ADVANCES IN CATALYSIS FOR HYDROCARBONS

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

ZEOCAT-3D

C123
VALORISING METHANE RESOURCES

BiZeolCat

Funded by
the European Union

These projects have received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement Nos. 814548, 814671 & 814557

A 3D-1D model for the simulation of catalytic reactors

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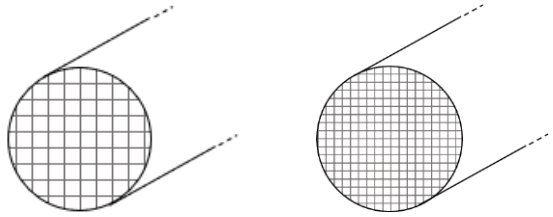
Introduction

- Non-oxidative methane dehydroaromatization (MDA) is one of the most promising processes for the direct conversion of biomethane into hydrogen and high-value aromatics (mainly benzene).

- The yield of the reactor, measured in terms of methane conversion, is influenced by multiple factors:
  1. operating conditions (e.g., temperature of the gas)
  2. geometry of the structure
  3. chemical properties of the catalyst

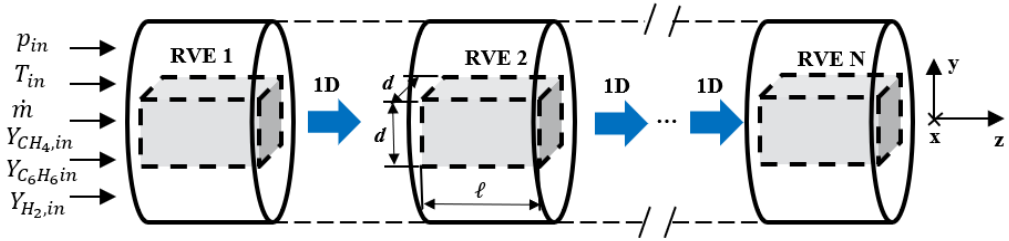
- The geometry and size of the catalyst plays a crucial role in the reactor design.



higher catalyst porosity → higher surface area (thus faster methane conversion) but also stronger pressure losses

Modelling approach

- Development of a 3D-1D model for simulating the MDA process in reactors from lab- to plant-scale.

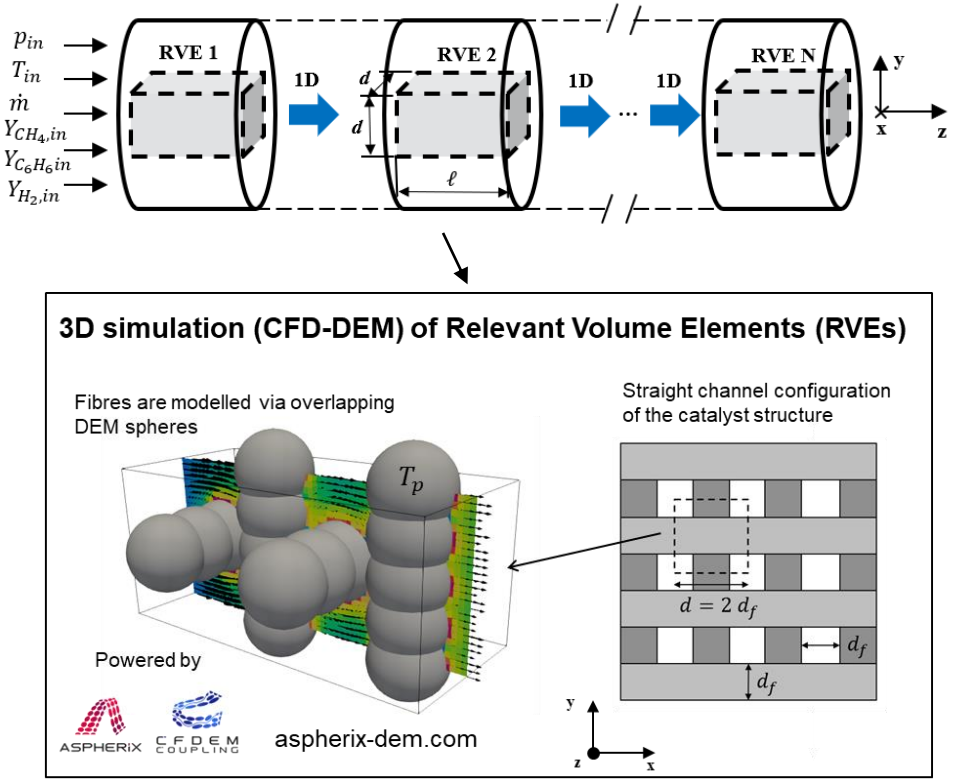


- The model focuses on:
  1. Fluid dynamics behavior of the system
  2. Effect of catalyst structure's size and operating temperature on the methane conversion and pressure drop.

- The MDA is modelled by considering only the main reaction, namely the reversible decomposition of methane ($\mathrm{CH_4}$) into hydrogen ($\mathrm{H_2}$) and benzene ($\mathrm{C_6H_6}$):

$$\mathrm{CH_4} \rightleftarrows \mathrm{C_6H_6} + \mathrm{H_2}$$

Hybrid 3D-1D method

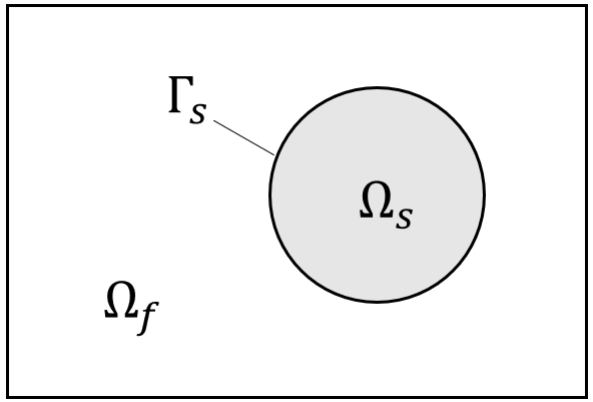


- The catalytic reactor is modelled by means of a combined 3D-1D approach.
- The 3D part of the model consists of particle-resolved CFD-DEM simulations of RVEs, while the 1D part consists of a low-order model connecting the RVEs
- The 3D model uses Aspherix® and CFDEM®coupling engines to solve the mass, momentum, energy transport and reaction kinetics.

Governing equations

Decomposition of the domain in the fictitious domain method.

$$\Omega = \Omega_s + \Omega_f$$



- CFD equations of compressible reacting multi-species fluid mixture

$$\begin{cases} \dfrac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{u}) = 0 \quad on\ \Omega, \\ \dfrac{\partial (\rho \boldsymbol{u})}{\partial t} + \nabla \cdot (\rho \boldsymbol{u} \otimes \boldsymbol{u}) = \nabla \cdot \boldsymbol{\sigma} + \rho \boldsymbol{g} \quad on\ \Omega, \\ \dfrac{\partial (\rho E)}{\partial t} + \nabla \cdot (\rho \boldsymbol{u} E) + \nabla \cdot (\boldsymbol{u} p) = -\nabla \cdot \boldsymbol{q} + \nabla \cdot (\boldsymbol{\tau} \cdot \boldsymbol{u}) + \rho \boldsymbol{g} \cdot \boldsymbol{u} + s_{E,c} + s_{E,p} \quad on\ \Omega, \\ \dfrac{\partial (\rho Y_i)}{\partial t} + \nabla \cdot (\rho Y_i \boldsymbol{u}) = \nabla \cdot \left(\alpha_i \nabla (\rho Y_i)\right) + s_{Y_i} \quad on\ \Omega. \end{cases}$$

- Boundary conditions

$$\begin{cases} \boldsymbol{u} = \boldsymbol{u_p} \ on\ \Omega_s \ \ and \ \ \boldsymbol{\sigma} \cdot \hat{\boldsymbol{n}} = \boldsymbol{t}_{\boldsymbol{\Gamma_s}} on\ \Gamma_s, \\ T = T_p \ on\ \Omega_s, \\ \sum_{i=1}^{m} Y_i = 1 \ on\ \Omega, \end{cases}$$

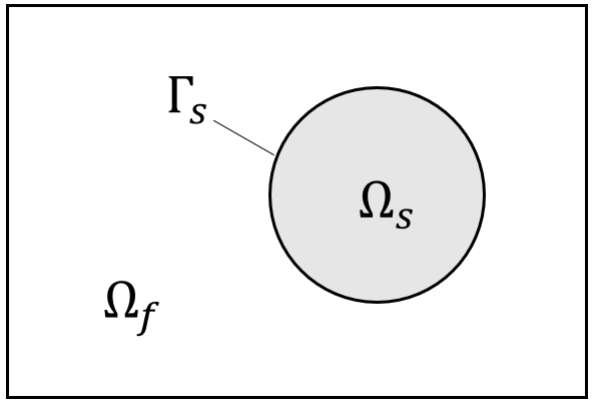
- DEM equations

$$\begin{cases} m_p \dfrac{\mathrm{d}\boldsymbol{v_p}}{\mathrm{d}t} = m_p \boldsymbol{g} + \sum_{j=1}^{n} \boldsymbol{f_j} - \int_{\Gamma_s} \boldsymbol{t}_{\boldsymbol{\Gamma_s}} \mathrm{d}\Gamma_s, \\ m_p c_p \dfrac{\mathrm{d}T_p}{\mathrm{d}t} = \sum_{j=1}^{n} \boldsymbol{q_j} - \int_{\Gamma_s} k \nabla T \cdot \hat{\mathbf{n}} \, \mathrm{d}\Gamma_s. \end{cases}$$

Governing equations

Decomposition of the domain in the fictitious domain method.

$$\Omega = \Omega_s + \Omega_f$$



- Chemical species concentration equations

$$\begin{cases} \dfrac{\partial(\rho Y_{CH_4})}{\partial t} + \nabla \cdot (\rho Y_{CH_4} \boldsymbol{u}) = \nabla \cdot \left(\alpha_{CH_4} \nabla(\rho Y_{CH_4})\right) + s_{Y_{CH_4}} \quad on\ \Omega, \\ \dfrac{\partial(\rho Y_{H_2})}{\partial t} + \nabla \cdot (\rho Y_{H_2} \boldsymbol{u}) = \nabla \cdot \left(\alpha_{H_2} \nabla(\rho Y_{H_2})\right) + s_{Y_{H_2}} \quad on\ \Omega, \\ \dfrac{\partial(\rho Y_{C_6H_6})}{\partial t} + \nabla \cdot (\rho Y_{C_6H_6} \boldsymbol{u}) = \nabla \cdot \left(\alpha_{C_6H_6} \nabla(\rho Y_{C_6H_6})\right) + s_{Y_{C_6H_6}} \quad on\ \Omega, \end{cases}$$

- The mass concentration sources $s_{Y_{CH_4}}$, $s_{Y_{H_2}}$ and $s_{Y_{C_6H_6}}$ are defined as follows:

$$\begin{cases} s_{Y_{CH_4}} = -6\, M_{CH_4}\left(k_f [\mathrm{CH_4}]^{\alpha} - k_r [\mathrm{H_2}]^{\beta} [\mathrm{C_6H_6}]^{\gamma}\right), \\ s_{Y_{H_2}} = 9\, M_{H_2}\left(k_f [\mathrm{CH_4}]^{\alpha} - k_r [\mathrm{H_2}]^{\beta} [\mathrm{C_6H_6}]^{\gamma}\right), \\ s_{Y_{C_6H_6}} = M_{C_6H_6}\left(k_f [\mathrm{CH_4}]^{\alpha} - k_r [\mathrm{H_2}]^{\beta} [\mathrm{C_6H_6}]^{\gamma}\right), \end{cases}$$

Governing equations – reaction kinetics

- The forward reaction rate constant is calculated based on the Arrhenius equation:

$$k_f = A\, e^{-\frac{T_a}{T}}$$

where A is the pre-exponential factor and T_a is the activation temperature. $k_f \neq 0$ only in the cells at the fluid-solid interface.

- The backward reaction rate is calculated as follows:

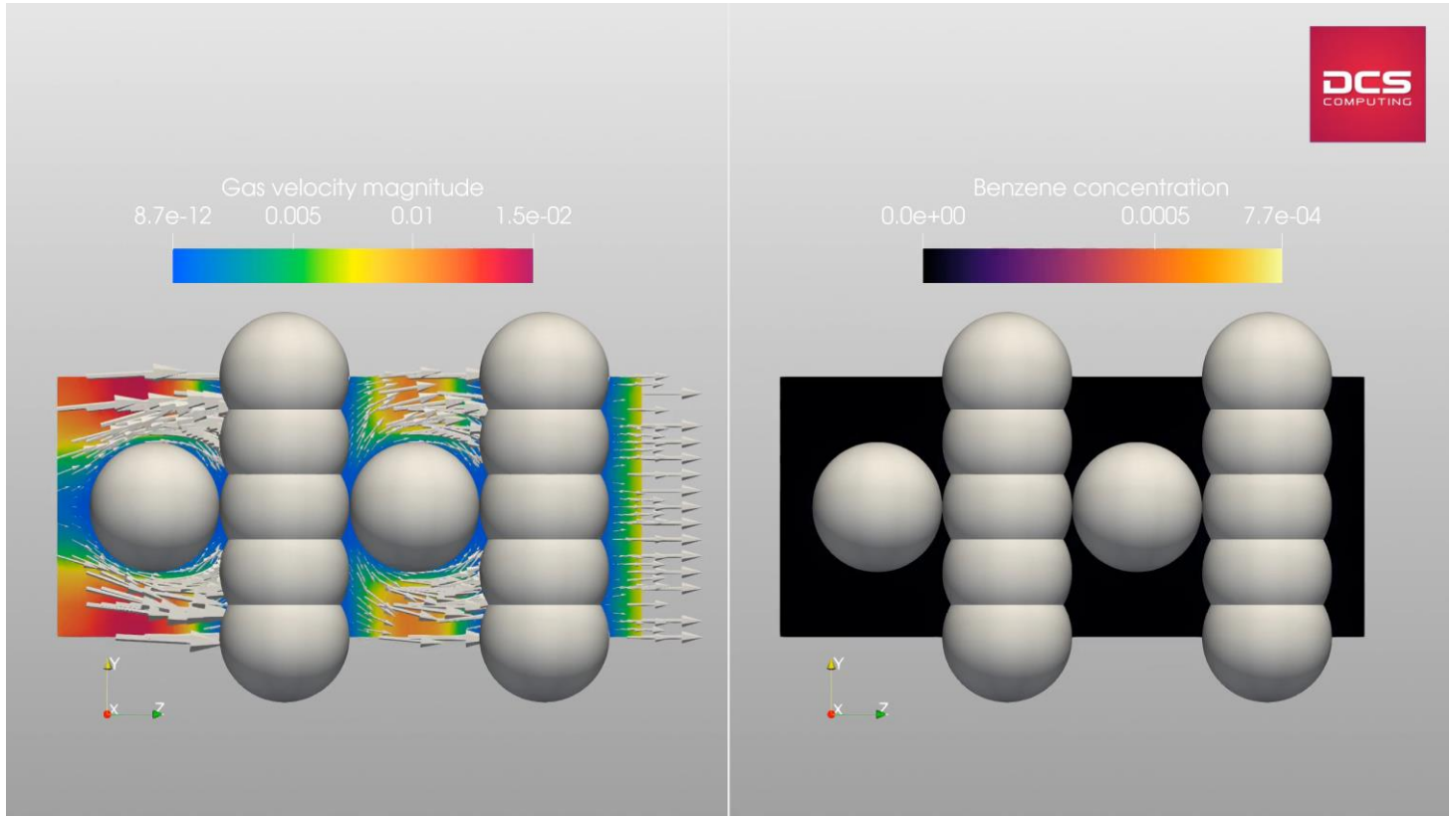
$$k_r = \frac{k_f}{K_c},$$

where K_c is the equilibrium constant. In what follows, we consider the equilibrium constant to be an exponential function of the temperature with the following form:

$$K_c = a\, e^{b\,T}$$

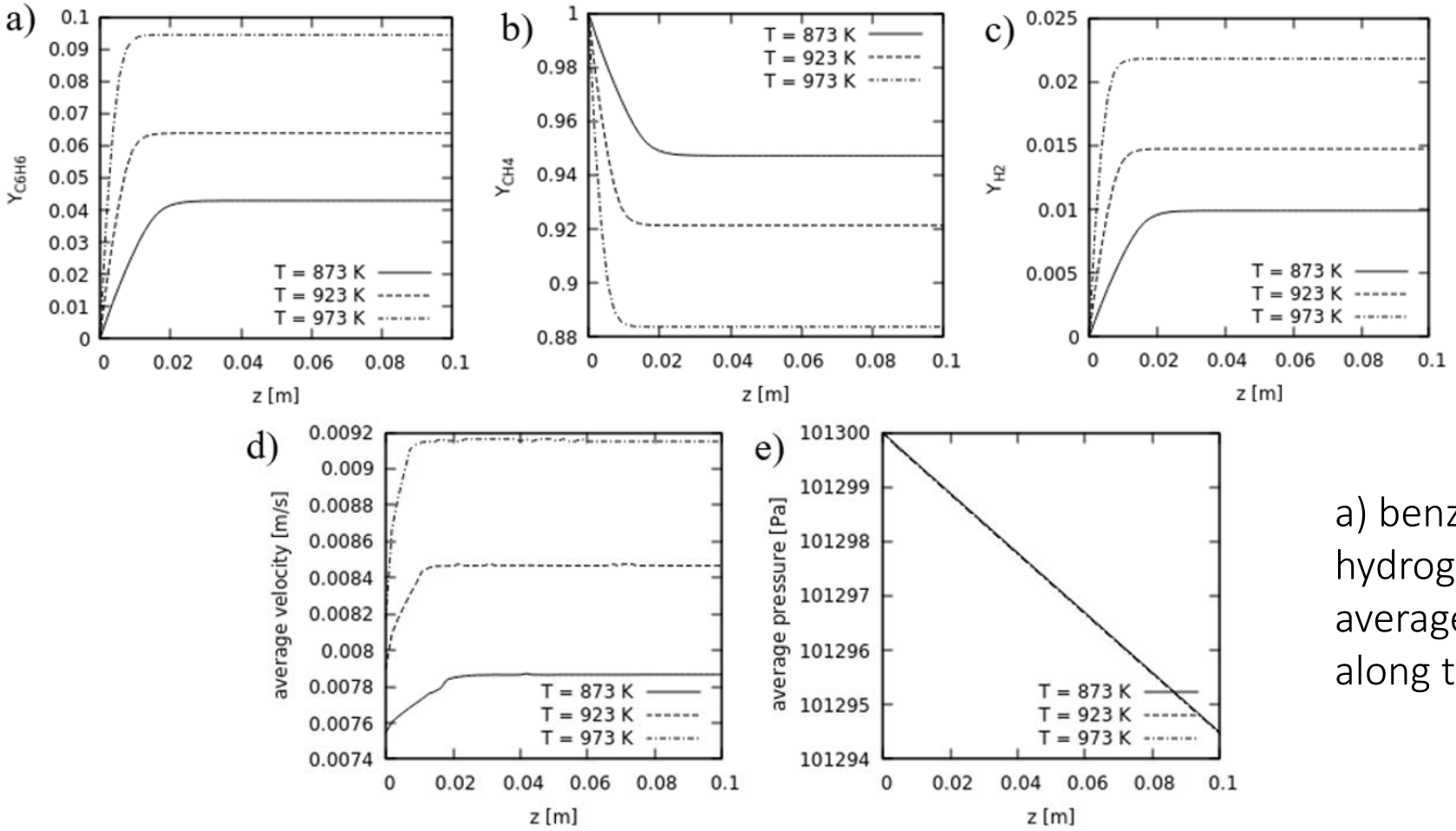
where a and b are user-defined coefficients that can be obtained, for example, by fitting experimental data.

3D simulation result



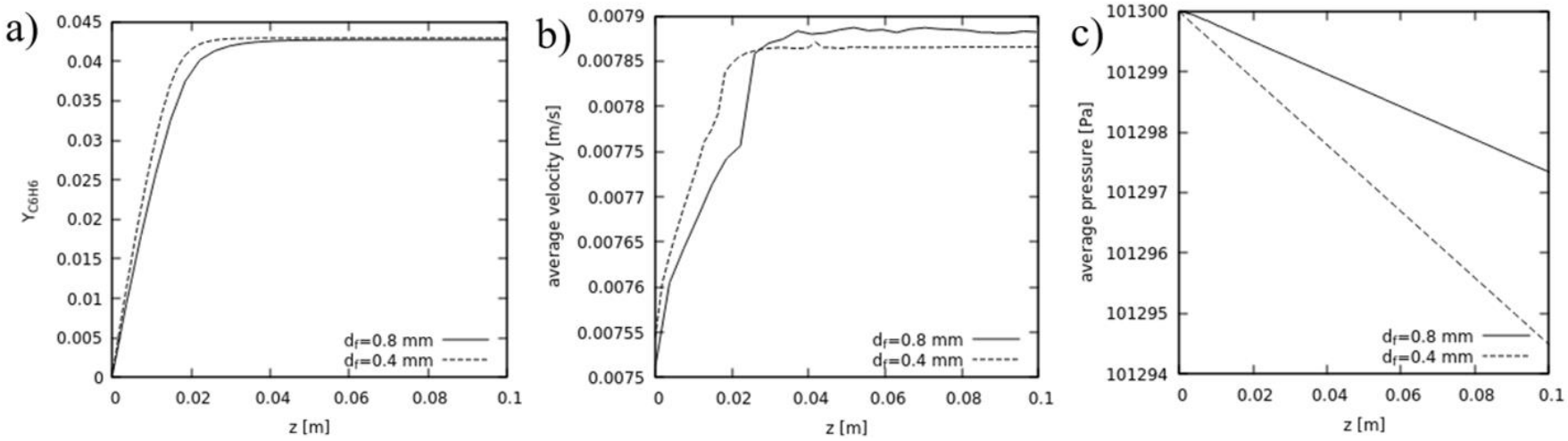
Section of (left) velocity and (right) benzene mass concentration in the middle of the RVE. .The result has been obtained from the simulation with catalyst size d_f= 0.8 mm and operating temperature T= 873 K.

3D-1D results - effect of operating temperature



a) benzene, b) methane, c) hydrogen mass concentration, d) average velocity and e) pressure along the reactor length.

3D-1D results - effect of catalyst size



a) benzene, b) methane, c) hydrogen mass concentration, d) average velocity and e) pressure along the reactor length.

Conclusions

- This work presents a **3D-1D model** for simulating the flow in **MDA reactors**.
- The MDA is modelled as a reversible methane decomposition into **hydrogen and benzene**, where the reaction rates are expressed via the **Arrhenius equations**.
- 3D simulation of relevant reactor sections using CFD-DEM simulations for accurately solve the physics of the problem.
- **1D** model to connect the **3D** solutions together and enable the simulation of industrial-relevant problems.
- Although the relative simplicity of the MDA model, the main features of the reactor flow seem to be captured, namely:
  1. the temperature dependence of the conversion rate and maximum methane conversion
  2. Dependence of pressure loss on the size of the catalyst structure

Acknowledgment

ZEOCAT-3D

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 814548

Coordinator: IDENER
Total cost and EC contribution: €6.764.020
Call: H2020-NMBP-ST-IND-2018
Funding scheme: RIA
Duration: from 2019-04-01 to 2022-09-30

THANK YOU

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