



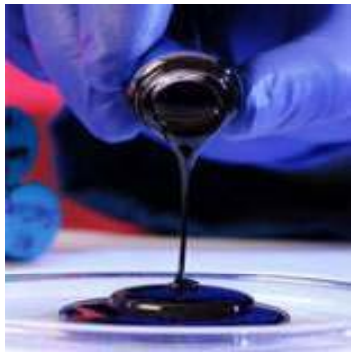


Successful Commercialisation of Zero/Low Rare-Earth FCC Catalysts

CatCracking.com

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Enriching Lives, *Everywhere.*™

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Overview

- Development of RE-Free and Low RE Catalysts
  - for HT/Low-Metal Feed Applications
  - for Resid Feed Applications

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- Development of RE-Free and Low RE Catalysts
  - for HT/Low-Metal Feed Applications
  - for Resid Feed Applications

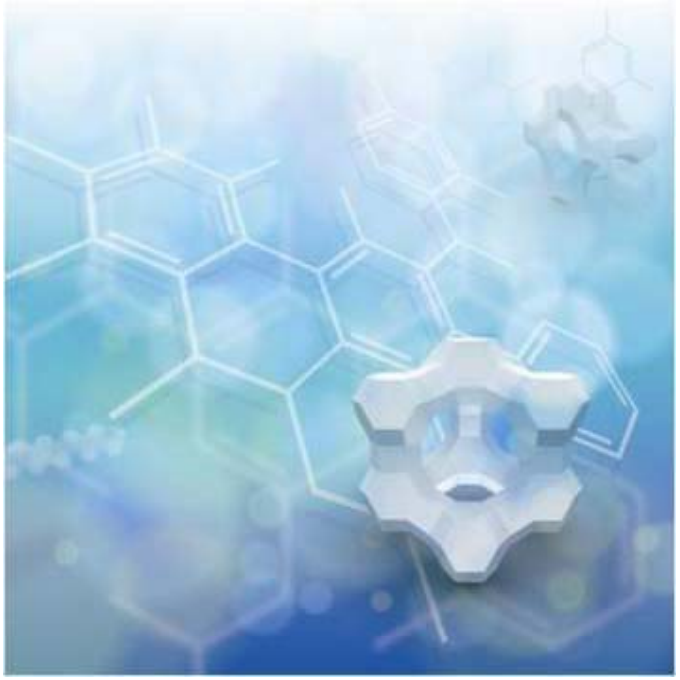
Grace Davison has developed the REplaceR family of RE-free FCC catalysts

Grace Davison RE-free technologies include:

- Z-21, a RE-free zeolite developed in 1997
- Z-22, a state-of-the-art RE-free zeolite developed in 2010

These RE-free zeolites can be used with the following EnhanceR technologies

- EAM, Acidity Modification
- EMR, Metals Resistance
- EPR, Pore Restructuring
- ESS, Structure Stabilisation



REp Lanthanum La 57 Atomic Weight = 138.91 Cerium Ce 58 Atomic Weight = 140.12 R™

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Overview

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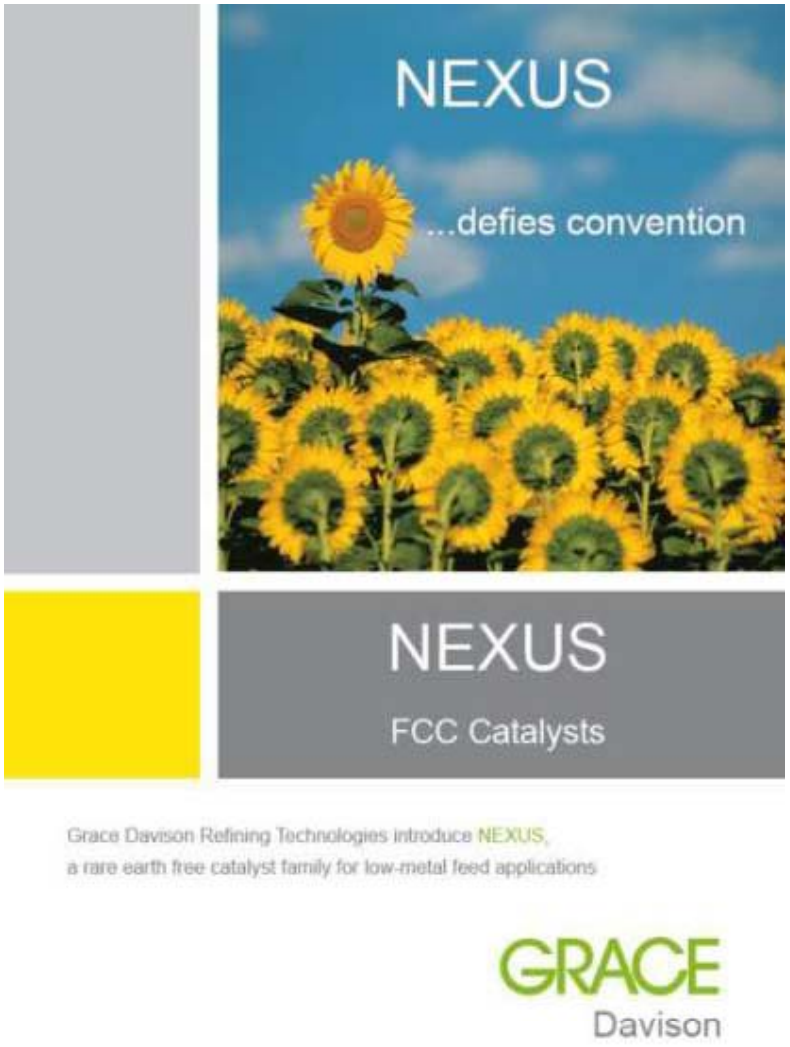
  - for Resid Feed Applications

NEXUS was the first RE-free catalyst family



NEXUS

- incorporates Z-21 zeolite
- RE-free catalyst for low-metal feed applications
- commercialised in 1997
- successfully used in 10 applications
- For example the following table shows the use of NEXUS at a refinery where maximum gasoline yield was the key objective

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NEXUS improved FCC product yields

	NEXUS-346	Competitor	Delta
Product Yields			
H_2	0.03	0.07	-0.04
Dry Gas	3.60	4.12	-0.52
LPG	16.25	18.19	-1.94
Gasoline	50.16	45.20	4.96
LCO	15.62	18.72	-3.10
MCB	7.98	7.68	0.30
Coke	4.72	4.56	0.16
Conversion	76.39	73.60	2.79

- Higher conversion
- Lower hydrogen yield
- Lower dry gas yield
- Higher gasoline yield

- Economic analysis showed a benefit to Refinery A of ca.1 million €/year
- Refinery A continued to use NEXUS

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REsolution is the successor to NEXUS

REsolution

- combines Z-21 zeolite with new matrix
- provides higher activity and bottoms upgrading compared to NEXUS
- RE-free catalyst for low-metal feed applications
- commercialised in 2010
- successfully being used in 7 applications
- for example…

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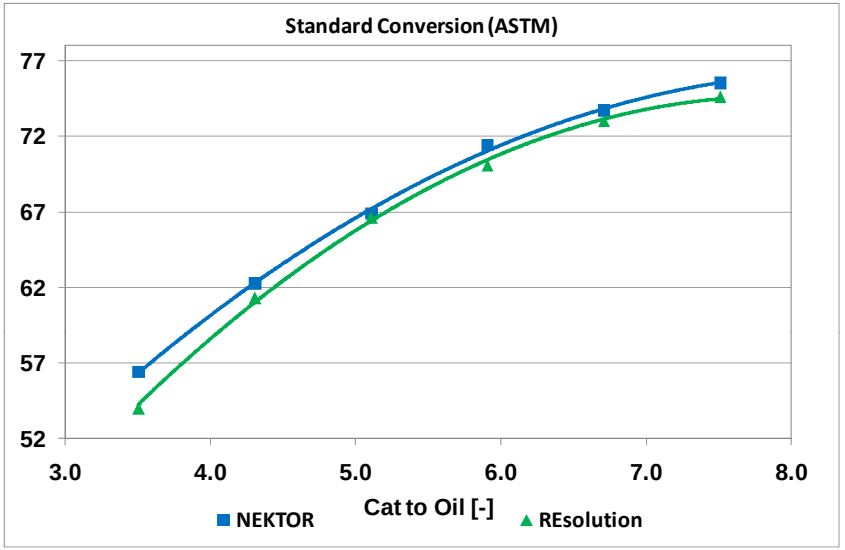
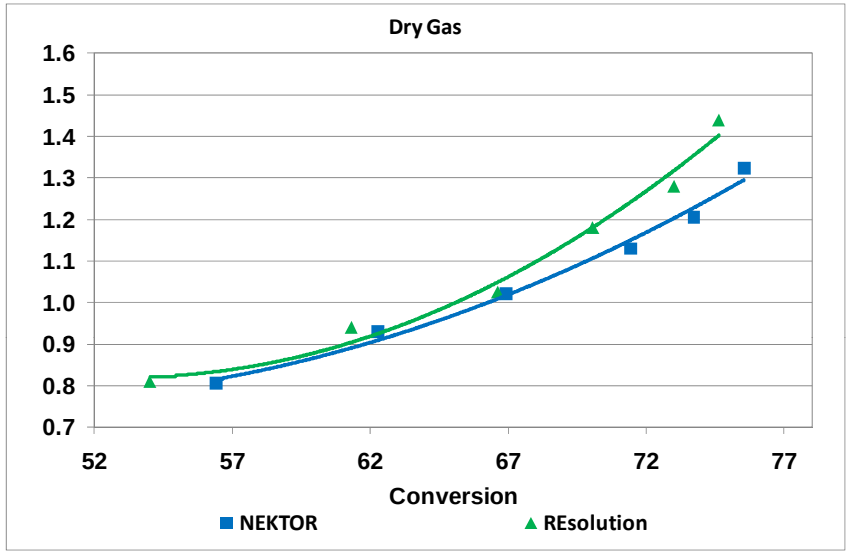
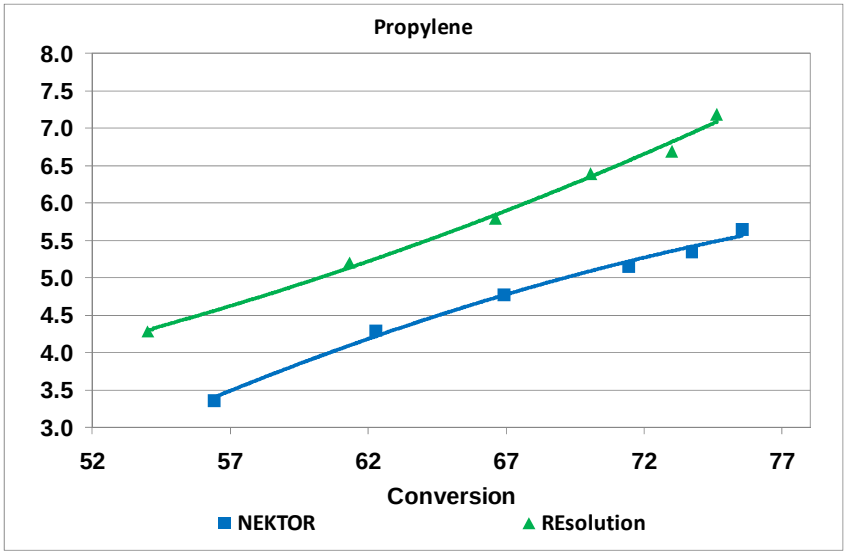
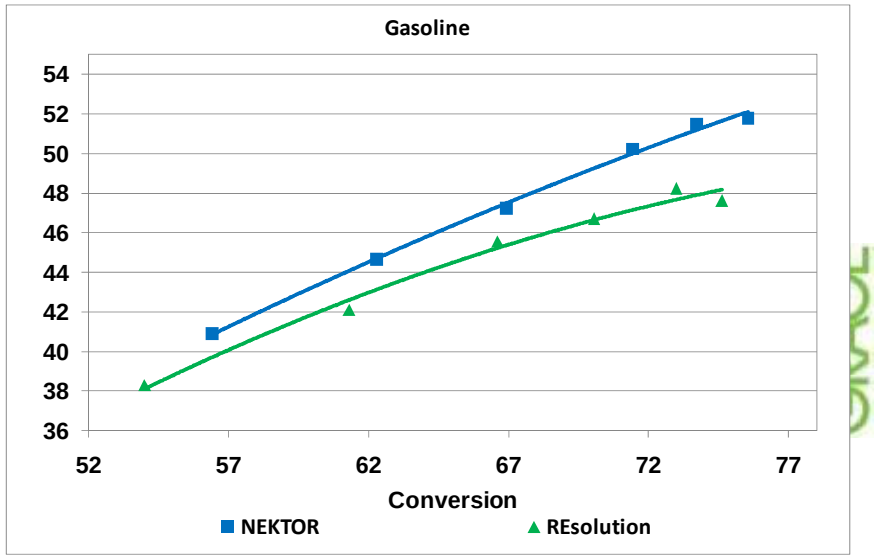
REsolution provides similar activity

ACE E-Cat Pilot Plant Testing, Ni+V ca. 1000 ppm



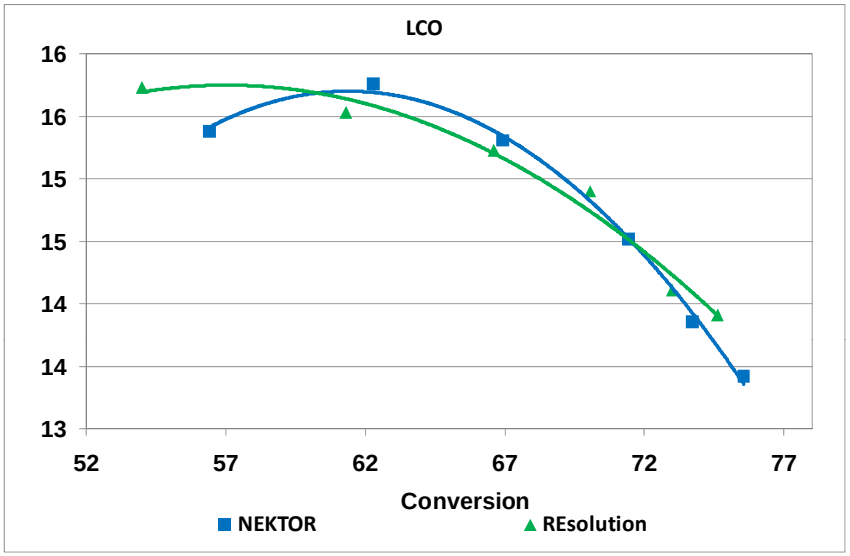


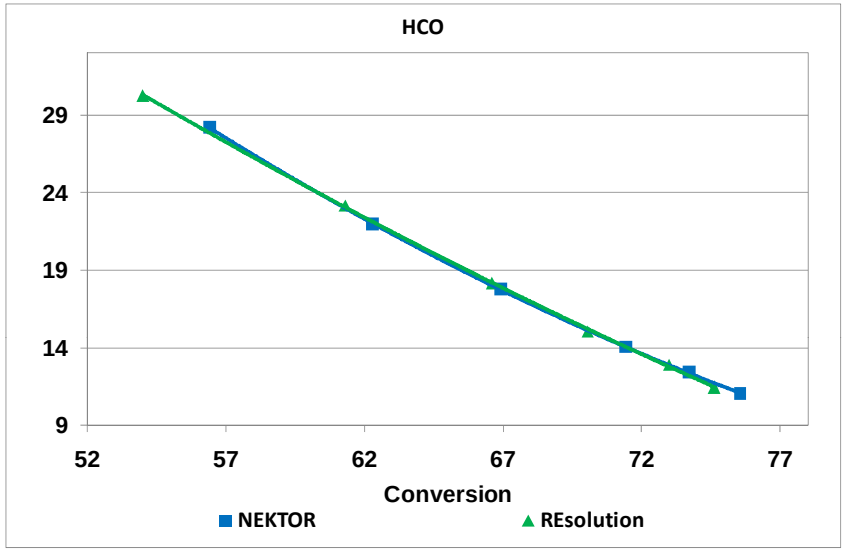


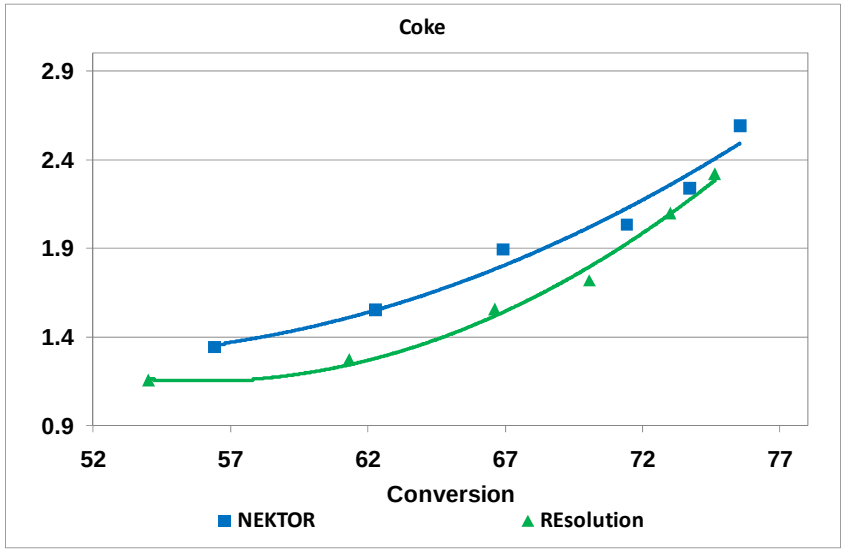


REsolution provides similar dry gas

ACE E-Cat Pilot Plant Testing, Ni+V ca. 1000 ppm



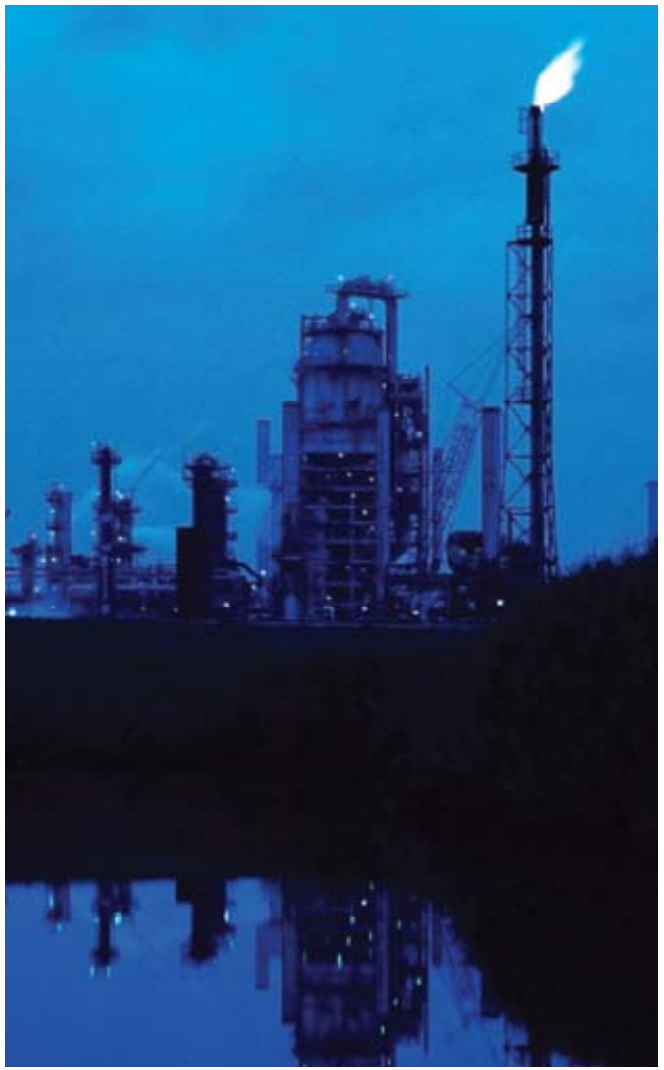




To summarise the commercial trial of REsolution

REsolution

- The trial is taking place at a refinery in central Europe
- Rare earth was reduced from 3.1 to 2.1 wt.% (30% change out) without affecting performance
- Catalyst change out has since reached 70% (3.1 to 0.9 wt.% rare earth) with even slightly improved performance observed
  - Higher iC4 selectivity
  - Similar bottoms upgrading
  - Similar dry gas
  - Lower delta coke



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Overview

- Development of RE-Free and Low RE Catalysts
  - for HT/Low-Metal Feed Applications
  - for Resid Feed Applications

REduceR is a RE-free catalyst for resid feed applications

Grace Davison Refining Technologies introduces REduceR, a rare-earth free catalyst that can be blended with resid catalysts for resid applications, thus reducing overall rare-earth costs

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Davison

REduceR

- combines new RE-free Z-21 and Z-22 zeolites with EnhanceR Metals Resistance Technology
- can be blended with RE-based resid catalysts without performance deterioration
- commercialised in 2011
- currently being used in over 10 applications

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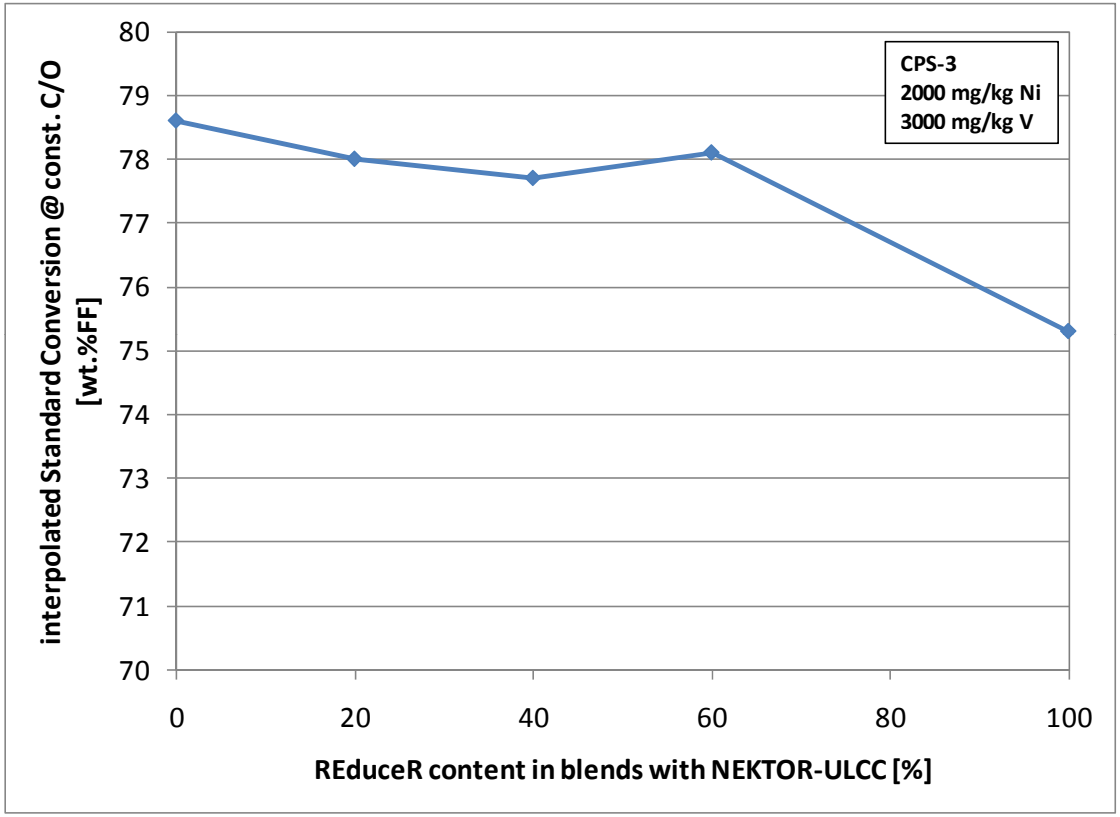
REduceR – Application in Blends

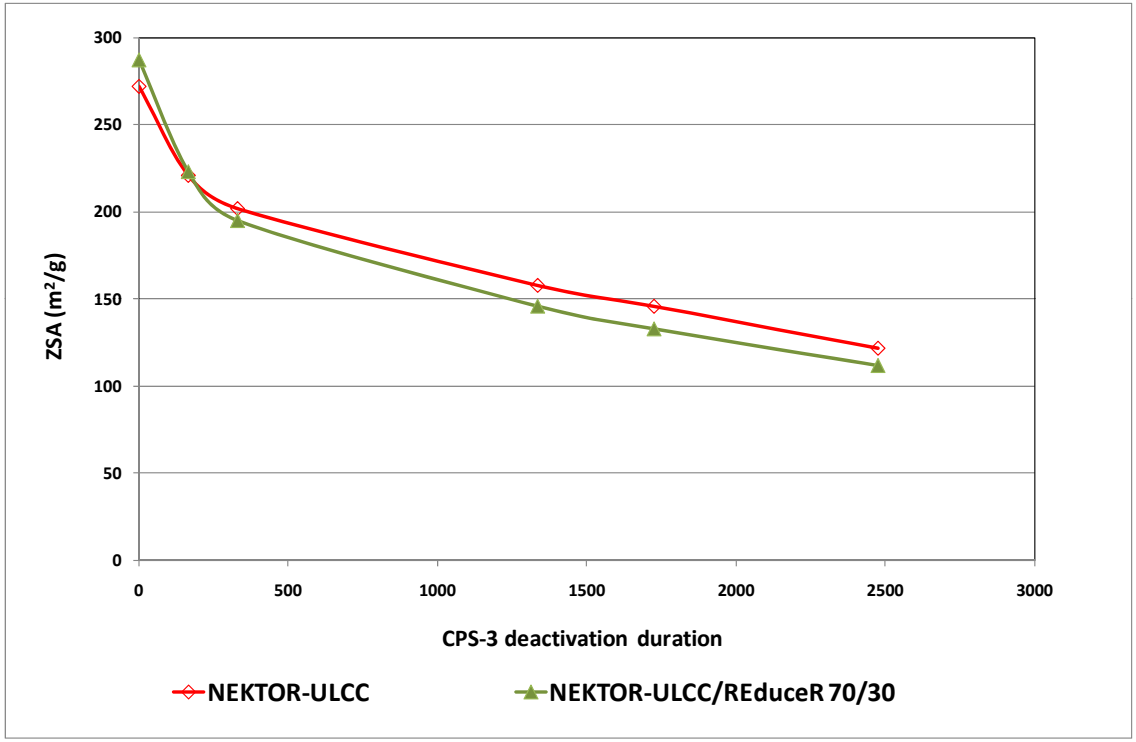
CPS-3 Deactivation Protocol, 2000 mg/kg Ni, 3000 mg/kg V



REduceR blends show very good activity retention
(even up to blends of 60%)

REduceR – Metals Tolerance

CPS-3 Deactivation Protocol, 4000 mg/kg Ni, 6000 mg/kg V



The REduceR blend shows very good ZSA retention even with a very severe, extended metals deactivation protocol

REduceR Commercial Trial

- In April 2011 Refinery B began to blend in 30% of the rare-earth free REduceR catalyst with the current NEKTOR catalyst

- The objective of the trial was to maintain the high performance whilst reducing catalyst rare-earth requirement (from 3.1 to 2.2 wt.%)

- Upon a successul performance at a 30% level the REduceR catalyst would then be tested at 50%

Refinery B – E-Cat MAT Study (60% Change Out)

	NEKTOR	70% NEKTOR 30% REduceR ca. 60% change out
MAT, wt.%	67	70
Gas Factor	5.1	3.2
H2 Yield, wt.%	0.35	0.25
Coke Factor	1.4	1.2
Ni, ppm	3532	3500
V, ppm	4157	4034
Na, wt.%	0.48	0.48
Fe, wt.%	0.43	0.58
Sb, ppm	138	469
Cu, ppm	41	33
RE2O3, wt.%	3.1	2.6

The REduceR blend provides high MAT, low GF, CF and H2 yields

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Refinery B – E-Cat MAT Study (60% Change Out)

	NEKTOR	70% NEKTOR 30% REduceR ca. 60% change out
Cat-to Oil	2.2	2.3
Conversion, wt.%	64	69
Hydrogen, wt.%	0.31	0.28
Propylene, wt.%	4.1	4.5
C4 olefins, wt.%	6.2	6.8
LPG, wt.%	14.3	16.8
Gasoline, wt.%	42.6	44.5
LCO, wt.%	17.2	15.6
HCO, wt.%	18.3	15.4
Coke, wt.%	4.7	4.7
Coke on catalyst, wt.%	2.13	2.04
RON	93.7	93.8
MON	80.9	81.5

The REduceR blend provides improved product yields

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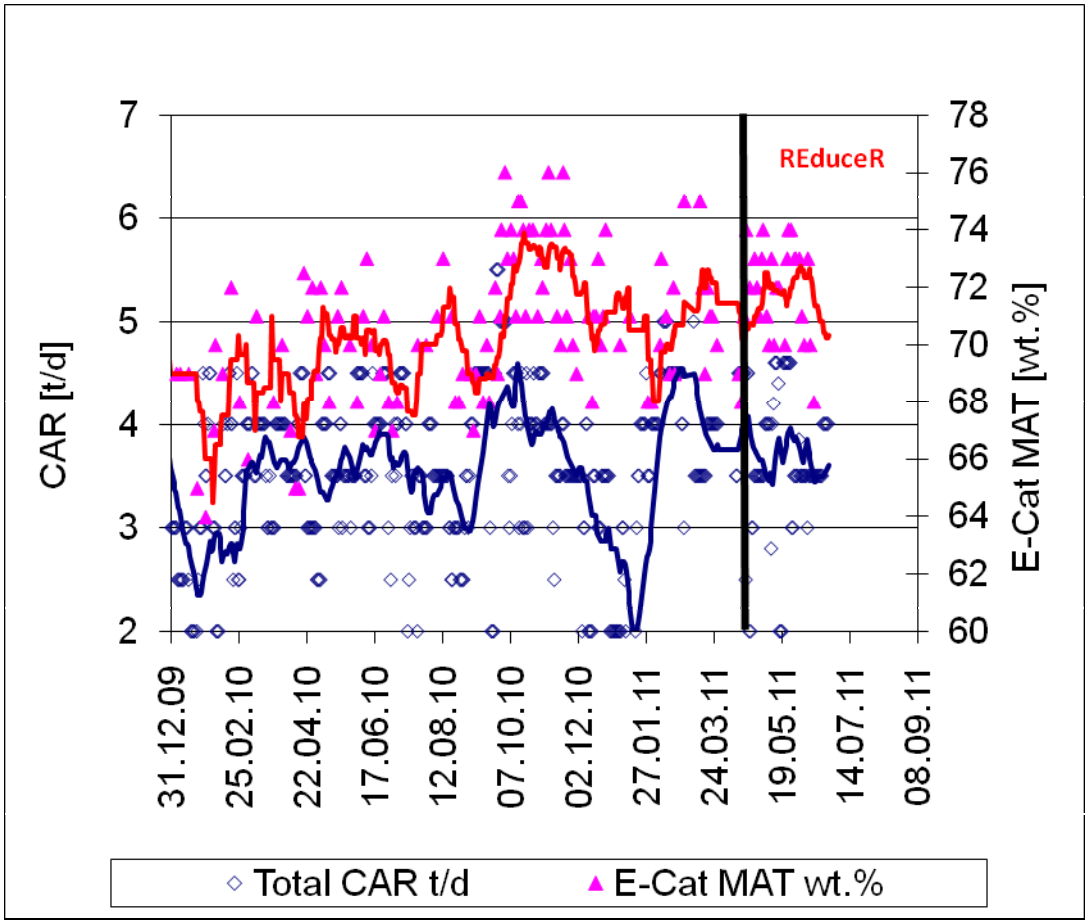
Refinery B – E-Cat Data (100% Change Out)



REduceR shows good activity retention at similar to lower CAR

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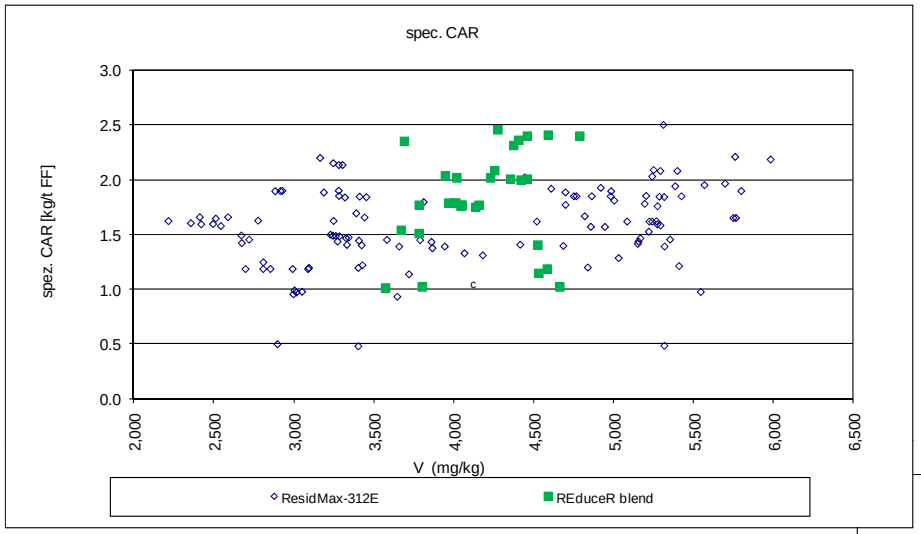
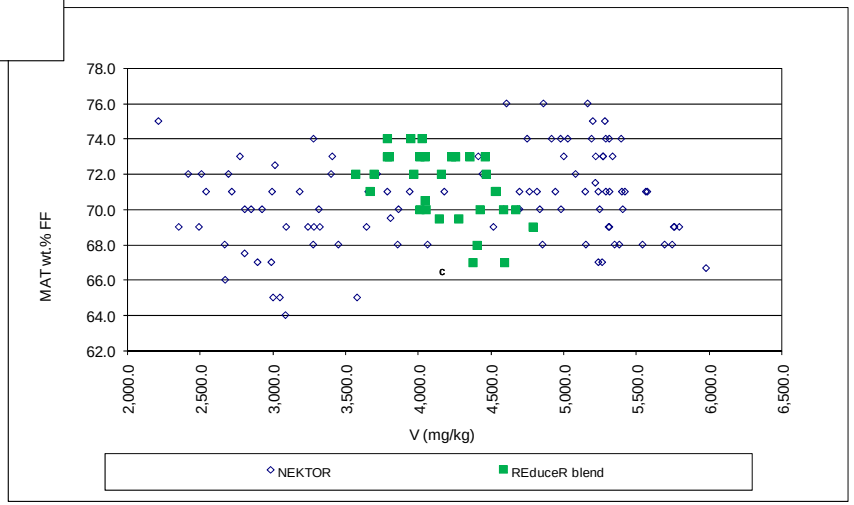
Refinery B – E-Cat Data (100% Change Out)





SCAR and MAT remained similar after addition of REduceR confirming good vanadium tolerance of REduceR

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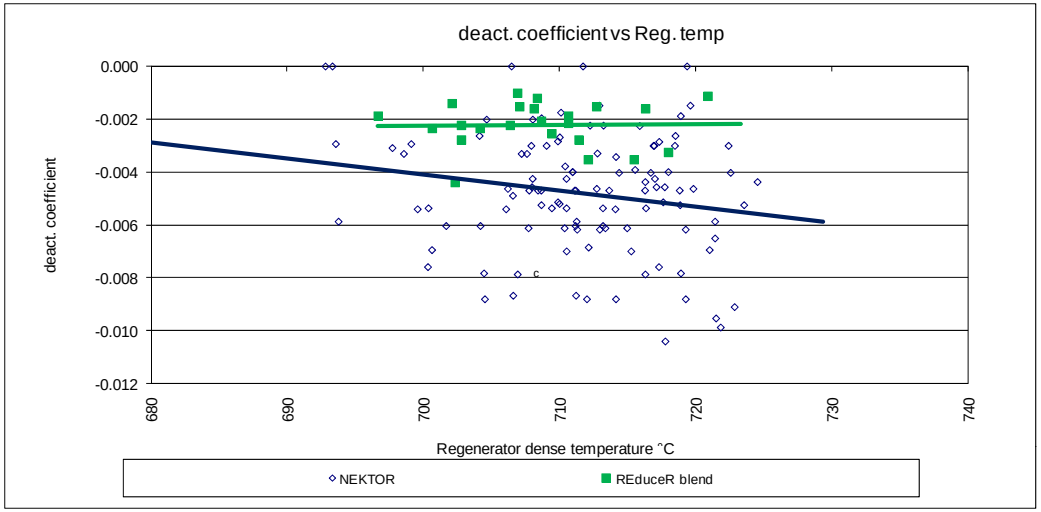
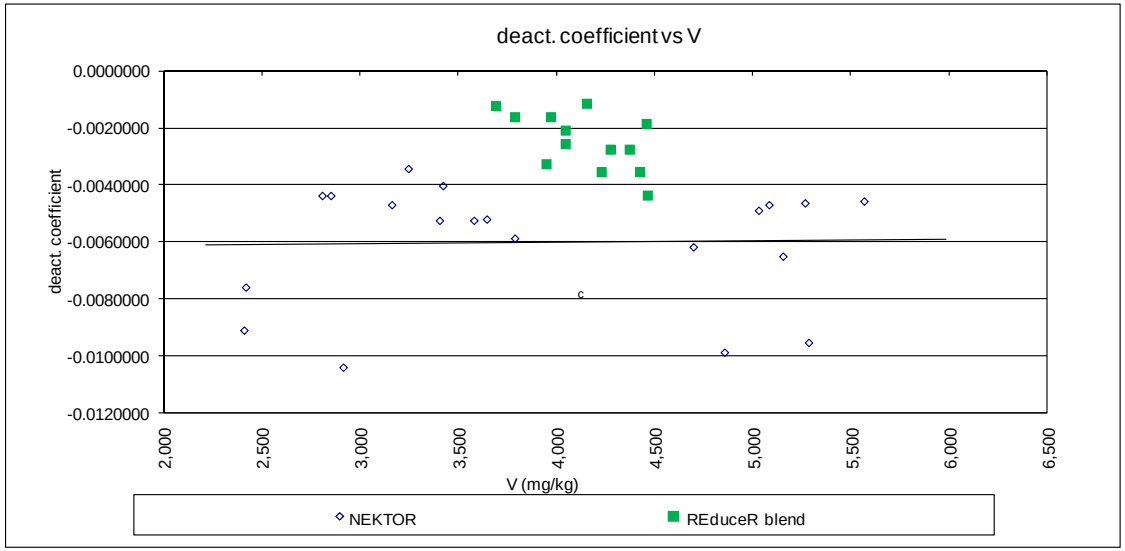
Refinery B – E-Cat Data (100% Change Out)





Intrinsic catalyst stability improved after addition of REduceR

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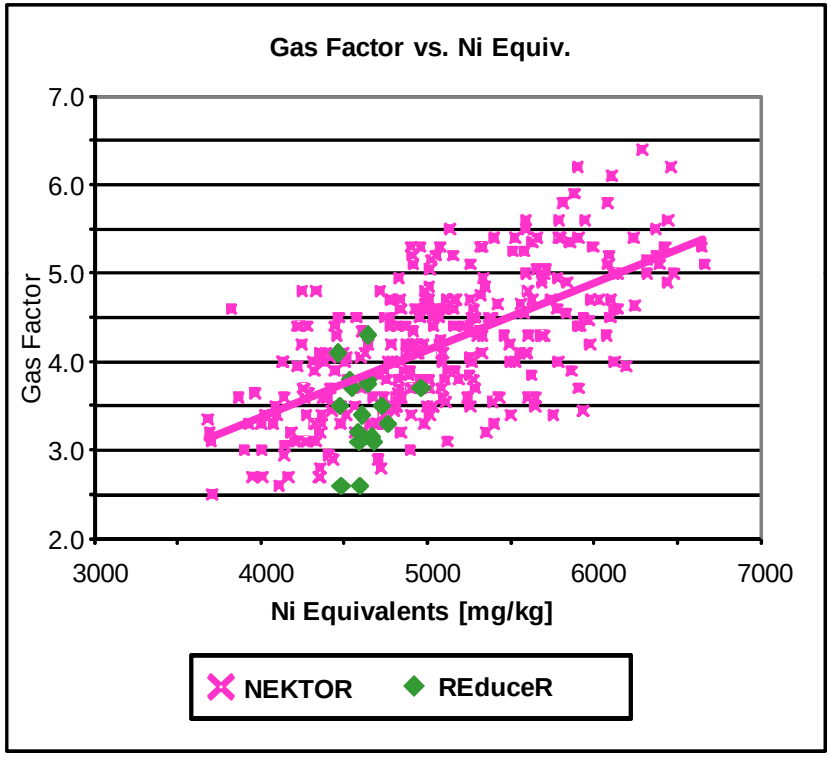
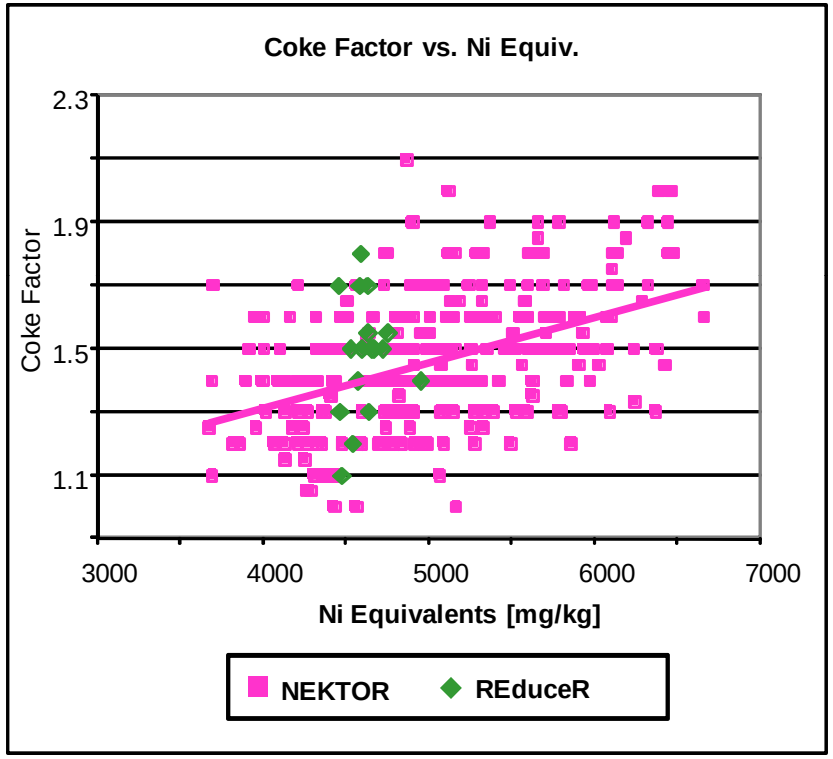
Refinery B – E-Cat Data (100% Change Out)

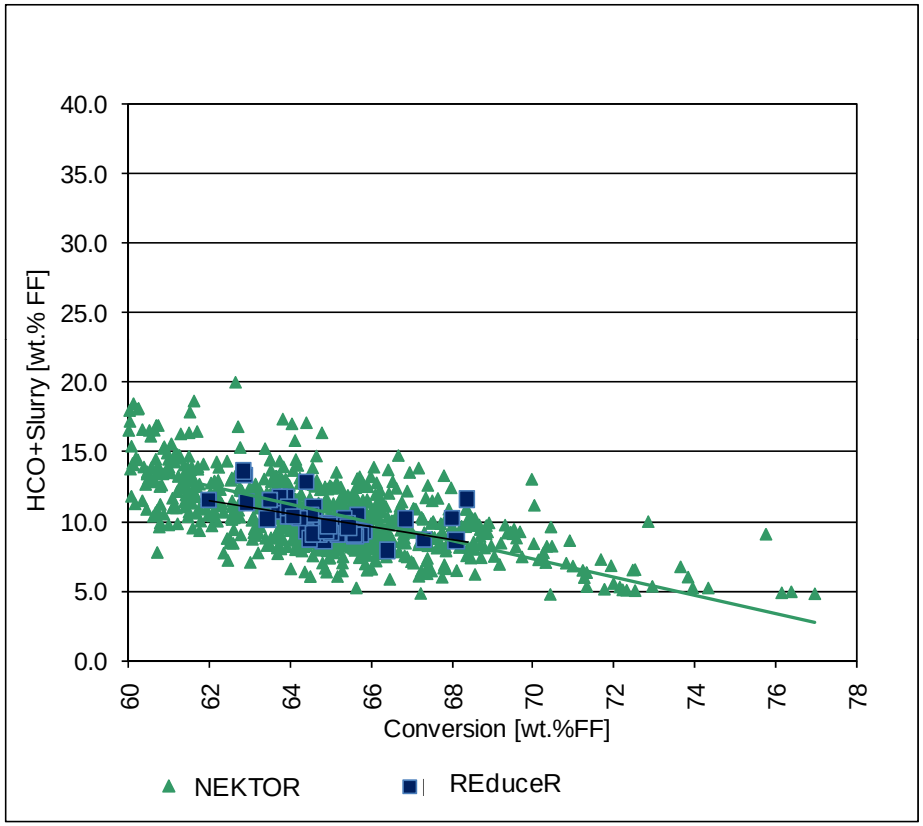
Commercial equilibrium catalyst (e-cat), Coke/Gas Factor vs. Ni equivalents





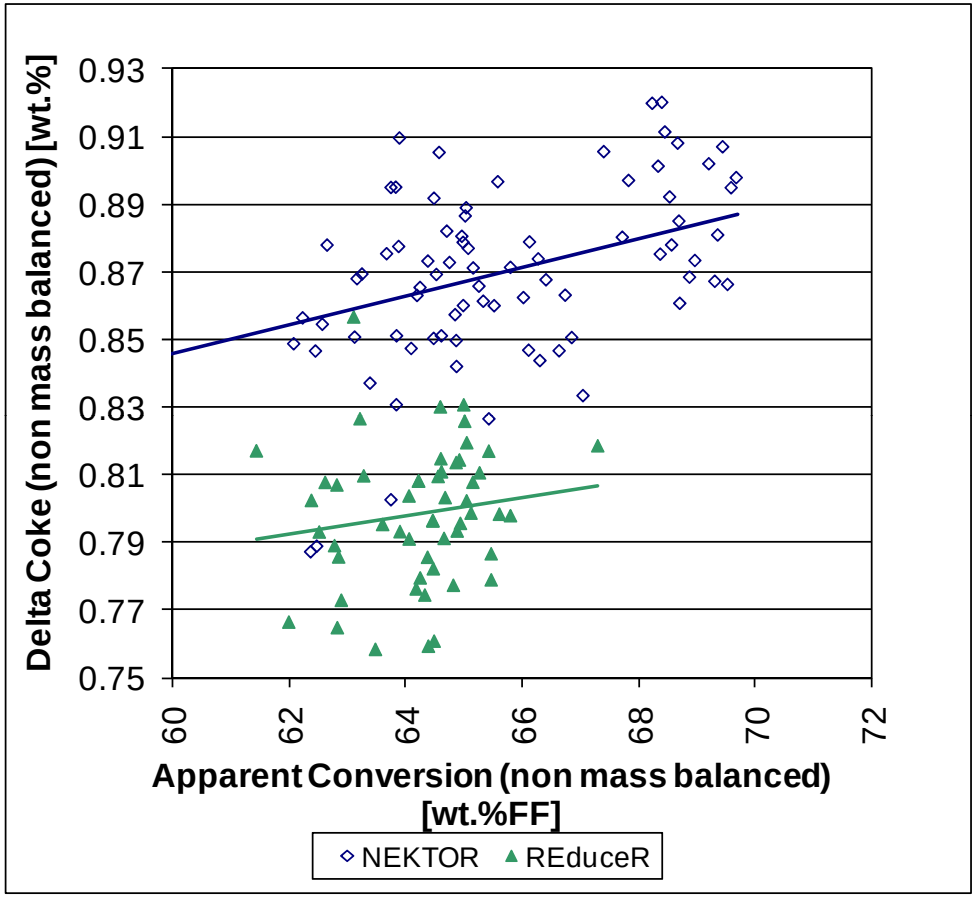
The good nickel tolerance of REduceR blends is confirmed at Refinery B

Refinery B – FCC Unit Data (100% Change Out)



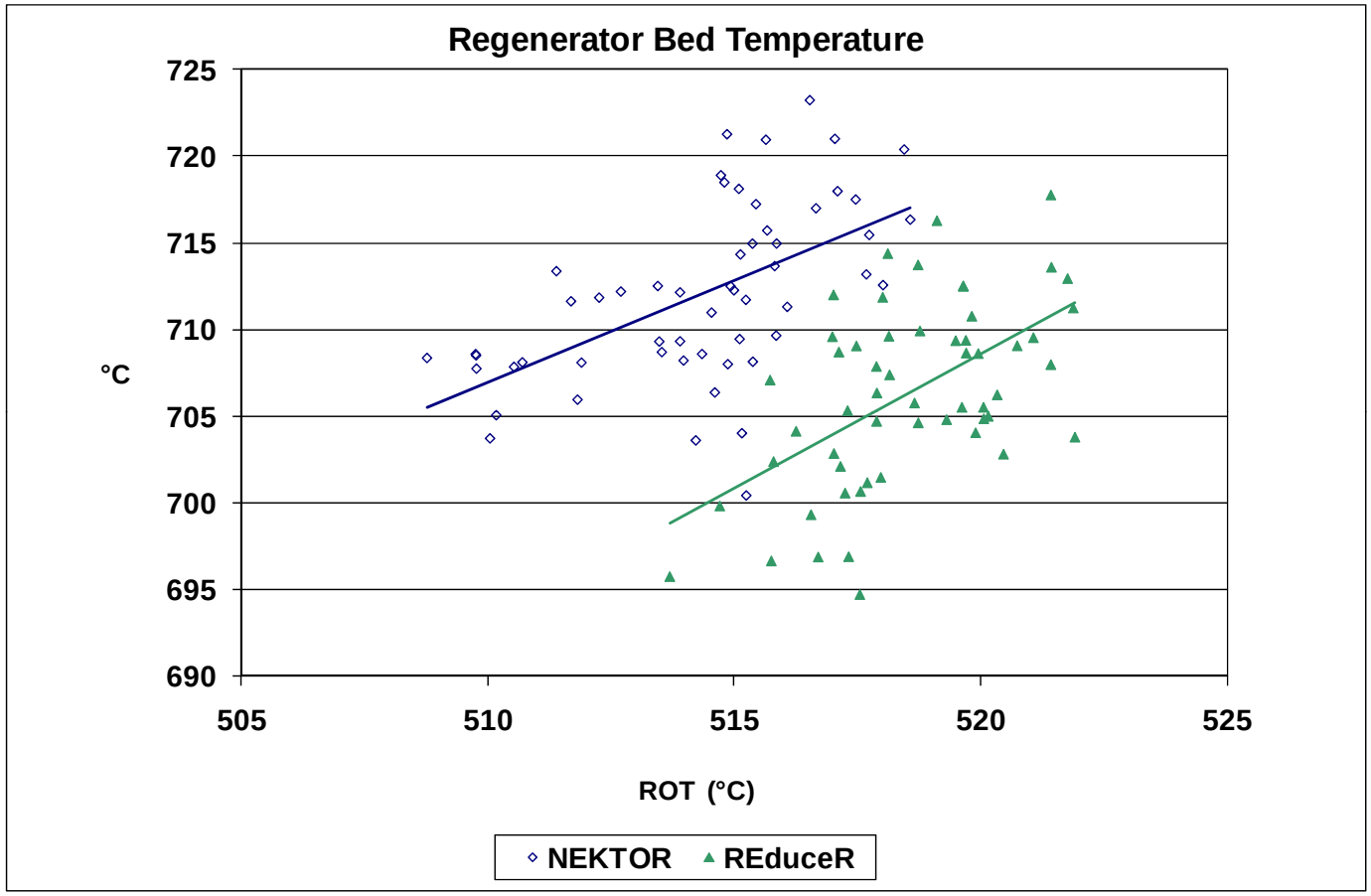
The REduceR blend showed similar bottoms cracking

Refinery B – FCC Unit Data (100% Change Out)



The REduceR blend showed a significant improvement in delta coke

Refinery B – FCC Unit Data (100% Change Out)



The REduceR blend reduced Regen Bed Temp

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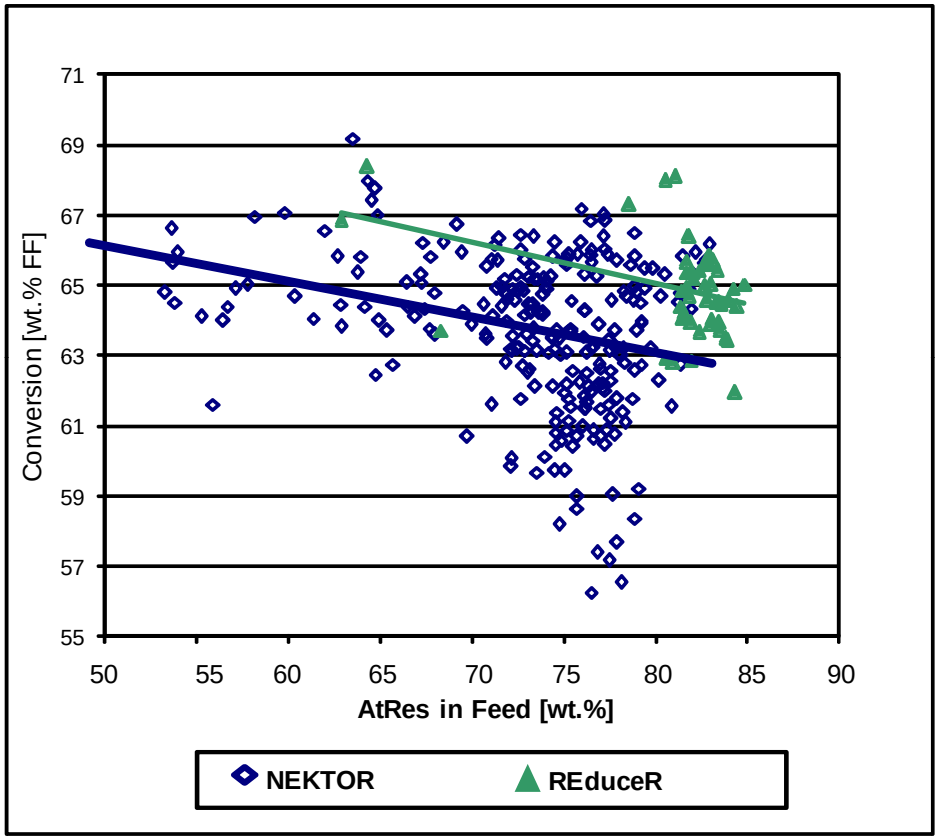
Refinery B – FCC Unit Data (100% Change Out)



The REduceR blend showed higher conversion at const AtRes content

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FCC Unit Data with 50% REduceR

To evaluate the catalyst performance the yields are calculated on the basis of constant feed properties and independent operating conditions

		NEKTOR	50% NEKTOR 50% REduceR
Cat-to-Oil	g/g	6.1	base + 0.4
Conversion	wt.%	74.5	base + 0.5
Hydrogen	wt.%	0.11	base + 0.02
C1+C2's	wt.%	2.2	base + 0.2
Propylene	wt.%	4.6	base + 0.4
C4 Olefins	wt.%	5.3	base + 0.6
LPG	wt.%	15.5	base + 2.0
Gasoline	wt.%	50	base - 1.6
LCO	wt.%	15.2	base - 0.2
Slurry	wt.%	10.3	base - 0.2
Coke	wt.%	6.4	base - 0.1
Delta coke	wt.%	1.05	base - 0.09
CAR	MT/D	base	base
e-cat Ni	ppm	base	base
e-cat V	ppm	base	base
Regen Bed Temp	°C	base	base - 15 °C

The key objectives of maintaining conversion and bottoms upgrading were clearly met, and were even increased

To summarise the commercial trial of REduceR at Refinery B

- A 30% blend of REduceR was added to a NEKTOR catalyst with the objective of maintaining performance whilst reducing catalyst rare-earth requirement

- Rare earth was reduced from 3.1 to 2.2 wt.%, and despite the high Ni+V, the excellent performance of NEKTOR was maintained and even improved

- Refinery B subsequently moved to 50% REduceR, and reduced the overall catalyst rare-earth content to 1.5 wt.%

- The key requirement of maintaining conversion and bottoms upgrading was not only achieved, they were even improved

Low/Zero Rare-Earth FCC Catalyst Reference List for EMEA

	Catalyst	Typical E-Cat Properties (June to August 2011)							
		Target RE Level (wt.%)	Ni (ppm)	V (ppm)	CaO (wt.%)	Fe (wt.%)	Na (wt.%)	MA (wt.%)	CRC (wt.%)
1	REsolution	0	237	403	0.03	0.30	0.30	66	0.02
2	REsolution	0	444	1171	0.03	0.37	0.27	72	0.07
3	REsolution	0	777	931	0.06	0.58	0.24	62	0.02
4	REsolution	0	409	836	0.10	0.67	0.10	61	0.14
5	REsolution	0	108	247	0.03	0.45	0.29	74	0.06
6	REsolution	0	na	na	na	na	na	na	na
7	REsolution	0	na	na	na	na	na	na	na
8	NADIUS + 50% REactoR	0.9	62	120	0.03	0.43	0.22	71	0.17
9	NADIUS + 80% NEXUS	0.5	356	1282	0.03	0.81	0.25	68	0.21
10	NADIUS + 45% REsolution	1.7	na	na	na	na	na	na	na
11	DieseliseR + 30% REduceR	2.4	2461	3273	0.06	0.55	0.32	71	0.19
12	NEKTOR + 30% REduceR	2.5	na	na	na	na	na	na	na
13	NEKTOR + 30% REduceR	2.5	2060	3632	0.07	0.37	0.34	71	0.20
14	NEKTOR + 30% REduceR	2.2	1545	2476	0.20	0.48	0.38	71	0.06
15	NEKTOR + 30% REduceR	2.2	2172	5003	0.07	0.40	0.49	70	0.12
16	NEKTOR + 50% REduceR	1.5	3736	4528	0.16	0.58	0.50	71	0.14
17	NEKTOR-ULCC + 30% REduceR	2.5	1813	2589	0.06	0.37	0.62	71	0.07
18	NEKTOR-ULCC + 30% REduceR	2.5	2420	3637	0.04	0.38	0.32	73	0.35
19	NEKTOR-ULCC + 50% REduceR	1.6	2550	1910	0.05	0.36	0.29	68	0.05
20	NEKTOR-ULCC + 30% REduceR	2.5	2883	4300	0.09	0.39	0.48	69	0.04
21	NEKTOR-ULCC + 50% REduceR	1.8	5321	2422	0.06	0.43	0.31	69	0.38
22	ResidCrackeR + 30% REduceR	2.5	6044	4937	0.08	0.49	0.38	64	0.11
23	ResidCrackeR + 50% REduceR	1.7	3547	4747	0.14	0.60	0.43	70	0.14

Rare-earth free catalyst technologies have received excellent market acceptance, and are performing well

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