

Membrane processes for Hydrogen separation and production

These membrane devices have been developed at ENEA Frascati laboratories for separation of hydrogen isotopes from tritiated water. Applied to the production of H₂ from biomass, the dehydrogenation process on which these devices are based, allows the achievement of higher hydrogen and syngas yields than traditional reactors. Furthermore, these processes represent the only solution available for some kind of biomass (i.e. olive mill wastewater) that cannot be treated via the conventional biological processes.

TRL 8

■ Description of the technology

Membrane devices for separation of hydrogen isotopes from tritiated water have been developed to operate in continuous processes characterized by high efficiency and increased safety. The membranes developed by ENEA have been tested at CEA Cadarache laboratories in a process for the treatment of housekeeping tritiated waste of JET in the frame of an EFDA task. Tritium was released from the waste in form of tritiated water that, in turn, was sent into a membrane reactor capable to recover tritium in molecular form.

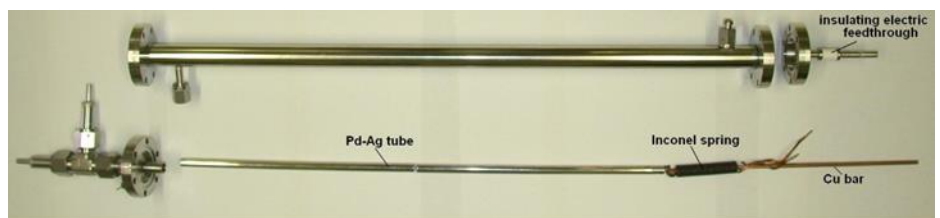
A membrane reactor, where hydrogen (one of the reaction product) is continuously removed via the membrane, can achieve reaction yields higher than conventional reactors (i.e. higher production of hydrogen and syngas from the same amount of biomass). Further, the use of Pd-based membranes allows the production of hydrogen of high purity (namely, 100%) such that required from specific applications (PEM fuel cells). Pd-alloys tube can be used for purifying the hydrogen produced via alkaline electrolyzers for both laboratory and industry (i.e., electronics, pharmaceuticals).

ENEA laboratories developed the know-how behind the Pd-membrane reactors (design, fabrication, characterization and process optimization) with specific expertise about: i) separators and membrane reactors for detritiation processes, and ii) membrane reactors for hydrogen production via dehydrogenation reactions (reforming of methane, ethanol and biomass, water gas shift of reformed streams). Pd-membranes operates in the temperature range 300-450 °C. In the fusion fuel cycle applications, permeator tubes are used to separate hydrogen isotopes from gas streams, while membrane reactors carry out the recovery of tritium from tritiated water via the water gas shift reaction or isotopic swamping. Main characteristic of these membrane units is the capability to extract the hydrogen isotopes with infinite selectivity.

When applied for the production of hydrogen via reforming, due the continuous removal of hydrogen (one of the reaction products) the Pd-membrane reactors are expected to work with reaction conversions higher than those achievable by traditional reactors or, in alternative, can yield the same amount of hydrogen but operating at lower temperature. For instance, the same hydrogen yield (around 50%) in ethanol steam reforming has been obtained in Pd-membrane reactors at 450 °C much below the operating temperature of traditional reformers (700-800 °C) thus involving significant advantages in terms energy efficiency and cost reduction



Internal view of the multi-tube membrane reactor built by ENEA for CEA laboratories (2017).



Pd-membrane reactor developed for JET soft housekeeping waste detritiation (JET Task Fusion Technology JW10-FT-2.35).

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■ Innovation and advantages of the offer

The innovation introduced in the Pd-membrane reactors for fusion fuel cycle applications consists of innovative mechanical design concepts (multi-tube modules, heating systems, compact size) and new joining techniques of Pd-tubes to steel parts. These developments allow operating detritiation processes in a continuous mode (then more efficiently and safely than the alternative processes based on the use of traditional reactors or on selective absorption in batch operations). In the tests carried out at CEA Cadarache laboratories (EFDA task on JET soft housekeeping waste detritiation) where D₂O was used instead of tritiated water, under the best operating conditions a Pd-membrane reactor exhibited very high extraction efficiency by recovering more than 90% of deuterium via isotopic exchange over the catalyst and permeation through the selective membrane.

■ Non-fusion Applications

Thanks to the validity of the technologies developed in the fusion, several applications in the field of (pure) hydrogen production (both membrane technology and process optimization) have been approached. Membrane reactors have been tested for the production of hydrogen and syngas from reforming of methane, ethanol and biomass. Reforming of olive mill wastewater via membrane processes allows to recover up to 3 kg of hydrogen per ton of wastewater. Although cost of Pd-alloy is still a hurdle in large scale applications, Pd-tubes can be applied in hydrogen generators for laboratory and other ultra-pure hydrogen devices. Furthermore, the processes based on dehydrogenation reactions represent the only solution available for some kind of biomass that cannot be treated via the conventional biological processes. This is the case of olive mill wastewater: the reforming process studied allows the reduction of the environmental pollution and its valorization for producing energy (hydrogen and syngas). Therefore, potential applications outside fusion concern: realization of small purifier for laboratory hydrogen generators, reforming of biomass for producing hydrogen and syngas. The technology and related know-how reach a TRL 8 in fusion and is available for demonstration in non-fusion.

■ EUROfusion Heritage

Researches at ENEA Frascati about Pd-membrane are carried out since 90's years in the frame of the programmes EFDA and then EUROfusion and in collaboration with CEA Cadarache and KIT (former TLK) Institutes. In this field, ENEA developed a relevant expertise moving from material development (diffusion bonding of Pd-Ag sheet for realizing thin-wall permeator tubes), then designing innovative Pd-membrane reactor (single and multi-tube finger-like configurations, heating systems, Pd-tubes joining) and, finally, developing detritiation processes via membranes.



Particular of a Pd-membrane module (15 tubes) before assembling