# *Modification of Mean Pore Diameter of Pre-treat Catalyst and Repurposing of Post Treat Catalyst for Improved Performance in LCO Hydrocracker*

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# New Reliance for a New India

Reliance Industries Limited

Reliance Industries Limited

India's most profitable company

1 Reliance O2C

**Largest and most complex single site refinery** at Jamnagar with 1.4 MMBPD crude refining capacity; **vertically integrated** portfolio across O2C value chain, among **lowest cost positions** and **global top 10 rankings in key products**

**Jio-bp** 51:49 fuel retail JV

A **global leader** and one of the **long-term winners**

2 Jio DIGITAL LIFE

**Largest** digital services provider in **India – 419.9 mn subscribers** (Jun'22)

**1st operator**[1] to **cross** 400mn subscribers in a **single country market**

Strategic investment by **Facebook & Google** and investments by **marquee financial investors** totaling to **$20bn for ~33% stake** in Jio Platforms Limited

3 Reliance RETAIL

**Largest Organized Retailer in India**

**208 mn registered customer base** with **a diversified product portfolio** of groceries, fashion & lifestyle, consumer electronics and connectivity across **15,866 stores across 45.5 mm sq. feet** (Jun'22)

Investments from Silver Lake Partners, KKR, GA, TPG, Mubadala, GIC, PIF and ADIA totaling **~$6bn for ~10% stake** in Reliance Retail Ventures Limited

**Three mega growth engines and a strong liquid balance sheet**

# Phenomenal Growth Journey – Now A Top 100 Global Company

Reliance Industries Limited

**Fortune Global 500 – 155th**

**Market Cap CAGR – 31% | Earnings CAGR – 25%**

## 1977-80 — $ 0.01 Bn

- IPO

## 1981-90 — $ 0.1 Bn

- Patalganga Complex
  - PFY
  - PSF
  - PTA
  - PX

## 1991-2000 — $ 4 Bn

- Cracker and Polymers @ Hazira
- Fiber Intermediates @ Hazira
- Jamnagar supersite - Integrated refinery & petrochem complex
- GDR Issue
- 50/100 Years Yankee Bond
- Upstream – PMT

## 2001-2010 — $ 50 Bn

- Jamnagar refinery & petrochem complex – 2
- Fortune Global 500
- IPCL acquisition
- Acquired broadband spectrum
- Launch of Reliance Retail
- KG-D6 discovery & commencement of production
- Recron Malaysia

## 2011-20 — $ 93 Bn

- Ethane project, ROGC, Gasifiers commissioned
- Innovative financing – perpetual bond, EXIM facilities
- Launched Jio, all-IP digital network
- India's largest Rights Issue
- Largest capital raise through asset monetization across Jio, Retail and fuel retailing
- KG D6 new production system

## 2021-22 — $ 230 Bn

- Retail crosses 15,000+ stores, 193 million customers
- Jio crossed 400+ Mn subscribers
- JV with ADNOC
- Launch of New Energy & New Materials
- Acquired REC Solar
- First ever jumbo US$ Notes issuance from India

# Reliance's Vision to be Net Carbon Zero by 2035

**Opportunity to accelerate New Energy and New Materials businesses based on RIL's vision of clean and green development**

- **Integrated Solar Photovoltaic module factory**
  - Establish and enable at least 100GW of solar energy by 2030
- **Advanced Energy Storage Battery factory**
  - Collaborate with global leaders in battery technology to achieve the highest reliability round-the-clock power availability
- **Electrolyser factory**
  - Manufacture modular electrolysers of highest efficiency and lowest capital cost
- **Fuel Cell factory**
  - Fuel cell uses oxygen from the air and hydrogen to generate electricity, emitting non-polluting water vapour

**Deploy next-gen technologies to combat climate change**

# Growth Engines for Sustainable Value Creation

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Jio DIGITAL LIFE

- **Best-in-class** digital services with pan-India all-IP mobile and FTTH connectivity
- Focus on **subscriber ramp-up**, **enterprise solutions**, **narrow-band IoT** and scaling-up of digital platforms

Reliance RETAIL

- Reliance is well-placed to leverage its online ecosystem and offline network to **maximize the reach across India's consumption strata**
- **JioMart** to create value for entire retail ecosystem by **partnering with** small merchants, kiranas and farmers

Reliance O2C

- **World-class, integrated O2C platform to sustain growth and profitability** through demand and commodity cycles
- O2C to maximize downstream, reduce transportation fuels and **create clean and green energy platforms**

New Energy

- Next big value creation engine – **New Energy and New Materials business**
- Technology and innovation focused partnerships in New Energy to achieve **Net Carbon Zero** by 2035

**Multiple engines of growth with focus on consumers and technology**

# Robust and Consistent Earnings

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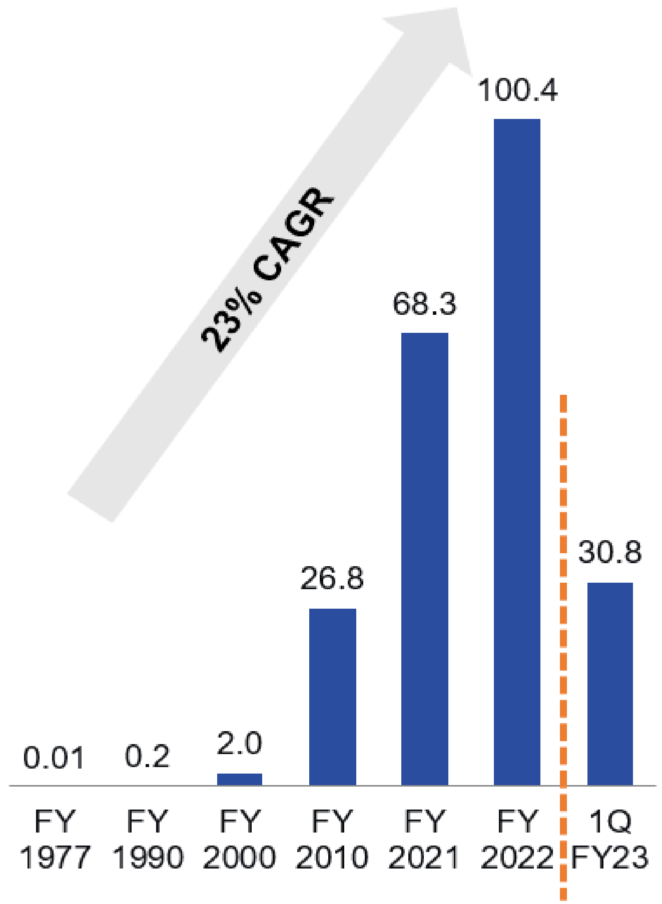
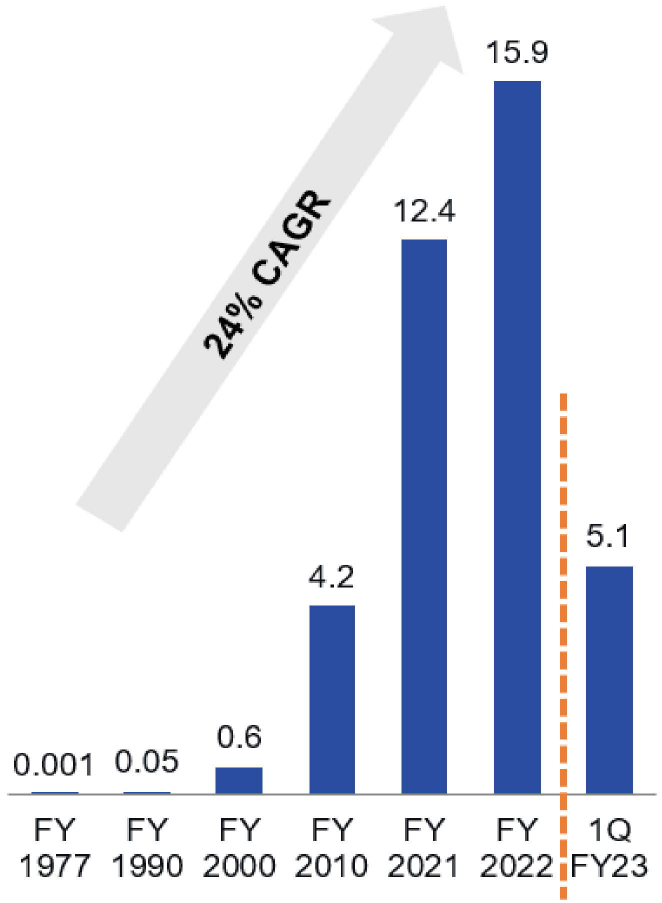
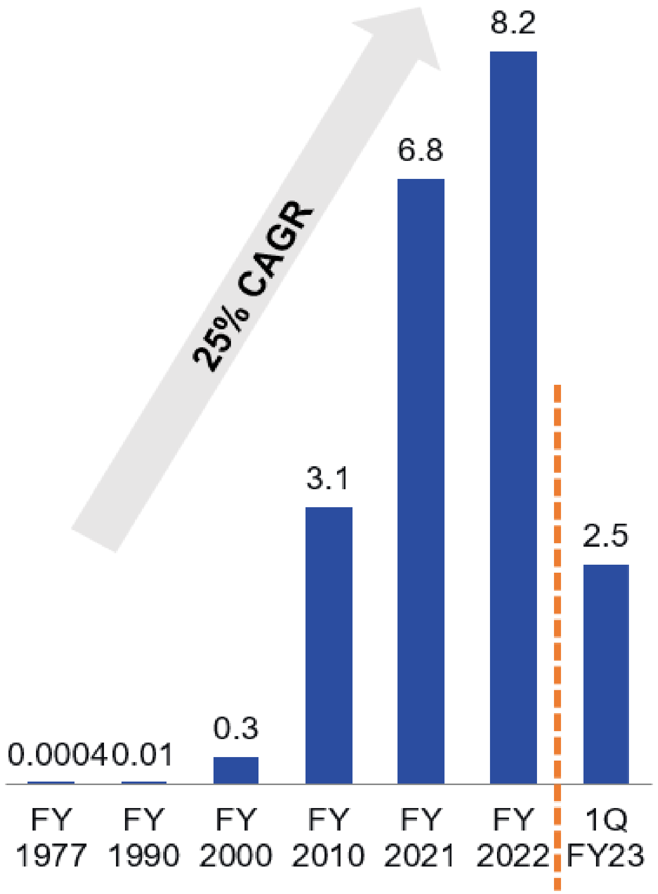
Revenue (US$ Billion)



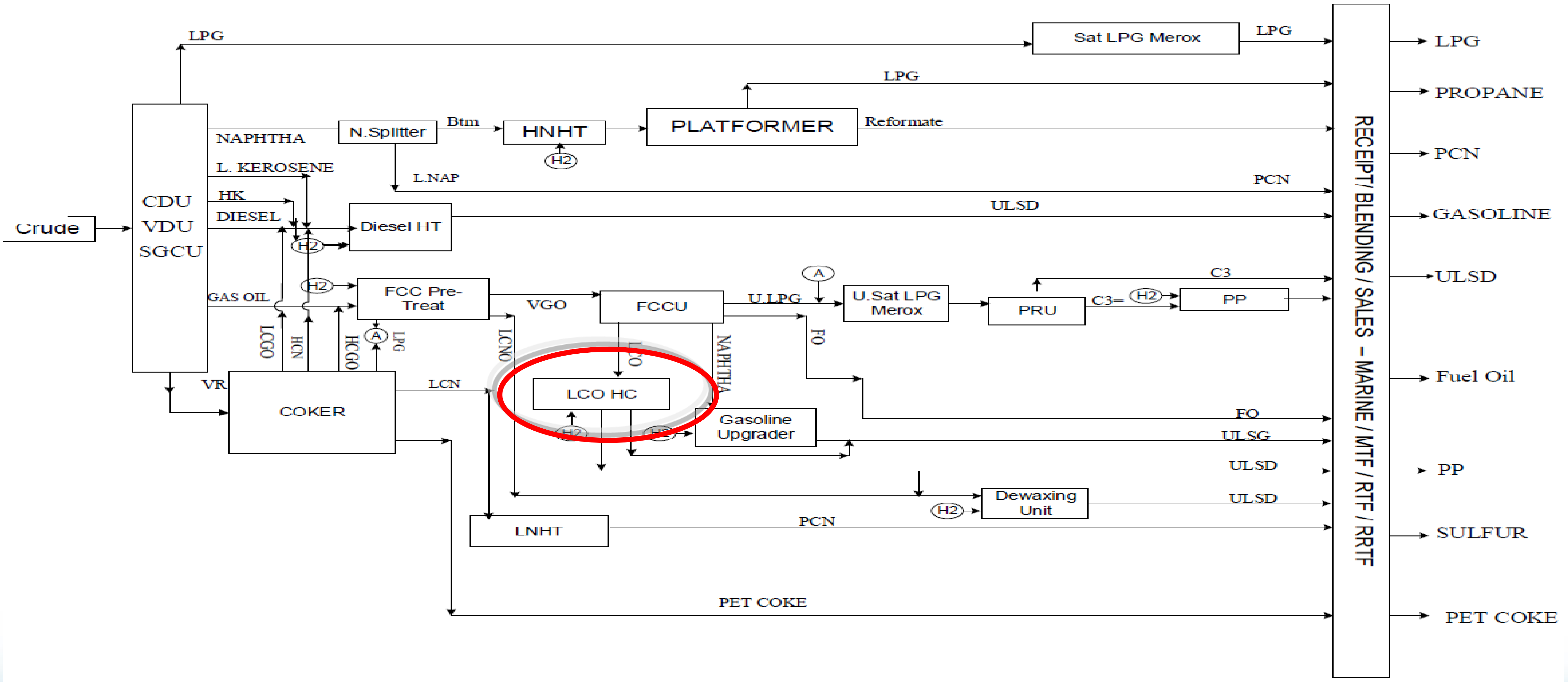

PBDIT (US$ Billion)




Net Profit (US$ Billion)




# LCO Hydrocracker Location in Refinery



# Why Hydrocracking?

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**Light Cycle Oil**

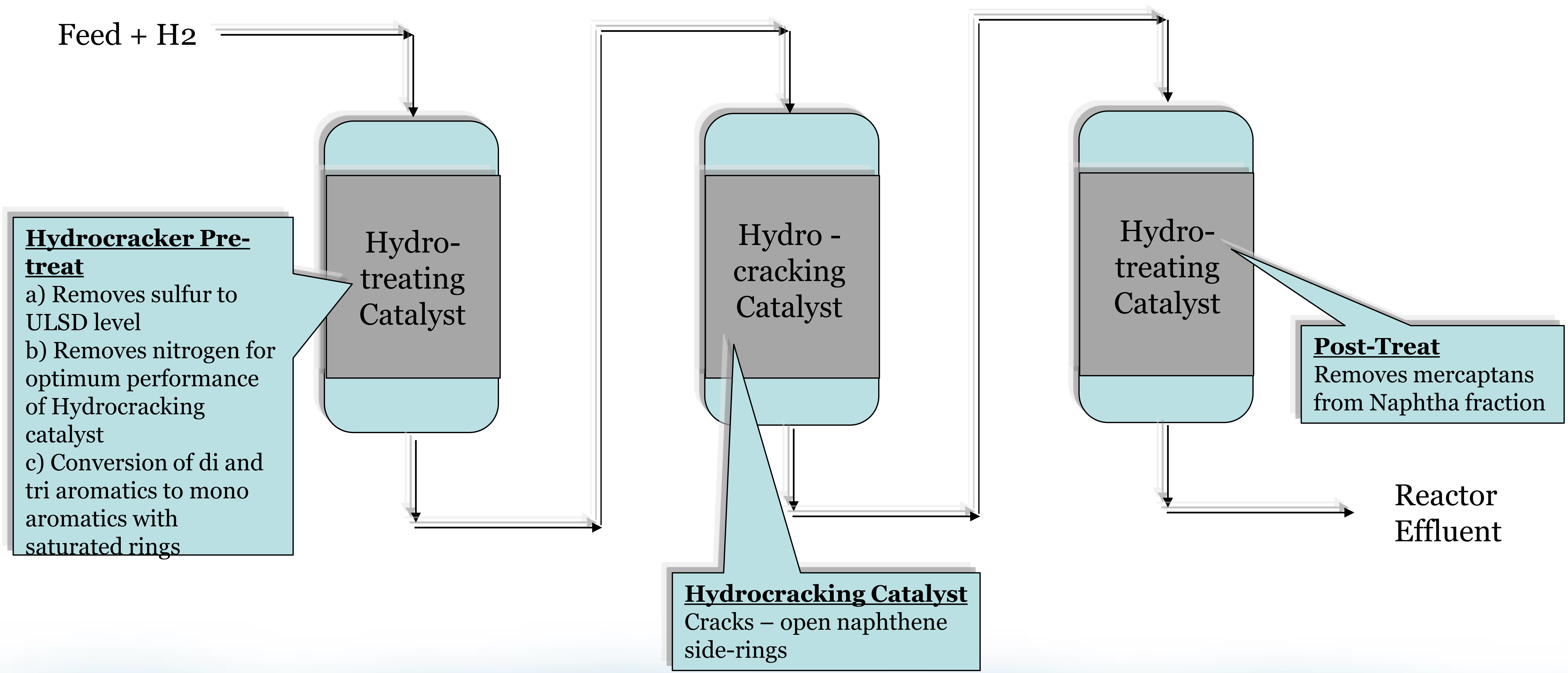
- Diesel Stream Generated from Fluidized Catalystic Cracker
  - High sulfur content (very high concentration of sterically hindered sulfur species), high nitrogen
  - High aromaticity – high density – poor cetane number
- Requires significant upgradation before blending to ULSD
  - Sulfur / Nitrogen removal
  - Density reduction
  - Cetane improvement

**Options for Upgradation**

- Hydrotreating
  - Removes sulfur and nitrogen
  - Reduces density as sterically hindered sulfur is removed via hydrogenation of Aromatic Rings
    - Extent of Density Reduction is small – stream still not blendable to ULSD
- Hydrocracking
  - Removes sulfur and nitrogen
  - Significant Density Boost – saturation of Aromatics Rings followed by Ring Opening
    - Conversion of some portion of LCO into hydrocarbon fractions boiling below 170 Deg C

Hydrocracking (Partial Conversion to 170 Deg C minus) – Suitable Option for Converting LCO to ULSD

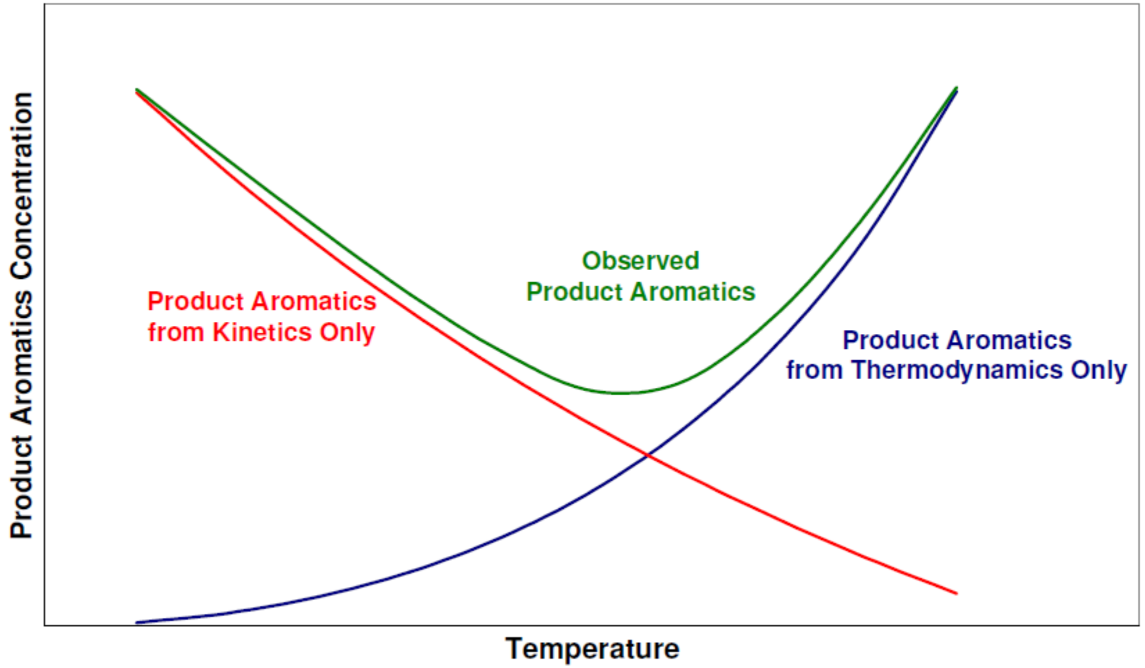
# LCO Hydrocracker Configuration




Three Processes: Pre-treatment (Hydrotreating) / Hydrocracking / Post-treatment (Hydrotreating)

# Pre-treat Catalyst

- Primary element of hydrocracking process
- Prepares the feed for hydrocracking catalyst
  - Removes sulfur to ULSD level
  - Removes nitrogen – prevents neutralization of acidic sites of zeolite in hydrocracking catalyst
  - Converts di and tri aromatics to mono aromatics with naphthenic side rings – easy to crack in hydrocracking catalyst

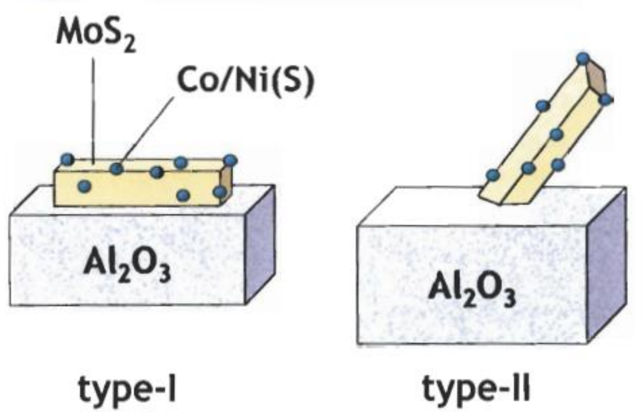



**Impact on Cycle Length**

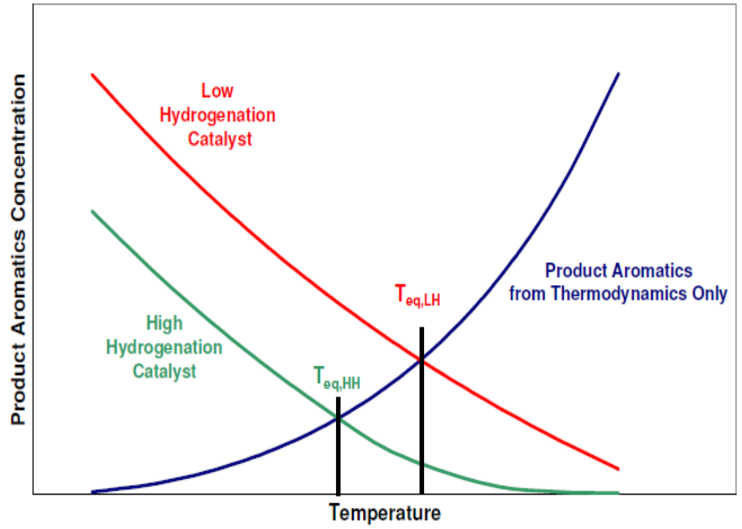
- High aromaticity of feed – hydrogenation of aromatic rings is equilibrium limited
- Lower aromatic saturation in EOR (operation beyond equilibrium point) results in nitrogen slip
- Hydrocracking function is severely affected
- Hydrotreating Catalyst performance decides LCO Hydrocracker Cycle Length

Performance of Pre-treat Catalyst – Key to Longer Cycle Length in LCO Hydrocracker

# Pre-treat Catalyst…




- LCO Hydrocracker requires Type II (high activity) NiMo catalyst
  - capable of higher hydrogenation at lower temperature
  - Better hydrocracking catalyst performance, longer cycle length




**<u>First Catalyst Cycle in RIL LCO Hydrocracker</u>**

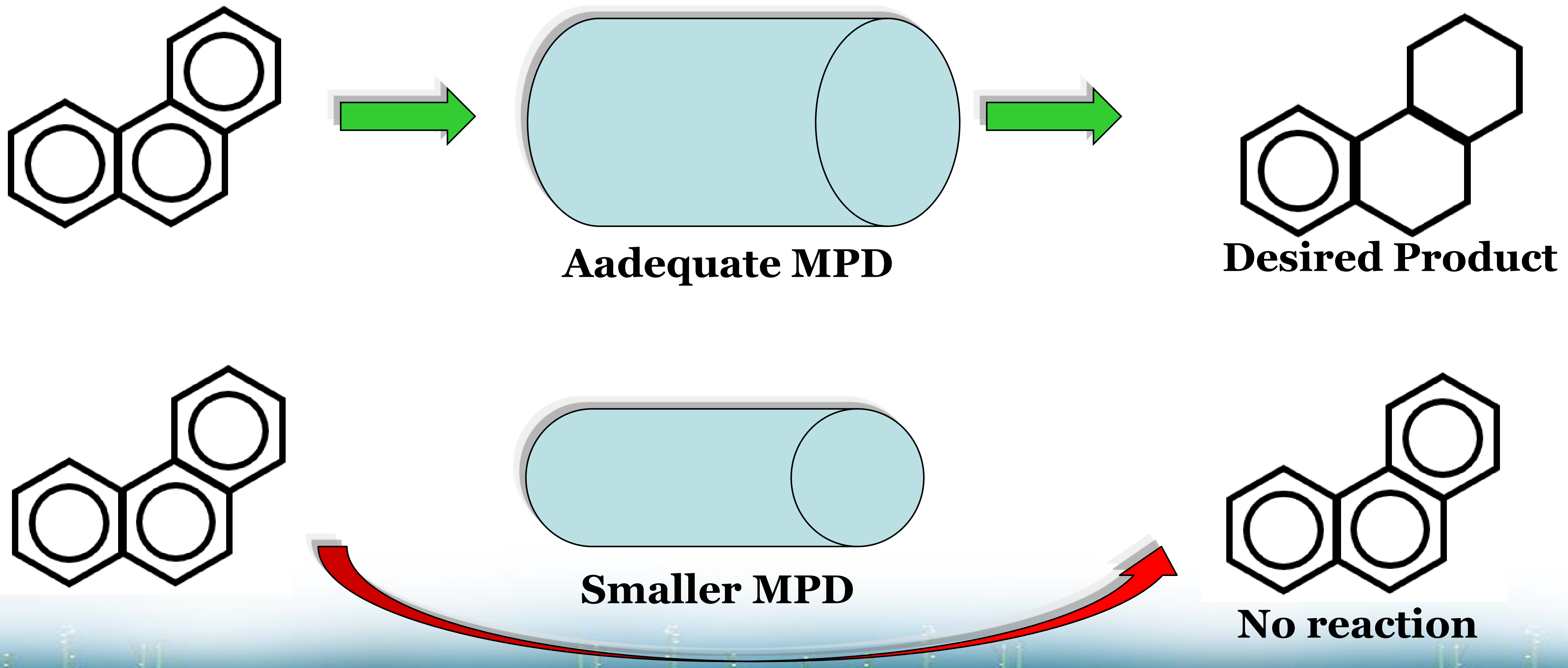
- Best NiMo type II catalyst for diesel service
- High activity zeolite based hydrocracking catalyst

<u>Actual Performance</u>

- Actual delta density lower than catalyst vendor estimation
- Higher hydrocracking catalyst severity than catalyst vendor estimation
- Unit started experiencing >10 ppm S in product in six months of operation

# Reason for Under-performance

- Active metal sites are inside pores present in the carrier.
- Contact between feed molecules and active metal sites is a must for reaction.
- If Mean Pore Diameter (MPD) of catalyst pore is smaller than the molecules, there will be no contact with active metal sites.



# Reason for Under-performance…..

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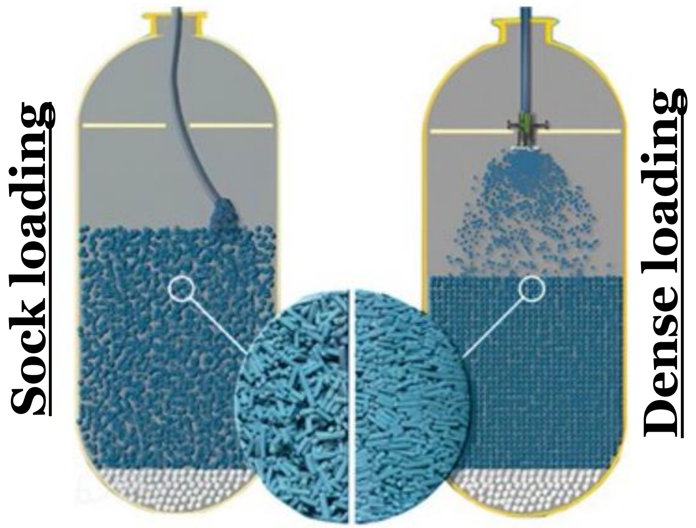
**Detailed Pilot Plant Study revealed the following:**

- Because of higher severity of RIL FCCs, di + tri aromatics are significantly higher in RIL LCO than most other refineries.
- Among all sour diesel streams, sterically hindered sulfur species concentration in LCO is the highest.
- As these molecules are bulky, MPD of the installed catalyst was not enough for easy access through the pores.
- As a result, bulky molecules simply bypassed the catalyst pores and ended up in product
  - High product sulfur
  - Lower naphthene rings for hydrocracking catalyst
- Slippage of organic nitrogen and lower concentration of naphthenes resulted in higher hydrocracking severity.
  - Lower Delta Density at design conversion
- To compensate for high product sulfur, hydrotreating catalyst severity was increased.
  - This resulted in shorter cycle length

Bigger Mean Pore Diameter – Critical for Better Performance of Hydrotreating Catalyst

# Implementation of Learning

- Re-engineering of the catalyst was done to increase Mean Pore Diameter of the catalyst for better access to metal sites
- Increase in Mean Pore Diameter decreases surface area.
  - Lower Surface Area – Lower catalyst activity
  - To compensate for reduced surface area, there is a requirement of loading more catalysts in hydrocracker pre-treat.
  - This was accomplished by converting one of the pre-treat beds from sock-load to dense-load




**Outcome**

- Lower product sulfur / lower nitrogen slip
- Higher naphthenic rings for hydrocracking catalyst
- Higher delta density / delta cetane
- Better cycle length

# Repurposing of Post Treat Bed

**Conventional Post Treat Bed**

- Post treat bed consists of low activity NiMo (type I) hydrotreating catalyst.
- Main purpose is to polish off any mercaptan that might have formed because of recombination in naphtha fraction

**Utilization of Post Treat Bed for Higher Delta Density / Higher Delta Cetane**

- Hydrocracking reactions happen at high temperatures.
- Typically, these temperatures are above aromatics saturation equilibrium.
- Cooling hydrocracking bed outlet to aromatic saturation equilibrium temperature at post treat bed inlet provides flexibility for further aromatics saturation
- Loading high activity NiMo catalyst (type II) in place of low activity type I catalyst maximizes saturation of remaining di aromatics.
  - Increased aromatics saturation – increased delta density / delta cetane

**Implementation in RIL LCO HC**

- High activity NiMo (type II) catalyst was incorporated in the post treat bed.
- The bed was operated at low temperature (closure to equilibrium) using bed inlet quench.
- Delta Density / Delta Cetane improved significantly because of repurposing the post treat bed.

# Conclusion

- Although LCO is a diesel range stream, it is quite different from conventional sour diesel streams.
- High severity in upstream FCC increases aromaticity in the stream.
- Concentration of sterically hindered sulfur species is also the highest in LCO.
- Above factors make LCO hydro-processing a difficult proposition.
- High activity NiMo (type II) catalyst is required
  - To convert di and tri aromatics to mono aromatics having naphthene rings
  - To meet ULSD sulfur target
  - To remove nitrogen from hydrocracking catalyst feed
- At the same time, Mean Pore Diameter (MPD) of the catalyst carrier is adequate for allowing access of molecules through the catalyst pores.
- Higher MPD reduces Surface Area of the catalyst. To compensate for that, part of pre-treat catalyst can be dense-loaded.
- Repurposing Post-treat Bed from conventional polishing bed to aromatic saturation bed will provide maximum benefit out of the unit in terms of higher delta density and higher cetane.

# Thank You