

HYDROGEN LIQUEFACTION

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Contents

- 1. Introduction
- 2. Process of Refining Source Hydrogen
 - 2.1 Pressure Swing Adsorption (PSA) Method
 - 2.2 Cryogenic Adsorption Purification Method
- 3. Ortho-Para Conversion Method
- 4. Liquefaction Process
 - 4.1 Hydrogen Liquefaction Process for Continuous Ortho-para Conversion
 - 4.2 Helium-Brayton Hydrogen Liquefaction Process
- Glossary
- Bibliography
- Biographical Sketches

Summary

This article describes the present status of hydrogen liquefaction around the world, illustrating a method of refining material gases necessary for liquefaction and the ortho-para conversion method. The paper also comments on typical liquefying processes.

1. Introduction

In 1898, J. Dewar of the United Kingdom was the first to succeed in the liquefaction of hydrogen. Liquefaction on an industrial scale started with the installation and operation of a system capable of producing 0.4 tons per day at Cryogenic Engineering Research Institute of the National Bureau of Standards (NBS) in Colorado, USA.

In the late 1950s, as space development became active; there was bulk demand for liquid hydrogen for fueling rocket engines.

Thus, liquefaction plants were constructed across the world: a plant capable of producing 30 tons per day ($17\,625\text{ L hr}^{-1}$) was built in 1959 at Air Products Inc., Florida, USA, followed by a plant capable of producing 600 L hr^{-1} at Air Liquide, in the suburb of Douai, northern France in the early 1960s, and then a plant for producing 730 L hr^{-1} in 1978 in Hyogo Prefecture, Japan.

Thereafter, no larger liquefaction plants were built in the United States, but larger plants

of 10 tons per day (5857 L hr^{-1}) and 1.45 tons per day (850 L hr^{-1}) were constructed in Europe and in Japan both in 1987. These are the largest liquefaction plants in each area today.

Hydrogen inherently has some unique physical properties, such as a very low density of 0.07 g cm^3 and latent heat of evaporation at 0.9 kJ/mol , as well as a low boiling point of 20.4 K at atmospheric pressure.

Because of these characteristics, during liquefaction appropriate measures must be taken, in addition to maintaining a low temperature.

Hydrogen refining and ortho-para conversion, which are particularly important measures, are described below, followed by an outline of the liquefaction process.

2. Process of Refining Source Hydrogen

Prior to liquefaction of hydrogen, impurities in the source hydrogen must be removed to 1 vppm ($= \text{ppm vol}\cdot\text{vol}^{-1}$) or below in total.

This is because of the possibility that the gaseous content of impurities other than helium may solidify at the temperature of liquid hydrogen and cause clogging of the liquefaction process system, as well as degrading the quality of the liquid hydrogen product.

In the industrial production, source hydrogen is available from: coke oven gas containing bulk hydrogen from steel industry; the partial oxidation of hydrocarbon obtained from oil refining; the steam reforming of offgas from ethylene plants; hydrogen as a byproduct of salt electrolysis from caustic soda or produced by reforming of raw materials such as methanol, ammonia or natural gas, etc.

Purities of source hydrogen thus obtained vary from about 50% to 99% and so must be improved by refining.

The optimum refining method must be selected according to the quality, quantity and volume of impurities contained.

These are summarized in Table 1. The PSA refinery method and the cold adsorption method, both of which are most frequently used for hydrogen liquefaction, are described below.

	Hydrogen source		Electrolysis	Coke oven gas	Ethylene off gas	Methanol		
Raw hydrogen	Pressure	kg/cm ² mmH ₂ O	50–500	25–30	15–30	9–30		
	Purity	%	99.5–99.9	50–60	50–97	75		
	Impurity	CmHn	N ₂	ppm	40	4–5 (%)	—	
			O ₂	ppm	10	—	—	
			CO	ppm	0.1	35–45 (%)	3–50 (%)	—
			CO ₂	ppm	0.1	1 (%)	—	2 (%)
			ppm	0.1	—	—	23 (%)	
Purifier & purified purity	Purifier		Deoxo• Desiccator	PSA				
	H ₂ purity	%	99.99–99.995	99.999–99.9995				
	Impurity	CmHn	N ₂	ppm	50	<10– <0.3		
			O ₂	ppm	<0.1	<1– <0.1		
			CO	ppm	<1	<1– <0.05		
			CO ₂	ppm	<1	<1– <0.05		
H ₂ O			°C	<–70	<–65– <–80			
Cryogenic purifier & purified purity	Purifier		Cryogenic purifier					
	H ₂ purity	%	<99.9999					
	Impurity	CmHn	N ₂	ppb	<10			
			O ₂	ppb	<50			
			CO	ppb	<10			
			CO ₂	ppb	<10			
H ₂ O			ppb	<100				

Table 1. Raw hydrogen purity, purifier and purified purity.

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Biographical Sketches

Takuji Hanada was born 1 January 1935, in Japan; he received his education from the Department of Mechanical Engineering, Hosei University; Joined Teikoku Sanso Co., Ltd. (1957–); Presently Air Liquide Japan Ltd. Adviser. Previous positions: Manager of Plant Designing Department (1970–1975); Deputy Manager of Plant Equipment Division (1975–1991).

Kunihiro Takahashi was born 28 January 1942 in Japan; he graduated from Chemical System Engineering Department, Faculty of Engineering, the University of Tokyo; completed master course with major in engineering, the University of Tokyo; joined Tokyo Gas Co., Ltd.; presently general manager of the Center for Supply Control and Disaster Management, Tokyo Gas Co., Ltd. Previous positions: appointed as a member of General Research Laboratory of Tokyo Gas Co., Ltd. (1967–1977); appointed as general manager of Technical Development Department, general manager of Engineering Department, and general manager of System Energy Department of The Japan Gas Association (1994–1997); appointed as a member of Sub-task-1-committee of WE-NET committee of New Energy and Industrial Technology Development Organization (1994–1997); has held present position since June 1997; studied research themes: research on production processes and catalysts for hydrogen-rich gas and methane-rich gas.