

## Technical Specification for the purchasing process of “Pre-Reforming” (PREF) 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 “Pre-Reforming” (PREF) catalysts used in the steam reforming process (SRM) of natural gas, propane, butane, or naphtha.

### 2. Description of Pre-Reforming Catalysts

The “Pre-Reforming” (PREF) section of Hydrogen Generation Units (HGU) is composed of fixed bed catalyst where the hydrocarbons compounds react with steam in presence of hydrogen to produce a mixture of CH<sub>4</sub>, CO, CO<sub>2</sub> and H<sub>2</sub> (synthesis gas) in an adiabatic reactor with typical inlet temperature range from 460°C to 500°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.

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. The pre-reforming catalysts must be able to process natural gas or naphtha. 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. Pre-Reforming Technical Requirements

4.1. The pre-reforming catalyst offered should be able to allow the operation of the hydrogen generation unit under conditions detailed in the Annex 1 for at least 36 months. The conditions accepted as indicators of the pre-reforming catalyst end of life is given in the Annex 1: Maximum inlet temperature; Maximum reactor pressure drop and maximum reactor outlet C<sub>2</sub><sup>+</sup> hydrocarbons compounds content. The SUPPLIER must inform the expect

performance at 36 months for each PETROBRAS' unit in accordance with Annex 2.

4.1.1. The catalysts must be in pre-reduced form.

4.1.2. SUPPLIER will be able to offer the product in different dimensions and formats to meet the indicators of the end of life for each hydrogen unit.

4.1.3. 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.

4.2. SUPPLIER must inform the characteristics of the offered product completing the template in Annex 3. The PREF products 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 pre-reforming catalysts offered the information listed below. All the information and documentation for the bidding purposes must be supplied in Portuguese or English languages:

4.4.1. 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 pre-reforming catalysts, in pre-reduced form, 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 - Pre-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 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 of personnel due to national health events, PETROBRAS may not perform one or more analyses 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**

<b>Refinery</b>	REFAP	RNEST
<b>Plant number</b>	U-704	U-35
Unit capacity (Nm <sup>3</sup> H <sub>2</sub> /d)	1,250,000	3,000,000
Composition (% mol)		
<b>Natural Gas</b>	<b>Principal feedstock</b>	<b>Principal feedstock</b>
CH <sub>4</sub>	89.16	88.98
C <sub>2</sub> H <sub>6</sub>	6.48	8.04
C <sub>3</sub> H <sub>8</sub>	1.69	1.69
C <sub>4</sub> H <sub>10</sub>	0.55	0.14
C <sub>5</sub> +	0.31	0.02
CO <sub>2</sub>	0.67	0.35
N <sub>2</sub>	1.14	0.78
RSH (ppmv)	<0.1 at preforming inlet	<0.1 at preforming inlet
H <sub>2</sub> S (ppmv)	<0.1 at preforming inlet	<0.1 at preforming inlet
Molecular Weight	18.17	17.91
<b>Recycle H<sub>2</sub></b>		
H <sub>2</sub>	99.90	98.63
CH <sub>4</sub>	0.10	0
CO	0	0
N <sub>2</sub>	0	1.37
<b>Naphtha</b>	<b>Alternative feedstock</b>	<b>Alternative feedstock</b>
Distillation ASTM D-86 (°C)		
IBP	37	38
10	53	50
30	73	63
50	81	79
70	106	95
90	163	120
FBP	195	150
Simulated (%mol)		
Paraffins	63.1	64.96
Olefins	1.0 (Note 2)	<0.6 (Note 2)
Naphthenic	29.5	31.77
Aromatics	7.2	3.20
Total Sulphur (ppm)	<0.1 (Note 1)	<0.1 (Note 1)
Specific gravity (20/4°C)	0.694	0.709
Molecular weight	97.93	91.51

Note 1: After hydrotreatment section.

Note 2: The hydrotreatment section use a CoMo catalyst. We can assume the olefins will be hydrogenated in this section.

### Annex 1: Feedstock and Process Information (continuation)

Refinery	REFAP	RNEST
<b>Plant number</b>	U-704	U-35
<b>Feed flow rate</b>		
Naphtha (std m <sup>3</sup> /h)	20.92	50.5
Natural Gas (kg/h)	17372	32444
H <sub>2</sub> /NG ratio (Nm <sup>3</sup> /kg)	0.13	0.16
H <sub>2</sub> /Naphtha ratio (Nm <sup>3</sup> /kg)	0.20	0.20
<b>Pre-reforming reactor</b>		
Steam/carbon (mol/mol)	2.5 (naphtha) / 2.1	2.3
Inlet temperature (°C)	490	490
Outlet pressure (kgf/cm <sup>2</sup> g)	27.3	27.0
Bed Diameter (mm)	2400	2800
Bed Height (mm)	2120	3860
Catalyst inventory (m <sup>3</sup> )	9.5	23.6
<b>Maximum pressure drop (kgf/cm<sup>2</sup>)</b>	0.5	0.5
<b>Maximum C<sub>2</sub><sup>+</sup> leakage (ppmv) - dry base</b>	1000	1000
<b>Maximum temperature (°C)</b>	520	520

Note 1: C<sub>2</sub><sup>+</sup> means any hydrocarbons with 2 or more carbon atoms

## Annex 2: Model of form to report the expect performance

### Simulation pre-reforming REFAP: Case naphtha

Catalyst type:		
Fixed data for simulation:		
Inlet pressure (kg/cm <sup>2</sup> g)	27.8	27.8
Inlet steam to carbon ration (mol/mol)	2.5	2.5
SIMULATION	SOR	AFTER 36 MONTHS
Reactor temperature (length % - °C)		
<b>Inlet</b>		
25%		
50 %		
75 %		
Outlet temperature (°C)		
Approach to equilibrium (°C)		
<b>Pressure drop (kgf/cm<sup>2</sup>)</b>		
Outlet gas composition (% v/v. dry base)		
H <sub>2</sub>		
CO		
CO <sub>2</sub>		
CH <sub>4</sub>		
N <sub>2</sub>		
<b>C2<sup>+</sup> (ppmv)</b>		

Note: For the purpose of mandatory technical requirement, only data relating to the campaign time of 36 months will be considered, in accordance with item 4.1.

### Simulation pre-reforming RNEST: Case NG

Catalyst type:		
Fixed data for simulation:		
Inlet pressure (kg/cm <sup>2</sup> g)	27.5	27.5
Inlet steam to carbon ration (mol/mol)	2.3	2.3
SIMULATION	SOR	AFTER 36 MONTHS
Reactor temperature (length % - °C)		
<b>Inlet</b>		
25%		
50 %		
75 %		
Outlet temperature (°C)		
Approach to equilibrium (°C)		
<b>Pressure drop (Kg/cm<sup>2</sup>)</b>		
Outlet gas composition (% v/v, dry base)		
H <sub>2</sub>		
CO		
CO <sub>2</sub>		
CH <sub>4</sub>		
N <sub>2</sub>		
<b>C2<sup>+</sup> (ppmv)</b>		



Note: For the purpose of mandatory technical requirement, only data relating to the campaign time of 36 months will be considered, in accordance with item 4.1.

### Annex 3: pre-reforming product characteristics

	Information from supplier	Requirements	Methods
Product Name		N/A	N/A
Pre-reduced		Yes	1
Could be used use with NG and Naphtha?		Yes	2
Could be heated in steam/H <sub>2</sub> over 250°C?		Yes	2
Form		Cylinders and tablets or rings with multiples holes	Visual inspection
Dimensions (mm)			
Tablets (D = diameter. L= length)		D (3.0 to 5.5) x L (3.0 to 5.5)	3
Rings with multiples holes D = diameter. L= length)		D ≤ 11; L ≤ 6.0	3
Bulk density (kg/L)		≥ 0.85	4
Composition (wt%)			
Ni expressed as NiO		≥ 40	5
Others		Inform	5
Impurities Sulfur Chlorine		inform	

- 1) Temperature Programmed Reduction (TPR): 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% H<sub>2</sub> in argon is passed over the catalyst between 100°C to 1000°C at a rate of 5°C/min. The consumption of H<sub>2</sub>, indicative of reduction of oxide species, is monitored by a thermal conductivity detector.
- 2) Review of documentation required and/or supplier answer. The heated could be done above dew point of steam and with steam/hydrogen molar ratio below 30 mol/mol. Note: It is known that high content of “free MgO” restrict this condition.
- 3) Value of 30 samples measured with pachymeter.
- 4) The “freely settled bulk density” is obtained using a 500 mL graduated cylinders with diameter at around 9 cm (reference ASTM D1895).
- 5) Determined by X-ray fluorescence spectrometry (XRF). Note: If the Si element is present

in the catalyst formulation, the supplier must indicate whether it is volatile or not, under conditions in Annex 1.

#### Annex 4: Additional requirements to product

	Requirements	Methods
Initial activity (methane conversion at 500°C) (%)	≥ 25%	6
Activity after thermal deactivation test (methane conversion at 500°C) (%)	≥ 20%	7
Mass increase in coke accelerated test (%)	< 30 %	8
Loss in initial activity after steaming test (%)	<10%	9
Fines generated in the loading test (%w/w)	< 3	10


- 6) The methane steam reforming activity is carried at atmospheric pressure using the commercial catalyst ground in mesh <100. The samples are subjected to pretreatment by heating from room temperature to 450°C at the rate of 30°C/min in argon flow. The steam reforming reaction are carried out at 450°C, 500°C and 550°C in a flow of methane and steam (steam/carbon of 2.2 mol/mol) diluted (1:1 v/v) with a flow of 10%H<sub>2</sub> in argon. The space velocity (VE) is 60,000 (L/kg.h) in dry base. The methane conversion obtained for different products are corrected to the same volumetric base (GHSV = 60,000 h<sup>-1</sup> in dry base) using a kinetic of first order and the catalyst density.
- 7) After measuring the initial steam reforming activity of methane, as described in item 8, the catalyst is subjected to heat treatment “in-situ” in an argon flow at 750°C for 6h. Next, the methane steam reforming activity is measured again as described in item 6;
- 8) The catalysts are tested in thermogravimetric analysis equipment (TGA). 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 650°C at the rate 10°C/min, maintained for 1h. The final mass é used to next step. Then the temperature is reduced to 350°C and measurements is taken of coke formation rates, by replacing the H<sub>2</sub>/argon stream with a synthetic stream consisting of 21.5% hydrogen; 27.3% CO; 42.9% CO<sub>2</sub> and 8.3% CH<sub>4</sub> 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 is associated to coke deposition.
- 9) The hydrothermal deactivation methodology consisted of loading 2.0 grams of the commercial pre-reformed catalyst ground on the -35 + 100 mesh in a bench unit reactor. The reactor heated at a pressure of 20 atm in a flow of H<sub>2</sub> from room temperature to 450°C at a rate of 300°C/h, when then the hydrogen was replaced by nitrogen and kept for 1h to purge the unit. Then the reactor was maintained at 450°C and 20 atm in nitrogen flow and water vapor corresponding to a water flow of 66 mL/h for 2 hours. At the end of the procedure, the reactor was cooled in a nitrogen flow to room temperature and the catalyst was exposed to air and its activity was measured according to item 6.
- 10) One hundred grams of pre-reforming catalyst 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:  $\%w/w = \text{fines} (< 24 \text{ mesh}) / \text{original mass sample} \times 100$ .

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

- 11) X-Ray diffraction (XRD): This technique is used for identification of crystalline phases present in the material.
- 12) Mechanical strength (CS): The extrudate 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, one pre-reforming product with previous experience at Petrobras will be used as reference.
- 13) Pore volume: The solid is impregnated with a water enough to fill the pores (incipient wetness technique).
- 14) Specific Surface Area: Determined by  $N_2$  adsorption-desorption at  $-196^\circ\text{C}$  in a Micromeritics ASAP 2400 or similar equipment. Prior to the analysis the samples are pretreated at  $300^\circ\text{C}$  in vacuum (reference: ASTM D3663).
- 15) Cyclohexane dehydrogenation. This test can be used in combination with DRX technique to estimate the metallic surface area.

## Annex 5 - Comprovante de entrega de amostra

 <b>PETROBRAS</b>	<b>COMPROVANTE DE RECEBIMENTO DE AMOSTRAS</b>	
	OPORTUNIDADE:	Catalisadores Pré-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)