

# **Technical Specification for the procurement (purchase) of catalysts for low severity hydrotreating units**

## **1 – Purpose**

This document provides information for a catalyst SUPPLIER interested in bidding on a supply contract for stacked bed catalytic systems (NiMo / CoMo) for the low severity hydrotreating units to produce Brazilian S10 diesel oil.

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 low severity diesel hydrotreating process is to produce full specified Brazilian S10 diesel oil from feedstocks compounded by straight run gasoil.

### **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<sub>2</sub>S, NH<sub>3</sub> 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 inventory cost will be selected and the catalytic evaluation performed by PETROBRAS with its own feed streams and in its own pilot plant facilities.

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.

Main catalysts must be supplied as extrudates with trilobe, quadralobe or similar shapes and average diameter ranging between 1.3 to 1.7 mm (1/20" to 1/15").

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 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 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**

<b>Property</b>	<b>Inert material</b>	<b>Guard bed</b>	<b>Activity grading</b>	<b>Poison trap</b>	<b>Main catalyst</b>
<b>Type of active phase <sup>(1)</sup></b>	-	X	X	X	X
<b>Type of support <sup>(2)</sup></b>	X	X	X	X	X
<b>Sock loading density, kg/m<sup>3</sup></b>	X	X	X	X	X
<b>Dense loading density, kg/m<sup>3</sup></b>	-	X	X	X	X
<b>Particle shape</b>	X	X	X	X	X
<b>Particle dimensions</b>	X	X	X	X	X
<b>Attrition index, % <sup>(3)</sup></b>	X	X	X	X	X
<b>Mechanical resistance <sup>(3)</sup></b>	X	X	X	X	X
<b>Stoichiometric sulfur required for sulfidation (wt%)</b>	-	X	X	X	X
<b>Packing weight</b>	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

### 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 3 and 4). This information represents average conditions of such industrial units and they will be used for testing the selected catalysts).

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

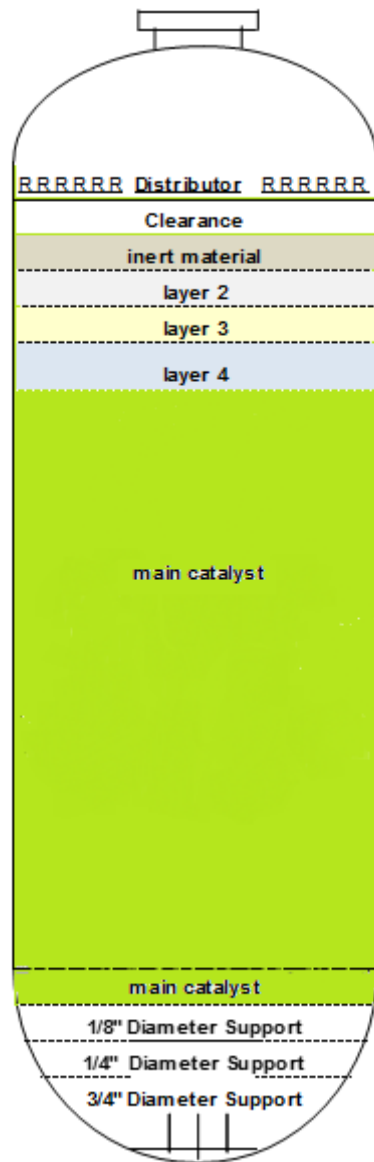
Parameter	HDT
Liquid Hourly Space Velocity (LHSV), h <sup>-1</sup>	1,3
Inlet H <sub>2</sub> total pressure, kgf/cm <sup>2</sup>	62
Total H <sub>2</sub> to feed ratio, Nm <sup>3</sup> /m <sup>3</sup>	245

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 1/4" and 1/8" diameter size, for top and intermediate beds, and 3/4", 1/4" and 1/8" diameter size for bottom of reactor beds. All unit beds are equipped with top-bed distributor trays suitable for gas-liquid or gas distribution. Depending on the distribution tray technology (old design), PETROBRAS will load a layer of spheres of 1/4" diameter size in the subsequent beds after the first. An illustration of a distribution of catalyst and other materials in a reactor can be seen in Figure 2.

As there are some limitations on hydrogen supply, the main catalyst system proposed by the supplier may have a maximum of 50% volume of NiMo catalyst in its composition.



**Figure 2** – Illustration of distribution of catalysts and other materials in a reactor of an ultra low sulfur diesel hydrotreating unit

The volume of guard bed and poison trap material shall be up to 10% of the overall catalyst volume (except for U-2700 which guard bed volume must be the same as informed in the PPU document). In addition, the Si trap shall be between 50% to 70% of this volume (guard bed and poison trap).

The **main catalyst** 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 catalysts prices) will be tested, using the catalyst samples provided by the SUPPLIER.

Supplier shall propose a convenient pack 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. The main catalyst system will be tested for initial activity. Main catalysts 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).

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 testing.



## 4.2 – Characteristics of feedstock and Procedures for catalyst testing

Main catalyst system will be tested with a feedstock obtained from a PETROBRAS' refinery.

Main characteristics of a typical feedstock are listed in Table 3:

**Table 3 – Main characteristics of hydrotreating feedstock**

<b>Properties</b>	<b>method</b>	<b>unit</b>	
specific gravity 20°C/4°C	ASTM D4052		0,8538
total sulfur	ASTM D5354	mg/Kg	3031
total nitrogen	ASTM D4629	mg/Kg	363
distillation (%v)	ASTM D86		
10		°C	232,0
50		°C	275,0
90		°C	330,5
95		°C	345,3
refractive index @20°C	ASTM D1747		1,4763

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 4. 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 catalyst system will be loaded as received, without previous treatment. The reactor will be pressurized with hydrogen at 60 kgf/cm<sup>2</sup> and then heated at 140°C at a rate of 25°C/h. The sulfidation procedure will consider SUPPLIER information and industrial unit limitations (such as minimum pressure for catalyst wetting, maximum furnace outlet temperature during sulfidation, etc.). After sulfidation, catalyst will be stabilized with test feedstock for at least 72h. At a given testing condition, product samples will be withdrawn when product density achieve constant values, within the analytical deviations as indicated by the corresponding standard methods.

Table 4 – Operating conditions for pilot plant testing

	Stabilization	Test 1	Test 2	Test 3
Pressure (kgf/cm <sup>2</sup> )	60	60	60	60
Temperature (°C)	340	340	355	370
LHSV (h-1)	2,8	1,3	1,3	1,3
H <sub>2</sub> to feed ratio (Nm <sup>3</sup> /m <sup>3</sup> )	245	245	245	245

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 20°C (ASTM D4052) less than 0,850 g/cm<sup>3</sup>, 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 specification will be considered as representative of the initial performance (SORT) of the main catalyst or main 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 355 °C, with a tolerance of + 2°C for considering experimental and analytical deviations of testing. Moreover, chemical hydrogen consumption shall not exceed 50 NL hydrogen/L feedstock with a tolerance of 10%, in order to cope with hydrogen supply limitations of such units.

## **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.

PETROBRAS shall provide the winner SUPPLIER with a summary of the evaluation results of its main catalyst system. 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.