



The REpLaCeR™ Family

Low and Zero Rare-Earth FCC Catalysts

Grace Davison Refining Technologies

GRACE

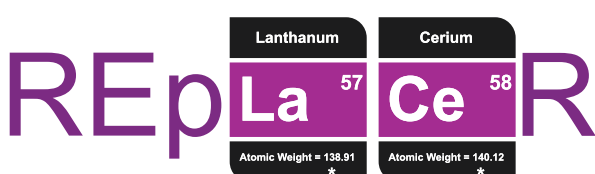
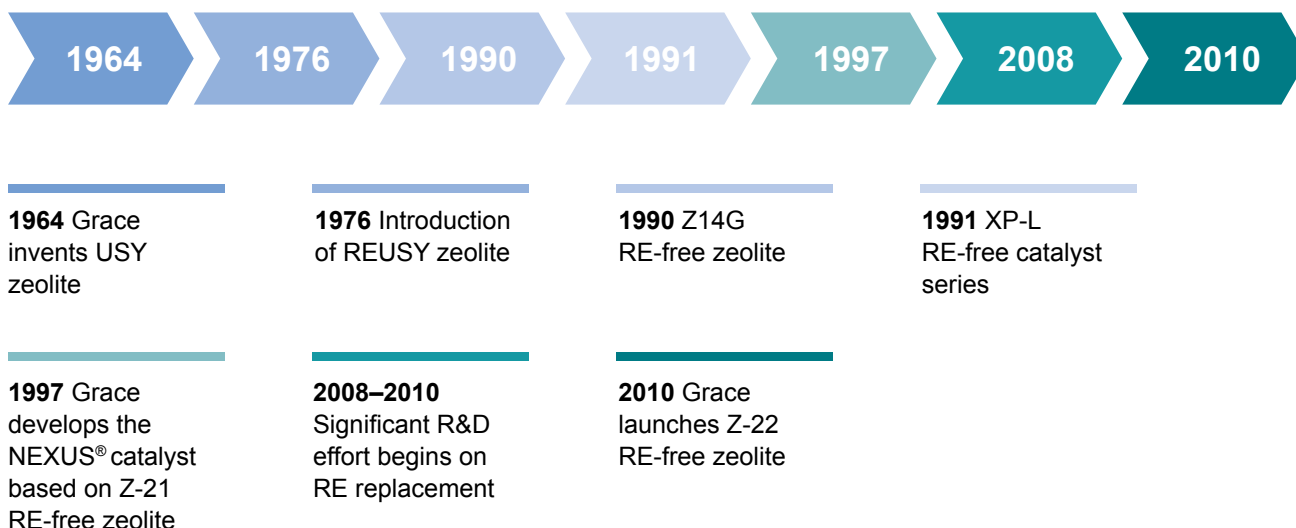
Rare-earth metals are an important component of FCC catalysts, as well as being a key raw material for many strategic industries with applications ranging from military devices to electronic components. In addition, they are essential constituents in newly evolving green technologies, such as hybrid cars and wind turbines. Rather ironically, rare-earth metals are not so rare, however they tend to be concentrated in hard to extract ore deposits. As a result, the world's supply comes from only a few sources; China alone accounts for 95% of the world's rare-earth metal output. Recent export quota restrictions on rare-earth metals from China have caused the price of rare-earth metals to rapidly rise.

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Grace Davison has a long history of providing innovation in the development of FCC catalysts, including the addition of rare-earth metals to stabilize the zeolite Y component of the FCC catalyst, which was revolutionary for catalytic cracking. As the only FCC supplier with flexible manufacturing platforms, Grace also has a successful history of developing rare-earth free FCC catalysts. We introduced new zeolite components that

enhanced gasoline octane in the 1990's, delivering activity and stability without the use of rare earth. Later in the 1990's Grace developed Z-21, a rare-earth free stabilized zeolite Y. Based on this new technology the NEXUS® catalyst family was commercialised in 1997, as a rare-earth free catalyst family for low-metal feed applications. The NEXUS® catalyst has since been used in 10 applications.

Figure 1: Grace's Long History of Zeolite Innovation



Grace Davison has now developed the REpLaCeR™ family of rare-earth free FCC catalysts, which are based on the following technologies:

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

Commercial Experience Using the NEXUS® Catalyst

In 2008, a refinery conducted back-to-back catalyst evaluations comparing the NEXUS® catalyst to a competitive rare-earth based FCC catalyst. The feed properties and operating parameters for both periods were similar. The key objective for the refinery was to maximize gasoline yield as well as reducing dry gas yield.

The FCC product yields obtained during back-to-back testing are shown in Table 1 (right). The NEXUS® catalyst provided higher conversion (2.8 wt.%), lower hydrogen yield (0.04 wt.%), a lower dry gas yield (0.5 wt.%) and a higher gasoline yield (5 wt.%). To summarise, the refiner considered the NEXUS® catalyst trial to be a complete success, realising a benefit of approximately 1 million €/year.

Table 1: FCC Product Yields Comparing the NEXUS® Catalyst with a Competitor's Rare-Earth Based Catalyst

Product Yields	Competitor	NEXUS®-346
H ₂	0.07	0.03
Dry Gas (-H ₂ S)	4.12	3.60
LPG	18.19	16.25
Gasoline C5-210 °C	45.20	50.16
LCO 210-360 °C	18.72	15.62
MCB 360+ °C	7.68	7.98
Coke	4.56	4.72
Conversion	73.60	76.39

New REsolution™ Catalyst Family Based on Z-21 Zeolite



Recently, Grace Davison has renewed efforts to develop new rare-earth free catalysts. This has involved further formulation development by combining the rare-earth free Z-21 zeolite with new matrices, resulting in the new catalyst family REsolution™. Rare-earth free REsolution™ catalysts are intended for low-metal feed applications, and represent a further improvement on the NEXUS® catalyst performance. Within each family of REsolution™ catalysts, the ability to independently adjust the activity and selectivities of zeolite and the matrix, as well as the ratio of zeolite/matrix activity allow for a tremendous degree of formulation flexibility. For low-metal applications REsolution™ catalysts will match/improve the performance of standard rare-earth based catalysts.

Within the first 6 months of commercialisation, the REsolution™ catalyst has been successfully used in seven refineries in the EMEA region. One such application is at Refinery A in central Europe. In February 2011 they switched from a NEKTOR™ catalyst with 3.1 wt.% rare earth to the rare-earth free REsolution™ catalyst. Figure 3 (page 6) shows ACE Ecat testing to evaluate the performance of the REsolution™ catalyst at a 30% change-out. As can be seen conversion, dry gas yield and bottoms upgrading were similar for the REsolution™ catalyst, whilst delta coke was lower. Table 2 (page 4) shows a comparison of the product selectivities in more detail, where the increased

LPG yields (at the expense of gasoline) can be attributed to the fact that more ZSM-5 additive was used during the REsolution™ period. The catalyst change out has now reached over 75% so the RE₂O₃ content of the Ecat has been reduced from 3.1 to 0.7 wt.% and the refinery are observing that the performance is not only maintained using the rare-earth free REsolution™ catalyst, it is actually improved. To summarise, they have observed similar bottoms upgrading and dry gas yield, as well as lower delta coke.

Figure 2: ACE Ecat Testing of Rare-Earth Free REsolution™ Catalyst

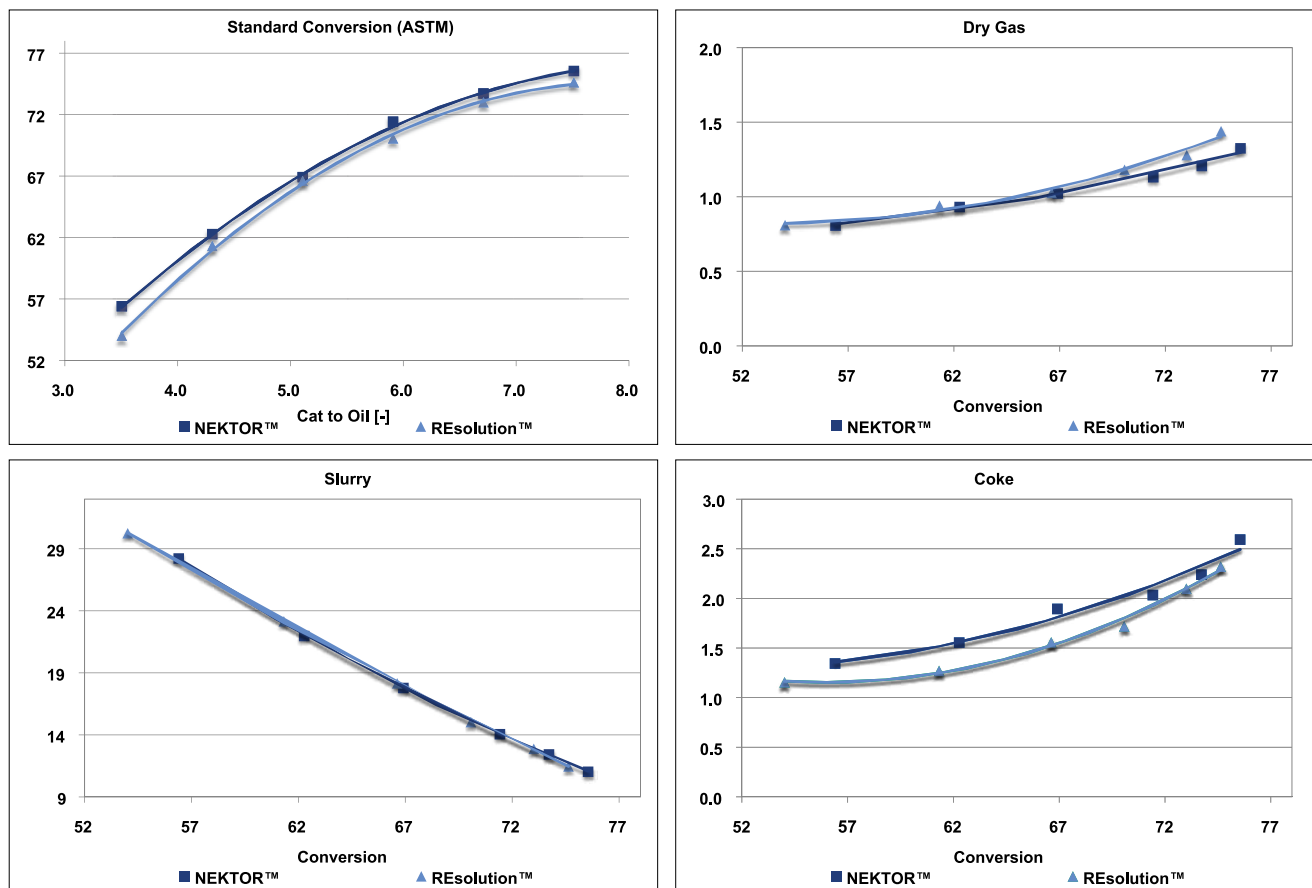


Table 2: ACE Ecat Testing of Rare-Earth Free REsolution™

ACE Ecat Data		NEKTOR™	REsolution™ (30% change-out)
Rare-earth	wt. %	3.1	2.1
Ni+V	ppm	754	626
Cat-to-Oil	g/g	4.8	5.0
Conversion	wt. %	66.0	66.0
Hydrogen	wt. %	0.04	0.04
Dry gas	wt. %	1.0	1.0
Propylene	wt. %	4.7	5.8
C4 Olefins	wt. %	6.7	7.2
LPG	wt. %	15.9	17.7
Gasoline	wt. %	46.9	45.0
LCO	wt. %	15.5	15.3
Slurry	wt. %	18.5	18.7
Coke	wt. %	1.7	1.5

Grace's Latest Zeolite Innovation – The Rare-Earth Free Z-22 Zeolite

Most recently, Grace Davison has achieved a breakthrough with a proprietary stabilisation process and a unique treatment step to boost acidity, resulting in Z-22, a state-of-the-art rare-earth free zeolite. Z-22 zeolite has been successfully produced in our manufacturing plants. The REactoR™ catalyst family utilizes the Z-22 zeolite, but also incorporates the EnhanceR™ processing technologies used in NADIUS™ (a rare-earth based first-generation EnhanceR™ catalyst for low-metal feed applications). ACE pilot plant testing (CPS-3 deactivation, metals free) demonstrates that both catalysts show similar selectivities in terms of dry gas, coke and bottoms upgrading, whilst the REactoR™ catalyst provides higher yields of LPG olefins at the expense of some gasoline yield. Commercial trials of the REactoR™ catalyst are in progress.

Table 3: ACE Testing Comparing NADIUS™ and REactoR™ Catalysts

CPS-3 deactivation, metals free	NADIUS™	REactoR™
Conversion, wt.%	75	75
LPG Olefins, wt.%	14.6	15.3
Gasoline, wt.%	51.0	50.3
Bottoms, wt.%	10.3	10.3
Coke, wt.%	1.7	1.6

The REpLaCeR™ catalyst is another new rare-earth free catalyst family that is based on the Z-22 zeolite, but this catalyst incorporates the processing technologies used in NaceR™ (a rare-earth based third-generation EnhanceR™ catalyst for low-metal feed applications). ACE pilot plant testing (CPS-3 deactivation, metals free) comparing the REpLaCeR™ and NaceR™ catalysts show that the REpLaCeR™ catalyst provides similarly high activity, slightly higher LPG olefin yields (at the slight expense of gasoline), as well as similar bottoms upgrading and lower coke yield. Commercial trials of the REpLaCeR™ catalyst are also in progress.

Table 4: ACE Testing Comparing NaceR™ and REpLaCeR™ Catalysts

CPS-3 deactivation, metals free	NaceR™	REpLaCeR™
Conversion, wt.%	75	75
LPG Olefins, wt.%	13.7	14.3
Gasoline, wt.%	50.4	50.0
Bottoms, wt.%	10.0	9.9
Coke, wt.%	2.6	2.1

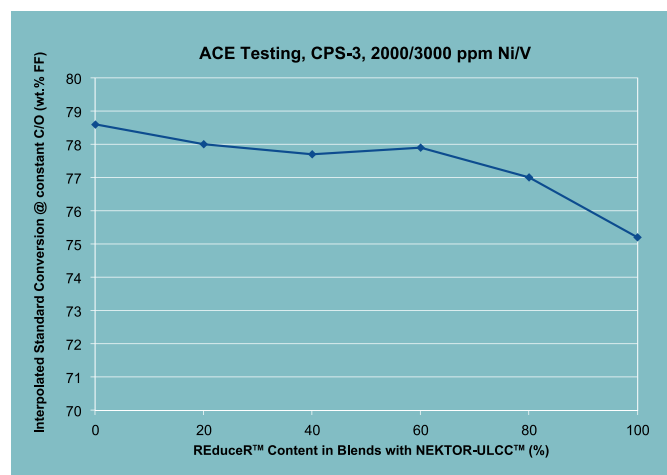
These ACE pilot plant results demonstrate that for low-metal applications the REactoR™ and REpLaCeR™ catalysts are suitable rare-earth free alternatives to established rare-earth based catalysts. Within these catalyst families the matrix type as well as the zeolite/matrix ratio can be varied. Additional formulation flexibility is possible, enabling fine tuning of the catalyst to suit FCCU-specific requirements regarding activity and selectivity. The REactoR™ and REpLaCeR™ catalysts are also manufactured with the proprietary Grace Davison alumina-sol binder system, which ensures low particulate emissions due to its excellent attrition resistance.

A Rare-Earth Free Catalyst for Resid Feed Applications

Due to the additional demands placed on the zeolite stability, the development of rare-earth free catalysts for the resid feed sector is much more challenging than for the low-metal feed sector, and rare-earth metals remains the most effective vanadium trap. However, processing technology involving metals resistance functionality has now been successfully applied to catalyst systems containing the Z-21 and Z-22 zeolites, resulting in the REDuceR™ catalyst family. The REDuceR™ catalyst can be used as a blending component with a rare-earth based resid catalyst, thus reducing the overall rare-earth requirement. Figure 3 (page 6) shows the activity retention of REDuceR™ catalyst blends with the NEKTOR-ULCC™ catalyst (ACE pilot plant, CPS-3 deactivation, 2000/3000 ppm Ni/V, constant cat-to-oil), and it can be seen that even up to blends of 60% REDuceR™ catalyst very good activity retention is obtained.

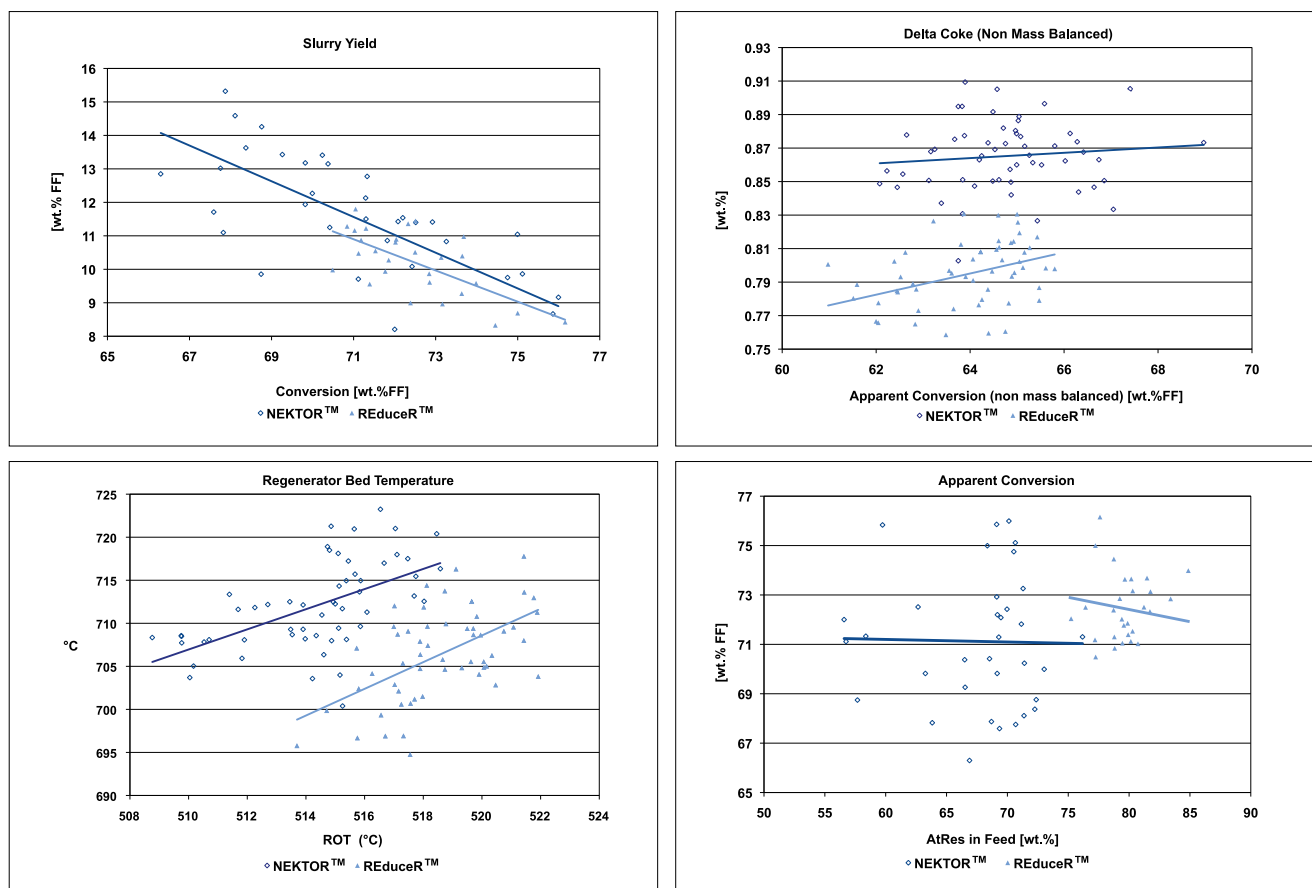


Figure 3: Activity Retention of REduceR™ Catalyst Blends for Resid Applications



The REduceR™ catalyst has been successfully commercialised, and is being used in more than ten European refineries. One such example is at Refinery B in central Europe, which processes a resid feedstock with typical Ecat Ni+V levels of > 7,000 ppm. This refinery was previously using a NEKTOR™ catalyst that contained ca. 3.1 wt.% RE₂O₃, and performed extremely well. In April 2011, Refinery B began to blend 30% of the rare-earth free REduceR™ catalyst with the NEKTOR™ catalyst, and the FCCU data shown in Figure 4 (below) shows that the REduceR™ catalyst blend provided similar/better bottoms upgrading, a lower delta coke, lower regenerator bed temperature and increased conversion at constant feed Atmospheric Residue content.

Figure 4: FCCU Data of the REduceR™ Catalyst Blend at 30%



Refinery B considered the performance of the REduceR™ catalyst to be such a success that they increased the blending ratio from 30% to 50%, thus reducing the overall rare-earth content of the catalyst to 1.5 wt.%. Table 5 (page 7) shows the FCCU product yields obtained with the 50% REduceR™

catalyst blend compared with the NEKTOR™ catalyst. For the purpose of evaluating the actual catalyst performance the yields shown are calculated on the basis of constant feed properties and independent operating conditions. The key objective of the refinery was to maintain conversion and bottoms

upgrading whilst reducing rare-earth content. As can be seen these key objectives were met, and in addition conversion and bottoms upgrading were even increased. The REduceR™ catalyst provided a similar coke yield but an improved delta coke, and allowed regen bed temperature to be decreased by 15 degrees C.

Figure 5: Rapid Market Acceptance of the REpLaCeR™ Family of Catalysts in the EMEA Region

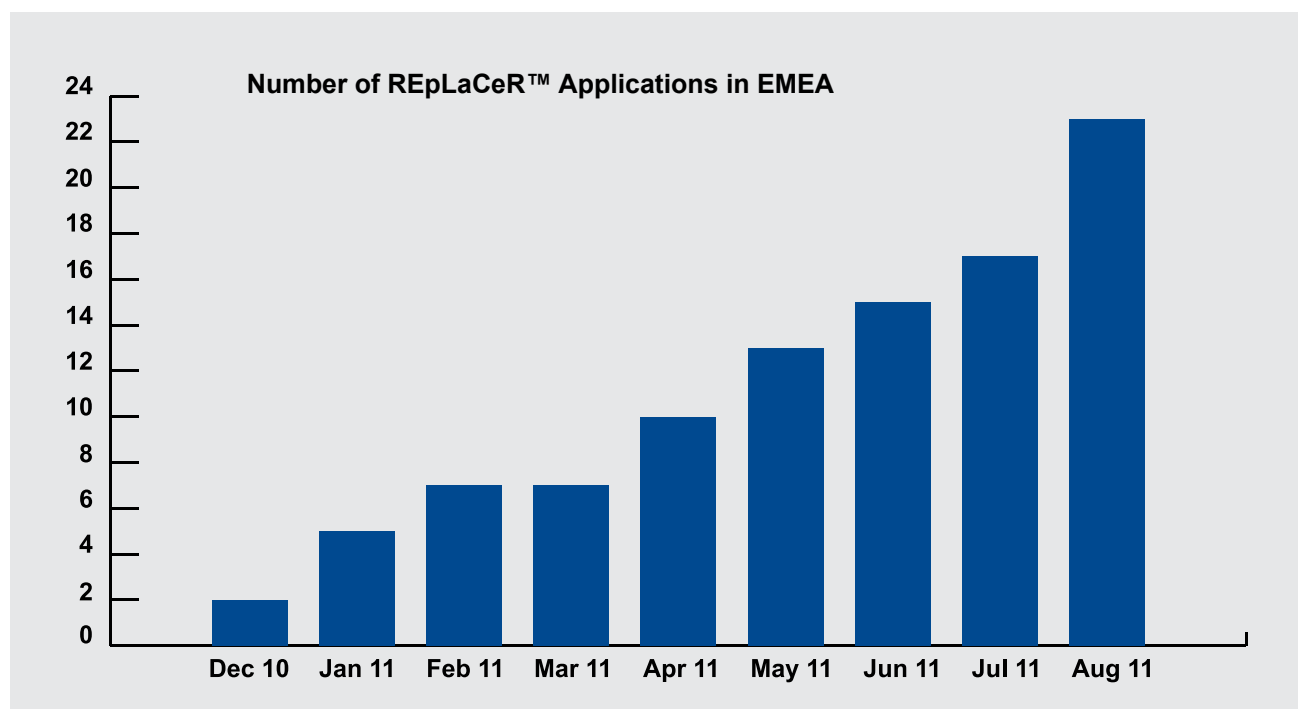


Table 5: FCCU Data of the REDuceR™ Catalyst Blend at 50%

		NEKTOR™	50% NEKTOR™ 50% REDuceR™
Cat-to-Oil	g/g	base	base + 0.4
Conversion	wt.%	base	base + 0.5
Hydrogen	wt.%	base	base + 0.02
C1+C2's	wt.%	base	base + 0.2
Propylene	wt.%	base	base + 0.4
C4 Olefins	wt.%	base	base + 0.6
LPG	wt.%	base	base + 2.0
Gasoline	wt.%	base	base - 1.6
LCO	wt.%	base	base - 0.2
Slurry	wt.%	base	base - 0.2
Coke	wt.%	base	base - 0.1
Delta coke	wt.%	base	base - 0.09
CAR	MT/D	base	base
Ecat Ni	ppm	base	base
Ecat V	ppm	base	base
Regen Bed Temp	°C	base	base - 15 °C



Summary

In 2011 Grace Davison Refining Technologies developed the REpLaCeR™ family of low and zero rare-earth catalysts:

- **REsolution™ catalyst:** a rare-earth free catalyst based on the Z-21 zeolite and a new matrix. The catalyst has undergone various successful commercial trials for low-metal feed applications.
- **REactoR™ catalyst:** a rare-earth free catalyst based on the Z-22 zeolite combined with the EnhanceR™ technologies used in the NADIUS™ catalyst. The catalyst is undergoing commercial trials with low-metal feed applications.
- **REpLaCeR™ catalyst:** a rare-earth free catalyst based on the Z-22 zeolite combined with the EnhanceR™ technologies used in the NaceR™ catalyst. The catalyst is undergoing commercial trials with low-metal feed applications.
- **REDuceR™ catalyst:** a rare-earth free resid catalyst based on either the Z-21 or Z-22 zeolite. The catalyst has undergone various successful commercial trials for resid feed applications and has shown to maintain and even improve performance with blends up to 50%.

Grace is a premier specialty chemical and materials company with more than 6000 employees located around the world. Our products are used by millions of people each day. Among many other things, we ensure the integrity of some of the world's major buildings and bridges, enhance the performance of your petroleum products and preserve the safety of your food.

Grace Davison has successfully pre-registered all REACH relevant substances. The next step is the ongoing preparation of the required registration dossiers and final registration of our substances. Now our customers can have confidence in REACH compliance and supply security beyond 2010.

Non-EU customers should contact us about their import needs.

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