Exceptional Stability through High Performance Hydroprocessing (HPC) Catalysts

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Southwest Process Technology Conference

Agenda

- Function of HPC Catalysts
- Composition of HPC Catalysts
- Catalyst Technology Development
- Importance of Stability
- Examples of Activity & Stability improvements

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Function of HPC Catalysts

- Purification of Petroleum Fractions (Hydrotreating):
  - Removal of S & N reduces pollution from gasoline & diesel
  - Saturation of aromatics improves Smoke point of jet and Cetane quality of diesel
  - Remove contaminants and inhibitors from feeds to downstream refinery processes such as FCC, reforming, etc.
- Conversion of Higher Boiling Molecules (Hydrocracking):
  - Isomerize long straight chain paraffins into branched paraffins to improve cold flow properties
  - Crack large molecules (680 ^{o}F plus) into smaller ones to be used as fuel or Lube oil base stocks
- As the name implies, these reactions occur in the presence of H_2 at elevated temperature and pressure

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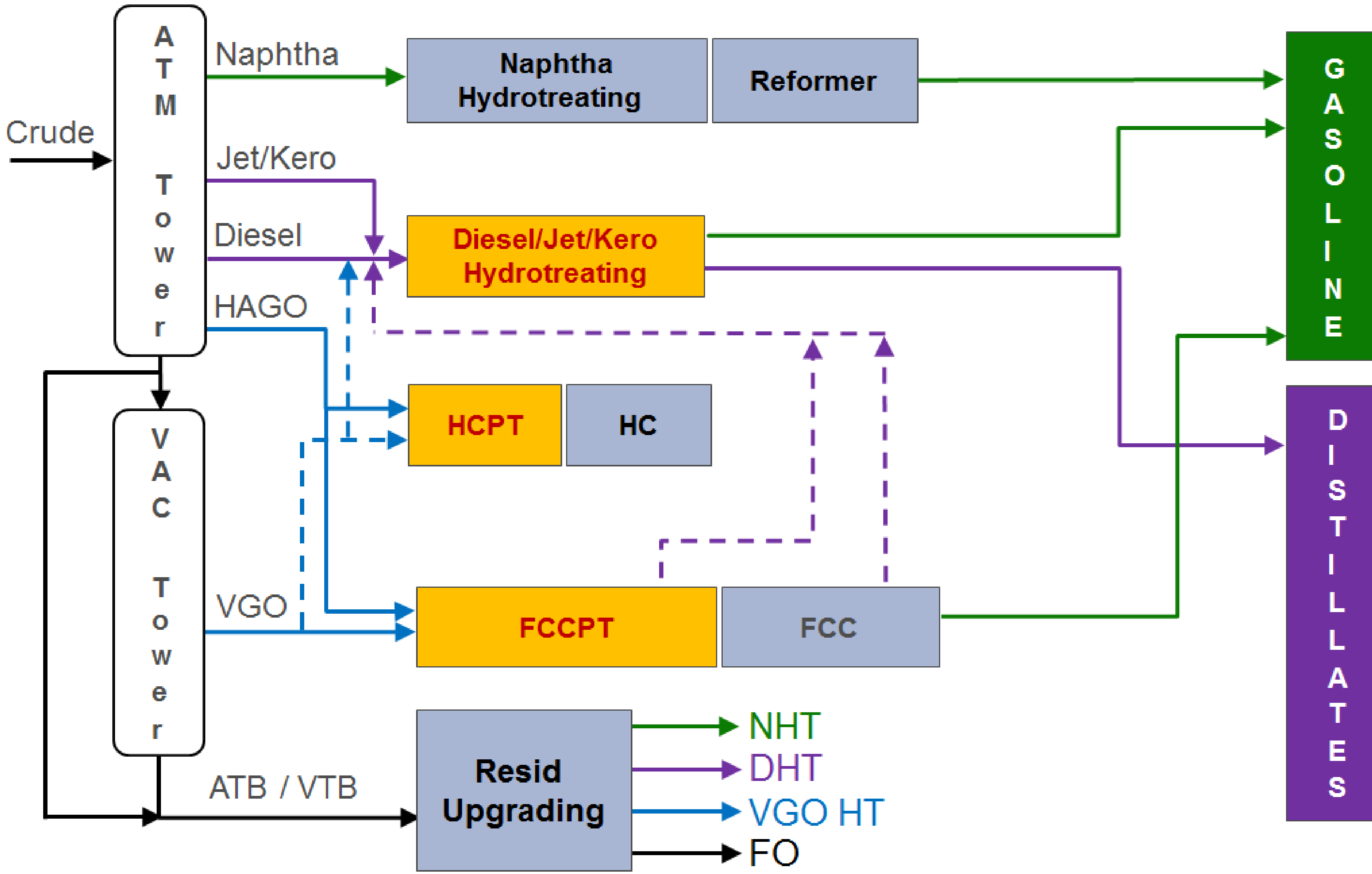
Crude
ATM Tower
Naphtha
Jet/Kero
Diesel
HAGO
VAC Tower
VGO
ATB / VTB
Naphtha Hydrotreating
Reformer
Diesel/Jet/Kero Hydrotreating
HCPT
HC
FCCPT
FCC
Resid Upgrading
NHT
DHT
VGO HT
FO
GASOLINE
DISTILLATES

Composition of HPC Catalysts

- Hydrogenation Function:
  - Made up of high activity metal sulfides such as Ni, Co, Mo (base metal) or Pt, Pd (noble metal)
- Cracking Function:
  - Provided by amorphous oxides (Alumina, Silica-Alumina) or by crystalline zeolites.
  - Ratio of cracking and hydrogenation functions is critical to optimize activity and selectivity.
- Binder (Alumina):
  - High surface area enabling good dispersion of active phase
  - High void fraction to enable easy access to active sites
  - Minimal activity to prevent undesirable reactions and good strength to avoid breakage
- Hydrocracking catalysts are bifunctional in nature and include hydrogenation & cracking activity

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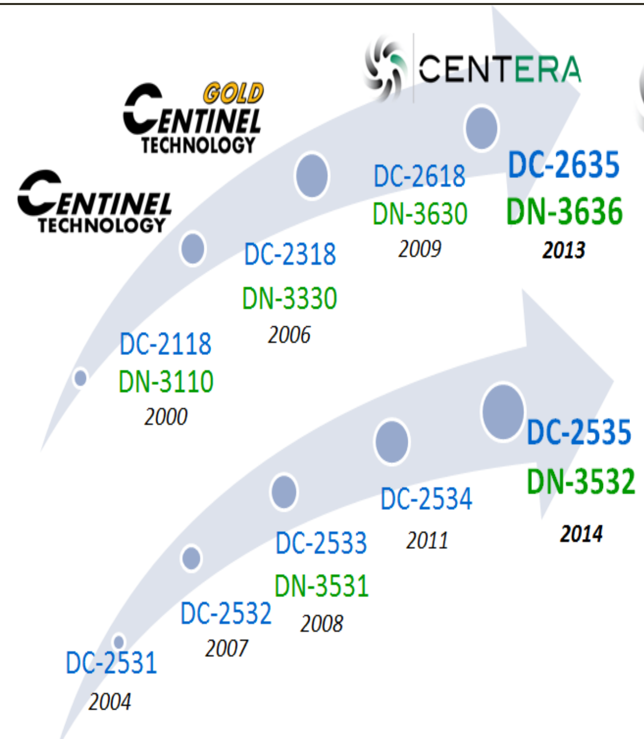
Catalyst Technology Development

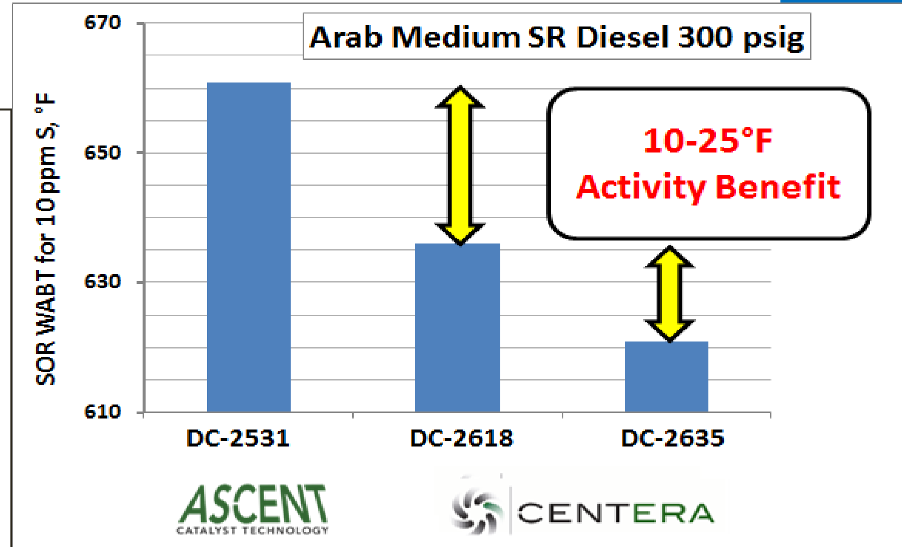


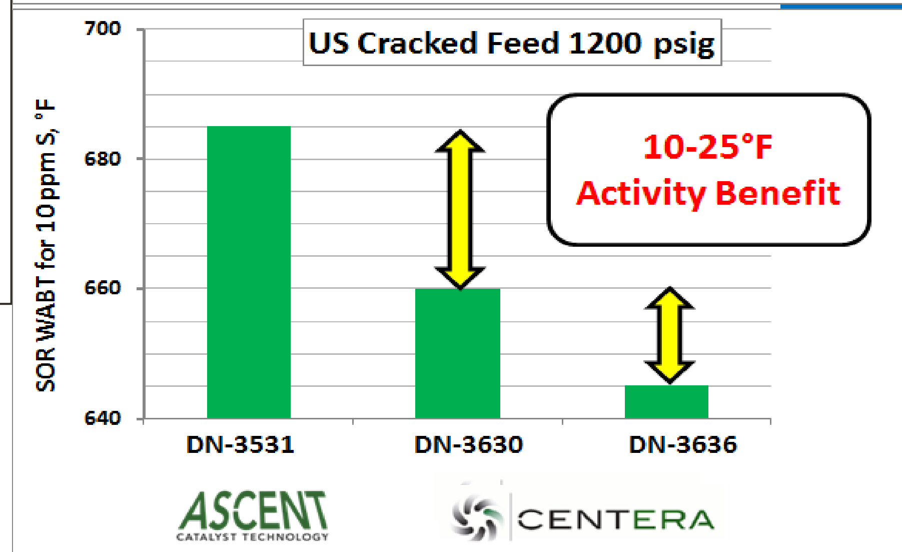
CENTERA

- Highest activity
- Type II catalyst

ASCENT CATALYST TECHNOLOGY

- High activity
- Lower H_2 consumption
- Conventional regeneration





Importance of Stability

- While activity gain is critical in catalyst development, truly successful performance combines good activity with low deactivation rate to enable either longer life or improved ability to process more difficult feeds
- Higher hydrogenation activity means lower propensity to form coke
- Physical properties of the binder play a critical role in catalyst stability:
  - High surface area for both availability of active sites and adsorption of poisons
  - High pore volume provides storage capacity for coke & metals in case of heavier feeds

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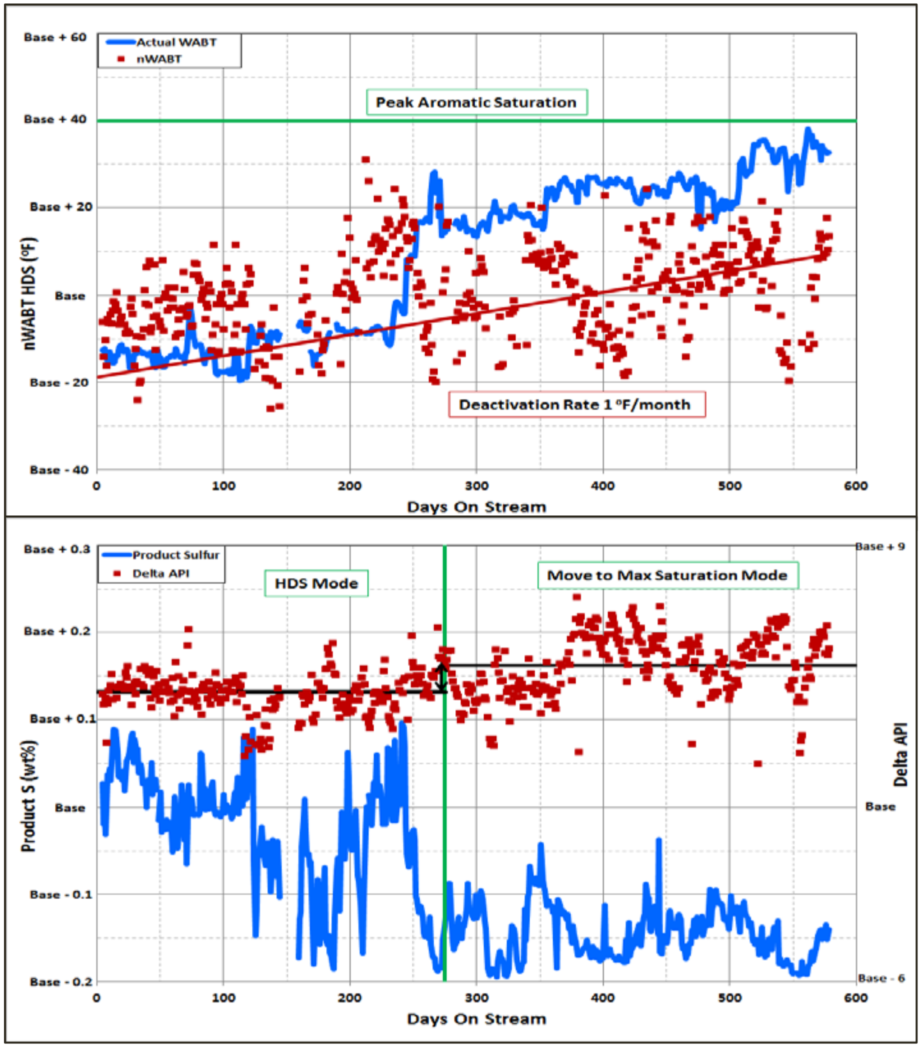
Increased resilience with more cracked feed and higher severity

	ASCENT™ DN-3551	CENTERA™ DN-3651
Feed Rate, kBPD	BASE	+ 10 %
% Cracked	**28 %**	**51 %**
Feed API	BASE	- 1.9
Feed Sulfur, wt%	BASE	+ 22 %
Feed Nitrogen, ppm	**BASE**	**+ 26 %**
Feed T95, ºF	BASE	BASE
Deactivation Rate, ºF/m	**1.2**	**1**

	HDS Mode	Aromatic Saturation Mode
WABT, ºF	BASE	+ 25 F
API Gain	**BASE**	**BASE + 0.8**
% HDS	BASE	+ 2 %
% HDN	**BASE**	**+ 8 %**
Diesel Sulfur	BASE	- 47 %
Deactivation Rate, ºF/m	BASE	No change

- This FCCPT unit processed higher rate & more cracked stock at similar deactivation rate (DR) compared to previous cycle
- Operating mode was changed to maximum saturation by increasing temperature resulting in significant improvement in FCC feed quality
- The exceptional stability of the current catalyst system means the DR continues to be low even at the higher severity

Excellent Stability with Increased Operating Severity



- Operating mode for this FCCPT unit was switched to maximum aromatic saturation to target higher volume swell & H_2 consumption
- Delta API was one number higher in Asat mode
- Deactivation rate was unchanged in spite of the higher severity

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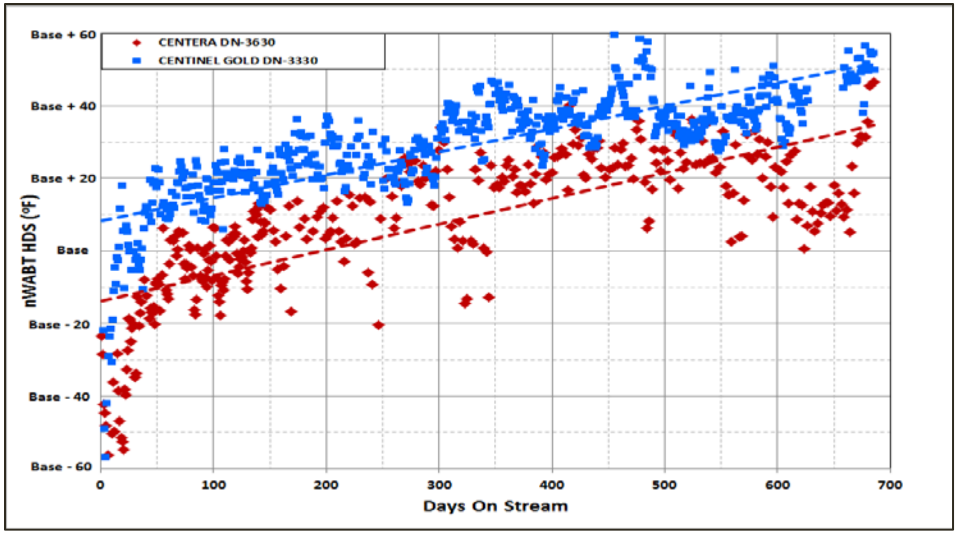
Stable performance with Heavier Feed in ULSD service



	CENTINEL ™ DN-3330	CENTERA™ DN-3630
Feed Rate, kBPD	BASE	+ 3%
Feed S, wt%	**BASE**	**+ 175%**
Feed N, ppm	BASE	+ 22%
Feed T90 / FBP, °F	**BASE / BASE**	**+ 22 / + 27 °F**

- New generation catalyst maintained a 15 – 20 °F activity benefit throughout the cycle
- Refinery was able to increase straight run diesel and LCGO end point
- Average feed was heavier with higher S and N; unit achieved higher margin while maintaining cycle life

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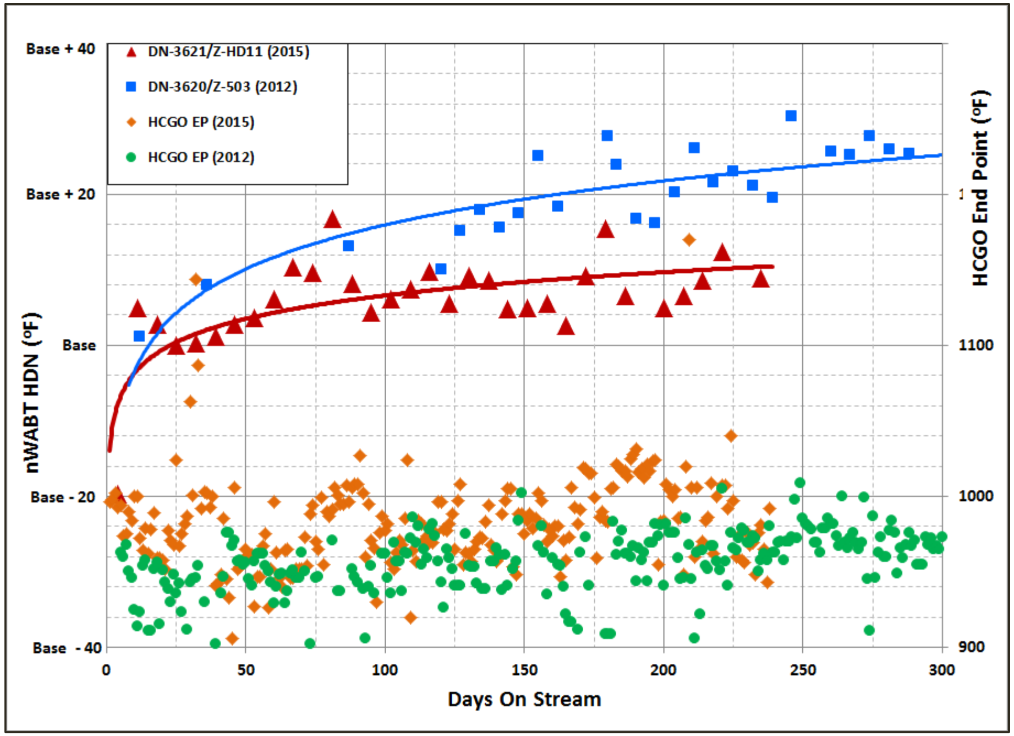
Improved HCR PT Activity & Stability with Heavier HCGO



- Pretreat reactor changed to a newer generation hydrotreating and ASA catalyst system
- The current system is 8 – 10 ºF higher in HDN activity with a 40% lower deactivation rate even though the HCGO end point is 20 – 40 ºF higher than last cycle
- Current exotherm is 20% higher indicating increased hydrogenation

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Excellent Stability leads to higher Diesel Yields

	ASCENT™ DN-3551 / CENTERA™ DC-2650	CENTERA™ DN-3651 / DC-2650
Feed Rate	BASE	+ 4 %
LCO Rate	**BASE**	**+ 37 %**
Feed API	BASE	- 1.0
Feed Sulfur	BASE	BASE
Feed Nitrogen	**BASE**	**+ 9 %**
H_2 Consumption	BASE	+ 11 %
Diesel Yield, % of FF	**47 %**	**52 %**
Diesel T95	**BASE**	**+ 10 ^oF**

- Another FCCPT unit that processes 100% cracked feed enjoyed large increase in diesel yield with a new generation catalyst load
- Unit was able to process more difficult feed (higher N, lower API) while maintaining yield throughout the cycle
- Diesel T95 was 10 ^oF higher along with higher consumption and thus increased volume swell

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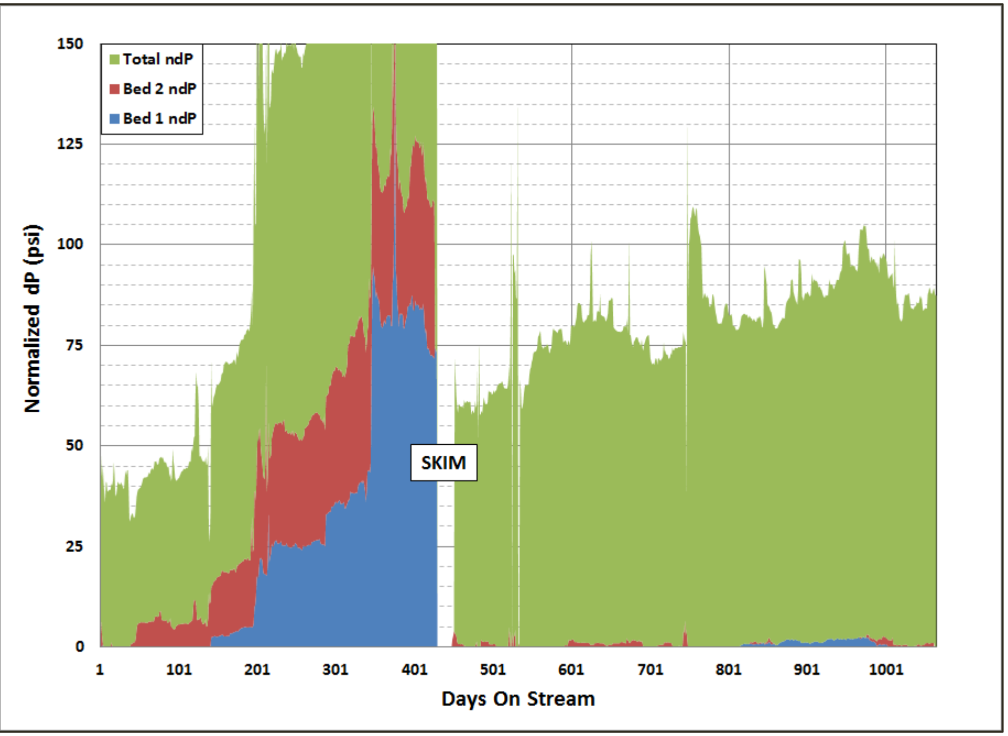
Resolve dP growth with optimized grading



- This unit suffered from chronic delta P growth
- Top two beds were skimmed halfway through the cycle due to high dP
- Delta P increase has been greatly reduced since the skim as a result of grading scheme optimization (smaller catalyst in filter tray, increased grading volume and layering)
- Unit is on track to achieve 60 months cycle life compared to original target of 36 months

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Summary

- In addition to catalyst activity, stability is a key performance indicator to ensure units meet turnaround timing and minimize unplanned downtime
- New catalysts enable refiners to process higher value and more difficult feed streams without sacrificing cycle life
- Units constrained by metals poisoning or delta P growth can be improved by a robust demet system or an optimized grading scheme and hardware options such as Shell Global Solutions HDTrays™ & Filter Trays™
- These products combined with Criterion's technical expertise help refiners maximize value from their assets

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