

TRITIUM RECOVERY FROM WASTE USING A PALLADIUM MEMBRANE REACTOR

Stephen A. Birdsell and R. Scott Willms
Los Alamos National Laboratory
MS C348, Los Alamos, New Mexico 87545

ABSTRACT

A large quantity of tritiated-water waste is produced worldwide and stored or disposed of in the form of tritiated water adsorbed on molecular sieve. The Palladium Membrane Reactor (PMR) has been developed to efficiently recover tritium from this water while greatly reducing the amount of water disposal. High tritium recovery and long-term operation have been demonstrated for this application. More recently, the PMR has been considered for use in processing mixed tritiated wastes. Although tritium experiments have not yet been done, non-tritium experiments with relevant hydrocarbons have been processed. Methanol, ethanol, octane, and gasoline have been processed with high hydrogen recoveries. The gasoline contained a wide distribution of hydrocarbons (27.2% aromatics, 6.5% olefins, and 66.3% saturated hydrocarbons) and 32.5 ppm sulfur, which demonstrates the robust potential of the PMR for mixed waste processing. Tritiated mixed wastes are available at Los Alamos for demonstration of the PMR. These wastes can be treated at Los Alamos without requiring a license since they were generated onsite and the tritium will be recycled. Plans for processing pure tritiated organics such as methanol, ethanol, propanol, and toluene are being made.

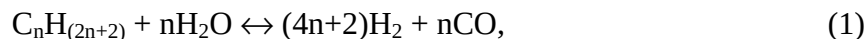
INTRODUCTION

Tritiated hazardous organics are generated in significant quantities at the Lawrence Berkeley National Laboratory (LBNL), the National Institute of Health (NIH), universities, pharmacology companies, the Los Alamos National Laboratory and various other institutions. Most of these wastes are generated in tritium labeling operations for biomedical applications and can sometimes be treated by waste disposal companies. Processing is accomplished by efficient oxidation of organics and subsequent release to the environment. Hence, tritium is released directly to the environment. Disposal companies are licensed to process the wastes based on, among other things, a maximum quantity of radiation that can be stacked per year. Thus, costs per Curie of disposal are extremely high. In some cases, such as at LBNL, wastes have accumulated for many years. Waste disposal services are available, but the costs for disposal of these large quantities are prohibitive.

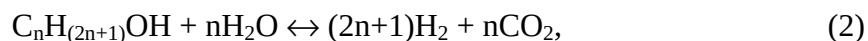
The palladium membrane reactor (PMR) followed by isotope separation, is a process with much potential for treating tritiated mixed wastes while recovering, essentially, all the tritium. The PMR converts water into a pure hydrogen isotopes stream and a carbon oxide waste stream. Tritium can then be purified from the hydrogen isotopes stream with an isotope separation system. In a demonstration with tritiated-water waste, 45,000 Ci were recovered from 2 L of water using a PMR/cryogenic distillation system. In an energy application, the PMR was used to process fuels such as methanol, ethanol, octane, and gasoline into a pure carbon dioxide stream and pure hydrogen stream. The gasoline contained a wide distribution of hydrocarbons (27.2% aromatics, 6.5% olefins, and 66.3% saturated hydrocarbons) and 32.5 ppm sulfur, which demonstrates the robust potential of the PMR for mixed waste processing. These fuels would be

considered hazardous wastes if it were necessary to dispose of them. Therefore, the PMR has been demonstrated, in 2 separate applications, to be effective at processing tritiated wastes and hazardous wastes. Many of the tritiated mixed wastes generated in the biomedical field (by for example, LBNL, NIH, universities, and pharmacology companies) are similar, from the perspective of processing, to the hydrocarbons tested with the PMR. Therefore, processing tritiated mixed wastes is a logical extension of the PMR

The palladium membrane reactor is an integrated catalytic-reactor/palladium-membrane. Catalysts are used to foster reactions such as alkane steam reforming



alcohol steam reforming



and aromatic reactions such as toluene steam reforming,



Since H_2O and CO are always present in steam-reforming environments, the water-gas-shift reaction



is also important. Due to thermodynamic limitations these reactions only proceed to partial completion (e.g., 40% conversion for methane reforming, Eq. 1). Therefore, a Pd/Ag membrane, which is exclusively permeable to hydrogen isotopes, is incorporated into the reactor (Fig. 1). Water and hydrocarbon are injected into the “catalyst side” of the PMR, where reactions such as Eqs. (1)-(4) occur. Pure hydrogen isotopes are produced in the permeate stream. Removal of H_2 from the reaction mixture causes equilibrium to move to the right in Eqs. (1)-(4). How far the equilibrium is moved depends on how much hydrogen is removed from the reaction mixture. By pulling a vacuum on the permeate side of the membrane, most of the hydrogen can be removed from the reaction mixture, enabling the reactions to proceed, essentially, toward completion.

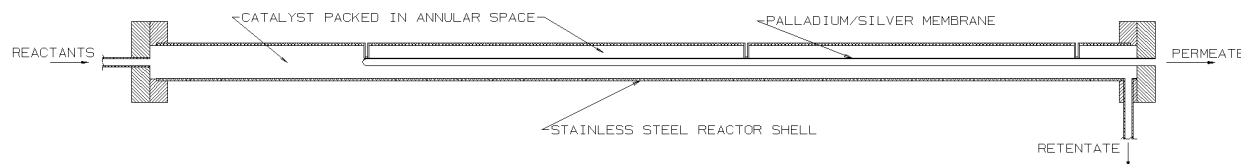


Figure 1. The Palladium Membrane Reactor.

Two types of PMRs have been investigated. The 1st stage PMR uses a scroll pump to achieve vacuums of about 1 mb in the permeate. The 2nd stage PMR uses a turbomolecular pump to achieve vacuums of about 10^{-6} mb. Staging results in more efficient operation than using a

single, larger reactor. For the non-tritium tests described below, both stages had a single Pd/Ag tube with dimensions of 0.635 cm outer diameter, 61.0 cm long, and wall thickness of 0.0178 cm. For the tritium tests, the PMRs were similar in design, but scaled-up by a factor of 6. Pt/ α - Al_2O_3 catalyst (Engelhard A-16825) was used in all of the PMRs.

The PMR has been under development at Los Alamos since 1992 (1-6). During this time, PMR performance has been characterized with respect to inlet conditions (i.e., hydrocarbon-to-water ratio), temperature, pressure, geometry, and catalyst type. This information has been analyzed and incorporated into a mechanistic model for use in design, optimization, and scale-up. Methane, methanol, ethanol, octane, and gasoline reforming and the water-gas-shift reaction have been investigated in non-tritium tests while methane reforming and the water-gas-shift reaction have been investigated in tritiated tests.

NON-TRITIUM TESTS

Fuel reforming (methanol, ethanol, octane, and gasoline) was done to demonstrate the applicability of the PMR to produce pure hydrogen in energy applications such as fuel cells. Non-tritium tests were also done with methane steam reforming and water-gas shifting in preparation for tritium experiments. This system was operated for 215 days (round-the-clock) over an 18-month period with high performance and reliability. Upwards of 99% recovery of injected hydrogen (in the form of hydrocarbon and water) can be produced as pure H_2 for each of the reactions investigated.

The water-gas-shift reaction (Eq. 4) is the dominant reaction when recovering hydrogen from water. In this application, water is injected into a PMR with the appropriate amount of CO such that most of the H_2 is produced in the permeate. Figure 2 shows the decontamination factor (DF = inlet hydrogen rate/outlet hydrogen rate) as a function of the inlet CO-to- H_2O ratio (CO: H_2O) for H_2O inlet rates ranging from 29-150 std. cm^3/min . For reference, DF=100 represents 99% recovery of hydrogen in the permeate, while DF= 340 represents 99.7% recovery of hydrogen in the permeate. PMR performance is strongly effected by the CO: H_2O . The optimum CO: H_2O occurs in the 1.1-1.2 range. If too much water is injected relative to the CO injection, then water breaks through to the outlet of the PMR. If too little water is injected, methane breakthrough occurs.

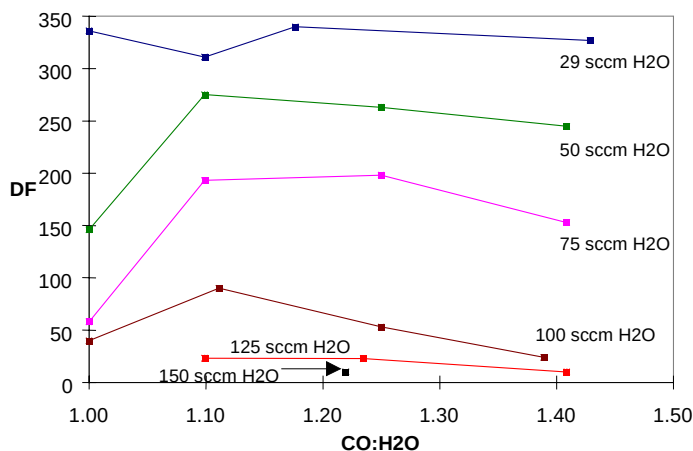
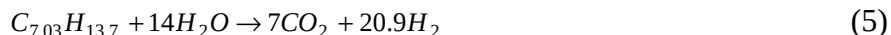


Figure 2. Decontamination factor versus inlet CO-to- H_2O ratio (530°C).

Gasoline is comprised of a wide-range of hydrocarbons, many of which are classified as hazardous material. Therefore, gasoline reforming will be the focus of this discussion. Details of the methane, methanol, ethanol, and octane reforming experiments can be found in (4). California Certification Fuel Phase II Reformulated Gasoline (RFG) from the Phillips Chemical Company was used in the experiments. The gasoline came with a certified analysis. A short description of the analysis is 27.2% aromatics, 6.5% olefins, and 66.3% saturated hydrocarbons. Carbon comprises 84.3 wt. %, hydrogen 13.7 wt. %, and the sulfur concentration is 32.5 ppm. This analysis gives an average molecular formula of $C_{7.03}H_{13.7}$ for gasoline.



This formula was used to determine how much water to inject relative to a given gasoline injection rate. Similar to the water-gas-shift reaction, if too much water is injected, hydrogen will breakthrough the PMR in the form of water. If too little water is injected, hydrogen will breakthrough in the form of hydrocarbons.

Figure 3 shows the gasoline-reforming performance at 550 and 575°C. Hydrogen production is much lower at 550°C, where 95% of the injected hydrogen is produced in the permeate, than at 575°C, where over 99% of the injected hydrogen is produced in the permeate. At 550°C, C_2H_6 was observed in the retentate with concentrations ranging from 50-400 ppm. The C_3H_8 concentration was 55 ppm. No peaks other than H_2 , CH_4 , CO , CO_2 , C_2H_6 and C_3H_8 were observed in this data. However, at temperatures below 550°C, numerous peaks are observed. This poor performance indicates that 550°C and below is too low for efficient operation.

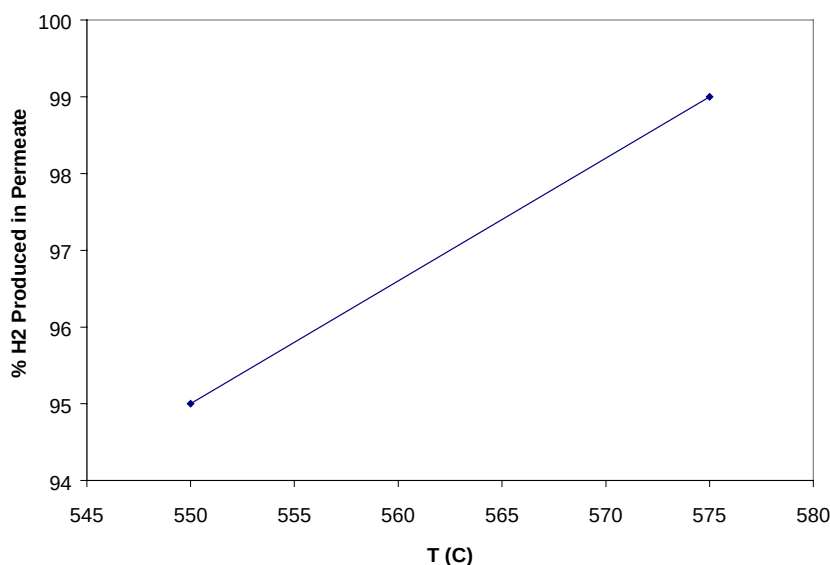


Figure 3. Gasoline steam reforming at a water injection of 6% in excess of stoichiometry.

TRITIUM TESTS

The above non-tritium tests were done on a test bench. Tritium tests were also done using a glove box system within a nuclear facility. Approximately 204 hrs. of steady-state PMR operation have been logged with high performance and reliability. Also, 30 start-up/shut-down

cycles were logged in the course of these demonstrations resulting in considerable operating experience.

The PMR was originally developed for fusion-fuel processing. This application involves steam reforming of tritiated methane and tritiated water (Eq. 1). A 2-stage PMR system was used in a 32-hr. test of the fusion-energy application. The 1st stage recovered approximately 99.7% of the hydrogen isotopes while the 2nd stage recovered approximately 99.9999% of the remaining hydrogen isotopes (overall recovery of 99.999998%). Details of this test can be found in (2).

In tritium facilities throughout the world, tritium wastes are typically oxidized to tritiated water and the water is adsorbed onto molecular-sieve beds for disposal in a waste repository. Tritiated water was removed from one such bed and processed with the PMR system. 2250 std. L of tritiated water were regenerated from the molecular sieve in 172 hrs. of testing. This demonstration resulted in the recovery of approximately 45,000 Ci of tritium and, essentially, complete removal of tritiated water from the bed. After processing with the PMR, the isotopes were fed into a cryogenic distillation system for production of pure T₂ and release of H₂ and D₂ to the environment.

A 2-stage PMR system was used to process the tritiated water for the first 21 hrs. of testing (3). Hydrogen-isotope recoveries were similar to those obtained in the fusion application. However, the 2-stage system achieves a higher recovery than is required for this application. Therefore, the remaining 151 hrs. of operation was done with a single-stage PMR, which is a more efficient system design. The exhaust of the PMR system must pass through a waste-treatment system before being stacked. Therefore, any hydrogen isotopes not recovered in the PMR system are collected on a molecular-sieve bed in the waste-treatment system. This bed will be processed with the PMR when it has been fully loaded with tritiated water. Thus, essentially no tritium is lost when reducing the PMR system to a simpler, more efficient single-stage system.

DISCUSSION

The PMR/isotope-separation process can be used to process tritiated mixed wastes while recovering the tritium for future use. Tritium recovery is desirable both from the perspective of reducing emissions and from the perspective of re-use. Existing processes for tritiated mixed waste disposal release the tritium to the atmosphere in the form of tritiated water. Tritiated water is 10,000 times more hazardous to humans than molecular tritium. Also, tritiated water is more likely to be concentrated in the local environment, by precipitation, than molecular hydrogen, which disperses in the atmosphere. Tritium is not produced in the US and is extremely valuable, with a commercial cost in the range of \$10,000/gm to \$30,000/gm. Therefore, it seems worthwhile to develop the PMR/isotope-separation process for tritiated mixed waste.

Several isotope separation techniques are available for the purification of tritium from hydrogen and deuterium. Chromatographic systems are used, but are only appropriate for small applications. Cryogenic distillation has been used by the US Department of Energy, and others around the world, for many years and is appropriate for this application. Another possibility is a semi-continuous chromatographic system that is in use at the Savannah River Site.

A PMR/cryogenic distillation system exists at Los Alamos. Also, tritiated mixed wastes awaiting disposal are stored at Los Alamos. Since these wastes were generated onsite and the tritium would be recycled with the PMR/cryogenic distillation process, it will not be necessary to obtain a license to do the demonstration. Among the wastes stored at Los Alamos are tritiated methanol, propanol, butyl acetate, and toluene. These wastes are among a list of the 17 most commonly generated wastes in tritium labeling operations for biomedical applications (7). Plans are being made to process these wastes.

CONCLUSIONS

The PMR has been demonstrated to efficiently process, in separate applications, tritiated wastes and hazardous wastes. After PMR processing, tritium was purified for reuse with a cryogenic distillation system. It is proposed to demonstrate this technology with tritiated mixed wastes. Los Alamos National Laboratory has tritiated mixed wastes in storage that are appropriate for PMR demonstration. Tritiated methanol, ethanol, propanol, and toluene are being considered for the demonstration. These wastes can be treated at Los Alamos without requiring a license since they were generated onsite and the tritium will be recycled. It is envisioned that after this technology is demonstrated at Los Alamos, it will be transferred to waste processing companies so that tritium recovery becomes the standard in tritiated mixed waste disposal.

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