Technical Specification for the procurement (purchase) of catalysts for the ultra low sulfur diesel (ULSD) hydrotreatment for units

1 – Purpose

This document provides information for a catalyst SUPPLIER interested in bidding on a supply contract for hydroprocessing NiMo catalysts system for use in the production of Brazilian S10 diesel oil (ULSD).

This document applies for the supply of fresh catalysts fabricated by the SUPPLIER itself or affiliated companies. Regenerated, rejuvenated, stabilized or used catalysts are not considered in this bid.

Information presented herein will allow any interested SUPPLIER 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 the 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 main objective of diesel hydrotreating process is to produce full specified Brazilian S10 diesel oil from feedstocks compounded by a mixture of straight run and cracked streams (such as LCO and coker gasoils).

2.1 – Reactions and simplified process scheme

Hydrotreating consists in a heterogeneous catalytic process in the presence of hydrogen, whereby the organic sulfur and nitrogen compounds are converted to H_2S, NH_3 and the corresponding hydrocarbons (hydrodesulfurization - HDS and hydrodenitrogenation - HDN, respectively). In addition, the olefins and aromatics can be saturated, known as olefin hydrogenation and hydrodearomatization reactions respectively.

A simplified scheme of a reaction section in ultra low sulfur diesel hydrotreating unit is presented in Figure 1.

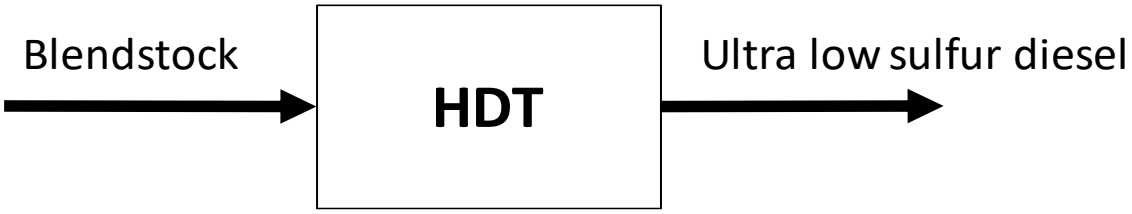

Figure 1 – Reaction section of an ultra low sulfur diesel hydrotreating unit

2.2 – Catalysts and other materials

For the purpose of this document, **catalyst** (written in bold typeface) refers indistinctly to any individual catalyst product or catalytic system, where catalytic system is any combination of catalysts, stacked in a definite order, as per the supplier proposal.

The process demands a **catalytic system,** loaded in a given order and designed to optimize the balance between desired reactions (hydrogenation), contaminant tolerance (silicon and arsenic poisoning, but not limited to these contaminants) and coke precursors conversion.
Main Catalyst(s) means the catalytic product(s) addressing hydrogenation and hydrogenolysis reactions. In addition to the main catalysts, the hydrotreating process demands 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, flow maldistribution, formation of gums and coke and localized temperature excursions, loaded at the top of first reactor;

iii. **activity grading**. consisting of a set of catalysts with different levels of activity, loaded on the top of catalytic bed, designed to prevent gums and coke formation or temperature excursions;
iv. ***poison traps***, designed to retain specific poisons (such as Silicon or Arsenic, but not limited to these contaminants), thus protecting the main catalysts.

PETROBRAS requires that **main catalysts** are tested previous to their use in industrial units. The complete catalytic system with lowest utilization 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.
PETROBRAS will select and acquire the **main catalysts** as well as inert, guard bed, activity grading and poison trap materials from the same SUPPLIER, as this is understood as taking part of a whole technical proposal.

3 – General requirements for catalysts supply

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

3.1 – Catalyst Characteristics

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 oxides.
The main catalyst system must be composed by NiMo catalyst. Main catalysts must be supplied as extrudates with trilobe, quadralobe or similar shapes. For this bid, the catalyst **nominal diameter shall be in the range of 2 to 2.5 mm.**
For each material, its shape, size and quantity to be used shall be clearly described on the technical proposal.

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, as catalyst data sheet, for all materials included in the bid (inert materials, guard bed catalysts, activity grading catalysts, poison traps and main catalysts), including at least the information about chemical and physical 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, including information on the safe handling, storage, disposal and toxicity of the materials supplied as may be required by law, such as Material Safety Data Sheets (MSDS). Although not required in the bidding step, SUPPLIER implicit 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** handling, storage, loading and unloading instructions;
- Recommended activation procedures for industrial plant;
- 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 for 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 (3)	x	x	x	x	x
Dense loading density, kg/m^3 (3)	-	x	x	x	x
Particle shape	x	x	x	x	x
Particle dimensions	x	x	x	x	x
Attrition index, % (4)	x	x	x	x	x
Mechanical resistance (4)	x	x	x	x	x
Stoichiometric sulfur required for sulfidation (SSU), wt%	-	x	x	x	x
Packing weight	x	x	x	x	x

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

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

(3) Dry basis density, i.e., disregarding any chelating agents

(4) Used standard method and units shall be indicated

3.3 – General operating conditions

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 4 and 5).

Table 2 – Typical operating conditions of a hydrotreating unit for ULSD

Parameter	HDT
Liquid Hourly Space Velocity (LHSV), h^{-1}	0.80
Inlet H_2 total pressure, kgf/cm^2	89
Total H_2 to feed ratio, Nm^3/m^3	255
Recycle gas H_2 content, vol %	97.2
Make-up Hydrogen Purity, vol %	99.99

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.

3.4 – Expected relative distribution of catalyst and other materials

The SUPPLIER shall recommend a set of inert material, guard bed, activity grading and poison trap catalysts for the service and feed composition herein described to be installed in the first bed of the unit.

All catalyst beds will be loaded over successive layers of ceramic spheres of 1/8” and 1/4” diameter size, for top and intermediate beds, and 1/8”, 1/4” and 3/4” diameter size for bottom of reactor beds. These ceramic spheres are not included in this scope of supply. All unit beds are equipped with top-bed distributor trays suitable for gas-liquid or gas distribution. An example of loading diagram of a diesel hydrotreating unit is shown in Figure 2.

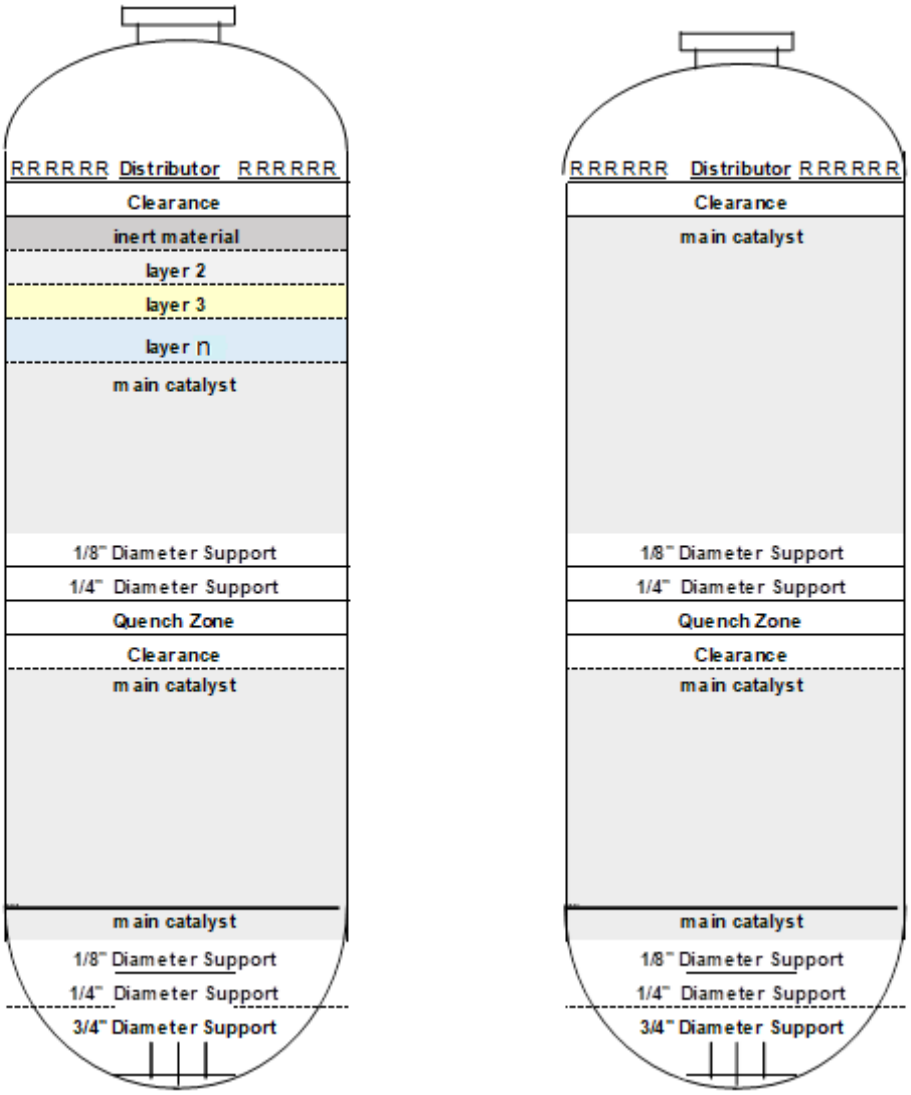

Figure 2 - Loading diagram of a typical HDT unit

The internal diameters of the reactors to be supplied by this catalyst bid are 4370mm.

The guard bed must comply with the size graduation considering the larger diameter of the main catalyst system. The total volume of guard bed is informed in PPU.

The volume of Si trap shall be between 60 to 65% of the total guard bed volume (guard bed and poison trap). Each layer of inert, guard bed, activity grading and poison trap materials shall have the minimum thickness of 150mm.

The **main catalysts and all other materials** shall be SOCK loaded.

4 – Procedure for testing and approving catalysts

Supplier shall propose a convenient package of catalysts for promoting a good gas-liquid distribution, gradual conversion of reactive species limiting exothermicity and trap of specified contaminants. Inert materials, guard materials, activity grading catalysts and poison traps will not be tested by PETROBRAS. The technical proposal will be evaluated regarding its adequacy to the proposed service and to the best practices of using such materials in hydrotreating technology for protecting the main catalyst beds.

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) will be tested by PETROBRAS, using the catalyst samples provided by the SUPPLIER.

The main catalyst system will be tested with a specific feed and in appropriate conditions for performance evaluation, for initial activity. Main catalyst system 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 catalyst system will be tested at fixed pressure, space velocity and gas-to-feed ratio and at different temperatures covering the intended SORT range of the HDT unit.

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

4.1 – Samples

The amount of sample provided shall not be inferior to 1L (one liter).

Samples delivered for testing must have the nominal diameter ranging from 1.3 to 1.6 mm (1/20” to 1/16”), in the same shape of the respective catalyst to be industrially supplied.

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

SUPPLIER must inform either metals concentration (for each one) or information about specific sulfur uptake for activation purposes and may provide specific instructions for pilot plant start up.

The address to send the sample and the contact data to be 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: Carmen Lucia Tavares da Silva
Bruno Martins Santos

SUPPLIER must certify that the sample was delivered at CENPES sending, through PETRONECT, the receipt presented in Annex I. The document must be signed by a PETROBRAS' technical representative. The delivery must respect the deadlines defined in the bid process.

4.2 - Catalyst properties

The SUPPLIER must also inform the volumetric proportion of each product suggested for the main catalyst system. This information will be called **Volumetric Proportion of Catalyst (vol %)**.

The information about sock loading density (kg/m^3), stoichiometric sulfur required for sulfidation - SSU (wt %) and volumetric proportion of catalyst (vol %) sent by the SUPPLIER will be used to calculate a parameter P (kg S /m^3 cat) as described below:

$$P = \sum_{k=1}^{n} (\boldsymbol{sock\ loading\ density} * \boldsymbol{SSU} * \boldsymbol{volumetric\ proportion\ of\ catalyst}) / \mathbf{10000}$$

The parameter will be calculated just for the main catalyst system and k represents each n catalyst proposed for the system.

The approval criteria is P ≥ 78 kg S / m^3 cat.

Main catalysts system that does not meet these criteria will not be approved and automatically not be considered for testing.

4.3 – Characteristics of feedstock and procedures for catalyst testing

Main catalyst system will be tested with a feedstock obtained from a PETROBRAS' refinery. The feedstock composition includes straight-run gas oil, light cycle oil (up to 4.3 wt %) and coker gas oil (up to 10.7 wt %) and it is representative of the service considered. Main characteristics of a typical feedstock are listed in **Table 4**.

Table 4 – Main characteristics of hydrotreating feedstock

Feedstock properties	
Density 20/4°C (g/cm^3)	0.8635
Refractive Index	1.4816
Sulfur (mg/kg)	3753
Nitrogen (mg/kg)	806
Si content (mg/kg)	1.0 (estimated)
ASTM D86 Distillation	
T10% (°C)	220
T50% (°C)	299
T90% (°C)	358
T95% (°C)	374
Aromatic distribution (n.d.M correlation)	
Aromatic carbons (wt %)	17.5
Naphthenic carbons (wt %)	29.8

Tests for assessment of initial activity of main catalyst system for hydrotreating application will be performed in a pilot-plant unit. Typical configuration and operational conditions are listed in

Table 5. Pilot plant tests will be performed with once through hydrogen flow (purity 99.99%). These parameters and ranges represent typical conditions for carrying such tests and shall not prevent PETROBRAS from using different conditions, if PETROBRAS deems necessary.

The SUPPLIER must suggest the activation procedures for pilot-plant tests. If not informed, the SUPPLIER implicitly accepts PETROBRAS' standard activation procedure.

The catalyst system to be tested will be loaded as received, without previous treatment and considering informed soak loading density for each product. The reactor will be pressurized with hydrogen at 89 kgf/cm^2 and then heated at 140°C at a rate of 25°C/h. The reactor will

be maintained in these temperature, pressure and hydrogen atmosphere conditions, during wetting with liquid feedstock.

Subsequent steps will consider SUPPLIER information for catalyst activation and industrial unit limitations (such as minimum pressure for catalyst wetting, maximum furnace outlet temperature during activation, etc.). After activation, catalyst will treat non cracked feedstock (SRGO) for 72h, in stabilization conditions described in **Table 5**.

The hydrotreating feedstock will be admitted and tests performed in the sequence presented in **Table 5**. At a given testing conditions, product samples will be withdrawn when product density achieve constant values, within the analytical deviations as indicated by the corresponding standard method (ASTM D4052).

Table 5 – Stabilization and Operating conditions for pilot plant testing

	Stabilization	**Test 1**	**Test 2**	**Test 3**
Pressure (kgf/cm^2)	89	89	89	89
Temperature (ºC)	340	340	350	360
LHSV (h^{-1})	0.8	0.8	0.8	0.8
H_2 to feed ratio (Nm^3/m^3)	255	255	255	255

After the stabilization of each catalytic test, samples of hydrotreated effluent will be analyzed in order to evaluate its performance according to the ULSD specification (section 4.4).

4.4 – Performance evaluation

Hydrotreated products will be characterized regarding the main properties for producing Brazilian S10 diesel: total sulfur content (ASTM D5354) less than 10 mg/kg, specific gravity at 20ºC (ASTM D4052) less than 0,850 g/cm^3, maximum distillation temperature of 95% v of the sample at 370°C (ASTM D86). At Petrobras discretion, other properties will be analyzed in order to obtain a more comprehensive characterization of the hydrotreated products.

The lowest reaction temperature for attaining all these specifications will be considered as representative of the initial performance (SORT) of the main catalyst or catalyst system. If necessary, data will be interpolated using adequate interpolating functions.

4.5 – Test approval criteria

Based on previous experience of PETROBRAS with similar catalysts and feedstocks for this application, the tested catalyst system will be validated if its SORT will be equal or below than 350°C, with a tolerance of + 2°C for considering experimental and analytical deviations of testing.

5 – Scope and Confidentiality

SUPPLIER shall provide required information, documentation and samples free of charge for the purpose of this procurement, 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 this procurement of catalysts process shall be used solely for this purpose.

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

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.

Samples will be tested according to commercial proposal ranking (best (lower) quotation first, and so on). For each sample successively tested, PETROBRAS shall provide the SUPPLIER with a summary of the evaluation results of the main catalyst system, indicating whether the system was accepted or not. However, PETROBRAS is under no obligation to provide information or data on PETROBRAS' proprietary know-how relating to these samples and/or processes.

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 will not return to SUPPLIER any documents or samples provided.

ANNEX I – Comprovante de entrega de amostra

PETROBRAS	**COMPROVANTE DE RECEBIMENTO DE AMOSTRAS**	
	OPORTUNIDADE:	Catalisadores HDT IV REPLAN
	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)