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

1 – Purpose

This document provides information for a catalyst SUPPLIER interested in bidding on a supply contract for hydroprocessing catalysts for use in the production of Brazilian S10 diesel oil (ULSD). The units to be supplied by this catalyst bid require a specific start-up procedure, due to their higher Minimum Pressurization Temperature.
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 covered by this specification.

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).
The units to be supplied by this catalyst require a specific start-up procedure due to their higher Minimum Pressurization Temperature. Reactor walls shall be heated up to 150°C before raising pressure up to the design value (120 kgf/cm^2). During this procedure, the

catalytic bed will be exposed to temperatures as high as 180°C, in hydrogen atmosphere, before wetting with liquid feedstock for a time up to 36 hours.

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 hydrodesaromatization reactions respectively.

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

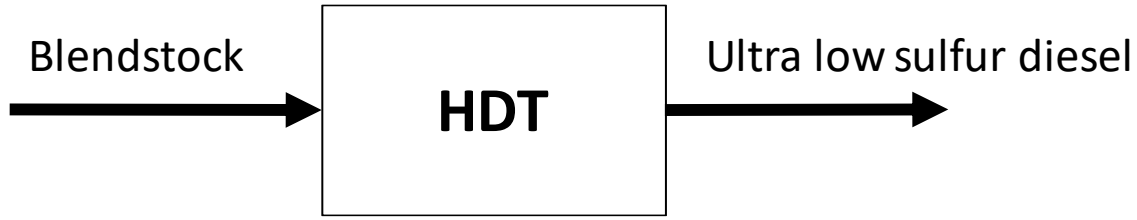

Figure 1 – Reaction section of an ultra low sulfur diesel hydrotreating unit

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 others 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

Main catalysts must be supplied as extrudates with trilobe, quadralobe or similar shapes and average diameter ranging between 1.3 to 1.6 mm (1/20” to 1/16”).

The supplier is free to offer the main catalyst in the oxide, pre-sulphided form or submitted to any other specific treatment. The Technical proposal must explicit and describe the specific treatment and in the economical proposal any cost related to it must be included. Samples delivered for testing must be in accordance with this option.

In case of adopting a pre-sulphided form, the main catalysts system 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.

TOTSUCAT CFP and Air Passivation Treatment **or equivalent catalyst pre-activation and passivation** technologies are preferred. Activation and passivation technologies different from Eurecat technology must be referenced with at least 5 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.

For each material, its shape and size shall be clearly described on the technical proposal and shall be the same for every unit included on the present bid.

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 [4]

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
Particle shape	x	x	x	x	x
Particle dimensions	x	x	x	x	x
Attrition index, % [3]	x	x	x	x	x
Mechanical resistance [3]	x	x	x	x	x
Stoichiometric sulfur required for sulfidation (wt%)	-	x	x	x	x
Packing weight	x	x	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) Used standard method and units shall be indicated

(4) For both oxide and pre-treatment form, if applied

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). This information represents average conditions of such industrial units.

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

Parameter	HDT
Liquid Hourly Space Velocity (LHSV), h^{-1}	1.1
Inlet H_2 total pressure, kgf/cm^2	120
Total H_2 to feed ratio, Nm^3/m^3	500
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. Units with two parallels trains of reactors lined up shall receive this set of materials in both first beds.

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.

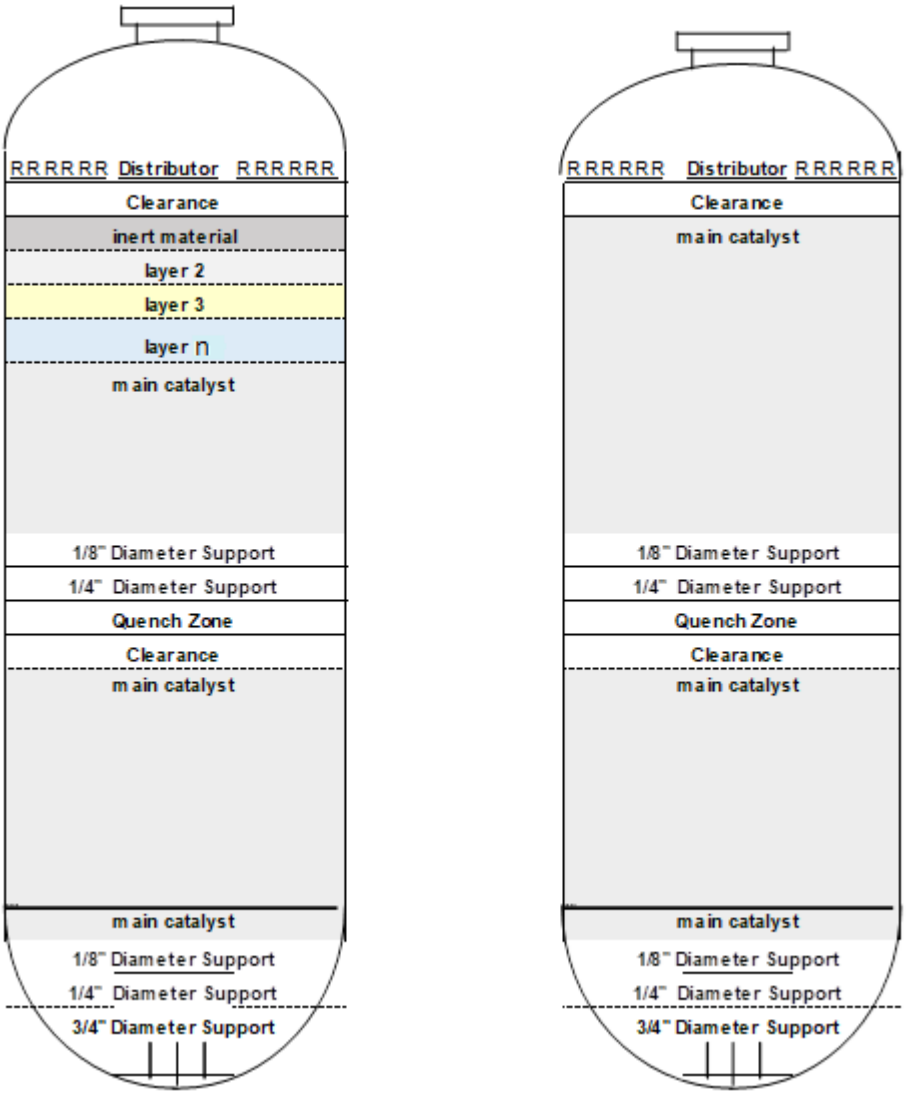

Figure 2 - Loading diagram of a typical HDT unit

The volume of Si trap, in the guard bed shall be between 50% to 70% of this 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 internal diameters of the first reactors, to be load with guard bed, of the units to be supplied by this catalyst bid are listed in table 3.

Table 3 – Internal diameter of the first reactors

Unit	Internal diameter (mm)
REDUC U-2800	3500
REPAR U-2313	4000
REVAP U-262	4000
REPLAN U-4283 *	3730

*This unit has two parallels trains of reactors lined up

The **main catalysts** shall be dense loaded. All other materials shall be sock loaded.

4 – Procedure for testing and approving catalysts

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 by PETROBRAS, using the catalyst samples provided by the SUPPLIER.

For the purpose of balancing between proposals offering oxide and sulfide form of the catalysts, Petrobras will adopt a leveraging factor comprising the costs of in-situ sulfiding and three days of mild feed processing (as catalyst stabilization period), in the form of an **additive cost of US$ 5.31 per kilogram of oxide form product**.

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 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 catalysts 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 units.

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).

For catalysts supplied submitted to a pre-treatment, the samples must be provided with the same pre-treatment. Exception will be accepted for pre-sulphided catalyst, that will be accepted the samples in the oxide form and sulfided by Petrobras (as per SUPPLIER instructions, if provided and deemed feasible).

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.

4.2 – 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 27 wt %) and coker gas oil (up to 30 wt %) and it is representative of the refineries and service considered. Main characteristics of a typical feedstock are listed in **Table 4**.

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.

Table 4 – Main characteristics of hydrotreating feedstock

Feedstock properties	
Density 20/4°C (g/cm^3)	0.8779
IR	1.4964
Sulfur (mg/kg)	3619
Nitrogen (mg/kg)	1513
Si content (mg/kg)	1.0 (estimated)
ASTM D86 Distillation	
T10% (°C)	229
T50% (°C)	278
T90% (°C)	353
T95% (°C)	372
Aromatic distribution (SFC*)	
saturated + olefin compounds (wt %)	60.7
monoaromatics (wt %)	21.2
diaromatics (wt %)	13.3
poliaromatics (wt %)	4.8

* Supercritical Fluid Chromatography

The catalyst system to be tested will be dense loaded as received, without previous treatment. The reactor will be pressurized with hydrogen at 120 kgf/cm^2 and then heated at 180°C at a rate of 25°C/h. The reactor will be maintained in these temperature, pressure and hydrogen atmosphere conditions, before wetting with liquid feedstock, for a time of 36 hours. Exception for catalyst system that will be supplied as pre-sulfided catalyst. For this oxide samples, after loading, the reactor will be pressurized with hydrogen at 120 kgf/cm^2, heated at 140ºC at a rate of 25°C/h and immediately wetting with liquid feedstock.

Subsequent steps will consider SUPPLIER information 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)	120	120	120	120
Temperature (ºC)	350	350	360	370
LHSV (h^{-1})	0,91	0,91	0,91	0,91
H_2 to feed ratio (Nm^3/m^3)	560	560	560	560

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 – 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 357°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.