

Technical Specification for the purchasing process of “Steam Reforming” (REF) catalysts for use in Hydrogen Generations Units (HGU)

1. Objective

The objective of this document is to specify the technical requirements for the process of purchasing “Steam Reforming” (REF) catalysts used in the steam reforming process (SRM) of natural gas, propane, butane, or naphtha.

2. Description of “Steam Reforming” (REF) Catalysts

The primary “Steam Reforming” (REF) section of Hydrogen Generation Units (HGU) is composed of a furnace with a variable number of metallic tubes (reactors), with a fixed bed catalyst where the hydrocarbons compounds react with water to produce a rich hydrogen gas (synthesis gas), in typical inlet temperature range from 450°C to 650°C and exit temperature range from 800°C to 950°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 and 2.

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).

3.1.2. The units where only natural gas is indicated as feedstock don't have alternative feedstock. In this case the suppliers should take in consideration that unexpected feedstock composition fluctuation or eventual contaminations with heavy hydrocarbon fractions can occur.

4. Reforming Technical Requirements

4.1. The catalysts offered should be able to allow the operation of the plant under optimum conditions for at least 48 months. The conditions accepted as

indicators of the catalysts end of run (EOR) are given in the Annex 2: Maximum reformer outlet temperature; Maximum reformer tube walls temperature; Maximum reformer pressure drop and maximum methane slip.

4.1.1. SUPPLIER must send the performance simulation at EOR used to fill the Annex 3. The information provided must fit the conditions defined in Annex 2, for each PETROBRAS' units.

4.1.2. The supplier must inform the type and volume of each catalysts used.

4.2. The relation between the equivalent diameter of the pellet (diameter of the sphere with the same volume) and the inner tube diameter of each unit must be less than or equal to 0,21.

4.3. The catalysts offered should be suitable for the type of feedstock of each hydrogen unit.

4.3.1. For the units that have naphtha or propane as an alternative feedstock the reformer inventory offered should be able to process efficiently naphtha or propane or natural gas, mixed or not, in any proportion. Part of the inventory of catalysts must contain potassium as a promoter to prevent deposition of coke. SUPPLIER must define the catalysts types, quantities, and the optimum reformer loading.

4.3.2. The maximum amount of catalyst without potassium or similar promoter used to reduce the coke deposition is 60%v/v, except to units REFAP/U-704 and RNEST/U-35 that has a pre-reforming section and can use 100% of not promoted catalyst. SUPPLIER must inform the different types and proportions between products for each unit.

4.4. SUPPLIER must inform the characteristics of the offered product completing the template in Annex 3. The REF products offered by SUPPLIER must have the minimum characteristics in all the items described in the Annex 4 and 5.

4.5.A representative product sample is requested to be evaluated by PETROBRAS in order to verify its compliance with the requirements described in Annex 4 and 5.

4.5.1. The sample amount required is around 1 kg.

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

4.5.3. 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)

4.5.4. SUPPLIER must certify that the sample was delivered at CENPES sending, through PETROCONNECT, the receipt presented in Annex 6. The document must be signed by a PETROBRAS' technical representative in accordance with items 4.5.1; 4.5.2 and 4.5.3. The delivery must respect the deadlines defined in the bid process.

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

4.6.1. 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).

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

4.6.3. Typical regeneration procedures to coke and/or sulfur (steaming).

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.

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 - Reforming 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 4.5) 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 Information

Refinery	REPAR	REPAR	RLAM	RPBC	RPBC	RECAP	REFAP	REFAP	REPLAN
Plant number	U-2600	U-22311	U-34	U-2311	U-22311	U-2311	U-702	U-704	U-241
Naphtha (std m3/h)	-	27	-	14	-	-	-	20.9	13.8
Natural Gas (Nm ³ /h)	4323	22851	3901	13000	29301	7759	9350	17372	11542
Natural Gas									
CO ₂ (% mol dry)	1.25	1.20	0.69	0.16	1.47	0.5	0.32	0.67	1.85
Naphtha									
IBP (ASTM D-86 oC)	-	48	-	67	-	-	-	37	41
10	-	81	-	77	-	-	-	53	54
30	-	105	-	83	-	-	-	73	63
50	-	109	-	90	-	-	-	81	73
70	-	118	-	98	-	-	-	106	83
90	-	122	-	108	-	-	-	163	98
FBP	-	135	-	120	-	-	-	195	120
PONA (%mol)	-		-						
Paraffins	-	64.8	-	56	-	-	-	69.74	97.3
Olefins		0.00		0	-	-	-	1.75	0.3
Naphtenics	-	29.1	-	39	-	-	-	21.02	-
Aromatics	-	6.1	-	5	-	-	-	7.5	2.4
Specific gravity (20/4°C)	-	0.73	-	0.72	-	-	-	0.70	0.71
Molecular weight (g/gmol)		103.9		96.0				97.9	85.6

Annex 1: Feedstock Information (continuation)

Refinery	REPLAN	REPLAN	REVAP	REVAP	REGAP	REDUC	REDUC	RNEST
Plant number	U-241A	U-4241	U-292	U-294	U-409	U-3900	U-1620	U-35
Naphtha (std m3/h)	13.8	-	3.6	-	-	-	-	50.5
Natural Gas (Nm ³ /h)	11542	29301	2746	18395	16042	9350	676.7	32444
Natural Gas								
CO ₂ (% mol dry)	1.85	1.47	0.64	0.87	0.87	0.32	0.4	0.35
Naphtha								
IBP (ASTM D-86 oC)	41	-	40	-	-	-	-	38
10	54	-	71	-	-	-	-	50
30	63	-	90	-	-	-	-	63
50	73	-	100	-	-	-	-	79
70	83	-	117	-	-	-	-	95
90	98	-	139	-	-	-	-	120
FBP	120	-	158	-	-	-	-	150
PONA (%mol)								
Paraffins	97.3	-	56	-	-	-	-	64.96
Olefins	0.3	-	0.6	-	-	-	-	<0.6
Naphtenics	0	-	35.2	-	-	-	-	31.77
Aromatics	2.4	-	8.2	-	-	-	-	3.20
Specific gravity (20/4°C)	0.71	-	0.72	-	-	-	-	0.709
Molecular weight (g/gmol)	85.6		101.6					91.51

Notes: a) The recycled H₂ in all units is 99.9%. except to U-1620 (93.6% H₂, 5.9% CH₄, 0.32% CO, 0.15% N₂); b) The sulfur amount in the inlet of reformer is less than 0.1ppmv (After hydrotreatment section).

Annex 2: Process and reformer information

	REPAR	REPAR	RLAM	RPBC	RPBC	RECAP	REFAP	REFAP
	U-2600	U-22311	U-34	U-2311	U-22311	U-2311	U-702	U-704
Steam/C ratio (mol/mol)	3.5	3.5	3.5	3	3.5	3.5	3	2.1
Inlet Temperature (°C)	510	510	510	480	510	510	485	625 a 650
Outlet pressure (kg/cm ²)	24	24.5	20.6	25.6	23.6	23.5	25.2	23.6
H ₂ /NG ratio (mol/mol)	0.05	0.05	0.05	0.05	0.05	0.03	0.05	0.05
H ₂ /Naphtha ratio (mol/mol)	0.25	-	0.25	0.25	-	0.25	-	0.20*
Maximum CH ₄ slip (%v/v)	5.17	5.01	4.1	8.86	4.77	4.69	8.14	2.6 (GN/GC)
Max outlet Temperature (°C)	850	850	850	842	850	850	840	910
Maximum reformer tube walls temperature (°C)	930	933	930	932	958	929	910	992
Maximum reformer pressure drop (kg/cm ²)	3	3.0	1.5	3.2	3.1	3	3.1	2.7
Furnace Type	Top fired	Top fired	Top fired	Top fired	Top fired	Top fired	Top fired	Side Fired
Catalyst inventory (m ³)	5.2	27.0	5.4	16.1	37.3	9.4	11.1	16.2
Heated height	10000	12000	9900	9200	11250	11500	12120	-
Number of tubes/Number of rows	64/2	264/6	64/2	160/4	312/6	96/2	112/4	132/2
Tube outside diameter	121.6	123.4	122.8	135	143.1	122.8	124	134.4
Tube inside diameter	101.6	101.6	101.6	101.6	114.3	101.6	101.6	108.1
Overall length	10648	12650	10500	12725	12075	12100	12720	14705
Load length	10400	12450	10300	12425	11612	11950	12500	13450

Annex 2: Process and reformer information (continuation)

	REPLAN	REPLAN	REPLAN	REVAP	REVAP	REGAP	REDUC	REDUC	RNEST
	U-241	U-241A	U-4241	U-292	U-294	U-409	U-3900	U-1620	U-35
Steam/C ratio (mol/mol)	3.5	3.5	3.5	5	4	4	3	5	2.3
Inlet Temperature (°C)	507	507	510	490	510	510	485	443	650
Outlet pressure (kg/cm ²)	23.9	23.9	23.6	23	25.5	25.6	25.2	27.9	23.3
H ₂ /NG ratio (mol/mol)	-	0.05	0.05	0.05	0.05	0.05	0.05	-	0.05
H ₂ /Naphtha ratio (mol/mol)	-	0.25	-	0.25	-	-	-	-	0.20*
Maximum CH ₄ slip (%v/v)	5.14	5.14	4.77	3.84	5.4	5.32	8.4	5.13	5.48
Max outlet temperature (°C)	850	850	850	815	830	830	840	779	915
Max reformer tube walls temperature (°C)	972	972	958	890	916	916	938	-	984
Maximum reformer pressure drop (kgf/cm ²)	3.3	3.3	3.1	4.5	3.4	3.4	3.1	3.1	2.7
Furnace Type	Top fired	Top fired	Top fired	Side fired	Top fired	Top fired	Top fired	Side Fired	Side Fired
Catalyst inventory (m ³)	14.8	14.8	37.3	4.4	20.2	20.4	11.3	1.38	37.5
Heated height	11031	11031	11250	10100	11500	11500	12120	-	13000
Number of tubes/rows	160/4	160/4	312/6	34/2	208/4	208/4	112/4	14/1	312/2
Tube outside diameter	131.6	131.6	143.1	152	121.6	121.6	127.6	-	136
Tube inside diameter	101.6	101.6	114.3	127.4	101.6	101.6	101.6	105	106.8
Overall length	11738	11738	12075	10784	12100	12100	12826	11601	-
Load length	11438	11438	11612	10100	11960	11894	12426	11382	-

Notes: a) Tube material: HP modified + Nb. except REFAP U-704 (25Cr, 35Ni, Nb,Ti); REVAP U-292 (Pyrotherm G24/24 Nb (IN-519)); RNEST U-35 (25Cr35NiNbTi). b) *The H₂/naphtha ratio in U-704 and U-35 is in Nm³H₂/kg naphtha.

Annex 3: Model of form to report the expect performance at 48 months.

<i>Location</i>	<i>Unit</i>	<i>CH₄ slip (%)</i>	<i>Outlet temperature (°C)</i>	<i>Maximum tube temperature (°C)</i>	<i>Pressure drop (kgf/cm²)</i>
REPAR	U-2600				
REPAR	U-22311				
RLAM	U-34				
RPBC	U-2311				
RPBC	U-22311				
RECAP	U-2311				
REFAP	U-702				
REFAP	U-704				
REPLAN	U-241				
REPLAN	U-241A				
REPLAN	U-4241				
REVAP	U-292				
REVAP	U-294				
REGAP	U-409				
REDUC	U-3900				
REDUC	U-1620				
RNEST	U-35				

Note 1: The conditions to simulate performance and the EOR conditions are provide in annex 1 and 2.

Annex 4: steam reforming product characteristics
(Obs: use this model for each product offered).

	Product 1	Product 2	Product x	Requirements	Note
Product Name				inform	N/A
Form				Multiples holes	1
Dimension (H x DO) mm				See note 2	2
Bulk density (kg/l)				≥ 0.8	3
Chemical Composition (wt%)					
Ni expressed as NiO				≥ 11	4
K expressed as K ₂ O				Inform	4
Others (description and amount)				inform	4
.					
.					
.					
Impurities (ppm)					
Sulfur				< 600	5
Chlorine				inform	6
Free SiO ₂				inform	4

- 1) Formats such as cylinders, spheres or fluted domed with multiple holes will be accepted. Single hole formats, such as raschig rings, will not be accepted. Visual Inspection.
- 2) Dimensions of the particle (H=Length; DO = external diameter). Value of 30 samples measured with pachymeter. The relation between the equivalent diameter of the pellet (diameter of the sphere with the same volume) and the inner tube diameter of each unit must be less than or equal to 0,21.
- 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 X-ray fluorescence spectrometry (XRF). Note 1: The silica and potassium should be in the form of fixed compounds. Volatile compounds under operating conditions, such as SiO₂ or KOH, at levels greater than 0.5% w/w, are not acceptable. The material can be analyzed by X-Ray diffraction (XRD) in order to help to identify the crystalline phases. Note 2: Part of the inventory of catalysts must contain potassium as a promoter to prevent deposition of coke.
- 5) Determined by combustion method.
- 6) Determined by ion chromatography.

Annex 5: Additional requirements to product

	Requirements	Methods
Initial activity (methane conversion at 550°C) (%)	≥ 30% (case 1) ≥ 40% (case 2)	7
Activity after thermal deactivation test (methane conversion at 550°C) (%)	≥ 27%	8
Mass increase in coke accelerated test (mg/mg.min)*100	< 0.7 (case 3) < 2.5 (case 4)	9
Broken particles in the loading test (%)	< 2	10

- 7) The methane steam reforming activity is carried at atmospheric pressure using the commercial catalyst ground in mesh <100 (the pellets will be ground entirely, and a homogeneous portion will be used, valid for eggshell products). The samples are subjected to pretreatment by heating from room temperature to 750°C at the rate of 30°C/min in 10% H₂/argon flow saturated with steam at 50°C. The temperature of 750°C was maintained for 2h to complete the reduction process. The steam reforming reaction are carried out at 500°C, 550°C and 600°C in a flow of methane and steam (steam/carbon of 2,2 mol/mol). The space velocity (VE) is 96000 (L/kg.h) in dry base. The methane conversion obtained for different products are corrected to the same volumetric base (GHSV = 96000 h⁻¹ in dry base) using a kinetic of first order and the catalyst density. The case 1 is valid for catalysts that promoted with potassium (used in the top of tubes). The case 2 is valid for catalysts without potassium (used in bottom of tubes).
- 8) After measuring the initial steam reforming activity of methane, as described in item 7, the catalyst is subjected to heat treatment “in-situ” with 10%H₂/argon flow saturated with steam at 50°C for 900°C for 4h. Next, the methane steam reforming activity is measured again as described in item 7;
- 9) The catalysts are tested in thermogravimetric analysis equipment (TGA). Before the test, the original pellets are maintained for 1 hour in deionized water with a water/catalyst ratio of 10:1 w/w followed by drying at 150°C. Typically, the tests are performed using 25 mg of catalyst ground in the range less than 170 mesh. Initially, a pretreatment step is performed by passing 40 mL/min of mixture containing 10% (v/v) hydrogen in argon saturated with water vapor at 15°C together with 40 mL/min of nitrogen with temperature programming ranging from 100°C to 750°C at the rate 10°C/min, maintained for 1h. Then the temperature is reduced to 350°C and measurements is taken of coke formation rates, by replacing the H₂/argon stream with a synthetic stream consisting of 2.9% hydrogen; 1.8% N₂; 13,2% CO; 15,0% CO₂; 43,6% CH₄; 0.4% C₃H₈, 0.1% nC₅ e 0.2% ethene saturated with water vapor at 15°C with temperature programming from 350°C to 700°C at a rate of 5°C/min. The increases in mass in the coking step, expressed as mg/(mg-catalyst.min) is associated to coke deposition. Case 3 is valid for catalysts with a high potassium content, typically used to process naphtha. Case 3 is valid for catalysts with a medium potassium content, typically used to process


heavy natural gas.

- 10) Thirty (30) pellets are dropped in a free fall of 1.5 m in a tube with a diameter of 7 cm under a metallic surface. After the drop the broken particles are counted and the value expressed as a percentage.

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

- 11) X-Ray diffraction (XRD): This technique is used for identification of crystalline phases present in the material.
- 12) Mechanical strength (CS): The extrudated radial crushing strength (reference ASTM D695-96) could be made to confirm an abnormal low catalyst strength (> 2% in simulated loading criterion in Annex 5). Typically, 30 particles of the catalyst are evaluated in the radical sense using a 500 kgf cell, speed of 1.3 mm / min. Values are normalized by the particle length and are expressed in kgf/cm and must be > 22 kgf/cm.
- 13) Pore volume: The solid is impregnated with a water enough to fill the pores (incipient wetness technique).
- 14) Specific Surface Area: 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).
- 15) Cyclohexane dehydrogenation. This test can be used to estimate the metallic surface area.
- 16) Coke resistance. The catalyst is reduced overnight at 650°C and 10 kgf/cm² with 6 mol/mol H₂/H₂O ratio. The reaction is conducted with a mixture of toluene and n-heptane (4:1 v/v), with steam/carbon ratio (SCR) of 4 mol/mol at 650°C and 25 bar. The steam/carbon ratio (SCR) is decreased in increments of 0.5 mol/mol until an increase in pressure drop is observed. Catalysts for use with naphtha should have increased in pressure drop (typically over 1kgf/cm²) for steam/carbon ratio (SCR) ≤1.5 mol/mol. This test can be performed when the test described in Annex 5 is not available.
- 17) Programmed Temperature Reduction (RTP): Typically, 0.3 grams of the previously ground catalyst (mesh <100) are initially pretreated at 400°C in Argon flow. Then a gas containing 10% H₂ in argon is passed over the catalyst between 100°C to 1000°C at a rate of 5°C/min. The consumption of H₂, indicative of reduction of oxide species, is monitored by a thermal conductivity detector. The product received at the refinery must have the same or better reducibility characteristics as the sample sent.

Annex 6 - Comprovante de entrega de amostra

	COMPROVANTE DE RECEBIMENTO DE AMOSTRAS	
	OPORTUNIDADE:	Catalisadores Reforma 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)