

Technical Specification for the purchasing process of “High Temperature Shift” (HTS) 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 “High Temperature Shift” (HTS) catalysts used to convert carbon monoxide in the steam reforming process (SMR) of natural gas, propane, butane, or naphtha.

2. Description of “High Temperature Shift” (HTS) Catalysts

The “High Temperature Shift” (HTS) section of Hydrogen Generation Units (HGU) is composed of one catalysts bed where the carbon monoxide (CO) reacts with water (H₂O) to produce hydrogen (H₂) and carbon dioxide (CO₂), (CO + H₂O = CO₂ + H₂), in an adiabatic reactor with typical inlet temperature from 320°C to 380°C.

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.

4. High Temperature Shift Technical Requirements

4.1. The HTS catalyst offered should be able to allow the operation of the hydrogen generation unit (HGU) under conditions detailed in the Annex 1 for at least 72 months. The conditions accepted as indicators of the HTS end of run (EOR) are given in the Annex 1: Maximum CO leakage; Maximum inlet temperature and Maximum reactor pressure drop. The SUPPLIER must inform the expect performance at 72 months for each PETROBRAS’ unit in accordance with Annex 2.

4.1.1. The SUPPLIER must send the performance simulation at EOR used to fill the Annex 2. The information provided must fit the conditions defined in Annex 1, for each PETROBRAS’ units.

4.1.2. The SUPPLIER should inform, at least, the following information:

Reactor outlet temperature (°C); Approach to equilibrium considered (°C); Temperature profile through the catalyst bed (°C); Reactor outlet gas composition (%vol dry base), by-products and expected pressure drop (kgf/cm²).

4.2. The SUPPLIER must inform the characteristics of the offered product completing the template in Annex 3. The HTS 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. If the supplier sent a representative sample of its product in Petronect invitation 7003455829, it is not necessary to send a sample of the same product. In this case, the supplier must attach to the process the previous receipt.

4.4.SUPPLIER must inform for the high temperature shift 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. Based on industrial information sent by PETROBRAS, make an evaluation of product's performance.

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

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

6. Disqualification Criteria

6.1. 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 - High Temperature Shift 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 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.
- 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

considering Annex 2 and 3.

Annex 1: Feedstock and Process Information

Refinery	REPAR	RPBC	RECAP	REFAP	REPLAN	REPLAN	REPLAN	REVAP	REGAP	REDUC	REDUC
Plant number	U-22311	U-2311	U-2311	U-702	U-241	U-241A	U-4241	U-292	U-409	U-3900	U-1620
Dry Feed flow (kmol/h)	4231.66	2245.58	1502.32	1551.91	2020.18	2020.18	5431.62	619.8	2963.97	1551.91	145.5
Feed gas (% mol dry)											
CH ₄	5.01	8.9	4.69	8.41	5.15	5.15	4.77	3.84	5.32	8.41	5.13
CO	12.47	11.88	12.56	12.29	12.71	12.71	12.56	12.61	10.5	12.29	9.01
CO ₂	9.62	9.39	9.65	8.91	9.24	9.24	9.62	9.77	11	8.91	13.15
H ₂	72.69	69.7	72.83	70.18	72.55	72.55	72.87	73.65	72.92	70.19	72.59
N ₂	0.21	0.13	0.27	0.21	0.35	0.35	0.18	0.13	0.26	0.2	0.12
Inlet steam/gas ratio (mol/mol)	0.62	0.60	0.62	0.59	0.63	0.63	0.62	0.96	0.74	0.59	1.03
GHSV (h ⁻¹) Note 1	3142	2338	3170	2304	3000	3000	3039	1841	2546	2304	1515
Reactor											
Height/diameter (mm/mm)	1.40	1.09	1.19	1.18	1.18	1.18	1.40	0.66	1.50	1.18	3.03
Inventory (m ³)	32.4	23.1	11.4	16.2	16.2	16.2	43	8.1	28	16.2	2.31
Outlet pressure (kg/cm ²)	23.6	24.3	22.5	23.9	22.9	22.9	22.8	22	24.6	23.9	27.6
Max Inlet temperature (°C)	371	371	371	371	370	370	371	380	371	371	370
Maximum reactor pressure drop (kg/cm²)	0.30	2.5	0.5	0.5	0.4	0.4	0.4	0.5	0.5	0.5	0.4
Maximum CO leakage (%v/v)	3.61	3.38	3.65	3.52	3.63	3.63	3.66	2.35	2.54	4.0	1.71

Note1: GHSV in dry base and using STP (20°C, 1 atm), 1mol = 24,0548l

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

<i>Location</i>	<i>Unit</i>	<i>Inlet Temperature (°C)</i>	<i>Pressure drop (kgf/cm²)</i>	<i>CO leakage (% v/v)</i>	<i>Approach (°C)</i>
REPAR	U-22311				
RPBC	U-2311				
RECAP	U-2311				
REFAP	U-702				
REPLAN	U-241				
REPLAN	U-241A				
REPLAN	U-4241				
REVAP	U-292				
REGAP	U-409				
REDUC	U-3900				
REDUC	U-1620				

Note: The conditions to simulate performance is provide in Annex 1. The inlet temperature is free, respecting the limit informed in Annex 1 (Maximum Inlet Temperature).

Annex 3: Product characteristics

	Information from supplier	Requirements	Methods and/or Observation
Product Name		N/A	N/A
Form		pellets	Visual inspection
diameter (mm)		between 5.0 and 9.5 mm	1
Length (mm)		between 3.5 and 6.2mm	1
Length/diameter (mm/mm)		Between 0.5 and 1.2	2
Bulk density (kg/l)		> 1.0	3
Specific surface area in the oxidized form (m ² /g)		> 30	4
Pore volume in the oxidized form (cm ³ /g)		> 0.15	5
Composition (wt%)			
Fe		> 53	6
Cr		> 5.0	6
Cu		> 0.8	6
Impurities			
Cr ⁶⁺ (ppm)		< 5000	7
S (ppm)		< 500	8
Na (wt%)		< 0.4	6

1) Medium average of 30 samples measured with pachymeter; 2) Relationship between length and particle diameter 3) The “freely settled bulk density” is obtained using a 500mL graduated cylinders with diameter at around 9 cm (reference ASTM D1895); 4) Determined by N₂ adsorption-desorption at -196°C in a Micromeritics ASAP 2400 or similar equipment. Prior to the analysis the samples are pretreated at 300°C in vacuum (reference: ASTM D3663); 5) The solid is impregnated with a water enough to fill the pores (incipient wetness technique); 6) Determined by Atomic Absorption (AA); 7) Determined by UV-Vis spectrometry using 1,5 difenylcarbazide, based on a modification of the ABNT NBR 13728-1996 method: One gram (1)g of the previously ground sample catalyst is left in contact with 100 ml of deionized water in an ultrasound bath at 35°C for 20 min. A portion of the solution is diluted and analyzed by UV-Vis spectrometry. Note: Qualitatively, if the color of the aqueous solution obtained by contacting 40 g of the sample in the original format with 100 mL of aqueous solution kept at 50°C for 10 min is yellow, experience shows that the product will be out of the desired specification, 8) Determined by combustion method.

Annex 4: Additional requirements to product

	Requirements	Methods and/or Observation
Initial Conversion (%)	> 20	9
Conversion after accelerated deactivation (%)	> 5.5	10
“HTS fines” generated in the loading (%w/w)	< 0.6	11
Mass loss at 600°C (%w/w)	< 17	12

9) Petrobras Method: The ground catalyst in the range of 150 to 100 mesh has the initial CO conversion activity measured under the conditions of T = 350°C, P = 1 atm, GHSV (h⁻¹) = 22143 (wet base), V/G = 0, 55 mol/mol using a gas with a composition (% v/v) of CO = 10%, CO₂ = 10%, CH₄ = 2%, H₂ = 78% in automatic equipment (Micromeritics AutoChem II). Note: In case of Micromeritics AutoChem II maintenance, alternatively the test will be carried out with the catalyst ground between 28 to 35 mesh, T = 350°C, P = 20 atm, V/G = 0.41 mol/mol, GHSV = 18400h⁻¹. The catalyst will initially be stabilized by operating at 430°C/6h.

10) Petrobras Method: The catalyst will be deactivated by exposition to 500°C at 6h in V/G = 0,55 mol/mol and after the activity expressed by CO conversion is measured at 350°C as previous reported in item 9.

11) One hundred grams of HTS 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.


12) By 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 (Mettler Toledo). Acceptable weight reduction is at maximum 15% w/w in flow of nitrogen until 600°C.

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

13) X-Ray diffraction (XRD): This technique is used for identification of crystalline phases present in the material. The technique could be used to identify the crystalline species of iron compounds and help to understand and confirm an abnormal loss of mass detected by TGA analyses. (Total mass loss over 15% w/w criterion in Annex 4).

14) 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 (> 0,6% w/w in simulated loading criterion in Annex 4 - item 11). In the case of this test, two HTS products with previous experience at Petrobras will be used as reference.

Annex 5 - Comprovante de entrega de amostra

 PETROBRAS	COMPROVANTE DE RECEBIMENTO DE AMOSTRAS	
	OPORTUNIDADE:	Catalisadores HTS 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)