**Technical Specification for the procurement (purchase) of catalysts for the cracked naphtha selective hydrodesulfurization process**

## 1 – Purpose

This document provides information for a catalyst SUPPLIER interested in bidding on a supply contract for units performing selective hydrodesulfurization of cracked naphtha (HDS-CN). Information presented herein will allow any interested parties to understand

- ✓ the objective of the process in which these catalysts can be used;
- ✓ general requirements of the catalysts;
- ✓ minimum performance parameters demanded from the catalysts;
- ✓ the procedure which PETROBRAS will use to assess performance of the catalysts and eventually approve or refuse their use;
- ✓ general requirements of the whole inventory that shall be referenced in the bid, including inert materials, guard bed catalysts, activity grading catalysts, main catalysts and poison traps.

## 2 – Process Information

The objective of cracked naphtha selective hydrodesulfurization (HDS-CN) process is to remove sulfur from the cracked naphtha stream, as to allow for the addition of the hydrotreated naphtha to a pool of commercial gasoline. It is of paramount importance that this process is selective, meaning that the reactors that will perform sulfur removal will also operate at conditions that promote simultaneous minimal saturation of olefins, thus preserving octane rating of the final product.

Prior to hydrodesulfurization, the feed stream needs to be treated for removal of diolefins, under such conditions that promote both conversion of diolefins to mono-olefins (but not the conversion of mono-olefins to paraffins) and the simultaneous conversion of light mercaptans into heavy sulfur compounds.

### 2.1 – Reactions and simplified process scheme

A HDS-CN unit is composed of two main reaction sections:

1) a selective hydrogenation pre-treatment section (PRE-TREAT) that processes the *full-range cracked naphtha (FRCN)* feed performing reactions of:

   - diolefin saturation to mono-olefins (with minimum saturation of mono-olefins to paraffins); and

   - thioetherification of mercaptans (also referred as sulfur shift)

2) a selective hydrodesulfurization section (HDS) that processes either the pre-treated FRCN feed or a heavy cracked naphtha (HCN) fraction of the pre-treated FRCN feed and removes sulfur from this stream while minimizing saturation of olefins.

A simplified scheme of a naphtha stream flow through reaction sections is presented in Figure 1.

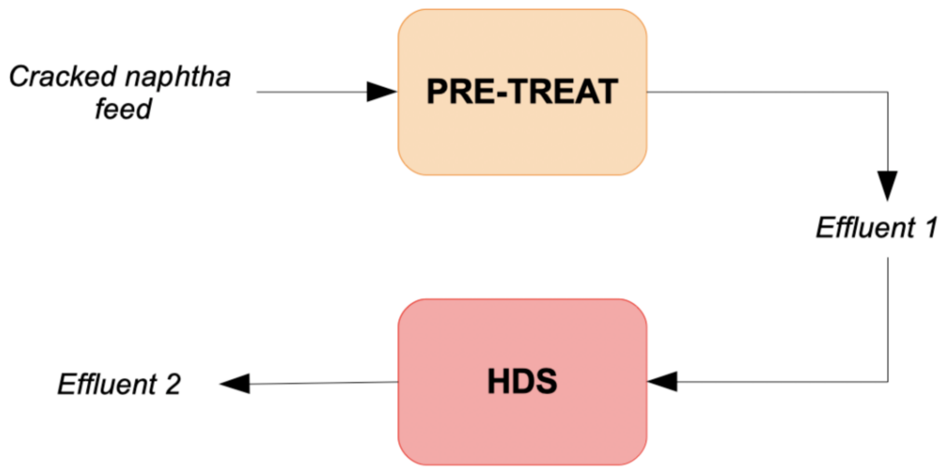


Figure 1 – Flow of a naphtha through the reaction sections of a cracked naphtha hydrodesulfurization unit

The pre-treatment section comprises two identical single catalytic bed reactors with a liquid distributor tray, as presented in Figure 2. These reactors are arranged in a lead-lag configuration, meaning that they can be operated:

a) in series, with any one reactor in the *lead* position;

b) alone, with the other reactor isolated for any reason

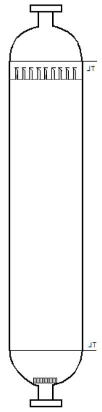

Figure 2 – General schematic of a single catalytic bed reactor with liquid distributor tray from the pre-treatment section

The HDS section contains two independent HDS stages, each one possessing a reactor with two symmetric catalytic beds, liquid distributor trays and quench injection between beds, as presented in Figure 3.

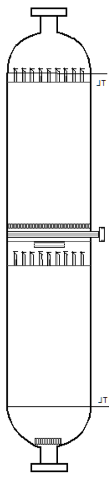

Figure 3 – General schematic of a two catalytic bed reactor with liquid distributor trays and quench injection from a HDS stage

Exception: The one exception to the configuration described above follows.
In this particular unit the pre-treatment section comprises two different single catalytic bed reactors with liquid distributor trays that operate exclusively in series, with the first pre-treatment reactor presenting a bed with 1/6 the volume of the second pre-treatment reactor. In this same unit the HDS section comprises two independent HDS stages, where the

reactors have two symmetric catalytic beds with no liquid distributor trays and the second stage reactor presents a total bed volume of 2/3 the bed volume of the first stage reactor.

### 2.2 – Catalysts and other materials

The process demands two specific catalysts, one for each reaction section (pre-treatment catalyst and HDS catalyst). These are the *main catalysts* loaded in the reactors.

Beyond the ***main catalysts***, reactors of each section shall include other materials, including

i. ***inert materials***, comprising inert particles loaded at the top of catalytic bed(s) and designed to prevent pressure drop build-up and/or flow maldistribution (*these materials shall not be confused with inert spheres, which are not considered in this scope*);

ii. ***guard bed materials***, comprising active catalysts designed to prevent pressure drop build-up and/or flow maldistribution and/or formation of gums, loaded at the top of catalytic bed(s);

iii. ***activity grading catalysts***, consisting of active catalysts similar to the main catalysts and designed to prevent formations of gums and coke and/or localized temperature excursions, loaded on the top of catalytic bed(s); and

iv. ***poison traps***, designed to retain specific poisons (such as Silicon or Arsenic, but not limited to these contaminants), thus protecting main catalysts.

PETROBRAS requires that **main catalysts** are tested previous to their use in industrial units. The complete catalytic system with lowest procurement cost, will be selected and the catalytic evaluation performed by PETROBRAS with its own feed streams and in its own pilot plant facilities. The **main catalyst** system samples must be provided together with the technical and economical proposal by the interested SUPPLIER without cost to PETROBRAS.

Inert, guard bed, activity grading and poison trap materials won't be tested and will be considered as taking part of the whole technical proposal.

## 3 – General requirements for catalysts supply

This section details several requirements for supplying catalysts to HDS-CN units. All information herein shall be taken into account when selecting materials included in a given bid, specially regarding catalysts that will be tested by PETROBRAS.

### 3.1 – Catalyst form

All materials, for all reactors, (i.e. guard bed materials, activity grading catalysts, poison traps and main catalysts containing Molybdenum, Cobalt and/or Nickel) must be supported in alumina or hydrotalcite.

Main catalysts and poison traps (containing Molybdenum, Cobalt and/or Nickel) must be supplied as RTU (*Ready-To-Use* – i.e, catalysts that are pre-activated and passivated, if deemed necessary). RTU catalysts must not demand a stabilization period (processing of an inert feed stream) upon start-up, as they are required to immediately admit cracked feedstocks.

As a reference, Eurecat and Chem32 offer respectively TOTSUCAT CFP and ThioCat CFT catalyst pre-activation and passivation technologies. Activation and passivation technologies different from these must be referenced with commercial previous experiences. Passivation method and agents must be easily removed or converted to non-interfering by-products at operating conditions. Air passivation is requested for the safe handling of the catalyst during the loading of the reactors.

### 3.2 – Required information and documentation

All information and documentation for the bidding purposes must be supplied in portuguese or English languages.

SUPPLIER must provide proper documentation for all materials included in the bid (inert materials, guard bed catalysts, activity grading catalysts, main catalysts and poison traps), including at least the information about chemical, physical and textural properties listed in Table 1.

Minimum documentation to be provided includes:

- Product data sheet
- Product MSDS
- Product safe handling instructions
- Product storage instructions
- Product disposal instructions
- Generic proposed loading diagram

PETROBRAS may demand other information for any material as may be required by law. Although not required in the bidding step, SUPPLIER implicitly agrees that, in case of being selected for supplying, all the material delivered must be accompanied by MSDS and other product specific documentation in portuguese language and complying with Brazilian standards (ABNT NBR 14725).

The SUPPLIER shall submit to PETROBRAS the recommended procedures for:

- Recommended catalyst loading and unloading instructions;
- Recommended unit start-up and shutdown procedures;
- Recommended emergency procedures.
- References of industrial use of each proposed catalysts/inert material.

Table 1 – Minimum technical information required about all materials

| Property | Inert material | Guard bed | Poison Trap | Activity grading | Main catalyst |
|---|---|---|---|---|---|
| **Type of active phase** (1) | - | x | x | x | x |
| **Type of support** (2) | x | x | x | x | x |
| **Stoichiometric sulfur required for sulfidation, wt%**(3) | - | - | x | x | x |
| **Sock loading density, kg/m$^3$** (4) | x | x | x | x | x |
| **Dense loading density, kg/m$^3$** (4) | - | x | x | x | x |
| **Specific surface area, m$^2$/g** | - | x | x | x | x |
| **Particle shape** | x | x | x | x | x |
| **Particle size** | x | x | x | x | x |
| **Attrition index, %** | x | x | x | x | x |
| **Mechanical resistance** | x | x | x | x | x |
| **Contaminant maximum uptake, %wt** | - | - | x | - | - |
| **Breakthrough onset for the contaminant, %wt** | - | - | x | - | - |
| **Packing weight** | x | x | x | x | x |
| **Ex - situ sulfidation contractor** | - | - | x | x | x |
| **Ex-situ treatment for cracked feed tolerance** | - | - | x | x | x |
| **Ex-situ treatment for compatibility with handling under air** | - | - | x | x | x |

(1) Describing metal constituents (e.g.: NiMo, CoMo, etc.)

(2) Describing chemical nature of support (e.g.: alumina, silica-alumina, hydrotalcite, etc.)

(3) Property of the oxide form of the catalyst, which shall be supplied as RTU

(4) Dry basis density, i.e., disregarding any chelating agents, for both oxide and RTU form (when applicable)

### 3.3 – General operating conditions and cycle length duration

SUPPLIER must consider that catalysts offered in a bid must perform adequately under typical operating conditions listed in Table 2, processing a feed stream with quality as defined in later sections of this document (see Table 4 and **Erro! Fonte de referência não encontrada.**).

Table 2 – Typical operating conditions of a cracked naphtha selective HDS unit

| Parameter | Pre-treatment section | HDS stage |
|---|---|---|
| **Spatial velocity, $h^{-1}$** | 1.7 – 2.8 | 2 – 3.3 |
| **Pressure, $kgf/cm^2$ g** | 24 – 27 | 16 – 19 |
| **$H_2$/FEED ratio, $Nm^3/m^3$** | 8 – 14 | 180 – 250 |
| **WABT SOR, ºC** | – | ≥ 250 * |
| **WABT EOR, ºC** | 216 | 307 |

* This figure is an estimate of the temperature at which a typical feed stream of the HDS section is completely vaporized, as HDS reactors must operate under gas phase conditions

SUPPLIER must attest that main catalysts will operate under such conditions, continuously providing a performance compatible with the approval criteria defined in Section 4.5 of this document and a cycle length of 1460 days (4 years) or longer. Cycle length is herein defined as the period elapsed between start-up of a unit loaded with main catalysts offered in a bid and a section or reactor achieving its EOR condition (WABT) as listed in Table 2.

### 3.4 – Expected relative distribution of catalyst and other materials

The SUPPLIER shall recommend a set of inert material, guard bed, activity grading catalysts for the service to be installed only in the pre-treatment reactors.
The volume of inert, guard bed and/or activity grading material shall be 10% of the catalyst volume of pre-treatment reactor.
FRCN feeds have been known to contain variable amounts of arsenic. The volume of poison trap shall be considered as 20% of the first HDS catalytic bed.

An example of loading diagram is shown in Figure 4.

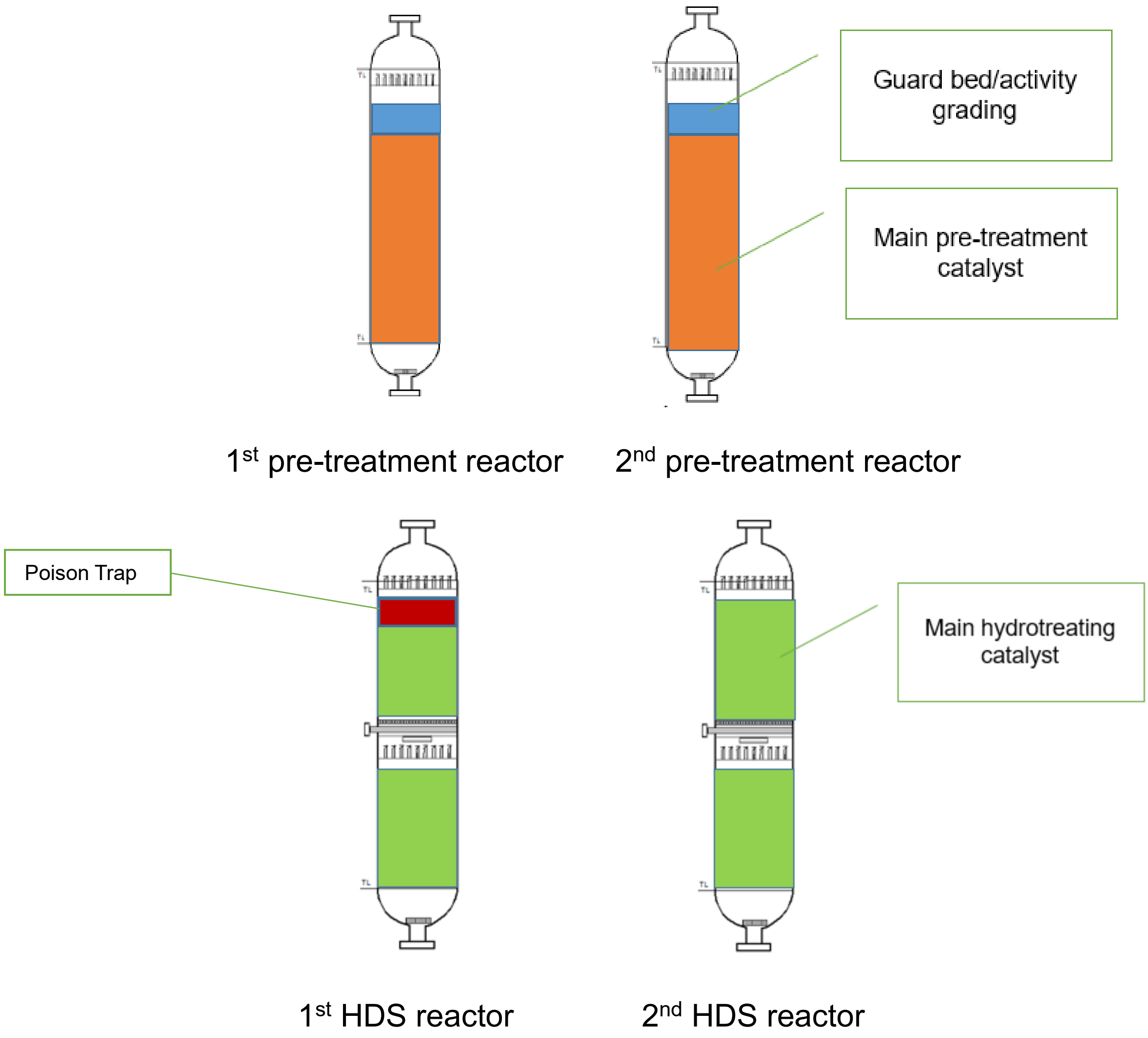


*Figure 4 - Loading diagram of a typical unit*

It might be considered the main catalysts as dense loaded and all other materials sock loaded.

## 4 – Procedure for testing and approving main catalysts

Main catalysts for both reaction sections will be tested, using catalyst samples provided by SUPPLIER.

Inert materials, guard materials, activity grading catalysts and poison traps will not be tested by PETROBRAS. However, data about all materials (see Table *1* for required information) included in a given bid will be technically evaluated by PETROBRAS to check whether each of these materials present the required features.

The main catalytic system with lowest inventory cost (that will be calculated considering inert materials, guard bed, activity grading, poison traps and main catalyst prices, including any pre-treatment that is needed) will be tested with a specific feed and in appropriate conditions for performance evaluation of each and all reactions demanded. It will be tested for initial activity and selectivity(ies) will be assessed with these results. Main catalysts will not be tested for stability under long term conditions, but short term stability (i.e., during the timeframe of initial activity testing) will be evaluated.

Main catalysts will be tested for initial activity at fixed pressure, spatial velocity and gas-to-feed ratio, at different temperatures.

The next subsections present requirements of the samples, conditions of testing (feed characteristics, unit description and operating conditions) and approval criteria.

**4.1 – Samples**

For testing purposes, catalyst samples may be provided as oxides (catalysts that demand *in situ* activation and stabilization) or as *ready-to-use* (RTU) catalysts – i.e., pre-activated: sulfided and passivated (if deemed necessary) so as to not demand any activation and/or stabilization procedures for testing. However, samples in RTU form are preferred, as SUPPLIER must provide active catalysts for industrial use in RTU form (see Section 3).

If the sample is provided as RTU, SUPPLIER shall attest that all procedures employed for pre-activation (and passivation, if necessary) of the sample are compatible with pre-activation (and passivation, if necessary) procedures of large scale volumes of catalyst, so that performances of the sample and a large scale batch are expected to be the same.

For samples provides as oxides, SUPPLIER must also inform either metals concentration (for each one) or information about specific sulfur uptake for activation purposes. In this case, SUPPLIER may provide instructions for activation and stabilization.

SUPPLIER may also include any start-up instructions deemed relevant to pilot-scale testing (e.g. regarding dry-up, wetting, etc.)

The amount of sample provided shall not be inferior to 1L (one liter), independent of catalyst form (oxide or RTU).

All samples shall be accompanied by proper documentation, including at least the information about chemical, physical and textural properties listed in Table 1, MSDS and any extra handling and storing instructions.

The address to send the sample and the contact data to be must placed in the shipment are showed below. In case of changes in this information, PETROBRAS will inform the participants through the appropriate channels.

PETROBRAS – Research and Development Center (CENPES)
Av. Horácio Macedo, 950, Cidade Universitária (Ilha do Fundão)
Rio de Janeiro – Brazil - ZIP Code: 21941-915
Attention: Marcus Vinicius Eiffle Duarte
Isabela Caldeira Leite Leocadio
Sandra Shirley Ximeno Chiaro

SUPPLIER must certify that the sample was delivered at CENPES sending, through PETRONECT, the receipt presented in Annex II. The document must be signed by a PETROBRAS' technical representative. The delivery must respect the deadlines defined in the bid process. If the supplier sent a representative sample of its product in Petronect invitation 7002908670, it is not necessary to send a sample of the same product. In this case, the supplier must attach to the process the previous receipt.

**4.2 – Catalyst properties**

SUPPLIER must attest that main catalysts supplied for each service meet PETROBRAS' requirements for both sock loading density $d_{SOCK}$ (considering RTU form) (expressed in $kg/m^3$) and stoichiometric sulfur uptake SSU (expressed in weight percentage). SUPPLIER must provide a figure for stoichiometric sulfur uptake SSU (expressed in weight percentage) of the oxide form of each main catalyst, calculated using catalysts metal composition and standard sulfiding stoichiometry equations, as presented below.

$$MoO_3 + 2\ H_2S + H_2 \rightarrow MoS_2 + 3\ H_2O$$

$$9\ CoO + 8\ H_2S + H_2 \rightarrow Co_9S_8 + 9\ H_2O$$

$$3\ NiO + 2\ H_2S + H_2 \rightarrow Ni_3S_2 + 3\ H_2O$$

The SSU must be calculated using only metal content of each catalyst and the stoichiometry equations, without any excess.

The product of both quantities $P = d_{SOCK} \cdot SSU$ will be calculated for the main catalyst. The minimum criteria is presented in Table 3. Main catalysts that do not meet these criteria will not be approved automatically, and not be considered for testing.

Table 3 **–** Minimum P required for main catalyst, by application

| **Application** | **Required** $P = d_{SOCK} \cdot SSU$ |
|---|---|
| **SHU** | ≥ 3.500 |
| **HDS** | ≥ 2.000 |

For both catalyst (SHU and HDS), industrial reference must include at least 1 commercial previous experience, including start of run and end of run dates, treating feedstock of full range naphtha (distillation range similar to that in table 4) with a minimum capacity of 1000 $m^3/d$.

### 4.2 – Tests of pre-treatment catalysts

Main catalysts for pre-treatment application will be tested with a full-range cracked naphtha (FRCN) feed obtained from a PETROBRAS' refinery dosed with a suitable mercaptan marker. Main characteristics of the FRCN feed are listed in Table 4. These ranges and figures represent lower and upper bounds or typical values for each characteristic of

PETROBRAS' FRCN streams and shall not prevent PETROBRAS from using a given feed with a given characteristic outside these ranges or significantly different from a typical value, if PETROBRAS deems necessary. Any characteristics not listed in **Erro! Fonte de referência não encontrada.** are not deemed by PETROBRAS as essential for performance evaluation of the catalyst for this application.

Table 4 – Main characteristics of the FRCN feed

| | |
|---|---|
| **Density @ 20/4 °C** | *0.7200 – 0.7600* |
| **Mercaptans, ppm** | *100* |
| **Olefins, %wt** | *20 – 50* |
| **Diene Value, g$I_2$/100g** | *2 – 6* |
| **SIM-DIST (ASTM D-2887), °C** | |
| **IBP** | *-10* |
| **10%** | *35* |
| **30%** | *70* |
| **50%** | *100* |
| **70%** | *140* |
| **90%** | *190* |
| **FBP** | *250* |

Tests for assessment of initial activity of catalysts for pre-treatment application will be performed in a pilot-plant unit. Typical configuration and operating conditions are listed in Table 5. These parameters and ranges represent typical conditions for carrying such tests and shall not prevent PETROBRAS from using different conditions, if PETROBRAS deems necessary.

Table 5 – Typical conditions for testing of catalysts for pre-treatment application

| | |
|---|---|
| **Reactor** | *Isothermal* |
| **Direction of flow** | *Upwards* |
| **Pressure, bar** | *$\geq 20$* |
| **LHSV, $h^{-1}$** | *2 – 6* |
| **$H_2$/FEED ratio, $Nm^3/m^3$** | *$\leq 20$* |
| **Temperature, °C** | *120 – 210* |

### 4.3 – Tests of selective hydrodesulfurization catalysts

Main catalysts for selective hydrotreatment application will be tested with a heavy cracked naphtha (HCN) feed obtained from a PETROBRAS' refinery. Main characteristics of the HCN feed are listed in Table 6. These ranges and figures represent lower and upper bounds or typical values for each characteristic of PETROBRAS' HCN streams and shall not prevent PETROBRAS from using a given feed with a given characteristic outside these ranges or significantly different from a typical value, if PETROBRAS deems necessary. Any characteristics not listed in Table 6 are not deemed by PETROBRAS as essential for performance evaluation of the catalyst for this application.

Table 6 – Main characteristics of the HCN feed

| | |
|---|---|
| **Density @ 20/4 ºC** | *0.7750 – 0.8150* |
| **Sulfur, ppm** | *600 – 1,300* |
| **Mercaptans, ppm** | *< 20* |
| **Nitrogen, ppm** | *150 – 350* |
| **Olefins, %wt** | *20 – 50* |
| **SIM-DIST (ASTM D-2887), ºC** | |
| **IBP** | *65* |
| **10%** | *90* |
| **30%** | *110* |
| **50%** | *140* |
| **70%** | *170* |
| **90%** | *210* |
| **FBP** | *250* |

Tests for assessment of initial activity of catalysts for selective hydrodesulfurization application will be performed in a pilot-plant unit. Typical configuration and operating conditions are listed in Table 7. These parameters and ranges represent typical conditions for carrying such tests and shall not prevent PETROBRAS from using different conditions, if PETROBRAS deems necessary.

Table 7 – Typical conditions for testing of catalysts for selective HDS application

| | |
|---|---|
| **Reactor** | *Isothermal* |
| **Direction of flow** | *Upwards* |
| **Pressure, bar** | $\geq 15$ |
| **LHSV, $h^{-1}$** | $\leq 3$ |
| **$H_2$/FEED ratio, $Nm^3/m^3$** | $\leq 300$ |
| **Temperature, °C** | $\geq 250$ |

### 4.4 – Performance evaluation

Each function of any catalyst will be evaluated through variation of a given concentration between feed and effluent streams. Each concentration will be measured by a proper quantitative assay.

Saturation of diolefins is evaluated through variation of conjugated diolefins concentration between feed and effluent streams, expressed as Diene Value (DV, in $gI_2$/100g) or Maleic Anhydride Value (MAV, in mg/g). These two measurements are interconvertible results of the same analytical assay.

Thioetherification (sulfur shift) of mercaptans is evaluated through variation of mercaptidic sulfur concentration (RSH, in weight parts-per-million, wppm) between feed and effluent streams.

Hydrodesulfurization of the naphtha stream is evaluated through variation of total sulfur concentration (S, in wppm) between feed and effluent streams.

Saturation of olefins is evaluated through variation of total olefin concentration between feed and effluent streams, expressed either as Bromine Number (BrN, in $gBr_2$/100g) or olefins weight percentage (O, in %) measured by an appropriate chromatographic method. For FRCN streams, O can be measured by gas chromatography (GC), supercritical fluid chromatography (SFC) or high performance liquid chromatography (HPLC). For HCN streams, O may be measured by SFC or HPLC, but not GC.

### 4.5 – Pilot Plant test approval criteria

For each application, performance indicators will be compared to a Reference Value (RV) defined at a given base temperature ($T_{BASE}$). For a given catalyst to be approved for a given application, each and all performance indicators shall meet or exceed (present a greater value) the corresponding RV's at predefined $T_{BASE}$'s.

There are 2 performance indicators for the pre-treatment application:

➔ dienes conversion: calculated using DV or MAV between feed and effluent of the tests

$$\text{Dienes conversion} = 100\,\frac{DV_{FEED} - DV_{EFFLUENT}}{DV_{FEED}}\,\text{or}100\,\frac{MAV_{FEED} - MAV_{EFFLUENT}}{MAV_{FEED}}$$

➔ sulfur shift: estimated through mercaptans conversion and calculated using mercaptans (RSH) concentrations between feed and effluent of the tests

$$\text{Mercaptans conversion} = 100\,\frac{RSH_{FEED} - RSH_{EFFLUENT}}{RSH_{FEED}}$$

Both performance indicators for the pre-treatment application shall represent global figures – i.e., measured as variations of the whole pre-treatment section, from its first to its last reactor. The base temperature for evaluating these indicators for the pre-treatment application is $T_{BASE}$ = 170 °C, and the reference values (RV's) to be met or exceeded for each indicator are

*Dienes conversion* ≥ *80%* and

*Mercaptans conversion* ≥ *95%*

There are 2 performance indicators for the selective hydrotreatment application:

➔ sulfur conversion: calculated using sulfur concentration between feed and effluent of the tests

$$Sulfurconversion = 100\,\frac{S_{FEED} - S_{EFFLUENT}}{S_{FEED}}$$

➔ selectivity: calculated as the ratio between sulfur conversion and olefins conversion between feed and effluent of the tests

$$\text{Olefins conversion} = 100\frac{O_{FEED} - O_{EFFLUENT}}{O_{FEED}} \text{ or } 100\frac{BrN_{FEED} - BrN_{EFFLUENT}}{BrN_{FEED}}$$

$$\text{Selectivity} = \frac{\text{Sulfur conversion}}{\text{Olefins conversion}}$$

Both performance indicators for the selective hydrodesulfurization application shall represent *per stage* figures – i.e., measured as variations of one single stage of selective hydrodesulfurization. The base temperature for evaluating these indicators for the hydrodesulfurization application is $T_{BASE}$ = 282 °C.

The RV to be met or exceeded by *Sulfur conversion* is a function of both sulfur concentration of the feed $S_{FEED}$ and target for sulfur concentration of the product of an industrial unit, which shall be referred to as $S_{TARGET}$. Considering a two-stage unit, it is possible to define a *minimum per stage sulfur conversion needed to treat a feed with* $S_{FEED}$ *and generate a product with* $S_{TARGET}$. Calculating from the general formula for sulfur conversion per stage (under equal conversions operating conditions):

$$X_S = 100\frac{S_{FEED} - \sqrt{S_{FEED}S_{TARGET}}}{S_{FEED}}$$

A calculation log for the $X_S$ formula is presented in Annex I.

$S_{TARGET}$ value is defined as 30.0 ppm. Considering such a target and normal premises about process operation, there is a relation between the minimum sulfur conversion demanded per stage $X_{STAGE}$ and the concentrations $S_{FEED}$ and $S_{TARGET}$:

$$X_{STAGE} = 100\frac{S_{FEED} - \sqrt{S_{FEED}S_{TARGET}}}{S_{FEED}} = 100\frac{S_{FEED} - 5.477\sqrt{S_{FEED}}}{S_{FEED}}$$

The RV to be met or exceeded by *Selectivity* (per stage) is fixed:

*Selectivity* $\geq$ *2.5*

Table 8 lists all approval criteria for performance test of main catalysts of both applications.

Table 8 – Approval criteria for each application

| Performance indicator | RV | $T_{BASE}$, °C |
|---|---|---|
| ***Application: pre-treatment*** | | |
| **Dienes conversion** | 80 | 170 |
| **Mercaptans conversion** | 95 | |
| ***Application: selective hydrogenation*** | | |
| **Sulfur conversion (*per stage*)** | $X_{STAGE}$ ($S_{TARGET}$ = 30ppm) | 282 |
| **Selectivity (*per stage*)** | 2,5 | |

All performance indicators may be evaluated by direct assessment at $T_{BASE}$ or by interpolation of results obtained at all temperatures tested, allowing for outlier removal. In the case of evaluation by interpolation, any good fit of experimental results may be used, thus not necessarily demanding the use of a kinetic model.

For illustration purposes, Figure 5 exemplifies the evaluation of test results through comparison of values obtained for 2 performance indicators and their respective RV's. At left, subfigure (a) depicts a performance indicator that exceeds the RV stipulated at $T_{BASE}$. At right, subfigure (b) depicts a performance indicator that does not meet the RV stipulated at $T_{BASE}$ – in this case, the respective main catalyst would not be approved.

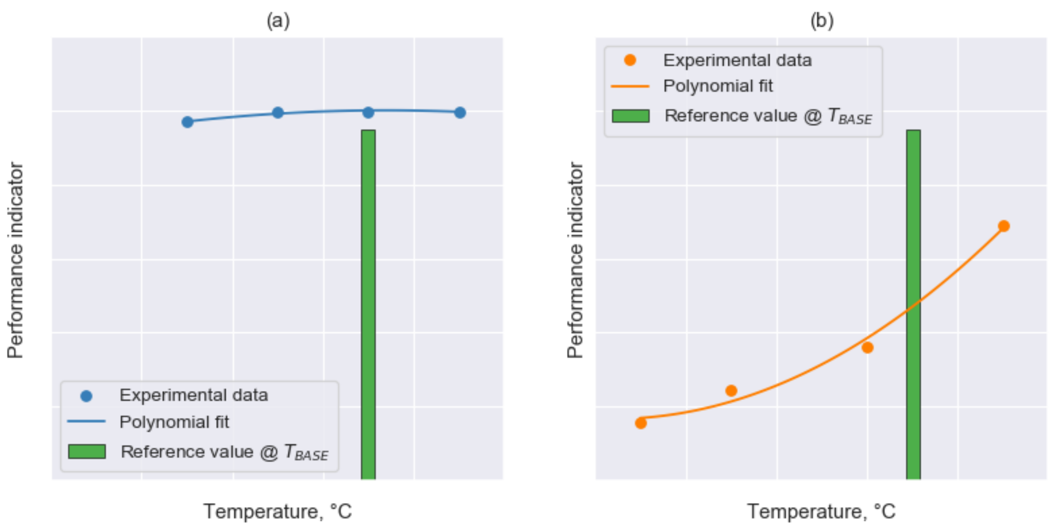


Figure 5 – Examples of test results. Subfigure(a) depicts a performance indicator that exceeds its RV. Subfigure (b) depicts a performance indicator that does not meet its RV.

**5 – Scope and Confidentiality**

SUPPLIER shall provide required information, documentation and samples free of charge for the purpose of qualification, i.e., assessing whether such catalysts are fit for use in PETROBRAS' industrial units according to testing procedures and approval criteria described in this document (see Section 4 – Procedure for testing and approving main catalysts).

Any and all information, documentation and samples provided by SUPPLIER in relation to the qualification process of catalysts for the HDS-CN process shall be used solely for the purpose of qualification.

SUPPLIER shall not use PETROBRAS' name nor any reference to PETROBRAS testing in connection with any outside publication related to the samples provided for qualification.

SUPPLIER grants no rights or license whatsoever to PETROBRAS hereunder with respect to any information provided.

PETROBRAS shall not give any portion of samples to any third party without prior written approval of SUPPLIER and will take all reasonable precautions to prevent loss or theft of any samples provided for evaluation.

PETROBRAS shall provide SUPPLIER with a summary of the results of its evaluation of samples provided. However, PETROBRAS is under no obligation to provide information or data on PETROBRAS' proprietary know-how relating to these samples.

PETROBRAS shall publicly disclose only the evaluation results required to comply with federal legislation in order to fulfill all requirements of the bidding process as regulated by Federal Law 13.303/2016.

PETROBRAS shall not return to SUPPLIER any documents or samples provided.

**ANNEX I – Memory log: minimum sulfur conversion allowable per stage ($X_{STAGE}$)**

A two-stage selective HDS unit presents sulfur conversions in each stage that are calculated as

$$X_1 = 100\frac{S_{FEED} - S_1}{S_{FEED}}$$

$$X_2 = 100\frac{S_1 - S_{TARGET}}{S_1}$$

where

- $S_{FEED}$ is the sulfur concentration of the feed stream of the first HDS stage;
- $S_1$ is the sulfur concentration of the effluent stream of the first HDS stage (feed of the second HDS stage); and
- $S_{TARGET}$ is the sulfur concentration of the effluent stream of the second HDS stage

Normally, a two-stage selective HDS unit operates under such conditions that result on approximately equal sulfur conversions in both stages. Thus it is normally assumed that under *normal operating conditions* both HDS stages present the same figure for sulfur conversion, which is referred to as $X_S$:

$$X_S \equiv X_1 \equiv X_2$$

From this assumption follows

$$\frac{S_{FEED} - S_1}{S_{FEED}} = \frac{S_1 - S_{TARGET}}{S_1}$$

Given that $S_{FEED}$ is an unknown but measurable quantity and $S_{TARGET}$ is an adjustable quantity (through manipulation of parameters such as each reactors temperatures, and others), $S_1$ is a variable dependent on both $S_{FEED}$ and $S_{TARGET}$ and can be calculated as

$$S_{FEED}S_1 - {S_1}^2 = S_{FEED}S_1 - S_{FEED}S_{TARGET}$$

$$S_{FEED}S_1 - S_{FEED}S_1 = {S_1}^2 - S_{FEED}S_{TARGET}$$

$${S_1}^2 - S_{FEED}S_{TARGET} = 0$$

$${S_1}^2 = S_{FEED}S_{TARGET}$$

$$S_1 = \sqrt{(S_{FEED}S_{TARGET})}$$

With this equivalence, under normal operating conditions each stage presents a sulfur conversion that is a function of $S_{FEED}$ and $S_{TARGET}$:

$$X_S = 100\,\frac{S_{FEED} - \sqrt{S_{FEED}S_{TARGET}}}{S_{FEED}}$$

**ANNEX II** – **Comprovante de entrega de amostra**

| PETROBRAS | COMPROVANTE DE RECEBIMENTO DE AMOSTRAS | |
|---|---|---|
| | OPORTUNIDADE: | Catalisadores HDS NC |
| | Nº DA OPORTUNIDADE: | Oportunidade Petronect nº ____________________ |

**Confirmamos o recebimento da(s) amostra(s) abaixo identificada(s):**

| Função do produto | Referência comercial | Volume Aproximado (l) |
|---|---|---|
| | | |
| | | |
| | | |
| | | |

**________________________________________, _____ de ______________ de ____________**
**(Local) (dia) (mês) (ano)**

**________________________________________________________________**
**(Nome completo do responsável pelo recebimento no CENPES)**

**________________________________________________________________**
**(Assinatura do responsável pelo recebimento no CENPES)**