Propane dehydrogenation in a packed-bed membrane reactor: What potential users expect from membrane reactor research

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Highlights

- No commercialization so far because of too low volumetric productivity.
- Design problem of simultaneous H_2 removal and heat supply should be addressed.
- Reaction engineering analysis helps to identify future development directions.

1. Introduction

Membrane reactors have been proposed for more than 20 years to intensify propylene production by propane dehydrogenation (PDH), the conversion of which is limited by the thermodynamic equilibrium and can be increased by the selective removal of the by-product hydrogen. Early attempts suffered from low hydrogen permeation rates and practical challenges of keeping membranes defect-free, and of sealing and connecting them to the reactor tubes. In the meantime, many material-related challenges have been overcome, and the preparation of ever more selective and thinner membranes is reported.[1]

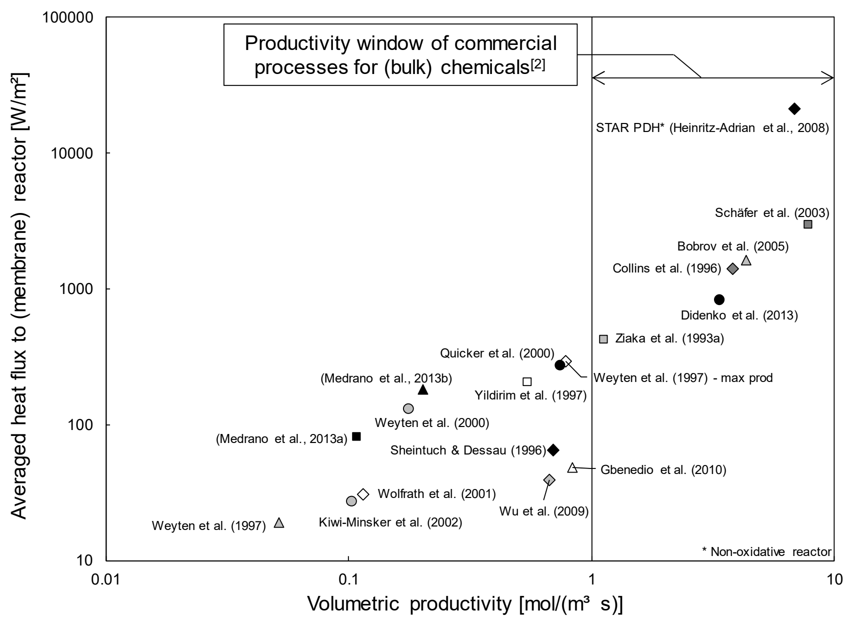

Figure 1. Averaged heat flux and volumetric productivity of membrane reactors for PDH reported in the open literature.

Still there is no implementation of membrane reactors for PDH on industrially relevant scale in sight, and even reports about piloting of PDH membrane reactors cannot be found in the open literature. What has prevented industrial development and commercialization of membrane reactor technology for PDH? Why have catalytic membrane reactors remained the subject of academic and publicly funded research for so long?

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Figure 1 gives answers to these questions; the volumetric productivity is too low compared to commercialized industrial processes. Many researchers have indeed concluded qualitatively that permeation rates are still too slow for coping with the PDH reaction, which is exemplified by reports of experiments at low space velocity.

Additionally, figure 1 reveals that the heat fluxes in lab-scale membrane reactors are one to three orders of magnitude smaller than in the tubes of a commercial PDH process ("STAR PDH"). This makes isothermal operation at lab scale easy, but obscures an intrinsic design problem for industrial membrane reactors. In-situ removal of H_2 keeps the reaction proceeding and requiring additional heat supply, while the available specific surface area that confines the catalyst bed needs to serve both, H_2 permeation and heat transfer. The role of heat supply in a membrane reactor for PDH was evaluated quantitatively in two recent papers[3,4] without discussing the practical implications of simultaneous H_2 removal and heat transfer for membrane reactor design.

2. Methods

The one-dimensional component and heat balances for packed-bed membrane reactors have two types of dimensionless groups. The Damköhler number, and heat and mass Stanton numbers characterize the physico-chemical properties of the system, while the reactor geometry and the portion φ of total surface area assigned to the membrane reflect the reactor parameters that can be manipulated for reactor design.

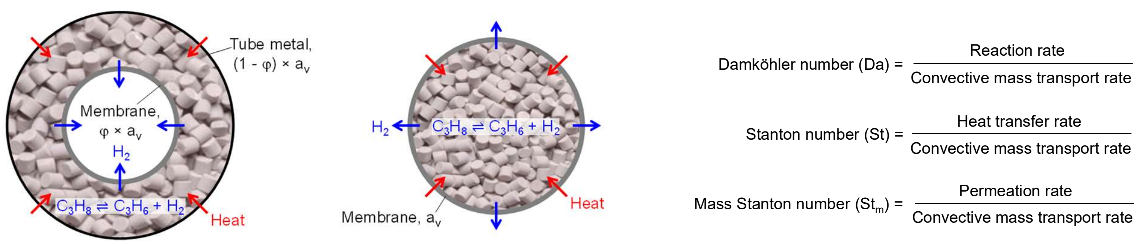

Figure 2. Membrane reactor with heat supply via separate surface (left), and via membrane together with H_2 removal (right).

Both the specific surface area a_v and φ are subject to practical constraints and need to be chosen wisely to optimize the membrane reactor performance with given Da, St and St_m for specific catalysts and membranes. Careful analysis will help to assess if their proper choice is enough to come to practically feasible membrane reactor designs, or if catalyst or membrane engineering need to extend the ranges of Da, St and St_m.

3. Conclusions

This contribution is meant as input from a potential industrial user of PDH membrane reactors to the membrane research community. Based on a reaction engineering analysis and a preliminary modelling study we hope to provide guidance to those aspects research on membrane reactors should focus at. We have chosen PDH as an industrially relevant model reaction, and hope to initiate a discussion between academia and industry for bringing catalytic membrane reactors closer to commercial application.

References

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Keywords
Propane dehydrogenation, membrane reactor, packed bed, dimensionless number.