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## FCC Process Role in Propylene Demands

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**Abstract** It is widely recognized that naphtha steam crackers are the largest current source of propylene. The yield of propylene from a naphtha cracker is approximately half the yield of ethylene 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 by-product. The availability of ethane at standard gas prices has attracted a large buildup of ethane-based steam cracker capacity, which produces very little propylene. As a result of buildup of ethane-based crackers, the propylene production rate from steam crackers is anticipated to fall, though the demand for propylene is expected to increase relative to the demand for ethylene. These market dynamics, if proven true, will result in a growing gap between propylene demands and propylene supplied from steam crackers, placing more emphasis and creating more opportunity for fluid catalytic cracking unit (FCC) units. The second largest source of propylene supplied for petrochemical application is from FCC units. The primary function of FCC units has typically been to produce gasoline. However, refiners have been taking advantage of the opportunity to produce and recover more propylene from FCC units by increasing the reaction severity via riser temperature, adding shape-selective catalyst, and installing propylene recovery units (PRUs). In this article propylene production methods are reviewed and comparisons between the methods are made.

**Keywords** demands, FCC, methods, process, propylene, steam crackers

### 1. Introduction

The market for propylene as a basic intermediate petrochemical continues to grow at average rates of 4–5% per year. The largest source of propylene supply to the petrochemical markets is steam crackers (as a by-product of ethylene), and the second largest source of propylene supply to petrochemical markets is refinery fluid catalytic cracking (FCC) units (as a by-product of gasoline and distillates). However, the FCC unit is becoming increasingly important as a source of propylene supply to meet future demand growth into the world petrochemical markets. Ethylene growth rates have lagged behind propylene growth rates and will continue to do so in the future. Similarly, the growth rate of transportation fuels is several times lower than propylene. Currently steam cracking and refinery operations constitute over 97% of the propylene produced today. Clearly alternative routes to propylene will gain prominence as producers seek to leverage their

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existing assets and available internal streams to find an optimum solution for meeting the demand for propylene. The process according FCC technology can be a solution to meeting the propylene gap in the future. The FCC unit continues to be the dominant conversion process in the petroleum refinery and increasingly its desired product slate is being shifted toward light olefins production. The product slate from the FCC units looks attractive when propylene is desired. Despite the technologies available to increase light olefins production in the FCC unit, intense research activity in this field is ongoing. The conventional FCC process is being modified to a high-severity FCC process suitable for an integrated refinery–petrochemical complex (Ma'adhah et al., 2000; Ino et al., 2004). The high-severity fluid catalytic cracking (HS-FCC) process can increase the yield of light olefins to 40 wt% of the product, versus the normal 4–10 wt% the process combines mechanical modifications with changes in process variables and catalyst formulation. The main operating regime of this novel refining process is high reaction temperature (about 600°C or more in riser), short contact time, high catalyst–oil ratio (higher than 10), and a special downflow reactor system (Ino et al., 2004).

## 2. FCC Process Description

The most common process is FCC, in which the oil is cracked in the presence of a finely divided catalyst that is maintained in an aerated or fluidized state by the oil vapors. The fluid cracker consists of a catalyst section and a fractionating section, which operate together as an integrated processing unit (Figure 1). The catalyst section contains the reactor and regenerator, which, with the standpipe and riser, forms the catalyst circulation unit. The fluid catalyst is continuously circulated between the reactor and the regenerator using air, oil vapors, and steam as the conveying media. A typical FCC process involves mixing a preheated hydrocarbon charge with hot, regenerated catalyst as it enters the riser leading to the reactor. The charge is combined with a recycle stream within the riser, vaporized, and raised to reactor temperature (900°F–1000°F) by the hot catalyst. As the mixture travels up the riser, the charge is cracked at 10–30 psi. In the more modern FCC units, all cracking takes place in the riser. The reactor no longer functions as a

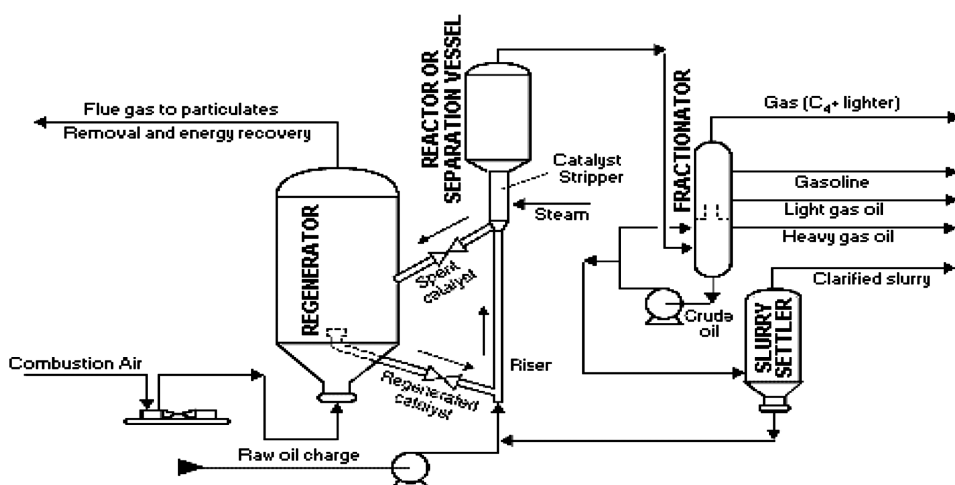


Figure 1. Fluid catalytic cracking process.

reactor; it merely serves as a holding vessel for the cyclones. This cracking continues until the oil vapors are separated from the catalyst in the reactor cyclones. The resultant product stream (cracked product) is then charged to a fractionating column where it is separated into fractions, and some of the heavy oil is recycled to the riser. Spent catalyst is regenerated to get rid of coke that collects on the catalyst during the process. Spent catalyst flows through the catalyst stripper to the regenerator, where most of the coke deposits burn off at the bottom where preheated air and spent catalyst are mixed. Fresh catalyst is added and worn-out catalyst is removed to optimize the cracking process.

### 3. Propylene Needs

Propylene is one of the fastest growing petrochemicals, driven primarily by the high growth rate of polypropylene. The consumption of propylene is 64% for polypropylene, 10% for acrylonitrile, 7% for propylene oxide, 9% for oxo-alcohol, and 10% for other.

Polypropylene demand currently is growing in some regions of world. Though 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, 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 (Bedell et al., 2004).

### 4. Feed Sources for Production of Propylene

Significant amounts of propylene can be made from feeds as light as methane to heavy oils from atmospheric tower bottoms (ATBs). In most cases it is unrealistic for the existing propylene producer to import large amounts of new feedstocks for propylene production; rather, the best source may be with low value or problematic internal streams within the producing refinery or steam cracker. Table 1 gives a summary of major propylene production technologies as a function of feed source. Currently steam cracking and refinery operations constitute over 97% of the propylene produced today. Clearly, alternative routes to propylene will gain prominence as producers seek to leverage their existing assets and available internal streams to find an optimum solution for meeting the demand for propylene (Ino et al., 2004).

### 5. Propylene Production from the FCC Process

In this section all methods for production of propylene from the FCC process will be reviewed.

#### 5.1. Change the Catalyst Type of FCC

Changing the catalyst type of FCC from gasoline mode to propylene mode is one method for increasing propylene in the FCC process. In this field many types of catalyst were given by companies; for example, Grace and Davison and Albemarle and other companies that are known worldwide (Nee and Lesemann, 2004).

**Table 1**  
Propylene production technologies

Feed	Process	Status	Ultimate C <sub>3</sub> H <sub>6</sub> yield % of feed
Methane	Indirect, methanol to olefins, methanol over custom catalyst	No commercial units yet	25–40
Ethylene + Butene	Metathesis, requires clean, high-purity olefins for reaction	Commercialized at Lyondell	90–95
Propane	Dehydrogenation	Several plants, but key is cost-effective propane pricing	80–85
Paraffins	Conventional steam cracking	Propylene recovered as a byproduct, the primary source of propylene	13–16
C <sub>4</sub> –C <sub>10</sub> olefinic	Olefins interconversion over proprietary ZSM-5 based	Sasol Superflex unit was started up in late 2005 catalyst	40–50
Gas oil	Conventional FCC unit	Second major source of propylene but fairly low fuels growth	4–7
Gas oil	High severity FCC unit with proprietary ZSM-5 based additives	Many variations, including KBR's Maxofin	15–25
ATB	High-severity resid FCC with specialized catalyst additives	No commercial units, although quite a bit of research by many	25–30

**5.1.1. Davison Catalysts: Propylene Maximization Technologies.** The use of ZSM-5-based additives is the most cost-effective way to increase propylene production in FCC units. Demand for these additives has increased steadily over the years and the industry has continued to move to lighter activity grades.

Davison Catalysts was the first catalyst manufacturer to supply ZSM-5 based additives for use in FCC units back in 1984, where their primary role was to enhance gasoline octane.

Since then the role of these additives has changed to that of optimizing the yields of high value C<sub>3</sub> = and C<sub>4</sub> = defines while at the same time capturing the boost is gasoline octane. Through continuous R&D efforts, Davison has maintained its position as the worldwide leading provider of ZSM-5-based FCC catalyst technologies. Developments by Davison Catalyst over the years have focused on increasing the intrinsic activity of ZSM-5 additives to enable refiners to more cost-effectively maximize yields of light olefins. With the upturn in the next petrochemical cycle, a further increase in the demands for ultra-high-activity ZSM-5 additives (>>25 wt% crystal) is expected as more FCC units operate to maximize propylene production (Nee and Lesemann, 2004).

**5.1.2. Olefins Max<sup>TM</sup>.** The first real breakthrough in the development of high-activity ZSM-5 additives came with the introduction of Olefins Max, the first such additive to contain 25% ZSM-5 crystal, which at the time was the maximum allowable under

license. This additive rapidly established itself as the benchmark for high-activity ZSM-5 additives and is still the most widely used in the refining industry, accounting for nearly half of all ZSM-5 used. In fact, an analysis of refiners that employ additives containing 25 wt% ZSM-5 crystal confirmed that Olefins Max is by far the additive of choice. The reason for the wide acceptance of Olefins Max is its performance relative to competitive products. Commercial data show that Olefins Max has higher activity per pound of additive compared with competitive products that also contain 25 wt% ZSM-5 zeolite. This activity difference is attributed to the proprietary ZSM-5 zeolite stabilization process employed by Davison Catalysts that ensures maximum ZSM-5 levels in the additive. Stabilization zeolite with phosphorus is a critical process in the manufacture of ZSM-5 additives. Refiners that utilize Olefins Max typically add it to the unit in the range of 3–5 wt% of fresh catalyst addition. However, several refiners have increased Olefins Max additions to levels well above 5 wt% and are getting as much as 16 vol% (9 wt%) propylene from their FCC units (Nee and Lesemann, 2004).

*5.1.3. Olefin Ultra.* The intrinsic activity of Olefins Ultra far exceeds even that of Olefins Max and it provides the highest activity per pound of any commercially proven ZSM-5 additive. The unique matrix system in Olefins Ultra not only ensures maximum activity per unit of ZSM-5 crystal but provides excellent attrition resistance properties. In fact, a major European refiner was able to reduce by almost half the addition of ZSM-5 additive and still achieve the desired yield of propylene. This enable the refiner to reduce fresh catalyst consumption by more than 10%. Olefins Ultra is the ideal choice for refiners wishing to maximize the production of propylene and butylenes from the FCC unit where high levels of conventional additives would be required that would otherwise result in dilution of circulating catalyst inventory. Olefins Ultra is currently being used successfully in 17 refineries around the world (Nee and Lesemann, 2004).

*5.1.4. Davison APEX Project: New Propylene Maximization Technology.* Davison Catalysts has also been actively working on a propylene maximization project with the aim to produce catalysts that give yields in excess of 15 wt% from the FCC unit. A new family of catalysts has subsequently been developed that will allow refiners to take propylene production to a new level. Using proprietary shape-selective zeolite and matrix technology, the catalysts developed within the APX project not only produce exceptional yield of propylene but demonstrate low coke make and good bottom cracking activity in the presence of contaminant metals (Nee and Lesemann, 2004).

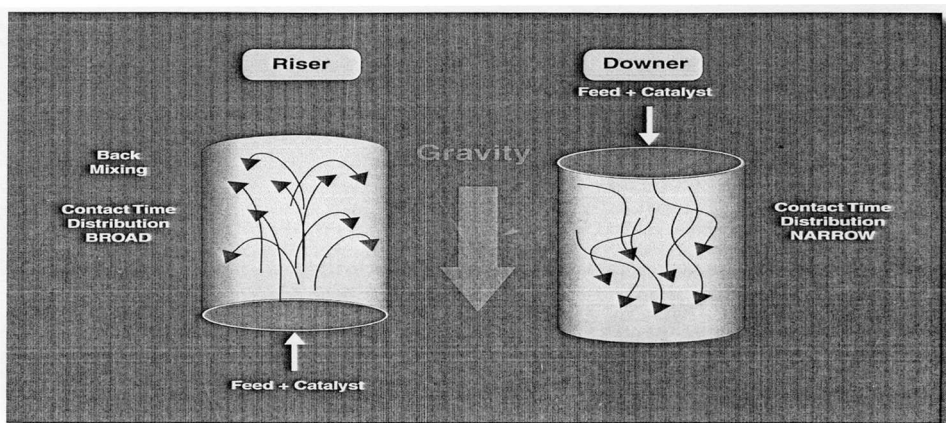
*5.1.5. Conclusion for FCC Catalyst/Additives Effects on Propylene Increasing in FCC Process.* The demands for propylene from FCC units will increase over the next few years to fill the supply gap that is developing as a result of a lag in steam cracker capacity expansion and an increase in the processing of light feedstocks (e.g., ethane in steam crackers). This will lead to opportunities for refiners to boost revenues by producing incremental propylene for sale into the petrochemicals market through the use of ZSM-5 additive technologies. Davison Catalysts is the leading supplier of high-performance ZSM-5 FCC additives. Olefins Max is the most widely used additive in the industry today by virtue of its performance versus competitive products. To meet the industry's need for additives with even higher activity, Davison introduced Olefins Ultra, which is now being used in 17 FCC units around the world (Nee and Lesemann, 2004).

## 5.2. High-Severity FCC

**5.2.1. Process Features of HS FCC.** The process scheme of the HS-FCC process consists of several steps such as reaction, stripping, regeneration, and separation. Oil feedstock is dispersed with steam and feed to the system and then contacted with the hot regenerated catalyst in a downer reactor and catalytically cracked. Coke deposited on the catalyst is stripped with steam and transferred to the regenerator where air is introduced and coke on the catalyst is removed by combustion. The hot regenerated catalyst is returned to the reactor via a catalyst hopper at a controlled circulation rate to achieve heat balance of the system (Ino et al., 2004).

**5.2.2. Downflow Reactor.** A downflow reactor system has been adopted for HS-FCC processes. The catalyst and the feed flow downward along with gravity to minimize back-mixing in the reactor and to obtain a narrower distribution of residence time. The selection of an optimum residence time allows the maximization of intermediate products such as gasoline and light olefins. The downflow reactor permits higher catalyst–oil ratio 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 downflow reaction would ensure plug flow without back-mixing. Because the FCC process involves successive reactions, the desired products such as olefins and gasoline are considered intermediate products. A suppression of back-mixing is the key to achieving maximum yield of these intermediates. Figure 2 shows the benefits of operating in a downflow mode (Ma'adhah et al., 2000; Ino et al., 2004).

**5.2.3. High Reaction Temperature.** Conventional FCC is typically operated at low to moderate severity (510°C to 530°C riser outlet temperature) with flexibility to swing between maximum gasoline and maximum distillate mode. Attempts to operate the FCC unit at high severity to produce more light olefin are not economically attractive because incremental light olefins will come at the expense of secondary cracking of gasoline. The secondary cracking of gasoline will result in excessive dry gas (C<sub>2</sub> and lighter) yields. Though the FCC unit has the capability of running at very high reactor temperatures, this



**Figure 2.** Benefits of downflow reactor in FCC operation.



approach is first being looked at to improve the conventional FCC process. The HS-FCC unit is operated under considerably higher reaction temperatures (550°C to 650°C) than conventional FCC units. Under these reaction temperatures, however, thermal cracking of hydrocarbons takes place cocurrently with catalytic cracking, resulting in increased undesirable products such as dry gas and coke (Aitani et al., 2000; Ino et al., 2004).

**5.2.4. Short Contact Time.** The time–temperature relationship in conventional FCC processes suggests that there is an optimum operating window. If the residence time is too short, the bottoms and long residence time promote dry gas production. The short residence time (less than 0.5 sec) of feed and product hydrocarbons in the downer should be favorable to minimize thermal cracking. Furthermore, undesirable successive reactions such as hydrogen transfer reactions, which consume olefins, are being 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 (Ino et al., 2004).

**5.2.5. High Catalyst–Oil Ratio.** In order to compensate for the decrease in conversion due to the short contact time, the HS-FCC process has to be operated at high catalyst–oil ratio (C/O), 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. Catalytic cracking proceeds simultaneously in FCC reactions. It is well known that the ethylene yield is lower and isobutylene yield is high in catalytic compared to thermal cracking at the same conversion. By increasing the catalyst–oil ratio, the effects of operating at high reaction temperature (thermal cracking) are minimized. High C/O increases conversion and decreases temperature drop during the endothermic cracking reaction. Therefore, a high C/O maintains heat balance and helps minimize thermal cracking, overcracking, and hydrogen transfer reactions (Aitani et al., 2000; Okuhara et al., 2001; Ino et al., 2004).

**5.2.6. Pilot Plant Study Experimental.** Experiments were conducted in a downer-type pilot plant with a capacity of 0.1 bbl/day. The pilot plant consists 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 tip 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. Catalyst circulation rate is calculated from the delta coke and coke yield. Typical design parameters of the pilot plant test are presented in Table 2. All tests were conducted at 600°C and a catalyst–oil ratio of 40 using a hydro-treated vacuum gas oil (VGO) of Arabian light origin. The base catalyst is a low cracking activity catalyst containing H-USY-type zeolite with low acid site density. The catalyst was modified with 10 wt% of a high-activity ZSM-5, supplied by Davison Catalysts. The ZSM-5 additive is widely used in the FCC process to increase octane and light olefins yields. The base catalyst and additive were deactivated with 100% steam at 810°C for 6 hr in a fluid-bed steamer before evaluation (Ino et al., 2004).

**5.2.7. Results of Pilot Plant Tests.** The base catalyst has a low-hydrogen transfer activity, which is preferred for light olefins production. However, operating at high reaction

**Table 2**  
Reaction conditions of downer and riser pilot plants

Parameter	Type of reactor	
	Downer	Riser
Reactor outlet temperature, °C	600	600
Pressure (stripper top), kPa	98	98
Hydro-treated VGO feed		
Rate, kg/h	0.4–0.2	0.7–1.0
Preheat, °C	280	280
Catalyst		
Proprietary catalyst		
Inventory, L	8	2
Steam pretreatment for 6 hr, °C	810	810
Circulation rate, kg/hr	13–40	13–18
Catalyst–oil ratio, kg/kg	13–40	13–30

temperature and high C/O ratio compensated for the low cracking activity of the base catalyst. Short contact time also suppressed hydrogen transfer reactions. Based on the intrinsic features of HS-FCC, maximum light olefins yield can be obtained by the combination of optimized catalyst system and operating conditions. The yields of light olefins, liquefied petroleum gas (LPG), gasoline, light cycle oil (LCO), heavy cyclic oil (HCO), and coke make are presented in Table 3 for conventional FCC and HS-FCC. In conventional FCC, the base catalyst yielded about 16 wt% light olefins and 43.4 wt% gasoline compared to 29 wt% light olefins and 45 wt% gasoline in HS-FCC. In the case

**Table 3**  
Comparison of ZSM-5 addition in conventional FCC and HS-FCC

Product yields wt%	Conventional FCC		HS-FCC	
	Base catalyst	Base + 10 wt% high-activity ZSM-5 additive	Base catalyst	Base + 10 wt% high-activity ZSM-5 additive
Dry gas	5.3	6.4	4.6	5.5
Propylene	7.5	13.0	10.7	18.4
Butylenes	8.8	13.6	16.1	17.8
Total C <sub>3</sub> -C <sub>4</sub> olefins	16.3	26.6	28.7	39.3
LPG	20.7	29.3	30.9	40.5
Gasoline	43.4	34.1	45.4	34.0
Light cycle oil (LCO)	15.0	15.4	9.4	9.3
Heavy cycle oil (HCO)	14.3	13.4	6.6	7.1
Coke	2.3	2.1	3.1	3.5

*Note.* Conventional FCC: pilot plant data generated in Davison circulating riser (DCR).  
HS-FCC: pilot plant data generated in DCR modified for “downer” mode.

of ZSM-5 addition, the yield of light olefins increased to more than 37 wt%, particularly propylene, which showed an increase of 72%.

The results showed that ZSM-5 is highly selective toward propylene relative to Y-Faujasite containing base catalyst. In both cases, the rise in light olefins was accompanied with a drop in gasoline yield because the addition of ZSM-5 accelerates the cracking of gasoline to lighter products. The addition of ZSM-5 is effective in catalytic systems where the base catalysts have low hydrogen transfer activity. The yield of light olefins for the base catalyst (with and without ZSM-5) increased with increasing conversion. However, increasing ZSM-5 additive content to 25 wt% showed a minor increase in the yield of light olefins (Fujiiyama, 1999, 2000; Ino et al., 2003, 2004).

**5.2.8. Concluding Remarks for HS-FCC.** With proper design and operation, the HS-FCC process is in the best position to produce light olefins for petrochemicals usage. As per process technology, reactor continuation has a major impact on operating requirements, conversion, and product selectivities. Catalytic cracking under high severity in a downer-type reactor boosts overall conversion and enhances the production of gasoline and light olefins. The results of preliminary economic evaluation show that the additional production of propylene and paraxylene plays a major role in the economics of the upgraded refinery with HS-FCC option (Ino et al., 2004).

### 5.3. Superflex Technology

**5.3.1. Superflex Overview.** Superflex is a fluidized catalytic cracking technology that converts olefinic streams from petrochemical or refinery sources to significant amounts of propylene and ethylene. Ideal streams can be

- Mixed C<sub>4</sub>s from a refinery or steam cracker, raffinate 1 or raffinate 2;
- Mixed C<sub>5</sub>s from a refinery or steam cracker, amylenes, treatment ameylene (TAME) feed, or raffinate;
- Light cracked naphtha from a steam cracker, FCC unit, coker or visbreaker;
- Olefinic streams from Fischer Tropsch or other processes

Lyondell Chemical Company (formerly Arco Chemical Company, Houston, TX) is the developer and owner of Superflex technology. In 1998, KBR became the exclusive worldwide licensor of Superflex. In this role, KBR is entirely responsible for supporting the technology, including the marketing, sales, development, engineering, and commercial aspects of Superflex. Superflex uses a fluid riser-type reactor, quite similar to an FCC reactor, to convert hydrocarbon feeds, typically in the C<sub>4</sub>-C<sub>8</sub> carbon range, to predominately propylene. Generally, the higher the olefin content of the feed, the higher the propylene yield. The original intent of the technology was to convert available, low-value streams to high-value petrochemical light olefins. In addition to propylene, the major by-products are ethylene and a highly aromatic gasoline stream. It has been proven that typical overall yields as a function of feedstock type. Overall, ultimate propylene plus ethylene yields between 50 and 70% can be achieved with olefinic feedstocks and the recycle to extinction of unconverted C<sub>4</sub>/C<sub>5</sub>s from the reactor. A simplified flowsheet for the Superflex process is shown in Figure 3. The reactor system employs elements of KBR'S FCC technology, backed by 65 years of experience and over 120 commercial units. After feed preheat, the feed is converted in the riser before the gas is separated from catalyst fines in the upper disengage. Heat is recovered from the gas, and the catalyst fines are removed in an oil wash column. The cooled gas is then sent to the recovery section for the production of

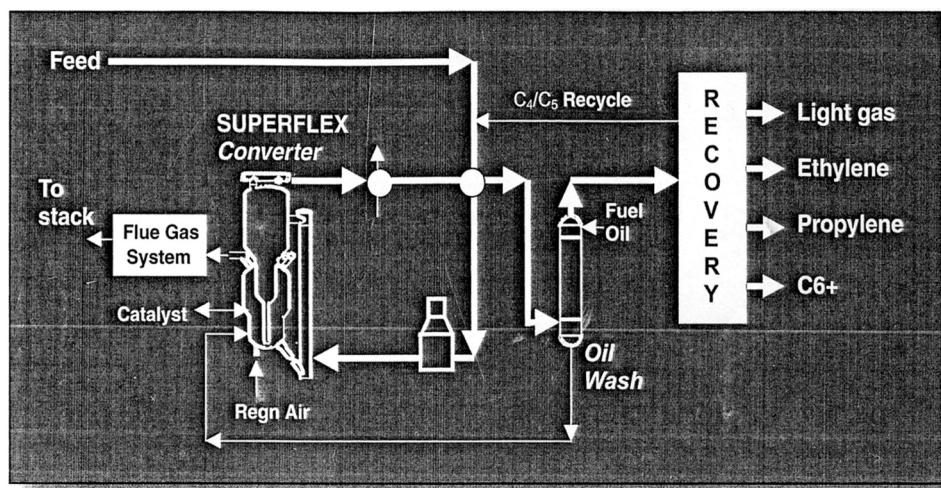


Figure 3. Simplified Superflex flow scheme.

polymer-grade olefins. Catalyst from the upper disengage is stripped and regenerated in the lower section of the KBR converter and the catalyst is returned to the riser reactor. Compared to similar interconversion processes, Superflex is clearly differentiated with several process advantages (Eng et al., 2004).

**5.3.2. Conclusions for Superflex Process.** Superflex technology will continue to play a strategic role in meeting future propylene demands in a cost-effective manner. Both refiners and ethylene plant owners will benefit from the conversion of low-value or problematic internal streams to high-value light olefins. Because of the robust and flexible nature of the technology, Superflex will enable the producer to convert a wide variety of low-cost feeds into higher margin propylene and ethylene (Eng et al., 2004).

## 6. Experimental Investigation in Fluidized Bed for Propylene Production

Experimental evaluation in a fluidized bed showed that HS-FCC is a method for changing operation condition of FCC to high-severity condition for increasing propylene yield in FCC processes. Adding ZSM-5 catalyst to FCC catalyst is one method for increasing propylene yield in FCC processes. The combination of HS-FCC with ZSM-5 will increase the yield of propylene (Farshi et al., 2006).

## 7. Conclusion

FCC process roles in supplying propylene demands in world were investigated in this manuscript. Different types of FCC processes were reviewed that can be categorized as follows:

1. Adding ZSM-5 catalyst additives or other appropriate additives as referred to in this manuscript to FCC catalyst.

2. Changing FCC catalyst from gasoline mode to propylene mode. Grace Davison, Albemarle, and Sud Chemie will be proposed appropriate catalyst/additive for propylene production in FCC process.
3. Changing the FCC operation condition to an HS-FCC process condition with a downflow reactor.
4. Using the new FCC Superflex process.

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