small portion s of strong Lewis acid sites. The ratio between Bronsted and Lewis acid sites may also be important for ethene selectivity & catalyst stability as well as other structure related factors.

Role of silicon & aluminium:

Source of Si & Al in the synthesis of SAPO-34 has effects on the catalytic performance in a MTO reaction. If synthesized from organic precursors, deactivation is more rapid with high methane formation. Acidic properties of SAPO-34 are closely related with silicon incorporation into the framework. Smith et al. revealed that there are two distinct acid sites in the sapo-34 unit cell: one in the eight-ring channel & the other in the six ring. Understanding the crystallization mechanism & the detailed distribution of Si & Al in the framework is essential for catalyst research. Si 'islands' cause acidic character to become strongly dependent on the topology of the material. Acidity directly relates to concentration of Si Island. Silicon precursors directly take part in the formation of crystal nucleus as well as in the growth of crystal grains. Fast crystallization enhances catalyst performance.

Effect of Coke:

During the MTO reaction, coke formation takes place which gets deposited on the catalyst. The pattern of coke distribution in a system with solids circulation differs strongly from that in fixed-bed reactor. In this section, we take into account the effect of coke deposition on reaction rate of various reactants & not necessarily the effect distribution pattern of coke over the catalyst, which may vary from one type of reactor to another & also affect their performance.

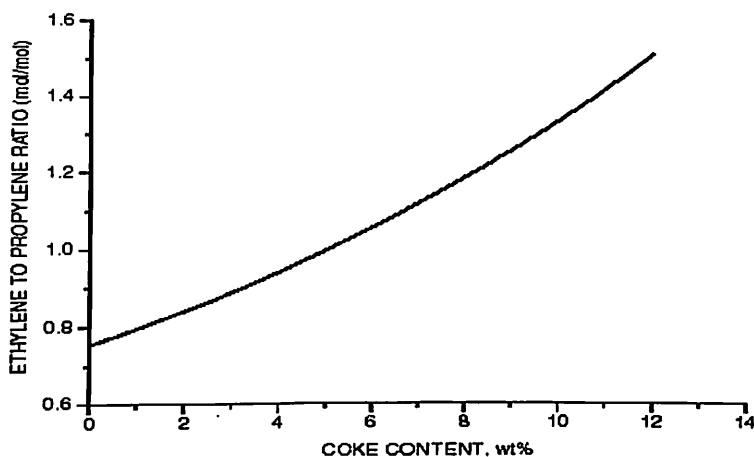## The Effect of Coke Content on Ethylene-To-Propylene Ratio.

Fig 1.10

Classification of Coke Deposit:

Based on the kinetic model of Bos et al., coke deposits fall under two categories,

- Inactive coke
- Active coke

Deactivation due to inactive coke:

Methanol conversion decreases significantly with an increase in coke deposit on the catalyst. According to Froment et al., the small pore molecular sieve SAPO-34 catalyst suffers from relatively rapid deactivation due to coke deposits that cause partial or complete pore plugging which reduces the concentration of active sites available to reagent molecules. So, reduction in the amount of active sites accessible to methanol molecules during reaction results in a decrease in methanol conversion.

Ratio of Active to Inactive Coke:

The coke deposited on the catalyst, termed as active coke, brings about an increase in the product selectivity by inducing transition state shape selectivity whereas the coke termed as inactive coke, formed during the methanol conversion process, when deposited on catalyst brings about a decrease in methanol conversion due to deactivation of active sites. The selectivity and yield depend on the ratio of active to inactive coke present at any given time. According to Soundararajan et al., ethylene yield goes through a maximum of 27.2 wt% at 5 wt% coke on catalyst. The initial increase in ethene yield can be explained in terms of the

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transition state shape selectivity. The decrease in the ethene yield beyond 5 wt% coke on the catalyst is a result of the reduced methanol conversion

Later on, with use of Sim Solv modeling and parameter estimation program with fluidized bed reactors having realistic dimensions it was found that in order to achieve ethene –to- propene ratio of 1 or higher, at least 7-8 wt% of coke must be present on the catalyst.

Empirical Correlation:

The coke content of the catalyst is the main factor governing the selectivity & activity of the catalyst. This effect is best described by an exponential dependence of all the reaction rate constants on the amount of coke on the catalysts. The mathematical representation suggested is as follows,

$$k_i(c) = k_i^0 e^{-\alpha_i C}$$

$k_i(c)$ = Reaction rate constant of the ith component.

α_i = Empirical constant for i[th] component.

C = Wt% of coke on the catalyst.

The larger the value of α_i, the more strongly the reaction rate decreases with increasing coke content. On the basis of shape selectivity effects, α_i is found to increase with increasing carbon number i.e., larger the molecule. Thus, the effect of coke on the selectivities i.e., the ratio of the rates of the reactions, can now be modeled by taking different values for the empirical constant α_i.

UOP – MTO PROCESS:

UOP –MTO Process
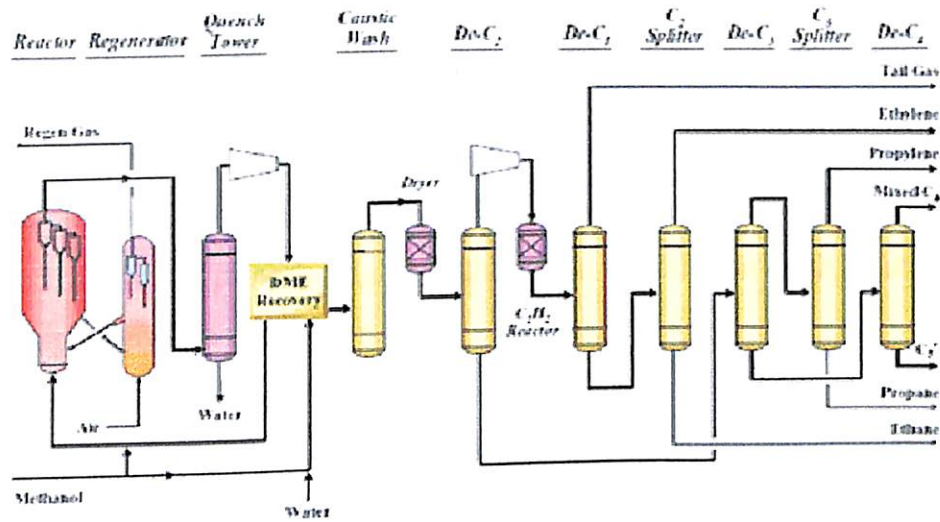
Fig 1.11

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 C_1-C_4 paraffins, hydrogen, CO and CO_2, as well as ppm levels of heavier oxygenates that are removed to ensure that the product olefins meet polymer-grade specifications.

The UOP/HYDRO 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 ATOFINA/UOP 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.

1.5. 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 feed stocks (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.

1.5. (A).OCC PROCESS FOR OLEFIN PRODUCTION

The OCC (Olefins Catalytic Cracking) process features fixed-bed adiabatic reactors. A swing reactor system is used for catalyst regeneration, performed in-situ using simple nitrogen regeneration to which small amount of air is added. The main characteristic of the process is the addition of steam to the reactor feed. The OCC process utilizes a tailor-made zeolite catalyst with high hydrothermal stability.

Propylene is one of the most important basic organic products, and the annual growth rates for propylene exceeds that of ethylene as a result of the huge growth in the propylene derivatives, e.g., polypropylene.

The naphtha steam cracking process-the main propylene source with about 70% share in the primary production, produces about twice as much ethylene as propylene. At higher P/E ratios, the total olefins yield drops to an uneconomically low level. Moreover, steam cracking process is also an expensive option because of the high capital investment.

Propane dehydrogenation could give a high yield of propylene, but the feedstock is only cost effective in some limited areas, making the process expensive and limiting

the production of propylene. Accordingly, olefin manufacturers are seeking cost effective options to increase the propylene production. One of the effective approaches for this purpose is to integrate the propylene production process into refinery or petrochemical plants, starting from a less valuable feedstock, such as catalytic cracking of mixed C4-olefins or higher carbon olefin.

In the present paper, the OCC (Olefins Catalytic Cracking) process that allows high selective production of propylene and ethylene by conversion of C4/C5 olefins from crackers and refineries is discussed in detail.

OCC reaction and principles
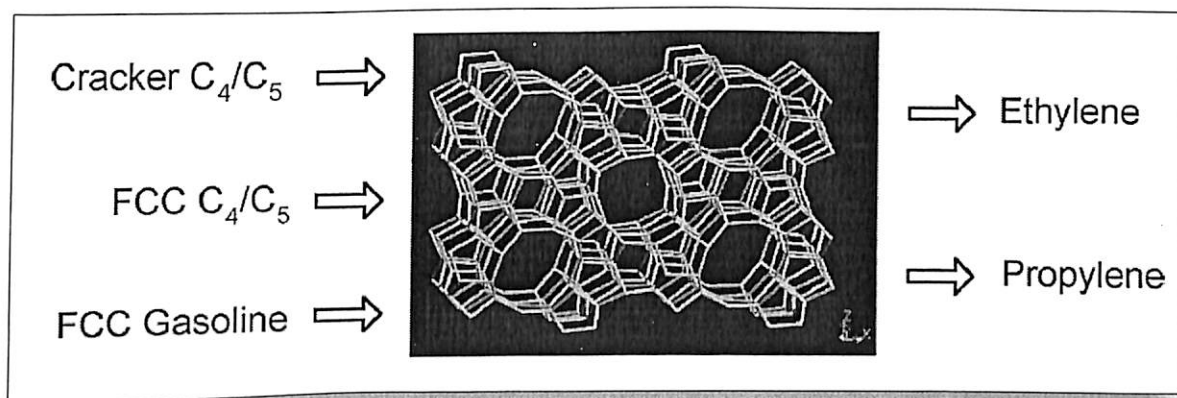
Fig 1.12

Fig.1.12 depicts the reaction scheme of OCC (Olefins Catalytic Cracking). Low value olefins from steam crackers or and refineries were catalytic cracked into propylene and ethylene on a shape selective ZSM-5 type zeolite catalyst at the temperature of 500-600°C.

The reaction principle for the OCC reaction can be explained simply as shown in Fig. 1.13 Take C4 olefins catalytic cracking as an example. C4 olefins are first di merized to form C8 transition species. Then, C8 transition species are catalytic cracked into the desired product following the carbonium formation and b bond scission mechanisms.

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Fig 1.13   **Mechanisms for OCC reaction**
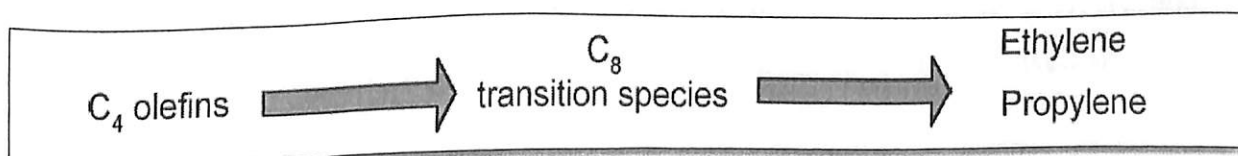
Feed stocks

The OCC process can operate with different feed stocks, especially those feeds that are available from steam crackers and refineries, the favourable feed stocks are as follows:

1. FCC or Coker C4 Olefins
2. FCC C5 Olefins
3. FCC gasoline
4. Steam cracking C4 Olefins (Butadiene extraction or Selective hydrogenation)
5. MTBE synthesis (FCC or Steam Cracker)
6. The mixture of the above hydrocarbons

The feedstock of OCC process is very flexible. There are several constraints for the feedstock of OCC process with respect to purity and composition. Feed stocks containing high or low concentrations of olefins can be processed. Obviously, feed stocks with higher olefins content are more favorable. Paraffin's, cycloalkanes, cycloalkenes and aromatics may be present in the feed stocks as these compounds are considered as non-convertibles. However, the feedstock should be controlled to less than 1.0wt% of diolefins; these components are contributed to coke formation.

OCC process features

The OCC (Olefins Catalytic Cracking) process features fixed-bed adiabatic reactors operating at temperatures 500-600°C and pressures 0.1-0.2MPa. A swing reactor system is used for catalyst regeneration, performed in-situ using simple nitrogen regeneration to which small amount of air is added. The main characteristic of OCC is the addition of steam to the reactor feed, the ratio of steam to hydrocarbon is typically between 0.5-2. It reduces the olefins partial pressure and improves the selectivity of propylene. Moreover, coking tendency as well as gum formation is suppressed efficiently.

OCC process:

A simplified process flow diagram of OCC unit is shown in Fig. 1.14 The liquid Feedstock containing olefins is vaporized and mixed with steam. The Hydrocarbon/steam mixture is further heated against the reactor effluent and in a fired heater before entering the fixed-bed reactor. By cooling the reactor effluent, steam is condensed and separated together with some gasoline by-products. The remaining vapor is compressed to do further separation. Most of C-4 fraction is recycled to the OCC reactor to increase the total propylene and ethylene yield. Part of the C4 fraction is purged to avoid the accumulation of paraffin's in the system. The C5 + fraction are cut to further process as paralysis gasoline. Separation facilities depend on how the unit is integrated into the processing system.
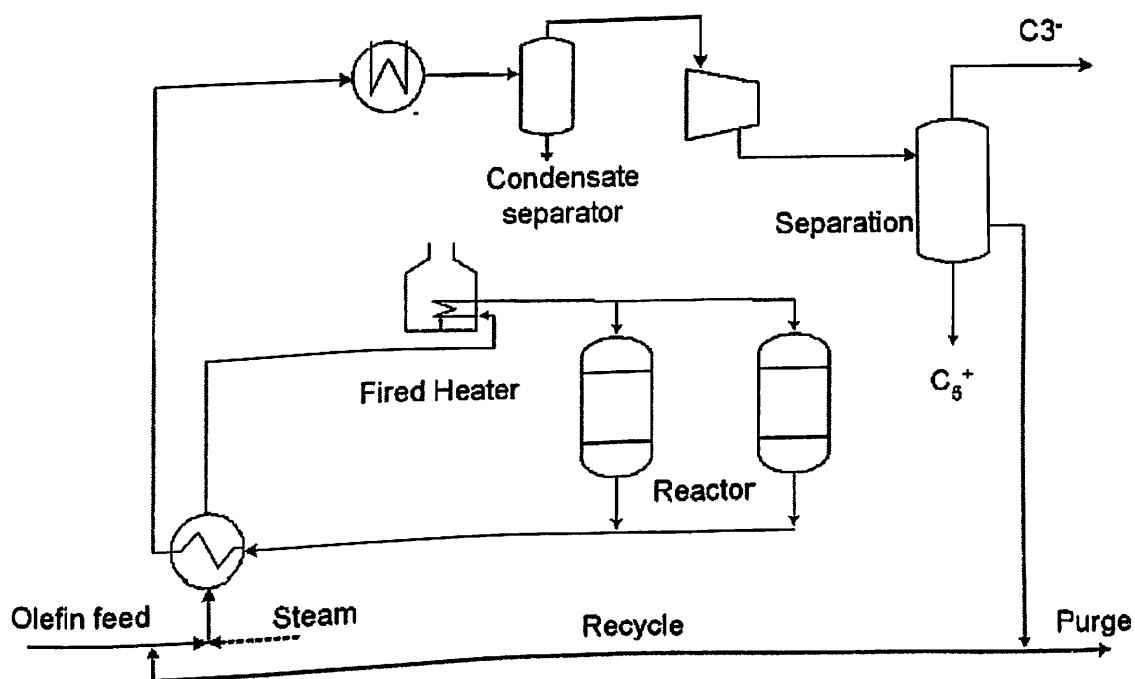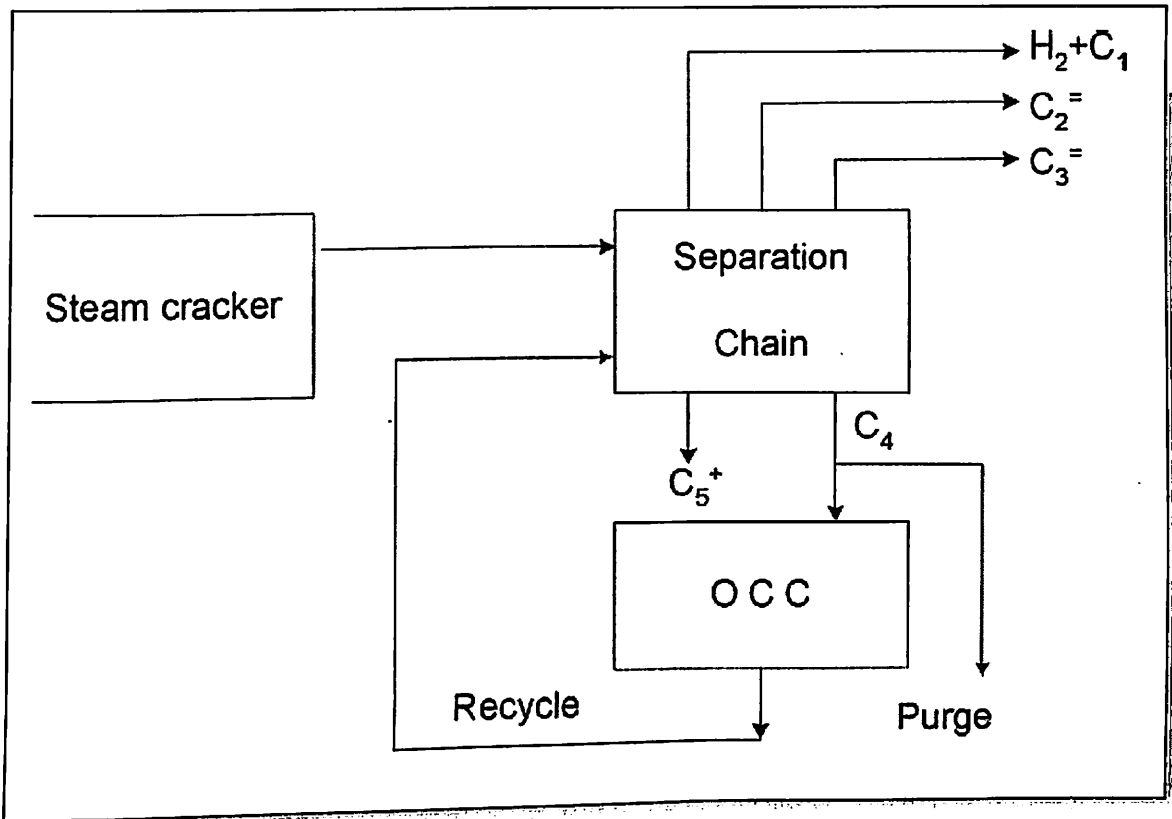

Fig 1.14   **Process flow diagram of OCC unit**
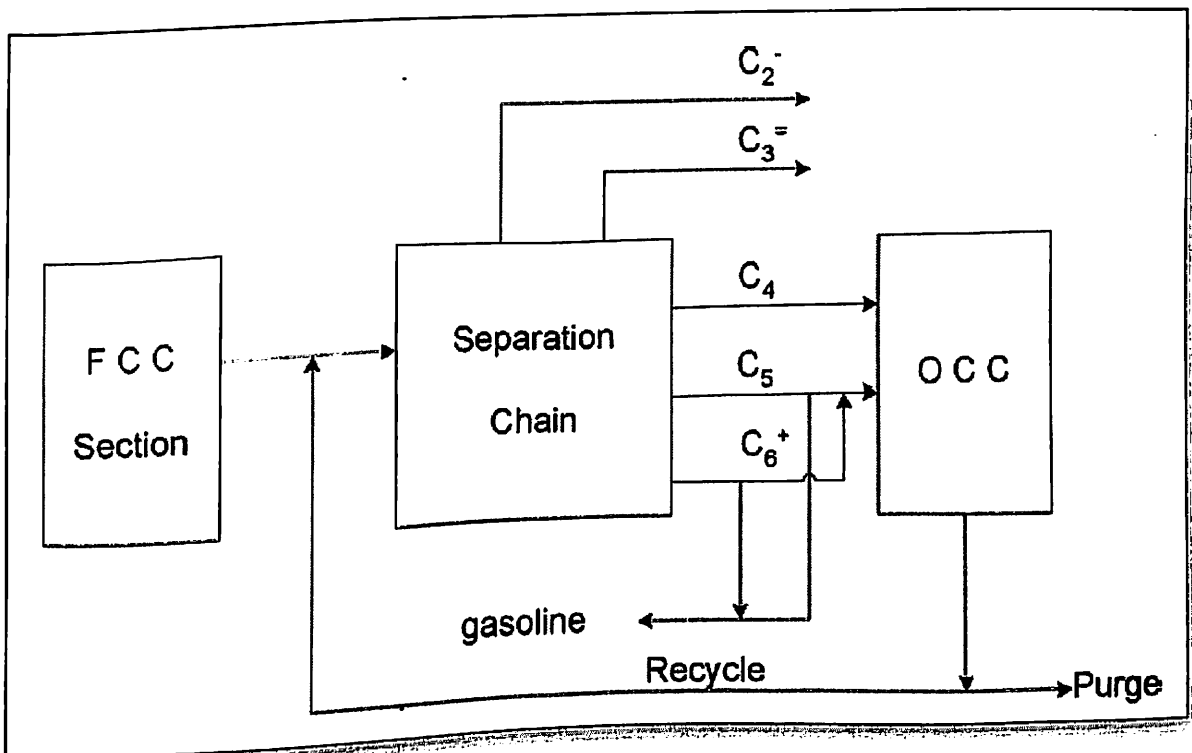
Fig 1.15 **Steam Cracker Integration**

Fig 1.16 **Refinery Integration**

Catalyst performance

The OCC process utilizes a tailor-made ZSM-5 zeolite catalyst with high hydrothermal stability, which is developed by SINOPEC SRIPT. In the optimized process conditions, the coking tendency in the OCC is very low. The catalyst exhibits high activity and stability. Thus, a fixed-bed adiabatic reactor system can be applied and no continuous catalyst regeneration is required. The catalyst cycle length is over 1000 hours. From laboratory and pilot plant experience, the catalyst lifetime is predicted to exceed one year. Typically 38-40wt% propylene and 13-15wt% ethylene are obtained in the pilot plant for per pass. The catalyst developed by SINOPEC for OCC process features the utilization of ZSM-5 zeolite with small crystal size, which is smaller than $0.5\mu m$. The effect of crystal sizes on the catalytic performance of ZSM-5 zeolite catalyst for OCC was studied, the results showed that the ZSM-5 zeolite with small crystal sizes showed better durability in the OCC process, which might be due to its high tolerance ability for coke. The typical yield of products from OCC reaction is shown in Tab.1.3 If the produced butylenes are recycled, propylene yield can be increased to 54wt.% and ethylene yield can be increased to 18wt.%. These given yield are related to the olefins content of the feed stocks. The catalyst exhibits little sensitivity to common impurities such as diolefins, sulphur compounds and nitrogen compounds. Catalyst regeneration is done in-situ. Nitrogen and amount of air are mixed and introduced into the reactor to burn the coke deposits on the catalyst.

Typical yield of products from OCC reaction		
	Typical yield (wt%)	
	Per pass	C_4-recycle
Propylene	38-40	54
Ethylene	13	18

Table 1.3

Applications

The OCC process was developed to utilize low value by-product streams containing olefins from steam crackers and refineries.

Steam cracker integration

There are several possible integration schemes for an OCC unit into a steam cracker. The simplest option is that product separation is done completely at the ethylene plant. The integration scheme is shown in Fig.1.15 C4 stream from butadiene extraction or selective hydrogenation or MTBE synthesis units are fed into the OCC unit. The effluent from the reaction section is processed by the separation of the ethylene plant.

To avoid the accumulation of paraffins in the system, part of the C4 fraction is purged in the option. This integration may be the most economic solution for a new plant, where additional capacity required to separate the effluent from OCC unit can be reserved in the ethylene plant. Therefore, no independent separation system for OCC unit is needed to build. Another option features integrating OCC unit with its own separation system. Only C3 - or C2 - fraction is processed by the separation system of ethylene plant. The option is favorable for an existing ethylene plant, where the additional capacity is limited.

Refinery integration

The refinery integration scheme is shown in Fig 1.16 The OCC converts C4 fraction or cracking gasoline to desirable light olefins, mostly propylene and ethylene. The volume of olefins in the gasoline stream is lowered from 45% to 15%, at the same time; the octane number is improved due to aromatics.

1.5. (B).OLEFIN METATHESIS

Olefin metathesis opens up new industrial routes to important petrochemicals, oleo chemicals, polymers and specialty chemicals. The most important applications of olefin metathesis in the field of petrochemicals are the olefins conversion technology (OCT) process (originally the Phillips triolefin process) and the Shell higher olefins process (SHOP).

In particular, naphtha steam crackers with an integrated metathesis unit are an interesting alternative for producing propene via the OCT process, as a high global demand for propene outpaces supply from conventional sources. In the polymer field, ring-opening metathesis polymerizations (ROMP) of cycloalkenes does an attractive process for making polymers possess special properties. Several industrial processes involving ROMP have been developed and brought into practice, such as the ROMP of cyclooctene, norbornene and dicyclopentadiene, leading To useful polymers. Metathesis of natural fats and oils and their derivatives offers possibilities for future developments in the oleo chemical industry, providing a contribution to a sustainable chemical industry. Moreover, in the light of the new metal–carbine metathesis catalysts, in particular the functional-group-tolerant well-defined ruthenium-based catalysts, it is to be expected that in the fine chemistry the metathesis reaction will soon find its way as a tool for the synthesis of agrochemicals, insect pheromones, fragrances, pharmaceutical intermediates, etc.

1. Introduction

Olefin metathesis is one of the very few fundamentally novel organic reactions discovered in the last 40 years. Among others, it opens up new industrial routes to important petrochemicals, polymers, oleo chemicals and specialty chemicals.

At Phillips Petroleum Co. this reaction was discovered serendipitously by Banks and Bailey 40 years ago, when they were seeking an effective heterogeneous catalyst to replace the HF acid catalyst for converting olefins into high-octane gasoline via olefin–isoparaffin alkylation'sWhen using a supported molybdenum catalyst, they found that, e.g. instead of calculating the paraffin, the olefin molecules

were split, and discovered that propene can be catalytically converted into ethene and butene.

Since then, industrial applications of the olefin metathesis reaction, including ring-opening metathesis polymerization enjoyed increasing interest, in particular in recent years. Here I will present an overview of the present situation. Pro-cesses known until 1997 have also been described elsewhere, including processes that are no longer commercial.

2. Industrial processes for the production of propene

Propene is obtained mainly from naphtha steam crackers globally about 70%) as a co-product with ethene, and as a co-product from gasoline-making from FCC units at refineries. Relatively small amounts are produced by propane dehydrogenation and by coal gasification via Fischer–Tropsch chemistry. Strong global demand for propene, however, presently outpaces supply from these conventional sources. Propene is used for about 60% for making polypropylene, and further for producing acrylonitrile, oxo alcohol, acrylic acid, etc.

The Phillips triolein process

An alternative route to propene is by applying the metathesis reaction for the conversion of a mixture of ethane and2-butene into propene. This process, called the Phillips tri-olefin process, which utilizes a heterogeneous catalyst sys- tem, was originally developed by Phillips Petroleum Co., USA, and operated from 1966 to 1972 for the conversion of propene into ethene and butene.

$$CH_2=CH_2 + CH_3CH_2=CH_2CH_3 \rightleftharpoons 2CH_3CH_2=CH_2$$
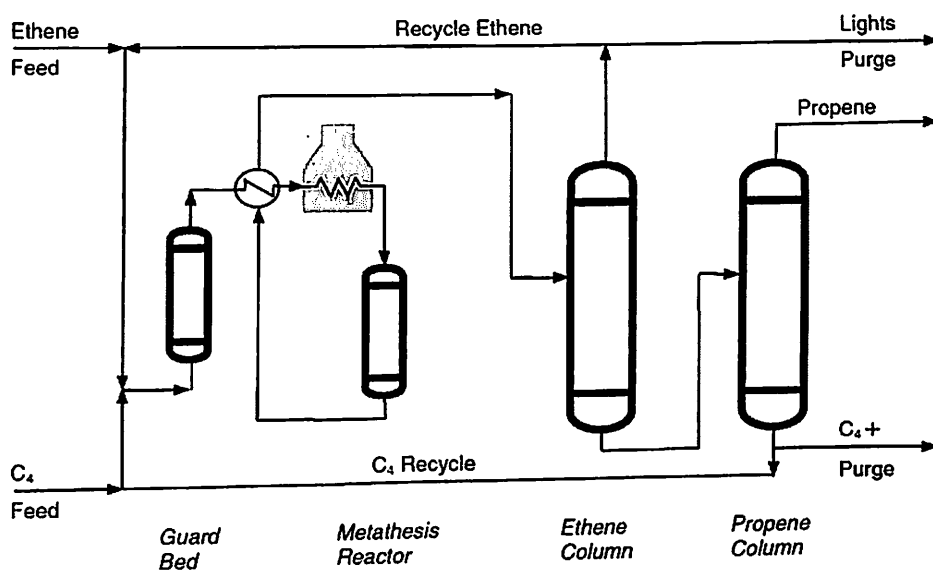
Olefin Metathesis

Fgi 1.17

1. Figure 1.17 shows a process flow diagram of the OCT process. Fresh C4 's plus C2 recycle are mixed with ethene feed plus recycle ethene and sent through a guard bed to remove trace impurities from the mixed feed. The feed is heated before entering the metathesis reactor.

2.The reaction takes place in a fixed-bed reactor over a mixture of WO3 /SiO2 (the metathesis catalyst) and MgO at >260 ° C and 30–35 bar.

3. 1-butene in the feedstock is isomerized to 2-butene as the original 2-buteneis consumed in the metathesis reaction. The conversion of butene is above 60% per pass and the selectivity for propene is >90%. The reactor is regenerated on a regular basis.

4. 1985, the Lyondell Petrochemical Co. started to operate plant in Channelview, Texas (USA) for the production of 136,000 t per year of propene. In their process, part of the ethene from ethane-cracking units is dimerized to 2-butene, using a homogeneous nickel catalyst developed by Phillips, which reacts with the rest of the ethene to produce propene.

5. The process has been retrofitted to the company's steam cracker in Channelview.

6. In particular, naphtha steam crackers with an integrated metathesis unit are an

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interesting alternative for producing more propene. In December 2001, BASF FINA Petrochemicals (a 60–40 joint venture between BASF and Atofina) brought on stream a world-scale steam cracker plant in Port Arthur, Texas (USA), which will integrate the OCT process to enhance the production of propene in relation to ethene. This plant produces 920,000 t per year of ethene and 550,000 t per year of propene, but when the metathesis unit is added (early 2004), it will adjust the output to 830,000 t per year of ethene and 860,000 t per year of propene.

7. Raw C2 and C4 feedstock's are supplied directly by the steam cracker, but additional C4's will be taken from the Sabina Chemicals' C4 splitter being planned by a joint venture of Shell Chemicals, BASF and Atofina; by-products are recycled to the cracker. Mitsui Chemicals will install the OCT technology to meet increasing propene demand in Asia. The propene capacity of its olefins plant at its Osaka Works in Japan will be increased by 140,000 t per year from 280,000 to 420,000 t per year. Completion of the project is expected in August 2004. The new unit will be the first plant installation in Japan to produce propene using the OCT technology.

8. By this revamp, the propene to ethene production ratio can be raised from 0.6 to >1.0. The OCT process will also be used at Shanghai Secco Petrochemical, a joint venture of BP Chemical, Sinopec and Shanghai Petrochemical Corporation, which is building a 900,000 t per year naphtha cracker integrated with an OCT unit to produce a total of 590,000 t per year of propene at Cajoling, China. The complex is scheduled for start-up in the first half of 2005.

9. PCS (Petrochemical Corp., Singapore), a joint venture between Shell Chemicals and Sumitomo Chemical, will use OCT metathesis technology to increase the propene output at its olefin units by 200,000–300,000 t per year.

1.6. HIGH-SEVERITY FCC: A NEW PROCESS TO MAXIMIZE PROPYLENE

A novel FCC process that maximizes propylene production is under development by research teams in Saudi Arabia and Japan. The process has been proven in a 30-BPD demonstration plant at Saudi Aramco's refinery, Saudi Arabia, and at a 500-BPD cold flow model at Nippon Oil Corporation, Japan. The high-severity FCC process combines mechanical modifications to conventional FCC with changes in process variables and catalyst formulations. The process main operating features are a down-flow reactor system, high reaction temperature, short contact time, and high catalyst to oil ratio. The paper highlights the features of the HS-FCC process and presents some results obtained from the 0.1 BPD riser and downer pilot plans and demonstration plant.

Propylene is used as a feedstock for a wide range of polymers, product intermediates, and chemicals. Major propylene derivatives include polypropylene, acrylonitrile, propylene oxide, oxo-alcohols, and cumene. These Derivatives account for almost 90% of global propylene demand and polypropylene alone has the largest volume. In 2005, global demand for propylene reached about 67 million tons and its annual demand growth is expected to increase by 4.8% up to 2010.

Currently, 30% of the world's propylene is supplied by refinery fluid catalytic cracking (FCC) operations and the remaining is co-produced from ethylene steam cracking of naphtha or other feedstocks. FCC continues to be the dominant conversion process for gasoline and light olefins production with a global capacity of 14.2 million BPD. Other sources of propylene in the refinery arise primarily from visbreaking and coking. Increasing the yield of the valuable light olefins, especially propylene and butenes, remain a major challenge for many refinery worldwide.

Conventional FCC units typically produce about 3-6 wt% propylene depending on feed type, operating conditions, and type of catalyst. Despite the technologies available to increase the propylene yield and other light olefins, intense research Activity in this field is still being conducted. As global demand for propylene

continues to grow, opportunities for new production routes continue to emerge.

Practically, there are several options to increase FCC propylene yield. These options include the use of high-selective FCC catalysts, ZSM-5 additives, high severity operation (higher reaction temperature), reprocessing (recycle) of FCC naphtha, and emerging propylene-oriented FCC processes. ZSM-5 additives can increase propylene to about 8 wt% while improvements in FCC catalysts, process design, hardware, and operation severity can boost propylene yield from 5% to 25% or higher.

SPECIAL FEATURES OF HIGH-SEVERITY FCC

The main objective of the high-severity FCC process is to produce significantly more propylene and high-quality gasoline. The special features of this new process (Table 1.4) include a down-flow reactor, high reaction temperature, short contact time, and high catalyst to oil (C/O) ratio. Since the FCC process involves successive reactions, the desired products such as olefins and gasoline are considered intermediate products. A suppression of back-mixing by using the downer reactor is the key to achieve maximum yield of these intermediates. Compared to conventional FCC processes, the HS-FCC has modifications in the reactor/regenerator and stripper sections.

Main Features of HS-FCC Process	
Main Feature	**Remarks**
Down-flow Reactor	• Minimizes back-mixing • Reduces undesirable by-products
High Reaction Temperature	• Operates at high temperatures (550 to 650°C) • Enhances thermal and catalytic cracking
High C/O Ratio	• Compensates reduced conversion • Enhances catalytic cracking
Short Contact Time	• Reduces thermal cracking • Reduces undesirable successive reactions

Table 1.4

Down-flow reactor:

A down-flow reactor system has been adopted for HS-FCC process. The downer permits higher C/O ratios because the lifting of catalyst by vaporized feed is not required. As with most reactor designs involving competing reactions and secondary product degradation, there is a concern over catalyst-feed contacting, back-mixing, and control of the reaction time and temperature. The down-flow reaction would ensure plug flow without back-mixing.

High-reaction temperature:

The HS-FCC unit is operated under considerably higher reaction temperatures (550 to 650oC) than conventional FCC units. Under these reaction temperatures, two competing cracking reactions, thermal cracking and catalytic cracking, take place. Thermal cracking contributes to the formation of lighter products mainly dry gas and coke while catalytic cracking increases propylene yield.

Short residence time: The short residence time (less than 0.5 sec) of feed and product hydrocarbons in the downer should be favorable to minimize the thermal cracking. Undesirable successive reactions such as hydrogen - transfer reactions,

which consume olefins, are suppressed. In order to attain the short residence time, the catalyst and the products have to be separated immediately at the reactor outlet. For this purpose, a high efficiency product separator has been developed capable of suppressing side reactions (oligomerization and hydrogenation of light olefins) and coke formation accelerated by condensation.

High C/O ratio:

In order to compensate the decrease in conversion due to the short contact time, the HS-FCC process is operated at high C/O ratio, in the range of 15 to 25. As mentioned earlier, the other advantage of operation at high C/O is the enhanced contribution of catalytic cracking over thermal cracking. By increasing the C/O ratio, the effects of operating at high reaction temperature (thermal cracking) are minimized. High C/O maintains heat balance and helps minimize thermal cracking, over-cracking, and hydrogen transfer reactions.

Comparison of typical product yields of conventional and HSFCC processes.
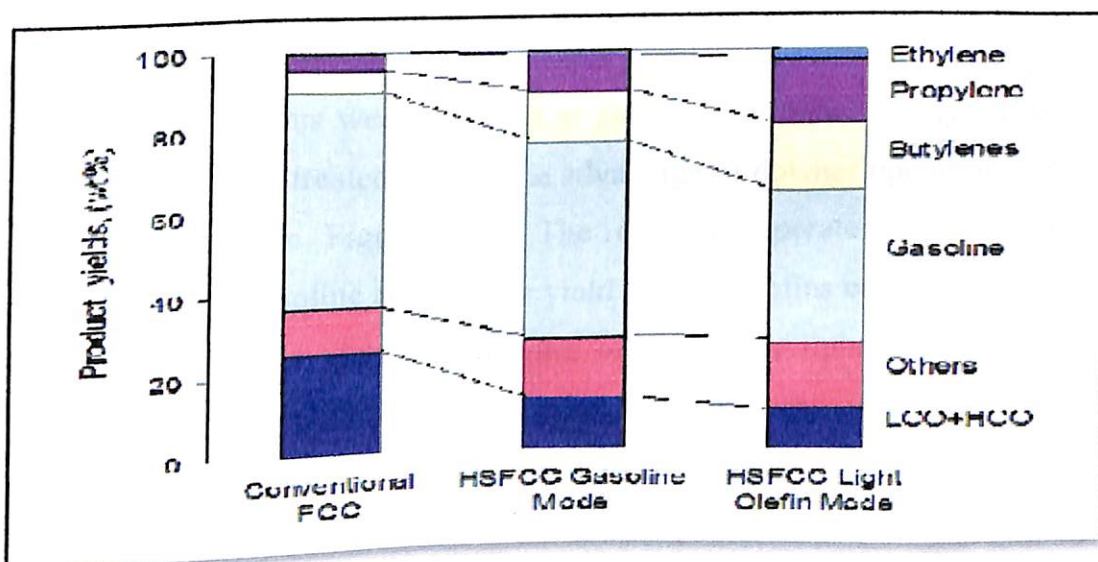

Fig 1.18

Figure 1.18 compares the typical product yields of conventional FCC and the two modes of HS-FCC. Compared to conventional FCC gasoline, the HSFCC gasoline has a higher octane number (about 100) and contains more Para-xylene. Para-xylene production, therefore, can be as much as 1.8-2.8 times more than in a conventional FCC. Conversely, the olefins content in the HS-FCC gasoline is less by 50-85 wt % depending on the operating severity.

Pilot plant results

Experiments were conducted in a 0.1 BPD pilot plant using various catalysts and Hydro treated vacuum gas oil (VGO) and untreated VGO. Figure 1.19 shows a schematic diagram of the downer pilot plant consisting of a downer reactor, stripper, regenerator, and catalyst hopper. Feed oil is charged into the upper part of the downer reactor together with dispersion steam. Regenerated catalyst is also charged to the top of the reactor from the catalyst hopper. At the outlet of the downer, product hydrocarbons are separated immediately from catalyst in the stripper, where heavy oil adsorbed on the spent catalyst is stripped by steam, and then spent catalyst is sent to the regenerator. The product yields from downer pilot plant were compared with a similar conventional riser type pilot plant. Both pilot plants were operated at similar conditions, catalyst (low-activity USY) and a hydro treated VGO. The advantage of downer operation over riser is clearly shown in Figure 1.21. The downer, operated at HS-FCC conditions, offers more gasoline at the same yield of light olefins compared to the riser. At the same gasoline yield, the downer offers higher light olefins yield. Several studies were conducted with different feed oils, catalysts and olefin boosting additive Combinations. The addition of 10wt% ZSM-5 additive was studied at 6000C and a C/O ratio of 40. The base catalyst was a low activity USY FCC catalyst.

Demonstration plant

Based on the results of the pilot plant, the technology was scaled to 30 B PD demonstration plant (Figure 1.22). The plant was operated for a period of about 18 months including several planned shutdown for inspection and modification. The main purpose of the operation was to confirm the operability of the feed nozzle and injection systems. The first stage product-catalyst separator was also a new design different from conventional cyclone separator. The operation of the demonstration plant was very successful and the obtained results were very close to those of the 0.1 BPD pilot plant. The demonstration plant consists of the following sections:

- Feed oil and catalyst mixer,
- Reaction section (downer reactor),
- Product and catalyst separator,
- Stripper,
- Regenerator with a riser-type lift line, and
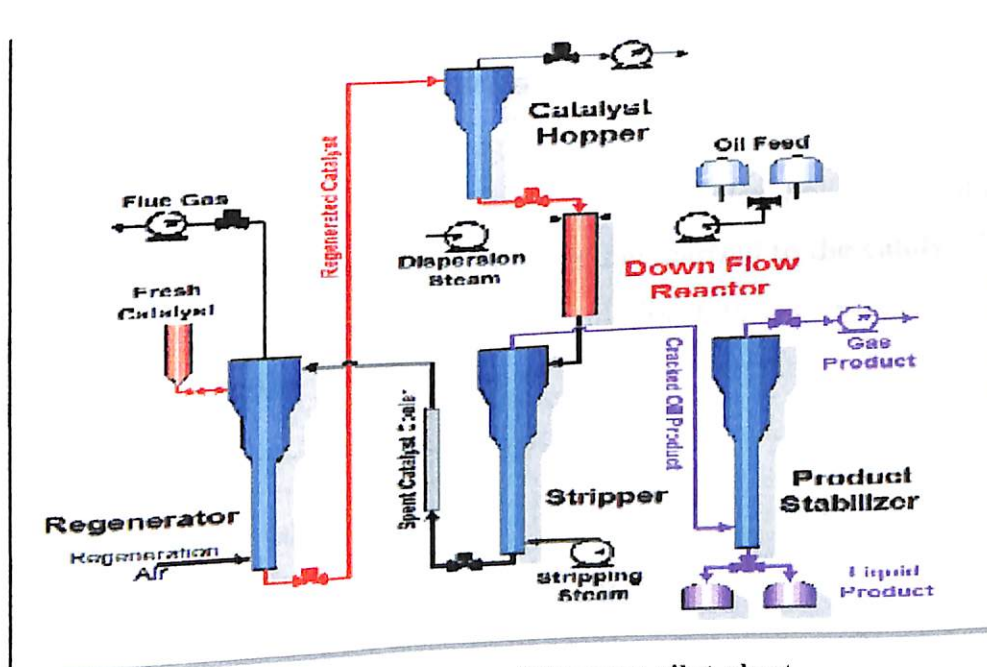- Catalyst hopper.

Figure 1.19   Schematic diagram of Downer pilot plant

Demo plant description:

Feed oil is charged to the mixing zone where it is mixed with the hot regenerated catalyst from the catalyst hopper. HP steam disperses the feed oil and the mixture moves downward through the reaction zone, where the liquid feed vaporizes and cracking reactions take place. The mixture of spent catalyst and hydrocarbon products, from the reaction zone, enters the gas solid separation zone. The spent catalyst is separated from the gas by centrifugal forces and the catalyst flows to the upper portion of the stripping zone. Hydrocarbon gases from the main separator feed a secondary separator, where the rest of the spent catalyst is separated from the product gas. Hydrocarbon gases then feed a product-recovery section. Catalyst separated in the secondary separator is directed to the stripping zone where heavy hydrocarbons adsorbed on the catalyst are removed using high-pressure stripping steam. Vapors of heavy products and un reacted feed oil stripped from the spent catalyst are withdrawn from the top of the stripping zone and sent to the recovery section after passing through the cyclone. The spent catalyst is transferred to the regenerator from the bottom of the stripper. Regenerator combustion gases lift the regenerated catalyst in the upper portion of the turbulent-phase fluidized bed to the cone-shaped acceleration zone and then to a riser-type lift line. The regenerated catalyst is then carried to the catalyst hopper located at the end of the lift line. Catalyst circulation rate is calculated from the delta coke and coke yield.
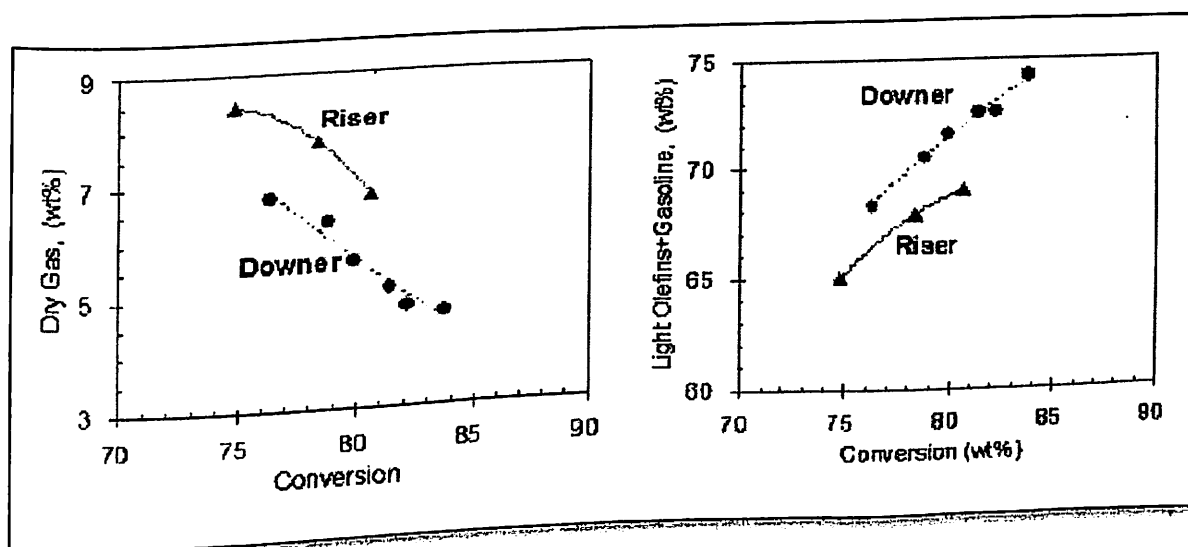

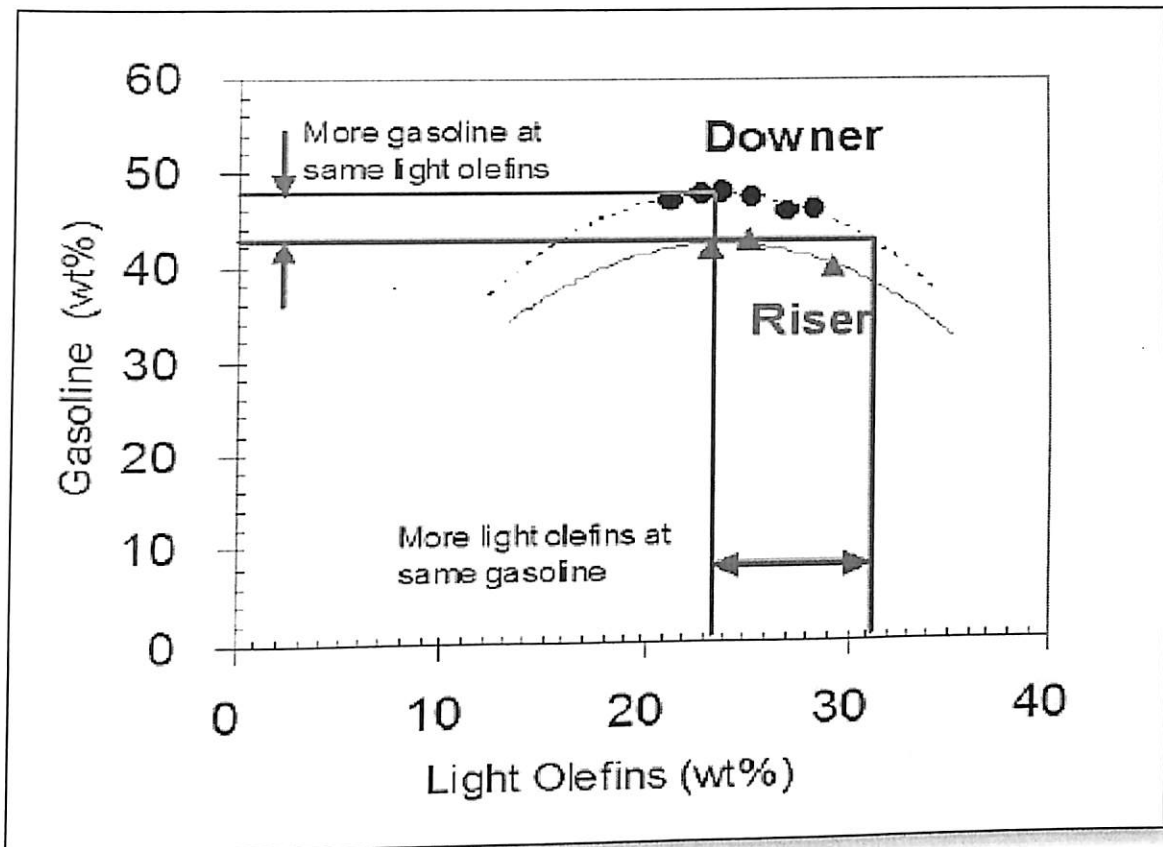**Fig 1.20   Comparison of product yields from Riser and Downer pilot plant**

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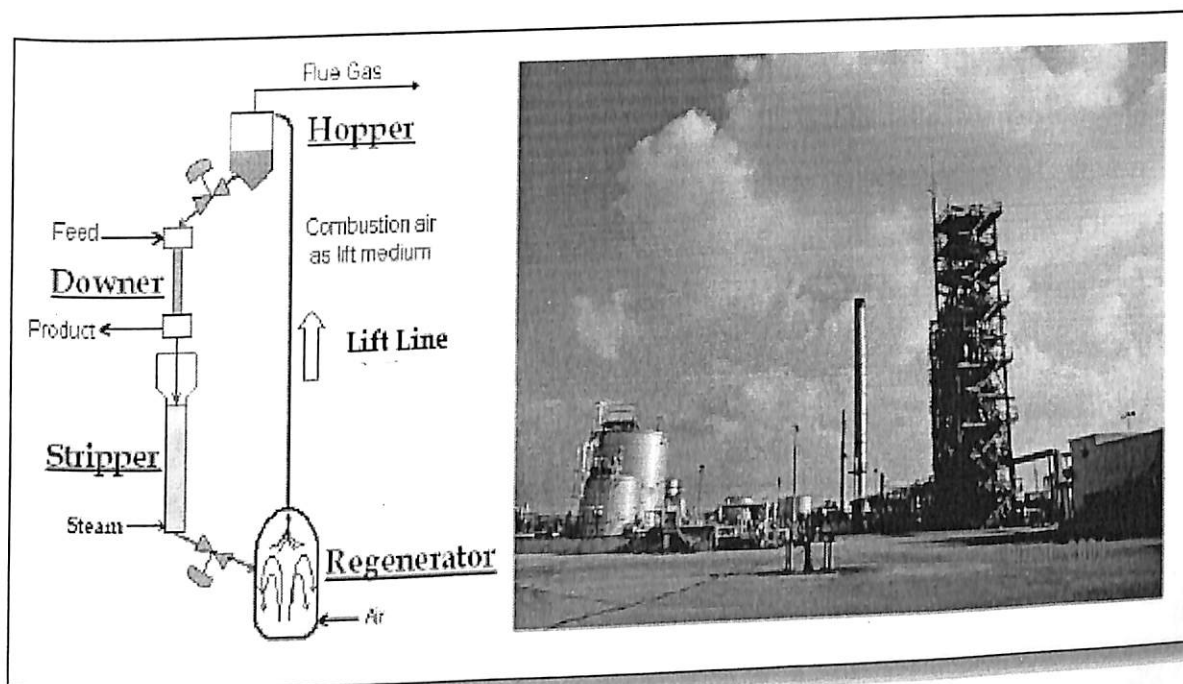*Figure 1.21*   **Advantage of Downer versus Riser for Light Olefins**

Figure 1.22   **Schematic diagram of 30 BPD HS-FCC Demonstration Plant at Saudi Aramco's Ras Tanura refinery**

EMERGING TECHNOLOGIES

New technologies like Deep catalytic cracking (DCC) and Non-regenerative catalytic cracking are emerging on the petrochemical horizons.

The DCC process developed by Research Institute of Petroleum Processing (RIPP) of China. DCC offers higher conversion of VGO to Propylene (typically 21wt %) as compared to conventional FCC. The DCC naphtha is rich in Benzene, Toluene and Xylenes (BTX) which may be recovered by solvent extraction as useful aromatic products. Main limitation of DCC process is that its gas oil would need severe hydro- treating due to very high aromatic content (typically 75wt %).

Non-regenerative catalytic cracking (NRCC), based on the concept of milli seconds catalytic cracking (MSCC), increases the yield of Propylene. The prime technological advantage of this process is higher throughput besides low coke formation.

1.7 DEEP CATALYTIC CRACKING (DCC)

DCC is a promising new technology for the production of light olefins from heavy feed stocks. It is especially attractive for producing propylene and butylenes and offers some competitive advantages of steam cracking and conventional FCC. The total yield of gaseous olefins in DCC process can be as high as 40% wt of the feed stock as against 10-15% wt obtained in conventional FCC. In DCC process, LPG is rich in propylene and butylenes. A DCC unit can be used for conventional FCC duty but the reverse is not possible. A DCC catalyst has the following essential features:

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

The DCC catalyst formulation is currently designed to optimize the formation of carbonium ions. This is because olefins tend to from carbonium ions easier than paraffin's

As the DCC process generates much larger quantities of gaseous product, its reactor

has a large diameter to prevent catalyst carry over. The operating conditions of DCC process are more severe than those of conventional FCC. However, the reaction temperature of DCC is much lower than that of steam cracking. The notable feature of DCC process is that coke formation is quite low.

A traditional reactor/regenerator unit design uses a catalyst with physical properties similar to traditional FCC catalyst. The DCC unit may be operated in two operational modes: maximum propylene (Type I) or maximum iso-olefins (Type II). Each operational mode utilizes unique catalyst as well as reaction conditions. DCC maximum propylene uses both riser and bed cracking at severe reactor conditions, while Type II utilizes only riser cracking like a modern FCC unit at milder conditions.

The overall flow scheme of DCC is very similar to a conventional FCC. However, innovations in catalyst development, process variable selection and severity enables the DCC to produce significantly more olefins than FCC in a maximum olefins mode of operation.

DCC Product Yield

Products, wt% FF	DCC Type I	DCC Type II	FCC
Ethylene	6.1	2.3	0.9
Propylene	20.5	14.3	6.8
Butylene	14.3	14.6	11.0
in which IC_4 =	5.4	6.1	3.3
Amylene	—	9.8	8.5
in which IC_5 =	—	6.5	4.3

Table 1.5

This technology is suitable for revamps as well as grass root applications.

Commercial plants: Currently seven units are in operation, six in China and one in Thailand.

Reference: Chapin, Letzsch and SwatYI "Petrochemical options from deep catalytic Cracking and the FCCU," 1998 NPRA, AM-98-44.

Licensor: Stone & Webster Inc., a Shaw Group Co. /Research Institute of Petroleum Processing.

Deep Catalytic Cracking

Product vapors ◄——————

— Reactor

Vapor and catalyst
— distributor

Flue gas ◄——————

Regenerator ——►

— Stripper

Combustion air ——►

——► Reactor riser

Regen. cat. ——
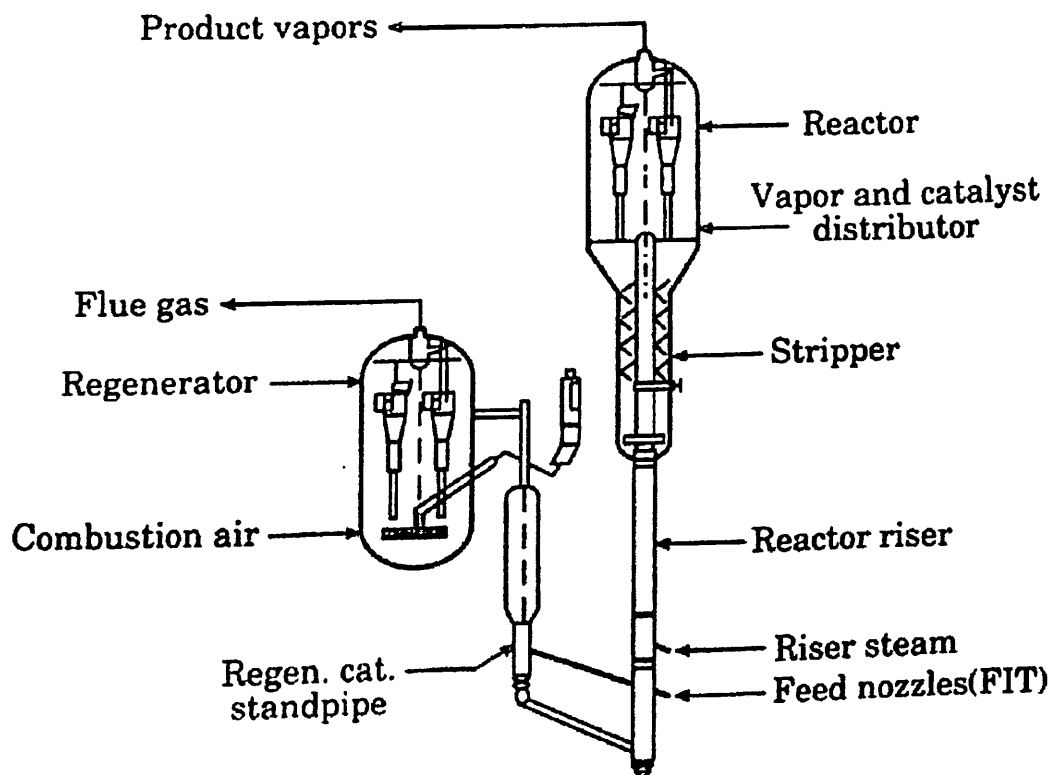standpipe

——► Riser steam
——► Feed nozzles(FIT)

Fig 1.23

1.8 NON-REGENERATIVE CATALYTIC CRACKING

R&D work NRCC is being actively pursued in USA. H-Transfer reaction can be minimized by keeping the contact time very low (<0.01 second) and increasing the cracking temperature to about 600oC. As a result the coke formation from gas oil feed is so low that upon 10,000 volume feed could be processed per volume of the catalyst while maintaining a conversion comparable to FCC.This would reduce the reactor size by a factor of 100.The gas yields can be increased by increasing the conversion above 70% and up to 80% of C3 – C4 products are olefins. However, there are still some unresolved problems of NRCC technology. e.g.,

High pressure drop due to increased space velocities.

➤ Rapid heat transfer to compensate for the cracking endothermicity without promoting thermal cracking.

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CHAPTER 2

COMPARISON OF PROPYLENE

PRODUCTION ROUTES

CHAPTER- 2

2.1 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 offers 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 feed stocks 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 feed stocks 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 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 the Figure given below. . 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 $40 per barrel. Near the low end of this range crude oil derived

feed stocks 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 feed stocks depends on expectations for long-term crude oil prices relative to natural gas based feed stocks. 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.

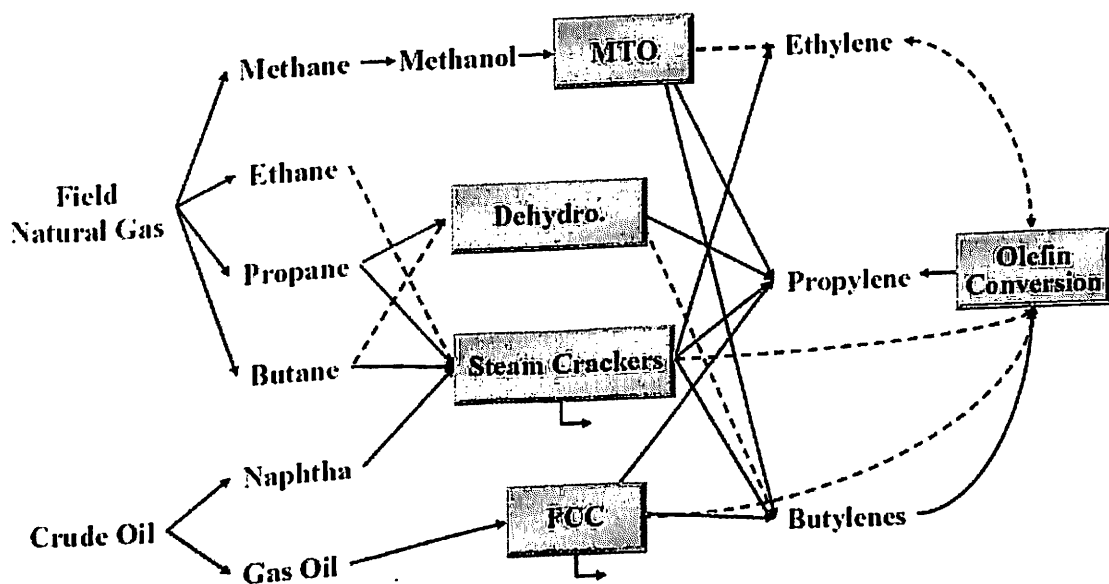## Feedstocks for Commercially Available Routes to Propylene

Fig 2.1

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,

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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.

2.2. 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.

Co-product Production

Fig 2.2

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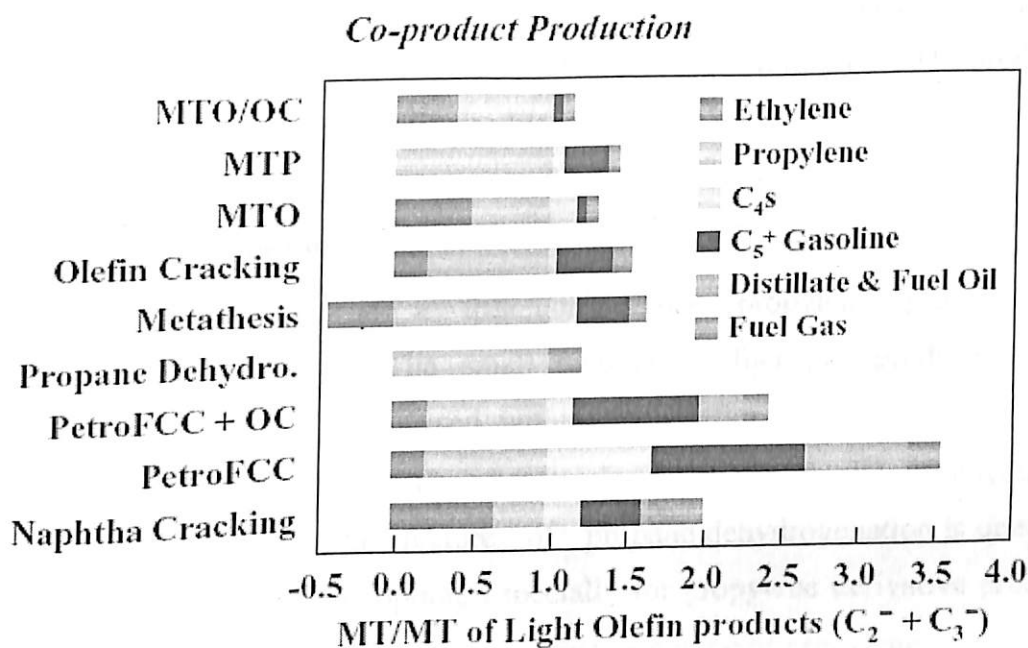
Naphtha cracking produces around 0.67 tons of ethylene and 0.33 tons of propylene for every ton of light olefin produced. In addition there are about 0.7 tons of C4+ byproducts that must be marketed to achieve good economics. Although not very selective towards propylene, naphtha cracking remains the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

FCC and Petro FCC 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 ATOFINA/UOP 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 feedstocks 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 ATOFINA/UOP Olefin Cracking process can be integrated with the UOP/HYDRO 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 C_4^+ 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.

2.3. 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.

CHAPTER 3

OUTLOOK

CHAPTER- 3

OUT LOOK

Fluid Catalytic Cracking (FCC) units are taking on an increasingly important role in the supply of light olefins, particularly propylene, to petrochemical markets refineries in Asia. Pushing the FCC operation to achieve these new levels of propylene requires careful consideration of unit capabilities, unit operations and catalyst technology. Propylene is a co-product of two refinery processes, steam cracking and fluid catalytic cracking (FCC). Steam crackers, where the primary product is ethylene, also supply two-thirds of the world's demand for polymer grade/chemical grade (PG/ CG) propylene.

Propylene demand growth in Northeast Asia will be strong over the next years, mainly driven by economic expansion in China. As steam cracking capacity expansions will not keep up with the demand growth, the region will increasingly need propylene derivative imports. North America is and will likely remain a net exporter of propylene and its derivatives due to its large FCC capacity base. However, refining capacity is tight in North America, and strong demand for transportation fuels has led to record prices for gasoline this year. The economic incentive for refiners to devote FCC capacity to propylene production in North America will rather diminish, and propylene exports from North America into other regions will decrease. Given the strong demand growth for propylene derivatives in Asia, this leaves the Middle East as a potential exporter of propylene derivatives into Europe.

As the economic incentive for increased propylene yields from FCC units is growing, FCC operators traditionally have the following options:

a) Use ZSM-5 additives

b) Increase riser temperature

c) Increase conversion

d) Change feed composition

ZSM-5 based additives, although introduced more than 20 years ago as a way to

increase the octane value of FCC gasoline, are now primarily being used to increase light olefins yields from the FCC unit. In fact, the use of these additives is by far the most effective way to increase light olefins yields, as typically only a few weight percent of additive in the inventory improve light olefins yields significantly. Basically, ZSM-5 cracks gasoline range olefin molecules into mainly C3 and C4 olefins. While ZSM-5 additives are formulated with different levels of ZSM-5 crystal, it is important to note that it is the actual activity that determines the effectiveness of the additive. Only optimized formulation and proper stabilization of the additive ensure that the FCC operator sees the full benefit in terms of yield optimization. The demand growth for propylene provides an attractive opportunity for FCC operators to improve profitability.

New options must be considered to meet the future propylene demands because conventional steam cracking technologies may be unable to close the gap between demand and supply. There are many alternatives available for increasing propylene production and each of these alternatives can be the best route to propylene for certain situations. Each producer should consider the key selection factors to help determine which route(s) to propylene is suitable for a particular project.

Considering South East Asia the following routes supply propylene in the following proportion.

1. Steam Cracking (Naphtha Cracking) – 70%
2. Fluid Cracking Unit – 30%

Propylene production in Southeast Asia is expected to grow by close to 4% annually between now and 2010, with FCC sourced propylene growing by about 10% per year. By the end of the decade, FCC units will provide more than 30% of all propylene in the region.

The Refiners should modify FCC technology so as to meet Propylene Demand and should go through DCC technology Developed by SINCOPEC and RIPP china.

DCC is the Extension of FCC for more active / shape selective and severe operation for more olefin production. DCC is important for interfacing refinery with petrochemicals.
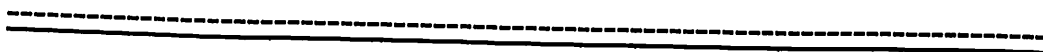
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