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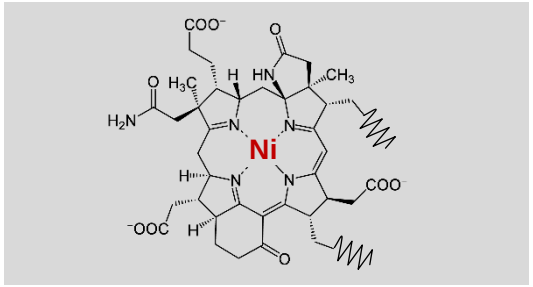
Boron-Based Technology: An Innovative Solution for Resid FCC Unit Performance Improvement

REFCOMM
GALVESTON
MAY 7-11 2018

Outline

- Development of BBT Platform
- BoroCat™
- Borotec™
- Boroflex™

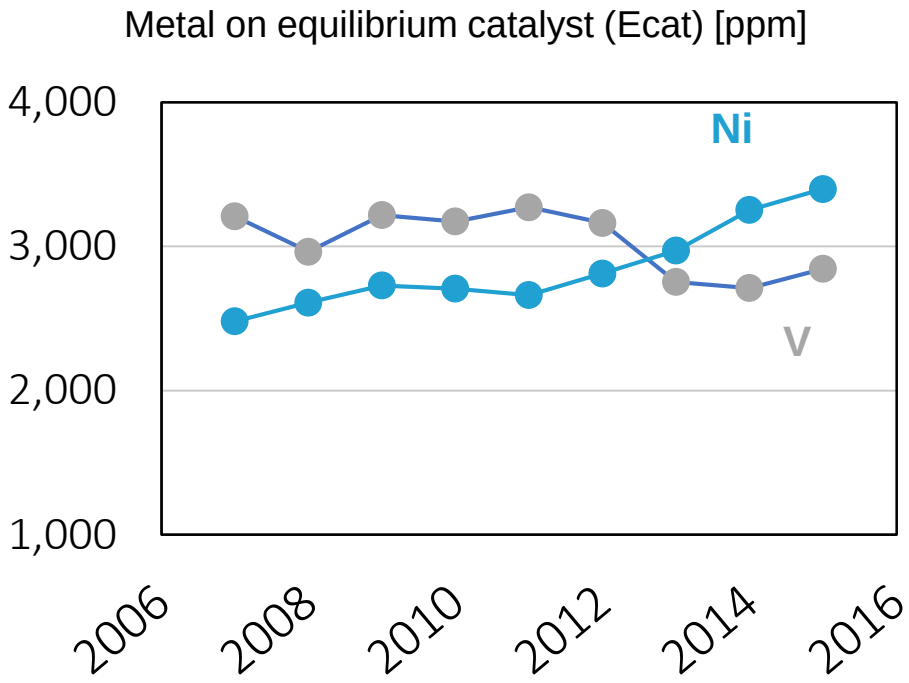
Shift in crude oil quality



Nickel, vanadium and iron are present in crude oil

Contaminant nickel present in FCC feed

Trend in contaminant metals



Increasing demand for catalysts that provide metals tolerance for optimized FCC unit performance

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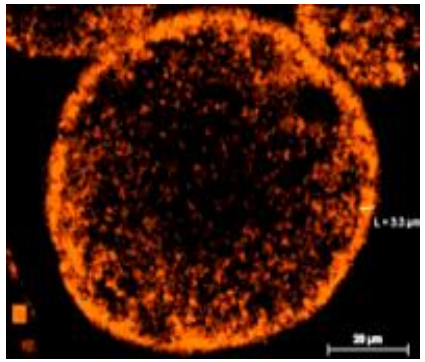
Global trend towards heavier more contaminated combined FCC feedstock

Nickel →



→ **Gasoline**

Nickel →

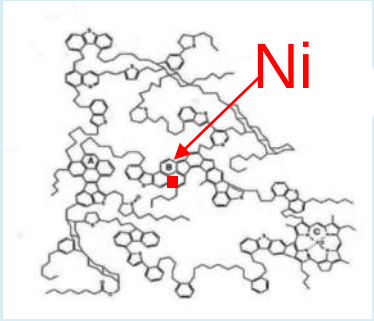
Side reactions:
hydrogen and coke

- During operation, nickel is deposited on the FCC catalyst
- Nickel accumulates especially on the outer surface of the catalyst
- In the FCC reactor, nickel metal catalyzes unwanted side reactions

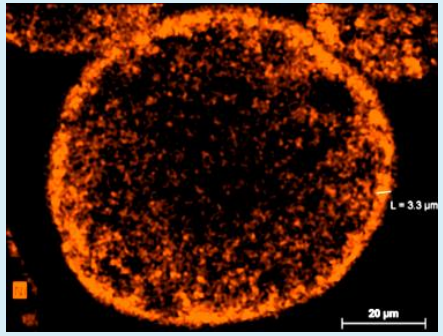
Improve Nickel Passivation for Resid Operations

Technology Objectives

- Create a new resid catalyst to minimize impact of contaminant Ni
- Improve conventional Ni passivation technologies
  - Specialty alumina – immobility
  - Antimony – operational concern



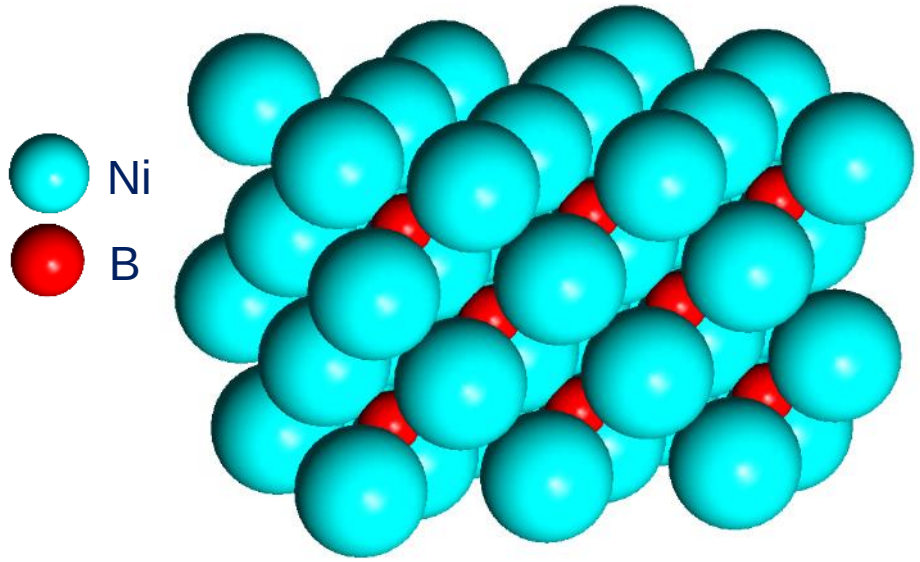
Typical metal-containing feed porphyrin

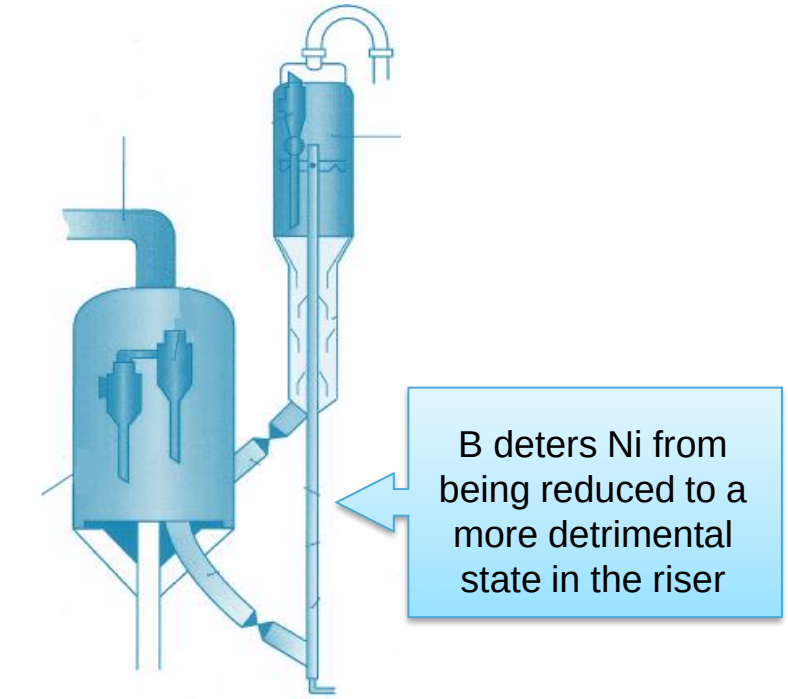


Elemental map of Ni on Ecat

A Novel Solution for FCC Refiners

Boron Mobile Under FCC Conditions, Migrates to Ni on the Catalyst





B deters Ni from being reduced to a more detrimental state in the riser

Introducing Boron-Based Technology (BBT)

BBT utilizes a novel chemistry for improved Ni passivation versus current technologies

- Boron migrates within the catalyst by solid state diffusion to passivate nickel
- Passivation of Ni confirmed by multiple spectroscopy studies

Performance Benefits

- Reduction in H_2 and delta coke

Nickel Passivation with BBT Confirmed in Multiple Lab Studies

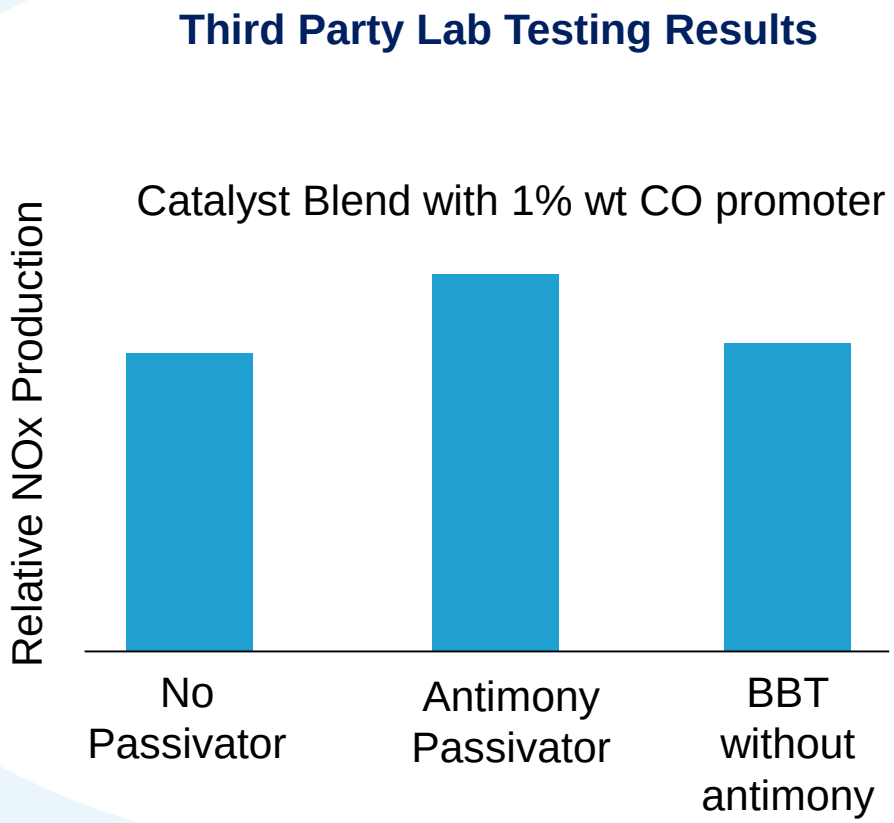
BBT versus Base Resid Catalyst: Relative Yield Shift Percentage @ 75% Conversion

		CPS (3000 ppm Ni; 3000 ppm V)	CMDU (3000 ppm Ni; 3000 ppm V)	Conventional Steam Deactivation (3000 ppm Ni)
H_2	%	-27	-27	-25
Gasoline + LCO	%	+0.8	+2.0	+4.0
Coke	%	-22	-13	-35%

BBT Passivates Nickel without Increasing NOx

Antimony use is not always possible in locations under strict NOx regulations.

Unlike antimony, BBT achieves Ni passivation without any increase in NOx



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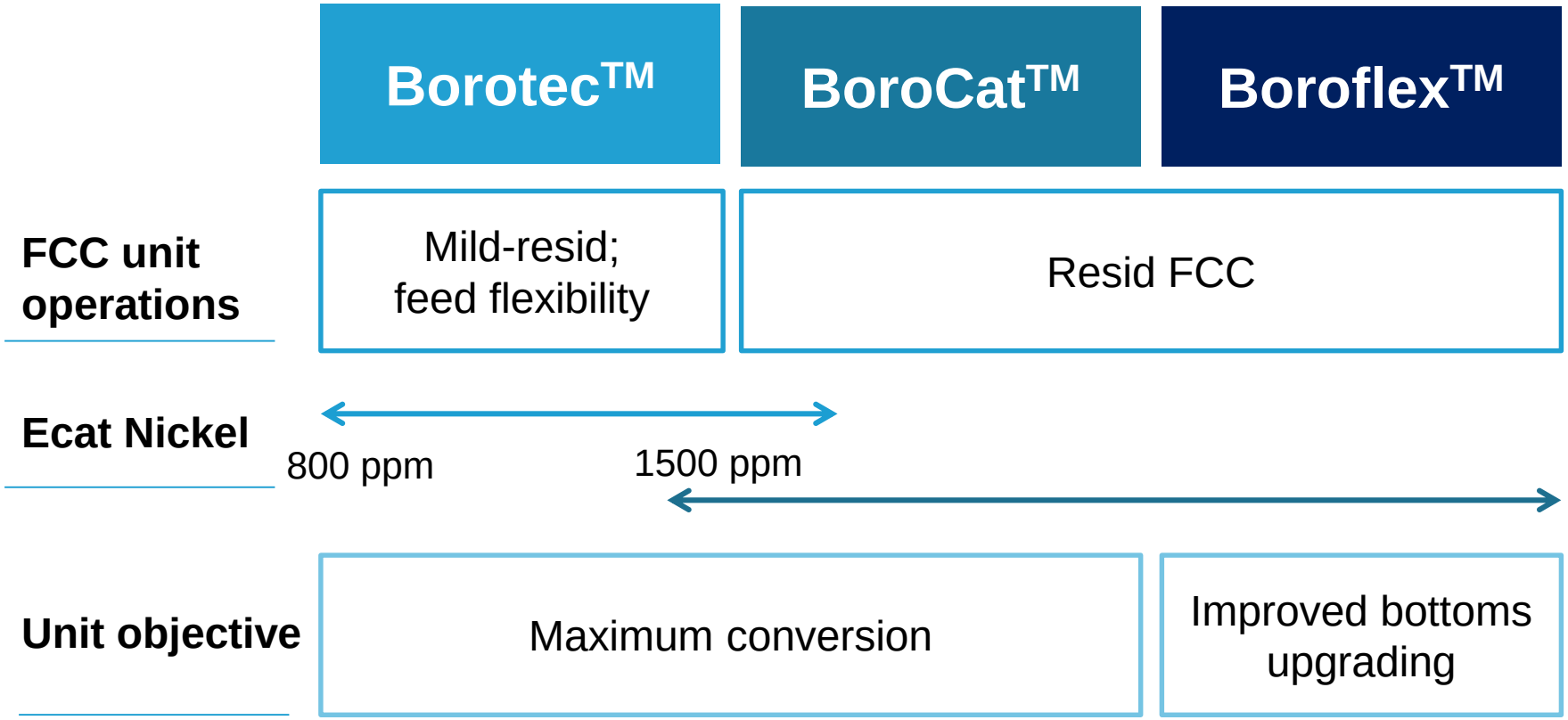
Products from the BBT Platform

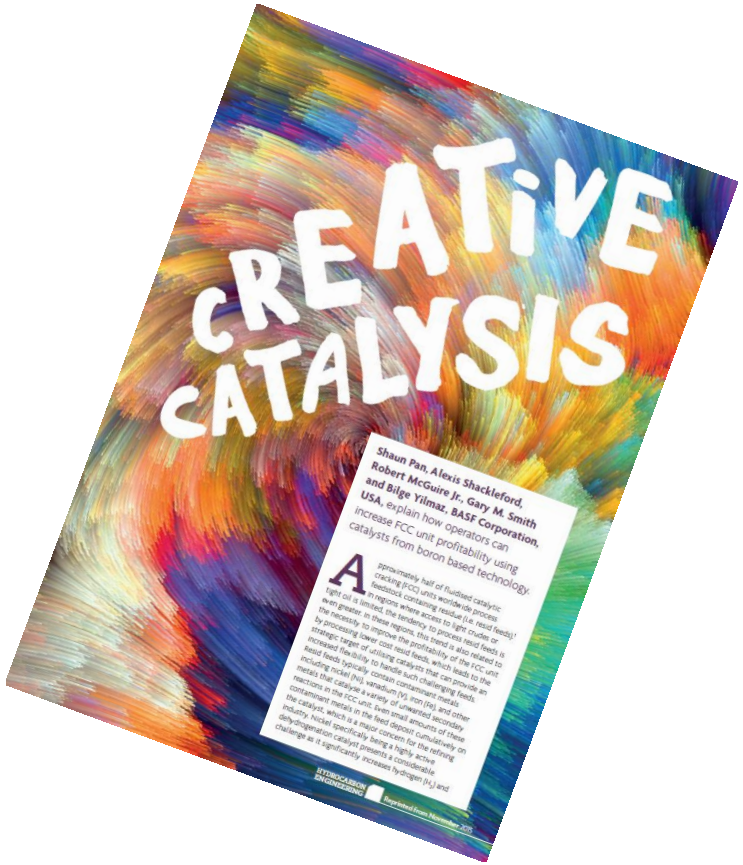


Outline

- Development of BBT Platform
- **BoroCat™**
- Borotec™
- Boroflex™

BoroCat™ – An innovative solution for nickel passivation in resid FCC units

- BoroCat is the first resid-FCC catalyst based on BASF's novel BBT platform.
- BoroCat is engineered to provide maximum metals passivation and superior product yields.
- BBT technology is used to passivate nickel and a proprietary pore architecture is used to minimize diffusional limitations of heavy feed molecules.



In multiple commercial trials, BoroCat reduced H_2 yield, reduced delta coke, increased gasoline yield and increased bottom upgrading

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Multiple Award Winning Catalyst Technology

Contenders:

Best Catalyst Technology

- BoroCat novel passivation FCC Catalyst — **BASF**
- EnviCat nitrous oxide abatement — **Clariant International Ltd.**
- ODH-Et oxidative dehydrognation of ethane — **Mexican Petroleum Institute**
- Molecular Highway bottoms upgrading — **Rive Technology**

2017 Edison Patent Award Winning Patents and Inventors

BASF Innovation Award

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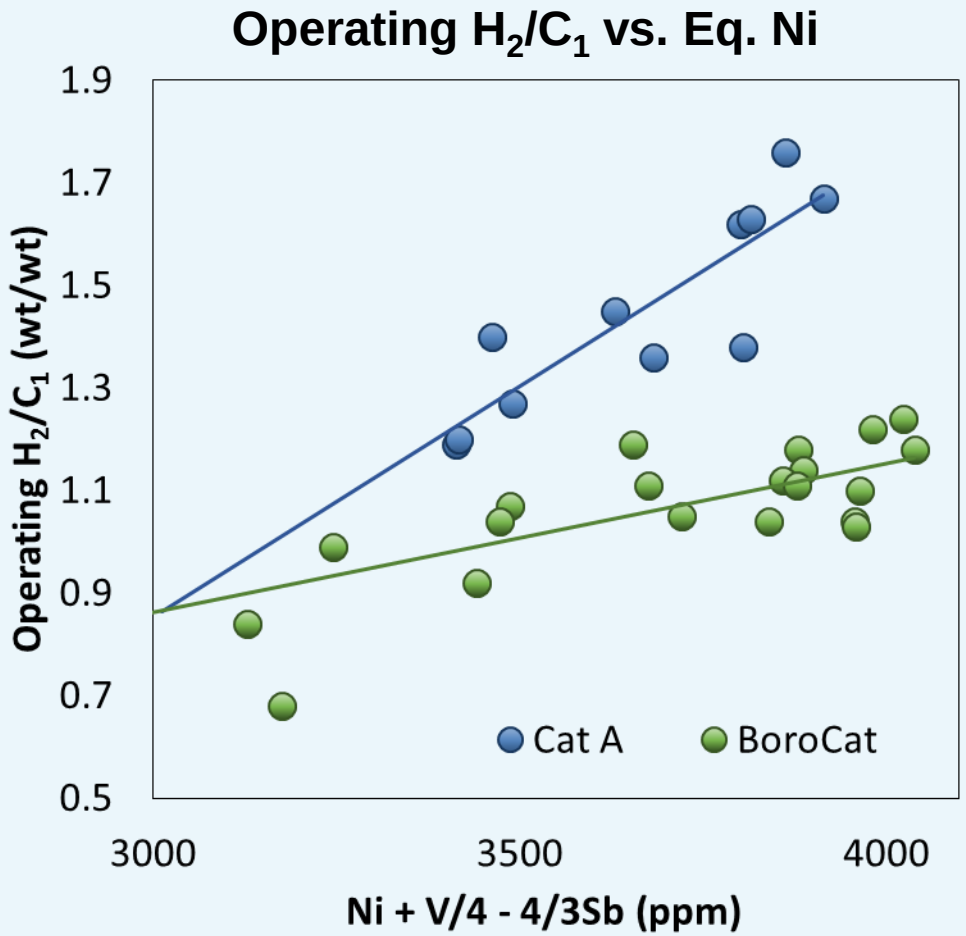
BoroCat Commercial FCC Trial #1

- Resid unit in Europe
  - API gravity: 24 – 27
  - Ecat Ni: 2700 – 3300 ppm
  - Ecat V: 1500 – 2000 ppm
- Switched to BoroCat for max gasoline yield

Result: Improved yield selectivity with lower H_2 and delta coke

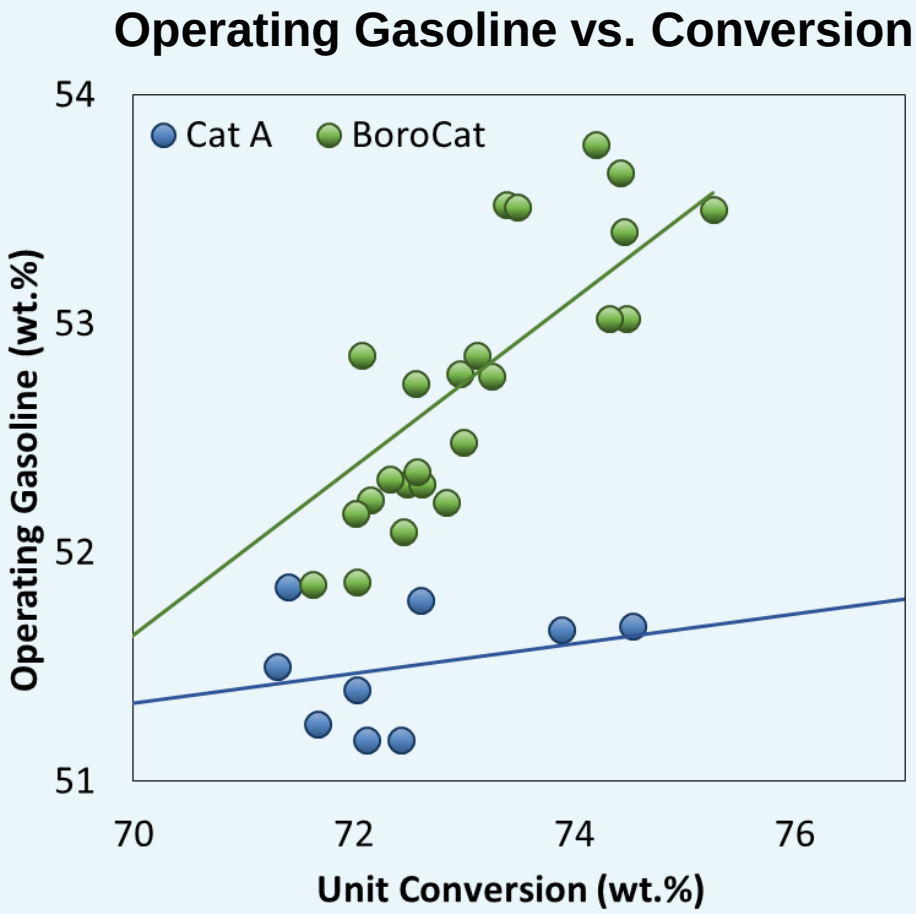
BoroCat Reduced Operating Hydrogen

- Operating H_2/CH_4 decreased with BoroCat at constant equivalent Ni



Operating Gasoline Selectivity Improvement with BoroCat

- Increase in operating gasoline yield with BoroCat at constant conversion



BoroCat Increases Gasoline and Unit Profitability

- **+3%** LPG and gasoline yields, higher conversion
- **26%** reduction of unwanted hydrogen
- **16%** coke reduction

Profitability improvement in line with customers' expectation

Outline

- Development of BBT Platform
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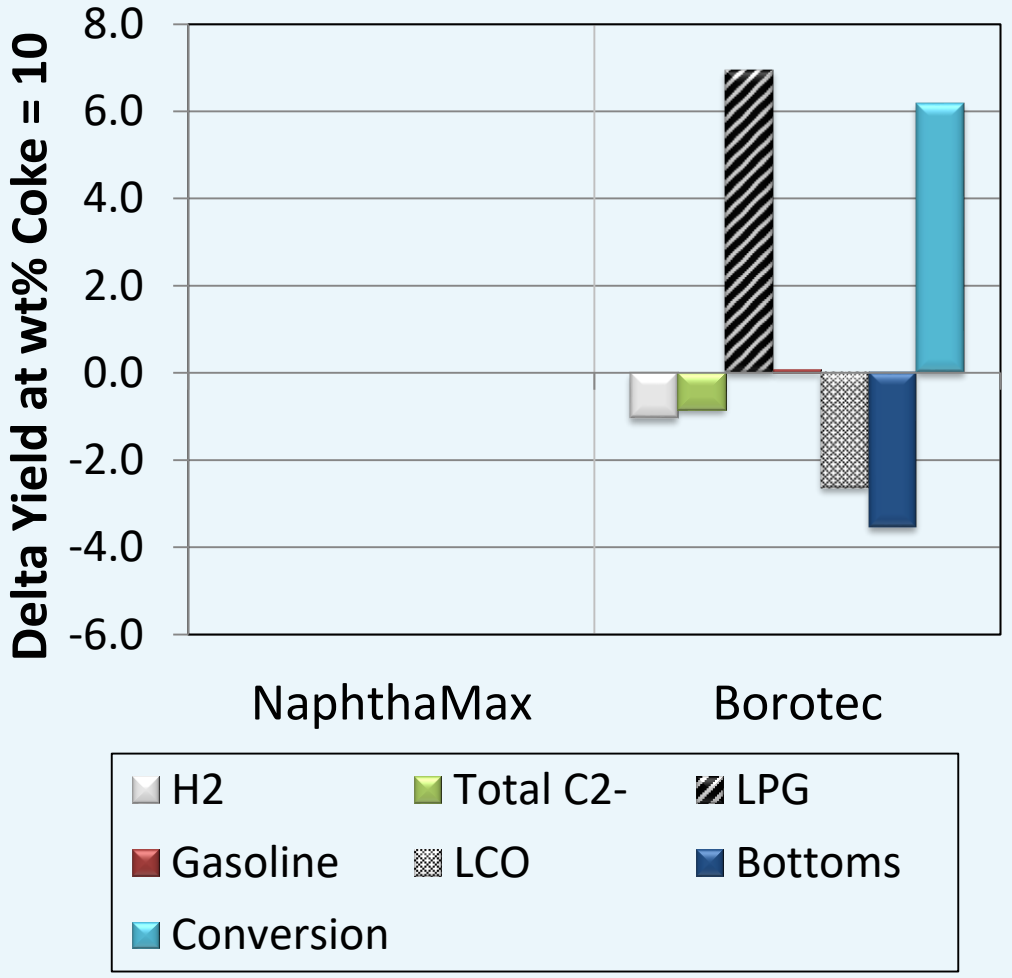
- **Borotec™**
- Boroflex™

Borotec Development

- Applies what made BoroCat™ successful for moderate metals levels
- High conversion, with good tolerance to metals, especially Nickel
- Testing shows vs. gasoil catalyst lower H_2 and delta coke, with improved liquid yield and LCO/BOT yield
  - CMDU Deactivation with 1,000 Ni & 1,500 V



Borotec Application

Borotec is optimal for high conversion, moderate resid feed applications with higher nickel level. Applications include:

- Units processing mild, moderate or hydrotreated resid feeds
- Unit processing variable feed quality needing flexibility with metals passivation as fresh nickel is most detrimental
- Ecat nickel levels 800-2,000ppm
- FCC units requiring metals passivation for lower hydrogen and delta coke
- FCC units desiring high conversion for improved liquid yields

Borotec Competitive Trial gives 0.23 $/bbl Uplift

- Better coke selectivity
- High activity at comparable V and Na levels
- Higher LCO/Bottoms
- Improved C3= and C4= olefin yield (after catalyst optimization for LPG= with a light olefins additive)

	Competitor	Borotec (Prior to Light Olefins Additive)
Conversion, wt.%	80.0	80.5
LPG, wt%	16.9	17
Gasoline, wt%	**54.0**	**54.5**
LCO, wt.%	14.2	13.9
Bottoms, wt%	5.9	5.6
LCO/BOT	**2.42**	**2.48**

While the initial Borotec gave high performance exceeding that of the competitive catalyst, BASF was able to further optimize the catalyst to give higher C3= and C4= resulting in 23 cents/bbl profit improvement over the competitive catalyst

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Boroflex: Boron based technology for Bottoms Upgrading and Distillate Maximization

Boroflex uses the latest in metals passivation technology along with a coke-selective matrix to provide bottoms upgrading for residue feedstocks.

- FCC units processing resid feedstocks looking to reduce slurry yield
- FCC units wanting higher yields of valuable liquid products of LPG (liquefied petroleum gas) olefins, gasoline and distillate products
- FCC units with severe metals contamination concerns targeting lower hydrogen and coke

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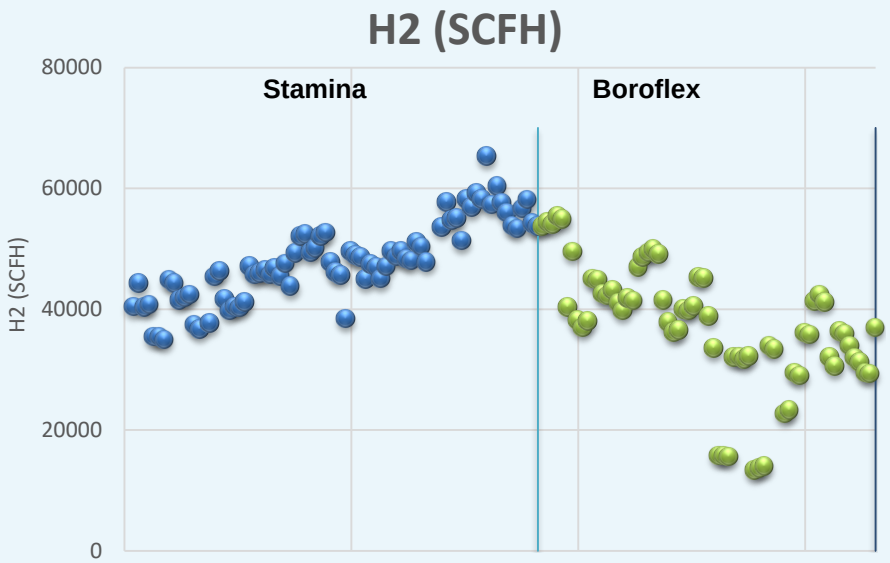
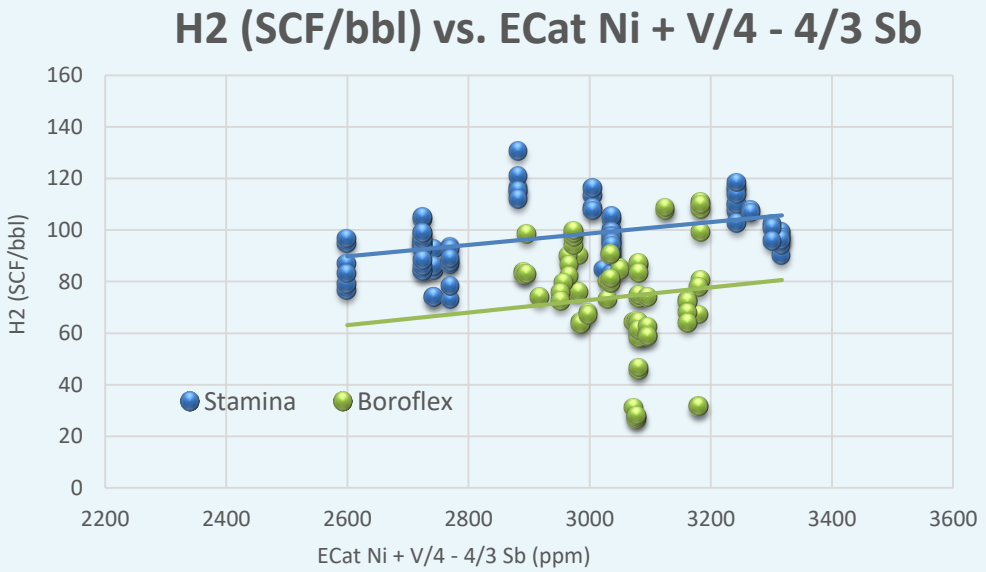
Boroflex Commercial FCC Trial #1

- Resid FCC unit in North America
- Feed: CCR 2-3% ; Ecat Ni 2,500-3,000 ppm; Ecat V: 1,000-1,500 ppm
- Incumbent catalyst: BASF's Stamina
- Objectives:
  - Lower H_2 and dry gas through improved Ni passivation
  - Increase gasoline yield
  - Maintain optimum bottoms upgrading

Boroflex Reduced Operating Hydrogen Yield

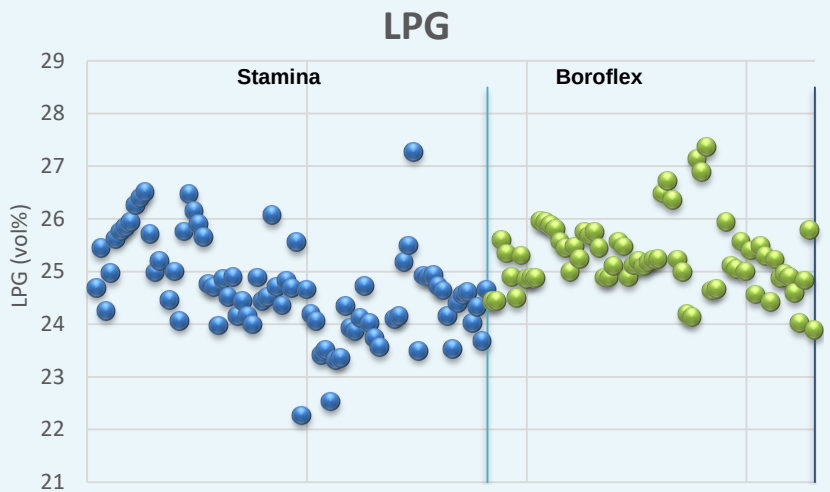
- Despite higher content of **fresh, more active Ni**, H_2 yield was reduced

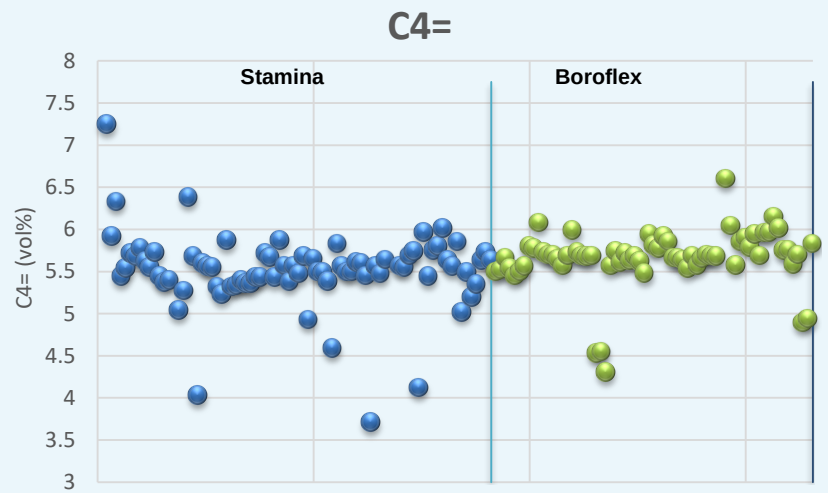


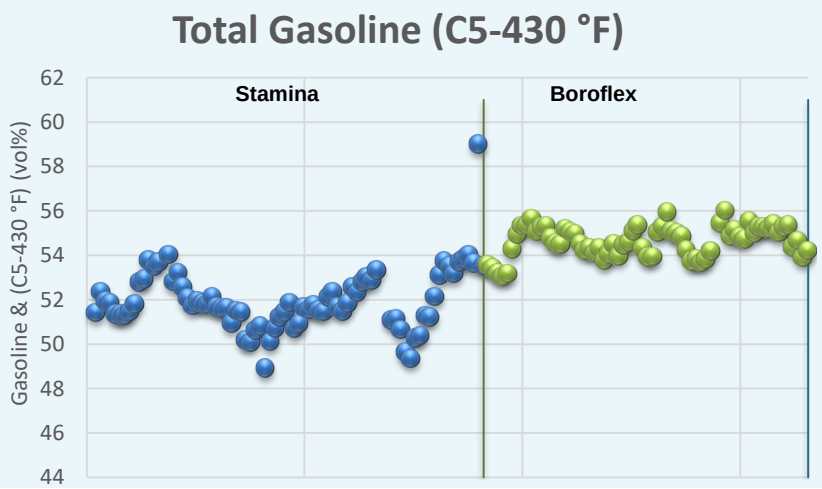


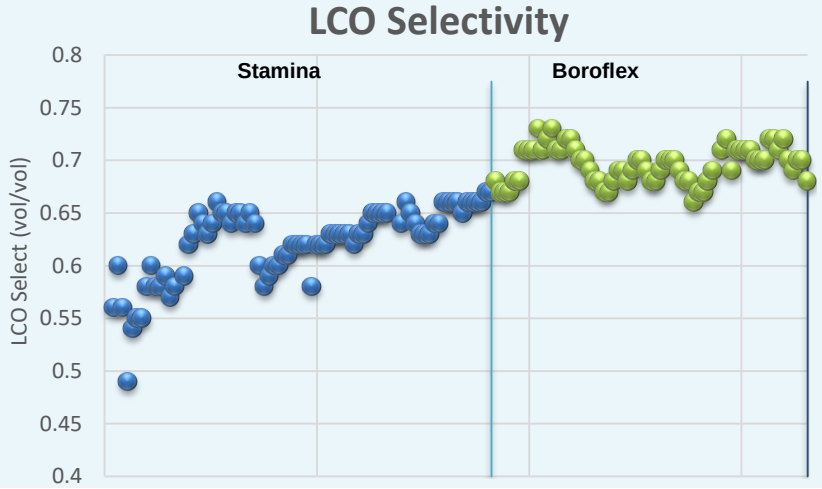
Boroflex Trial: Operating gasoline yield increased

- C4 olefinicity maintained (butylenes selectivity valuable!)
- Gasoline make and LCO selectivity improved



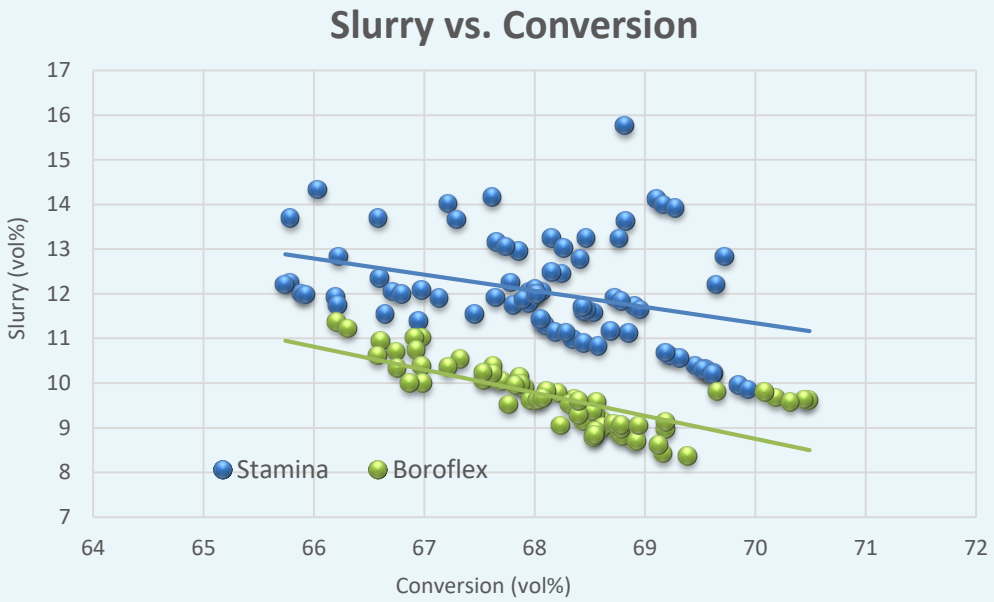


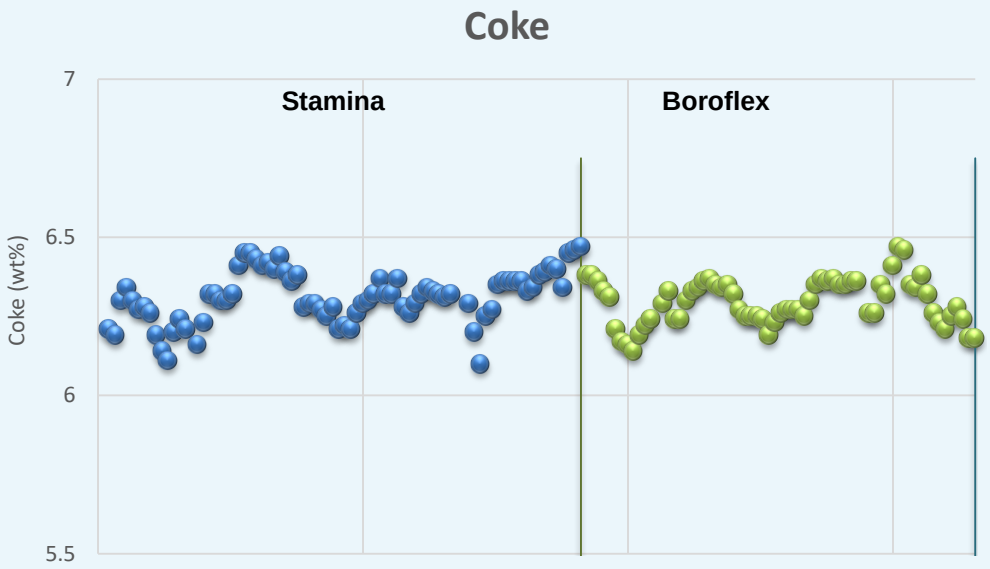




Boroflex Trial: High level of bottoms upgrading

- High level of bottoms upgrading
- Coke remained fairly consistent





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Increase in unit profitability from Boroflex

- Using normalized operating yields and KBC modeling, refinery saw an overall **$0.23/bbl** increase in profitability by switching to Boroflex
- Unit saw similar conclusions in ACE yields (with even larger magnitude)

Operating Yield	Overall Delta
H_2	-0.08
C3	0.02
C3=	0.09
nC4	0.03
iC4	0.13
C4=	0.15
Gasoline	0.65
LCO	-0.38
Bottoms	-0.47
Coke	-0.12
Total C3+ Yield	0.23

Boroflex Commercial Trial Part 2

- Resid FCC unit in North America
- Boroflex vs. another supplier's premium catalyst with new/innovative bottoms upgrading technology
- No olefins additive
- Objectives:
  - Lower H_2 and dry gas
  - Improved olefin selectivity holding overall LPG constant
  - Increase gasoline yield
  - Improve bottoms upgrading

Boroflex Commercial Trial Part 2

- Boroflex gave superior yields
  - H_2 and dry gas decreased
  - Propane decreased (positive for the LPG limited unit)
  - Olefinicity increased
  - Gasoline increased
  - Bottoms decreased, LCO/BOT increased
- Boroflex saw significant improvement in all yields for **0.97-1.30 $/bbl** (seasonal)

Operating Yield (wt%)	Supplier A	Boroflex
Dry Gas	2.8	2.5
Propane	2.1	1.6
Propylene	7.7	8.2
n-Butane	1.2	1.3
Iso-Butane	4.4	4.2
Total Butylene	4.2	5.5
LPG	19.6	20.8
Gasoline	39.3	39.9
LCO	19.0	21.2
Bottoms	13.6	9.5
LCO/BOT	1.4	2.2
Coke	5.8	6.0

Conclusions and Path Forward

BBT platform uses the novel chemistry of boron for passivation of contaminant Ni

- Increased FCC unit profitability & yield selectivity
- No increase in unit NOx emissions

Borotec	***BoroCat***	***Boroflex***
Ecat Ni between 800 – 2,000 ppm	Ecat Ni exceeding 1,500 ppm	Ecat Ni exceeding 1,500 ppm
Target objective: maximum conversion, flexible crude slate	Target objective: maximum conversion resid feeds	Target objective: maximum bottoms upgrading resid feeds
Used in multiple refineries worldwide	Used in multiple refineries worldwide	Multiple North American refinery trials
Flexible for changing crude slate or mild resid feed for improved yields	Maximize liquid yields with lower hydrogen and delta coke	Best bottoms upgrading with lower hydrogen and coke
0.23 $/bbl benefit shown	Up to 0.38 $/bbl benefit shown	Up to 1.30 $/bbl benefit shown

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