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Heavy Water: A Manufacturers’ Guide for the Hydrogen Century

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Once the third most ubiquitous substance in the Universe, to most people deuterium is either unknown or an arcane curiosity. But, as heavy water, it has a crucial role in the CANDU®[1] reactor concept. As an isotope of hydrogen, its separation from normal hydrogen is surprisingly easy but its extremely low natural abundance makes such separation relatively expensive. Accordingly, Atomic Energy of Canada Limited (AECL) has worked extensively over the last 40 years on the development of the industrial processes with affordable economic characteristics. Three groups of processes attracted significant efforts and produced technically gratifying results. The most recent effort has brought a family of processes based on water-hydrogen exchange to industrial demonstration. They create potential synergies with industrial production of hydrogen, which many expect will become a major component of the energy systems of the 21st Century.

In the Beginning

Deuterium provides part of the evidence on conditions at the Big Bang origin of the Universe. Only three simple substances are believed to have formed as atomic matter coalesced out of the primordial plasma: light hydrogen (or protium, to distinguish the common hydrogen isotope) constituted about 75% and the balance was almost all helium. A mere 0.0013% emerged as deuterium, the heavier and stable isotope of hydrogen[2]. Unlike all heavier elements and isotopes, the Universe’s supply of both hydrogen and deuterium appeared once and for all. The stellar processes that create everything else are built from the hydrogen isotopes. But while a protium atom has relatively small risk of undergoing fusion inside a star, deuterium is completely consumed within seconds, a testament to its utility as a fuel for fusion.

Now stars are not a major component of the Universe’s mass and so have made little inroads on the deuterium content of the Universe since then but interesting local variations have developed. Small rocky planets like Earth have lost hydrogen to space rather prolifically. By preferentially retaining the heavier isotope, deuterium has become enriched to around 0.0155% in Earth’s oceans. (As much drier planets, Mars has attained almost 0.1% and Venus a spectacular 2.2% of the heavier isotope.)

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[1] CANadian Deuterium Uranium

[2] Protium has an atomic mass of 1. Deuterium adds a neutron to the single proton of hydrogen nuclei and so has a mass of 2. Tritium, the third isotope, has two neutrons, hence atomic mass 3 and is unstable, decaying to helium-3 with a 12.3-year half-life.

Who cares?

So deuterium is a minor component of all the hydrogen in us and around us. It is apparently harmless, varying gently in surface water from 0.0130% in arctic surface water to 0.0162% in the Nile in Egypt—the latter, an effect of naturally occurring fractional distillation. Why should anyone want to extract it? In small amounts, it is useful as a tracer of chemical and biochemical reactions and as a protium-free substance for magnetic resonance imaging. The dominant use, however, arises from its properties as a neutron moderator.

Nuclear reactors depend on a chain reaction in which neutrons from an initial fission induce at least one further fission. At the high velocity with which they emerge from fission, neutrons are far less likely to produce a new fission event than if they are first slowed to much lower speeds, the process call moderation. This process is essential for the design and operation of "thermal" nuclear reactors, which predominate in today's nuclear power plants. For the number of collisions needed to slow neutrons from "fast" to "thermal" speeds, protium is unbeatable. In that respect, protium in the form of normal ("light") water is the best moderator and is the reason that light-water reactors have relatively small moderator volumes. (The oxygen in water is, conveniently, invisible to neutrons.) Protium, however, is also fairly effective in absorbing neutrons with the result that a chain reaction can only be sustained if the uranium fuel is enriched in fissile nuclei (usually U-235) by around a factor of four above U-235's natural 0.7% abundance. Deuterium, though requiring more collisions and hence a larger volume of moderator, slows neutrons with a much lower risk of capture. Minimal capture means that natural uranium can fuel a reactor moderated with deuterium in the form of heavy water[3]. So designers of thermal reactors have a fundamental choice: either, isotopically enrich the uranium fuel in fissile atoms; or, isotopically enrich the moderator in deuterium. The first option is an ongoing requirement. The second, which is the choice of the CANDU® is close to being a one-time operation since only around 0.5%/a of the heavy water is lost from a CANDU.

How best to separate heavy water?

While it is merely an isotope of hydrogen, separation of deuterium from protium is easy compared to some separations of different elements. Both physical and chemical processes abound where the two isotopes behave distinctively. Indeed, considering the great natural dilution of deuterium (below one part in 6000), the ease with which it can be extracted is reflected in a price of only around 300 $/kg D_2O. By way of comparison, from a typical natural abundance of around one-sixth that of deuterium in protium, gold extracted from rock costs over 6000 $/kg to extract.

To provide some perspective on the factors affecting the economics of D_2O production processes, consider fractional distillation of water. This is the simplest deuterium

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[3] On the rare occasions when neutrons are absorbed by deuterium, two times out of three, an atom of tritium is formed. The third neutron behaves advantageously, fissioning the deuterium nucleus and ejecting a protium atom and two neutrons.

separation process. At 13 kPa (51°C), the vapour pressure of the deuterated form of water is reduced by 5.5% compared to undeuterated water. Or, to introduce the concept of the separation factor, α:

$$\alpha = 1.055 = \frac{\textit{deuterium concentration in the liquid}}{\textit{deuterium concentraion in the vapour}}.$$

α is a function of temperature, falling as temperature rises. Because it is only 1.015 at the normal boiling point of water, use of distillation under vacuum is very attractive. Figure 1 illustrates the simplicity of this process. Water is boiled and condensed at opposite ends of a contacting tower, which is filled with a highly wettable packing, usually made of phosphor bronze. Throughout the contacting tower, liquid and vapour are brought into repeated contact. The falling liquid water becomes steadily enriched in deuterium while the rising vapour becomes steadily depleted. Though the separation factor is quite small, repeated contact amplifies the effect. It is common for such a system to have the equivalent of some hundreds of equilibrium contacts – i.e. increments of packing in which the exiting liquid and vapour are in equilibrium with each other.

The process could hardly be simpler. Heat is applied at the bottom; cooling at the top. There are no moving parts and it is almost totally sealed. The only adjunct processes required are a small system to eject any air inleakage and good purification of the water feed to eliminate anything that could corrode or coat the packing.

The limitation of water distillation lies in the quantities of water that must be evaporated. Because the separation factor is relatively small, the internal flows between the boiler and the condenser must be around 13 times larger than the feed flow. This is not a serious problem for small quantities of recovered water but it is huge detraction from the possible use of water distillation for primary production of D_2O when factored onto the already large volumes associated with the low concentration of deuterium in natural water. For D_2O production, around 100 000 times the product rate would have to be boiled and condensed. The temperature at which this heat of vaporization must be applied is admittedly fairly low but, even if heat were free, the volume of packing to handle immense vapour flows is prohibitively expensive.

Note though that processes that are unsuited to primary D_2O production can be useful for other separations of hydrogen isotopes. Thus, water distillation has been used almost invariably to reprocess the small escapes of D_2O in CANDU reactors that are recovered by dryers because the volumes are low.

For primary production, vacuum distillation is uncompetitive because (1) the separation factor is too small and (2) the energy requirement too large. This process does however also have advantageous features: (1) the exchange rate is fast; (2) a liquid and a vapour are involved and so countercurrent contact is possible; and (3) the feed, water, is available in unlimited amounts.

Those five characteristics provide quite a comprehensive framework to assess the suitability of a physical or chemical process for D_2O production. Table 1 compares some of the other possible processes for D_2O production against those five criteria. Those that make a process uneconomic are shown in bold. Process strengths are shown in italics.

Table 1: D_2O Production Processes Overview

Process	Separation Factor	Energy Needed	Natural Exchange Rate	Countercurrent Flows	Feed
Distillation of H_2O	**1.015 to 1.055**	**Very high**	Moderate	Yes	*Water*
Distillation of Liquid H_2	*~1.5*	Moderate	Slow	Yes	**Very pure H_2**
Water electrolysis	*5 to 10*	**Very high**	Fast	**No**	*Water*
Laser Isotope Separation	*Huge; can be > 20 000*	Moderate?	**Slow**	Unimportant	**CFCs**
Water-Hydrogen sulphide exchange	1.8 to 2.3	**High**	*Fast*	Yes	*Water*
Ammonia-hydrogen exchange	*2.8 to 6*	Moderate	**Slow – catalyst needed**	Yes	H_2
Aminomethane-hydrogen exchange	*3.5 to 7*	Moderate	**Slow – catalyst needed**	Yes	H_2
Water-hydrogen	2 to 3.8	Moderate	**Almost nonexistent – catalyst needed**	Yes	*Water*

Table 1 contains a wide range of process types, all capable of producing D_2O, but reveals no economically outstanding process. Each process has strong and weak points.

Water electrolysis has a high separation factor but the only way to apply it repeatedly is to recombine the oxygen and hydrogen and then repeat the electrolysis, which is very energy intensive. (Strictly speaking, electrolysis depends not on equilibrium but on a kinetic isotope effect in which H is evolved much faster than D. While the separation factors for the other processes are precise thermodynamic values and functions of temperature, the rate-determined ones for electrolysis and laser isotope separation depend on details of the equipment.)

Laser isotope separation offers tantalizing possibilities. Figure 2 illustrates the concept, which is based on the different resonant frequencies of bonds ending in a protium and deuterium atom. In theory, one could tune a laser to the exact frequency of a deuterated bond, break it, and so free deuterium with exquisite selectivity. However, rupturing a chemical bond with a single photon requires UV energies and those are not available with reasonable energy efficiency or cost. This impasse was circumvented by the discovery by Marling[4] at Lawrence Livermore Laboratories that a cascade of IR photons could be just as selective if the photons were tuned to the first transition above the electronic ground state. Extensive follow-up by AECL at Chalk River confirmed the principle and revealed its limitations. The simple molecules that are available industrially on a sufficient scale—water, hydrogen, ammonia and methane—are not susceptible to this process. So an intermediate transfer step would be required for a practical process, the photo-selective molecule being re-deuterated by contact with water. Even with perfect selectivity, one photo-selective molecule would be destroyed for every atom of D released. So most chemicals could be eliminated as simply more expensive atom-for-atom compared to D. Any losses of undeuterated molecules would further curtail the price range of suitable working molecules. The photo-selective substance has to be amenable to a countercurrent re-deuteration process, either as a gas or a liquid virtually immiscible with water and yet capable of exchanging D and H atoms with water. (The alternative of contact of a liquid with steam would use excessive amounts of energy.) All these things considered, the most interesting molecules were found to be cholorofluorocarbons. Separation factors up to 26 000 were measured. Unfortunately, quite apart from chlorofluorocarbons being excoriated for their damage to the Earth's ozone layer, review of the exchange step to replenish the D content of the active molecule placed this process somewhere between impracticable and uneconomic.

For any extraction process, the initial step, which treats the entire deuterium-carrying feedstock, must be simple. But the LIS approach to deuterium extraction illustrates that simplicity in itself is not necessarily sufficient. Countercurrent contact between water and the working molecule is simple enough but would have to sit precariously between easy transfer of H and D without substitution of –OH for –H or significant losses of the working molecule to solution in the effluent water. Assuming the working molecule was gaseous – rates of exchange for gas-liquid contact are usually faster than those for liquid-liquid exchange – this step would benefit from high pressure but the laser dissociation step needs low pressure so flow of the working molecule that is at least as large as the water feed would need to be compressed and expanded.

Processes Based on Chemical Exchange

The remaining processes in Table 1 all depend on the separation factors between two chemical species influencing a reaction of the type:

$$\mathrm{HX + DY \Leftrightarrow DX + HY.}$$

Monothermal versus Bithermal Processes

One species is a gas, the other a liquid. Quite large separation factors exist for the pairs of chemical species listed and they can be exploited in two approaches: monothermal and bithermal processes. These are illustrated in Figure 3.

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[4] Marling, J.B., Herman, I.P., and Thomas, S.J., *J. Chem. Phys.*, 72, 5603, 1980.

Monothermal processes are very simple. Equilibrium favours deuterium in the liquid species. So, by converting the liquid into the gas, the gas can then be used to enrich the incoming liquid in D. The effect can be amplified by countercurrent flow of the liquid, prior to its conversion, with the gas, after conversion. Quite short exchange columns can achieve high deuterium enrichments because the gas enters the exchange column at the same concentration as the liquid leaving it and so is far removed from equilibrium. Note too that a substantial part of the deuterium in the liquid can be extracted since the D concentration in the gas leaving can be as low as $1/\alpha$ of the feed concentration. There is only one problem with monothermal processes: a simple conversion process has to exist and it has to be very low cost since it will have to treat the entire feed flow. For two of the four processes in Table 1, there is no practicable conversion process. However, both water and ammonia can be converted into hydrogen. Ammonia is comparatively easy to dissociate thermally, requiring 45 kJ/mol. Plants using this monothermal process have been built in India and Argentina.

Water is much harder to dissociate, requiring 240 kJ/mol. Allowing that 100 ppm of the deuterium in the feed water could be extracted, 10 000 moles of feed water would produce one mole of D_2O. With a molecular weight of 20, the energy associated with thermodynamically perfect dissociation would be 120 GJ/kg D_2O. So, using electrolysis with electricity at a very low cost of 3 ¢/kW.h, the energy cost would be 1000 $/kg D_2O.

Bithermal processes are somewhat more complex but they avoid the need for chemical conversion. They exploit the inverse relationship between separation factor and temperature. So the cold tower of a bithermal process enriches the liquid in D and strips D from the gas. The liquid then passes to the hot tower where α is smaller. Consequently, some of the deuterium in the liquid is forced back into the gas and the hot tower progressively depletes the liquid and enriches the gas in D. Where liquid is the feedstock, the gas is recycled. (This is usually the case but gas-fed bithermal processes are just as feasible.) Note that extraction of D from the feedstock is limited by the ratios of α in the hot, α_h, and cold, α_c, conditions. The maximum extraction is $(1 - \alpha_h/ \alpha_c)$, much less than the $(1 - \alpha_c)$ of the monothermal process. Further, not only is a hot exchange column needed, but the cold exchange column is lengthened too because the gas concentration entering it is much lower than occurs with the monothermal process.

Which Chemical Pair?

The four pairs listed in Table 1 have emerged as the options of choice. None is ideal.

Girdler-sulphide

The water-H_2S combination is the basis of the bithermal Girdler-Sulphide (G-S) process. This process has produced far more heavy water than any other in Canada and worldwide. The G-S process had not been easy to deploy and AECL and Ontario Hydro put much effort into mastering it: problems with foaming were overcome with the development of antifoaming agents to add to the feed water; corrosion and erosion occurred and were overcome by choice of materials and control of process conditions; the reasons for poor contact efficiency between the gas and the water were explored and improved; and the process was modelled in great detail, allowing more effective operation. As a result, by around 1980, four Canadian plants were operating very successfully, producing over 2000 tonnes of D_2O a year and glutting a fading market for new reactors with their output. Three plants were quickly taken out of service and the last half of the fourth plant ceased operation in 1997.

The G-S process was a triumph of engineering stubbornness: it uses large amounts of steam energy (>10 Mg/kg D_2O); H_2S is highly toxic and corrosive; and the separation factor does not vary greatly over the rather narrow range of temperatures than can be used. The only upside for the G-S process is that the exchange reaction is fast and occurs without a catalyst.

Ammonia-hydrogen and aminomethane-hydrogen

The other three pairs all need catalyst assistance. Ammonia-hydrogen and aminomethane-hydrogen are closely related and both depend on ammoniacal alkali metal salts to catalyse the reaction (KNH_2 in ammonia). Even with these, the reaction is still rather slow and complex mechanical agitation is needed to provide adequate transfer rates. To exploit the effect of temperature on separation factors, refrigeration is needed and the energy demands of the process are significant. By substituting aminomethane (CH_3NH_2) for ammonia (NH_3), AECL developed a superior bithermal process during the 1970s. Aminomethane has faster kinetics and a rather wider temperature range. An industrial prototype of this process was about to be committed in 1979 when the demand for D_2O suddenly turned down.

Both monothermal and bithermal ammonia plants have been built and successfully operated. Some depend on hydrogen plants for their feedstock and some on water-ammonia exchange to replenish the deuterium content of the ammonia. Though less hazardous than H_2S, ammonia and aminomethane are both toxic.

Water Hydrogen

How much simpler it would be if one could use the water-hydrogen pair. As Table 1 indicates, water and hydrogen do not, however, exchange hydrogen isotopes without a catalyst and a good catalyst is the key to applying this system. That requirement apart, this pair has many attractive features: it operates in a moderate temperature range; there are no toxicity or corrosion issues; and both substances are available as feedstocks on a large scale. Water-hydrogen exchange was, in fact, applied to produce up to 6 tonnes/a of D_2O in Trail, B.C., between 1944 and 1956. However, the catalyst undermined its economics.

Water and hydrogen will exchange hydrogen isotopes in the presence of various metal catalysts. Platinum has long been recognized as the most effective metal for this purpose. However, because of the low solubility of H_2 in water, even a thin film of water reduces catalyst activity to near zero. To get round this impasse, the Trail plant used a succession of co-current contacts between hydrogen and superheated steam, each contacted separated by a condenser and a boiler/superheater. There was thus no natural countercurrency in the process and it was hugely energy-intensive.

Development of a "wetproofed" catalyst by AECL has been the key to processes based on water-hydrogen exchange. The idea is very simple: apply a film to the catalyst surface that is water-repellent but will permit ready passage of water vapour and hydrogen. In practice, developing really effective catalysts with high activity and long life has been a major undertaking spanning over three decades. However, AECL now has effective catalysts and continues to enhance their performance.

Monothermal water-hydrogen

If electrolytic hydrogen were being produced on a large scale (> 100 MW), the addition of a monothermal water-H_2 process to produce heavy water would produce D_2O at an unbeatable price. This process is known as Combined Electrolysis and Catalytic Exchange (CECE). Alas, while electrolysis is widely used to produce hydrogen of high purity in small quantities, large-scale production by electrolysis has been very unusual. (See, however, below.) Large-scale production of hydrogen is preponderantly produced by steam-methane reforming (SMR), whose basis is the reaction:

$$CH_4 + 2H_2O \Rightarrow 4H_2 + CO_2.$$

Here again, water is converted into hydrogen. So there is again the possibility of a monothermal process, which we refer to as the Combined Industrial Reforming and Catalytic Exchange (CIRCE). This is illustrated in Figure 4. Obviously, it is much more complex than CECE. It is also more demanding in a number of ways: (1) the water flow is half that of the hydrogen, which means that the two species come closer to equilibrium in transferring deuterium into the liquid; (2) the whole SMR must be a tightly closed system to contain material enriched in deuterium by a factor of 10 to 20; and (3) traces of carbon monoxide normally present in SMR-hydrogen must be eliminated since CO poisons the exchange catalyst. These are all tractable issues, demonstrably so with the successful operation of a prototype plant by AECL at a small SMR in Hamilton, owned by Air Liquide Canada (Figure 5).

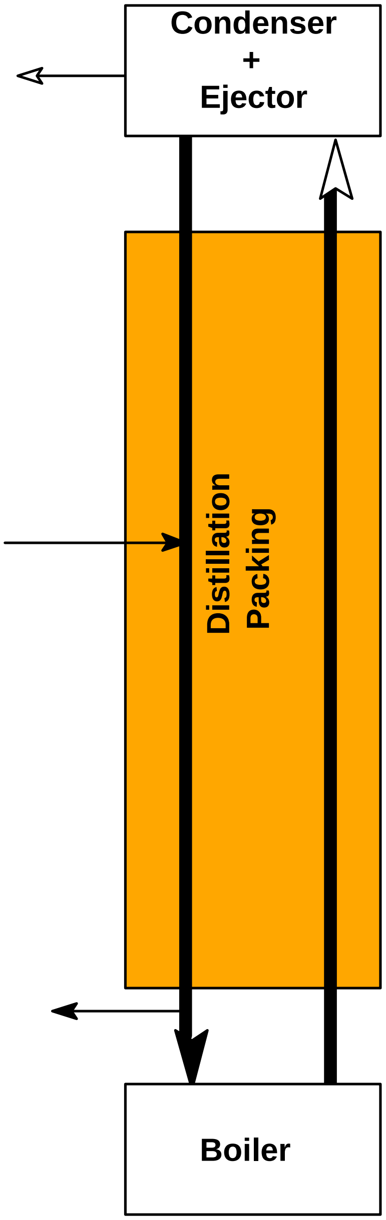
The prototype is a comprehensive demonstration of the technology: beside the CIRCE first stage, it incorporates a bithermal water-hydrogen second stage (producing 10% D) and a CECE third stage to complete the enrichment to reactor-grade (99.72 mole%) D_2O.

Another prototype plant at AECL's Chalk River Laboratories has recently completed qualification of the CECE process for use as a heavy-water upgrader (at around half the cost of water distillation) and for tritium removal from heavy water.

Where Next?

By mid-2002, the prototype CIRCE plant at Hamilton should have completed the demonstration of this process for heavy-water production. Large SMR plants are ubiquitous. Successful operation of the prototype plant, taken together with ongoing work to lower the cost of the exchange catalyst, will provide the anchor process for future D_2O production. However, the CECE process would always be better if only electrolysis were used for large-scale production of H_2.

Now H_2 is much touted as *the* fuel for the new century. Burned in fuel cells, it is free from the polluting effects of VOCs and NOx. If it were produced electrolytically from electricity produced by nuclear or other low-CO_2-releasing sustainable technologies, it could be the ultimate transportation fuel source to redress greenhouse gas emissions associated with traditional fuels or hydrogen produced by SMR technology. The combination of nuclear electric generation—water electrolysis—and D_2O production by CECE is an alluring possibility.



Water Distillation

Figure 1.

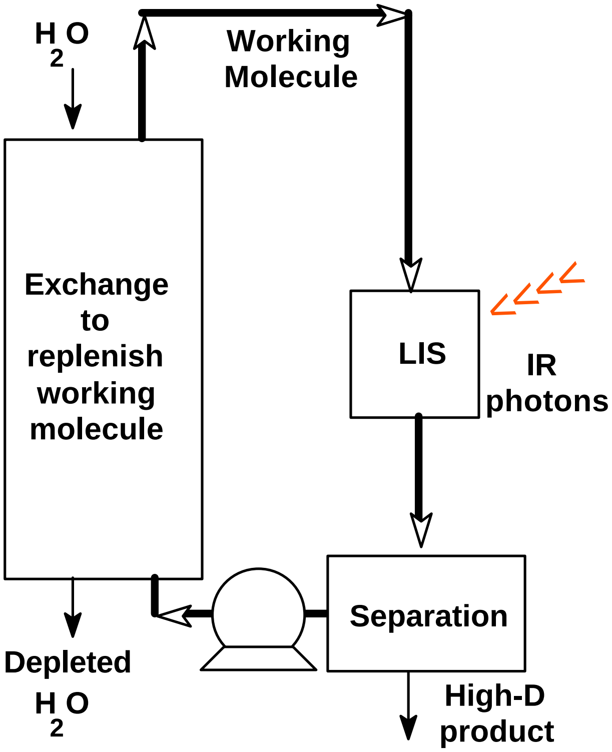

H2O
Working Molecule
Exchange to replenish working molecule
LIS
IR photons
Separation
Depleted H2O
High-D product

Figure 2.

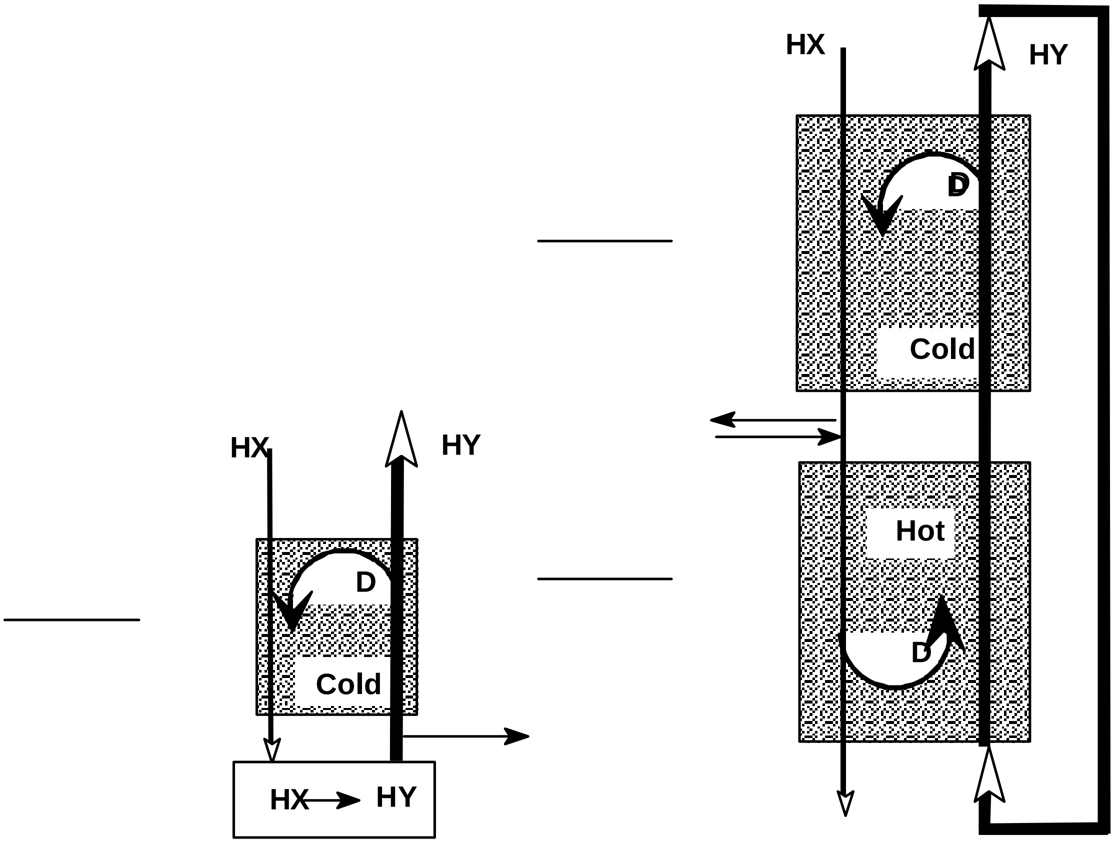


Figure 3.

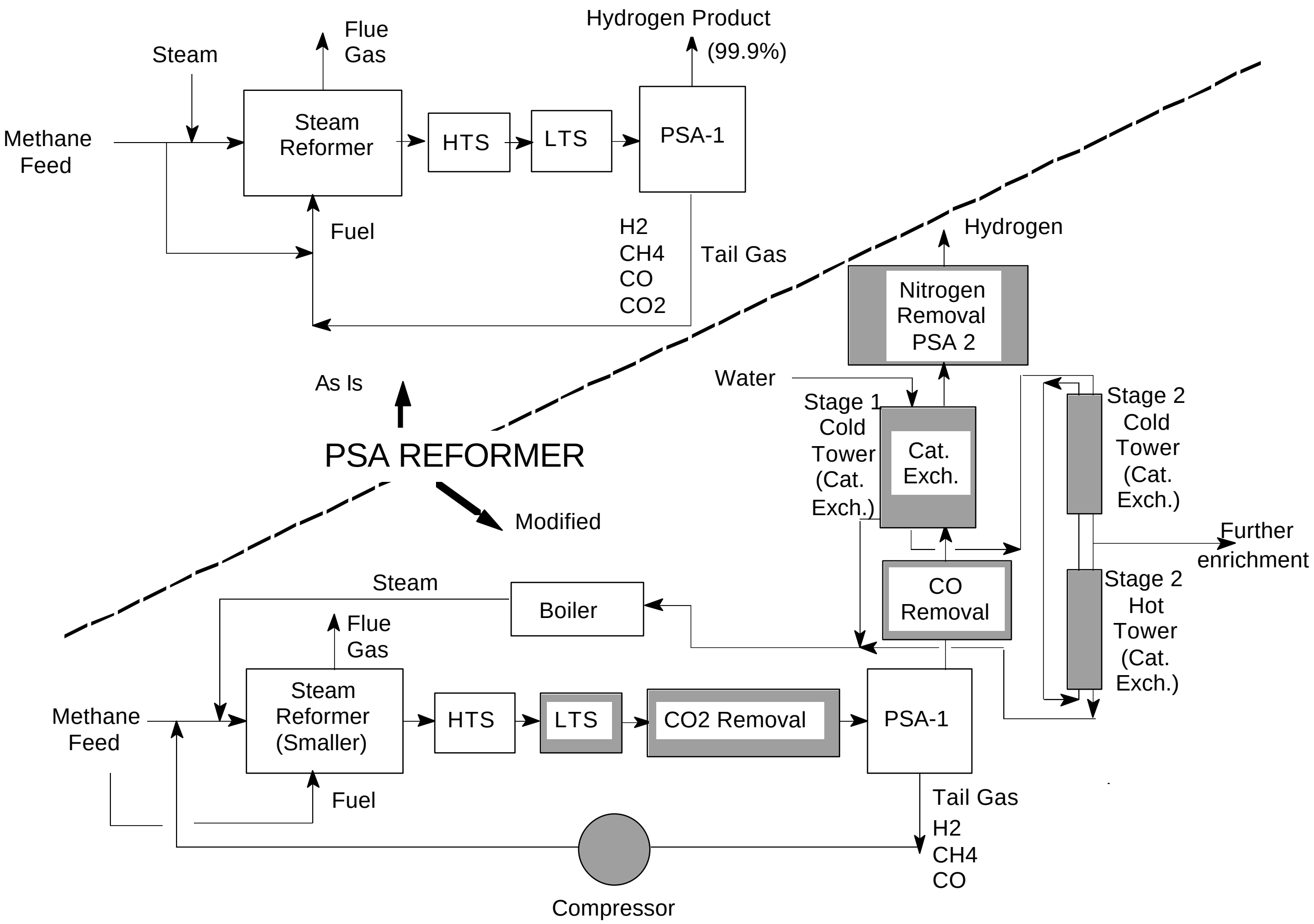

Steam
Flue Gas
Hydrogen Product
(99.9%)
Methane Feed
Steam Reformer
HTS
LTS
PSA-1
Fuel
H2
CH4
CO
CO2
Tail Gas
Hydrogen
Nitrogen Removal PSA 2
As Is
Water
Stage 1 Cold Tower (Cat. Exch.)
Cat. Exch.
Stage 2 Cold Tower (Cat. Exch.)
PSA REFORMER
Modified
Further enrichment
CO Removal
Steam
Boiler
Flue Gas
Stage 2 Hot Tower (Cat. Exch.)
Methane Feed
Steam Reformer (Smaller)
HTS
LTS
CO2 Removal
PSA-1
Fuel
Tail Gas
H2
CH4
CO
Compressor

Figure 4.

Figure 5.