Design of a membrane reactor for continuous production of 1,1 diethoxy butane – a bio-based oxygenated diesel additive

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DESIGN OF A MEMBRANE REACTOR FOR CONTINUOUS PRODUCTION OF 1,1 DIETHOXY BUTANE - A BIO-BASED OXYGENATED DIESEL ADDITIVE

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INTRODUCTION

The use of biofuels in car engines has become one of goals towards a sustainable development. Acetals seem to be good candidates to enhance the cetane number of biodiesels [1]. 1,1 diethoxy butane is produced via acetalization reaction between butanal and ethanol.

2 Ethanol + Butanal ⟷ 1,1 Diethoxty butane + Water

Both reactants can be obtained from renewable sources. Ethanol via fermentation, and butanal via partial oxidation or dehydrogenation of fermented (renewable) n-butanol. The acetalization reaction presents thermodynamic limitations: conventional reactor conversions are around 40% at kinetically acceptable ranges [2]. To overcome these limitations, innovative reactors shifting the equilibrium are required. Membrane reactors are a promising option: continuous removal of water from the reaction mixture, increases the conversion of the product butanal.

Here different processes based on dehydration membranes and different reactors types are presented, in order to develop a heterogeneously catalyzed continuous process for 1,1 diethoxy butane production at a semi pilot scale (7 L/h feed flow rate).

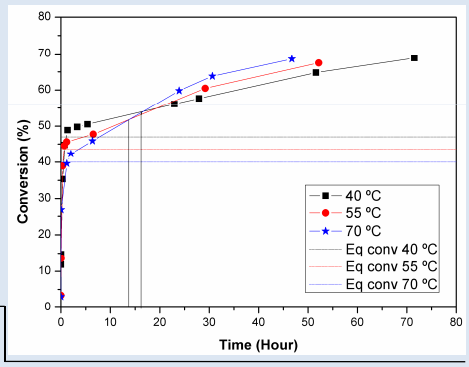
EXPERIMENTAL WORK

Experimental data using HybSi® dewatering membranes and Amberlyst 47 resins as catalysts have been used to develop a heterogeneously catalyzed continuous process for 1,1 diethoxy butane production at a semi pilot scale.

Kinetic data ⟹ Conventional batch reactor

Permeance data ⟹ Batch dehydration experiments of the involved quaternary mixture at different temperatures.

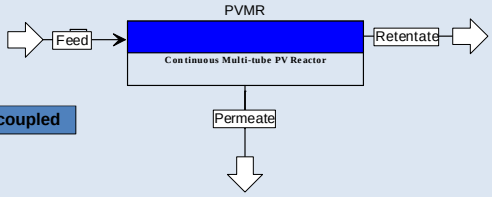
Experimental semi-batch experiments (where the reaction and separation take place in the same unit) show that water removal by membrane reactors shift the equilibrium conversion to the product side. These experiments were simulated by a "semi-batch" model validating the previously obtained permeance and kinetic data [3].

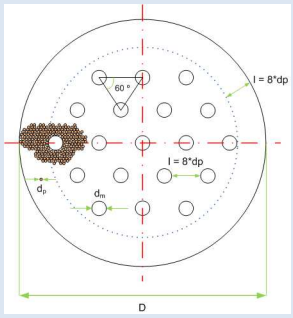


MEMBRANE REACTOR – CONCEPTUAL DESIGN

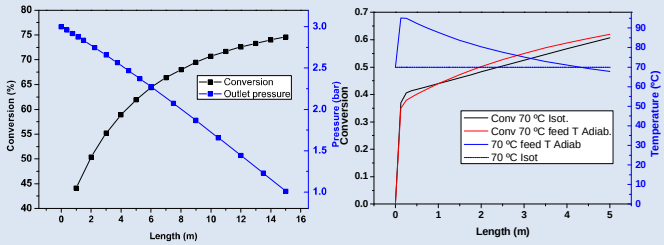
In all configurations hydrodynamics play an important role to avoid concentration and temperature polarization. Assumptions considered in this design are:

- Concentration/temperature polarization is negligible.
- Plug flow profile in the reactor.
- Main mass transport resistance is in the selective top layer of the membrane.
- Permeate is collected in the tube and perfectly mixed.





1. Multi Tube Plug Flow Membrane Reactor: Reaction and pervaporation are coupled



Required conditions:

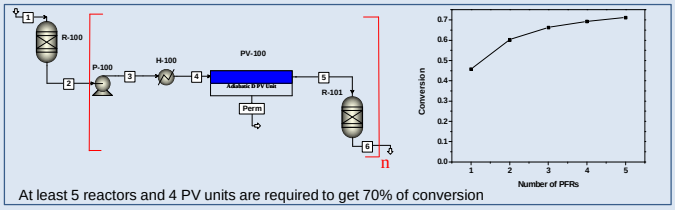
- Pipe to pipe distance is $8 \times d_p$ to avoid wall effects
- In all simulations Re > 10 to avoid conc. polarization

Results:

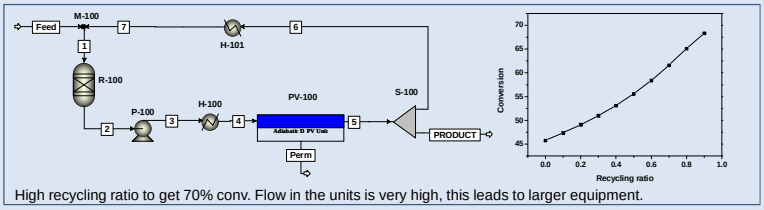
- Pressure drops are very high
- Extremely long reactor
- Very different reaction and pervaporation rates

2. Plug Flow Reactor (PFR) + Pervaporation module (PV)

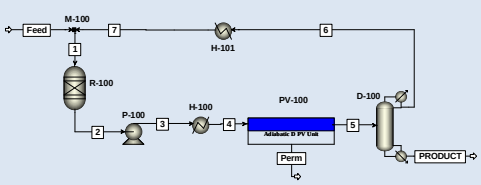
Uncoupled reactor and pervaporation modules ⟶ more efficient pervaporation process ⟶ ↑ m^2/m^3 (no catalyst particles along membrane tubes)



At least 5 reactors and 4 PV units are required to get 70% of conversion



High recycling ratio to get 70% conv. Flow in the units is very high, this leads to larger equipment.



- Water removal in the PV unit avoids azeotrope formation in the distillation column, this simplifies downstream separation from very complex separation to a very simple and easy one.
- Very pure acetal is easy to obtain.
- Only non reacted components are recycled: low recycle flow rate, thus smaller dimensions of the equipment.
- Reasonable membrane area is required.
- In pervaporation high selectivity for water is very important. HybSi® has shown high selectivity for water.

Summarizing table

* 7 L/h of feed flow rate

Model type	Conversion	PV length	Mem. Area (m^2)
MPFMR	74.6	15	0.66
PFR + PV in series	70.6	2.45	1.00
PFR + PV + recycle	71.0	0.6	1.60
PFR + PV + Dist	~100	2	0.81

CONCLUSIONS

- Dehydration membranes shift the reaction to the product side achieving much higher conversions than the equilibrium.
- Reasonable membrane area is need to remove the water formed in the reaction.
- In coupled membrane reactor the catalyst is highly active at the studied temperature range. This leads to a mismatch between water generation and water removal through the membrane.
- The uncoupled process of reaction and pervaporation is better because the different rates of transformation and separation can be controlled separately.
- The combination of a PV module and distillation column leads to almost 100% of conversion. The efficient water removal avoids many azeotropes that are formed, leading to an easy and much simpler separation process.

[1] M.R. Capeletti, L. Balzano, et all. *Appl. Catal.* (2000) 198 L1-L4
[2] I. Agirre, V.L Barrio, B. Güemez, J.F Cambra. and P.L Arias., *IJCRE*. (2010), A86
[3] I. Agirre, M.B. Guemez, A. Motelica, H. van Veen, J. Vente, P.L. Arias. *J. Mem. Sci.* (2011), 371, *179-188*