Membrane-Assisted Chemical Looping Reforming reactor for combined ultra-pure H\textsubscript{2} production and CO\textsubscript{2} capture

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Highlights

- Combination of two technologies in a new reactor that is here fully developed
- Ultra-pure H\textsubscript{2} (>99.99%) is recovered using Pd-based membranes
- Environmentally friendly concept with cost of H\textsubscript{2} similar to conventional technology
- Efficient heat integration that allows 91% CO\textsubscript{2} capture

1. Introduction

Globally, more than 95% of the hydrogen is worldwide produced from fossil fuels [1], with the steam methane reforming of methane (SMR) as the most used technology. Around 90% of this hydrogen is used for ammonia production (50%), methanol and refining industries. Giving a closer look to the ammonia industry, about 80% is used for fertilizers, which points out the strong effect of cost of H\textsubscript{2} production on basic products in the agriculture sector. Besides, the SMR technology is a highly energy-intensive process, thus also responsible for a large contribution to the anthropogenic emissions to the atmosphere. With the aim of reducing the CO\textsubscript{2} emissions associated with hydrogen production, a new reactor concept that combines advantages of two different technologies, namely membrane reactors for H\textsubscript{2} production and Chemical Looping for CO\textsubscript{2} capture, has been proposed and demonstrated at lab scale [2]. This reactor concept is named Membrane-Assisted Chemical Looping Reforming (MA-CLR), and has been demonstrated using natural gas as fuel source, though it could also be powered by renewable fuel sources like biogas (thus even leading to negative carbon emissions). Chemical Looping is a technology where a solid (metal) oxide circulates and transports heat and oxygen between two reactors operated at different atmospheres, oxidizing (air reactor) and reducing (fuel reactor), and avoids at any point in the process the mixing of fuel and air, which facilitates CO\textsubscript{2} sequestration. In the fuel reactor the endothermic fuel conversion occurs, and by integrating H\textsubscript{2} selective membranes, the hydrogen produced can be recovered as pure product. This hydrogen recovery allows achieving high yields at lower temperatures by shifting the equilibrium reactions towards the products. In this work the main results of the experimental demonstration of the new reactor concept will be presented and discussed together with a detailed techno-economic evaluation of the process.

2. The reactor concept

The entire reaction system consists of two fluidized bed reactors connected by a riser column and gas sealing units. The air reactor is 15 cm in height and 5 cm in diameter, and is in its turn connected to the riser column of 2 m in height in order to drive the solids towards the fuel reactor, which is 20 and 6.5 cm in height and diameter, respectively. Inside this unit, a commercial Ni-based catalysts supplied by Johnson Matthey is used as heat and oxygen carrier and as catalyst for the reforming reaction occurring in the fuel reactor. Immersed in the fuel reactor, three metallic supported Pd-based membranes prepared at Tecnalia (Spain) have been used for the selective H\textsubscript{2} separation. These membranes have been previously tested for several hundred hours to verify their stability in time. Experiments have been carried out at different operating conditions, viz. temperature, inlet composition and inlet gas flow rates, and the results have been compared with an in-house developed phenomenological model. Furthermore, a techno-economic assessment of this technology has been performed using Aspen Plus, and the results have been compared for the same plant size as the conventional SMR technology with and without integration of CO\textsubscript{2} capture.
3. Results and discussion

The influence of the different operating conditions has been assessed through a detailed experimental study. Some of these results are presented in Figure 1, where the influence of the temperature and the amount of oxygen fed in the air reactor is evaluated in terms of fuel conversion. The use of membranes largely improves the performance of the reactor, and H2 recoveries above 30% have been measured. This recovery could be increased by working at higher pressures and with more membranes. In the same research line, a detailed techno-economic assessment has been carried out by investigating the cost of H2 production of the reactor concept projected at industrial scale and comparing the results with conventional SMR technology [3]. The results show that the overall efficiency of the process would be 82%, which is very similar to what is achieved with state-of-the-art conventional technology without CO2 capture (81%) and much higher than the conventional technology when integrating CO2 capture (67%). When referring to costs, H2 could be produced in the MA-CLR at a cost of 0.213 €/Nm³, almost identical as produced nowadays (0.216 €/Nm³) with the advantage that 91% of the carbon emissions would be avoided. If CO2 is to be captured in the conventional SMR, then the cost of H2 production would increase to 0.282 €/Nm³, indicating the potential of the here presented and demonstrated MA-CLR.

![Figure 1. Fuel conversion as function of different operating conditions for the unit operated with (MA-CLR) and without (CLR) membranes](image)

4. Conclusions

In this work a new reactor concept has been proposed and successfully demonstrated at lab scale. This technology has the potential to produce ultra-pure H2 at operating conditions far from conventional reformer units, with the addition that it achieves high carbon capture rates. Despite the fact that the technology is still in a first stage of development, these promising results, also supported by the results from a techno-economic analysis advise further research in order to bring the technology to the market. The recommended guidelines for further development involve the improvement of existing membranes in order to allow operation at slightly higher temperatures, and more fundamental understanding and engineering development of pressurized circulating beds.

References


Acknowledgements

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Keywords

H2 production; Membrane Reactors; CO2 capture; Chemical Looping.
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**Personal data**

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### Dr. in Chemical Engineering

**My profile**

- Chemical Engineer with experience in R&D on the field of novel processes for H₂ production and their subsequent scale up.
- Multi-task capabilities and always willing to participate as team-worker.
- Very good communication skills, with many presentations in international events as well as teaching/supervision related activities in academia.
- Used to write and handle reports in time.
- More than 18 scientific publications and more than 25 conference contributions.

### Office and computing

- Microsoft Office: Advanced level
- Aspen Hysys and Aspen Plus: Advanced level
- Matlab: User level

### Languages

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### Personal grants and awards

- **2017:** PhD with the distinction ‘cum laude’ at Eindhoven University of Technology. More information can be found [here](#).
- **2017:** Best poster presentation at International Conference on Catalytic Membrane Reactors (ICCMR13) in Houston, USA.
- **2015:** Best oral presentation at International Conference on Catalytic Membrane Reactors (ICCMR12) in Szczecin, Poland.
- **2013:** Personal competitive grant for four years contract at University of Zaragoza (ES) as doctoral candidate as published the 8th February 2013 in the Official Circular in Aragon (BOA).
- **2012:** Second best average grade in Chemical Engineering at University of Zaragoza (ES).
**Work experience** (more details in the appendix)

- **January 2017-Up to date. Researcher at Eindhoven University of Technology (NL).**
  
  *Participation in the following projects: 1) “MEMERE: Methane activation via integrated membrane reactors” EU Horizon 2020 call SPIRE-05-2015; 2) “PROMECA: Process intensification via through the development of innovative membranes and catalysts” EU Horizon 2020*
  

- **January 2013-January 2017. Researcher at Eindhoven University of Technology (NL) with a doctoral fellowship.**
  
  *Project associated: “ClingO2: Chemical looping reforming for pure hydrogen production with integrated CO2 capture” Project (VIDI 12365)*
  
  *Main activities:* Development of a new membrane reactor from fundamental research to lab-scale demonstration. In this period I have done activities related to process optimization, techno-economic analysis, development of experimental techniques and experimental operation among others. I have also been involved in process design, P&ID of the novel concept and in preparation of documentation and reports.

- **July 2011-December 2012. Research assistant at University of Zaragoza (ES)**
  
  *Project participation: (1) “New process to obtain aromatics employing methane from natural gas” and (2) “Process integration by reactor development for glycerol reforming and selective oxidation reactors” Project (CTQ2010-15568).*
  
  *Main activities:* In this period I have done activities related to catalyst preparation and characterization, process optimization and experimental evaluation at lab scale of a reactor concept patented at the University of Zaragoza.

**Teaching activities at Eindhoven University**

- **Process Design course (Bachelor).** Lecturer and responsible of tutorials
- **Advance Separation Technology (Master).** Responsible of tutorials
- **Separation Technology ( Bachelor).** Responsible of tutorials

**Academic background**

- **2013-2017: PhD in Chemical Engineering at Eindhoven University of Technology (NL)**
- **2011-2012: Post-Master in Introduction to Research in Chemical Engineering and Environmental Technologies at University of Zaragoza (ES)**
  
  *Average mark: 8.86/10 and Post-Master Thesis qualified with Cum Laude (9.7).*

- **2011-2012: Master on Chemical Engineering at University of Zaragoza (ES)**
  
  *Average mark: 7.97/10 and Master Thesis qualified with Cum Laude (9.7).*
  
  *Award: 2nd best average mark in Chemical Engineering promotion 2011.*

- **2009-2009: Bachelor on Industrial Technical Engineering; specialized in Industrial Chemistry at University of Zaragoza (ES)**
  
  *Average mark: 7.06/10 and Bachelor Thesis qualified with Excellent (9.0).*
Appendix CURRICULUM VITAE, José A. Medrano

References

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- Dr. F. (Fausto) Gallucci
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- Dr. D.A. (Alfredo) Pacheco Tanaka
  Senior researcher, Materials for Energy and Environmental Area, Tecnalia Research and Innovation, San Sebastian (ES)
  Mail: alfredo.pacheco@tecnalia.com

Scientific publications

Journal articles


**Editorials**


**Book Chapter**


**Other research-related activities**

**Conferences** (* contributions presented by myself)


25. J.A. Medrano*, I. Julian, J. Herguido, M. Menendez. “Dual process intensification: membrane reactor coupled to a two-zone fluidized bed reactor (TZFBR) for the catalytic propane dehydrogenation”, in 11th
International Conference on Catalysis in Membrane Reactors (ICCMR11), 7-11 July 2013, Porto, Portugal. Oral presentation.


Courses


3. Course on Particle Image Velocimetry, 10-14 March 2014, German Aerospace Center (DLR), Gottingen, Germany.


**Workshops**


**Supervision of students**

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