

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

2. Description of “Low Temperature Shift” (LTS) Catalysts

The “Low Temperature Shift” (LTS) section of Hydrogen Generation Units (HGU) is composed of one catalysts bed where the carbon monoxide reacts with water (H₂O) to produce hydrogen (H₂) and carbon dioxide (CO₂), ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) in an adiabatic reactor with typical inlet temperature range from 190°C to 230°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. Low Temperature Shift Technical Requirements

4.1. The LTS 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 36 months. The conditions accepted as indicators of the LTS 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 36 months for each PETROBRAS’ unit in accordance with Annex 2. The LTS catalysts offered should be for low methanol production.

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).

- 4.1.3. The product offered may have a guard bed product on top of it to capture sulfur or chloride, limited to less than 10%v/v of the total volume of the bed, with the minimum characteristics described in Annex 5.
- 4.2. The SUPPLIER must inform the characteristics of the offered product completing the template in Annex 3. The LTS 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 to verify its compliance with the requirements described in Annex 3 and 4.
 - 4.3.1. The sample amount required is around 1kg.
 - 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 showed below. In case of changes in this information, Petrobras will inform the participants through the appropriate channels.

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Av. Horácio Macedo, 950, Cidade Universitária (Ilha do Fundão)
Rio de Janeiro - Brazil - ZIP: 21941-915
Attention: Roberto 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 6. 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 low 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 batch 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 - Low 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 (LTS section)

<i>Refinery</i>	<i>REVAP</i>	<i>REDUC</i>
Plant number	U-292	U-1620
Dry Feed flow (kmol/h)	664.7	155.94
GHSV (dry base) h-1	2076.5	2076.5
Feed gas data (% mol dry)		
CH4	3.59	4.79
CO	2.35	1.71
CO2	18.52	18.97
H2	75.43	74.42
N2	0.11	0.11
Inlet steam/gas ratio (mol/mol)	0.83	0.89
Outlet pressure (kg/cm ²)	21	27.2
Maximum Inlet temperature (°C)	220	210
Maximum reactor pressure drop (kg/cm ²)	0.5	0.4
Maximum CO leakage (%v/v)	0.31	0.26
Reactor dimension		
height/diameter (mm/mm)	0.628	0.628
Inventory (m ³)	7.7	2.16

Annex 2: Model of form to report the expect performance at 36 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>
REVAP	U-292				
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		Cylinders (tablets, pellets)	Visual inspection
diameter (mm)		between 3.0 and 6.0 mm	1
Length (mm)		between 2.5 and 5.0mm	1
Length/diameter(mm/mm)		Between 0.5 and 1.1	2
Bulk density (kg/l)		≥ 1,05	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%)			
Cu expressed as CuO		> 35	6
Zn expressed as ZnO		> 20	6
Al expressed as Al ₂ O ₃		> 8	6
Promoter (Cs, K or others) to low methanol subproducts		Must be present. < 2	6
Other promoters and binders as Ca La, Ce and others		allowed	6
Impurities			
Cl (ppm)		< 150	9
S (ppm)		< 450	8
Na (ppm)		< 1000	7

- 1) Value 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 X-ray fluorescence spectrometry (XRF); 7) Determined by Atomic Absorption (AA); 8) Determined by combustion method (LECO); 9) Determined by ion chromatography.

Annex 4: Additional requirements to product

	Requirements	Methods
CO Initial Conversion (%)	≥ 60	10
CO conversion after 1 ^o thermal accelerated deactivation teste (%)	≥ 28	10
CO conversion after 2 ^o thermal accelerated deactivation test (%)	≥ 20	10
CO Initial Conversion after chlorine doping (%)	≥ 40	11
CO conversion after 1 ^o thermal accelerated deactivation teste with chlorine doping (%)	≥ 18	11
CO conversion after 2 ^o thermal accelerated deactivation test with chlorine doping (%)	≥ 15	11
Temperature in order to have more than 90% of H ₂ consumption in TPR test	< 200°C	12
Fines generated in the loading test (%w/w)	< 0,4	13

10) 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 = 200°C, P = 1 atm, GHSV (h⁻¹) = 12000 (dry base), V/G = 0, 55 mol/mol using a gas with a composition (% v/v) of CO = 3%, CO₂ = 15%, CH₄ = 2%, H₂ = 80% in automatic equipment (Micromeritics AutoChem II). The catalyst is previously reduced in 10%H₂/argon at 230°C with rate of 1°C/min, P= 1 atm with GHSV (-1) at about 10.000 h⁻¹. The first deactivation step is carried out at 430°C in H₂ for 4h, after which the measurement condition of the initial conversion is returned. The second deactivation step is like step 1. 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 = 200°C, P = 20 atm, V/G = 0.60, GHSV = 26300h⁻¹ (wet base). The catalyst is previously reduced at 200°C for 14h in 1%H₂ in N₂ with 1°C/min rate. The first deactivation step is carried out at 350°C /12h, after which the measurement condition of the initial conversion is returned. The second deactivation step is like step 1. The minimum CO conversion in this test becomes 70% v/v, 65% and 55%, respectively. **11) Petrobras Method:** The catalyst ground in the range of 150 to 100 mesh is impregnated by the pore volume method with a aqueous solution of HCl in order to have 500 ppm of chorine in the catalysts sample. After the activity of the catalyst is tested as previous reported in item 9. **12) In Temperature Programmed Reduction (TPR) test,** approximately 0.2 g of sample is treated at 150°C overnight in a vacuum and after at 300°C with a heating ramp of 5°C/min for 1 hour. The sample is cooled to room temperature in an argon flow and then reduced in 10% H₂ in Ar, with a flow rate of 50mL /min with a heating ramp of 2°C/ min. The H₂ consumption is monitored by thermal conductivity detector. **13) One hundred grams of LTS 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:

14) X-Ray diffraction (XRD): This technique is used for identification of crystalline phases present in the material. This analysis does not imply disqualification.


15) 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). This analysis does not imply disqualification.

16) 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 (> 0.4% w/w in simulated loading criterion in Attachment 4). In the case of this test, two LTS products with previous experience at Petrobras will be used as reference.

Annex 5: Guard bed

Product based on copper oxide, having form and dimensions as described in Annex 3, Fines generated in the loading test and reducibility characteristics as described in Annex 4 (method 11).

Annex 6 - Comprovante de entrega de amostra

 PETROBRAS	COMPROVANTE DE RECEBIMENTO DE AMOSTRAS	
	OPORTUNIDADE:	Catalisadores LTS 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)