

Dual flow reactor for acid gas cracking and methane conversion simulation with COMSOL Multiphysics®

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Abstract

The chemical industry faces increasing pressure to reduce energy consumption and greenhouse gas emissions. Traditional reactor designs often require external heating or cooling, leading to significant energy losses. A promising approach is the dual-flow reactor, which integrates an exothermal and an endothermal reaction within a single heat exchanger-like structure. This design enables direct heat transfer between the two reaction zones, minimizing external energy demand and enhancing process efficiency.

In this study, a comprehensive model of such a dual-flow reactor is developed using COMSOL Multiphysics®.

The model couples turbulent flow, heat transfer, and reaction kinetics to simulate the interaction between the exothermal and endothermal reaction zones. The reactor geometry is designed to ensure thermal contact without mass transfer between the two streams, allowing for efficient heat exchange and process intensification.

The model is used to investigate the impact of key parameters, including reactor dimensions, mass flow rates, and the selection of reaction pairs. For this, H₂S based and CH₄ based reactions are investigated. The results demonstrate the potential of the dual-flow reactor concept to significantly reduce energy requirements in industrial processes, paving the way for more sustainable chemical production.

Introduction

To reduce energy consumption in energy intensive processes, an opportunity resides in the sharing of heating and cooling requirements of a pair of continuous process. This could advantageously replace independent heating and cooling methods. Provided that the two processes operate at compatible temperatures, the heating of the former can be achieved by the cooling of the latter.

Prior to testing a pair of process in an experimental setup, a numerical approach is selected to model the behaviour of an industrial scale setup. The goal being to assess the general concept, the physics is implemented and solved in a large-size dual reactor. Two different pairs of process are assessed: acid gas cracking/combustion and methane conversion/water vapor generation. Acid gas cracking chemistry is described in [A], and the kinetics proposed in this paper are employed. Acid gas combustion is described in [B], and the kinetics are similarly used. The methane conversion kinetics are more complex, especially in the presence of oxygen, and the kinetics described in [C, D and G] are used. Finally, water vaporization is described using a thermal approach.

After describing the geometry in the first section, the physics and the chemistry is described in the second part. Finally, results are presented before outlining the main conclusions and the next steps.

1. Dual reactor geometry

In the dual reactor setup, only the heat is shared between the two processes. Therefore, reactants and products of each process flow in two independent regions, while a heat conductive wall separates them. To promote heat exchange, the heat conductive wall has a large surface area, similarly to a conventional heat exchanging device.

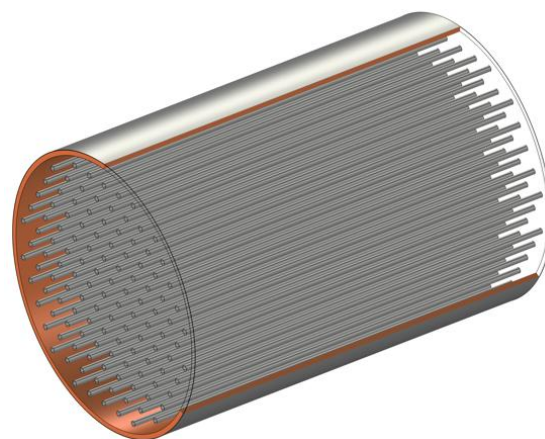


Figure 1. Dual reactor geometry (121 tubes, 5.56cm diameter tubes)

The design studied is presented in Figure 1. One process occurs in the 121 5.6cm diameter tubes, while the other occurs around the small diameter tubes but within the large vessel envelop. This

vessel diameter is 270 cm. The length of the heat exchange region is 410cm. The 121 tubes are made of silicon carbide. The vessel wall has an internal layer of refractory bricks and an outer layer made of steel.

2. Physicochemical description and computing

To model the reactor behaviour, fluid flow, heat transfer, reaction rate and species distribution must be solved together in the different fluid domains. In the solids, reactor behaviour is characterized by the heat conduction. However, at the solid surface, convection and surface-to-surface radiative heat fluxes are applied.

2a. Fluid flow and heat transfer

In the fluid domains, weakly compressible Navier-Stokes equations are solved with a k-epsilon turbulence equation. A counter-current flow strategy is applied, and a mass flow rate is imposed at the inlet of each reactor. No slip walls are assumed, and the outlet sets the reference pressure at 0 Pa. The flow equations are not detailed here, but the velocity field $\mathbf{u}$ is determined. The relative pressure is also obtained, and as its order of magnitude is small compared to the device operating pressure, compressibility heat is not accounted for in the heat transfer and the chemical reaction is considered within isobar conditions. However, the variation of fluid mix density ρ is important, which justifies compressibility assumption in the fluid flow computation. Finally, the turbulent kinetic energy k_{NS} is used to compute effective fluid heat conduction and fluid species diffusion.

The velocity field is applied to the heat equation to account for the convection heat transfer, and the temperature T is solved for:

$$\rho C_p \mathbf{u} \nabla T + \nabla(-k \nabla T) = Q_{process}$$

With C_p the fluid mix heat capacity and k its heat conductivity. $Q_{process}$ is the heat of the applicable process. $Q_{process} > 0$ indicates an exothermic process while $Q_{process} < 0$ describes an endothermic process.

In the solids, the heat equation simply becomes $\nabla(-k \nabla T) = 0$ with k the solid conductivity. Surface to surface radiative heat transfer is applied between the internal surfaces of the reactor, and the view factors are computed using COMSOL's Heat Transfer module. Moreover, a nucleate boiling flux [H] is applied to the walls in contact with water. For practical reasons, it was decided to solve solids and fluids using two different temperatures in COMSOL. At the interface, the convective flux is applied to conserve energy: this flux is the key to

the dual reactor idea. For the 3D simulations, a heat transfer coefficient relevant to the flow conditions is applied. For the 1D simulations, a Nusselt dependent pipe flow expression is used at the inner wall of the small tubes, and a cylinder in cross flow external forced convection is used.

2b. Geometrical assumptions

To account for the complex heat transfer in the vessel and the tubes, a 3D computation is considered at first. This approach can be solved for in a 30° portion of the full reactor, for the acid gas process pair. Indeed, the process can essentially be described using 2 reactions and 7 species. Unfortunately, this 3D approach is too expensive for methane conversion: several hundred of reactions and species are involved to various degrees. Even the simplified set of kinetics used require solving a few dozens of reactions and a dozen species. For such a process, only a 1D approach is affordable within industrial time scale: therefore, the acid gas reaction pair is computed for both 3D and 1D assumptions to evaluate the validity of the latter.

Acid gas combustion reaction is a fast and local process which turns cold large density reactants into hot low density unburned reactants and products. Such a phenomenon requires large mesh density and therefore, this reaction is computed along a short 1D geometry representing the local region near the nozzle. After the combustion is completed, the flame temperature and species composition are known and can be applied at the inlet of the actual 3D geometry to compute a non-reactive flow.

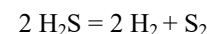
2c. Acid gas chemistry

The transport of concentrated species i is:

$$\nabla \cdot \mathbf{j}_i + \rho(\mathbf{u} \cdot \nabla) \omega_i = R_i$$

With $\mathbf{j}_i$ the species flux, ω_i the species mass fraction, $R_i = \nu_{ij} r_j$ its reaction rate, ν_{ij} the stoichiometric coefficient of species i in reaction j , and r_j the reaction kinetics of reaction j .

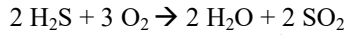
The acid gas (H₂S) cracking generates hydrogen and sulphur. All species are considered in their gaseous state:



For this reaction, $r = (k_f p_{\text{H}_2\text{S}} p_{\text{S}_2}^{0.5} - k_r p_{\text{H}_2} p_{\text{S}_2})$, with $k_f = A_{fcrack} \exp(-E_{fcrack}/(RT))$ the forward rate constant, $k_r =$

$A_{rcrack} \exp(-E_{rcrack}/(RT))$ the reverse rate constant, where A is the preexponential factor, E the activation energy, the subscript f stands for forward, r for reverse and $crack$ for acid gas cracking reaction. The variables $p_{\text{H}_2\text{S}}$, p_{S_2} and p_{H_2}

are the partial pressures of respectively H_2S , S_2 and H_2 . Reaction properties are described in [A]. The acid gas combustion generates water and sulphur oxide:



For this reaction, $r = k_f p_{\text{H}_2\text{S}} p_{\text{O}_2}^{1.5}$, with $k_f = A_{f\text{comb}} \exp(-E_{f\text{comb}}/(RT))$ the forward rate constant, where the subscript comb is for acid gas combustion reaction and p_{O_2} is the partial pressure of O_2 . Reaction properties are described in [B]. With the nitrogen present in the air flow, only 7 species are described. At the inlet of the cracking tubes, the mass flow rate is 214 kg/h of H_2S . At the inlet of the combustion vessel, the mass flow rates are 10t/h of H_2S , 4.7t/h of O_2 and 15.1t/h of N_2 .

2d. Methane conversion chemistry

As stated previously methane conversion involves a large number of species and reactions. This is particularly true in the present context of oxidative coupling of methane (OCM).

Whereas the geometry of the tube and vessels is simplified to a 1D approach, the description of the species becomes tedious and error prone. For this reason, the 38 reaction and 24 species system is defined using CHEMKIN file format. The transport properties come from ANSYS generic transport file [E], the thermodynamic properties come from the University of Galway/ARAMCO 2018 database [F], but the kinetics file is created specifically for this work and based on [C, D and G]. They all follow the pattern presented with acid gas reactions, although the pressure operating conditions may vary for the purpose of the study: therefore, pressure fall-out behaviours are based on [C, D and G] and described within the CHEMKIN type files. The inlet stream of gas is 12.1 t/min of CH_4 and 360 t/min of O_2 at 750°C . Operating pressure is 20 bars. Water flow is approximately 60 kg/min

3. Results

3a. Acid gas processes

Both combustion and cracking of H_2S naturally occur in Claus process. Dual flow reactor allows for a better selection of the different reaction products. H_2S reactions and flows are computed in the domain described. Figure 2 describes the parameters of the H_2S combustion which is computed in 1D. For the inlet conditions considered, most of the combustion occurs between 2 and 3 cm after O_2 and H_2S meet. The flame temperature computed is about 1470°C for the assumptions listed. This temperature would decrease if volume radiative heat emission were considered, but the current result is sufficient for the goal of this project.

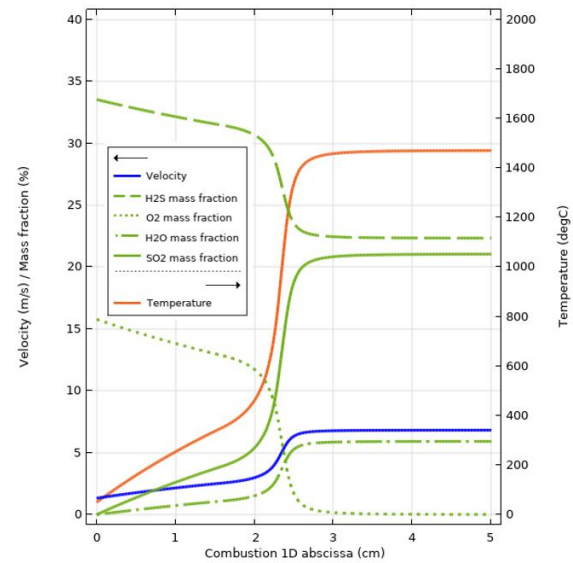


Figure 2. H_2S combustion flow velocity, temperature, and chemical composition along flame abscissa.

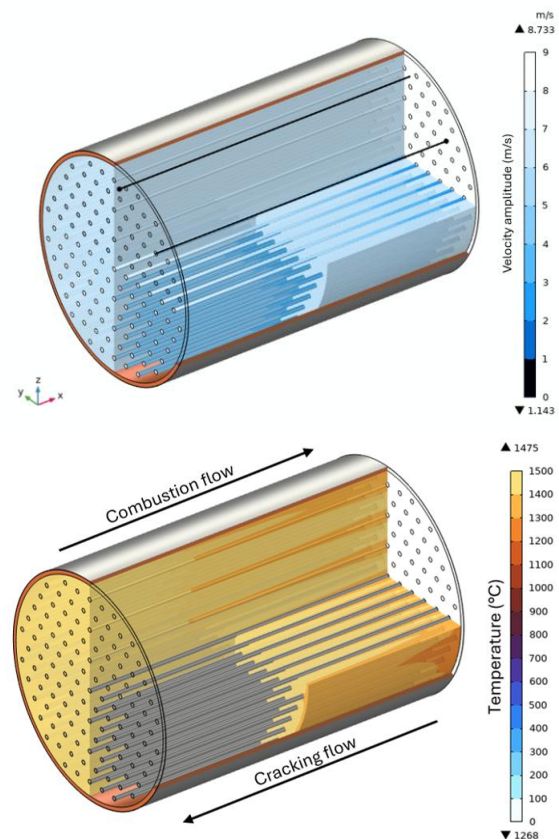


Figure 3. (Top) Unburned H_2S , H_2O and SO_2 flow velocity in vessel; H_2S , H_2 and S_2 flow velocity in the tubes. (Bottom) Unburned H_2S , H_2O and SO_2 temperature distribution in the vessel.

The unburned H_2S and combustion products are then applied to the inlet of the vessel. In this vessel,

the non-reactive flow is computed, and its heat is transferred to the tubes as can be seen in Figure 3. The tubes, heated by the stream of hot gas, provide heat for the H_2S cracking to occur within them. To analyse the cracking flow behaviour, it is important to distinguish different metrics: they are detailed in Figure 4. They allow for analysing the stream in the whole section as an average, and to focus specifically on the central and outer gas layers.

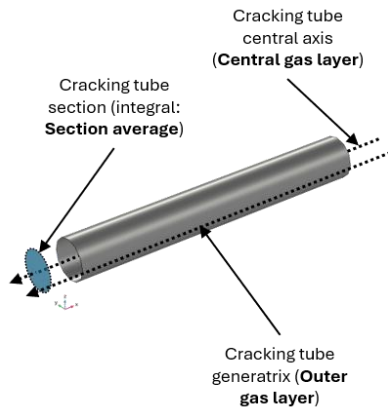


Figure 4. Cracking tube characteristic metrics: section average, central axis, tube generatrix.

Using such metrics, Figure 5 shows the temperature and cracking H_2 yield. The combustion flow temperature decreases as it shares its heat with the cracking stream. Reversely, the cracking stream section average temperature increases along the cracking tube abscissa. However, a large difference is visible between the outer layer and the central layer temperatures. While the former increases immediately after contact with hot tube wall, the latter increases slowly. Similarly, the outer layer H_2 yield is high, and the central layer H_2 yield is low. However, this effect can be reduced by using smaller diameter tubes. Depending on the tube diameter, the central layer may never be hot enough to trigger H_2S cracking, but adapted tubes show low temperature and yield difference across the tube section.

This low difference is good news for the H_2S dual reactor process: with a carefully designed device, it is technically feasible to use the heat of combustion to generate cracking. This low difference is also good news for the computation of methane conversion process. Indeed, with the carefully designed device – i.e. with small enough tube diameter – a 1D computation of the OCM should generate accurate results.

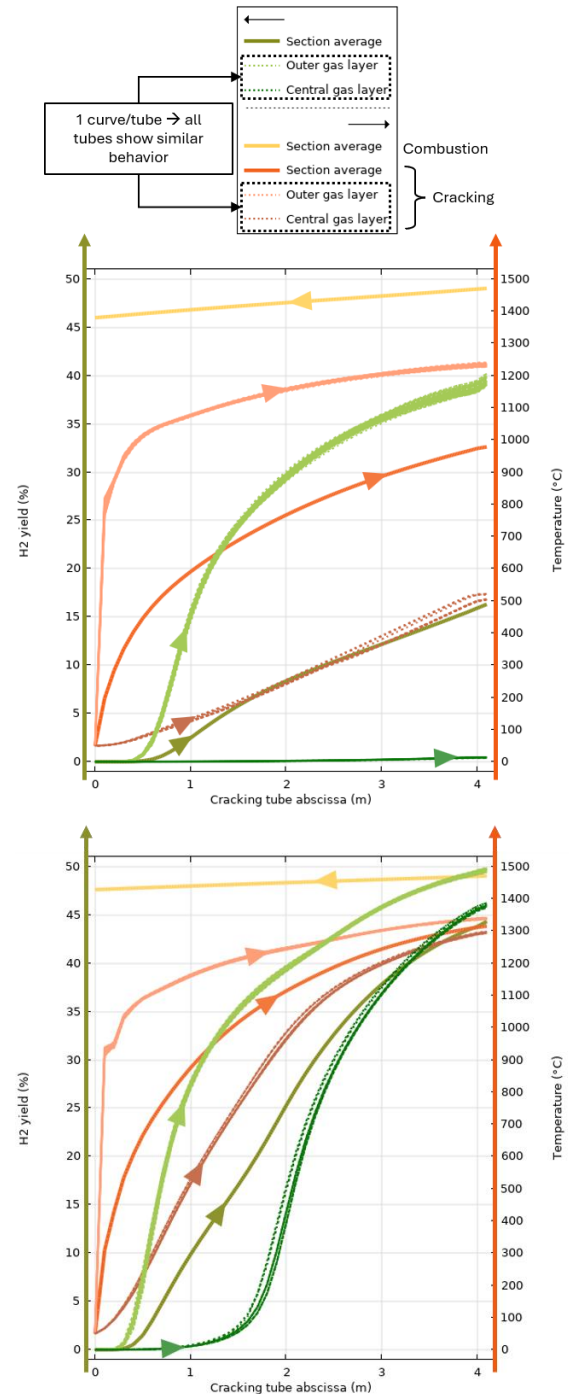


Figure 5. H_2 yield and temperature in cracking tubes, using the different characteristic metrics. Top: 5.6cm diameter tubes, bottom: 2.8cm diameter tubes, arrow: flow direction.

3b. Methane conversion process and water vapor generation.

Because the water vaporization draws a lot of energy, the tubes hosting the OCM stream are sleeved at their inlet side. The sleeve is considered as a perfect insulator, and it leaves the last part of

the tube for heat exchange to occur. This is known as the contact region, and the contact length is varied to design the species selectivity.

Figure 6 shows the OCM flow velocity, flow temperature, and mass fraction of CH_4 and O_2 . O_2 is progressively consumed by different reaction in the first half of the tube, but the consumption rate increases approximately and reaches a maximum at 2.5m in the stream before O_2 disappears from the flow. This rapid consumption is accompanied by an increase in temperature. Were the contact length longer the flow would be cooler, or shorter, the flow would be warmer.

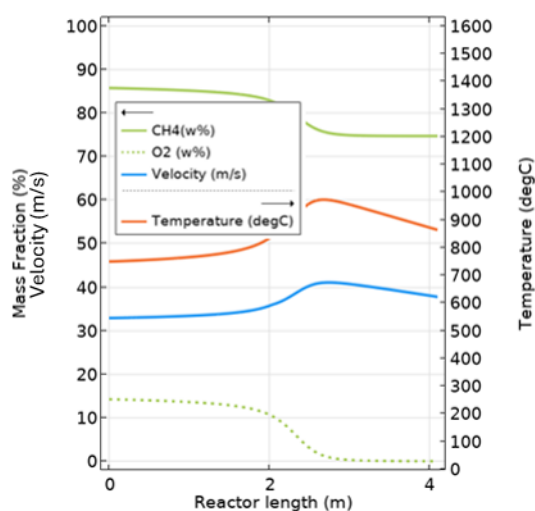


Figure 6. OCM flow velocity, temperature, and chemical composition along reactor length for a 2.1m contact length (i.e. a 2m sleeve length).

Figure 7 shows a synthetic view of the output species composition, depending on the contact length. Whereas contact length does not influence oxygenated products, decarbonated and hydrocarbon product are different between a long and a short contact length. A short contact length promotes H_2 , C_2H_2 , C_2H_4 and C_3H_6 , whereas a long contact length reduces their production. Longer contact length increases the production of C_2H_6 mainly.

Depending on the desired production, different reactor sleeves are selected. Water vapor generation is always successful in this process pair: only the vapor flow rate changes depending on the contact length.

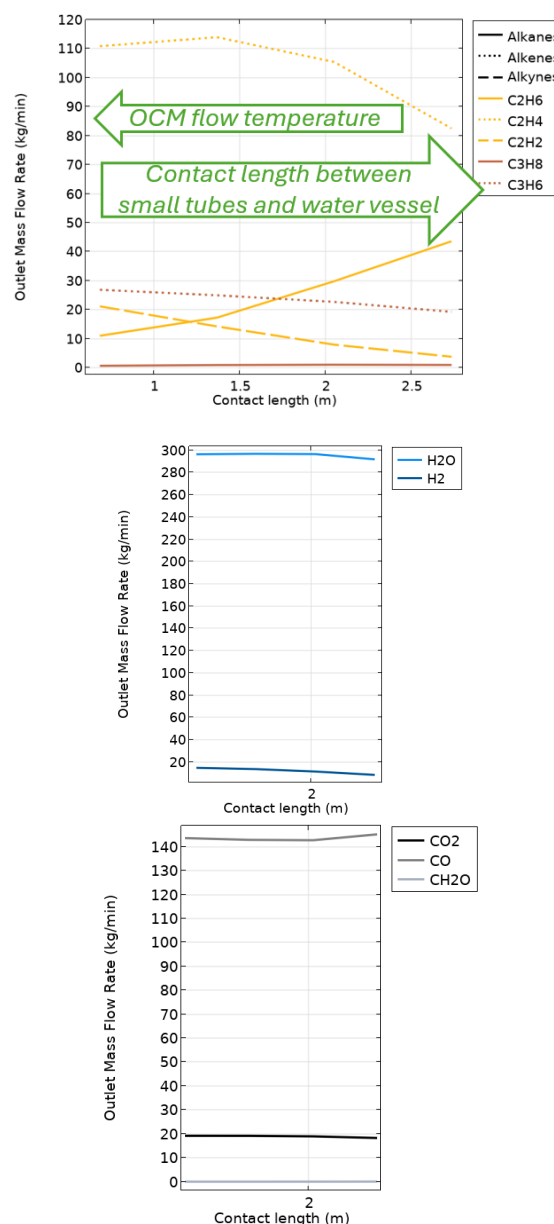


Figure 7. Output mass flow rates of the different OCM products, for various contact lengths. Top: hydrocarbons, middle: decarbonated, bottom: oxygenated.

Conclusions

Leveraging reaction kinetics availability in the literature for specific process pairs, a numerical model of a dual flow reactor is developed. It is then applied to different process pairs. One process provides the heat to the other and receives cooling in return. If carefully designed, such a continuous flow equipment can produce large throughput for both processes with minimal supplementary energy use.

Acid gas treatment can be done using such a device, and the efficiency can be improved by carefully selecting the tube dimensions. With this system, the

valuable H₂ generated in the classical Claus process can be isolated and used for other purposes.

OCM is also a relevant process for a dual flow reactor. In addition to designing the tube diameter, it is possible to choose the reactor production profile by varying the heat contact length between the water filled vessel and the OCM tubes.

When designing a dual flow reactor, the simulation results prove to be a valuable decision support tool. While it cannot replace experimental tests and pilot lines, these results allow for narrowing down the relevant configurations to explore experimentally. Indeed, it allows for fast iteration rate, and suitable physics informed first guesses.

References

[A] Hawboldt, K. A., Monnery, W. D., & Svrcek, W. Y. (2000). New experimental data and kinetic rate expression for H₂S pyrolysis and re-association. *Chemical Engineering Science*, 55(5), 957-966.

[B] Zarei, S. (2018). A modified kinetic reaction scheme for Claus reaction furnaces in oil refineries. *Innov Ener Res*, 7(215), 2576-1463.

[C] Chen, Q., Couwenberg, P. M., & Marin, G. B. (1994). Effect of pressure on the oxidative coupling of methane in the absence of catalyst. *AIChE journal*, 40(3), 521-535.

[D] Tsang, W., & Hampson, R. F. (1986). Chemical kinetic data base for combustion chemistry. Part I. Methane and related compounds. *Journal of physical and chemical reference data*, 15(3), 1087-1279.

[G] Tsang, W. (1987). Chemical kinetic data base for combustion chemistry. Part 2. Methanol. *Journal of physical and chemical reference data*, 16(3), 471-508.

[H] Pezo, M. L., & Stevanović, V. D. (2016). Numerical prediction of nucleate pool boiling heat transfer coefficient under high heat fluxes. *Thermal Science*, 20, S113-S123.

[E] ANSYS Chemkin transport database

[F] AramcoMech3.0 (2018)

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