# Catalytic cracking process enhances production of olefins

## A FCC technology and catalyst formulation selectively crack a wide range of feeds, including residue, to yield high quantities of light olefins

DALIP SONI and M RAMA RAO *Lummus Technology*
G SAIDULU, D BHATTACHARYYA and V K SATHEESH *Indian Oil Corporation*

The primary purpose of the fluid catalytic cracking (FCC) process historically has been to convert low-valued, heavier petroleum streams into gasoline, alkylation feed (eg, isobutane and butene) and, to a lesser extent, other distillate products. While other light olefins were always produced, the low volumes did not attract much attention because of separation costs and modest product margins.

In the last decade, production of propylene from FCC units (FCCUs) has grown significantly and is now approaching 20–30% of all propylene produced worldwide.[1] Key drivers of this surge in production include the price spread between propylene and gasoline, and increased demand for propylene. To maximise the propylene yield from FCCUs, significant improvements have been made in catalyst formulation and process technology. This relatively new strategy for the on-purpose production of FCC propylene will help meet approximately 5% of the annual growth rate in worldwide demand for propylene.[1]

Early attempts to increase production of light olefins from the FCCU were based primarily on process variables, but the poor selectivity of this approach resulted in excess production of dry gas and coke. By the 1970s, researchers found that non-Y zeolites could also co-produce light olefins ($C_2=$ to $C_5=$), often at the expense of gasoline. Table 1 shows the chronology of development for catalysts and additives to enhance the production of light olefins in FCCUs.

This article discusses the growth of on-purpose production of light olefins

| Timeline of the use of zeolites in higher FCC olefins production | |
|---|---|
| **Year** | **Event** |
| 1970 | ZSM-5 in FCC invented |
| 1974 | USY in FCC invented |
| 1983 | ZSM-5 commercialised in cracking |
| 1986 | Zeolite Beta in FCC invented |
| 1990 | First on-purpose olefins production via ZSM-5 |
| 1995 | Indmax FCC process invented |
| 2003 | Indmax process commercialised |

**Table 1**

from the FCCU and the approaches employed. Specifically, the Indmax FCC (I-FCC) process will be addressed, including its benefits, the underlying concepts, the chronology of its development and commercialisation.

## Approaches to production of increased olefins

### Process variables

Some of the variables of the FCC process employed in the production of olefins include a higher severity operation, recracking of cracked material and partial catalyst recycle. A high severity operation is achieved by a high reaction temperature, with or without a higher residence time. The general concept for a higher severity operation is to overcrack (beyond the maximum gasoline mode) and produce increased quantities of light olefins.[2] The length of contact time depends on the type of catalyst employed. A longer contact time results in excessive production of dry gas and coke, and may also result in reduced selectivity for light olefins due to hydrogen transfer reactions.

A high severity operation with a short contact time overcomes the drawbacks of a longer contact time. Short contact time produces less dry gas and coke, and provides a higher selectivity to light olefins. However, it requires a catalyst formulation that can deliver the desired levels of conversion and yield for light olefins.

Recracking cracked material such as naphtha can yield incremental light olefins. This recracking can be done in the same or a separate riser reactor. Injecting in the same riser reactor has been used for upgrading visbreaker or coker naphtha in FCC risers. Recycling FCC naphtha to the same riser reactor has also been applied, but the yield of dry gas increases.

In the partial catalyst recycle approach, part of the spent catalyst is recycled back to the reaction section to increase the catalyst-to-oil ratio. The drawback is that the catalyst's dynamic activity is lower than when a higher catalyst-to-oil ratio is achieved with all-regenerated catalyst. This may result in lower levels of conversion and selectivity to light olefins.

### Catalyst variables

Since the 1960s, the refining industry has used various X and Y zeolites as the primary cracking catalyst in FCC.[3,4] Benefits of greater stability and better selectivity quickly led to the exclusive use of Y zeolites. The phase-out of lead in fuels convinced researchers to seek alternative routes to increase gasoline octane. Several versions of Y zeolites were used, and these are listed in Table 2.

Many methods were applied to dealuminate Y zeolite in order to balance activity, stability, gasoline yield and octane. The use of Y zeolite

| Benefits and drawbacks of zeolite catalysts | | |
|---|---|---|
| Catalyst | Pros | Cons |
| Ultrastable Y (USY) | More $C_3$=/$C_4$=; less coke | Poor stability |
| RE-USY | Improved stability vs USY | Limited olefin potential |
| ZSM-5 | Excellent $C_3$= yields | Poor conversion activity; additive dilution effect |
| Zeolite Beta | Enhanced $C_4$= | High cost; poor stability |

**Table 2**

| Typical yield of olefins for the I-FCC process | | |
|---|---|---|
| | wt% of feed | wt% in $C_2$ & lighter |
| Ethylene | 3–7 | 40–50 |
| | | wt% in LPG |
| Propylene | 12–24 | 40–50 |
| i-Butylene | 4–5 | 8–12 |
| Other butylene | 5–12 | 20–25 |

**Table 3**

for increased production of olefins focused on Ultrastable Y (USY), achieved mainly through its reduced zeolite unit cell size and decreased framework Al content.[5,6] At constant conversion, USY catalysts yield more $C_3$-$C_4$ olefins, higher octane gasoline, and less gasoline and coke. One patent[7] showed that the olefin yield reached a maximum at a unit cell size of 24.15–24.20 Å. Figure 1 shows the olefin yield as a function of unit cell size. Unfortunately, USY is less active and stable than its REY counterpart. RE-USY can achieve benefits similar to USY, but with about 35% higher activity than USY.[8]

Currently, the popular approach to olefin production is the use of ZSM-5 additive.[s] ZSM-5 was first explored as a stand-alone FCC catalyst, but was found to be lacking in conversion activity — not surprising for a zeolite of medium pore size. It was later proved that ZSM-5 enhances gasoline octane when used as an additive to the main FCC catalyst, due to the ability of ZSM-5 to produce more olefins.

While early use of ZSM-5 focused on octane enhancement, the use of larger quantities of ZSM-5 for on-purpose propylene production started in the 1990s. Refiners have since increased their reliance upon ZSM-5, to the point where it is now used in almost 20% of FCC capacity worldwide. This approach has proven to be a relatively inexpensive route to propylene.

ZSM-5 can be used as a separate additive or as an integral part of the FCC catalyst. Each approach has its benefits and drawbacks. Since the two

## The process uses a catalyst that is selective in cracking molecules of different shapes and sizes to yield light olefins

zeolites (Y and ZSM-5) age at different rates, the separate additive method can adjust better for this effect. However, the additive can build up in the FCC inventory to the point where this dilution can reduce the overall conversion performance of the catalyst mix. Using the integral, single particle approach, Y zeolites need to have some extra activity — so-called activity giveaway — which may not
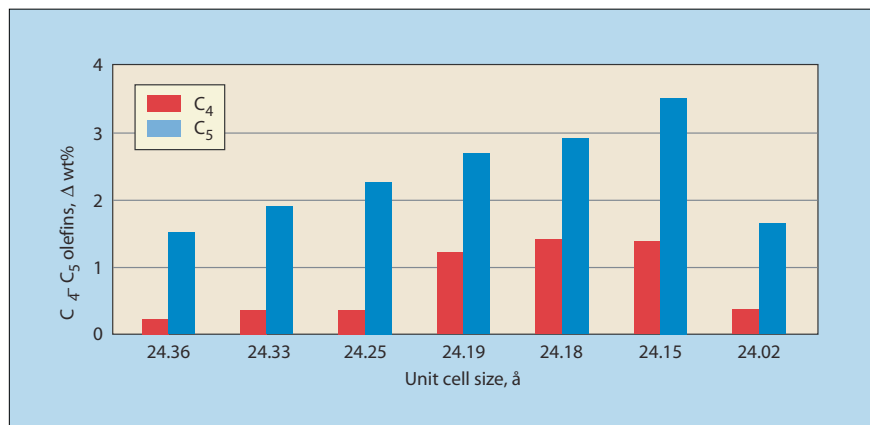
be easily achieved. This approach also does not offer the flexibility to change the percentage of ZSM-5 in the total catalyst inventory in the event of changes in feedstocks or fluctuations in market demand.

The generally accepted mechanism for ZSM-5's utility is the secondary conversion of heavier gasoline olefins to lighter ($C_3$ and $C_4$) olefins as well as isobutane.[10,11,12] The gasoline paraffins have been shown to be 100-fold less reactive than the olefins.[13] Feedstock plays a key role in the abundance of gasoline olefins. For example, highly paraffinic crudes such as Minas are the most responsive to ZSM-5, while aromatic crudes such as San Joaquin are significantly less effective for octane boost and olefin production.

### Indmax FCC (I-FCC) process

The Indmax process, developed by Indian Oil Corporation (IOCL), is a breakthrough in FCC technology for converting heavy feeds, including residue, to light olefins.[14] This process overcomes the drawbacks or limitations of just adding ZSM-5.

The Indmax process employs a riser reactor system along with a catalyst stripper and catalyst regenerator, just like a conventional FCCU. The process uses a proprietary catalyst formulation that is very selective in cracking molecules of different shapes and sizes to yield high quantities of light olefins.

The catalyst formulation is unique and very different from what has previously been used in FCC or RFCC operations. This approach provides the flexibility to tailor the formulation to meet the challenges of market fluctuations in feedstock properties or product demand. The catalyst



**Figure 1** Incremental olefin yields for various USY catalysts
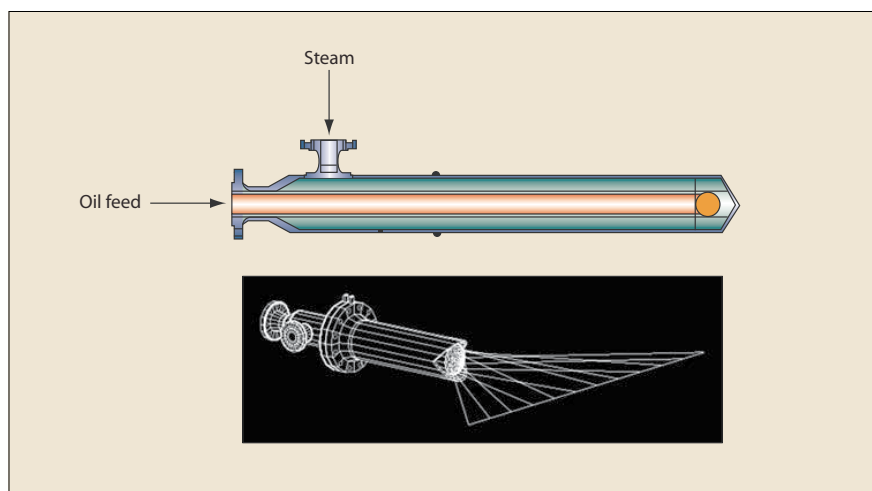
**Figure 2** Schematic of Micro-Jet injectors

formulation is specific to each operation, and depends on feedstock characteristics and product objectives. Research studies have been conducted for various feedstocks to determine light olefin yields and selectivity. Table 3 summarises the range of olefins yields and selectivities that can be obtained from different feedstocks and operations.

The Indmax catalyst formulation is also tolerant of metals and can operate with a high vanadium concentration on the equilibrium catalyst. The ability to process feeds with a high metals level is important for residue operations.

The process utilises a higher riser reactor temperature (530–600°C), a higher catalyst-to-oil ratio (12–20), and a lower hydrocarbon partial pressure to achieve high conversion and selectivity to the production of light olefins. Since all the cracking reactions take place with a short contact time in the riser reactor, with a high catalyst-to-oil ratio and all high activity regenerated catalyst, the selectivity to light olefins is high. The LPG produced contains up to 50 wt% propylene and 12 wt% isobutylene. Total olefins in liquefied petroleum gas (LPG) can be as high as 80 wt%. The process can accept feedstocks ranging from hydrotreated vacuum gas oil to residue, with feed Conradson carbon residue (CCR) as high as 10 wt%.

The first commercial unit to adopt the Indmax process was commissioned in 2003 at the Guwahati Refinery of IOCL in Assam, India. With a capacity of 100 000 tonnes per annum, it has been producing the desired product yields to the required specifications. The feedstock is a mixture of atmospheric tower bottom (ATB) and coker heavy gas oil (CHGO). In addition, coker naphtha (CN) is injected into the same riser reactor. The composition of the feedstock is summarised in Table 4. The CCR in the combined heavy feed (ATB+CHGO) is 3.75 wt%. The unit operates in complete combustion without a catalyst cooler, which demonstrates the delta coke selectivity — it produces less delta coke — of the Indmax catalyst.

A number of test runs performed in this unit achieved high conversion and a propylene yield of 17.2 wt% of the total feed. The coke selectivity of the catalyst keeps the regenerator temperature low — even without a catalyst cooler — which results in a high catalyst-to-oil ratio that in turn provides high conversion and selectivity to light olefins (propylene and ethylene).

Lummus Technology, a CB&I company (Lummus), is the exclusive licensor of the I-FCC technology. The

I-FCCU is designed by Lummus with basic information developed by IOCL. Process features include:

● **Micro-Jet feed injectors** These injectors promote selective catalytic cracking reactions by thoroughly contacting the feed with the hot regenerated catalyst and rapidly vapourising it. In the Micro-Jet injector design, the inherent energy of the feed dispersion steam is used to shear the feed into small droplets. Figure 2 is a schematic of the Micro-Jet injector. It consists of a double pipe, wherein the oil flows through the centre pipe and steam flows through the annulus. The cylindrical flow of oil is turned into thin films as it flows past a device attached at the end of the centre pipe. The thin films of oil are then hit by several jets of dispersion steam flowing in the annulus. The small droplets formed are then ejected into the riser through a specially engineered tip that generates several microjets designed to achieve the best exit velocity when entering the riser. Micro-Jet injectors provide a higher conversion and yield of light products, while minimising dry gas and delta coke.

Each individual jet is angled so that all the jets collectively form a flat fan spray pattern for maximum coverage of the riser cross-section. This provides uniform distribution of feed across the riser. The angle of injection is chosen to achieve thorough dispersion of oil in the catalyst. The injection velocity is high enough to penetrate the catalyst mass, yet does not cause catalyst attrition and erosion of the riser

● **Riser design** Riser residence time and velocity are selected to promote catalytic cracking reactions, to minimise undesirable thermal cracking reactions and to increase selectivity to olefins. Riser residence time is determined through pilot plant tests and kinetic model studies. The riser diameter, and hence the velocity, is determined by means of a computer model, by tracking volume expansion as the reaction mixture flows up the riser. The riser design approaches plug flow conditions with minimum slip, which enhances selective catalytic cracking reactions and hence selectivity to light olefins

| Indmax unit feed composition | | |
|---|---|---|
| **Feed** | | |
| | ATB | 50% |
| Feed composition | CHGO | 30% |
| | CN | 20% |
| Feed density | | |
| (ATB+CHGO) | | 0.9456 |
| Coker naphtha | | 0.7164 |
| CCR (ATB+CHGO) | | 3.75 wt% |

**Table 4**

● **Reaction termination device (RTD)**
Direct-coupled cyclones are fitted to the end of the riser reactor to recover product vapours at the end of the riser and terminate the reactions (Figure 3). Most of the catalyst is thrown against the cyclone wall straight after exiting the riser reactor and so separates from the product vapours. This leaves little time for bimolecular hydrogen transfer reactions that would resaturate the olefins produced in the riser.

The primary cyclone operates at a pressure lower than that in the cyclone containment vessel or reactor. As a result, the recovery of products at the end of the riser is almost complete and the post-riser residence time is minimal. This further helps to preserve the olefins produced in the riser reactor. In addition, entrainment of the product vapours with the spent catalyst is minimal. This reduces production of delta coke and hence holds down the regenerator temperature, which helps to increase the catalyst-to-oil ratio that is critical to achieving high yields of light olefins

● **Modular grid (MG) catalyst stripper**
This stripper design has flat baffles, which are angled and orientated so that the entire cross-sectional area of the stripper is available for catalyst flow and the maximum surface area is available for catalyst and stripping steam contact (see Figure 4). The baffles are assembled and built as modular grids that can be installed in the stripper vessel by simply stacking them one over another. These grids can be inspected easily in place through manholes provided in between the stacks. The MG stripper is efficient even when catalyst flux is high.

When the aim is to produce light olefins from heavier feedstocks with high CCR and metals content, then excessive coke production, a high regenerator temperature, high dry gas production and high catalyst make-up rates are to be avoided. The Indmax catalyst's low selectivity for delta coke and dry gas, along with its high tolerance for metals, in conjunction with hardware design improvements, enable the I-FCC process to handle these feedstocks. It is worth noting that the I-FCC process can convert residue feedstocks with
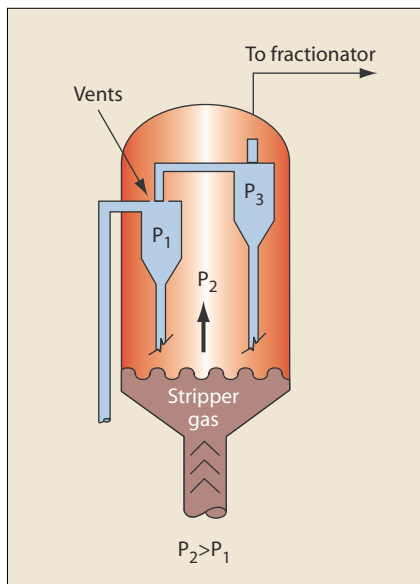


**Figure 3** Reaction termination device

CCR up to 5 wt% without a catalyst cooler, and CCR up to 10 wt% with a catalyst cooler.

In 2007, Lummus Technology and the IOCL R&D Centre completed the design of an 85 000 bpsd I-FCCU at IOCL's Paradip Refinery in Orissa using hydrotreated VGO feed. The unit, scheduled for startup in 2012, will aim for a maximum propylene yield and will also produce an increased quantity of ethylene as feed to the downstream petrochemical complex. The design of another 15 000 bpsd unit at IOCL's Bongaigaon Refinery, Assam, with a residue feed and the aim of producing LPG/propylene and high octane gasoline, was recently completed.

## Conclusion

The I-FCC process's catalyst formulation, hardware design and operating strategy can upgrade heavy feeds (including residue) for a high yield of light olefins such as propylene, ethylene and butylenes.
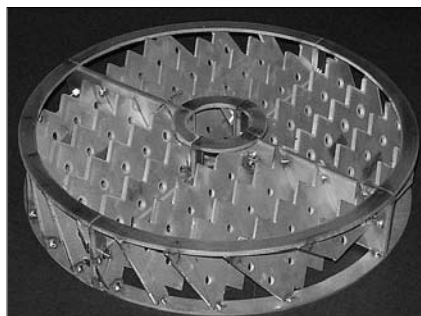


**Figure 4** Modular grid stripper internals

The process involves only riser cracking. The operation can easily be adjusted, depending on the demand and pricing of products. It enables changes to the proprietary catalyst formulations to respond to changes in feedstock properties or product selection. The I-FCC process produces low levels of delta coke and dry gas, even with residue feeds that contain high levels of CCR and metals contaminants. The need for a catalyst cooler is in many situations eliminated.

**References**
1  CMAI News, 12 Nov 2001.
2  Hutchinson D, Hood R, Catalytic cracking to maximize light olefins, *Pétrole Et Techniques*, Mar-Apr 1996, 29.
3  US 3 140 249 (to Socony Mobil), 7 Jul 1964.
4  US 3 140 251 (to Socony Mobil), 7 Jul 1964.
5  US 3 595 611 (to W R Grace), 27 Jul 1971.
6  US 3 957 623 (to W R Grace), 18 May 1976.
7  US 5 549 813 (to Texaco), 27 Aug 1996.
8  Buchanan J S, Adewuyi, *Applied Catalysis A: General*, 134, 1996, 247–262.
9  US 3 758 403 (to Mobil), 11 Sept 1973.
10  Rajagopalan K, Young G W, *Am. Chem. Soc. Symp. Ser.*, 375, 1988, 34.
11  Madon R J, *J. Catal.*, 129, 1991, 275.
12  Buchanan J S, *Appl. Catal.*, 74, 1991, 83.
13  Haag W O, Lago R M, Weisz P B, *Discuss. Faraday Soc.*, 72, 317, 1981.
14  Upadhyay, *et al*, Successful demonstration of Indmax process for conversion of residues to LPG and high octane gasoline, Petrotech 2005, New Delhi, Jan 2005.

**Dalip Soni** is Director, FCC Technology, at Lummus Technology, Houston, Texas. He has a master's degree in chemical engineering from Oklahoma State University.
*Email: dsoni@cbi.com*

**Rama Rao Marri** is Principal Process Engineer at Lummus Technology, Houston, Texas. He is a co-inventor of the Indmax FCC process. He has a Master's degree in chemical engineering from the Indian Institute of Technology, Kanpur.
*Email: ramarao@cbi.com*

**G Saidulu** is Deputy Manager, Research, at the R&D Centre of Indian Oil Corporation, Haryana, India. He has a masters degree in chemical engineering from the Indian Institute of Technology, Kanpur. *Email: saidulug@iocl.co.in*

**V K Satheesh** is Deputy Manager, Research, at the R&D Centre of Indian Oil Corporation. He has a master's degree in chemical engineering from the Indian Institute of Technology, Kanpur. *Email: satheeshvk@iocl.co.in*

**Debasis Bhattacharyya** is a Senior Research Manager at the R&D Centre of Indian Oil Corporation. He has a master's degree from the Indian Institute of Technology, Kanpur. *Email: bhattacharyad1@iocl.co.in*