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Innovative use of catalyst and operating conditions increases on-purpose olefin production

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Fluidized catalytic cracking (FCC) technology was developed to increase gasoline production derived from crude-derived vacuum gasoil (VGO) and, in some cases, atmospheric resids. This continues to be the primary objective. According to a Purvin and Gertz study, as of 2010, cracking-based conversion accounts for approximately 50% of the world's refining capacity with an additional 10%–15% for the North American refining market. As fuels market needs to evolve, FCC technologies are being repurposed to produce high-grade petrochemical feedstocks along with transportation fuels. This article investigates FCC evolving operations to meet future market needs.

MARKET OVERVIEW

In general, demand for clean transportation fuels will outpace demand growth for other refined products; this is an encouraging projection for the conversion-based refiners. Conversely, data indicates that the outlook for US gasoline demand to 2020 shows a lower overall demand and a gradual decline (Fig. 1). This demand behavior can be explained by a number of factors:

- A sharp price increase since 2004 causing the first wave of demand destruction
- The post recession recovery for US gasoline demand in 2010 is nearly 8% lower than its peak in 2004. It is expected to decline to less than 0.5%/yr.
- Ethanol blending is displacing petroleum-derived gasoline. From 2000–2009, ethanol usage as a gasoline blendstock steadily increased to its present average level of 4.5 vol%.
- The Energy Independence and Security Act (EISA) was signed into law by President Bush in December 2007. The EISA mandates, among other items, transportation efficiency improvements that include:
 - By 2016, the CAFE (corporate average fuel economy) standards for new light duty vehicles will increase by 40%.
 - The Renewable Fuels Standard (RFS) calls for a total of 36 billion gallons/yr of renewable fuel by 2022.
 - Propagation of hybrid power train technologies.

Worldwide propylene. In contrast to gasoline, the 10-year outlook in global propylene demand will outstrip co-production from available ethylene crackers, FCC units and other sources. This anticipated supply gap is expected to be filled through additional on-purpose propylene production from FCC units and other on-purpose cracking solutions. Fig. 2 provides the expected

propylene demand and supply contribution by source. Although conventional-fuels-based FCC yields approximately 4 wt%–6 wt% of propylene; operating conditions, catalyst system and technology via revamps can increase propylene yields by as much as 5 wt%. In addition, new technologies are now available for both revamp and new unit applications and that enable propylene yields over 20 wt%. The fundamental question remains, what is the most economic propylene production solution from an FCC that takes into account the following:

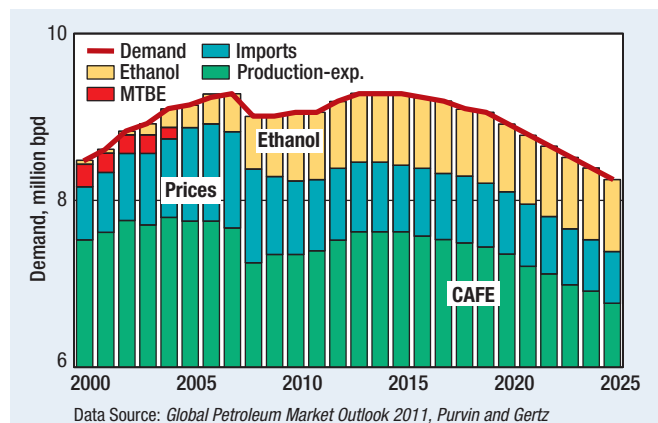


FIG. 1 Gasoline demand growth and ethanol contribution.

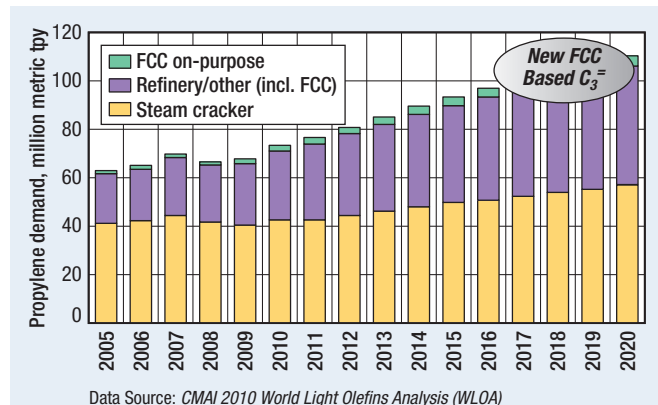


FIG. 2 Expected worldwide propylene demand.

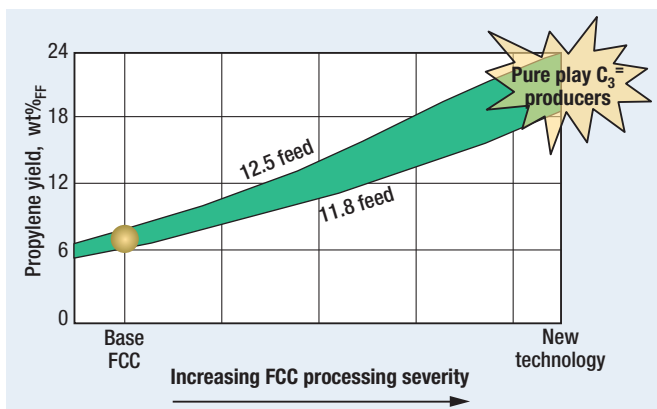


FIG. 3 FCC propylene yield as a function of feed and reactor severity.

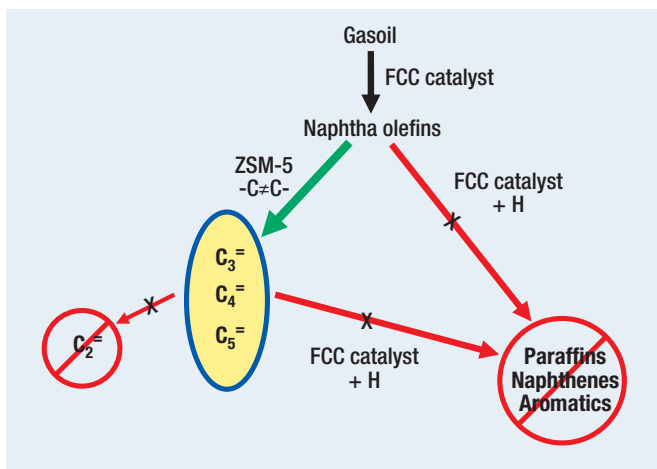


FIG. 4 FCC reaction pathways to produce olefins.

1. **Expected fuels demand.** Propylene production from an FCC has a direct negative impact on the quality of fuel products produced, in particular FCC naphtha. The impact is measured in terms of reduced naphtha yield and a shift in its molecular composition,

2. **The highest propylene yield achievable given feedstock quality.** The total potential for propylene from a particular FCC feed is determined largely by its hydrogen content.

CHEMISTRY OF PROPYLENE PRODUCTION

As the operating (reactor) severity of the FCC is increased, liquefied petroleum gas (LPG) and propylene production increases. Propylene production is accomplished through the cracking of olefinic naphtha to lower molecular weight olefins. Fig. 3 shows that there is a broad, continuous range of propylene yield from FCC technology for a gasoline operation at 4 wt%–6 wt% propylene to a petrochemical operating mode exceeding 20wt% propylene yield. This figure summarizes the general relationship between yields for propylene at increasing operating severities for different quality feedstocks.

Operating variables and chemical principles. Propylene production from an FCC unit is framed by several factors that when combined with licensed technology provide the means for propylene/petrochemical modes of operation. These factors include:

FCC feed quality is the most critical parameter in determining propylene production potential. There is a strong positive correlation between the FCC feed hydrogen content and propylene yield. Feeds that are richer in hydrogen are capable of producing more propylene largely due to increased feedstock conversion. Furthermore, this potential for propylene is harnessed by the FCC technology and process conditions. The continuum of propylene yield as a function of technology and operating conditions is conveyed in Fig. 3.

The feed hydrogen content is responsible for the width of the band in Fig. 3. Refiners with upstream feed-pretreating capability may be able to leverage this condition to further extend propylene production capacity.

Unit conversion drives propylene yield and is closely related to feed hydrogen content. Propylene yield increases nearly linearly with conversion. A conversion increase is typically accomplished via rising reactor temperature and catalyst-to-oil ratio for a given feed and catalyst system.

In the catalyst system, two elements that must be considered are the formulation of cracking catalyst USY zeolite and the level of pentasil within the system. As shown in Fig. 4, the first function of the catalyst system is VGO conversion to naphtha olefins. The second function of a high-propylene catalyst system is a pentasil function to rapidly crack the naphtha olefins into light olefins. Pentasil containing additives (ZSM-5) can increase propylene yield by a factor of two to three depending on the pentasil quantity. While ethylene co-production is generally understood, this is a kinetically controlled process that must be moderated for propylene maximization.

An additional consideration is the formulation parameters that mitigate hydrogen transfer reactions of olefins to paraffins and aromatics. The level of USY zeolite and its rare earth exchange directly impacts hydrogen transfer reactions.

The pentasil and the cracking catalyst must function cooperatively as a system, and the pentasil quantity must be balanced with the characteristics of the cracking catalyst.

Reactor hydrocarbon partial pressure can shift the FCC reaction equilibrium to favor low molecular weight olefins. The reduced partial pressure is achieved collectively with lowering operating pressure and the addition of reactor steam. An FCC utilizing new propylene technology fundamentals can operate at much lower partial pressure than a typical FCC while producing 50% higher propylene yields for the same feed, catalyst and conversion.

A major engineering study was conducted to determine the relationship between propylene yield and plant cost. Larger equipment is required to process the increased molar flow and to ensure the larger vapor volumes resulting from the higher light-ends yields. These principles can also be applied to existing units, though a partial pressure floor is imposed by throughput and equipment design. Results of this study are data, as shown in Fig. 5. The data describe the relationship between propylene yield and relative plant cost for a reduction in partial pressure.

Equilibrium. Pilot plant and commercial studies have determined that commercial-scale FCC operation at high severity and with a ZSM-5 enhanced catalyst system produces light olefins in an equilibrium distribution. This equilibrium limit was determined by extensive monitoring of high propylene FCC units, bench-scale pure compound studies and circulating riser pilot-plant testing. Fig. 6 shows the distribution of light olefins by carbon number in the riser effluent (red bars).

Equilibrium calculations indicate that the light olefin products distribute by molecular weight and that this distribution is governed by thermodynamic equilibrium. Superimposing the distribution of light olefins from an equilibrium model calculation (blue bars) on the data from an FCC operating in enhanced LPG operating mode shows the C_3 – C_5 olefins to be nearly in equilibrium. This observation suggests that the reactions producing light olefins may be controlled by equilibrium. To achieve propylene yields significantly in excess of 12 wt% for an average FCC feedstock, we must consider technology that acts to shift the equilibrium.

To test the hypothesis of equilibrium-limited propylene, C_3 – C_5 olefins were independently added to a VGO feed and processed in a circulating pilot plant with a high ZSM-5 equilibrium catalyst. The results validated the equilibrium hypothesis. When propylene is added to the VGO feed, the net propylene yield decreased from over 10 wt% to less than 4 wt% while at the same time, the net yield of C_4 – C_8 olefins increased measurably. The independent addition of 1-butene decreased the net yield of total butenes and increased the net yield of propylene. The testing also showed that ethylene is also influenced by equilibrium, although not to the same extent, as residence time has the dominating effect. A comparison of the equilibrium calculations against the commercial unit data confirms that an equilibrium model of FCC reactions can be used as an accurate predictive tool. *In short, reactions producing light olefins are controlled by an equilibrium mechanism and the thermodynamic equilibrium limits propylene production from the FCC.*

Based on this evaluation, a three-year comprehensive pilot plant, modeling and commercial benchmarking program were used to develop two models to handle the full spectrum of low to high-propylene FCC operations—the VGO and resid model and the olefin re-cracking model. The former augments the traditional yield and heat balance calculation with the effects of ZSM-5 interactions with reaction variables, while the latter describes riser cracking of light naphtha C_4 – C_{10} olefins over ZSM-5 modified catalyst systems.

COMMERCIAL APPLICATION

Considering that a base fuels FCC operation produces ex-reactor propylene yields in the range of 4wt%–6 wt%, we examine the requirements to further increase reactor propylene yield. Three categories can be defined that are characterized by the extent of scope, with each requiring additional capital and operational expense. For simplicity, these brackets do not consider the refiner's base operation and configuration in terms of open capacity or propylene specific equipment. Considerations for open and available capacity include, but are not limited to:

- **Reactor section** to address the additional molar flow
- **Regeneration section** to address additional coke make due to higher operating severity
- **Recovery section** to address change in vapor liquid distribution and propylene recovery
- **Treating section** to meet the polymer-grade propylene product requirements.

Incremental reactor propylene yield above the Base Case is bracketed according to these factors:

- 3% to 5%—Achieved through modifications to the catalyst system (use of shape selective ZSM-5 additive, modifying the cracking catalyst formulation) and an increase in reactor temperature. Typically, such increases require only modest changes to the recovery section and a metallurgical check to determine capacity to accommodate the reactor temperature increase.

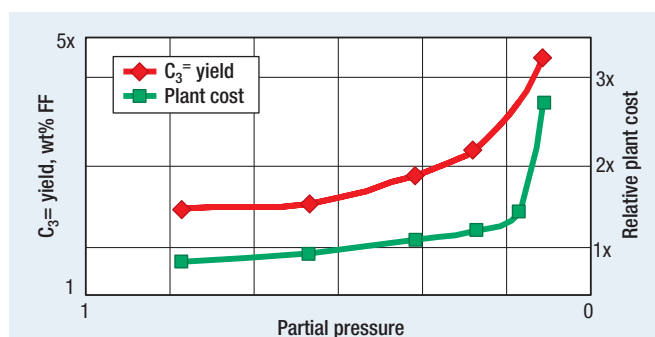


FIG. 5 Plant cost as a function for propylene yield.

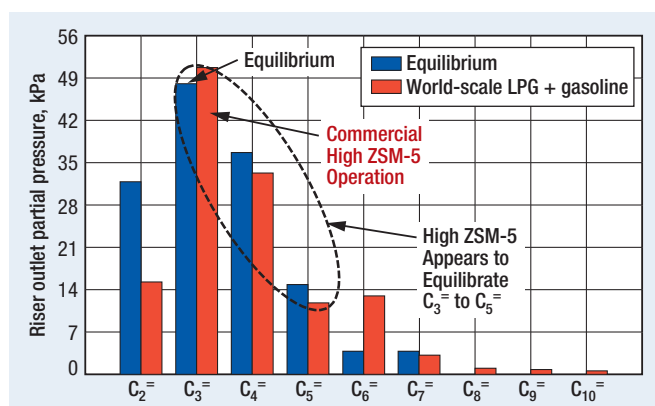


FIG. 6 FCC light olefin equilibrium distribution.

- 5% to 9%—Same as list in item a, along with reduced hydrocarbon partial pressure. This is achieved by lowering the reactor pressure and/or adding reactor steam. Implementation may require modifications to enable additional wet-gas-compression capacity, main column condensing capacity and sour-water condensing capacity.

- Greater than 9+%—Same as in item b, along with targeted recycle (LPG and light naphtha) and may also wish to consider the applicability of new maximum propylene technology. This represents the ultimate propylene production scenario and will require reconfiguration of the gas concentration unit to facilitate use of the targeted recycle. The new propylene technology will require extensive reactor/regenerator section modifications since a second reactor will be added.

European refiner. This refiner operates a stacked configuration FCC unit that was designed in 1960 for low conversion of VGO. This unit was the subject of a subsequent technology upgrade and feed capacity revamps over the last 40 years. In the late 1990s, the refiner commissioned a hydrocracker, resulting in a higher quality feed. Subsequently, an FCC revamp was commissioned to handle the higher conversion and increased yield of propylene associated with better quality feed.

Prior to the feed quality change and unit revamp, the unit yielded approximately 4.5 wt% propylene, and a marginal increase was expected with the hydrogen-rich feed. A major revamp was conducted as a high-conversion enabler. The scope of the revamp included adding a new riser separation system with improved feed distributors. This revamp enabled a conversion increase that resulted in a 4 wt% increase in propylene yield.

The refiner is considering further propylene production increases in conjunction with the catalyst manufacturer that would produce a propylene yield of nearly 13 wt%. This exemplifies increases in propylene yield that can be achieved as a result of FCC technology upgrades that enable *effective* increases in conversion and improvements to selectivities, a tuned catalyst system and feed quality improvements.

Other refiner. A refiner replaced its 1940s thermal catalytic cracking (TCC) unit reaction section with a new high propylene FCC process so that it could substantially increase its propylene production through a simultaneous reactor-regenerator technology upgrade and a feed rate increase. Although a total reactor-regenerator replacement was required, the product-recovery section was revamped for higher propylene yield and recovery, and a propylene-recovery unit was installed. It was commissioned to produce 140,000 metric tpy of polymer-grade propylene. The new propylene-focused FCC unit was a major revamp of an obsolete cracking technology that substantially increased polymer-grade propylene production. This refiner has achieved more than 16 wt% propylene using an Arabian Light VGO.

Existing FCCs can be, and have been, converted for operations at or near high propylene FCC conditions. Recently, a newer FCC operating with enhanced LPG yields revamped its reactor section

TABLE 1. Spent catalyst recycle impact on unit heat balance

	Base	Base + reactor process
Reactor temp, °F	990	990
Coke, wt%	5.3	5.2
Regenerator temp, °F	1,234	1,301
Cat/oil ratio (Rx-Reg), lb/lb	10.7	8.0
Cat/oil ratio (Riser), lb/lb	8.1	15.7
Delta coke, wt%	0.50	0.65

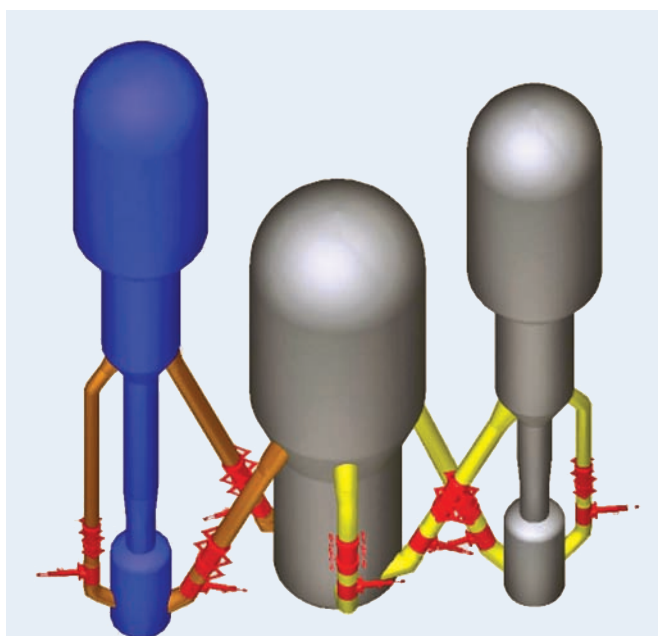


FIG. 7 Latest maximum propylene technology configuration.

to emulate the new high propylene FCC operations. As a result of this technology upgrade, this unit achieved an 18% increase in its propylene yield.

The new high propylene FCC technology utilizes low partial pressure, high reactor temperature, a ZSM-5 catalyst system and features spent catalyst recycle technology. The spent catalyst recycle technology recycles carbonized, active catalyst from the stripper to the riser mix zone where it is mixed with regenerated catalyst. Since the recycled catalyst is heat balance neutral, the spent catalyst recycle can facilitate a significant increase in the riser catalyst-to-oil ratio. This technology also helps to suppress the riser inlet temperature, which in turn reduces dry gas yields, and the higher catalyst-to-oil ratio contributes associated with its operation to higher conversion. It allows the catalyst/oil ratio to be increased well beyond typical limits imposed by a traditional FCC heat balance. This enables a higher ZSM-5 content in the riser at any specific ZSM-5 concentration in the circulating equilibrium catalyst inventory. Furthermore, applying the spent catalyst technology with a ZSM-5 enhanced catalyst system works to improve the catalyst's effectiveness, thus increasing conversion of light naphtha olefin and selectivity from the catalyst-to-oil increase.

More on spent catalyst recycle technology. This technology can be used as a revamp option and can produce similar benefits including selectivity improvement and dry-gas management. In addition, because of its heat balance neutral effect, the net effect of the spent catalyst recycle is a delta coke increase that manifests as a regenerator temperature increase. This can prove to be invaluable for refiners processing severely hydrotreated feeds or is operating at a very low delta coke. Symptomatic of low delta coke operation is after burn and elevated carbon monoxide (CO) in flue gas that may require the elevated excess oxygen, an inefficient practice, and the use of CO promoter. Table 1 summarizes actual pre/post data for an FCC unit where the spent catalyst recycle technology was added to address the low regenerator temperature. Since its 2005 commercialization, the technology is operating in six units and is being designed or is in construction for an additional 12 units.

Commercial application. Because propylene production is equilibrium limited, recycling higher molecular weight olefins can be used as another technique to maximize propylene yields. The linking of reaction equilibrium concepts with reactor and regenerator technologies results in the latest maximum propylene FCC technology. This latest technology—highest-yield propylene FCC process—uses a multi-stage reactor system comprising a primary hydrocarbon feedstock reaction stage, and a secondary recycle reaction stage utilizing a common regeneration stage with continuous circulation of fluidized catalyst between both reactor stages and the regeneration stage. The reactor/regenerator section is shown in Fig. 7. This system uses two reaction stages primarily to overcome equilibrium limitations to propylene yield and selectivity, and secondarily to maximize product flexibility. For propylene production relative to the severity/feed quality continuum, the highest-yield technology is represented at the far right side of Fig. 8 for those refiners that choose to maximize the production of propylene.

This technology extends propylene yields to greater than 20 wt%. This substantial shift is achieved by the second reactor that cracks C_4^+ olefins to propylene. The second riser can be part of a major revamp, but plot plan considerations require case by

case evaluation. This latest technology provides the ability to deliver the maximum propylene yield from the conversion of traditional FCC feeds. It can be the ultimate solution to those refiners whose primary objective from their FCC has shifted to maximize propylene production.

The critical technology features of the latest maximum propylene process technology are:

- **Maximum riser containment.** Each reactor riser is designed with its own proprietary riser termination device (RTD) and high-flux stripper to minimize post-riser vapor residence time. The post-riser reactions that occur at high reactor temperatures that can favor propylene production are accompanied by non-selective gas yields and the undesirable hydrogen transfer of olefins to alkanes.

- **High catalyst to oil riser reactors.** The reactors apply tightly contained riser reactor systems that operate at a very high (15–30) catalyst-to-oil ratio. Riser reactors were chosen over fluidized-bed reactors to minimize dilute-phase dry-gas formation and minimize hydrogen transfer reactions that are promoted by the extensive backmixing of fluidized bed reactors.

- **Second-stage riser cracking.** The spent catalyst recycle reactor technology allows the second riser catalyst-to-oil ratio to increase beyond typical limits imposed by heat balance. This enables a higher ZSM-5 content in the riser at any specific ZSM-5 concentration in the circulating equilibrium catalyst inventory. Fig. 9 shows the second riser butene conversion and propylene yield increase with C/O ratio well beyond the 5–9 available from a traditional reactor configuration (without reactor technology). This increases conversion per pass and decreases recycle in the unit against a specific propylene production target, and enables direct conversion of butenes to propylene in the second riser without an intermediate step of polymerization.

- **Product recovery and targeted recycle.** Effluent from each reactor is routed to independent main columns and partially integrated gas concentration. The first stage reactor effluent is routed to a standard main column with LCO, HCO and slurry products.

Naphtha and lighter material are taken overhead to an enhanced absorption based product recovery system. This recovery system recovers propylene and produces a superheated C₄-light naphtha stream that is feed to the second stage reactor. The second stage reactor effluent is quenched in a small column that preheats the fresh feed. The unconverted naphtha and C₄-reaction products are routed to a depropanizer and debutanizer.

This multi-stage reactor and product separation system can be the most capital selective design; this configuration produces the

greatest yield of propylene per unit cost of production. It can provide exceptional performance through the reduction of non-reactive diluents from the second-stage feedstock, which consists of only convertible species or those that participate in the equilibrium shift.

In a comparative study of 500,000 metric tpy propylene (50,000 bpsd fresh feed) units, application of the reactor technology required 12% less capital and 7% less operating cost per unit of propylene relative to a comingled product recovery system design. The lower expenses were due to decreased equipment sizes and the associated energy consumption. Moreover, the reactor technology produces a net reactor propylene yield in excess of 20 wt%, which exceeds the capability of currently available traditional FCC technologies.

REFINING/PETROCHEMICAL INTEGRATION OPTIONS

The FCC refining community will be faced with many interesting challenges over the next few decades. A shrinking forecasted US gasoline demand, coupled with potential economic and legislative factors will likely reshape the future for refining conversion. This will leave US refiners with the challenge of how to best utilize the expected open capacity while preserving the fixed asset base. As propylene demand grows, refiners can leverage their FCC technology through implementation of the concepts outlined in this article.

Propylene's remarkable demand growth requires new technologies to capture growth opportunities. Until recently, refiners were able to capture incremental shifts that had been met with success for meeting local demand. The first principles for propylene production from an FCC unit lend well to understanding the propylene potential, reactor conditions and catalyst selection for achieving incremental in propylene production shifts. In particular, the influence of equilibrium and the introduction of equilibrium manipulation augment these first principles. Potential propylene yields in excess of current practice and convention underscore the necessity for new technology offerings that allow the refiner to achieve propylene yields well in excess of the current commercial experience. **HP**

ACKNOWLEDGMENT

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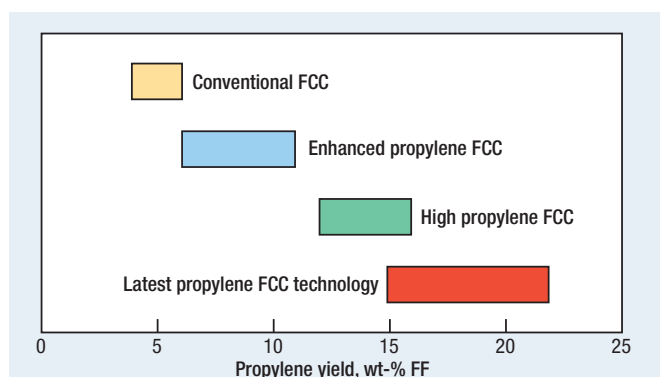


FIG. 8 Mapping new reactor technology on the propylene continuum.

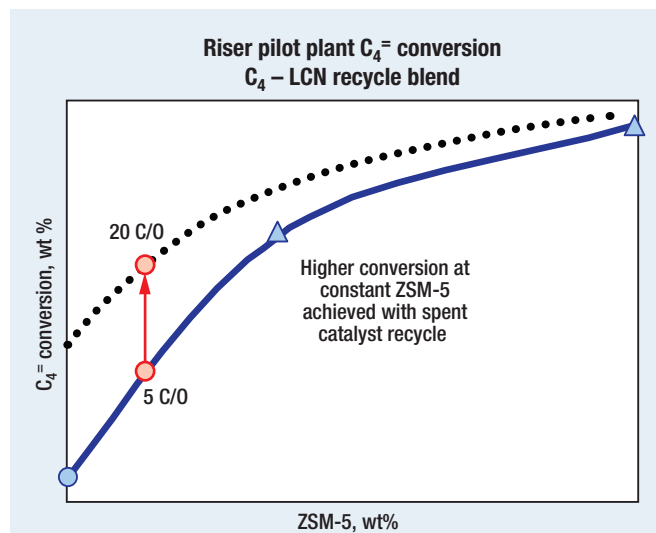


FIG. 9 New reactor process contribution to butene conversion.