Technical Specification for the qualification of catalysts for the cracked naphtha selective hydrodesulfurization process

Revision: 3
Date: 2019-11-28
Number of pages: *19*

1 – Purpose

This document provides information for a catalyst SUPPLIER interested in qualifying products for eventually 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.

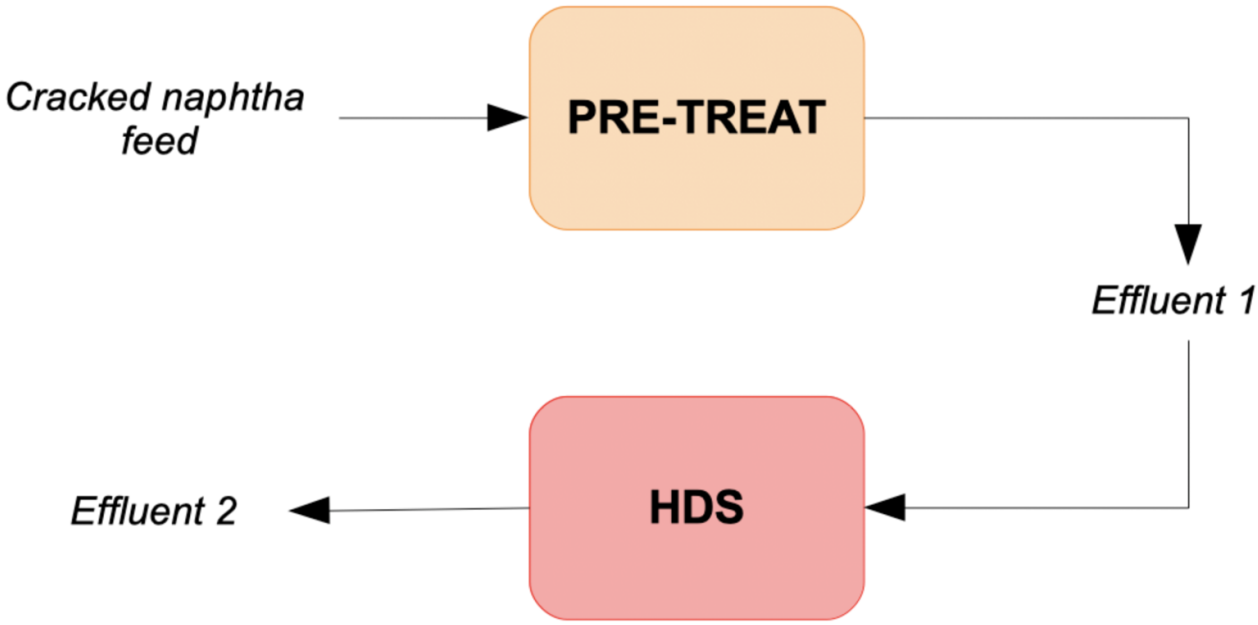

Figure 1 – Flow of a naphtha through the reaction sections of a cracked naphtha hydrodesulfurization unit

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 qualified (tested and approved) previous to their use in industrial units*. These tests are performed by PETROBRAS with its own feed streams and catalyst samples provided by any interested SUPPLIER.

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 active materials (i.e. guard bed materials, activity grading catalysts, poison traps and main catalysts containing Molybdenum and/or Nickel and/or Cobalt or any other metal) must be supplied as RTU (Ready-To-Use). For instance Eurecat's TOTSUCAT CFP and Air Passivation Treatment or equivalent catalyst pre-activation and passivation technologies. Activation and passivation technologies different from Eurecat technology must be referenced with commercial previous experiences.

3.2 – Required information and documentation

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**. PETROBRAS may demand other information for any material.

SUPPLIER must also provide all safety-related documentation for all materials as supplied (RTU form, in the case of active catalysts), including

- MSDS
- instructions for handling, storing, loading and unloading

Table 1 – Minimum technical information required about all materials

Property	**Inert material**	**Guard bed**	**Activity grading**	**Poison trap**	**Main catalyst**
Type of active phase (1)	-	x	x	x	x
Type of support (2)	x	x	x	x	x
Sock loading density, kg/m^3	x	x	x	x	x
Dense loading density, kg/m^3	-	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	-

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

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

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 Tables 3 and 4).

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

Parameter	Pre-treatment section	HDS stage
Spatial velocity, h^{-1}	2,5	3
Pressure, kgf/cm^2 g	27	19
H_2/FEED ratio, Nm^3/m^3	12	200
WABT SOR, ºC	–	$\geq$ 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 1.460 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

Finally, SUPPLIER shall take into account typical relative distributions of different materials loaded in reactors of pre-treatment and HDS sections listed in **Table 3**. These figures are guidelines for loading proposals and may be overridden for specific cases (e.g., a strong and specific contamination at a given feed stream) by SUPPLIER's suggestion and with PETROBRAS agreement.

Table 3 – Typical relative distribution of materials loaded in reactors of HDS-CN unit

Material	Pre-treatment	HDS
Inert material	≤ 5%*	≤ 7%*
Guard bed	≤ 5%	-
Activity grading material	≤ 2%	-
Poison trap	-	≤ 5%
Main catalyst	90 – 95%	90 – 100%

* Estimate does not consider the volume loaded below inferior tangent line of the reactors

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.

In addition to mandatory catalytic tests performed by PETROBRAS, references of industrial use on the same application may be requested.

Each main catalyst will be tested with a specific feed and in appropriate conditions for performance evaluation of each and all reactions demanded. Each catalyst 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*, even though short term stability (i.e., during the timeframe of initial activity testing) may 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.

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.

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.)

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 **Table 4** 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, gI_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	≥ 20
LHSV, h^{-1}	*2 – 6*
H_2/FEED ratio, Nm^3/m^3	≤ 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 °C	*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), °C	
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	≥ 15
LHSV, h^{-1}	≤ 3
H_2/FEED ratio, Nm^3/m^3	≤ 300
Temperature, ^oC	≥ 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 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 – 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} = 270 °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.

Definition of this S_{TARGET} value is complex, as it varies with the current legislation established value for the sulfur concentration on commercial gasoline C and the actual composition of the gasoline produced by each refinery under a certain set of conditions. To avoid this complexity, it is assumed a maximum limit for this target, which shall be referred to as $\tilde{S}_{TARGET}$with a value of 66.7 ppm, which represents the greatest sulfur concentration allowable on the product of the HDS unit that yields a gasoline C product with 50 ppm sulfur under the ethanol addition rules in force in the period up to June 2019. 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:$\tilde{S}_{TARGET}$:

$$X_{STAGE} = 100\frac{S_{FEED} - \sqrt{S_{FEED}S_{TARGET}}}{S_{FEED}} = 100\frac{S_{FEED} - 8.167\sqrt{S_{FEED}}}{S_{FEED}}$$

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

Selectivity $\geq$ *3*

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

Table 8 – Approval criteria for each application

Performance indicator	RV	T_{BASE}, ºC
Application: pre-treatment		
Dienes conversion	80	170
Mercaptans conversion	95	
Application: selective hydrogenation		
Sulfur conversion (*per stage*)	X_{STAGE}	270
Selectivity (*per stage*)	3	

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 2 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.

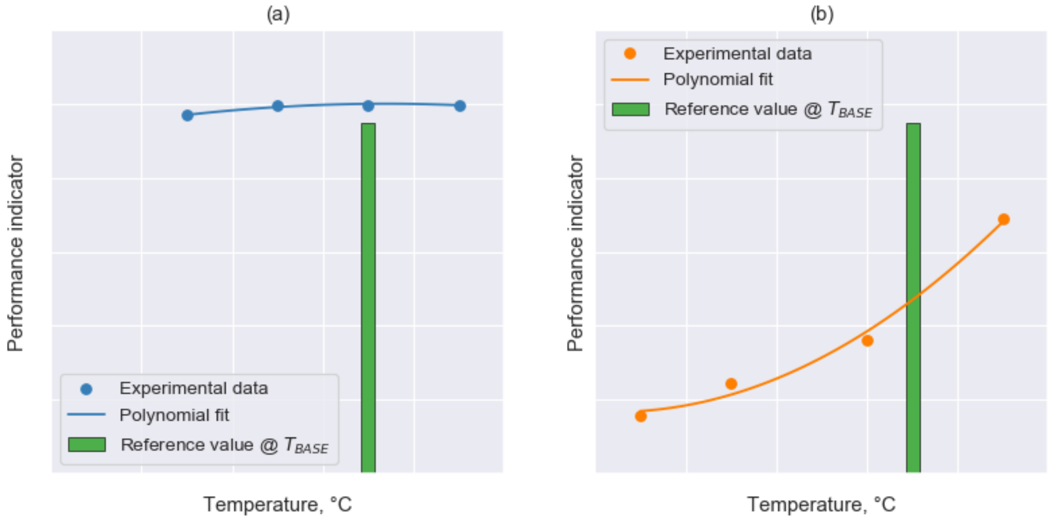

Figure 2 – Examples of test results. Subfigure(a) depicts a performance indicator that exceeds its RV. Subfigure (b) depicts a performance indicator that does not meet its RV.

5 – Scope and Confidentiality

SUPPLIER shall provided 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}:

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