

Challenges in diesel hydrotreating catalyst selection

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Selecting the best diesel hydrotreating catalyst is complex due to several factors:

- Diesel hydrotreating net conversion is typically less than 5.0 wt% without dewaxing, making it difficult to distinguish the best catalyst based on yield gaps alone.
- Hydrogen consumption is considerably lower than that of hydrocracking, making the assessment more challenging because the differences between vendors can be minimal.
- Predicting product properties with different estimators makes direct comparisons less useful, particularly in terms of volume swell.
- Catalyst activity is estimated using kinetic models, but each vendor has their own models and assumptions, leading to comparison biases.

Economic Importance of Catalyst Selection

Catalyst loading strategies for light cycle oil (LCO) processing must consider factors like olefin saturation, metal loading/dispersion, and pore structure to handle contaminants and ensure reactor stability.

Choosing the optimal catalyst can increase refining profits, extend unit cycle lengths, improve product quality, and reduce energy consumption. Some specific economic benefits include:

- Increasing refining profit by processing more refractory and less expensive feed components.
- Maximising unit cycle length to avoid unplanned shutdowns.
- Improving product quality and yield by lowering product

sulphur, nitrogen, density, and total aromatics, and increasing cetane number.

- Reducing energy consumption by minimising the energy required to initiate chemical reactions and maximising heat recovery.

High-Throughput Catalyst Testing

Avantium's high-throughput parallel testing technology allows for efficient and accurate testing of multiple catalyst systems, providing high-quality data with minimal waste. Single pellet single string reactors (SPSRs) help minimise axial dispersion and ensure reproducible reactor loading. Avantium's micro-pilot plant allows for highly efficient testing of catalysts for fixed-bed processes, producing the highest data quality with low amounts of feed.

Realistic scaling down of diesel hydrotreaters for lab testing involves adjusting parameters like hydrogen partial pressure and hydrogen-to-oil ratio and including demetallisation catalysts when necessary. The first step in designing an effective catalyst testing programme involves a comprehensive review of the commercial operation.

Independent testing is essential to accurately determine catalyst performance, avoiding reliance on vendor predictions and ensuring reliable data for economic evaluations.

This article summarises two recent case studies illustrating how our independent catalyst testing was utilised to identify the most effective diesel hydrotreating catalyst.

Case Study 1: Benchmarking nine catalyst systems

Testing often reveals discrepancies between predicted and actual catalyst performance, emphasising the need for independent testing to uncover true catalyst efficiency.

In the first case study, catalyst vendors offered various combinations of base metals and stacking strategies. Some vendors proposed 100% nickel-molybdenum (NiMo) for the maximum hydrodesulphurisation (HDS)/ hydrodearomatisation (HDA) activity, while others used combinations of cobalt-molybdenum (CoMo)/ NiMo to balance the hydrogen consumption and provide

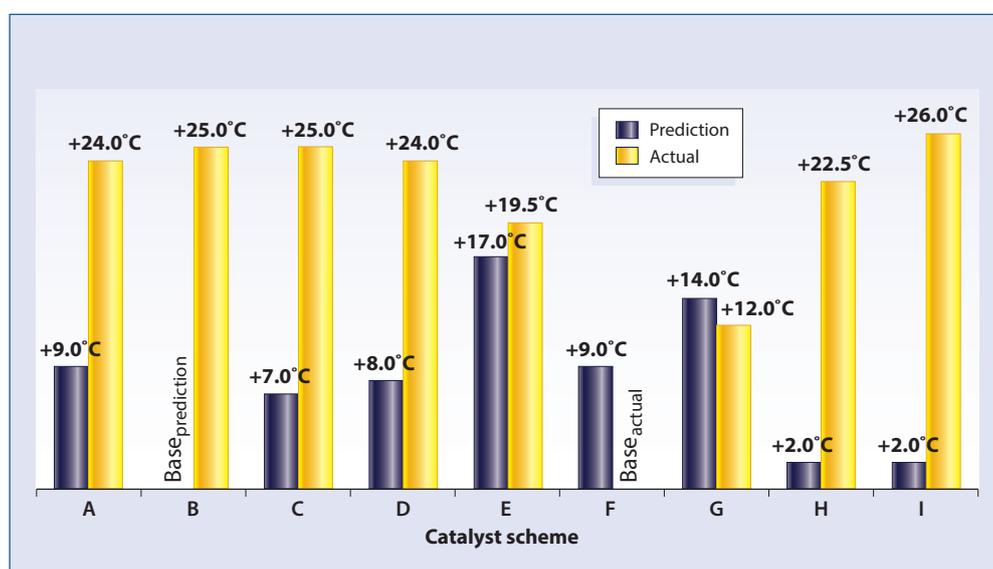


Figure 1 WABT requirements for 8 ppm product sulphur

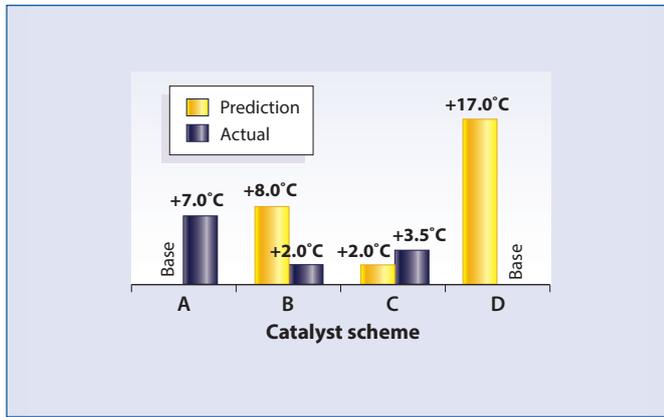


Figure 2 WABT requirements for 10 ppm product sulphur

more HDS stability over the operating cycle. In total, nine catalyst loading schemes (including the incumbent loading scheme) were compared.

In a conventional catalyst test system, it will take much longer to finalise the results as only a few catalyst systems can be tested at the same time. With 16 parallel reactors in Avantium's proprietary Flowrence¹ system, the whole study was conducted in less than two months with comparable results to the commercial-scale unit.

The project was executed in accordance with protocols from catalyst vendors, ensuring good mass balance and data consistency. For quality assurance, Avantium used duplicate reactors for the catalyst systems to ensure good repeatability.

The key highlight here is to find the catalyst system that can process the feed blend of 25% LCO over the 60-month catalyst cycle length and, at the same time, stay within the hydrogen consumption limit (dictated by the size of the make-up hydrogen compressor). This amount of LCO is relatively high compared to standard diesel hydrotreating units.

Since the refinery had never processed this high percentage of LCO before, this study can also be considered proof of concept for whether the economic drive from the linear programming (LP) planning tool can be implemented in the real world.

The predicted weight-averaged bed temperatures (WABTs) were based on different kinetic models and assumptions. While some catalyst vendors offered attractive catalyst activity on paper, with others being more conservative (such as higher WABT), the reality turned out to be quite different, as demonstrated in **Figure 1**.

During the proposal stage, Catalyst scheme F was conservatively estimated to be 9°C lower than that of Catalyst scheme B. However, in reality, Catalyst scheme F was by far the best performer, with 25°C better activity than Catalyst scheme B, which is also among the poorest performers. The same observation applies to Catalyst schemes E and G to a certain extent, where their actual activity is top tier while being underestimated on paper.

Case Study 2: Benchmarking four catalyst systems

In this case, four catalyst schemes were tested with the objective of processing 5 vol% LCO. According to all the

catalyst vendors, the catalysts could handle this amount of LCO for the intended cycle duration. After the first test results with 5 vol% LCO + 95 vol% SR diesel, a very high catalyst deactivation rate was observed. It became clear that none of the catalyst schemes could handle the LCO and would not last the 36-month cycle in the commercial unit.

As seen in **Figure 2**, although there were activity gaps between catalyst systems, the relative differences were not that large. The differences in WABT between catalyst systems will be a matter of cycle months, not years.

More importantly, based on the test data, no catalyst system would meet the required cycle length with this operating scenario. In this case, the most conservative catalyst scheme on paper, Catalyst scheme D, turns out to be the best performer in real life.

On the contrary, a seemingly attractive catalyst scheme on paper, Catalyst scheme A is a poor choice, as it required the highest WABT to achieve 10 ppm product sulphur based on the actual test results.

More importantly, based on the test data, no catalyst system would meet the required cycle length with this operating scenario. In this case, the most conservative catalyst scheme on paper, Catalyst scheme D, turns out to be the best performer in real life

Conclusion

Without independent catalyst testing, it is extremely difficult to select the right diesel hydrotreating catalyst for your application. Real-world catalyst testing reveals the true catalyst performance and provides refiners with reliable data for their economic evaluation.

A parallel catalyst testing system benefits both refiners and catalyst vendors by allowing one catalyst vendor to offer/test more than one catalyst loading scheme, increasing the chance of getting better catalyst loading schemes. The data obtained from pilot plant testing can also be used for kinetic modelling to gain more insights into actual catalyst performance.

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Reference

¹ Flowrence is a registered trademark for Avantium's high-throughput catalyst testing systems.

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