ON-PURPOSE PROPYLENE FROM OLEFINIC STREAMS

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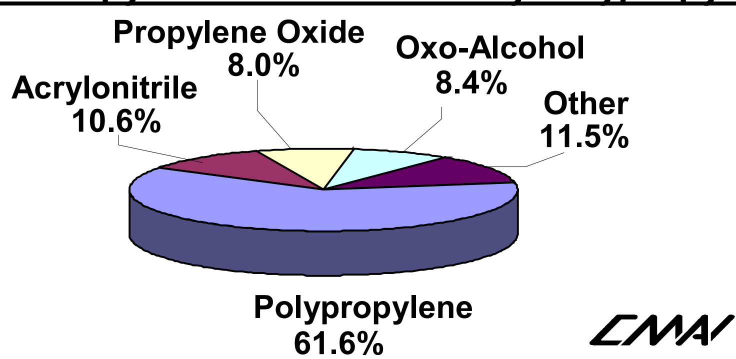
Abstract

ExxonMobil recently completed development of a new, on-purpose propylene technology based on catalytic naphtha cracking, called the ExxonMobil PCC^{SM} Process. This process offers significant advantages over prior systems. The development of this technology was driven by the need for increased volumes of propylene to supplement supplies of propylene currently produced as co-products in Steam Cracking and Fluid Catalytic Cracking. The primary feedstocks for this process are olefinic naphtha streams from Cat Crackers, Cokers, and Steam Crackers, typically used as gasoline blend stocks. These streams can have high sulfur contents and it is expected that additional processing will be needed to meet future regulations in countries required to produce low sulfur gasoline. Hydrotreating, the likely candidate for sulfur reduction, requires hydrogen and consumes olefins, which not only adds to operating expense but also reduces the octane value of the product going to gasoline blending. The PCC Process provides a means of converting olefin molecules in these naphthas to high value ethylene, propylene, and (optionally) butylene prior to hydrotreatment, thereby reducing hydrogen consumption and octane loss in conjunction with upgrading lower value naphtha olefins to high value chemical products.

Propylene needs

Propylene is one of the fastest growing petrochemicals, driven primarily by the high growth rate of polypropylene (Figure 1). Polypropylene demand currently is growing in the U.S. at 6 %/yr, and in some regions of the world the growth rate is considerably higher.

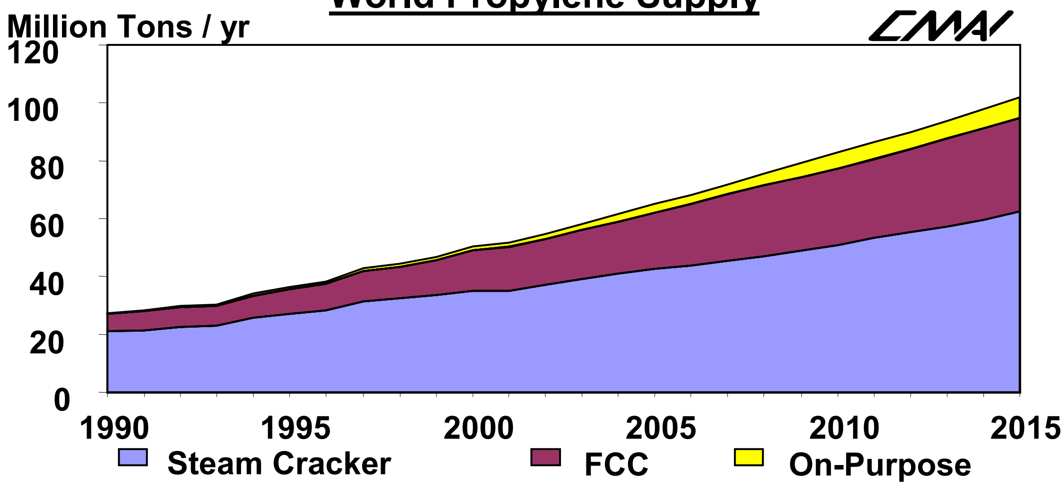
Figure 1
50M Ton Propylene Market Driven by Polypropylene



While steam cracking continues to supply most of the world's propylene, there is an increasing need for propylene from other sources. The growth in steam cracker capacity is driven by the need for ethylene, and co-product propylene production is not keeping up with propylene demand growth. Furthermore, co-product propylene production from steam cracking is determined largely by the feedslate and much of the new steam cracking capacity is based on ethane feed, which produces little propylene.

Propylene production from FCC units is the second most important source of worldwide petrochemical propylene supply (Figure 2). As demand has increased, Refiners have been able to increase propylene production in FCC's by optimizing catalyst and operating conditions. In particular, use of ZSM-5 catalyst additive is increasing as Refiners find it profitable to boost FCC propylene production. In the U.S., FCC propylene has in fact surpassed steam cracker propylene as the largest source of U.S. petrochemical propylene supply.

Figure 2
World Propylene Supply



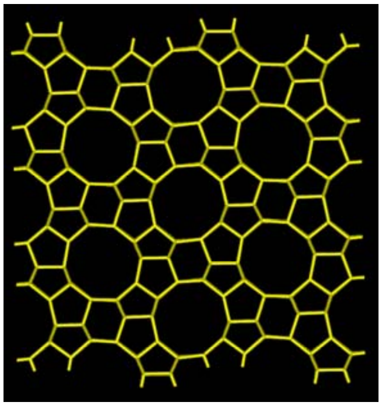
However, the potential for production of propylene in existing Refinery FCC's is limited (by the capacity of the units and the cost to debottleneck to accommodate increased volumes of gas). New on-purpose propylene technologies will be required to provide the additional supplies of propylene needed to meet the growth projections. Several on-purpose propylene technologies are available, such as propane dehydrogenation and metathesis, but have seen only limited applicability. Propane dehydro requires high investment and both technologies require opportunistic feedstock economics. A newly emerging technology involving catalytic cracking of olefinic naphthas and/or C4's can now be considered as well.

Olefin Cracking for Propylene

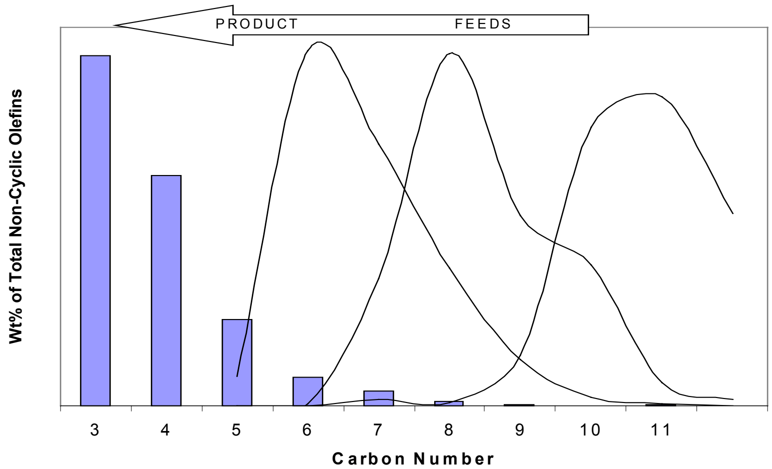
Catalytic cracking of olefinic streams to produce primarily propylene along with ethylene and butylenes has been described by several companies in recent years, including Mobil (MOI℠), Kellogg Brown & Root (SUPERFLEX℠) and Lurgi (PROPYLUR®). These processes are characterized by the use of ZSM-5 catalysts to convert higher molecular weight olefins and paraffins to lighter olefins.

ZSM-5 is an aluminosilicate zeolite having a pore size of 5.1 to 5.6 Angstroms. This pore size provides shape selectivity by limiting access to the interior of the catalyst to mostly linear (non-branched or mono-methyl) paraffin and olefin molecules. The active sites in the zeolite catalyst promote cracking. The resulting distribution of C_3 and higher olefins approaches equilibrium, with propylene being the olefin product having highest yield (see Figure 3). Ethylene also is produced, but its yield is largely dependent on reaction conditions. Reaction chemistry and the use of ZSM-5 catalyst favor conversion of the olefinic molecules, but depending on severity more or less paraffin conversion may occur also.

Figure 3
Reaction Equilibration in Catalytic Naphtha Cracking



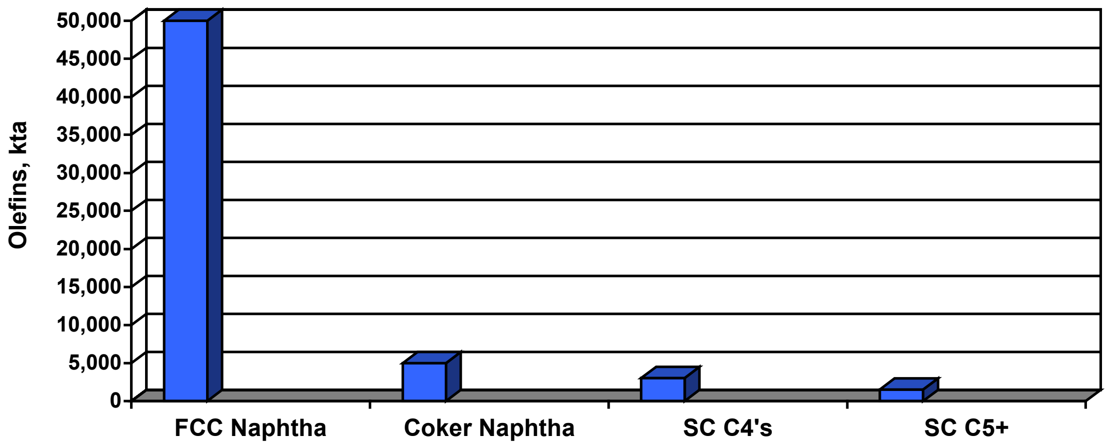
ZSM-5
3D(10x10x10)
5.3 x 5.6 Å, 5.1 x 5.5 Å



Feedstock Considerations

Modern polypropylene units require about 300 thousand metric tons per year (300 kta) of propylene per train. Production of such large volumes of propylene from olefinic naphtha and C4 cracking requires large volumes of olefinic feedstock. Such large quantities of olefinic feedstock molecules can be obtained from FCC's (cat naphtha), Cokers (coker naphtha), and steam crackers (C4's and pyrolysis gasoline). But by far, the largest source of olefinic feedstock molecules is cat naphtha from FCC, with steam crackers lagging far behind (see Figure 4).

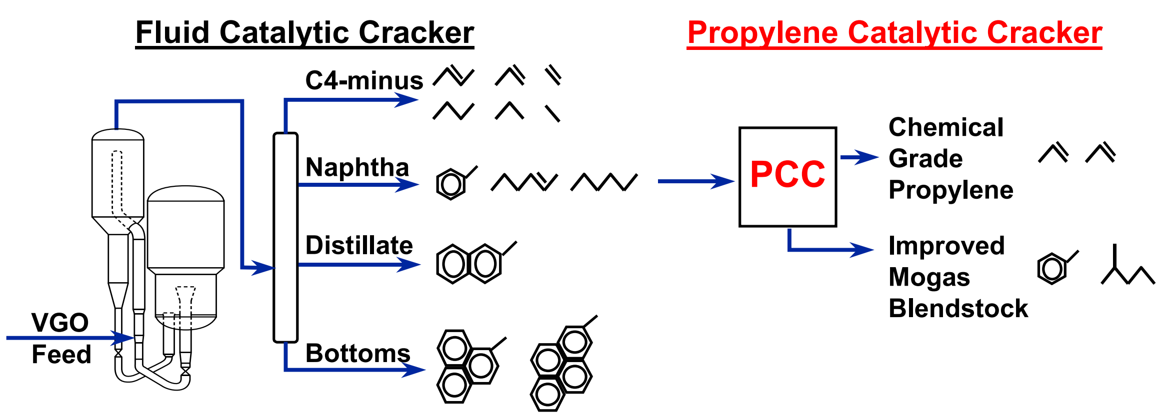
Figure 4
U.S. Olefin Feedstock Potential



Depending on the FCC feed, processing conditions, and naphtha cut range, cat naphtha may contain 20-60% olefins, which makes it ideal for catalytic conversion to propylene. Figure 5 illustrates the relationship of an integrated process scheme.

Figure 5
PCC Integration with FCC

- **FCC: Primarily catalytic cracking of side chains and saturated rings**
- **PCC: Selective catalytic cracking of olefins provides advantage**
- **Improved Mogas to meet emerging regulatory environment**



However, while cat naphtha is a good feedstock for catalytic conversion to propylene, it also is a prime gasoline component. Refiners rely on its octane content to blend gasoline. Nonetheless, there are synergies with Refining associated with processing this stream to convert its olefin content to propylene.

Cat naphtha typically contains sulfur, the amount of which depends on the feed sulfur content and on whether or not the FCC feed is hydrotreated. Future gasoline regulations in the U.S. and Europe are expected to require significant reductions in gasoline sulfur levels (to 50 wppm, or less). In most locations this will require treating cat naphtha to reduce its sulfur level. The most likely option available to Refiners today involves hydrotreatment.

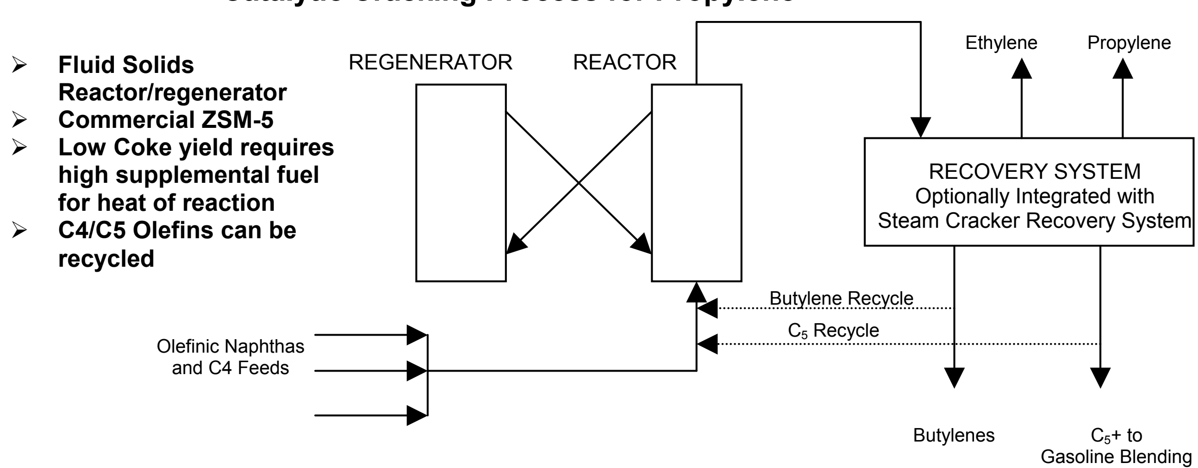
Hydrotreatment, however, also saturates olefins and results in a loss in cat naphtha octane. This octane loss can be a significant debit in Refinery economics. Technologies such as the ExxonMobil SCANFining^{SM} Process can minimize the amount of olefin saturation and thereby minimize the resulting octane loss.

Catalytic conversion of cat naphtha olefins to propylene before hydrotreatment converts most of the contained olefins to light olefins, thereby further minimizing the potential for octane loss in hydrotreatment. Also, the catalytic conversion step increases the octane level of the naphtha. The catalyst can crack only the mostly linear (and therefore low octane) olefin and paraffin molecules, thereby concentrating the higher octane aromatics. This, plus isomerization and some additional aromatics formation, provides an increase in octane level of the residual naphtha.

Facilities Description

An economical unit for processing large volumes of olefin-containing feedstocks to produce world-scale quantities of on-purpose propylene requires appropriate selection of reaction system for the production, and downstream processing facilities for the recovery, of the desired petrochemical products. A fluid solids reactor/regenerator configuration is well suited for such large capacity units. Figure 6 shows a conceptual flowplan for a typical fluid solids catalytic naphtha cracking facility to produce on-purpose propylene.
Feed naphtha obtained upstream of a Refinery desulfurization facility (if present) is

Figure 6
Catalytic Cracking Process for Propylene



preheated and is injected into the reactor of a fluid solids reactor/regenerator system. The hot, regenerated catalyst contacting the preheated feed supplies the necessary sensible heat to complete preheating the feed to reaction temperature, and supplies the necessary heat of reaction.

These fluid solids systems can use commercially demonstrated ZSM-5 fluid solids catalysts, such as those employed commercially in FCC as catalyst additives. Coke make on this type of catalyst when cracking naphtha is low, requiring a means to provide supplemental fuel to burn in the regenerator to supply the necessary sensible heat and heat of reaction.

Reactor effluent is cooled and vapors are compressed for product recovery. Once-through yields of ethylene and propylene typically are in the range of 10-20 wt.% and 30-40 wt.% on feed olefin content, respectively. If so desired, reaction severity can be increased to crack more of the feed paraffin content in order to increase the yield of propylene and other light olefins. Butylene yield is typically about $^{2}/_{3}$ that of propylene (Figure 3). Butylenes can be recovered as product, or can be recycled (optionally with unconverted C_5+) for additional propylene production. The characteristics of ZSM-5 (Figure 3) provide the mechanisms to oligomerize and recrack butylenes to produce a distribution of light olefins favoring propylene yield. The choice between recycling butylenes or not depends on the market for co-product butylenes and is site specific.

Since the reactant species are mostly olefins, and the Refinery naphtha streams typically contain only 20-60 wt.% olefins, a large portion of the product slate is comprised of unconverted naphtha. In addition, some aromatics are formed in the reaction zone (the amount depends on the conditions and technology employed). While the more olefinic C_5 cut may be recycled if desired, a major benefit of this process is the production of an increased octane, reduced olefin content naphtha which would be recovered for blending into gasoline. If naphtha feed desulfurization were required prior to installation of this process, the product naphtha stream can be processed in this desulfurization unit for cleanup en route to gasoline blending.

Propylene is produced at concentrations ranging from 85% to 90% of the C_3 stream, depending on the technologies and catalysts employed. Further processing, including fractionation and contaminant removal, is required to supply polypropylene feed.

Ethylene can be recovered in order to achieve maximum economic benefit. The ethylene concentration in the C_2- stream is considerably greater than in similar streams produced from conventional FCC, making it more suitable for processing in steam cracker recovery facilities.

Supplemental Feeds

While well suited for large volumes of cat naphtha feed, these naphtha cracking facilities can accommodate smaller volumes of supplemental feeds at low incremental investment. An integrated Petrochemical producer therefore would find it economical to design their naphtha cracking unit to accommodate those olefinic naphthas and C4's which otherwise would require costly processing to meet increasingly stringent fuel quality requirements. Such supplemental feeds can include:

- Coker naphtha
- Visbreaker naphtha
- Pyrolysis naphtha from steam cracking
- Steam cracked C4's
- MTBE raffinate
-

As in the case of recycled butylenes, the characteristics of ZSM-5 (Figure 3) provide the mechanisms to oligomerize and recrack butylenes to produce a distribution of light olefins favoring propylene yield.

An advantage of a fluid solids system is that it is robust with respect to feed quality considerations. Catalyst circulation through the regenerator provides a mechanism to regenerate the catalyst by removing coke deposits. This provides the flexibility to process a variety of feed streams having a broad range of qualities, such as diolefins, aromatics, or heavy ends that could contribute to catalyst fouling and deactivation in a fixed bed configuration. Specifically, steam cracked C4's containing butadiene can be processed in this type of facility without necessity for selective butadiene hydrogenation, if desired. This provides a very attractive means of converting steam cracked C4 co-product to additional propylene in locations where the market for such C4's is limited.

New ExxonMobil PCC^{SM} Process

The criteria for a commercially viable on-purpose propylene process based on naphtha cracking can be summarized as follows:

- Economical investment, operating cost
- Reliable and demonstrated reaction system and catalyst
- Selectivity to high value co-products
- Production of residual naphtha having desired properties for gasoline blending

ExxonMobil Chemical Co. conducted an evaluation to compare different catalytic naphtha cracking technologies against these criteria. This evaluation confirmed the need for a new process to achieve the desired characteristics listed above. Together with its affiliate, ExxonMobil Research and Engineering Co., an improved process concept was identified and subsequently was progressed through the development phase.

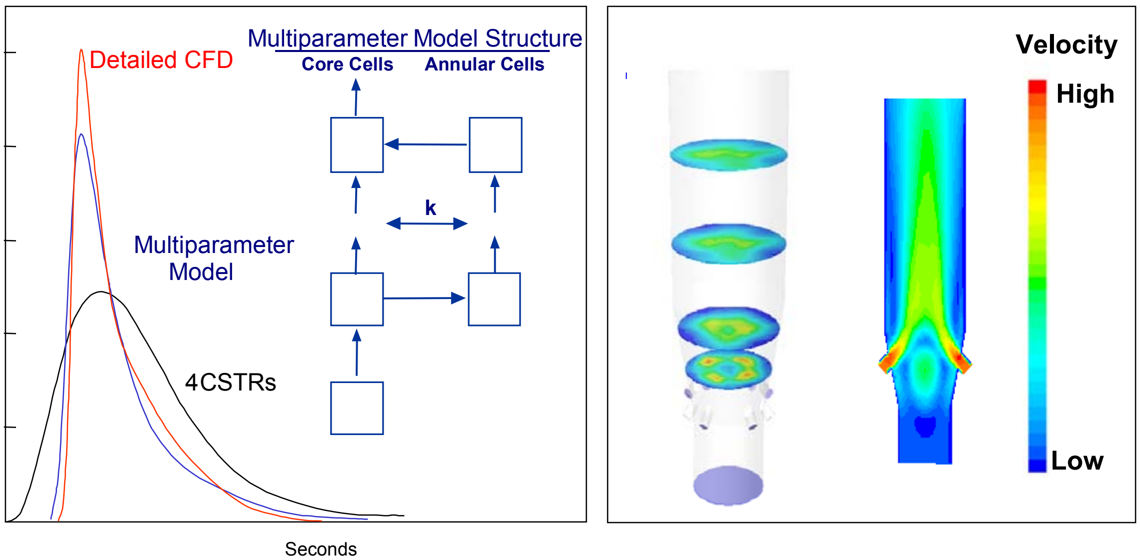
ExxonMobil now is pleased to announce the development of a new fluid solids naphtha cracking process called the ExxonMobil PCC^{SM} Process (where PCC stands for Propylene Catalytic Cracking). The PCC Process employs an optimum catalyst, reactor design, and patented combination of optimum operating conditions to achieve a high degree of reaction selectivity. These provide PCC with economic advantages over prior fluid solids configurations.

The key distinction between PCC and prior fluid solids technologies is the use of a patented combination of selective reaction conditions, proprietary equipment, and catalyst designed to crack feed into propylene and other light olefins. These patented conditions and process configuration are designed to minimize the downgrade of gasoline molecules to low value fuel components.

Figure 7
REACTOR / REGENERATOR SCALE-UP

Based on extensive ExxonMobil FCC scale-up experience

- **FCC pilot plant tracer / hydrodynamic vs Commercial unit data**
- **Computational Fluid Dynamics analysis of riser**



These conditions also produce product C_2 and C_3 streams that are highly concentrated in olefin content, resulting in lower investment for product recovery. Specifically, the PCC reactor produces propylene at the concentration required for Chemical Grade propylene (95%), thereby avoiding costly product fractionation. In addition, the optimized conditions minimize the production of aromatics, which will be an important consideration in meeting future gasoline regulations. These characteristics provide PCC with economic advantages over prior fluid solids configurations, as well as alternate on-purpose propylene technologies, and are summarized in Table 1.

Table 1
Characteristics of PCC vs. Other Naphtha Cracking Processes

	ExxonMobil PCC	Other Fluid Bed Processes	Fixed Bed	Propane Dehydro
Robust Reaction Environment	Yes	Yes	No	Yes
Feed Flexibility	Yes	Yes	Limited	No
Selective Olefin	Yes	No	Unknown	Not Applicable

conversion				
Propylene recovery cost	Low	High	Unknown	High
Residual naphtha aromatics content	Moderate	High	Unknown	Not Applicable

ExxonMobil recently has completed the development of this new PCC Process. The development program has involved extensive testing in ExxonMobil's pilot facilities (Figure 8). PCC technology builds upon ExxonMobil's extensive background in FCC and in the production and recovery of propylene and ethylene from FCC and steam cracking facilities (Figure 9, 10).

Figure 8
Large 1.5 bbl/d riser pilot plant used in the development of the PCC Process

ExxonMobil Chemical currently is developing plans to implement this technology at one of its own Petrochemical sites, as well as evaluating making the technology available for licensing.

Conclusions

A fluid solids process has been found to be preferable for on-purpose production of large volumes of propylene from olefinic streams, as needed for world-scale polypropylene units. This type of facility can process a variety of feeds, including preferably Refinery cat naphtha, steam cracker pygas, olefinic C4's, and other Refinery or Chemical plant olefinic streams. ExxonMobil has developed and optimized the design of its new PCC Process in order to provide a cost effective, best in class on-purpose propylene process by building on its FCC and olefin production experience.

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Appendix

Figure 9

EXXONMOBIL FCC EXPERIENCE

- 1.6 Mbbl/d FCC capacity owned and operated by ExxonMobil
  - 28 operating units
- Total of 71 FCC units designed by EMRE including Licensee units
- ExxonMobil Process Research Labs(EMPR)
  - Catalyst Development
  - Process Development
- ExxonMobil Research and Engineering (EMRE)
  - Process Development, Engineering, Reactor Design

FLEXICRACKING Unit

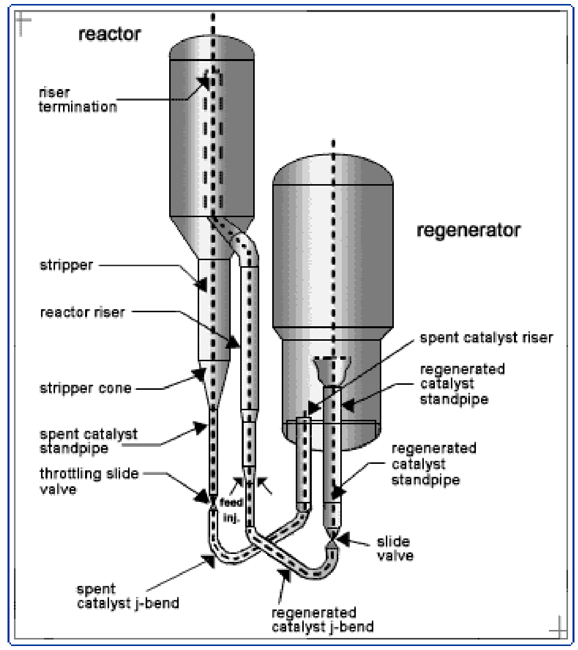

Figure 10

EXXONMOBIL CHEMICAL EXPERIENCE

- 5th largest Chemical company on World-wide basis
- One of the largest world-wide producers of olefins; over 8 Mt/yr Ethylene, 4.5 Mt/yr Propylene capacity
- Highly integrated with Refining;
  - Greater than 50% Propylene recovered from FCC's
  - Steam Cracker feeds, by-product integration
- Design and Technology support for Olefin facilities