Hybrid catalyst loading reduces fill cost and carbon footprint

Using rejuvenated catalyst in a hybrid load significantly lowers fill cost and CO_2 footprint while providing the performance advantages of latest generation fresh catalyst

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When faced with the task of selecting catalysts for an upcoming hydrotreater turnaround, refiners usually consider replacement with either fresh catalyst or regenerated/rejuvenated catalyst. When the anticipated feedstock, treating severity, and cycle length requirements are unchanged from the current cycle, refilling the catalyst with regenerated or rejuvenated catalyst is a good option. Regeneration of Type I catalysts and rejuvenation of Type II catalysts typically restores >90% of original fresh catalyst activity – generally adequate for replicating the performance of a prior cycle with the same fresh catalyst.

If, on the other hand, the upcoming cycle offers an opportunity to capture higher margins by increasing throughput, processing a more challenging feedstock, or stretching cycle length (for instance, to meet a planned turnaround), replacing the catalyst with the latest generation fresh catalyst may be justified. The latest generation fresh catalyst will typically deliver 15% or higher activity than the previous generation. That extra catalyst activity can be translated into higher throughput, longer cycle length, lower product sulphur/nitrogen or the capability to process a more difficult feedstock.

Hybrid loads

There is a third option for catalyst selection, which is less often considered – the hybrid catalyst load. A hybrid catalyst load utilises a combination of prior generation rejuvenated catalyst and latest generation fresh catalyst to reach an activity level indistinguishable from a full load of latest generation fresh catalyst. The use of rejuvenated catalyst in a hybrid load significantly reduces both the catalyst fill cost and its CO_2 footprint while simultaneously providing all the performance advantages of latest generation fresh catalyst.

At first glance, one might expect a hybrid catalyst load to have an activity level proportional to the fraction of rejuvenated and fresh catalyst in the loading multiplied by their respective activities. A hybrid load is able to outperform the arithmetic average activity of the constituent catalysts by exploiting differences in sulphur reactivity and reaction kinetics as a function of the catalyst's position in the reactor.

A variety of sulphur types are present in most hydrotreater feedstocks, but the type and content can vary significantly, depending on feedstock source and type. **Figure 1** shows some of the sulphur types as well as their reactivities. Mercaptans, sulphides, and disulphides typically have extremely high reactivity. Thiophenic sulphur compounds are less reactive and become progressively less so when connected to one or two benzene rings. The least reactive sulphur compounds are dibenzothiophenes with steric hindrance from one or more alkyl groups adjacent to the thiophenic sulphur. The difference in reactivity between most reactive and least reactive sulphur species is massive – more than 100x.

The least reactive sulphur molecules clearly benefit from, and in many cases require, high catalyst activity to increase the removal rate, but what about the most reactive sulphur molecules? In a unit designed to remove sulphur with low reactivity, the most reactive sulphur hardly benefits from higher catalyst activity. The highly reactive sulphur components of a feedstock are quickly hydrotreated at the top of such a unit in a small fraction of the unit's overall catalyst volume.

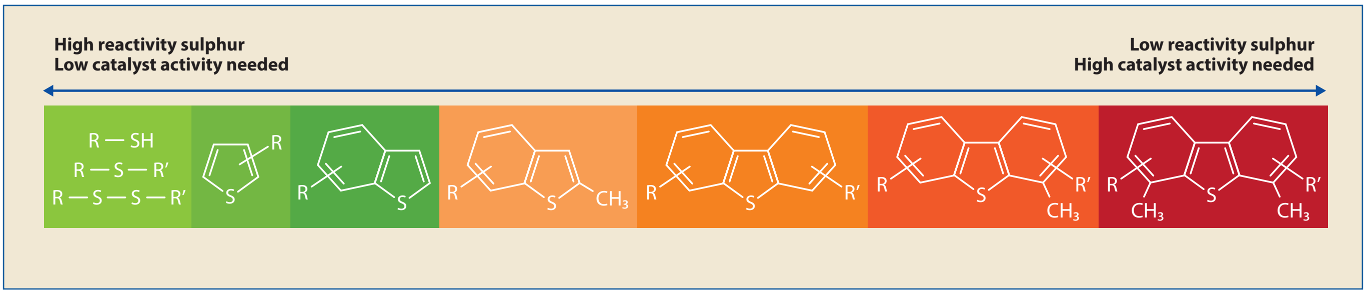

Figure 1 Sulphur types and their reactivities

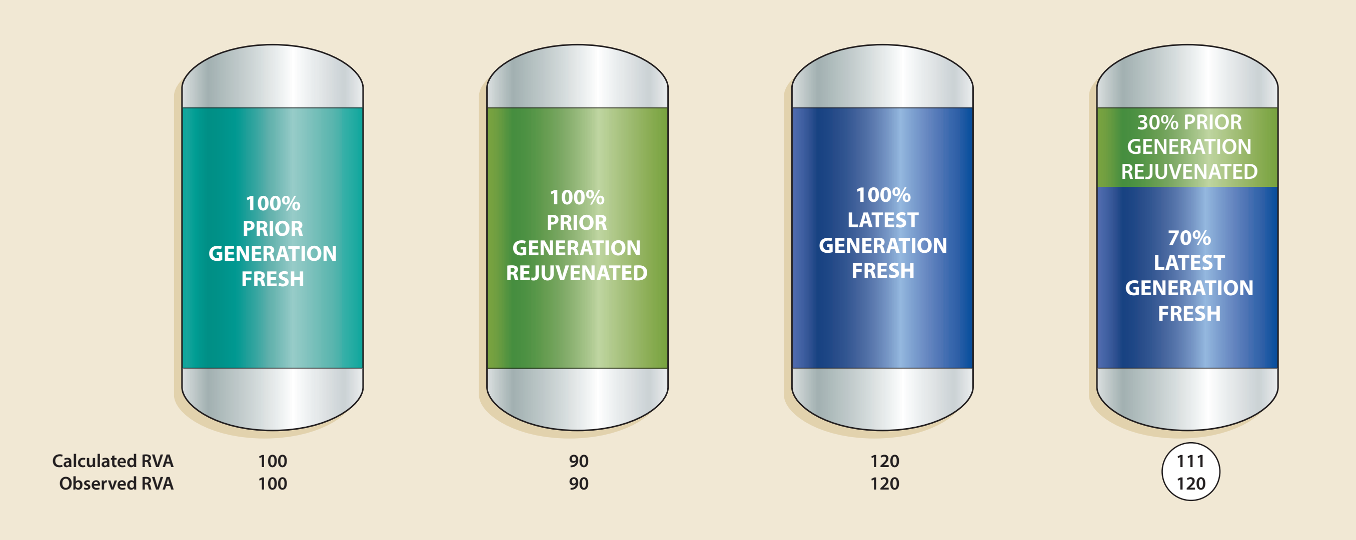

Figure 2 The arithmetic average activity expected from filling 30% of a reactor's volume

The rate of removal for these compounds is more generally limited by the rate of mass transfer of reactants into and reaction products out of the catalyst's pore structure. The catalyst's intrinsic activity is seldom a limiting factor for the removal of these species. This aspect of desulphurisation behaviour can be exploited in a hybrid load by employing a lower cost rejuvenated catalyst in that part of the reactor where intrinsic catalyst activity does not limit a unit's overall desulphurisation performance.

Maximising intrinsic activity

The observed activity of a unit using a hybrid catalyst loading is higher than the calculated value from arithmetically averaging the relative activity of the constituent catalysts. As shown in **Figure 2**, the arithmetic average activity expected from filling 30% of a reactor's volume with a prior generation rejuvenated catalyst (RVA 90) and 70% with a latest generation fresh catalyst (RVA 120) is RVA 111.

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However, the observed activity for that same catalyst system will be RVA 120, which is identical to the activity expected from filling the reactor with 100% latest generation fresh catalyst. Desulphurisation in the highly reactive sulphur regime at the top of the reactor is not limited by intrinsic catalyst activity. The higher intrinsic activity of a latest generation fresh catalyst is mostly lost in this regime, such that a prior generation rejuvenated catalyst performs at essentially the same level.

These sulphur reaction regimes are present in all ultra-low sulphur diesel (ULSD) hydrotreaters and many FCC feed pretreatment (FCC-PT) hydrotreaters. Those are ideal units to exploit the benefits of hybrid loading. In both applications, the feedstock to be processed contains a full range of sulphur molecules from high to low reactivity. In ULSD units, since the product sulphur must be below 10 ppm, it is required to remove almost all the lowest reactivity sulphur compounds.

In an FCC-PT unit, the product sulphur requirement is generally higher, so some or all the lowest reactivity sulphur can remain untreated. The operating conditions of both applications will generate a reaction regime where the highest reactivity sulphur molecules are not limited by intrinsic catalyst activity. Hybrid loading techniques will be effective in these units to gain the performance expected from a full load of high-activity catalyst, plus the cost savings expected from reusing catalyst.

Loading rejuvenated catalyst

Since high intrinsic catalyst activity is not necessary to remove high reactivity sulphur molecules, and since those same molecules react at the top of the catalyst bed, how can the catalyst loading be optimised? The upper part of the reactor, where desulphurisation of high reactivity sulphur dominates, is not a reaction regime where highly active catalysts will be utilised to their full potential. Since the performance benefit of fresh catalyst cannot be fully utilised in this reaction regime, its cost-effectiveness is compromised. A more cost-effective approach is to load a less expensive catalyst in this regime.

A rejuvenated catalyst is a smart choice for use at the top of a reactor since it has sufficient activity for the reaction regime and is significantly less expensive than fresh catalyst. A rejuvenated catalyst within one to two generations of the latest generation will have a suitable activity level to perform well. **Figure 3** shows the performance gain expected from Type I and Type II rejuvenated catalysts relative to the activity of their original fresh state.

Rejuvenation boosts the activity of Type II catalysts to at least 90% of the original fresh level, and it typically boosts the activity of Type I catalysts by 15% or more above the level of the original fresh. The increased activity for Type I rejuvenated catalysts, well above the original fresh activity, is a consequence of the rejuvenation process transforming a Type I active phase to a more active Type II active phase morphology. The enhanced activity of Type I rejuvenated catalysts significantly expands the available volume of used catalyst suitable for use in hybrid loads.

While the activity of regenerated Type I catalyst would, in most cases, be too low to use in a hybrid load, rejuvenation of that same catalyst renders it suitable for use. When compared to the activity of regenerated catalyst, both Type I and Type II catalysts benefit greatly from rejuvenation. This activity gain expands the fraction of total reactor volume in which they can be deployed in a hybrid load without impacting overall unit performance.

Importance of pilot plant testing

Determining the catalyst volume where sulphur removal is dominated by desulphurisation of high reactivity sulphur molecules is difficult without extensive pilot plant testing. While the quantity of highly reactive sulphur for a given feed can be measured using sulphur speciation techniques, the position in the catalyst bed where desulphurisation shifts from a largely mass transfer limited regime to a largely activity limited regime is difficult to predict precisely.

In addition, the exact volume and position of the two reaction regimes will shift somewhat with variations in feedstock or operating conditions. Fortunately, it is not necessary to precisely determine at what point in the reactor desulphurisation becomes activity limited. Limiting the volume of fresh catalyst displaced by rejuvenated catalyst will slightly reduce the cost-effectiveness, but it guarantees performance will be as expected. The volume of rejuvenated catalyst used in subsequent cycles can be increased as experience with hybrid loading increases.

Industrial experience has shown that at least 25% of the catalyst volume at the top of the reactor can be filled with rejuvenated catalyst without a negative impact on unit performance. This is especially true when the activity difference between the rejuvenated catalyst and fresh catalyst is relatively small – less than 25%. The smaller the difference in relative activity between the two catalysts, the less chance that overall unit performance will be adversely affected by the displacement of fresh catalyst with rejuvenated catalyst. For instance, rejuvenated catalyst from a previous generation will typically have 20-25% lower activity than latest generation fresh catalyst. That difference in activity would allow 30% or more of the reactor volume to be filled with rejuvenated catalyst without reducing overall unit performance.

A common question about hybrid loads is who will be responsible for providing technical support for the unit. Refiners with a large, experienced technical staff may prefer to design and support a unit using a hybrid load on their own. Catalyst manufacturers are usually willing to support hybrid loads when they are involved in the process of catalyst selection and design of the catalyst loading diagram. It should be noted that often it is the refiner who must initiate the dialogue with a fresh catalyst manufacturer about their interest in considering options for hybrid loads. The catalyst manufacturer may not propose an option for hybrid catalyst loading unless the refiner proactively expresses interest.

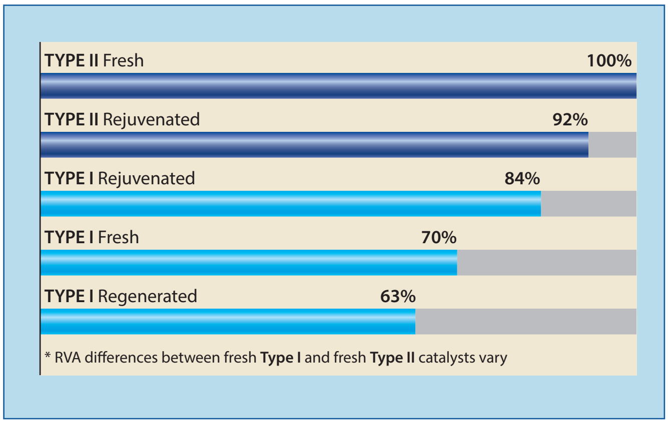
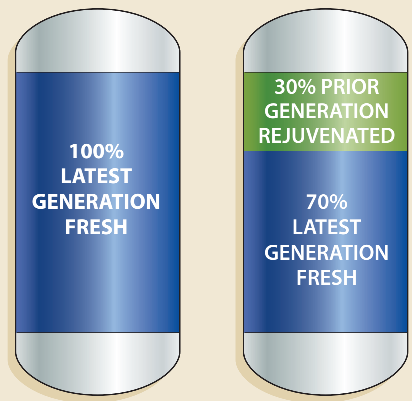


Figure 3 Performance gain expected from Type I and Type II rejuvenated catalysts relative to activity of original fresh state

Savings with hybrid loads

A main driver for most refiners to consider hybrid loads is the savings in catalyst expenditures, typically one of their largest controllable costs. **Figure 4** shows the characteristics of a hybrid load compared to a conventional load of fresh catalyst. In terms of observed activity and expected cycle length, there is no difference. The hybrid load delivers 100% of the activity and 100% of the cycle length expected from a full fresh catalyst load. The cost of the hybrid load is significantly less.

The actual difference can vary depending on the price of molybdenum, cobalt, and/or nickel at the time of purchase. However, a typical savings level is 50% for that fraction of the reactor loaded with rejuvenated catalyst. The reduction in cost will be even greater if the refiner supplies the



	Conventional	Hybrid
Observed RVA	100%	100%
Relative cycle length	100%	100%
Relative fill cost	100%	85% / 80%*
Relative CO_2 footprint	100%	80%

* if reusing own catalyst

Figure 4 Characteristics of a hybrid load compared to a conventional load of fresh catalyst

catalyst to be rejuvenated from their own inventory of previously used catalyst. In that case, the only costs incurred are for regeneration and rejuvenation treatments applied to their spent catalyst.

Reducing CO_2 footprint

While the main driver for a refiner to reuse catalyst will generally be cost savings and effective use of assets, it must be noted that there is also a positive impact on CO_2 footprint from catalyst reuse. Compared to the overall CO_2 footprint generated to manufacture fresh catalyst, regeneration and rejuvenation of a spent catalyst saves more than 60% in CO_2 footprint. The CO_2 footprint to manufacture a fresh catalyst from raw materials is like the CO_2 footprint from the removal of residual carbon from a spent catalyst. The main difference in CO_2 footprint is generated by the manufacturer of the raw materials used in fresh catalyst.

Hybrid loads are a painless and well-proven method to control catalyst fill costs while still capturing the performance benefits of fresh catalyst

Mining, refining, and purifying the metals required to manufacture fresh catalysts are highly energy-intensive processes. These energy-intensive processes are obviously unnecessary when reusing catalyst since they remain the same as on the original fresh catalyst. Figure 4 shows the 20% reduction in CO_2 footprint for the hybrid load as compared to a full fresh load. Reuse of catalysts, especially in a hybrid load where there are no downsides in terms of unit performance, is an easy way to practice circularity and environmental responsibility. As time passes, the CO_2 footprint reduction aspect of hybrid loads is expected to become increasingly important in accessing the economics of catalyst reuse.

Hybrid loads are a painless and well-proven method to control catalyst fill costs while still capturing the performance benefits of fresh catalyst. The fill cost savings are especially large when a refiner reuses catalyst they already own. The performance of a hybrid load is virtually indistinguishable from that of a full load of fresh catalyst. Finally, hybrid loading promotes circular economies and responsible catalyst management – an increasingly important consideration for many refiners.

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