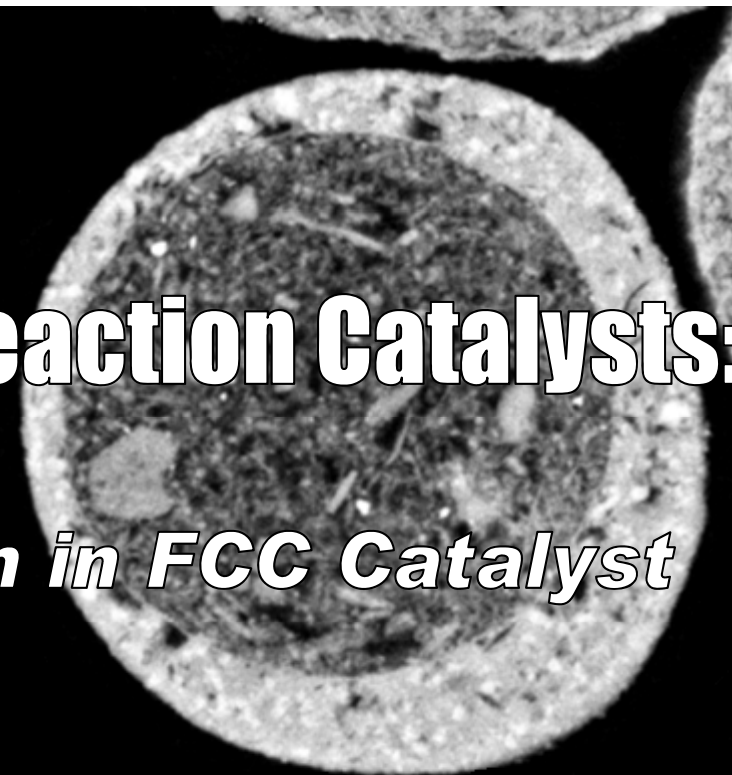




Multi-Stage Reaction Catalysts:

A Breakthrough in FCC Catalyst Technology



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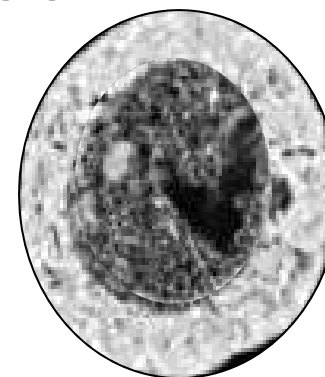
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MORE PRODUCTION - LESS RISK

Multi Stage Reaction Catalysts

An Innovative Manufacturing Technology Platform



- Many commercial processes take advantage of staged reactions with different catalytic attributes
 - Common Refinery example – staged bed hydrotreating reactors
- How can we do this in a circulating system like FCC?



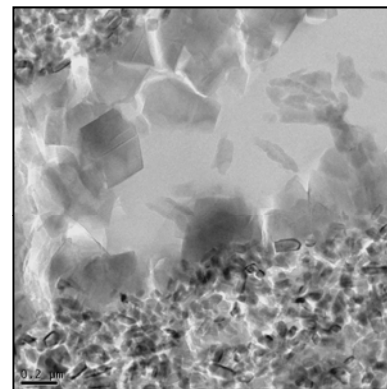
- Through Innovation in FCC Manufacturing!
- BASF Multi-Stage Reaction Catalyst (MSRC) combines two or more FCC catalyst functionalities within a single catalyst particle

Current BASF Resid FCC Technology

Flex-Tec®

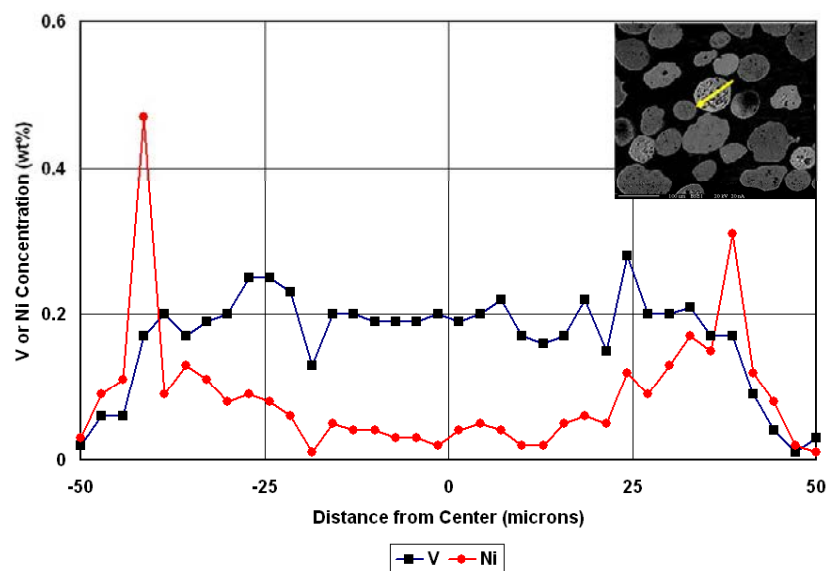
FCC catalyst for severe resid applications

- Optimized DMS structure
 - Enhanced diffusion of heavy molecules
- Separate particle vanadium trap
- Integrated specialty alumina that passivates nickel thus reducing the metal catalyzed formation of hydrogen and coke
 - This specialty alumina is distributed throughout the catalyst particle but as we will see on the next slide nickel mainly deposits on the outermost portion of the catalyst

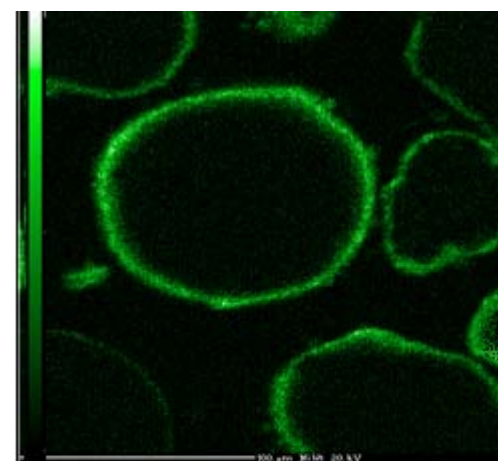


ECat (Equilibrium Catalyst) Analysis

Electron micro-probing



Scanning Electron Microscopy (SEM)

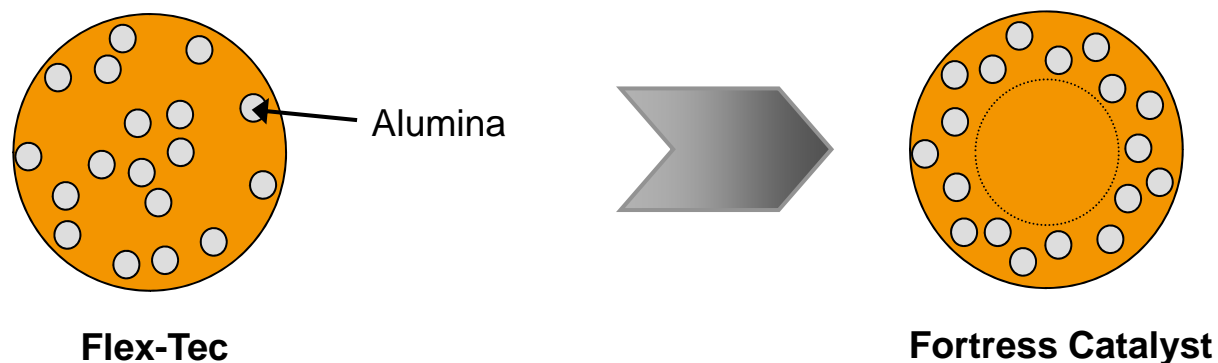


 Nickel

- Vanadium is located throughout particle
- Nickel is concentrated in the outer-layer of catalyst (5-10 micron)

MSRC Approach

Can we improve upon the DMS based Flex-Tec by distributing the specialty alumina where nickel is predominantly located?



Yes: By using a two stage technology with increased alumina content in outer-stage and none in the inner-stage

Fortress™

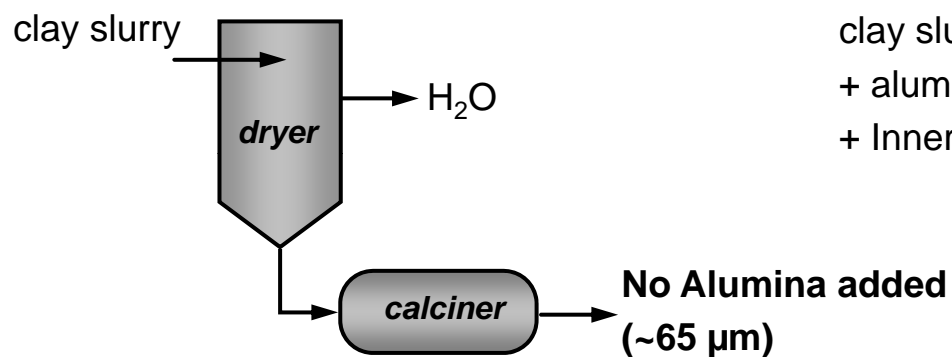
- **Fortress™** is the first product off the new MSRC platform
- DMS based product with improved metals tolerance for lowest H₂/dry gas generation and lowest coke selectivity
- Designed for resid application with high metals



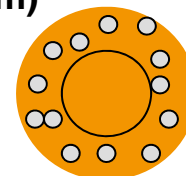
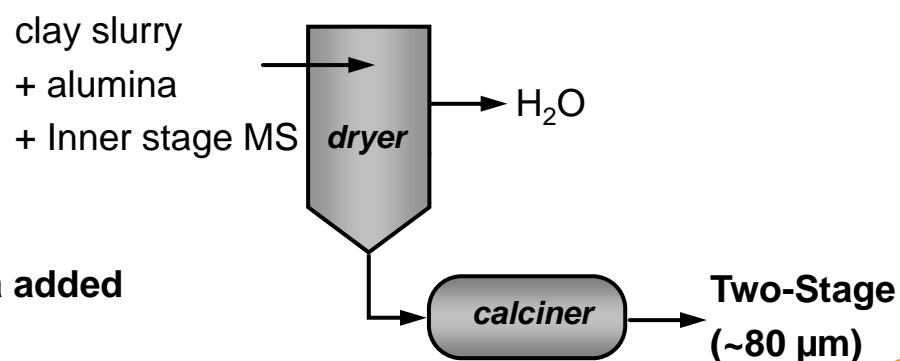
Multi-Stage Reaction Catalysts

Fortress Production Process

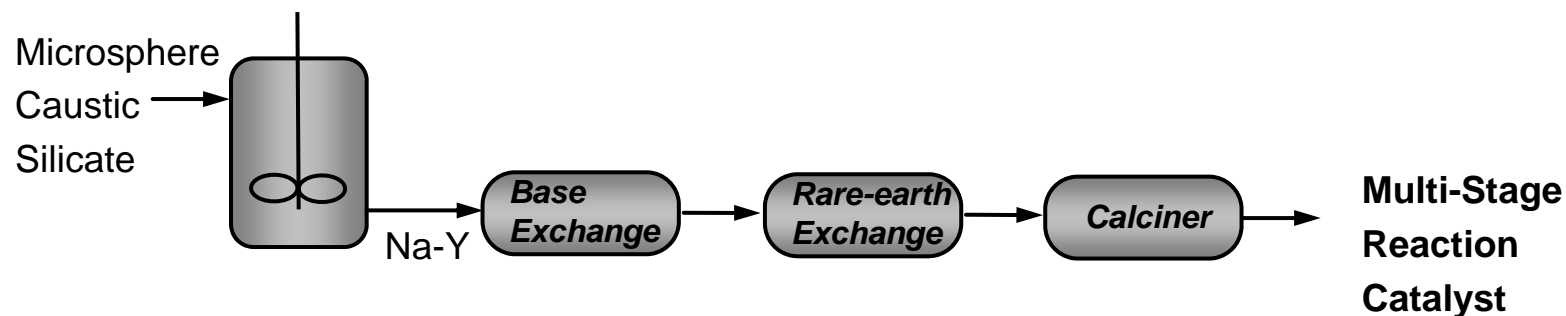
Step 1: Inner stage microsphere



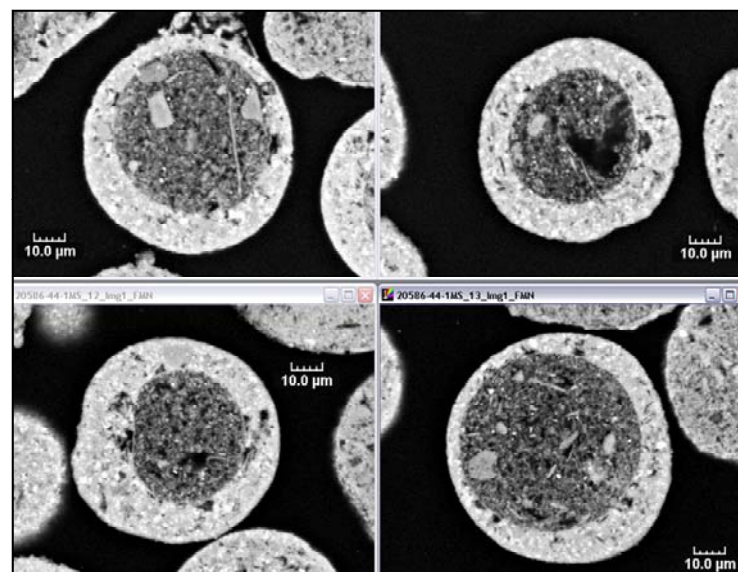
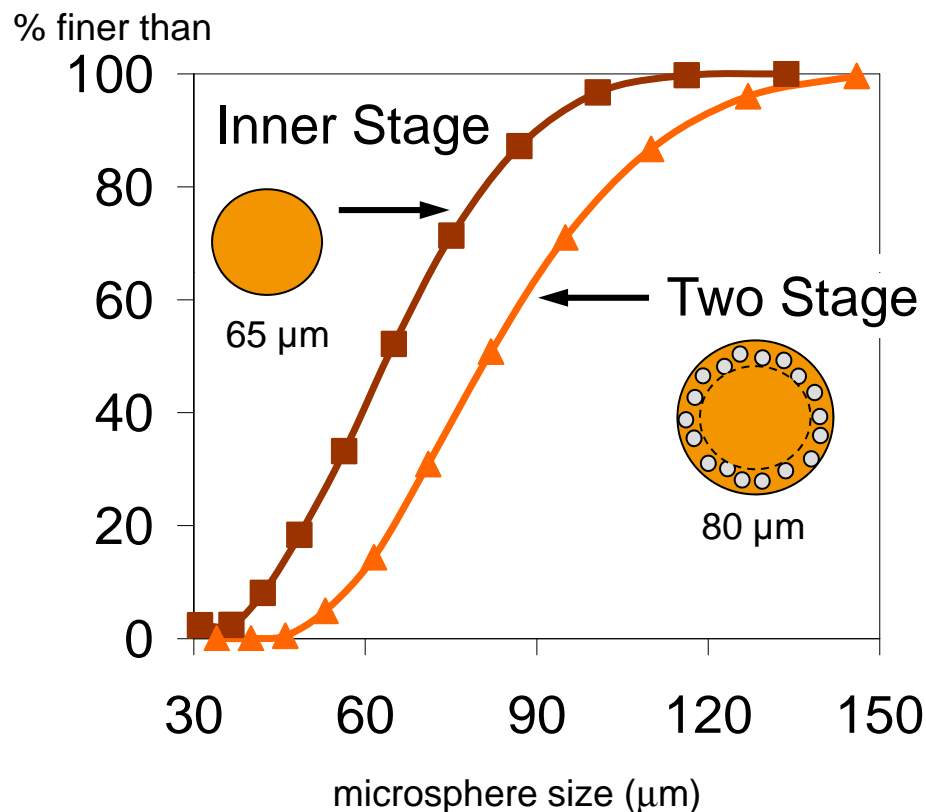
Step 2: Outer stage microsphere




Step 3: Zeolite crystallization and after-treatment



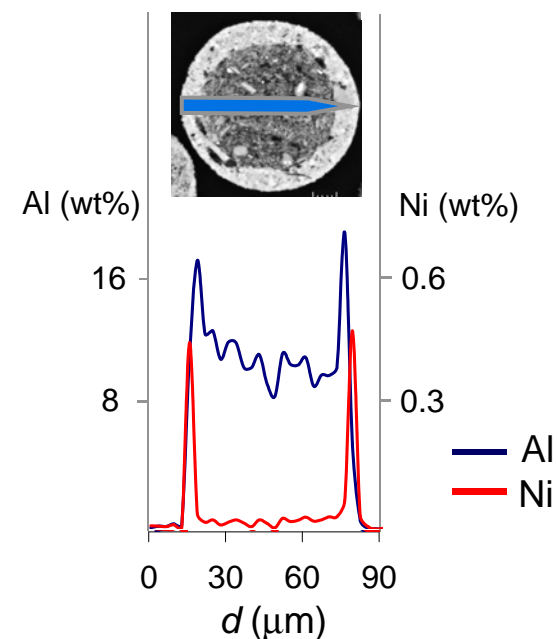
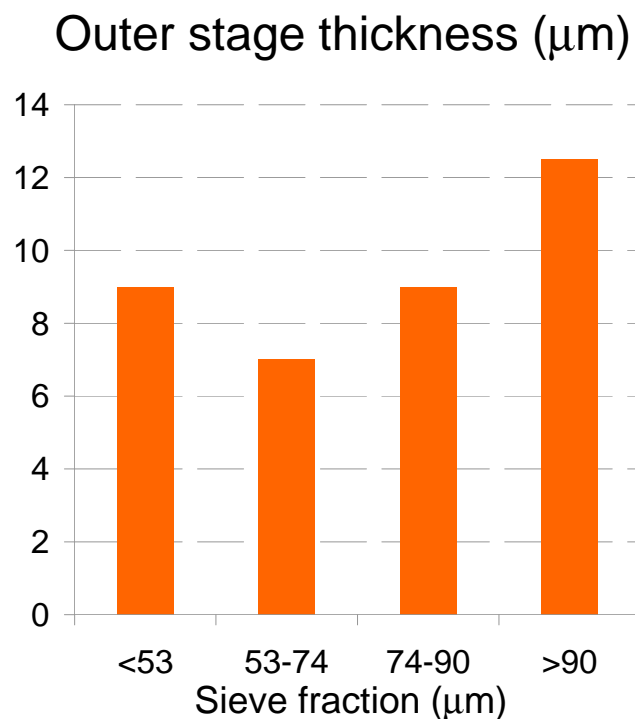
Catalyst Development



- Technology unique to BASF  first microsphere formed, then zeolite grown across the interface and acts as the binder
- Attrition resistance comparable with current FCC catalyst grades

Catalyst Development

- The outer-stage is enriched with specialty alumina to make it more effective at nickel passivation over Flex-Tec
- Outer-stage thickness is consistent for all catalyst diameters (~9 microns)



Fortress™ Lab Performance

- The properties of Fortress are equivalent to Flex-Tec
- Metals free ACE testing at constant conversion shows similar selectivities indicating no diffusion barrier

Catalyst Properties

	Flex-Tec	Fortress
TSA (m ² /g)	300	301
MSA (m ² /g)	72	69
APS (μm)	76	76
Na ₂ O (wt%)	0.22	0.20
Roller (wt% loss/h)	18	16

Metals Free ACE Testing

	Flex-Tec	Fortress
Hydrogen (wt%)	0.055	0.055
Total C4- (wt%)	17.14	17.46
Gasoline (wt%)	50.15	49.95
LCO (wt%)	15.74	16.1
Bottoms (wt%)	14.26	13.9
Coke (wt%)	2.67	2.53

Fortress™ Lab Performance

- The fresh catalyst was deactivated by Cyclic Metals Deactivation Unit (CMDU)
- Testing in an ACE unit using a resid feed showed hydrogen and coke selectivity benefits with Fortress

CMDU Deactivated Catalyst

	Flex-Tec	Fortress
Ni (ppm)	2797	2718
V (ppm)	1133	1050
Steamed TSA (m ² /g)	115	123
Steamed MSA (m ² /g)	36	38
ZSA/MSA	2.2	2.2

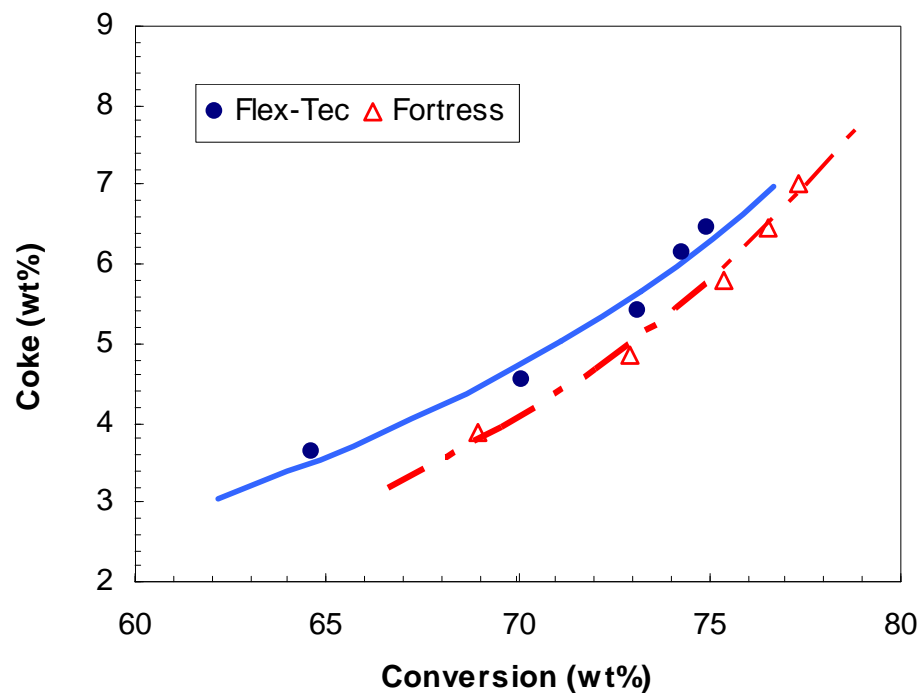
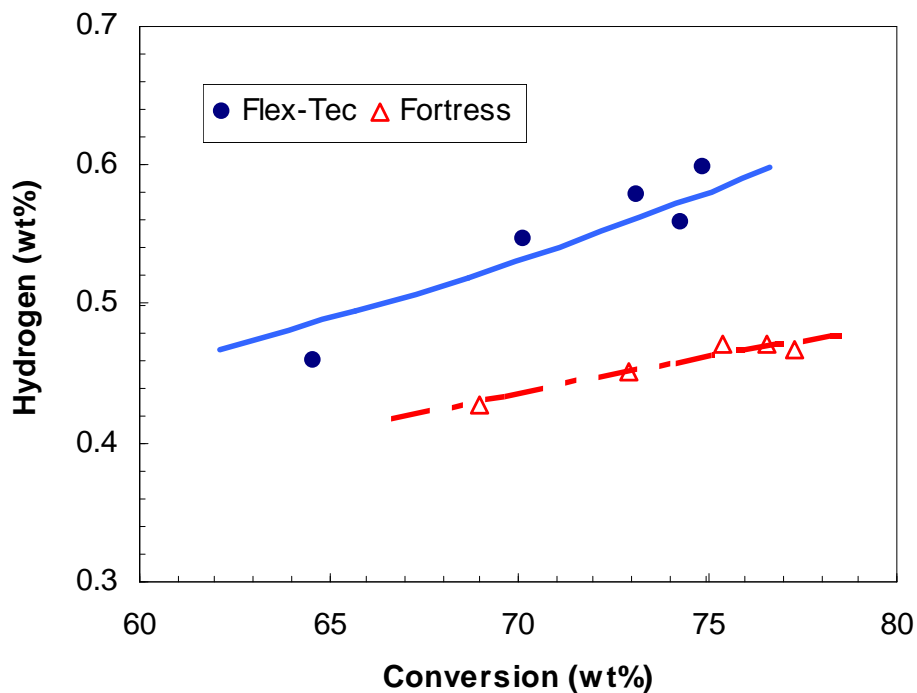
ACE Testing

	Flex-Tec	Fortress
Hydrogen (wt%)	0.53	0.44
Total C4- (wt%)	15.32	15.11
Gasoline (wt%)	49.44	50.41
LCO (wt%)	20.14	20.15
Bottoms (wt%)	9.86	9.85
Coke (wt%)	4.71	4.05

Fortress™ Lab Performance

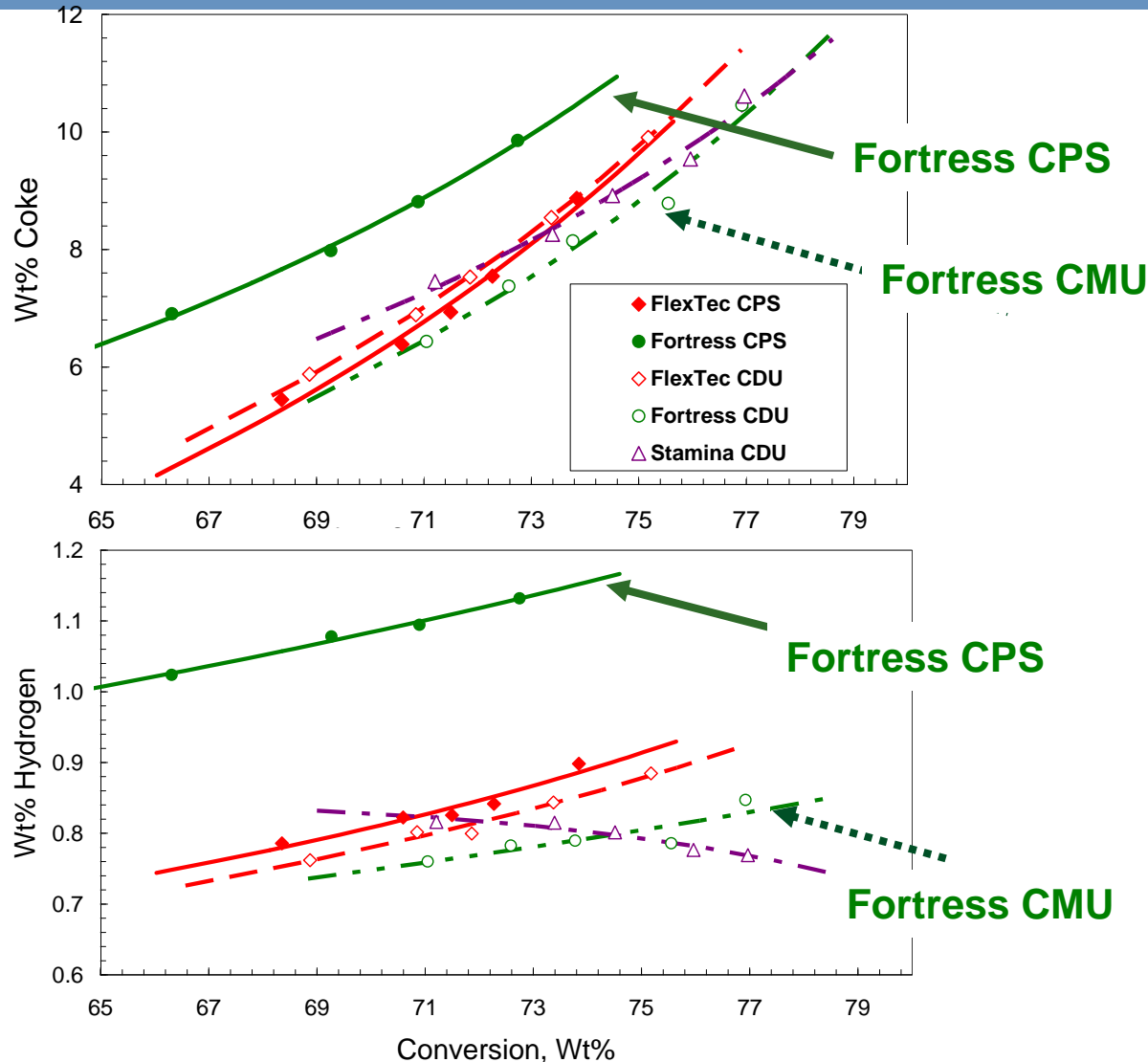
ACE Testing with CMDU Deactivation

- 20% lower hydrogen yield
- 10% lower coke yield



CPS vs CMDU Testing (5000 ppm Ni, 1000 ppm V)

Bias against FORTRESS with CPS deactivation



- Uniformity of nickel distribution with CPS deactivation creates a clear bias in testing for Fortress.
- Exaggerated H₂ and coke yields with lab dispersed Ni
- Inner-stage of Fortress does not passivate against contaminate metals because they are not dispersed in the particle interior in commercial operation
- Ni = 5000 ppm
- V = 1000 ppm

Fortress™ Commercial Trials



- Fortress is being trialed in two locations
- Both locations had been using purchased ECat for metals flushing that was removed prior to the start of the trial for the best comparison
- Data shown covers the most advanced trial

- **Commercial Trial 1**
 - Resid, short contact time unit located in the US
 - Deep partial burn
 - Low reactor severity
 - Primary constants: wet gas compressor and air blower limited

Fortress™ Commercial Trials

- Typical ECat properties before and after the purchased ECat was removed

With Purchased ECat

FACT	71 wt%
Nickel	7400 ppm
Vanadium	2600 ppm
Delta Iron	0.23 wt%
Antimony	2000 ppm
Carbon on Catalyst	0.2-0.5 wt%
Equivalent Nickel	5600 ppm

Without Purchased ECat

FACT	71 wt%
Nickel	8900 ppm
Vanadium	2700 ppm
Delta Iron	0.30 wt%
Antimony	2300 ppm
Carbon on Catalyst	0.2-0.6 wt%
Equivalent Nickel	6800 ppm

Equivalent Nickel is calculated using the equation below

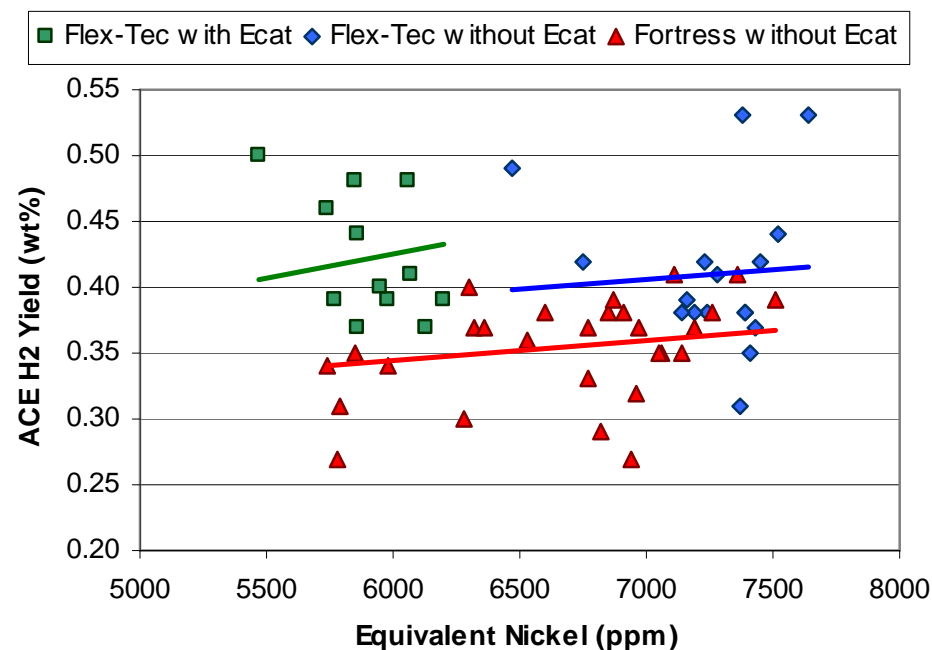
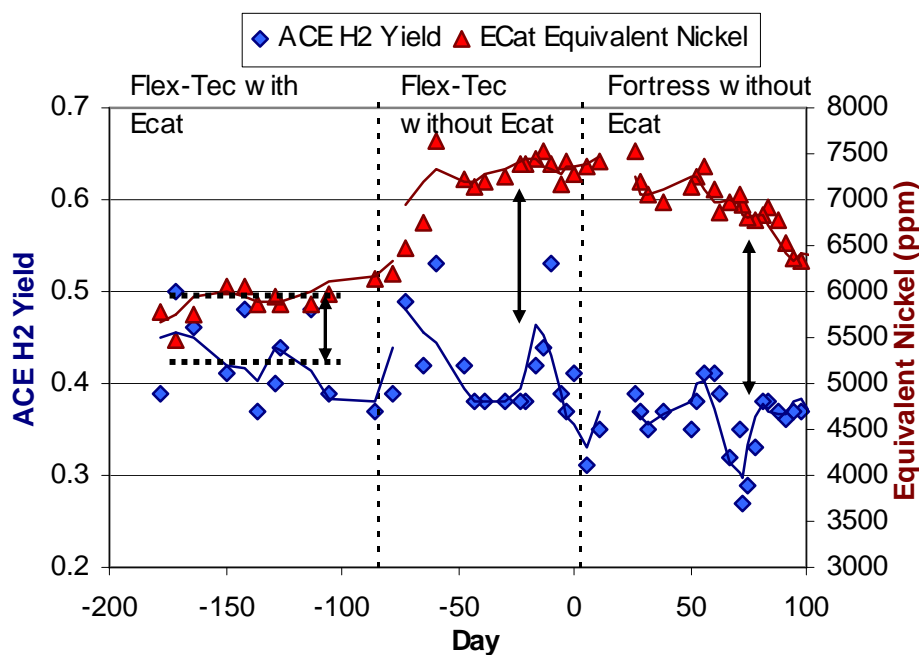
$$Ni + \frac{V}{4} + \frac{Fe}{10} + 5 \cdot Cu - \frac{4}{3} Sb$$

Commercial ECat Results

Reduced ACE Hydrogen Yield with Fortress



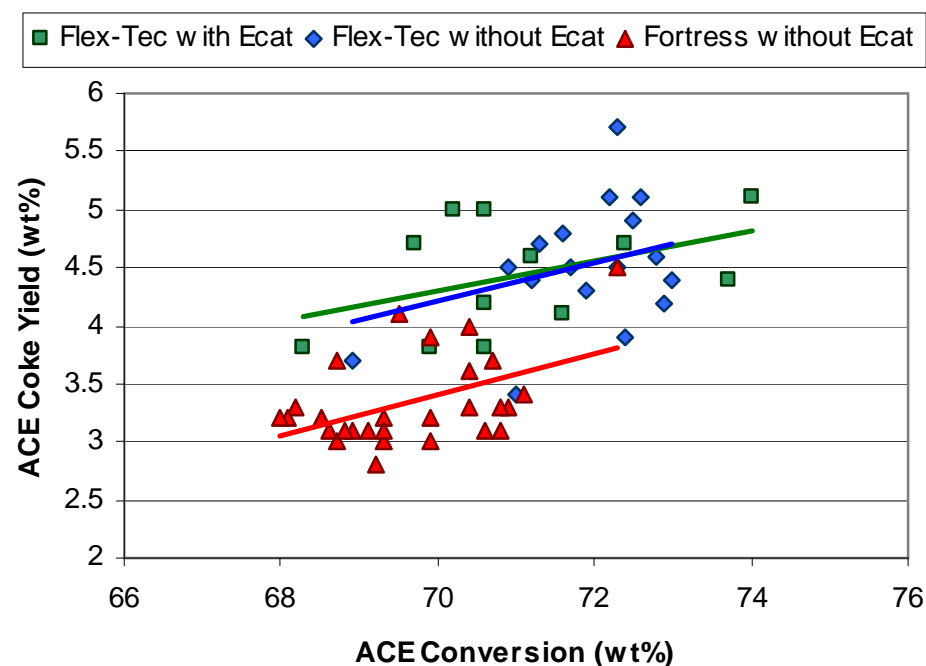
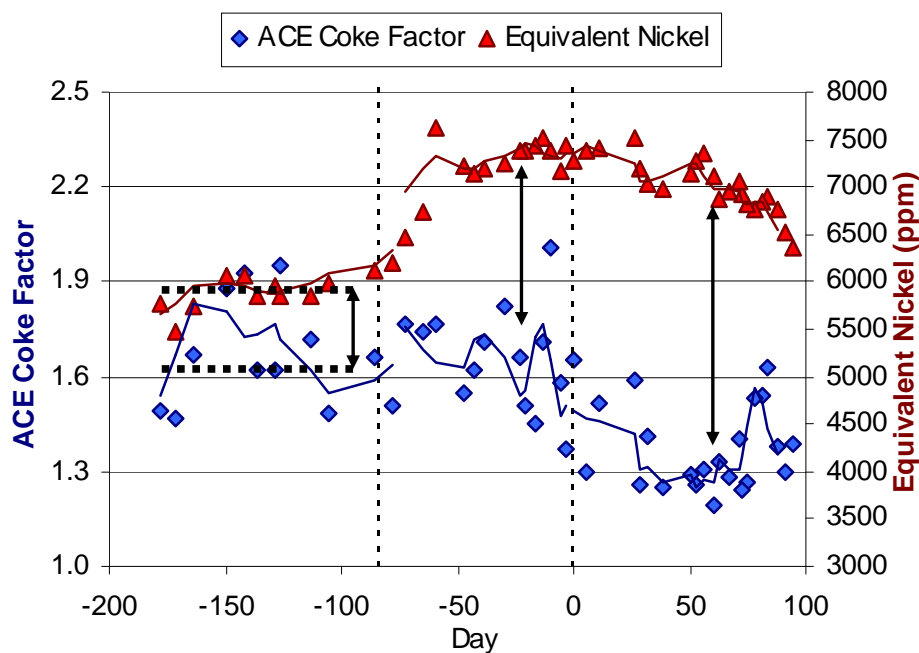
- Removing of the purchased Ecat did not increase hydrogen yield despite the large increase in metals
- The ACE hydrogen yield has decreased by 12% (0.41 wt% to 0.36 wt%) with the catalyst change from Flex-Tec to Fortress at similar nickel equivalents



Commercial ECat Results

Improved ACE Coke Selectivity

- As with the hydrogen yield, removal of the Ecat didn't increase coke yield
- The coke yield for the same conversion decreased by 17% (4.2 wt% to 3.5 wt%) with Fortress

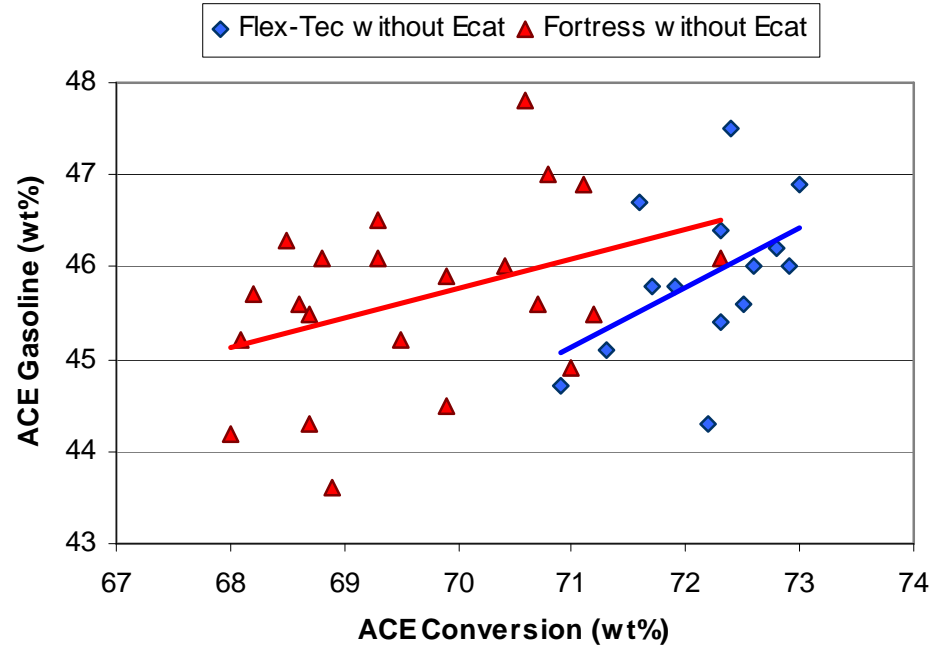
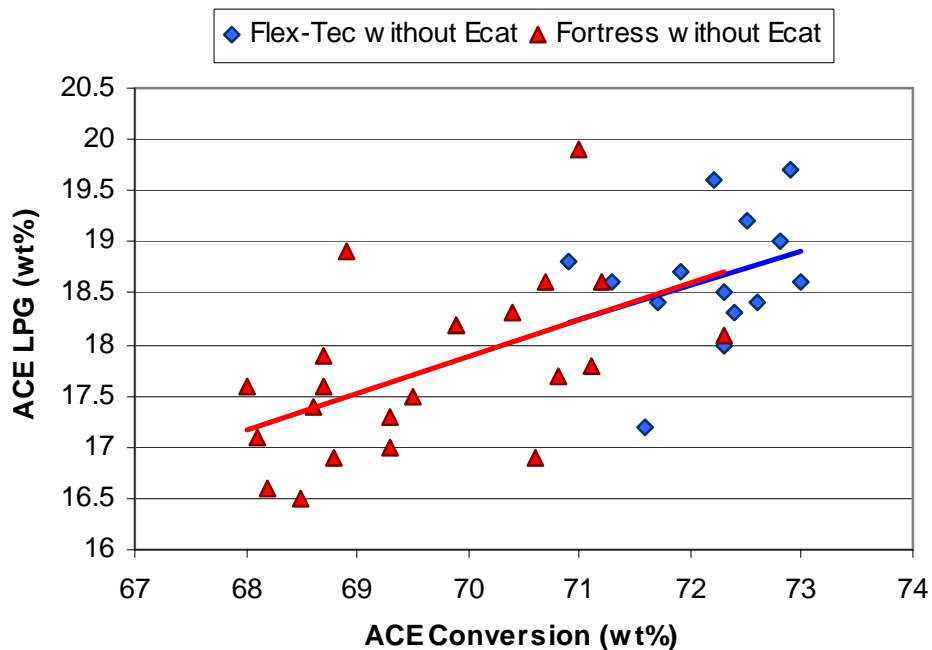


Commercial ECat Results

Higher ACE Gasoline Selectivity with Fortress



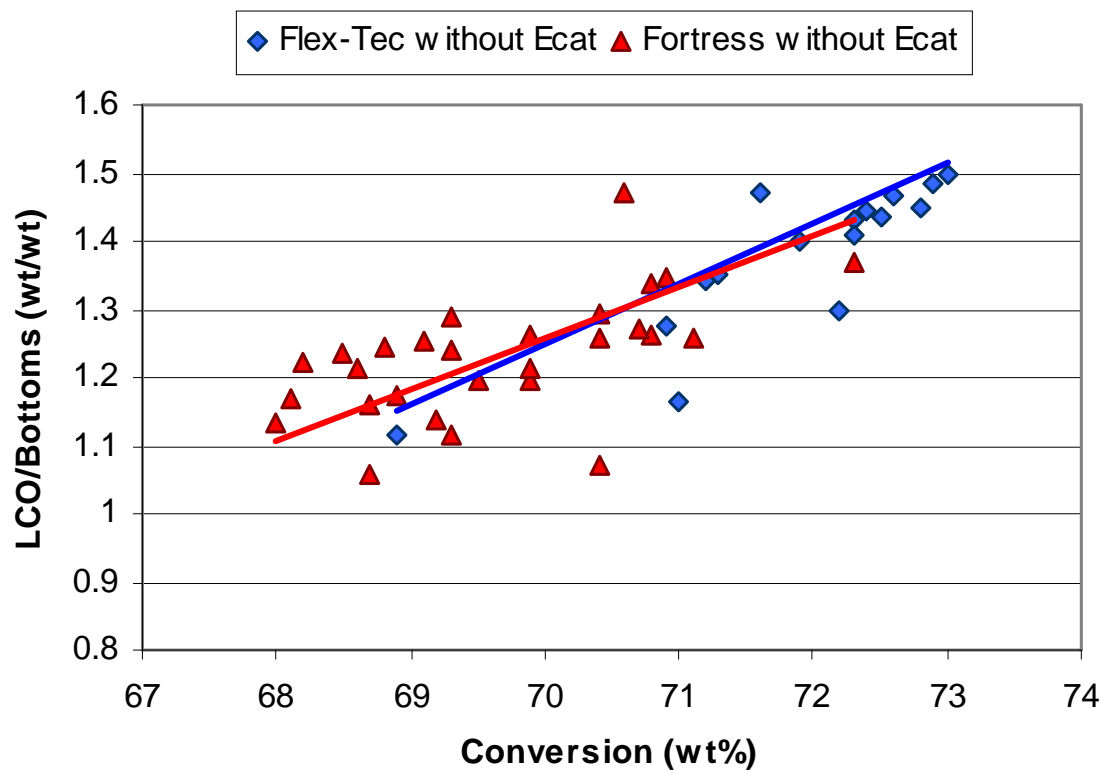
- Gasoline yield increased by 0.5 - 1 wt%
- LPG selectivity did not change going to Fortress
- The yield increase comes from the decrease in hydrogen and coke



Commercial ECat Results

Bottoms Selectivity

- No change in bottoms selectivity

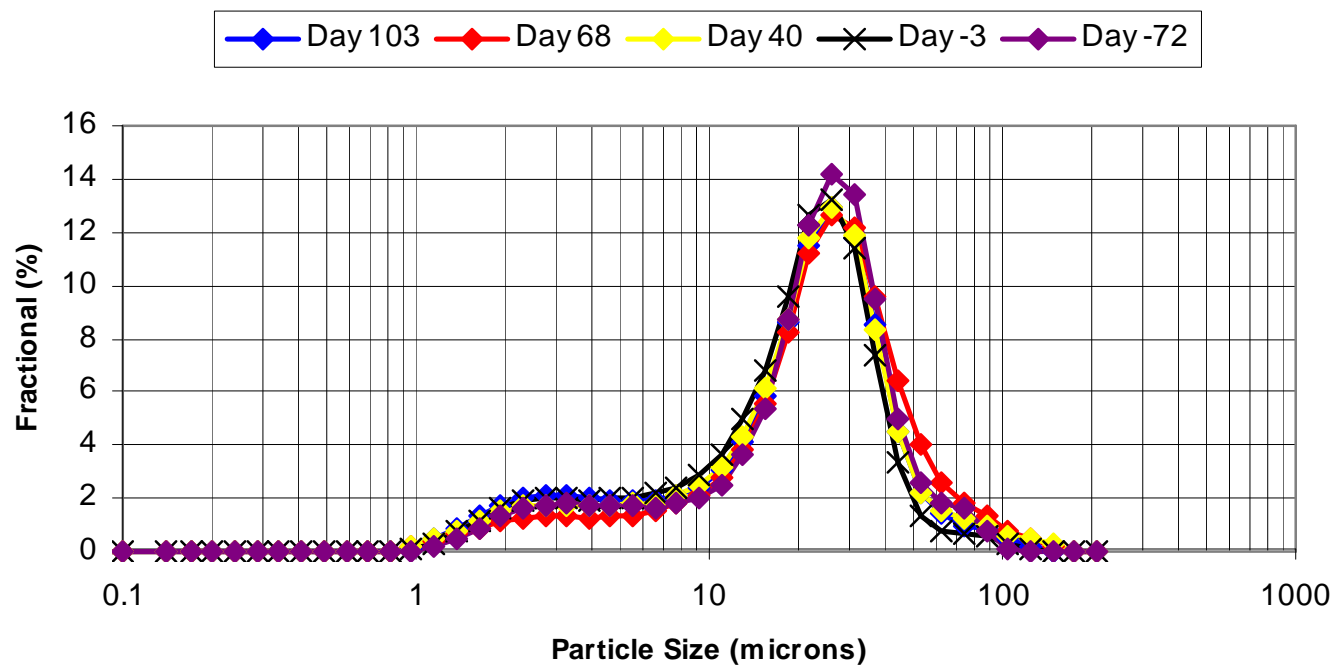


Commercial Results

No Increased Attrition



- The ESP fines particle size analysis shows no shift with the changeover to Fortress
- The cyclone loss peak is greater than the attrition peak, no loss problem with either catalyst



Commercial Results

Post Audit ACE Study

- A post-audit ACE study using the refiners feed
- The ACE temperature was set to 995°F and variable cat/oil ratio to generate yield response curves

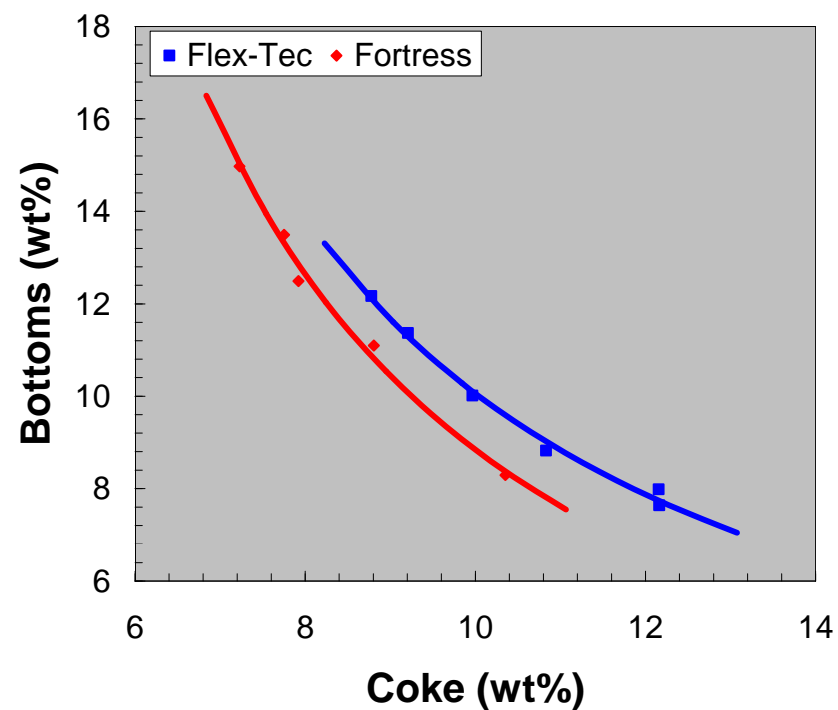
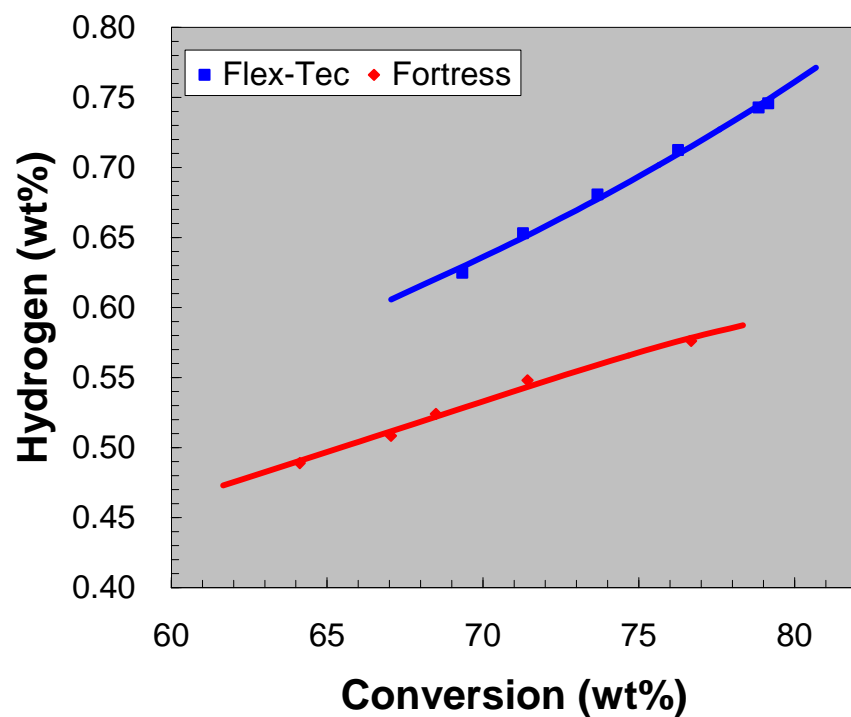
Feed Properties

API Gravity	23
Concarbon	3.0 wt%
Sulfur	0.2 wt%
K Factor	11.8
Nickel	8.7 ppm
Vanadium	2.4 ppm
Iron	2.4 ppm

Commercial Results

Post-Audit ACE Study

- The post audit ACE study validates the ECat trend results of the improved metals tolerance of Fortress resulting in lower hydrogen and coke



Second Commercial Trial

- The second commercial Trial of Fortress is also a comparison with Flex-Tec with the purchased ECat removed prior to the trial
- The unit is operating well, but it is too early for results
- Due to the lower metals level, the expected benefit is less than at Trial 1

With Purchased ECat

FACT	71 wt%
Copper	70 ppm
Nickel	2700 ppm
Vanadium	2200 ppm
Delta Iron	0.9 wt%
Antimony	600 ppm
Equivalent Nickel	3400 ppm

Without Purchased ECat

FACT	69 wt%
Copper	70 ppm
Nickel	3500 ppm
Vanadium	3200 ppm
Delta Iron	1.1 wt%
Antimony	900 ppm
Equivalent Nickel	4200 ppm

MSRC-CORE

- Second catalyst offering from BASF under the MSRC manufacturing platform
- CORE's highly stable zeolite outer stage reduces diffusion path length which
 - Improves selectivity
 - Delivers high bottoms conversion with low coke
 - High gasoline and light olefin yields
- CORE is engineered to provide coke selectivity and gasoline yields on par with NaphthaMax[®] III with lower rare earth
- The inner stage of CORE serves as the anchor for the highly active outer stage
- Currently undergoing manufacturing trials and scheduled to be ready for commercial trials by 4Q 2011

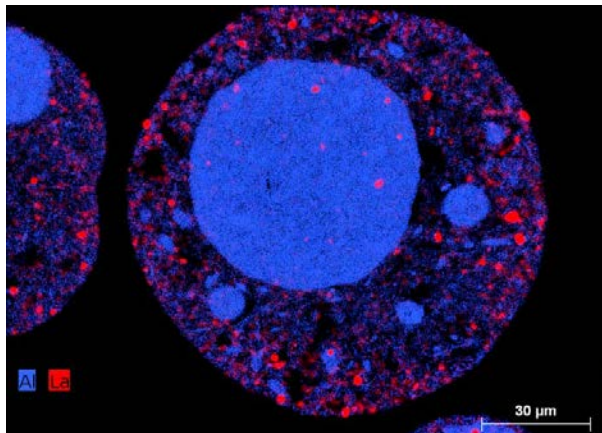
Improving Mass Transfer

Diffusion path length as only viable option

Reduce the Thiele modulus, ϕ_2

To improve effectiveness of catalyst

$$\phi_2 = \frac{r}{3} \sqrt{\frac{k' \rho_{cat} C_s}{D_e}}$$

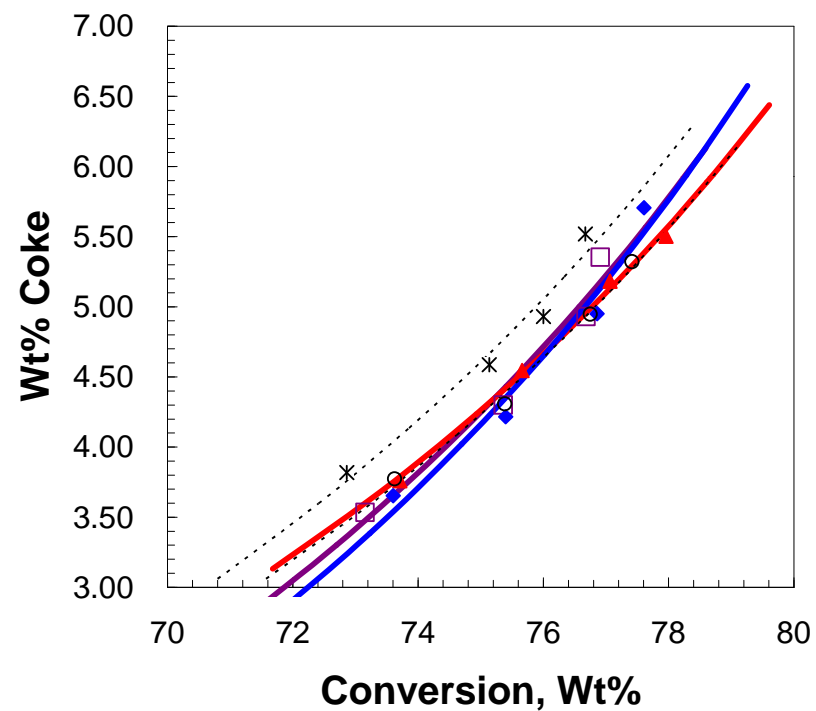
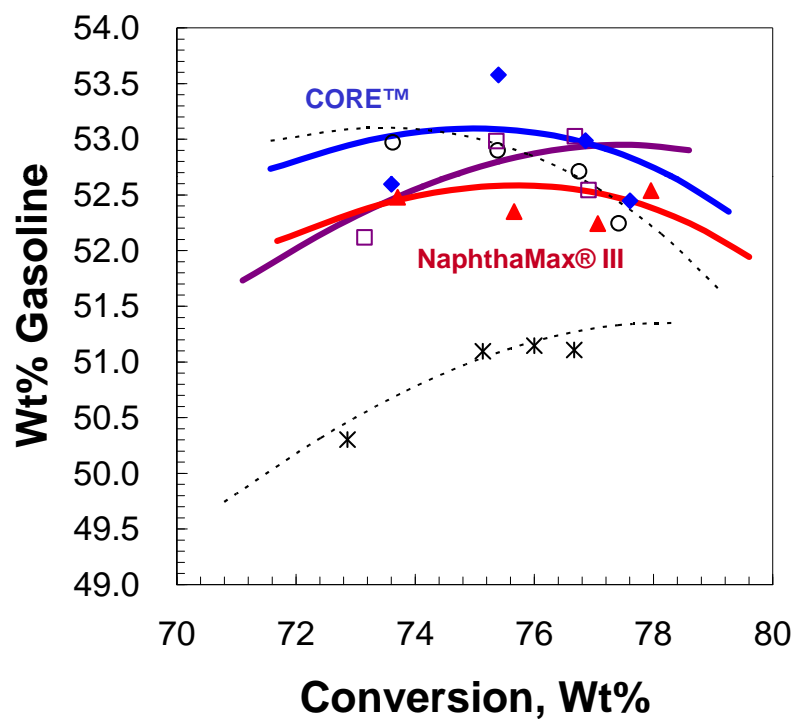


- Increase diffusivity D_e via porosity
 - Already gave us DMS
- Decrease activity (k')
 - Uneconomical
- Decrease diffusion path length (r)
 - Diameter fixed by cyclones
- Dual stage approach:
 - Inactive inner stage reduces (r)
 - Particle retained in the FCC
 - Less zeolite is offset with improved zeolite stability

A Winning Combination

- Multi-Staged Reaction Catalyst (MSRC) approach
 - An outer stage of highly stable and active zeolite improves mass transfer by reducing the diffusion path length
 - A stable core serves as an anchor for the active outer stage. Attrition properties are comparable to NaphthaMax III products
- Highly stable and active zeolite yields a reduction on RE usage
 - 25% reduction in zeolite leads to 25% reduction on RE
- Result is DMS-like yields with no penalty for lower RE

Circulating Riser Pilot Unit Catalytic Data



Yields match NaphthaMax III with 25% lower REO

Summary

- BASF has introduced an innovative new FCC catalyst manufacturing platform, Multi-Stage Reaction Catalyst (MSRC)
- Fortress™, the first MSRC product, has been successful commercialized
- Laboratory testing, refinery trial results, and post-audit testing all demonstrate the improved metals passivation benefits of Fortress
- CORE™, the second product, is in commercialization and offers potential for REO reduction
- BASF will be introducing exciting new technologies from the MSRC platform in the future!



The Chemical Company

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