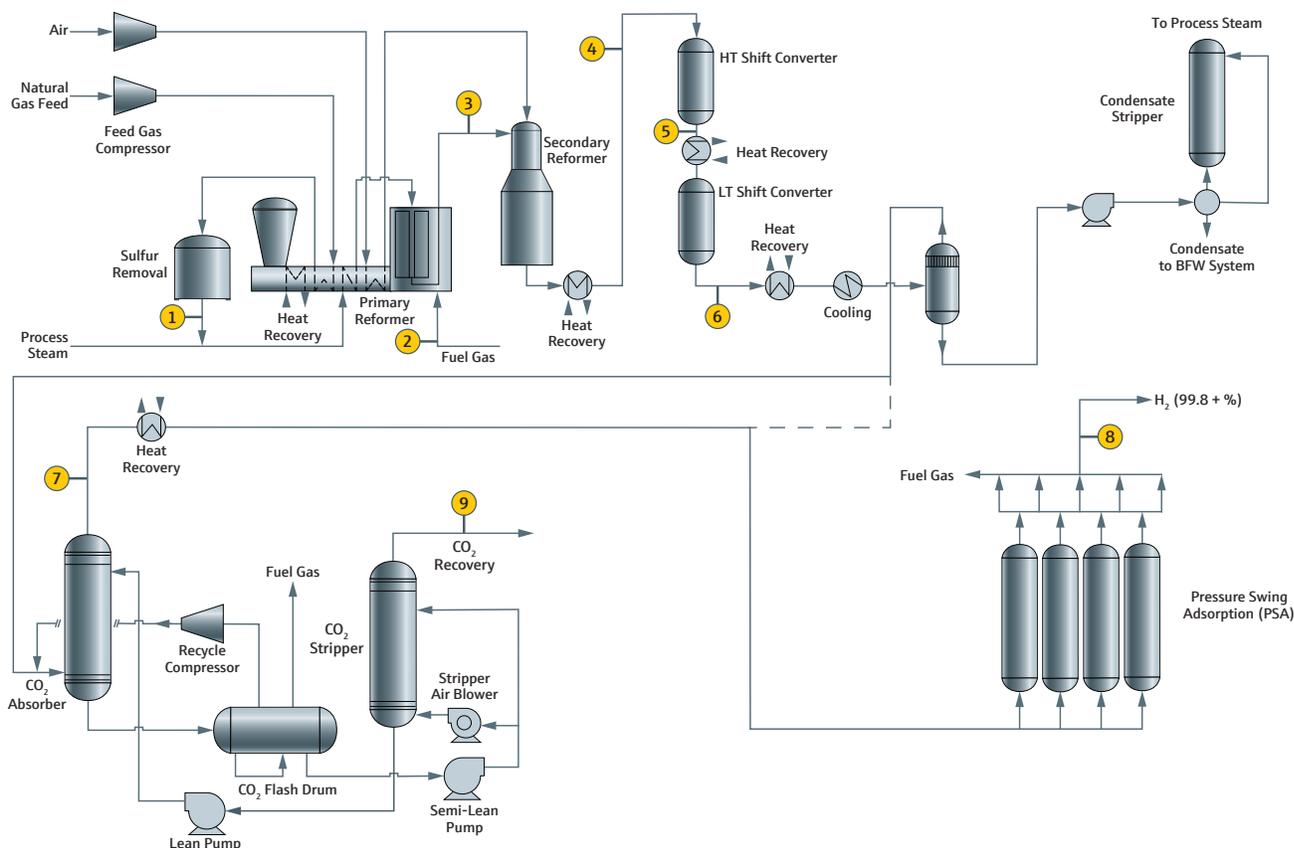


Application Note

Captive hydrogen production analytics overview

Hydrogen production and main uses Hydrogen is the simplest and most abundant element on earth. In 2013, the annual production of hydrogen was estimated to be about 55 million tons with its consumption increasing by approximately 6% per year. Production is primarily from Steam Methane Reforming (SMR) of natural gas and much of this hydrogen is used in petroleum refineries, in the production of ammonia for fertilizers, and in methanol production, as well as in food processing. Close to 50% of the global demand for hydrogen is produced via SMR of natural gas, about 30% from oil/naphtha reforming from refinery/chemical industrial off-gases, 18% from coal gasification, 3.9% from water electrolysis, and 0.1% from other sources.[1]

The overall hydrogen production process Modern refineries often rely on third-party bulk gas suppliers to obtain 'merchant' hydrogen.* There are also many refineries that produce 'captive' hydrogen for use in numerous hydrotreating and hydrocracking processes that are essential for refinery operation. The majority of this hydrogen is produced via SMR of natural gas inside the refinery battery limits (ISBL). The output of the SMR is syngas, which is a mixture of H_2 and CO . The CO is converted into CO_2 and additional H_2 using water-shift reactors. When recovery and sequestration of CO_2 are required, the syngas is purified by removing CO_2 via a CO_2 absorber. In most refineries, Pressure Swing Adsorption (PSA) are used in the final H_2 purification process (see Figure 1). Gas loops are commonly used to recover unused H_2 .



A Simplified Process Diagram Showing the Main Process Units for the Generation of Captive Hydrogen Inside the Battery Limits (ISBL) of a Refinery

* See the general HyCO Production Overview Application Note (HYO)

1. Hydrogen Production Technologies: Current State and Future Developments, C.M. Kalamaras and A.M. Efsthathiou, Conferences Papers in Energy, Vol 13 (2013), Hindawi Publishing Corp., Article ID 690627.

Process analytical challenges There are several streams that are typically analyzed in real time during the hydrogen manufacturing process, and the analysis results form the basis for controlling and optimizing the main process units. Although most of the streams are relatively easy to analyze using traditional on-line analyzer techniques such as GC, MS, and photometry, in several cases steam content and the process conditions are severe enough require special sample conditioning techniques. With these challenging samples, the ability to obtain reliable sampling and analysis is often compromised. The use of the Optograf Analyzer, combined with the OptoDRS Sampling Interface, is a unique and robust solution for these challenging streams.

The solution: Optograf™ Analyzer and OptoDRS™ or OptoAST™ System The Optograf Analyzer provides the unique spectroscopic ability to analyze the mononuclear diatomic gases H₂ and N₂, which allows measurement of all the streams shown in the typical “Stream Service” list below. Speciation is achieved without any columns, valves, stream switching or the need for carrier gas. In addition, the OptoDRS and OptoAST modules are based on the pipe-centric concept of performing the process sampling, sample conditioning, and measurement in a single, integrated module that can be installed at the sample tap. Below is a list of typical process conditions and the process sampling interfaces recommended by Kaiser Optical Systems, Inc., for each of the streams analyzed on-line. The OptoDRS sampling module is uniquely capable of dealing with the preconditioning of hot, dirty (particulates) and moisture-saturated samples, such as those found in the reformer and shift-converter streams, whereas the OptoAST module can interface to relatively dry and clean process samples at line temperature and pressure (up to 150 °C/1000 psig). As such, only minimal sample conditioning is required, while avoiding any need for sample transport to the analyzer in a shelter, because the optical probe sensor transmits spectral information via an optical fiber to the analyzer.

	Stream Service	Key Measurement Parameter	Pressure* (barg)	Temp* (°C)	Recommended Sampling Interface
①	Natural Gas Feed to Primary Reformer	Carbon Number	26	25	OptoAST
②	Fuel Gas to Reformer Furnaces	BTU	6	40	OptoAST
③	Raw Syngas – Primary Reformer Outlet	Composition/CH ₄	36	800	OptoDRS
④	Raw Syngas – Secondary Reformer Outlet	Composition/CO	35	370	OptoDRS
⑤	High Temperature Shift Converter Outlet	Composition/CO	34	445	OptoDRS
⑥	Low Temperature Shift Converter Outlet	Composition/CO ₂	32	220	OptoDRS
⑦	CO ₂ Absorber Outlet – Feed to PSA	Composition/CO ₂	31	25	OptoAST
⑧	PSA Unit H ₂ Stream	Composition/H ₂ /N ₂	18	30	OptoAST
⑨	CO ₂ Absorber Recovery Stream	CH ₄ Impurities	5	30	OptoAST

Table 1: Summary of the Typical Streams analyzed on-line in a Hydrogen plant

* Pressure and Temperature values listed are for typical process unit outlet streams.

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