El hidrógeno como vector energético: necesidades metrológicas en su producción, transporte, almacenamiento y uso.

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Universidad de Valladolid

METROLOGÍA PARA EL PACTO VERDE

10 DE NOVIEMBRE DE 2021

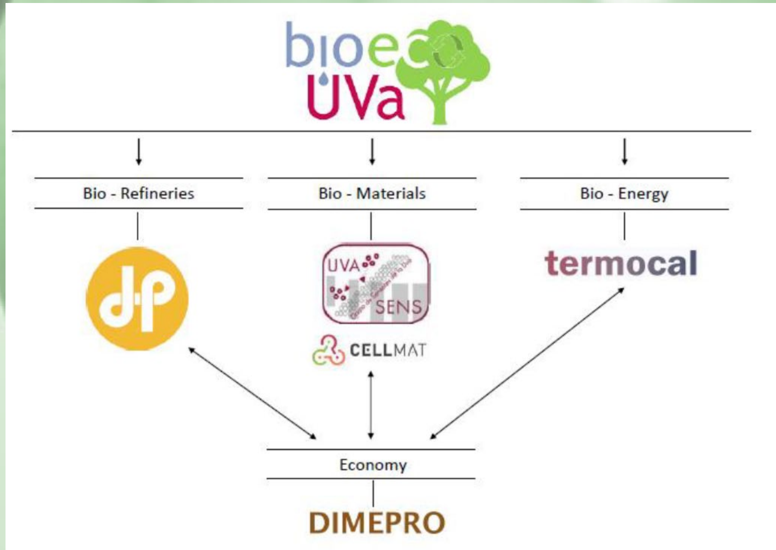
El hidrógeno como vector energético. Motivación.




TermoCal
TERMODINÁMICA
Y CALIBRACIÓN

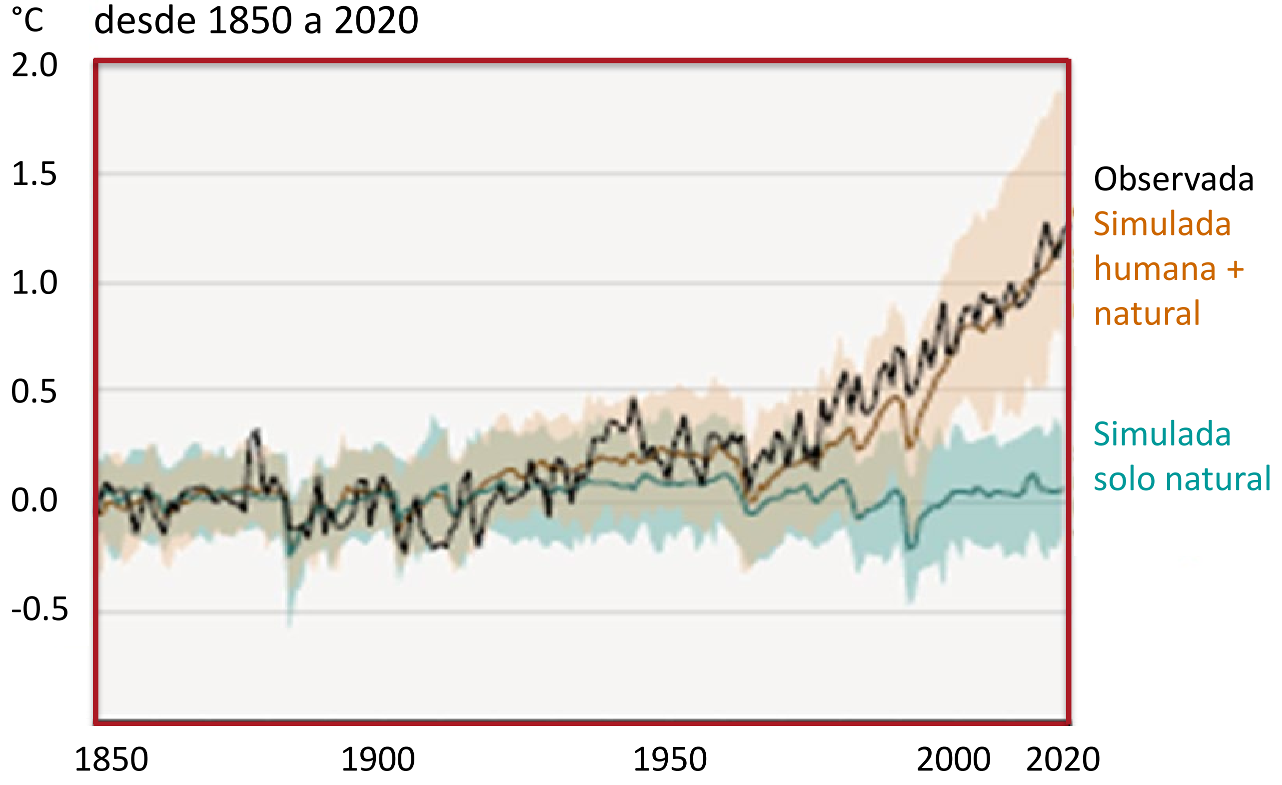



1) **Fundamental Metrology**
2) **Thermophysical Properties and Phase Behaviour** of multicomponent fluid mixtures over wide ranges of temperatures, pressures and chemical compositions
3) **Exergy analysis** of systems and processes



La influencia humana en el clima es clara

Cambio en la temperatura global media anual de la tierra observada y simulada utilizando factores naturales + humanos y naturales solo desde 1850 a 2020

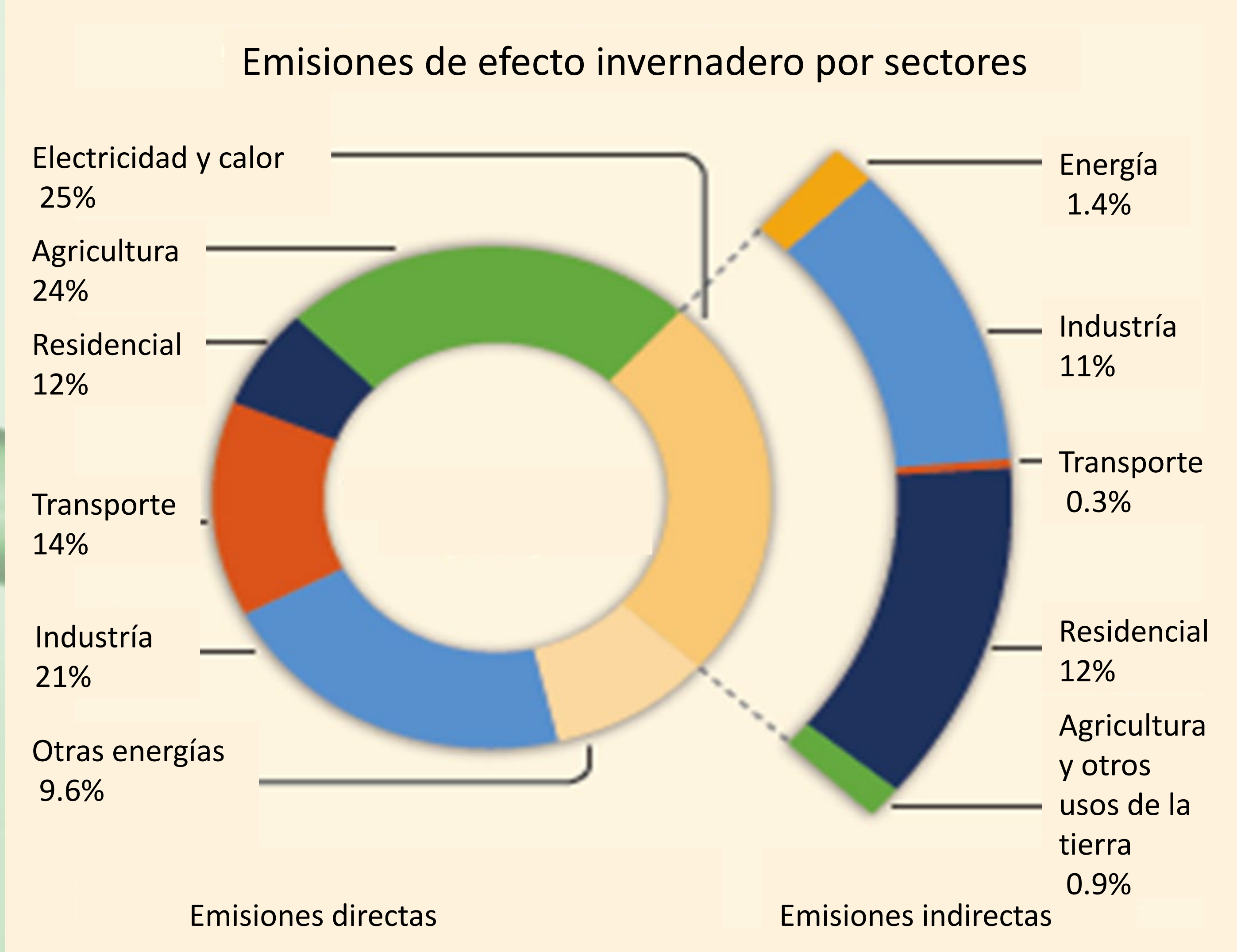


Last IPCC Report. AR6 2021. The Physical Science Basis (August 2021)

El hidrógeno como vector energético. Motivación.

¿Qué podemos hacer?

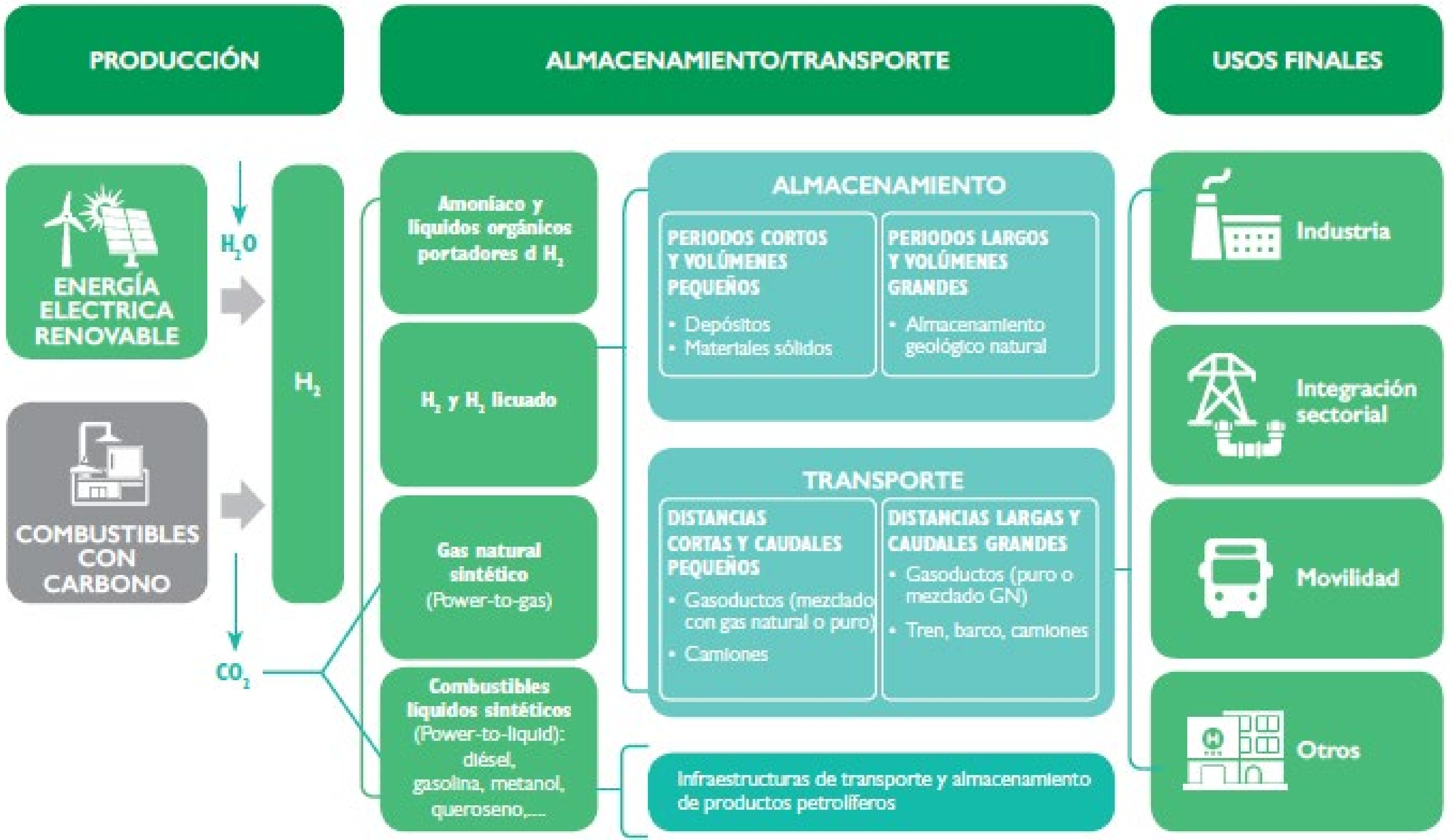
Aumentar el uso de energías renovables
Vectores energéticos como el hidrógeno
Ahorro energético
Aumento en la eficiencia
……….



El hidrógeno como vector energético. Motivación.

El hidrógeno como vector energético. Motivación.

Figura 1. Etapas de la cadena de valor del hidrógeno.



Marco estratégico de energía y clima. Ministerio para la transición ecológica y el reto demográfico. 2020.

El hidrógeno como vector energético. Motivación.

Cadena de valorización del hidrógeno

Producción
Electrolisis
Derivado de
combustibles fósiles
(Termoquímica)

→

Almacenamiento
Compresión
Licuefacción
Químico

+

Transporte
Tubería
Camión
Barco
Tren

→

Uso
Calor
Electricidad
Transporte
Materia prima industrial

Economía sostenible

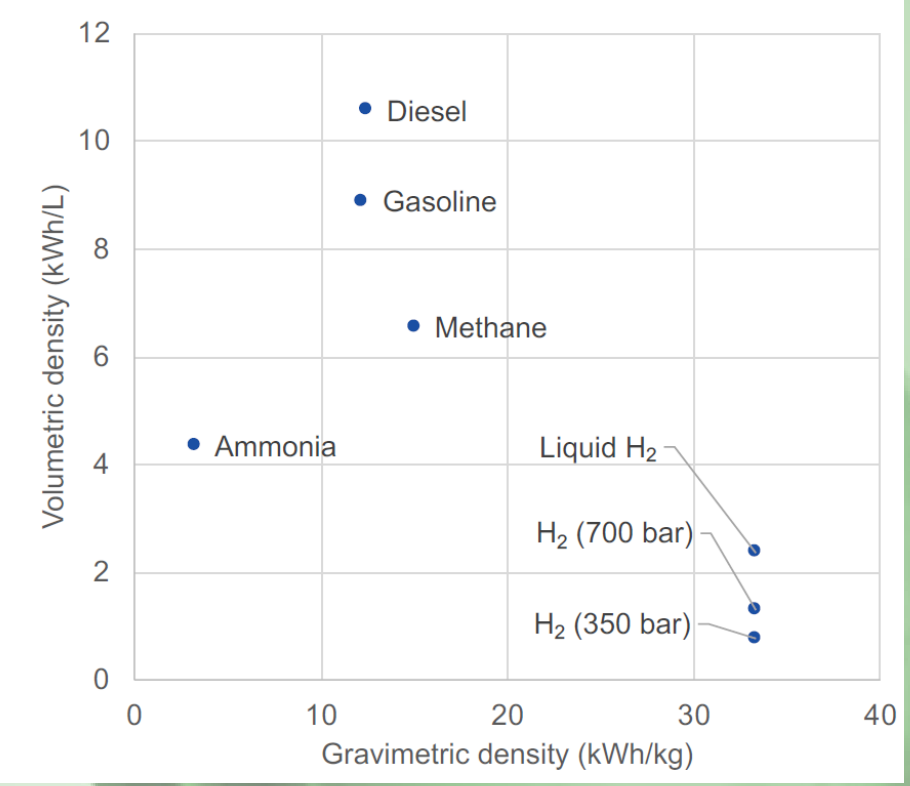
Suministro | **Demanda**

PROPIEDADES	**Ejemplos**
Equilibrio de fases	**H_2 + CO_2 ...**
Propiedades termodinámicas de una fase: densidad, velocidad del sonido …	**H_2 + CH_4 ...**
Propiedades de transporte: viscosidad, coeficientes de difusión …	**H_2 , H_2 + tubería …**

Comparación del LH_2 y el LNG (LCH_4)

	LH_2 (H_2)	LNG(LCH_4)
Boiling point K	20.3 (-253℃)	112 (-162℃)
Saturated liquid density kg/m^3	70.8	442.5
Saturated gas density kg/m^3	1.34	1.82
Critical temperature K	32.9	190
Critical Pressure MPa	1.28	4.60
Latent heat kJ/L (kJ/kg)	31.4 (444)	226(510)
Surface tension mN/m	1.98	12.9
Thermal cond. mW/(m K)	119	184
Prandtl Number	1.34	2.21
Lower heating value MJ/L(MJ/kg)	8.5 (120)	22.1 (50)

Reference : REFPROP NIST Standard Reference Database 23, version 9.0

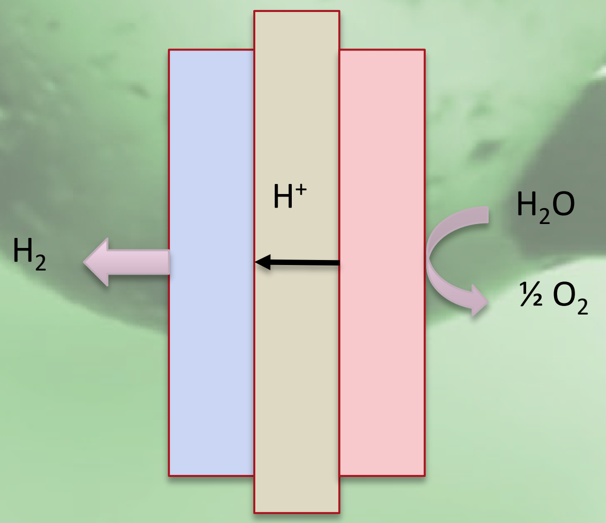


El hidrógeno como vector energético: producción, ejemplos

RENOVABLE

Electrolizador PEM

Cátodo - Ánodo +



Membrana de intercambio de protones.

p.e. Membrana polisulfonada

NO RENOVABLE + CCS

$CH_4 + \frac{1}{2}\ O_2 \rightleftarrows CO + 2\ H_2$

Oxidación parcial

$CH_4 + H_2O \rightleftarrows CO + 3\ H_2$

Reformado con vapor

$CH_4 + CO_2 \rightleftarrows 2\ CO + 2\ H_2$

Reformado con seco

$3\ C + O_2 + H_2O \rightleftarrows H_2 + 3\ CO$

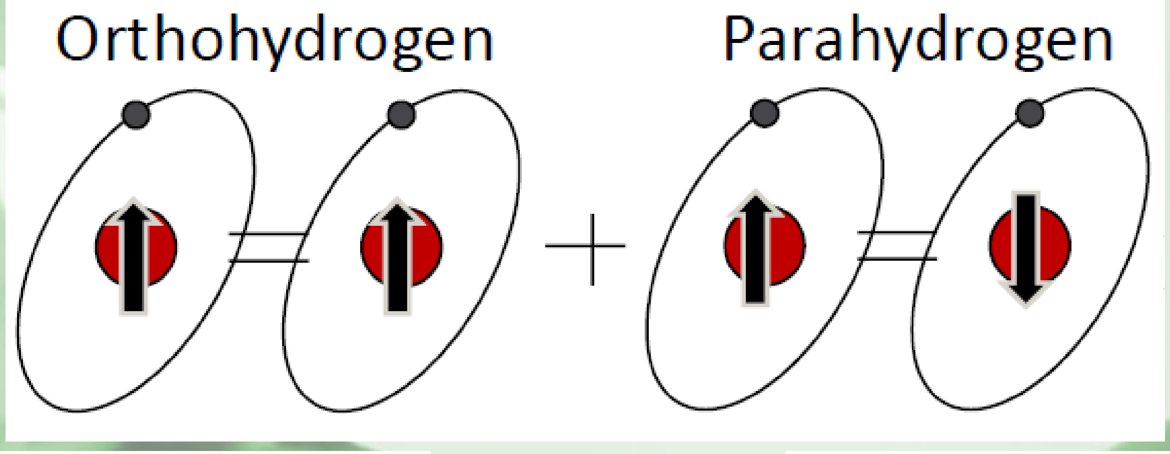
Gasificación de carbón

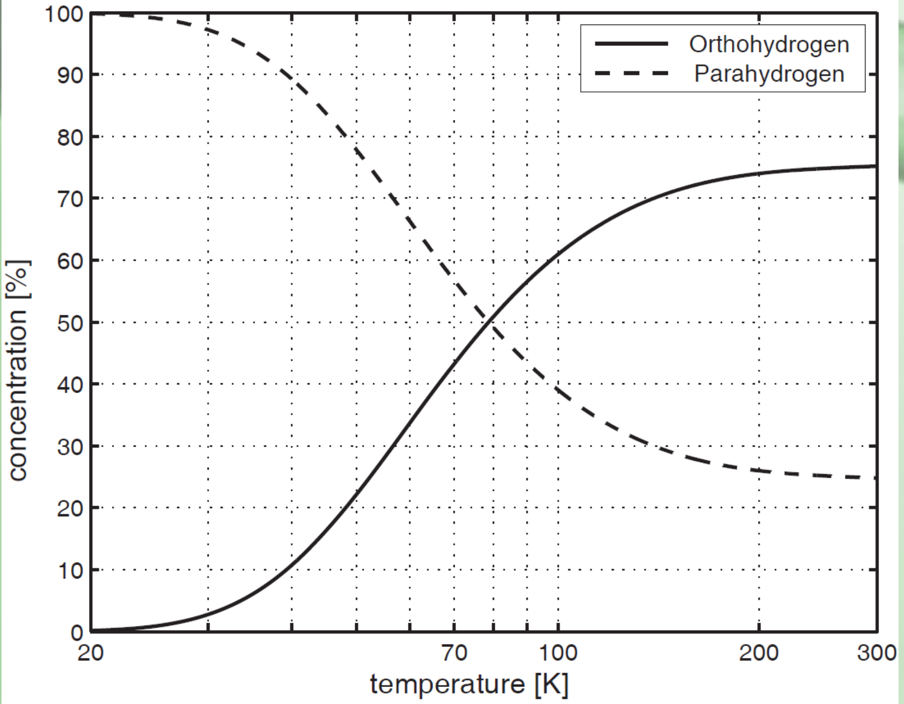
…

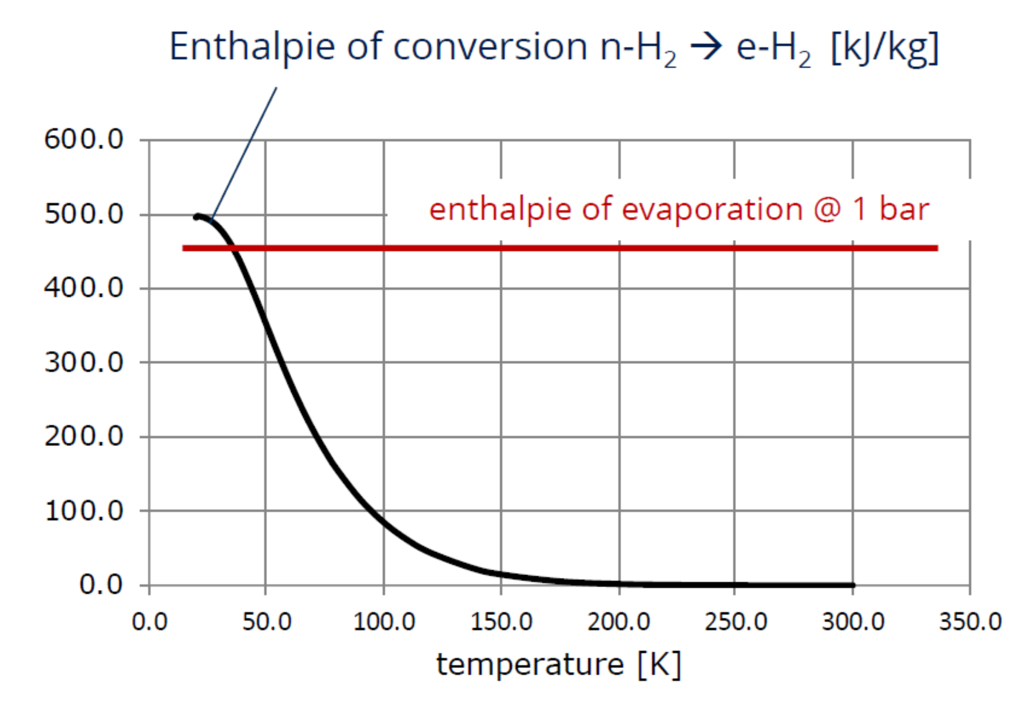
Gasificación biomasa

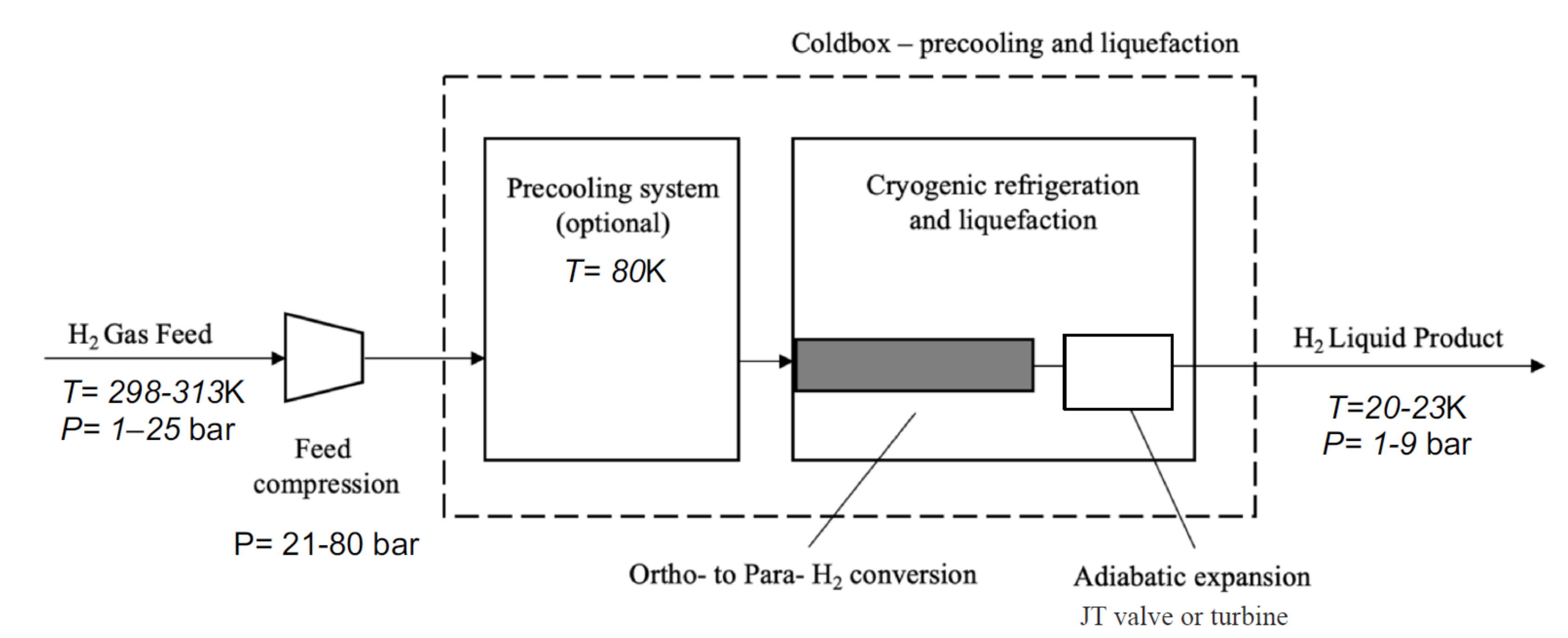
H_2

Formas alotrópicas del hidrógeno

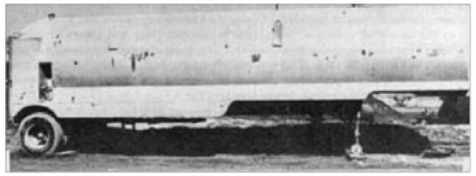






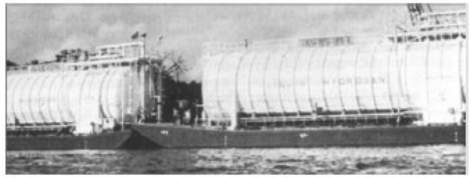

Coldbox – precooling and liquefaction
Precooling system (optional)
T= 80K
Cryogenic refrigeration and liquefaction
H2 Gas Feed
T= 298-313K
P= 1–25 bar
Feed compression
P= 21-80 bar
H2 Liquid Product
T=20-23K
P= 1-9 bar
Ortho- to Para- H2 conversion
Adiabatic expansion
JT valve or turbine

El hidrógeno como vector energético: almacenamiento, transporte.

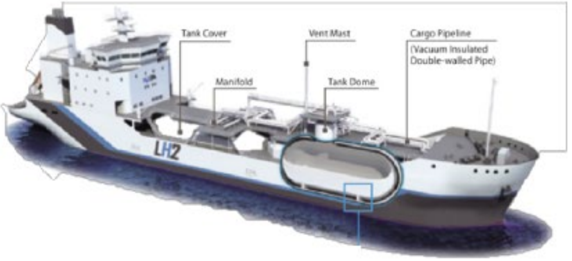


1978: 1-axle semi-trailer
for highway transportation

Air Products LH_2 tanker,
0.4-6.7 tonnes LH_2



NASA LH_2 transportation
by barge to the Kennedy
Space Centre



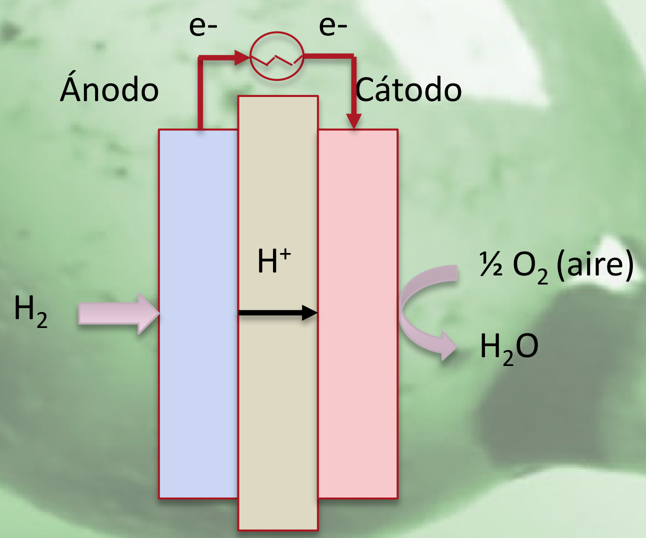
KHI LH_2 transport
88.5 tonnes LH_2 from Victoria
to Japan in 16 days

NASA LH_2 tank at Kennedy Space Centre

	Hydrogen	Natural gas
Flammability Limits (in air)	4-74%	5.3-15%
Explosion limits (in air)	18.3-59.0%	5.7-14%
Minimum ignition energy (mJ)	0.02	0.29
Adiabatic flame temperature in air (K)	2045	1875

El hidrógeno como vector energético: uso.

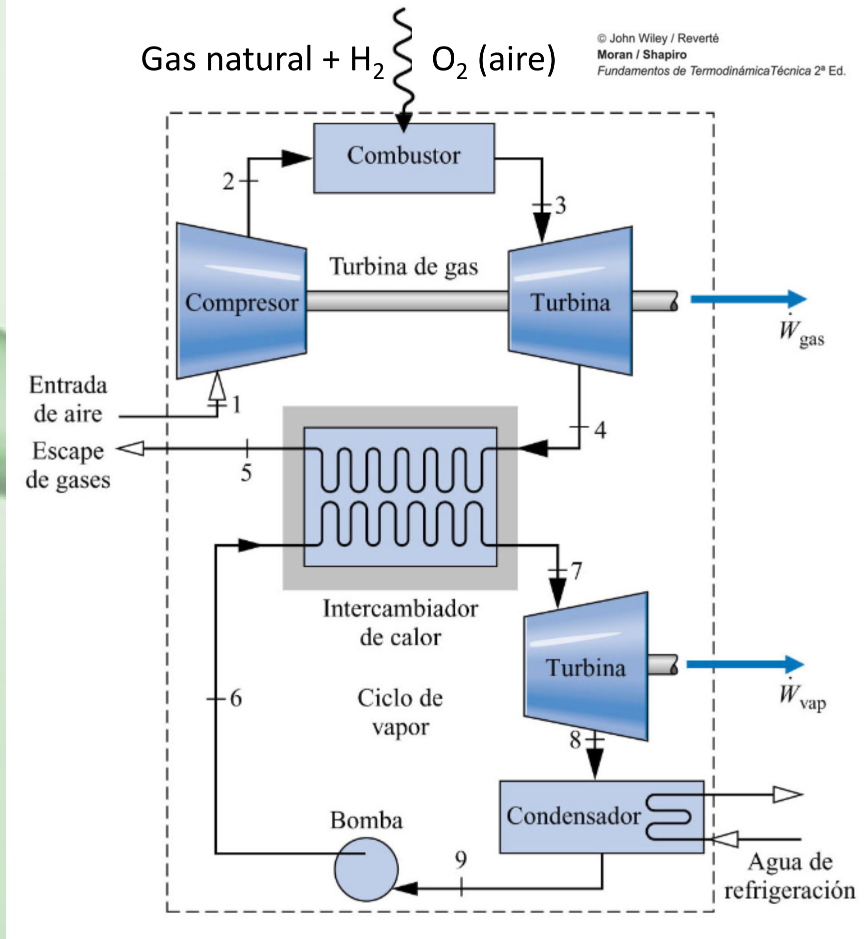
Pila de combustible PEM



Membrana de intercambio de protones.

p.e. Membrana polisulfonada

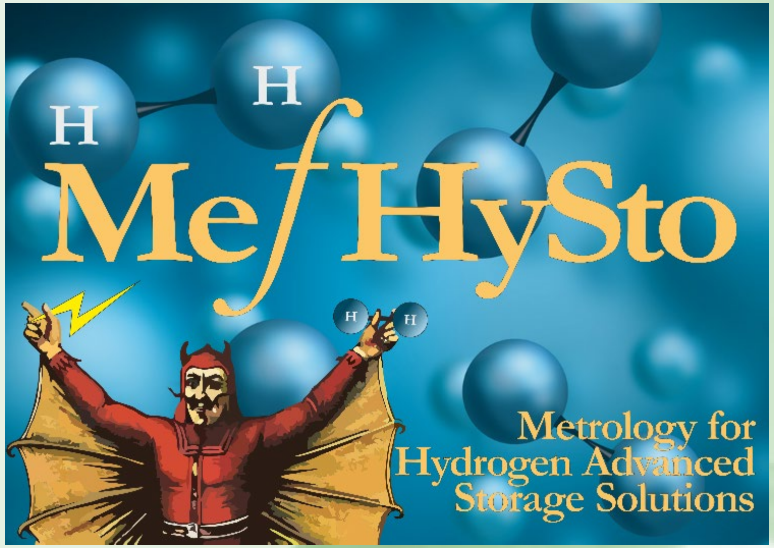
Ciclo combinado



¿Qué hacemos?

Comienzo: 01 Junio 2020

Duración: 36 meses

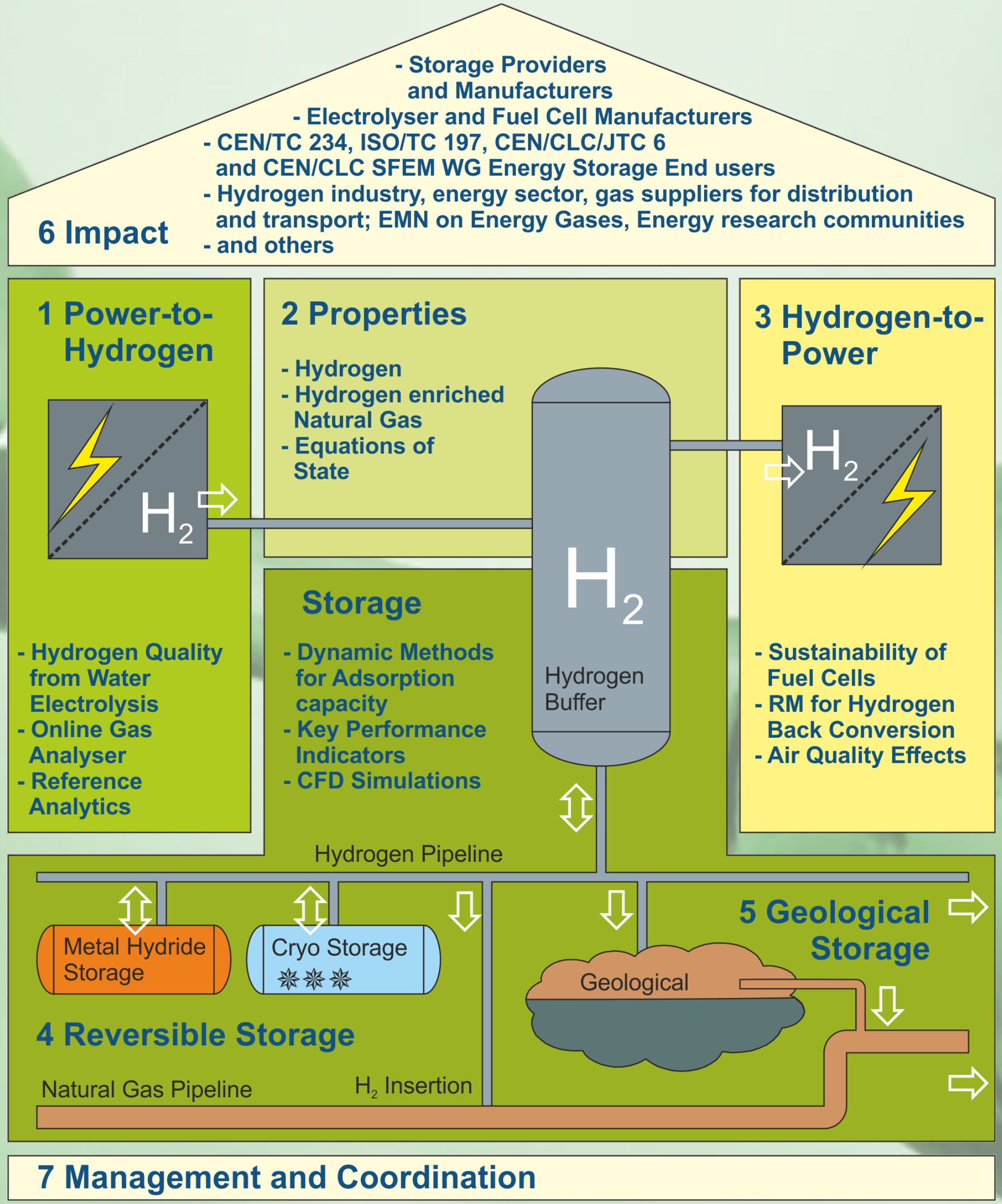


Coordinador: BAM (DE)

Participantes: BAM (DE), NPL (UK), CMI (CZ), PTB (DE), CA (FR), UVa (ES), MTH (FR), FHA (ES), RA (ES), MPG (DE), ERIG (BE), UDC (ES), DBI (DE), DVGW (DE).

Objetivo: Proporcionar soluciones de estandarización para tecnologías avanzadas de almacenamiento de hidrógeno mediante medidas trazables y técnicas validadas, que permitan el cumplimiento del objetivo energético de la UE para las energías renovables en el 2030 y los requisitos de la Directiva Europea de Energías Renovables 2018/2001.

El hidrógeno como vector energético: necesidades metrológicas.



El hidrógeno como vector energético: necesidades metrológicas.

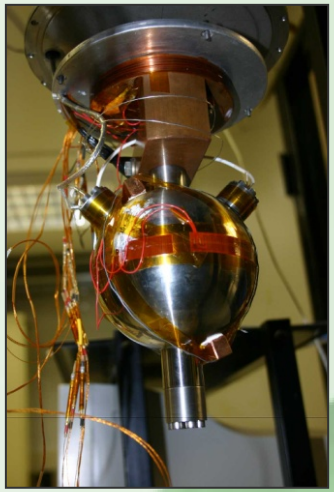
VELOCIDAD DEL SONIDO

RESONADOR ESFÉRICO

$u^2 = (\partial p / \partial \rho)_S$

$Cp, \beta_\alpha, \gamma_\alpha$

Humedad, f

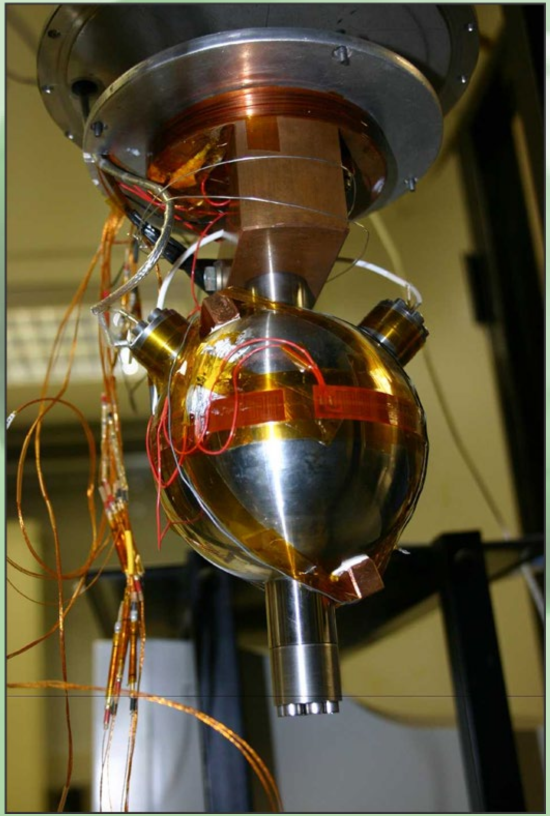


DENSIDAD

DENSÍMETRO SUSPENSIÓN MAGNÉTICA

P, ρ, T

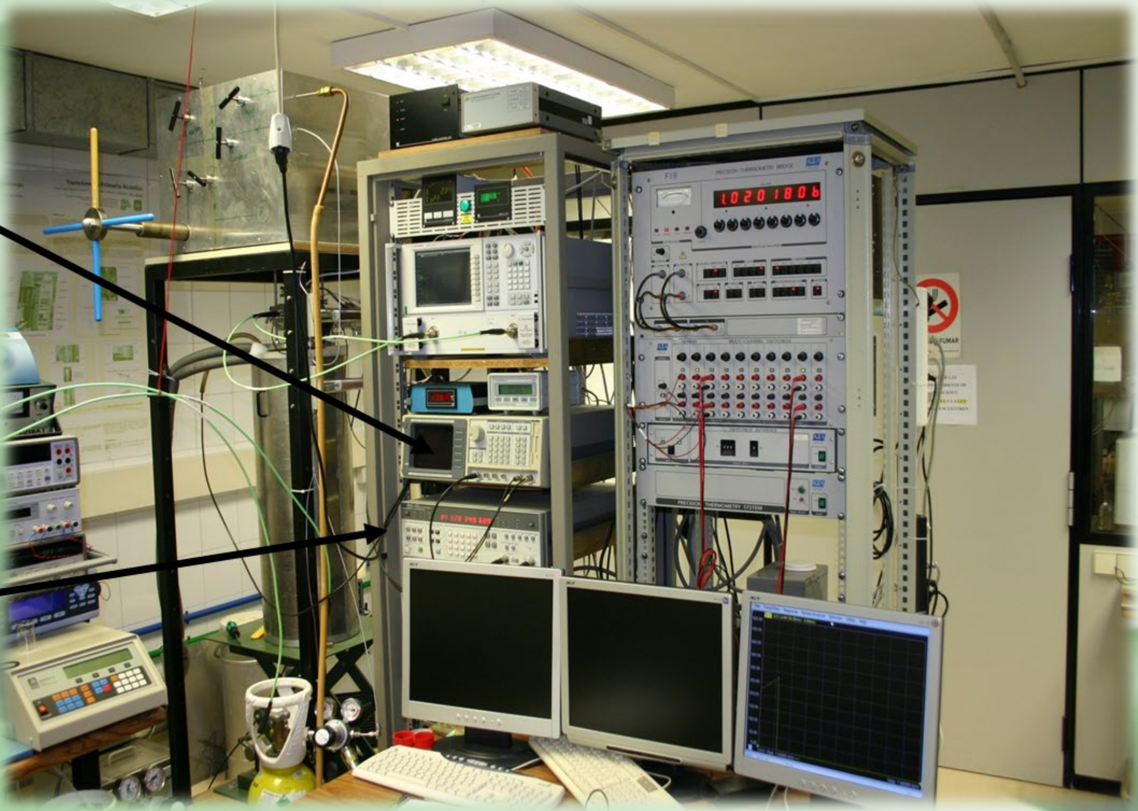
Resonador esférico



El hidrógeno como vector energético: necesidades metrológicas.

Analizador acústico

Generador acústico

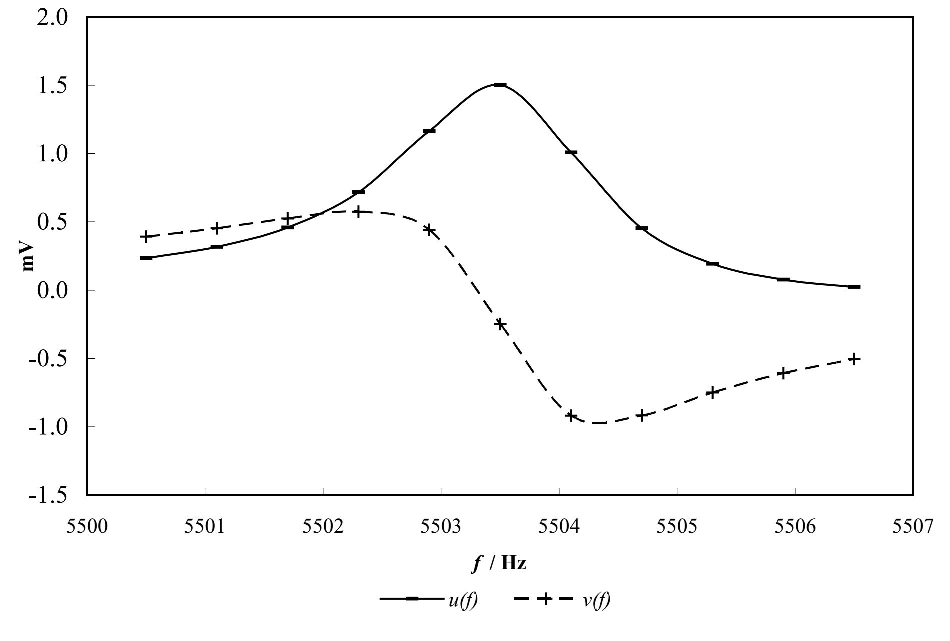


Presión	<20 MPa
Temperatura	250 - 500 K
Incertidumbre	(k=2)
Velocidad del sonido	0.02%
Presión	0.015%
Temperatura	4 mK

Evaluación de la velocidad del sonido a partir de la frecuencia de resonancia

$$u = \frac{f_{\ln}\xi_{\ln}}{2\pi a}$$

u: Velocidad del sonido
f_{ln}: frecuencia de resonancia del modo *l,n*
ξ_{ln}: eigenvalor para el modo *l,n*
a: radio



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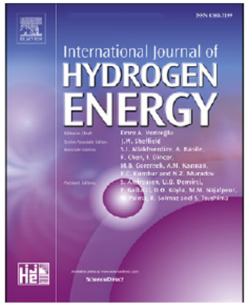

Speed of sound for three binary ($CH_4 + H_2$) mixtures from p = (0.5 up to 20) MPa at T = (273.16 to 375) K

Daniel Lozano-Martín [a], *M. Carmen Martín* [a], *César R. Chamorro* [a], *Dirk Tuma* [b], *José Juan Segovia* [a,*]

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[b] *BAM Bundesanstalt für Materialforschung und -Prüfung, Berlin, 12200, Germany*

HIGHLIGHTS

- Experimental speeds of sound for (methane + hydrogen) mixtures are reported.
- An accurate spherical resonator was used for the measurements.
- Experimental data were fitted to a virial-type equation.
- Heat capacities and virial coefficients were obtained from the speed of sound data.
- The results were compared with reference EoS such as GERG 2008 and AGA8.

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J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Speed of sound data, derived perfect-gas heat capacities, and acoustic virial coefficients of a calibration standard natural gas mixture and a low-calorific H_2-enriched mixture

Daniel Lozano-Martín [a], David Vega-Maza [a], Alejandro Moreau [a], M. Carmen Martín [a], Dirk Tuma [b], José J. Segovia [a,*]

[a] TERMOCAL Research Group, Research Institute on Bioeconomy (BioEcoUVa), University of Valladolid, Escuela de Ingenierías Industriales, Paseo del Cauce 59, 47011 Valladolid, Spain
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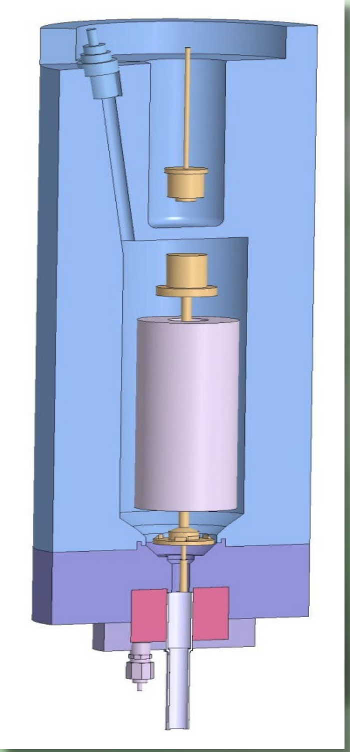
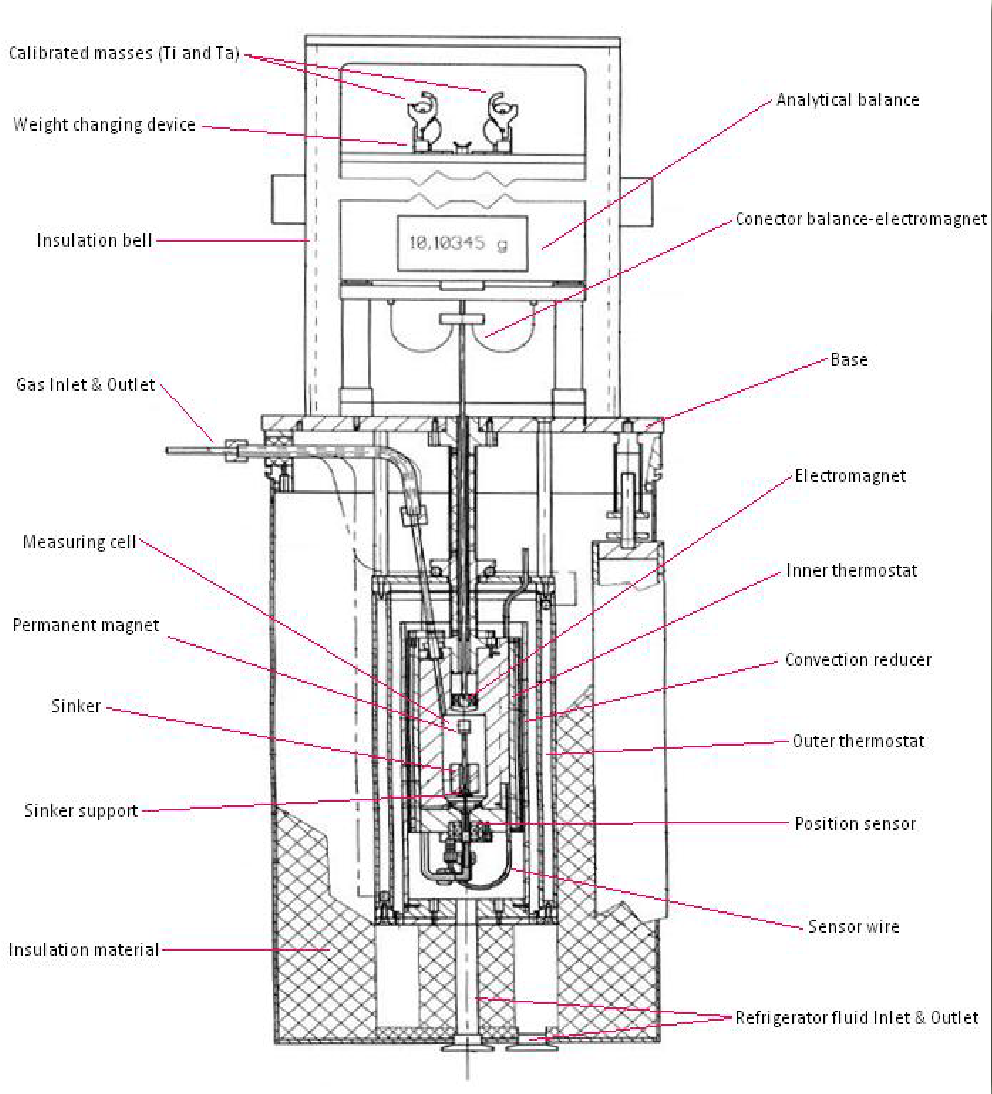
Acoustic virial coefficients

A B S T R A C T

This work aims to address the technical aspects related to the thermodynamic characterization of natural gas mixtures blended with hydrogen for the introduction of alternative energy sources within the Power-to-Gas framework. For that purpose, new experimental speed of sound data are presented in the pressure range between (0.1 up to 13) MPa and at temperatures of (260, 273.16, 300, 325, and 350) K for two mixtures qualified as primary calibration standards: a 11 component synthetic natural gas mixture (11 M), and another low-calorific H_2-enriched natural gas mixture with a nominal molar percentage $x_{H_2} = 3\%$. Measurements have been gathered using a spherical acoustic resonator with an experimental expanded ($k = 2$) uncertainty better than 200 parts in 10^6 (0.02%) in the speed of sound. The heat capacity ratio as perfect-gas γ^{pg}, the molar heat capacity as perfect-gas $C_{p,m}^{pg}$, and the second β_a and third γ_a acoustic virial coefficients are derived from the speed of sound values. All the results are compared with the reference mixture models for natural gas-like mixtures, the AGA8-DC92 EoS and the GERG-2008 EoS, with special attention to the impact of hydrogen on those properties. Data are found to be mostly consistent within the model uncertainty in the 11 M synthetic mixture as expected, but for the hydrogen-enriched mixture in the limit of the model uncertainty at the highest measuring pressures.

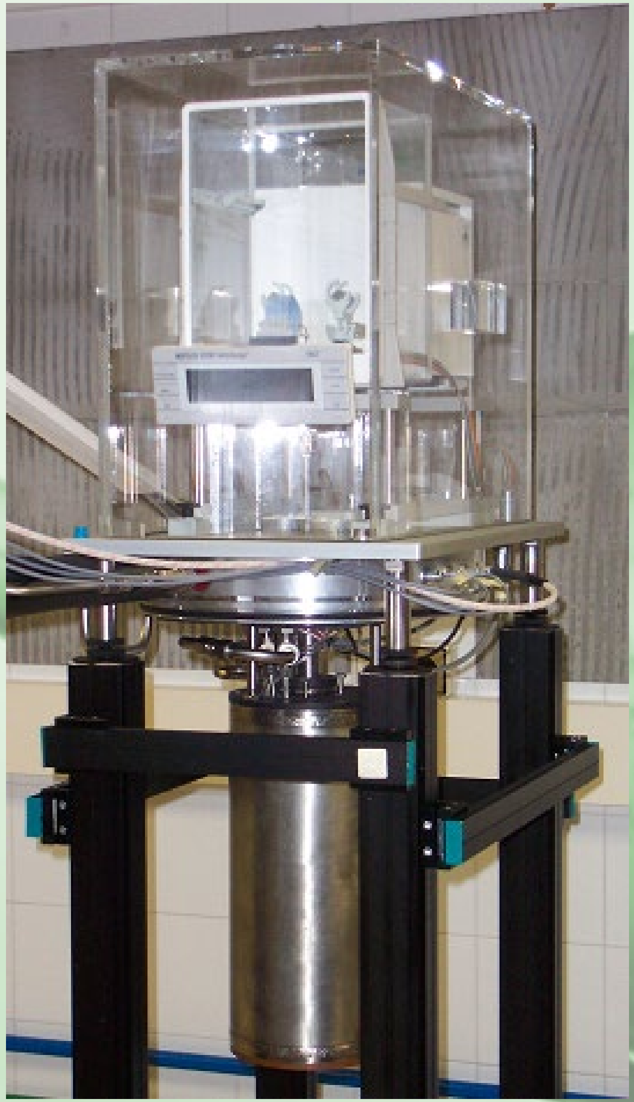
Densímetro de flotador





Presión	<20 MPa
Temperatura	250 - 400 K
Incertidumbre	(k=2)
Densidad	0.02-0.34%
Presión	0.015%
Temperatura	4 mK

Densímetro de flotador



El hidrógeno como vector energético: necesidades metrológicas.

Journal of chemical & engineering data

Article

Cite This: *J. Chem. Eng. Data* 2018, 63, 1613−1630

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Accurate Experimental (p, ρ, and T) Data for the Introduction of Hydrogen into the Natural Gas Grid (II): Thermodynamic Characterization of the Methane−Hydrogen Binary System from 240 to 350 K and Pressures up to 20 MPa

Roberto Hernández-Gómez,[†] Dirk Tuma,[‡] Eduardo Pérez,[†] and César R. Chamorro[*,†]

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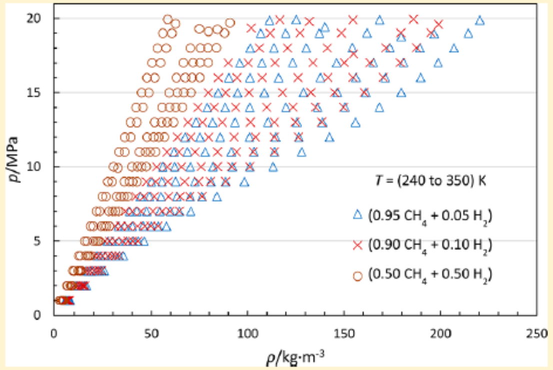
ABSTRACT: Most of the experimental density data of the methane−hydrogen binary system available at the time of the development of the equation of state for natural gases and related mixtures, GERG-2008, at temperatures above 270 K were limited to hydrogen contents higher than 0.20 (amount-of-substance fraction). On the contrary, for mixtures with hydrogen contents lower than 0.20, experimental data were limited to temperatures below 270 K. This work intends to close the gap and provides accurate experimental (p, ρ, and T) data for three binary mixtures of methane and hydrogen, (0.95 CH_4 + 0.05 H_2), (0.90 CH_4 + 0.10 H_2), and (0.50 CH_4 + 0.50 H_2), at temperatures of 240, 250, 260, 275, 300, 325, and 350 K, thus extending the range of available experimental data to higher temperatures for mixtures with hydrogen contents lower than 0.20 and, accordingly, to lower temperatures for mixtures with hydrogen contents higher than 0.20. The density measurements were performed by using a single-sinker densimeter with magnetic suspension coupling at pressures up to 20 MPa. Experimental data were compared to the corresponding densities calculated from the GERG-2008 and the AGA8-DC92 equations of state, respectively. The experimental data are within the uncertainty of both equations of state, except at the lower temperatures of 240 and 250 K and pressures over 14 MPa for the mixtures with a hydrogen content of 0.05 and 0.10, respectively. The virial coefficients $B(T, x)$ and $C(T, x)$, as well as the second interaction virial coefficient $B_{12}(T)$ for the methane−hydrogen binary system, were also calculated from the experimental data set at temperatures from 240 to 350 K using



El hidrógeno como vector energético: necesidades metrológicas.

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Accurate experimental (p, ρ, T) data of natural gas mixtures for the assessment of reference equations of state when dealing with hydrogen-enriched natural gas

Roberto Hernández-Gómez [a], Dirk Tuma [b], Daniel Lozano-Martín [a], César R. Chamorro [a,*]

[a] Grupo de Termodinámica y Calibración (TERMOCAL), Dpto. Ingeniería Energética y Fluidomecánica, Escuela de Ingenierías Industriales, Universidad de Valladolid, Paseo del Cauce, 59, E-47011 Valladolid, Spain

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EMPIR EURAMET

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GOBIERNO DE ESPAÑA MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Junta de Castilla y León