

OXIDATIVE COUPLING OF METHANE IN A GAS-SOLID VORTEX REACTOR

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Abstract

New reactor technologies are key enablers to make oxidative coupling of methane (OCM) one of the most important chemical processes in the chemical industry because they allow to resolve the heat and mass transfer limitations that are encountered in traditionally used fixed bed reactor types. In this work the gas-solid vortex reactor is proposed as a promising reactor technology for OCM. CFD simulations show that the narrow residence time distributions and efficient heat management in the GSVR can give rise to C₂ yields ~25 %.

Keywords

oxidative coupling of methane, gas-solid vortex reactor, computational fluid dynamics

Introduction

Oxidative coupling of methane is considered one of the most promising routes to directly convert methane into more valuable hydrocarbons. The uncertain economics related to the tradeoff between conversion and C₂ selectivities is an important reason why OCM is currently not industrially applied (Vandewalle et al., 2018b). In the last decades, numerous studies have focused on developing a viable catalyst that has the potential to improve the low C₂ yields. However, so far, the research on catalyst development has not led to any major breakthrough. One of the reasons is that next to the catalyst aspects, reactor design is of crucial importance for OCM. The lack of an appropriate reactor is one of the primary reasons why OCM has not been commercialized at industrial scale.

Previous studies based on bifurcation theory (Sun et al., 2018; Vandewalle et al., 2018a) have shown that the key features of an ideal OCM reactor are high thermal backmixing (i.e. high effective thermal conductivity) and low species backmixing (i.e. narrow residence time distributions). Narrow residence time distributions, i.e. plug flow behavior, is necessary to control and maximize the selectivity towards the intermediate products ethane and ethylene. High effective thermal conductivity creates the opportunity to exploit the bifurcation behavior and operate an OCM reactor autothermally, in this way utilizing the

reaction heat in the best possible way. Both these characteristics can be obtained in the gas-solid vortex reactor (GSVR) that is studied in this work. In a gas-solid vortex reactor in a static geometry, gas is injected tangentially via a number of inlet slots (see Figure 1). The swirling gas transfers its momentum to the particles in the reactor chamber, which in turn start rotating. A fluidized state is obtained when the drag force exerted by the gas balances the apparent weight of the particles in the centrifugal force field.

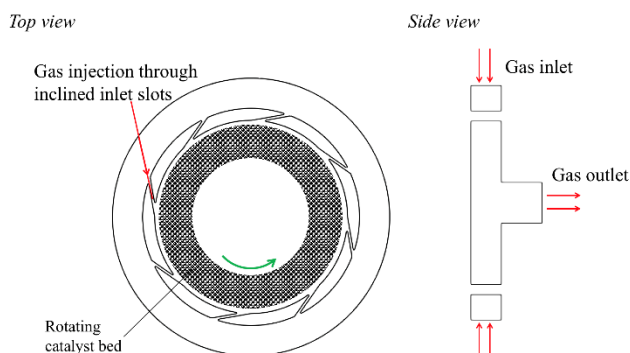


Figure 1. Gas-solid vortex reactor in a static geometry.

In contrast to conventional gravitational fluidized beds, higher gas throughput, lower residence time, more uniform beds, higher slip velocities and hence better heat and mass transfer can be achieved in this reactor type. Therefore, the GSVR is an excellent candidate for process intensification. As the reactor can combine short residence times and narrow residence time distributions with optimal heat transfer characteristics, it is a very promising technology for OCM.

In this work, the open-source CFD package OpenFOAM is used to simulate an adiabatic gas-solid vortex reactor using an Euler-Euler approach. Detailed microkinetic models are used for different types of catalyst (Sn-Li/MgO, Mn/Na₂WO₄/SiO₂, Sr/La₂O₃). The effect of operating conditions and reactor geometry is evaluated.

Methodology

The simulated GSVR geometry is adopted from the work of (Gonzalez-Quiroga et al., 2017). It basically consists of a cylindrical unit positioned along a vertical axis with eight gas injection slots of 1 mm width, equally distributed over the circumferential wall and tangentially inclined at a 10° angle. A reactor diameter of 80 mm and length of 15 mm are defined.

The reactive two-phase flow in the GSVR is simulated with an Euler-Euler approach using the open-source CFD package OpenFOAM. A dedicated solver was developed, coupling OpenFOAM and Cantera, the latter being used as mechanism interpreter. This allows to use detailed microkinetic models. In this work, the microkinetic model consists of 39 gas phase reactions and 26 catalytic reactions (Kechagiopoulos et al., 2014). The same model can be used for different catalysts (Sn-Li/MgO, Mn/Na₂WO₄/SiO₂, Sr/La₂O₃), provided the kinetic parameters are adjusted accordingly. The GSVR is simulated as an adiabatic unit.

Results and discussion

Non-reactive simulations show that narrow residence times can indeed be obtained in the GSVR. Plug flow behavior for species/mass transport is indicated by the quasi parallel streamlines (see Figure 2) and a simulated Péclet number $\gg 1$.

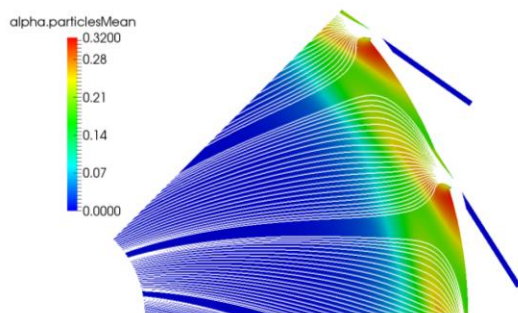


Figure 2. Gas streamlines, shown on top of the catalyst volume fraction field. Simulated conditions: 16-slot GSVR, 75 m/s

slot velocity ($CH_4:O_2 = 4$), 11.2 g catalyst particles (2300 kg/m³, \varnothing 500 μ m)

Preliminary reactive simulations also indicate a good thermal mixing in the reactor, without hot spot formation. High C₂ selectivities \sim 75% can be obtained, but in the non-ignited state, methane conversion is limited because of the very small residence times (<5 ms) in the catalyst bed. Employing the effects of ignition/extinction behavior, the methane conversion can be increased while maintaining a high C₂ selectivity, and at the same time working at lower inlet temperatures.

Conclusion

In this work a new reactor technology is proposed for the oxidative coupling of methane (OCM). A gas-solid vortex reactor (GSVR) combines the two most important features required in an ideal OCM reactor: good heat management and narrow residence time distributions. This allows to utilize the exothermic reaction heat in the best possible way while also maximizing the selectivity towards intermediate C₂ products. Computational Fluid Dynamic simulations are used to optimize and design the GSVR specifically for OCM. The CFD simulations show that the narrow residence time distributions and efficient heat management in the GSVR can give rise to C₂ yields \sim 25 %.

Acknowledgments

LAV acknowledges financial support from a doctoral fellowship from the Fund for Scientific Research Flanders (FWO). The computational work was carried out using the STEVIN Supercomputer Infrastructure at Ghent University, funded by Ghent University, the Flemish Supercomputer Center (VSC), the Hercules Foundation and the Flemish Government – department EWI.

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