Technical Specification for the purchasing process of "Hydrotreatment" (HDT) catalysts for use in Hydrogen Generation Units (HGU)

1. Objective

The objective of this document is to specify the technical requirements for the process of purchasing "Hydrotreatment" (HDT) catalysts used in the steam reforming process (SRM) of natural gas, propane, butane, or naphtha.

2. Description of "Hydrotreatment" (HDT) Catalysts

The "Hydrotreatment" (HDT) section of Hydrogen Generation Units (HGU) is composed of a fixed bed catalyst where the organic sulfur compounds react with hydrogen to produce H_2S in an adiabatic reactor with typical inlet temperature range from 350ºC to 390ºC.

3. Feedstock and Process Information

3.1. The main characteristics of the feedstocks for each hydrogen plant, the main process data in the EOR (End of Run) conditions and the catalysts inventories are showed in the Annex 1.

3.1.1. All the units where naphtha and natural gas are indicated as the feedstock have the capability to process naphtha or natural gas separately or mixed, in any proportion. In this case, natural gas is considered the main feedstock and naphtha the alternative feedstock (that will be used in 30% of the campaign time).

4. Hydrotreatment Technical Requirements

4.1. The hydrotreatment catalyst offered should be able to allow the operation of the hydrogen generation unit under conditions detailed in the Annex 1 for at least 72 months. The conditions accepted as indicators of the HDT end of run (EOR) are given in the Annex 1: Maximum inlet temperature; Maximum reactor pressure drop and maximum reactor outlet organosulfur compounds content of 0,1 ppmv. The SUPPLIER must inform the expect performance at 72 months for each PETROBRAS' unit in accordance with Annex 2.

4.2. The SUPPLIER must inform the characteristics of the offered product completing the template in Annex 3. Only CoMo/alumina type catalysts will be accepted, and regenerated catalysts will not be accepted. The HDT product offered by SUPPLIER must have the minimum characteristics in all the items described in the Annex 3 and 4.

4.3. A representative product sample is requested to be evaluated by PETROBRAS in order to verify its compliance with the requirements described in Annex 3 and 4.

4.3.1. The sample amount required is around 1 kg.

4.3.2. The samples forwarded must be free of cost to PETROBRAS.

4.3.3. The address to send the sample and the contact data to be must 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: Roberto Carlos Pontes Bittencourt (BK12)
Vivian Passos de Souza (CXA3)

4.3.4. SUPPLIER must certify that the sample was delivered at CENPES sending, through PETRONECT, the receipt presented in Annex 5. The document must be signed by a PETROBRAS' technical representative in accordance with items 4.3.1; 4.3.2 and 4.3.3. The delivery must respect the deadlines defined in the bid process.

4.4. SUPPLIER must inform for the hydrotreatment catalysts offered the information listed below. All the information and documentation for the bidding purposes must be supplied in Portuguese or English languages:

4.4.1. The Material Safety Data Sheet (MSDS) written in Portuguese. 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).

4.4.2. Information about loading, normal operation, unloading and disposal of the material.

5. The winner of the bid must provide the information below, when requested:

5.1.1. Based on industrial information sent by PETROBRAS, make an evaluation of product's performance.

5.1.2. Send the quality certificate of each bath of the inventory provided.

5.1.3. Reply to PETROBRAS' queries in case of operation problems.

6. Disqualification Criteria

6.1.1. The non-compliance with the requirements described in the section 4 will imply that the product will not be considered technically approved.

7. Packing

7.1. The catalysts shall be packed in drums or big bags.

8. Scope and Confidentiality

8.1. 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 – Hydrotreatment Technical Requirements).

8.2. 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.

8.3. 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.

8.4. SUPPLIER grants no rights or license whatsoever to PETROBRAS hereunder with respect to any information provided.

8.5. 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.

8.6. PETROBRAS shall provide the winner SUPPLIER with a summary of the evaluation results of its catalysts. However, PETROBRAS is under no obligation to provide information or data on PETROBRAS' proprietary know-how relating to these samples and/or processes.

8.7. 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.

8.8. PETROBRAS will not return to SUPPLIER any documents or samples provided.

8.9. The product sample forwarded (item 4.3) must be free of obligations to sign "Test and Evaluation Agreement" or other confidentiality agreements.

9. Force Majeure and Acts of God

9.1. In the event of force majeure such as, but not restricted to, the temporary closure of R&D units, equipment maintenance or restrictions on the movement personnel due to national health events, PETROBRAS may not perform one or more analysis described in this document. In this case, the respective item will be evaluated only based on technical information provided by SUPPLIER.

Annex 1: Feedstock and Process information (HDT section)

Refinery	REPAR	REPAR	RLAM	RPBC	RECAP	REFAP	REPLAN	REPLAN	REPLAN	REGAP
Plant number	U-2600	U-22311	U-34	U-2311	U-2311	U-704	U-241	U-241A	U-4241	U-409
Naphtha (std m^3/h)	-	27	-	14	-	20,9	13,8	13.8	-	-
Natural Gas (Nm^3/h)	4323	22851	3901	13000	7759	17372	11542	11542	29301	16042
H2/NG ratio (mol/mol)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0,05	0,05	0,05
H2/Naphtha ratio (mol/mol)	-	0.25	-	0.25	-	0.20	0.25	0,25	-	-
Natural Gas										
CO_2 (% mol dry)	1.25	1.20	0.69	0.16	0.5	0.67	1.85	1,85	1,47	0,87
RSH (ppmv)	4	7	0.4	0	10	10	3	3	7	5,7
H_2S (ppmv)	6	3.3	5.2	15	10	11	7	7	3,2	5,5
Naphtha										
IBP (ASTM D-86 ºC)	-	48	-	67	-	37	41	41	-	-
10	-	81	-	77	-	53	54	54	-	-
30	-	105	-	83	-	73	63	63	-	-
50	-	109	-	90	-	81	73	73	-	-
70	-	118	-	98	-	106	83	83	-	-
90	-	122	-	108	-	163	98	98	-	-
FBP	-	135	-	120	-	195	120	120	-	-
PONA (%mol)	-		-							
Paraffins	-	64.8	-	56	-	69.74	97.3	97,3	-	-
Olefins		0.00		0	-	1.75	0.3	0,3	-	-
Naphtenics	-	29.1	-	39	-	21.02	-	0	-	-
Aromatics	-	6.1	-	5	-	7.5	2.4	2,4	-	-
Sulfur (ppm w)	-	0.2	-	0.1	-	40	60	60	-	-
Specific gravity (20/4ºC)	-	0.73	-	0.72	-	0.70	0.71	0,71	-	-
Molecular weight (g/gmol)		103.9		96.0		97.9	85.6	85.6		
CoMo reactor										
Outlet pressure (kgf/cm^2g)	27.4	28.8	22.4	29.6	27.8	31.3	28.3	28.3	27.6	30
Bed Diameter (mm)	1500	2000	1050	1700	1700	2000	2000	2000	2800	2200
Bed Height (mm)	1410	4090	2830	3195	2020	3320	3550	3550	5770	4440
Inventory (m^3)	2.5	12.8	2.5	7.20	4.50	10.67	11.10	11.10	35.30	16.80
Maximum pressure drop (kgf/cm^2)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Maximum temperature (ºC)	400	400	400	370	400	380	400	400	400	400
Maximum organosulfur escape (ppmv)	0.1	0.1	0.1	0.1	0.1	0.1	0,1	0.1	0.1	0.1

Note: H_2/naphtha ratio to U-704 is in Nm^3H_2/kg naphtha

Annex 2: Model of form to report the expect performance at 72 months.

Location	*Unit*	*Inlet Temperature (°C)*	*Pressure drop (kgf/cm²)*	*Maximum organosulfur escape (ppmv)*
REPAR	U-2600			
REPAR	U-22311			
RLAM	U-34			
RPBC	U-2311			
RECAP	U-2311			
REFAP	U-704			
REPLAN	U-241			
REPLAN	U-241A			
REPLAN	U-4241			
REGAP	U-409			

Note: The conditions to simulate performance is provide in Annex 1; the inlet temperature could be between 300°C and maximum inlet temperature (Annex 1).

Annex 3: HDT product characteristics

	Information from supplier	Requirements	Methods and/or Observation
Product Name		N/A	N/A
Form		Rings, extrudates, spheres	Visual inspection
Outside Diameter (OD) (mm)		between 2.0 and 5.0 mm	1
Length/diameter(mm/mm)		Between 1 and 4	2
Bulk density (kg/L)		≥ 0.50	3
Total surface area (m^2/g)		≥ 100	4
Composition (wt%)			
Co expressed as CoO		≥ 2,8	5
Mo expressed as MoO_3		≥ 8,8	5
Balance		alumina	5
Impurities (wt%)			
Ni + Zn		< 0.2	5
Fe + Si		< 0.2	5
Sulphur (S)		< 0.1	6

1) Value of 30 samples measured with pachymeter; **2)** Relationship between length and particle diameter. A content equal to or greater than 90% of the particles must respect this relationship **3)** The "freely settled bulk density" is obtained using a 500 mL graduated cylinders with diameter at around 9 cm (reference ASTM D1895); 4) Determined by N2 adsorption-desorption at -196 ºC in a Micromeritcs ASAP 2400 or similar equipment. Prior to the analysis the samples are pretreated at 300 ºC in vacuum (reference: ASTM D3663); 5**)** Determined by X-ray fluorescence spectrometry (XRF) and/or Atomic absorption (AA); 6**)** Determined by combustion method.

Annex 4: Additional requirements to product

	Requirements	Methods
Fines generated in the loading test (%w/w)	< 3	7

7) One hundred grams of CoMo product is dropped into a tube plastic onto a metal surface placed in the bottom from a height of 1.5m. The sample is sieved in -24 mesh and the amount of fines is calculated as: %w/w = fines (< 24 mesh)/original mass sample x 100.

The following analysis, at Petrobras discretion, may be carried out to identify issues related to compliance with mandatory items and understanding of possible failure:

8) X-Ray diffraction (XRD): This technique is used for identification of crystalline phases present in the material.

9) Thermogravimetric analysis (TGA): This technique measures the amount of weight change of a material, either as function of increasing temperature, or isothermally as a function of time, in an atmosphere of a selected gas. Typically, equipment used at Petrobras is TGA/SDTA 851 (Metter Toledo).

10) Mechanical strength (CS): The extrudated radial crushing strength (reference ASTM 6175) and the bulk crushing strength (reference ASTM D7084-4) could be made to confirm an abnormal low catalyst strength (> 3% w/w in simulated loading criterion in Annex 4). In the case of this test, two HDS products with previous experience at Petrobras will be used as reference.

11) Pore volume: The solid is impregnated with a water enough to fill the pores (incipient wetness technique).

12) Activity test: Before the test, the catalysts are heated to 400oC in H_2 flow for 4h. The temperature is then reduced to 360 ºC and a feed containing 1% DMDS in heptane is fed to the reactor. After pretreatment, a synthetic naphtha consisting of 10% toluene in n-heptane balance and containing 15 ppm of sulfur as thiophene is treated over an HDT catalysts at 20 kgf/cm^2, T=360 ºC, LHSV = 2.0 h^{-1}. After 48 hours of operation, the amount of organosulfur in the exit of reactor must be less than 0.1 ppm.

Annex 5 – Comprovante de entrega de amostra

PETROBRAS	COMPROVANTE DE RECEBIMENTO DE AMOSTRAS	
	OPORTUNIDADE:	Catalisadores HDT UGH
	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)