ADVANCES IN CATALYSIS FOR HYDROCARBONS

RESULTS FROM ZEOCAT-3D, C123 & BIZEOLCAT EU RESEARCH PROJECTS

ZEOCAT-3D

C123
VALORISING METHANE RESOURCES

BiZeolCat

Funded by
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ADVANCES IN CATALYSIS FOR HYDROCARBONS

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ZEOCAT-3D

Biogas upgrading using a gas-liquid contact membrane process: Modelling, simulation and membrane wetting estimation

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Outline

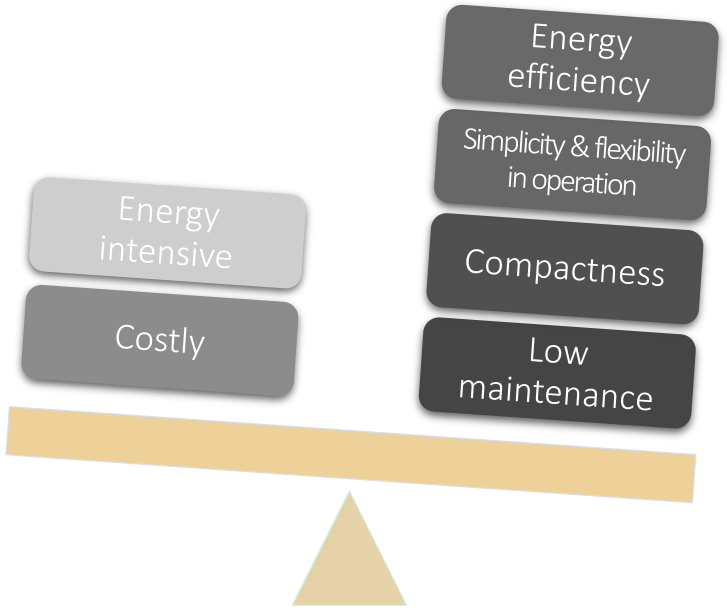
- Methodology and aims
  - Gas-liquid contact membrane system for CO_2 removal
- Modelling of the membrane-based gas absorption process under isothermal operation
  - 2-D formulation in the fiber; 1-D in the shell-side; coupling using BCs
  - Mass transfer resistances in the shell-side and the membrane including wetting
  - Reaction rate term in the shell-side
- Results
  - CO_2 removal for various flowrates
  - Membrane wetting estimation
  - Use of shell-side mass transfer correlation and parametric analysis
  - Dynamic response of the system
- Conclusions

Methodology and aims

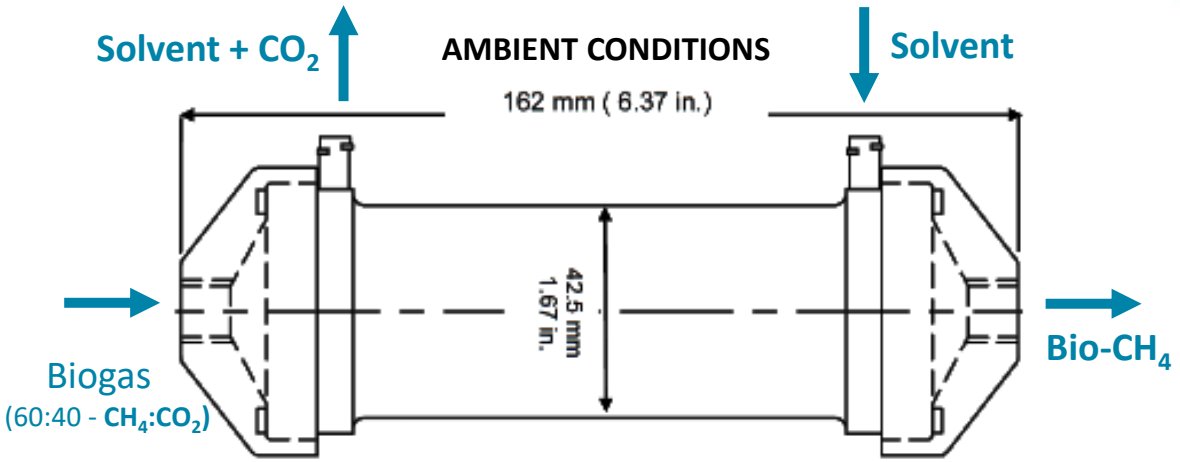
MEMBRANE-BASED GAS ABSORPTION

Conventional amine technologies

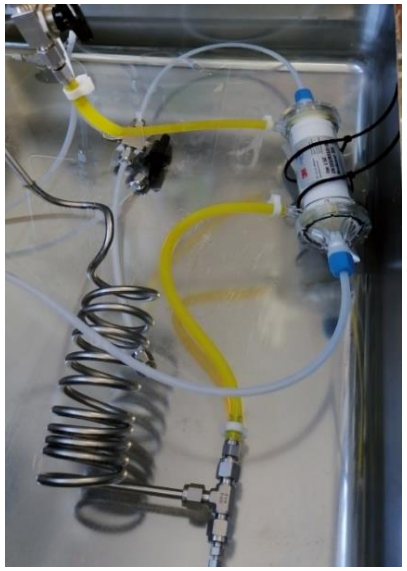
Membrane-based CO_2 capture



Certain advantages of membrane-based gas absorption compared to conventional equipment



3M Liqui-Cel 1.7x5.5 MM at CERTH



- ✓ 7400 polypropylene hollow fibers (*OD/ID: 300/220 μm*)
- ✓ Pore size: 40 nm
- ✓ Specific surface area: 3600 m^2/m^3
- ✓ Active surface area: 0.58m^2
- ✓ Parallel flow

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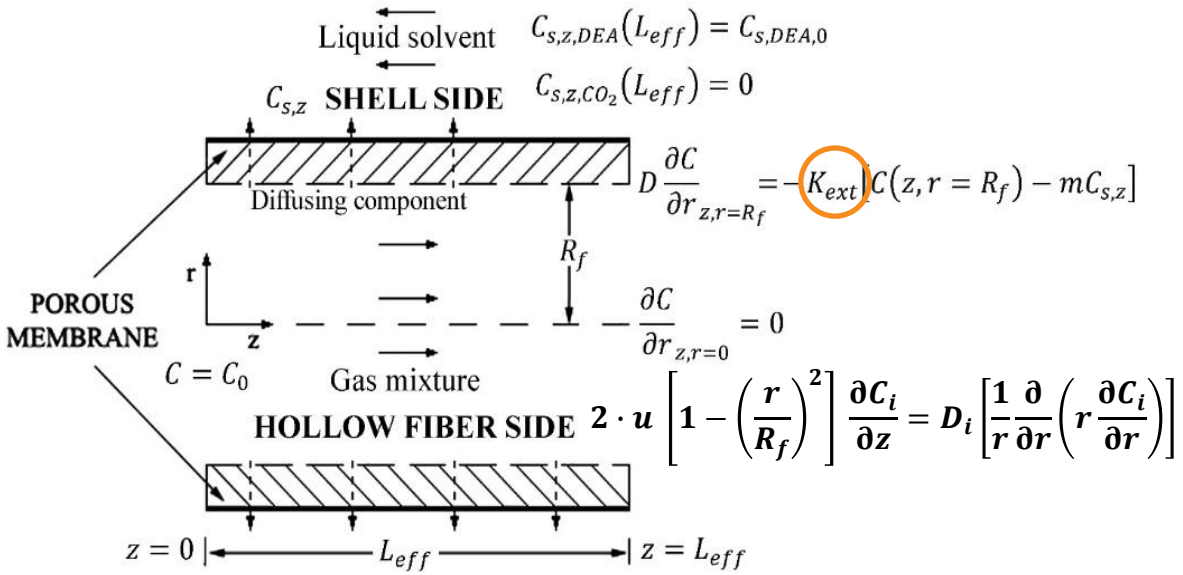
Modelling

CO_2 absorption using gas-liquid contact membrane process

$$-u_{int}\frac{\partial C_{s,z,i}}{\partial z} = -n_i \cdot Rate_i(z) + a_v \cdot MembraneFlux_i(z)$$



- Binary mixture CO_2-CH_4 ~(40-60%) in the fibers

When no shell-side equations are necessary analytical solutions exist see:
G. Pantoleontos, I.M. Anagnostara, M. Syrigou, A.G. Konstandopoulos. Solutions of the mass continuity equation in hollow fibers for fully developed flow with some notes on the Lévêque correlation, Carbon Capt. Sci. Technol. 2 (2022) 100027

- Resistance-in-series[1] concept to calculate K_{ext}:

$$\frac{1}{K_{ext}} = \frac{l_m}{D_{eff,j}}(1-wett) + \frac{\tau \cdot l_m}{\varepsilon_f \cdot D_{j,amine} \cdot E}\cdot wett + \frac{m}{E \cdot k_{s,o}}$$

- Overall reaction rate[2] between CO_2-DEA

$$CO_2 + 2R_2NH \rightarrow R_2NCOO^- + R_2NH_2^+$$
$$Rate = k_R \cdot [CO_2] \cdot [DEA]^2$$

- Wetting calculation by matching experimental data and computational output for various gas and liquid flowrates using 0.25M DEA
- SPSE gPROMS ModelBuilder 7.0 is used

[1] For the shell-side correlation, $k_{s,o}$, see Costello et al. J. Membrane Sci. 80 (1993) 1-11.

$$Sh_s = (0.53 - 0.58\varphi) \cdot Re_s^{0.53} \cdot Sc_s^{0.33}$$

[2] For the reaction rate and enhancement factors see Hikita et al. Chem. Eng. J. 13 (1977) 7-12 (valid for 0.174-0.719M); Danckwerts, Gas-liquid reactions, 1970

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Results – CO_2 removal for various flowrates

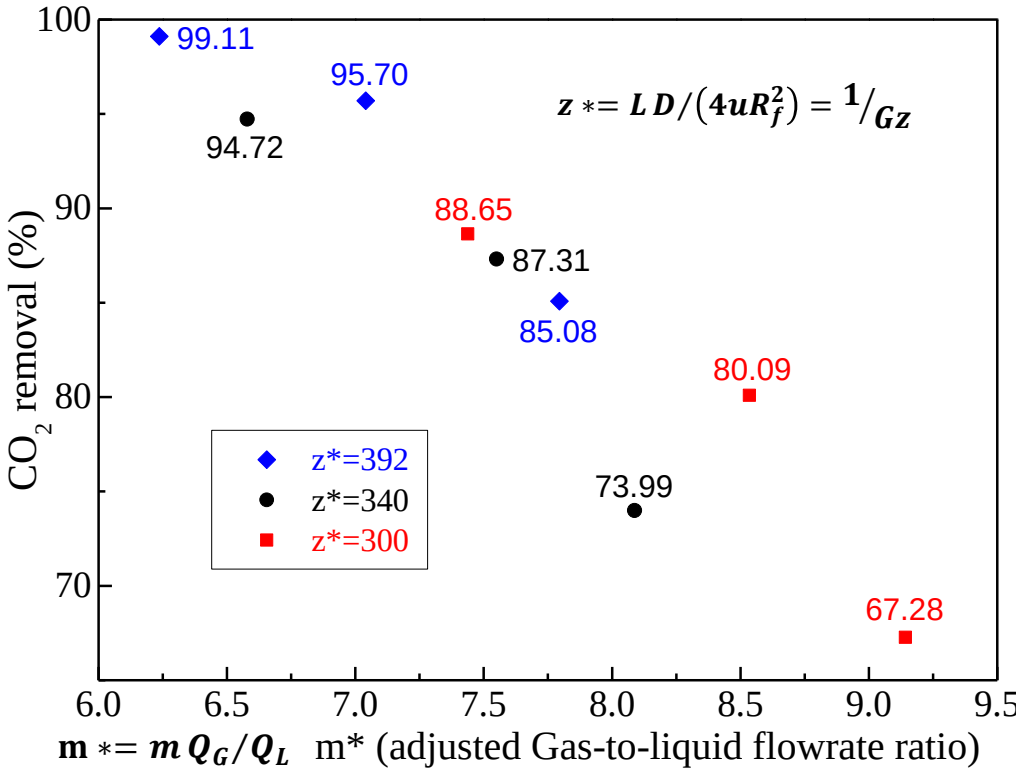
- The gas feed contains 41.2-41.9% CO_2, 58.8-58.1% CH_4 (fiber-side)
- Aqueous solution of DEA 0.25M in the shell side
- Gas flowrates 102.44– 130.8 LPH and the liquid flowrates 16.8–21 LPH
- Experiments are carried out at 24.5-28.5 °C and 1 Atm

No.	T (°C)	Q_{Gin} (lph)	Q_{Gout} (lph)	Q_l (lph)	$CO_{2,in}$ (%)	$CO_{2,out}$ (%)	**CO_2 removal (%)**
1	**28.5**	**102.4**	67.4	**16.8**	41.2	9.35	**85.08**
2	**28.5**	**102.4**	62.7	**18.6**	41.2	2.90	**95.70**
3	**28.5**	**102.4**	61.0	**21.0**	41.2	0.62	**99.11**
4	**24.5**	**116.5**	82.2	**16.8**	41.2	15.20	**73.99**
5	**25.5**	**115.7**	75.0	**18.3**	41.6	8.15	**87.31**
6	**25.5**	**115.7**	71.5	**21.0**	41.6	3.56	**94.72**
7	**24.5**	**131.7**	96.3	**16.8**	41.7	18.70	**67.28**
8	**25.5**	**130.8**	88.9	**18.3**	41.9	12.30	**80.09**
9	**25.5**	**130.8**	84.5	**21.0**	41.9	7.38	**88.65**

$$\boldsymbol{CO_2 Removal}\ (\%) = \boldsymbol{b_1} \cdot \mathbf{m}* + \boldsymbol{b_2} \cdot \sqrt{\mathbf{z}*} + \sum_{j=3}^{6} \boldsymbol{b_j} \cdot (\mathbf{z}*)^{j-3}$$

Coefficients	*Values*	*Stand. error*	*Coefficients*	*Values*	*Stand. error*
b_1	**-8.37×10^{0}**	1.24×10^{0}	b_4	**-3.27×10^{4}**	8.32×10^{3}
b_2	**6.36×10^{5}**	1.62×10^{5}	b_5	**3.26×10^{1}**	8.32×10^{0}
b_3	**-3.63×10^{6}**	9.22×10^{5}	b_6	**-1.94×10^{-2}**	4.97×10^{-3}

- For the 3M Mini Module 1.7x5.5 high CO_2 removal even at high gas-to-liquid flowrate ratio (6.25 adj. GtL for No. 3 → 99%) and at very small DEA concentrations
- CH_4 diffusion into the liquid flow is negligible in all experimental sets, according to the experimental measurements and mass balance calculations



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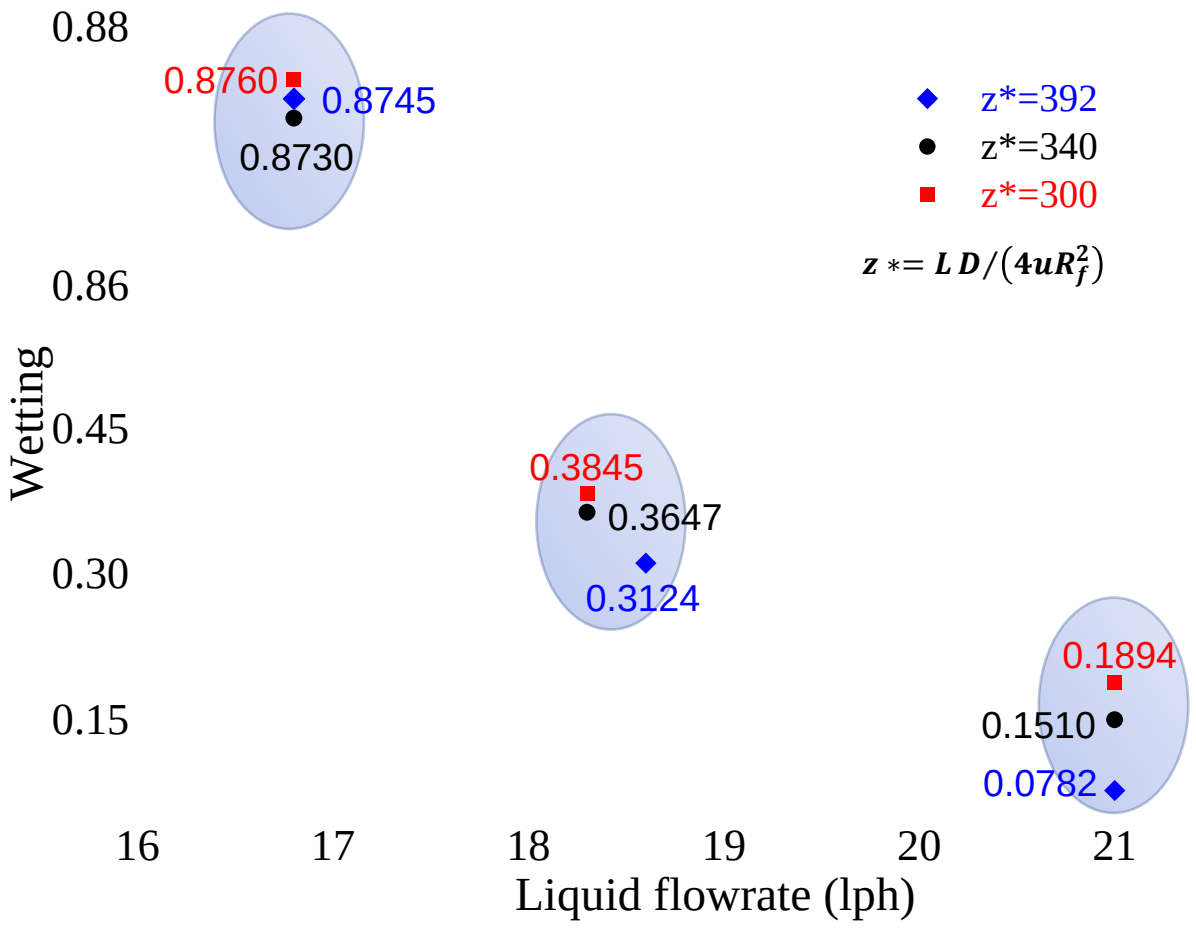
Results – Membrane wetting estimation



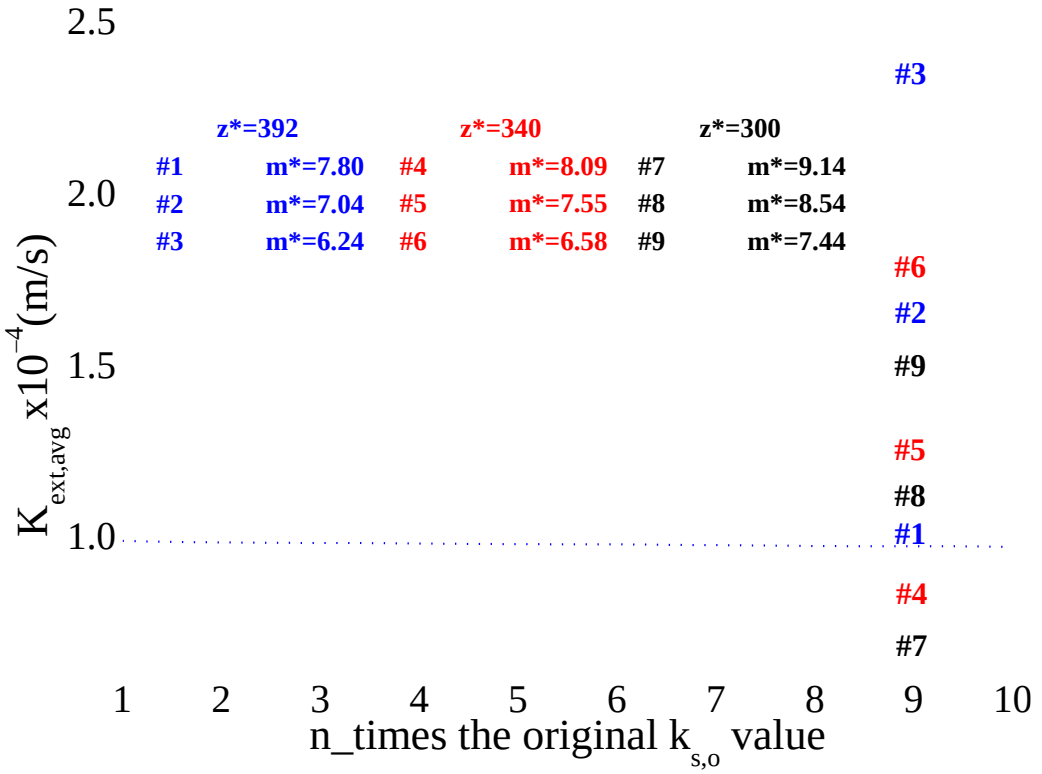
$$\frac{1}{K_{ext}} = \frac{l_m}{D_{eff,j}}(1 - \boldsymbol{wett}) + \frac{\tau \cdot l_m}{\varepsilon_f \cdot D_{j,amine} \cdot E} \cdot \boldsymbol{wett} + \frac{m}{E \cdot k_{s,o}}$$

- Wetting calculation by matching experimental data and computational output for various gas and liquid flowrates using 0.25M DEA
- Application of the Hikita (reaction rate) – Costello (shell-side correlation)
- The calculated wetting values are concentrated close to each other for the same liquid flowrate regardless of the gas mixture flowrate (z*)
- Increasing liquid flowrate leads to smaller wetting values relative to gas-filled portion the membrane resistance (see also Pantoleontos et al.[1])

❖ Reaction rate by Hikita et al. Chem. Eng. J. 13 (1977) 7-12
❖ Shell-side mass transfer correlation by Costello et al. J. Membrane Sci. 80 (1993) 1-11.

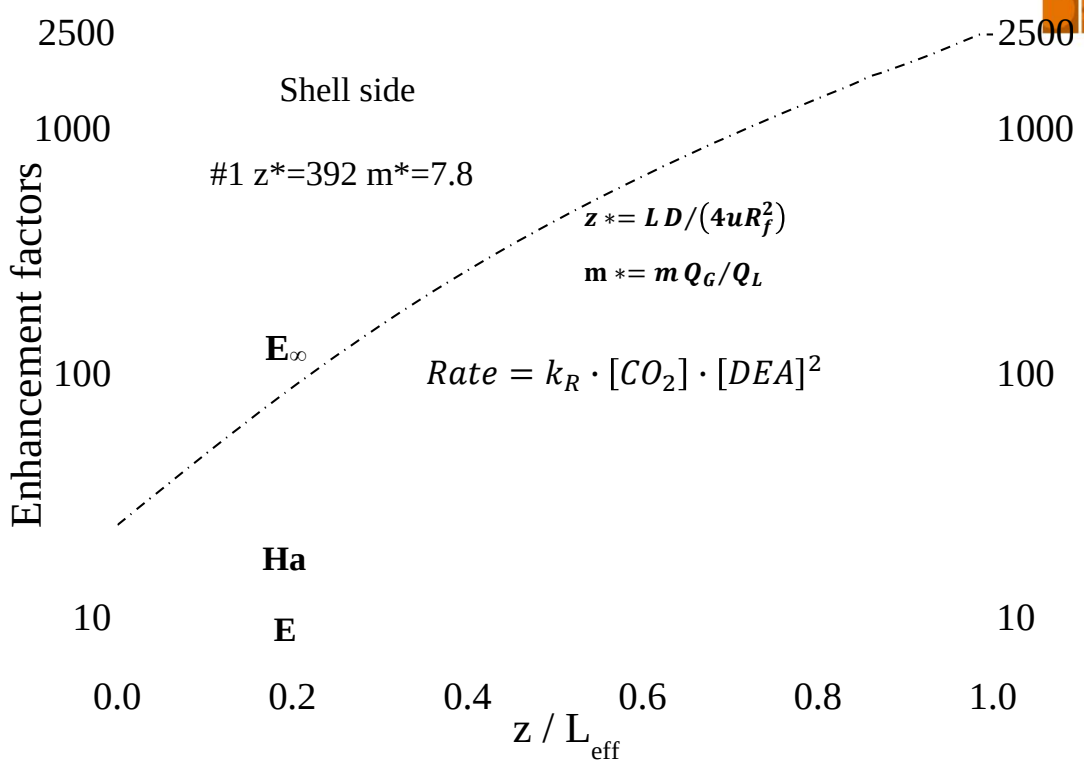
[1] Pantoleontos, G., Theodoridis, T., Mavroudi, M., Kikkinides, E.S., Koutsonikolas, D., Kaldis, S.P., Pagana, A.E., Can. J. Chem. Eng. 95 (2017) 1352-1363.

Results – Parametric analysis



$$K_{ext,avg} = \frac{1}{L_{eff}} \int_0^{L_{eff}} K_{ext} dz$$

- The $K_{ext,avg}$ is hardly altered for different $k_{s,o}$ values → the absorption performance mainly depends on the reaction rate

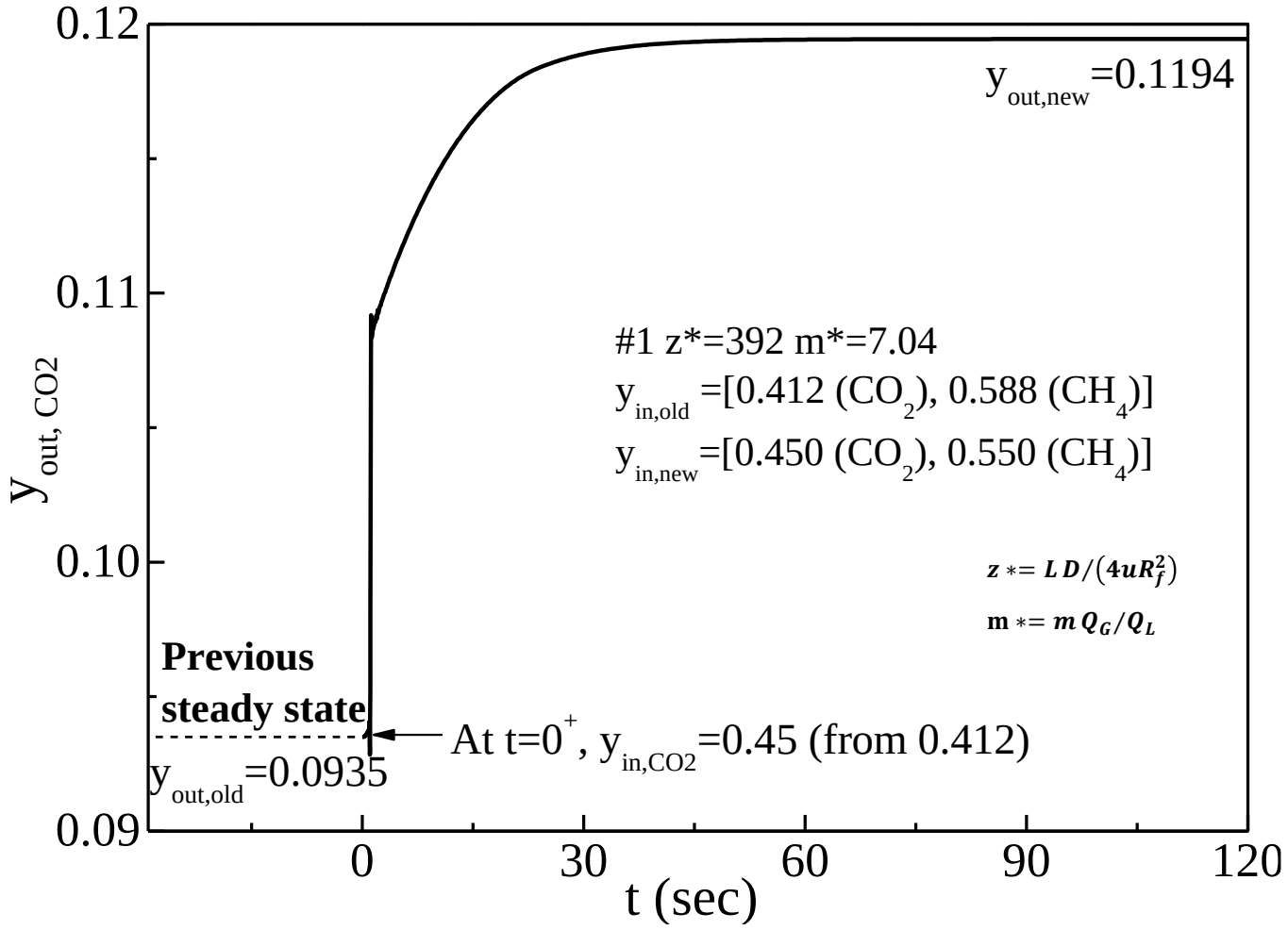


$$(Ha)^2 = \frac{1}{k_{s,o}^2}\left[k_R \cdot D_{CO_2,DEA} \cdot C_{s,z,DEA}^2\right]$$

When $\boldsymbol{E \approx Ha} \longrightarrow \boldsymbol{k_s = E \cdot k_{s,o} \approx C_{s,z,DEA} \cdot \sqrt{k_R \cdot D_{CO_2,DEA}}}$

- The design of experiments can be guided by a single pair of z*-m* regardless of the shell-side mass transfer correlation

Results – Dynamic response



- Variation of the biogas composition
- Dynamic response of the module performance for a step-change in biogas composition (from y_{in}= 0.412 to 0.45)
- Retain the same liquid flowrate → switch from a matching-case (wetting estimation) to a fixed-wetting case (simulation)
- A new steady state is reached after almost two minutes
- Fast transients will be also the case for a larger unit

❖ Reaction rate by Hikita et al. Chem. Eng. J. 13 (1977) 7-12
❖ Shell-side mass transfer correlation by Costello et al. J. Membrane Sci. 80 (1993) 1-11.

Conclusions

- Gas-liquid contact membrane system is capable of removing >95% CO_2 from a biogas mixture and completely recovering bio-CH_4 using DEA 0.25M at GtL flowrate ratios ~6
- Mass transfer model of sufficient fidelity (2-D formulation in the fiber; 1-D in the shell-side) including all relevant mass transfer resistances (membrane wetting; shell-side correlations; enhancement factors)
- Membrane wetting estimation by matching experimental data with the computational output
  - Two wetting "patterns": the wetting depends mainly on the liquid flowrate; the relative contribution of the liquid-filled part of the membrane resistance decreases for higher flowrates
- Parametric analysis of the shell-side mass transfer correlation reveals that it affects the wetting computational estimation
- The apparent shell-side mass transfer coefficient mainly depends on the reactive conditions
- Dynamic analysis reveals that the gas-liquid contact membrane process after a composition step-change reaches a new steady state after two minutes

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Thank you for your attention

ZEOCAT-3D

Development of a bifunctional hierarchically structured zeolite based nano-catalyst using 3D technology for direct conversion of methane into aromatic hydrocarbons via methane dehydroaromatization

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