Captive hydrogen: production analytics overview

HyCO 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.

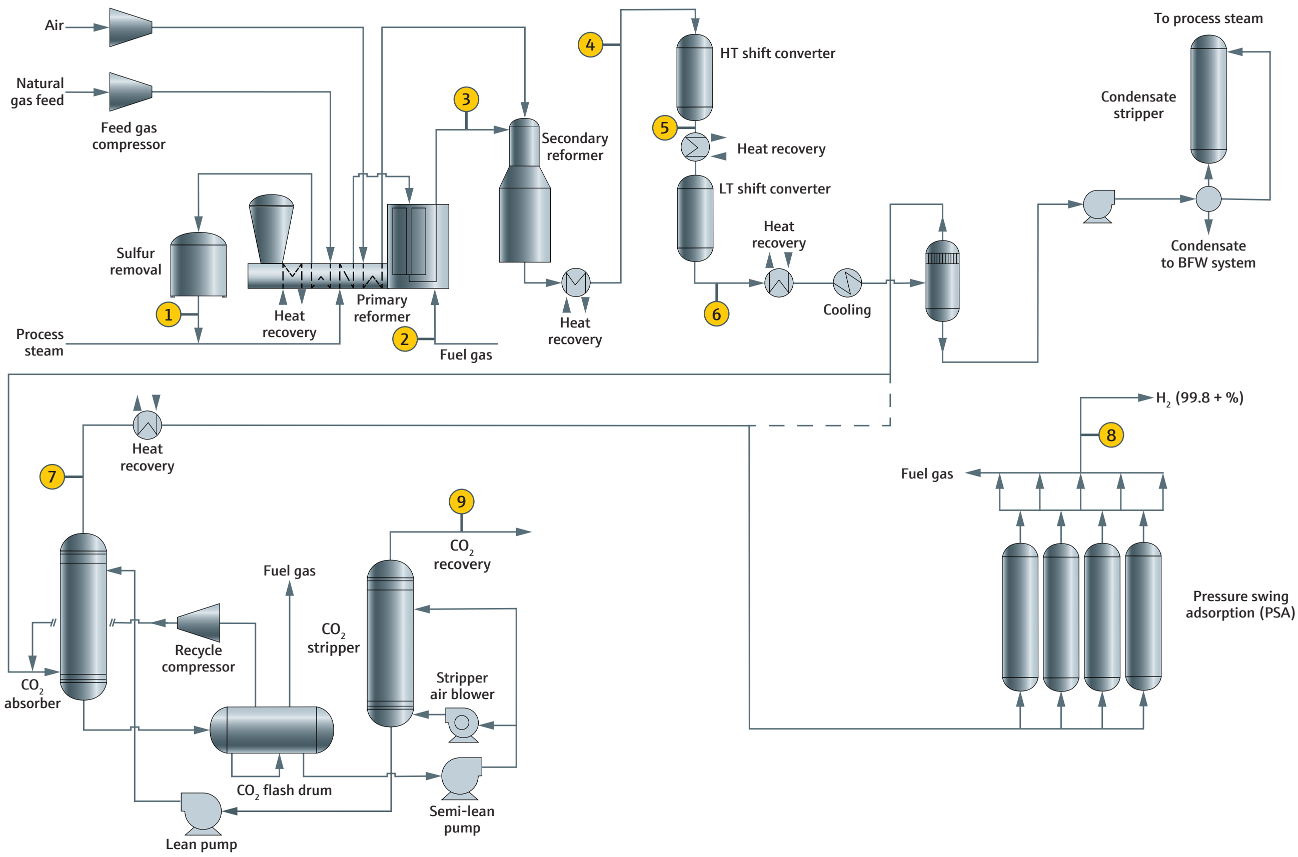

Figure 1: A simplified process diagram showing the main process units for the generation of captive hydrogen inside the battery limits (ISBL) of a modern refinery

Reference

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

*See the general Merchant hydrogen: production analytics overview

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 to require special sample conditioning techniques. With these challenging samples, the ability to obtain reliable sampling and analysis is often compromised. The use of the Raman Rxn5 analyzer combined with a well-designed sample conditioning system is a robust solution for these challenging streams.

The Raman Rxn5 analyzer The Raman Rxn5 analyzer provides the unique spectroscopic ability to analyze the mononuclear diatomic gases H_2 and N_2, 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. The Raman Rxn5 analyzer uses fiber optic cables of up to 150 meters in length to connect an Rxn-30 probe to the analyzer. The use of fiber optic cables allows the gas probe to be interfaced with a sample conditioning system near a sample tap point, so that no gas needs to be transported to the analyzer via expensive and high maintenance heated gas transfer lines. No potentially toxic or explosive gas mixtures are ever brought at or near the analyzer, eliminating the lag time associated with long sample transport runs. The safety of personnel is also enhanced because they do not need to come into contact with process gas to perform any routine maintenance on the analyzer. With a properly designed sample conditioning system, gas composition measurements can be made at temperatures up to 150 °C and pressures of up to 1000 psia. The ability of the Rxn-30 probe to measure under these conditions simplifies the sample conditioning required, and often allows the sample to be returned to the process after non-destructive Raman measurement, eliminating costly flaring.

	Stream service	Key measurement parameter	Pressure* (barg)	Temp* (°C)
❶	Captive hydrogen: natural gas feed to primary reformer	Carbon number	26	25
❷	Captive hydrogen: fuel gas to reformer furnaces	Btu	6	40
❸	Captive hydrogen: raw syngas – primary reformer outlet	Composition/CH_4	36	800
❹	Captive hydrogen: raw syngas – secondary reformer outlet	Composition/CO	35	370
❺	Captive hydrogen: high temperature shift converter outlet	Composition/CO	34	445
❻	Captive hydrogen: low temperature shift converter outlet	Composition/CO_2	32	220
❼	Captive hydrogen: CO_2 absorber outlet – feed to PSA	Composition/CO_2	31	25
❽	Captive hydrogen: PSA unit H_2 stream	Composition/H_2/N_2	18	30
❾	Captive hydrogen: CO_2 absorber recovery stream	CH_4 impurities	5	30

Table 1: Summary of the typical streams analyzed on-line in a captive hydrogen plant

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