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Hydroprocessing catalyst selection—Part 2: Considerations and best practices for catalyst testing

Hydroprocessing catalysts are an essential part of the refinery involved in the treatment/conversion of most petroleum fractions, ranging from naphtha to residue. Hydrotreating catalysts help refiners meet fuel regulations and enhance the performance of downstream catalysts and processes, [e.g., naphtha reforming or fluid catalytic cracking (FCC)] by removing sulfur (S), nitrogen (N) and metals from their feedstocks, as well as improving product properties by hydrogen (H) addition. Moreover, hydrocracking catalysts further improve refiners' profits by converting low-value streams [e.g., vacuum gasoil (VGO)] into high-value fuels and chemical feedstocks. Therefore, the selection of hydroprocessing catalysts requires great care from refiners to ensure maximum asset utilization and profitability.

Part 1 of this article, which appeared in the May issue of *Hydrocarbon Processing*, discussed pitfalls in planning and selecting the catalyst evaluation method, and provided best practices to guide refiners towards an optimal hydroprocessing catalyst selection.

Part 2 discusses critical aspects of a hydroprocessing catalyst testing program and presents readers with best practices/suggestions to ensure a successful benchmarking campaign.

Industrial vs. laboratory-scale fixed-bed reactor. While refiners conduct a catalyst testing campaign to assist their catalyst selection process, experimental aspects remain that require great care and consideration to ensure meaningful results and minimum biases between catalyst vendors.

First, the laboratory-scale fixed-bed reactor should effectively simulate phenomena in the commercial-scale reactor. In most hydroprocessing applications, the trickle flow regime is pre-dominant. Scientists/engineers have proposed experimental techniques to minimize the effects of non-ideal flow behaviors on the performance of a laboratory-scale reactor.[4] For example, a minimum value of reactor-to-particle diameter ratio must be ensured to reduce wall effects. Typically, laboratory-scale fixed-bed reactors have a higher than usual length-to-diameter ratio than commercial reactors for good similarities between two different scales.

The differences between these two different scales are summarized in **TABLE 2.** Even with perfect hydrodynamics, other experimental factors can still cause discrepancies between the laboratory-scale experiment and the commercial process. In the authors' hydroprocessing experience, the laboratory-scale unit's overall performance was often poorer than the commercial one. Other critical experimental aspects are discussed here to better explain how discrepancies can occur, as well as the practical solutions to address them.

LHSV vs. WHSV. Linear hourly space velocity (LHSV) is a widely accepted parameter to connect a laboratory-scale reactor with a commercial one. LHSV is a ratio between volumetric feed flowrate (m^3/hr) and reactor volume (m^3)—as such, the typical unit of LHSV is 1/hr.

TABLE 2. Differences between industrial and laboratory-scale fixed-bed reactor

Parameter	Industrial-scale reactor	Laboratory-scale reactor
Diameter	1 m–6 m	0.2 cm–4 cm
Length	10 m–50 m	0.5 m–2 m
Flow distribution	Requires flow distribution devices to wet the catalyst beds evenly	Using inert material is enough to promote good flow distribution and catalyst wetting
Mode of operation	Non-isothermal: requires interbed cooling or quenching in many cases	Isothermal: no need of interbed cooling, ideal for kinetic study
Axial dispersion	Negligible	Significant in some cases
Catalyst wetting	Very good	Generally poorer
Mass and heat transfer	Very good	Generally poorer
Channeling and wall effects	Negligible	More significant in most cases

Despite its popularity, the authors do not fully agree with using this parameter to simulate the commercial-scale reactor for multiple reasons, especially for scale-down applications (e.g., refinery catalyst benchmarking).

Two primary techniques are available to pack the catalyst inside a commercial-scale reactor: sock loading and dense loading. The catalyst amount for a fixed volume can differ by up to 20% by employing a different loading technique. In other words, the difference in overall activity could be as high as 20%. This discrepancy is particularly crucial for catalysts with extrudate shapes, while the same effect is less pronounced for spherical ones. It is not uncommon to see different catalyst vendors propose a different catalyst loading technique for the same reactor.

Additionally, different catalysts have a unique loading density from different designs and materials.

For these reasons, the authors recommend that every scientist/engineer adhere to weight hourly space velocity [(WHSV), m^3 of feed/hr/kg of catalyst] to improve the similarity between two different scales. Using a specific WHSV for each catalyst vendor is the best option.

Care must be taken which catalyst weight basis is referred to when specifying WHSV (e.g., wet or dry). Modern hydrotreating catalysts usually contain the organic additive (typically organic acid) to promote Type II active sites. Although this organic additive decomposes during the catalyst activation, it contributes 16 wt%–30 wt% of the fresh catalyst weight, depending on the level of metal contents.

H_2 partial pressure and H_2-to-oil ratio. In the authors' experience, typical maximum pressures for laboratory-scale units vary between 160 barg and 175 barg. Despite the use of pure H_2 being prevalent in laboratory-scale experiments [which also diminishes hydrogen sulfide (H_2S) inhibition effects], this pressure limitation still impacts the hydrogenation level, N slip control and the deactivation rate in high-pressure hydrocrackers and residue hydrotreaters (see **TABLE 3** for typical pressure ranges).

Additionally, this limit also affects some product properties from poorer hydrogenation (e.g., cetane number or smoke point). Theoretically, this constraint also impacts the cracking activity, but the effect is only marginal. It is uncommon to see poorer product qualities from a laboratory-scale experiment compared with a commercial unit.

To compensate for lower H_2 partial pressure, the H_2-to-oil ratio can be proportionally increased during the test campaign. For example, if the H_2 partial pressure is off by 10%, the H_2-to-oil ratio should be increased by the same proportion. **Note:** A higher H_2-to-oil ratio cannot fully compensate for lower H_2 partial pressure, but it will surely help.

For most cases, refiners use their actual H_2-to-oil ratio as a target for their pilot plant testing campaign. In the authors' experience, recycle gas flows are notoriously incorrect. The actual gas molecular weight can significantly differ from the one used in the distributed control system (DCS) calculation. This flowmeter does not impact the material balance across the unit; therefore, it is rarely corrected by the refinery. Moreover, the recycle gas sample is seldom taken for units without an amine scrubber due to a high H_2S level; a cartridge of lead acetate is required when taking the sample to lower H_2S concentration to an acceptable level. To calculate a realistic H_2-to-oil ratio, the molecular weight difference must be considered (the uncorrected recycle gas flow reading can be off by up to 20%).

Catalyst loading scheme. Various assumptions have been used for the catalyst loading scheme, such as:

- Replacing the demetallization catalysts with the main hydrotreating catalysts
- Excluding the demetallization catalysts.

The main argument to support these assumptions is that the test campaign is relatively short, therefore demetallization catalysts are not needed (e.g., negligible metal deactivation). This reasoning might be valid if different main hydrotreating catalysts are benchmarked for an R&D program. However, this is not the case for the refinery catalyst benchmarking program, where the ratio between the demetallization catalysts and the main hydrotreating catalysts varies with catalyst vendors.

The catalyst vendor that proposes more demetallization fraction will be given extra activity advantages during the test campaign if the refiner adopts the first assumption. On the contrary, the catalyst vendor with less demetallization fraction will be less affected by excluding the demetallization catalysts if the refiner goes with the second assumption. Some demetallization catalysts have fairly high activity. Excluding them from the test campaign can distort the results.

For example, the catalyst loading scheme with more demetallization fraction tends to require a higher degree of reaction temperature increment than the one with less demetallization fraction, therefore a higher tendency of thermal cracking and crossing aromatics saturation equilibrium.

For these reasons, it is recommended to include both the

TABLE 3. Typical process conditions of various hydrotreating and hydrocracking processes[5]

Application	Petroleum fraction	Reaction phase	LHSV (h^{-1})	H_2 partial pressure, bara	Temperature, °C	H2/Oil (Nm^3/m^3)	H_2 consumption (Nm^3/m^3)
Hydrotreating	Naphtha	Vapor	3–8	10–20	320	60	2–10
	Kerosene	Vapor/Liquid	2–5	20–30	330	80	5–15
	Gasoil	Vapor/Liquid	1.5–4	25–40	340	140	20–40
	VGO	Vapor/Liquid	1–2	50–90	360	210	50–80
	Residue	Vapor/Liquid	0.2–0.5	80–130	370–410	> 525	100–175
Hydrocracking	VGO	Vapor/Liquid	0.5–1.5	90–200	380–430	1,000–2,000	150–300
	Residue	Vapor/Liquid	0.1–0.5	120–210	400–440	1,000–2,000	150–300

demetallization and main hydrotreating catalysts, where applicable, to minimize biases between catalyst loading schemes. Effort must be made to achieve a realistic ratio between the demetallization and main hydrotreating catalysts.

Finally, assumptions should be clearly communicated with all catalyst vendors about your assumptions. In one instance, a major hydrocracking catalyst suppliers missed an email about the loading scheme assumptions and suffered from an extremely high pretreating temperature during the catalyst benchmarking campaign. That catalyst supplier even sent its R&D expert to Germany to investigate the issue only to discover that they did not read the email closely enough.

Feedstock. A catalyst supplier once conducted a pilot plant testing campaign for a VGO hydrocracker and included 1% condensate residue (fuel oil blending component). This condensate residue contains a high level of asphaltene, but the refinery nonetheless tried to convert a small amount of it for additional profit. The result is shown in **FIG. 4.** In this case, the reactor inlet is small, and there is no feed filtration system.

Be careful with the choice of feedstocks during the hydroprocessing catalyst testing program. A dirty feed can easily plug a small flow channel and fail the experiment. In this case, the condensate residue merely contributes to product yields, H_2 consumption and product properties. Excluding it from the short-term running campaign would be best, considering the damage it could create to the laboratory-scale system. A filtration system will help, but is no guaranteed solution for dirty feed. For coker oils, maintain positive N_2 pressure from the sample point until the laboratory to prevent subsequent gum formations from olefinic compounds.

In addition to site-specific feedstocks, refiners may further save feed shipment costs by asking the independent laboratory to provide non-specific sulfiding oil for catalyst activation. These independent laboratories usually have leftover sulfiding oil from their previous campaigns.

To better reflect the commercial operation, refiners may also consider adding dimethyl disulfide (DMDS) to simulate the effects of H_2S in the recycle gas.[3] Other species, such as quinoline, can also be added to the feedstock to adjust feed composition.

Recycle operation and recycle cutpoint (RCP). Many hydrocrackers employ a recycle stream to optimize product

FIG. 4. Foulants at the reactor inlet during a hydrocracking pilot plant testing campaign.

yields (**FIG. 5,** top). The product fractionator separates products from the unconverted oil (UCO) in the commercial unit, then recycles UCO back to the reactor for product yield adjustment. Consequently, UCO gets a second chance to be hydrogenated and converted into products, which usually means product quality improvements.

Unfortunately, most independent laboratories cannot perform a true recycle operation. Instead, a simulated recycle operation is usually achieved by feeding a UCO sample from the actual unit to the pilot-scale reactor and adjusting the single-pass conversion across the pilot-scale reactor to match the reality (**FIG. 5,** bottom).

Although this simulated recycle operation seems fair on the surface, as every catalyst vendor is under the same assumption, it can still somehow create biases between each catalyst loading scheme. For example, the catalyst system with a better hydrogenation function than the incumbent one (where the UCO sample is taken from) will experience product quality disadvantages, and vice versa for the loading scheme with a poorer hydrogenation function (e.g., free aromatics saturation from the existing unit).

This can also distort the product qualities for different combined feed ratios (CFRs) and overall conversions to certain degrees. CFR is a ratio between the total reactor feed and fresh feed. A higher CFR means more UCO is recycled back to the reactor inlet. In reality, the smoke point and cetane number usually improve when the overall conversion increases (e.g., from better aromatics saturation/ring-opening). Nonetheless, the laboratory experiment gave the opposite results for the cetane number, as seen in **FIG. 6.** This discrepancy is from the fact that a higher overall conversion operation (98%) has a higher percentage of UCO, and this simulated recycle stream does not have a second chance to be hydrogenated/ring-opened, but is already converted to products during the first pass.

Moreover, the RCP between diesel and UCO is higher in laboratory-scale experiments, with much sharper fractionation (e.g., much less overlap between diesel and UCO). In many commercial units, the separation between diesel and UCO is poor by nature from lower internal reflux at the point of separation. Moreover, the maximum heater duty can also limit the actual RCP.

From **FIG. 7,** VGO and UCO from the refinery contain around 10%–16% of diesel (defined as a portion with the boiling point below 370°C), while UCO from the pilot plant only has 4%–5% of diesel. This fact implies that the true conversion of a laboratory-scale experiment is lower than that of a commercial-scale operation. In a sense, hydrocracking catalysts are under less conversion stress in a laboratory-scale experiment.

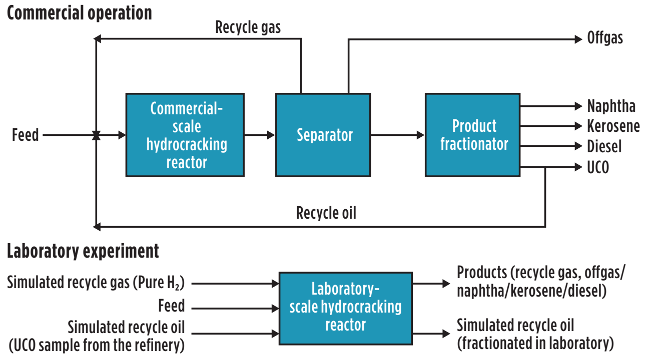

FIG. 5. A single-stage hydrocracker with recycle, commercial operation vs. laboratory.

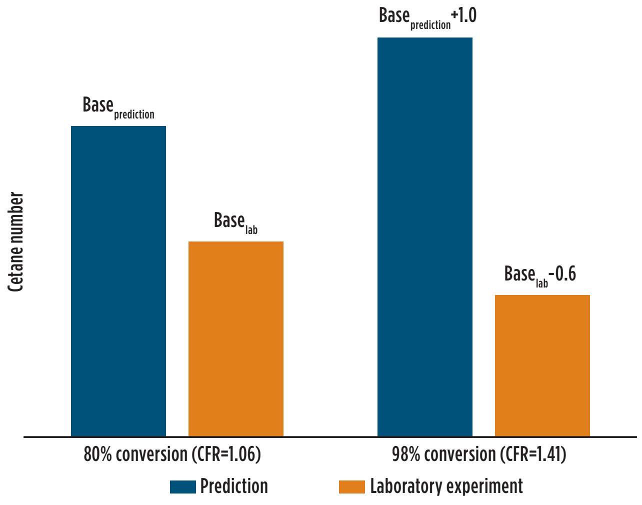

FIG. 6. Cetane number for different overall conversions (and CFRs), prediction vs. laboratory.

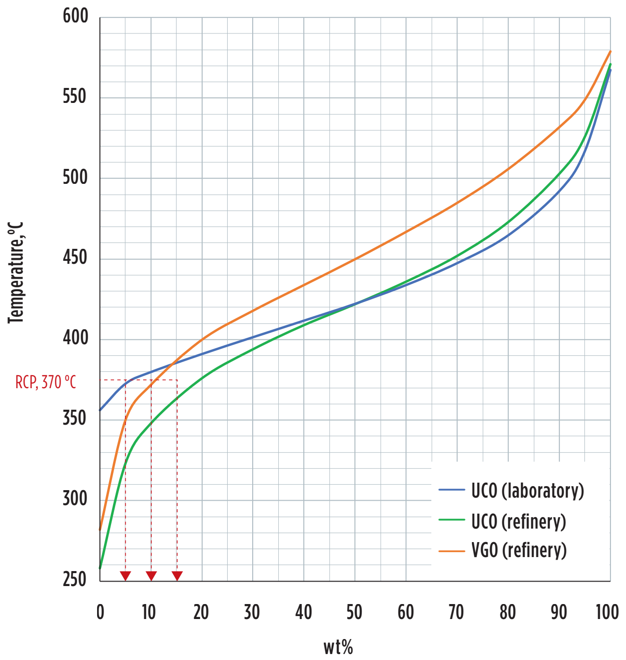

FIG. 7. UCO and VGO distillation by simulated distillation analysis (ASTM D2887), refinery vs. laboratory.

TABLE 4. An example of product cutpoints from ITB

Product	Boiling range, °C
Light naphtha	C5–90
Heavy naphtha	90–145
Kerosene	145–210
Diesel	210–370
UCO	370–Endpoint

In the authors' experience, these hydrogenation and conversion discrepancies are not that serious. Using oil with lower aromatic contents might help alleviate hydrogenation gaps [e.g., a UCO sample from the start-of-run or gas-to-liquid (GTL) liquid with a similar boiling range]. **Note:** Refiners may consider tailoring the RCP of the hydrocracking catalyst testing campaign to match the operating unit, to better reveal the actual performances. Nonetheless, a meaningful comparison between each catalyst loading scheme is still possible despite all mentioned deviations.

Product cut point and properties. Refiners usually specify product cut points between products as guidelines for independent catalyst testing laboratories (**TABLE 4**). However, this does not mean that these product cut points completely agree with other product specifications. For example, the minimum specification of cetane number is 60. During the pilot plant testing campaign, the cetane number will be different for each catalyst vendor despite the same product cut points. To what degree is a better question.

Catalyst vendor A might possess an excellent hydrogenation function and achieve a cetane number of 62, while catalyst vendor B can only offer the cetane number of 58 at the standard product cut points.

To better compare each catalyst vendor, adjusting the cut point between kerosene/diesel to standardize every catalyst vendor is recommended (e.g., target the cetane number of 60). The catalyst vendor with a cetane number > 60 will gain additional diesel from kerosene using this standardization, and vice versa. The wider the gap is, the more diesel gain or loss will be seen. **Note:** The minimum cetane number specification varies with refineries and applications.

A better question is how to standardize the cetane number or other product properties (**FIG. 8**). The most practical solution is to input product yields and properties into the process simulator, then recut each product to match your product specification target.

Depending on the experiment, this product property standardization might or might not change the ranking of each catalyst vendor. For example, suppose the catalyst vendor that is taking the lead already has the highest diesel yield and cetane number with the standard product cut points. In that case, the cetane number standardization will not change the ranking.

Mass balance. Regardless of how proficient the independent catalyst testing laboratory is, there will always be mass balance errors in the real world. In a laboratory-scale experiment, even minor errors can significantly affect the critical parameters (e.g., chemical H_2 consumption). For example, a +/– 2% error is acceptable in the commercial-scale plant, but the same error magnitude could lead to significant errors in elemental balances for laboratory-scale experiments. Ideally, all the key elemental balances, including carbon, H, S and N, should be close to 100% for hydroprocessing applications.

Liquid flow is based on weight measurement for both feeds and products, while gas flow is measured by a flowmeter and an online gas chromatography (GC) analyzer. Typically, gas flowmeters have lower accuracy and are notorious sources of mass balance errors. Additionally, routine activities, including product sampling, sample transfer and product fractionation, can also result in light liquid product losses. As such, measured product flows tend to be less than feed flows, especially in hydrocracking applications (**FIG. 9**). To what degree is a more interesting question.

Typically, the error magnitude increases with processing severity (e.g., catalyst acidity or conversion level). For example, a naphtha selective hydrocracker makes more light products than a diesel selective one, therefore resulting in poorer mass balances from more offgas and naphtha. For a commercial catalyst benchmarking campaign, these mass balance errors can lead to million dollars difference in revenue from misleading product yield structure and chemical H_2 consumption.[5]

As illustrated in **FIG. 9,** the pretreating section alone (highlighted in blue) made minimal light ends, thus closer to 100 wt% mass balance. For this data set, the error magnitude is less than 0.5 wt% for all data points (exclude the catalyst

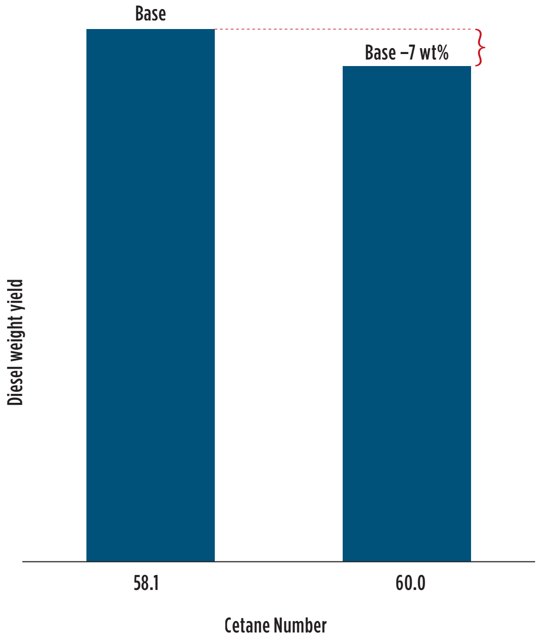

FIG. 8. Diesel yield correction by standardizing cetane number from 58.1 to 60.

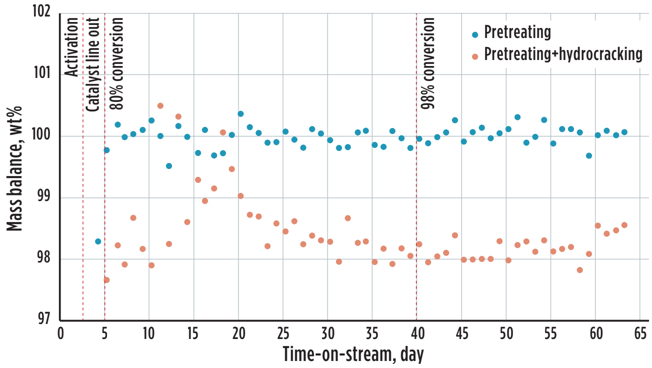

FIG. 9. Overall mass balance vs. time-on-stream of a hydrocracking catalyst benchmarking campaign.

TABLE 5. A demonstration of how data reconciliation could minimize errors for a 54,000-bpd hydrocracker

ΔChemical H_2 consumption, raw-reconciled	80% conversion	98% conversion
wt%	0.12	0.14
Tpd	9.5	11.2
$ MM/cycle	17	20.1

line-out period). Conversely, the hydrocracking section (highlighted in orange) further increased light ends yield and mass balance errors, up to 2.3 wt%.

As a best practice, the authors recommend including a scaling factor into mass balance equations to improve the mass balance of every element. **Note:** The mass balance equations shown below are for demonstration purposes only and are specifically for hydrocracking applications. It is assumed that 100% sulfur and N in the feedstock are converted into H_2S and ammonia (NH_3), respectively, to simplify the mass balance equations.

The overall mass balance equation is shown in Eq. 1:

$$F_{feed} + F_{chemical\ hydrogen} = k_{scaling} \times (F_{gas\ product} + F_{liquid\ product}) + F_{H_2S} + F_{NH_3} \tag{1}$$

The H mass balance equation is shown in Eq. 2:

$$\begin{aligned} F_{chemical\ hydrogen} = {} & k_{scaling} \times (C_{hydrogen,gas\ product} \times \\ & F_{gas\ product} + C_{hydrogen,liquid\ product} \times F_{liquid\ product}) + \\ & [(2 \times AM_H)/(MW_{H_2S})] \times F_{H_2S} + \\ & [(3 \times AM_H)/(MW_{NH_3})] \times F_{NH_3} - C_{hydrogen,feed} \times F_{feed} \end{aligned} \tag{2}$$

The carbon mass balance equation is shown in Eq. 3:

$$C_{carbon,feed} \times F_{feed} = k_{scaling} \times (C_{carbon,gas\ product} \times F_{gas\ product} + C_{carbon,liquid\ product} \times F_{liquid\ product}) \tag{3}$$

Based on the authors' experience, it is impossible to achieve 100% mass balance for every species. Focusing on the H and overall mass balance (e.g., target 100%) for hydroprocessing applications is recommended, as these two mass balances will directly impact chemical H_2 consumption and product yields (**TABLE 5**). As such, the carbon mass balance will be a resultant. In most cases encountered by the authors, the carbon balance nonetheless improved, although it was not perfect.

Where applicable, use multiple data sets of elemental composition (either by EA or NMR) to ensure consistent final ranking results. As a precaution, this data correction practice should be carefully performed to avoid any misleading results from the data correction itself; performing this when the raw mass balance errors exceed 2.0 wt% is not recommended.

Takeaways. Although the economic direction is clear—e.g., maximize middle distillate from a hydrocracker—multiple price sets should always be used to rank hydroprocessing catalysts. This sensitivity analysis ensures the robustness of the final ranking against market fluctuations.

While key ideas presented here are based on hydroprocessing applications, they can be modified/tailored to match other catalyst applications, as well (e.g., elemental balance and data correction technique). HP

NOMENCLATURE

$k_{scaling}$, scaling factor: > 1.00 in case of product loss or < 1.00 in case of product gain
$F_{chemical\ hydrogen}$: mass flowrate of H_2 consumed by chemical reactions or chemical H_2 consumption
$F_{gas\ product}$: mass flowrate of the gas product
$F_{liquid\ product}$: mass flowrate of the liquid product
F_{feed}: mass flowrate of the liquid feed
F_{H2S}: mass flowrate of H_2S, calculated based on the feed flowrate assuming 100% sulfur removal
F_{NH3}: mass flowrate of ammonia, calculated based on the feed flowrate assuming 100% N removal
$C_{hydrogen,\ gas\ product}$: H content of the gas product
$C_{hydrogen\ ,liquid\ product}$: H content of the liquid product
$C_{hydrogen,\ feed}$: H content of the liquid feed
$C_{carbon,\ gas\ product}$: carbon content of the gas product
$C_{carbon,\ liquid\ product}$: carbon content of the liquid product
$C_{carbon,\ feed}$: carbon content of the liquid feed
MW_{H2S}: molecular weight of H_2S, 34.08 g/mol
MW_{NH3}: molecular weight of NH_3, 17.03 g/mol
AM_H: atomic mass of H, 1.01 g/mol

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