Technical Specification for the purchase of catalysts for the coker naphtha hydrotreatment process (KN-HDT)

1 Purpose

This document provides information for a catalyst SUPPLIER interested in bidding on a supply contract for units performing hydrotreatment of coker naphtha (KN-HDT).

The scope of this document applies to the supply of fresh catalysts. Regenerated, rejuvenated, stabilized or used catalysts are not allowed in this bid.

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 supply;
- ✓ minimum performance parameters demanded from the catalysts;
- ✓ the procedure which PETROBRAS will use to assess the quality of the proposals 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 Objective of the process

The objective of coker naphtha hydrotreatment (KN-HDT) process is to remove sulfur and nitrogen as well as saturate olefinic compounds from the coker naphtha stream. The hydrotreated stream may be blended into commercial gasoline or be fed to naphtha reforming units. In this latter case the capture of silicon is of paramount importance, besides total sulfur and nitrogen content of the hydrotreated stream.

2.1 Reactions and simplified process scheme

A KN-HDT unit is composed of three reaction sections:

1) A pre-treatment section (PRE-TREAT) that processes the coker naphtha to hydrogenate the diolefins, to prevent gum formation on the main hydrotreatment reactors.
2) A hydrotreatment section, where the above stream is fed diluted with straight run naphtha and hydrotreated to remove olefins, nitrogen and sulfur, and also to capture silicon.

3) A post-treatment section, where conditions are set to remove remaining sulfur compounds (mercaptan hydrogenation).

*For RNEST unit, there is not a post-treatment reactor

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

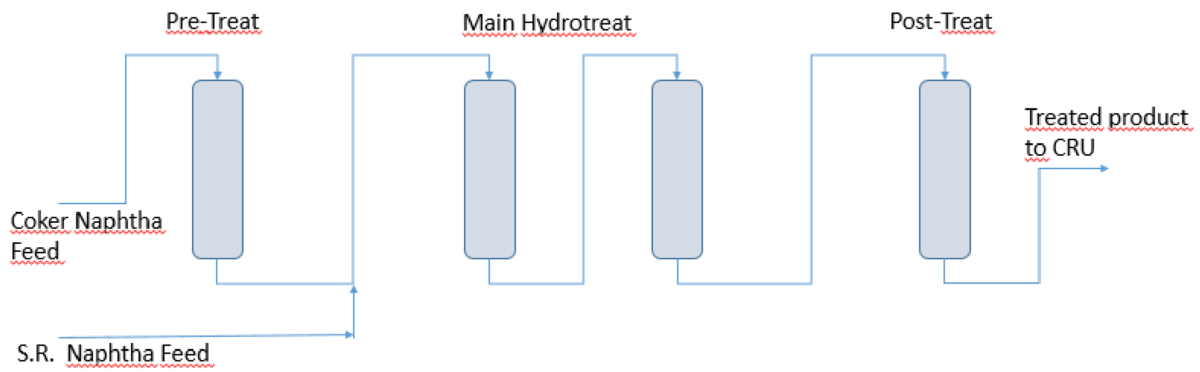

Figure 1 – Flow through the reaction sections of a coker naphtha hydrotreatment unit

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 supplier proposal.

The process demands several catalysts for each reaction section (pre-treatment, hydrotreatment and post-treatment catalyst). These are the *main catalysts* loaded in the reactors, which for the purpose of this process shall be constituted of Nickel and Molybdenum supported on alumina.

Besides 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. For the purpose of this process, poison traps also shall be constituted of Nickel and Molybdenum supported on alumina.

3 Data on the considered units

The unit considered within the scope of this process is located at RNEST refinery, whose specific data is summarized on **Attachment I**:

A general description of these units is as follows:

- One diolefin hydrogenation reactor. This reactor typically operates between 170 and 200ºC, promoting hydrogenation of the most reactive compounds which otherwise could lead to gum formation and fouling of the preheat train or main reactors.
- One or more main hydrotreatment reactors. These reactors typically operate between 300 to 380ºC to perform olefin saturation, plus sulfur and nitrogen removal through hydrogenation. Exothermicity due to olefin hydrogenation is controlled either by using recycle gas quench, SRN quench or hydrogenated product recycle. On units where the product is fed to a naphtha reformer, a higher activity catalyst may be used on a layer at the bottom of the second reactor, to complete nitrogen removal. Poison trap may be compounded with the main hydrotreating catalysts to achieve the desired silicon retention. The distribution of active phase shall be balanced such that the top catalytic bed of the first main hydrogenation reactor performs a significant degree of olefin saturation at Start Of Run (SOR) conditions.
- One post-treatment reactor to reduce mercaptidic sulfur so that total sulfur content is below 0,5 wppm throughout the whole catalyst cycle. This reactor operates at a temperature lower than main hydrotreatment reactors outlet temperature, typically in the range between 290 and 320ºC. A specific catalyst may be used in this reactor.

*For RNEST unit, there isn't a post-treatment reactor

Specific information on the unit considered in this Technical Specification is summarized in attachment I. This attachment contains:

- A summary description of the unit and process flow.
- Unit-specific targets such as product specification and cycle length constraints.
- Feedstock characteristics
- Summary of operating conditions
- Reactor / bed volumes

4 General requirements for catalysts supply

This section details several requirements for supplying catalysts to KN-HDT units. All information herein shall be taken into account when selecting materials included in a given bid.

4.1 Catalyst form

Main catalyst for all reactors 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. Acknowledge that process feed is totally vaporized at the inlet of hydrotreating reactor(s) at normal SOR conditions. Air passivation is requested for the safe handling of the catalyst during the loading of the reactors.

Catalyst is to be **sock-loaded**.

4.2 Catalysts packaging

Catalysts shall be packaged and shipped in suitable containers.
Note: the packaging shall prevent the catalyst to come into contact with air, so as to preserve

its characteristics.

4.3 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 SUPPLIER shall submit to PETROBRAS:

- 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 documentation to be provided includes:

- Product data sheet
- Product MSDS
- Product safe handling instructions
- Product storage instructions
- Product disposal instructions

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 materials delivered must be accompanied by MSDS and**

other product specific documentation in Portuguese language and complying with Brazilian standards (ABNT NBR 14725).

SUPPLIER shall submit to PETROBRAS:

- 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	Activity grading	Poison trap
Type of active phase (1)	-	x	x	x
Stoichiometric sulfur uptake, %wt	-	x	x	x
Type of support (2)	x	x	x	x
Sock loading density, kg/m^3 (3)	x	x	x	x
Dense loading density, kg/m^3 (3)	-	x	x	x
Specific surface area, m^2/g	-	x	x	x
Particle shape	x	x	x	x
Particle dimensions	x	x	x	x
Attrition index, %	x	x	x	x
Mechanical resistance (4)	x	x	x	x
Silicon maximum uptake, %wt (4)	-	x	x	x
Silicon Breakthrough onset, %wt	-	x	x	x
References of commercial use of the offered products	x	x	x	x
Packing weight	x	x	x	x

Packing type (drums/ big-bag/other)	x	x	x	x
Product sulfided ex-situ? (yes/no)	**-**	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

Table 2 – Minimum technical information required about all materials (cont.)

Property	**Main diolefin catalyst**	**Main hydrotreating catalyst**
Type of active phase (1)	x	x
Stoichiometric sulfur uptake, %wt	x	x
Type of support (2)	x	x
Sock loading density, kg/m^3 (3)	x	x
Dense loading density, kg/m^3 (3)	x	x
Specific surface area, m^2/g	x	x
Particle shape	x	x
Particle dimensions	x	x
Attrition index, %	x	x
Mechanical resistance (3)	x	x
Silicon maximum uptake, %wt (5)	x	x
Silicon Breakthrough onset, %wt	x	x
References of commercial use of the offered products	x	x

Packing weight	x	x
Packing type (drums/ big-bag/other)	x	x
Product sulfided ex-situ? (yes/no)	x	x
Ex - situ sulfidation contractor	x	x
Ex-situ treatment for cracked feed tolerance	x	x
Ex-situ treatment for compatibility with handling under air	x	x

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

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

(3) For both oxide and RTU forms

(4) Used standard method and units shall be indicated

(5) Inform silicon uptake in SOR and EOR conditions

5 Minimum performance parameters demanded from the catalysts

The requested cycle length is four years (48 months). SUPPLIER must attest that main catalysts will operate under such conditions, continuously providing a performance compatible with the approval criteria defined in Section 7 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 **Attachment I**.

6 Assessment of the proposals

6.1 Minimum Technical Specifications

Technical proposal for the catalyst system, considering dienes hydrogenation reactor, main reactors and post-treatment reactor, including:

- Guard bed catalysts (for each section/reactor)
- Main catalysts (including silicon trap, for each section/reactor)
- Proposed reactors loading diagram
- Estimated Start Of Run Temperature (SORT).

- Estimated Deactivation rates (ºC/month) for both sulfur and nitrogen conversion.
- Estimated Silicon pick-up capacity of each catalyst and the whole catalyst system, at operating conditions. Estimated silicon breakthrough, as a fraction (percentage) of overall silicon pickup capacity.
- Estimated unit cycle length, based on HDS and HDN.

6.2 Technical proposal qualification:

Proposals will be technically evaluated for consistency through the following parameters:

a) Completeness of required product documentation.
b) Completeness of Item 7 (General requirements of the whole inventory) requisites.

6.3 Criteria for disqualification

a) Failure to comply with the minimum technical specifications will imply in disqualification of the proposal.
b) Inconsistency between the proposal and the specific requisites will imply in disqualification of the proposal.
c) insufficient silicon uptake capacity will imply in disqualification of the proposal.

7 General requirements of the whole inventory:

SUPPLIER must indicate, according to the specific unit objectives, and within the limits informed, the proper composition for the grading beds, guard beds and main catalyst beds, as needed.

a) For diolefin hydrogenation reactors, inert and activity grading material shall occupy no more than10% of the catalyst volume of this reactor.
b) For the first main hydrogenation reactor, inert and activity grading material shall occupy no more than 10% of the overall catalyst volume of this reactor.
c) For main hydrogenation reactors, SUPPLIER shall propose a composition between silicon trap and main hydrotreating catalyst(s) which best suits the process objectives according to the specifications described in Attachment I. Silicon trap shall be limited to a maximum of 30% of total volume of these reactors. Petrobras will use 40 m^3 of an inert silicon trap that has already been purchased. PPU volume for this purchase already considers this information. For silicon uptake capacity, assume that this

existing inert silicon trap has zero (0) silicon uptake capacity.

d) Silicon trap shall be an active material, constituted of Nickel and Molybdenium over alumina. Stoichiometric sulfur value required for complete sulfiding of the silicon trap must have a minimum value of **1,8**% wt, on dry basis. Silicon trap shall be loaded only in the main hydrogenation reactors.

e) The main catalysts for diolefin, hydrotreatment and post-treatment reactors shall be an active material, constituted of Nickel and Molybdenium over alumina. Stoichiometric sulfur value required for complete sulfiding of the catalyst must have a minimum value of **7,5**% wt, on dry basis.

ATTACHMENT I

RNEST U-33

The RNEST U-33 was designed so that a mixture of KN and SRN (combined naphtha feed) is fed directly into the preheat train, together with hydrogen recycle into a diolefin hydrogenation reactor, and two main hydrotreatment reactors. Heating of the combined feed to reaction conditions is performed by furnace heating of a recycle hydrotreated stream mixing upstream of the first main hydrotreatment reactor. Hydrogen recycle quench is used between hydrotreatment reactors and between reactors' catalytic beds to control reaction heat release.

General Unit Information

The volume of catalyst to be considered in each reactor are:

	R-33001	R-33002	R-33003
Catalyst Loading	Sock	Sock	Sock
1st Bed catalyst volume (m3)	21	59	70
2nd Bed catalyst volume (m3)	-	60	80

Obs. Petrobras will use 40 m^3 of an inert silicon trap that has already been purchased. That's the reason PPU total volume is lower than reactors total catalyst volume ($V_{PPU} = (V_{R-01} + V_{R-02} + V_{R-03} – 40\ m^3) * 1,1$ (according to note 6)).

Typical Feedstock Characteristics and Operational Conditions

Stream	**Straight-run Naphtha**	**Coker Naphtha**
Feedstock Rate, m^3/d	1470	1530
Density 20/4 ºC, kg/m^3	778.9	720.1
Sulfur, wtppm	700	3020
Nitrogen, wppm	2.3	156
Silicon, wtppm	1	5
Bromine Number, g Br2/100 g	-	78
Diene Value, g I2/100g	-	5.0

Reactor	R-33001		R-33002		R-33003	
	SOR	EOR	SOR	EOR	SOR	EOR
Maximum Operating Temperature, °C	371		380		383	
Pressure, kgf/cm²g	38.46		35.58		34.31	
H_2/Feed (Nm^3/m^3)	215	217	268	210	268	210

Product Quality

	Combined Naphtha Feed, Downstream R-328301	Hydrotreated Naphtha
Sulfur, wtppm	-	< 10
Nitrogen, wtppm	-	< 10
Silicon, wtppm	-	0
Diene Value, g I2/100g	≤ 1	0
Bromine Number, g Br2/100 g	-	< 1.0

Unit flowsheet