Maximize propylene from your FCC unit

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


Fluidized catalytic cracking (FCC) technology was developed to increase gasoline production derived from crude-derived vacuum gasoil (VGO) and, in some cases, atmospheric resid. 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 increases 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:
  o By 2016, the CAFE (corporate average fuel economy) standards for new light duty vehicles will increase by 40%.
  o The Renewable Fuels Standard (RFS) calls for a total of 36 billion gallons/yr of renewable fuel by 2022.
  o 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 revamps 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:

- Propagation of hybrid power train technologies.
- The Renewable Fuels Standard (RFS) calls for a total of 36 billion gallons/yr of renewable fuel by 2022.
- 20% increase in corporate average fuel economy (CAFE) standards for new light duty vehicles by 2016.
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FIG. 1 Gasoline demand growth and ethanol contribution.

FIG. 2 Expected worldwide propylene demand.
**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.

**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:

**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.

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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 C3–C5 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, C3–C5 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 C4–C8 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 pylene FCC operations—the VGO and resid model and the olefin 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.

**COMMERICAL APPLICATION**

Considering that a base fuels FCC operation produces ex-reactor propylene yields in the range of 4–6 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:

*a.* 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.

*b.* 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.

*c.* 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 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 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>
<thead>
<tr>
<th>TABLE 1. Spent catalyst recycle impact on unit heat balance</th>
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<tr>
<td>Reactor temp, °F</td>
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<tr>
<td>Coke, wt%</td>
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<tr>
<td>Regenerator temp, °F</td>
</tr>
<tr>
<td>Cat/oil ratio (Rx-Reg), lb/lb</td>
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<tr>
<td>Cat/oil ratio (Riser), lb/lb</td>
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<td>Delta coke, wt%</td>
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**FIG. 7** Latest maximum propylene technology configuration.

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 reconverts C₄⁺ olefins to propylene. The second riser can be part of a major revamp, but plot plan considerations require case by case.
REFINING DEVELOPMENTS

SPECIAL REPORT

The conventional FCC process produces the lowest 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.

ACKNOWLEDGMENT