IGNITION IN ADIABATIC REACTORS FOR OXIDATIVE COUPLING OF METHANE

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Abstract

A high effective heat conductivity of the catalyst bed and a narrow residence time distribution are the key requirements for any reactor for oxidative coupling of methane (OCM). Bifurcation analysis shows that this allows a steady state adiabatic and autothermal conversion of methane fed at near ambient temperature by utilizing the thermal power of the exothermic reactions while also maximizing the selectivity towards intermediate C_2 products. A gas-solid vortex reactor (GSVR) with a rotating dense fluid bed meets these two requirements, making it a very promising reactor candidate for OCM.

Keywords

oxidative coupling of methane, gas-solid vortex reactor, bifurcation analysis, CFD

Introduction

Oxidative coupling of methane (OCM) is considered one of the most promising routes to directly convert methane into more valuable hydrocarbons. However, OCM suffers from the conversion-selectivity problem typical for many selective oxidation processes: due to oxidation of the C_2 products in secondary reactions high methane conversions correspond to poor C_2 selectivities and a large yield of undesired CO_x products. This tradeoff between conversion and C_2 selectivity is the main reason why OCM is currently unable to achieve the 30-35 % C_2 yields that are suggested to make the process industrially relevant. From the 1980s onwards, researchers have been searching for a viable OCM catalyst, which primary role is to initiate methane activation and to suppress deep oxidation reactions that have a lower apparent activation energy and are thermodynamically favored over the desired coupling reaction. Although research on catalyst development is numerous, so far it has not led to any major breakthrough to improve C_2 yields.

One of the reasons is that next to the catalyst aspects reactor design is of crucial importance. Reactor engineering is also important to tackle the second challenge for OCM, namely the extreme exothermicity of the process. Because of the large adiabatic temperature rise and hence high values of the Zeldovich number, an OCM reactor of practical importance is always operated in the runaway region. This can be deduced from the following runaway criterion (Balakotaiah and Luss, 1991):

$$\frac{E}{RT_0}\frac{(-\Delta H_r)r(T_0,C_0)}{T_0}\left[\frac{d_t}{4U}+\frac{d_p}{6h}\right] < 0.368f(\phi_0)$$

where E is the intrinsic activation energy [J mol^{-1}], R the universal gas constant [J mol^{-1} K^{-1}], T_0 the inlet temperature [K], $(-\Delta H)$ the reaction heat [J mol^{-1}], $r(T_0,C_0)$ the intrinsic reaction rate at inlet conditions [mol m^{-3} s^{-1}], d_t the tube diameter [m], d_p the pellet diameter [m], U the overall heat transfer coefficient [W m^{-2} K^{-1}], h the fluid-pellet heat transfer coefficient [W m^{-2} K^{-1}], $f(\phi_0)$ a function of the Thiele modulus at inlet conditions which accounts for the impact of intraparticle diffusion on the runaway locus. For many practical situations, and especially for OCM where the adiabatic temperature rise is so large, this criterion cannot be satisfied unless the reaction mixture is extremely diluted, which also negatively affects the reactor performance and productivity.

Thermal effects, such as the existence of multiple steady states, are dominating in every OCM reactor and should be exploited to achieve a better reactor performance. An understanding of the ignition and extinction, e.g. via bifurcation analysis, is therefore of crucial importance when designing novel reactors for OCM.

Ignition / extinction in an adiabatic OCM reactor

The ignition / extinction behavior of OCM has been studied via bifurcation analysis by (Sun et al., 2018) and (Vandewalle et al., 2018a). In these studies, three different adiabatic reactor models are considered: a plug flow reactor (PFR), a continuously stirred tank reactor (CSTR) and a lumped thermal reactor (LTR) model. The latter represents the limiting case with zero backmixing (cf. PFR behavior) for species and perfect thermal backmixing (cf. CSTR behavior). The bifurcation behavior in these reactor types is compared with a focus on methane conversion, C_2 yields and their dependence on operating conditions such as inlet composition, inlet temperature and space time.

Among the three investigated reactor types, the LTR shows the highest product yields and the lowest extinction temperatures, which allows autothermal operation at a much lower inlet temperature compared to a PFR and CSTR. This indicates 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. a narrow residence time distribution. The latter, i.e. plug flow behavior, is necessary to control and maximize the selectivity towards the intermediate C2 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.

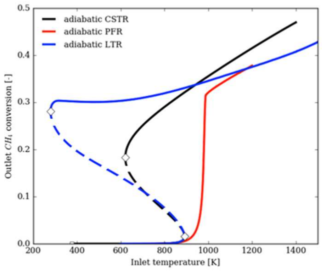

Figure 1: Comparison of the methane conversion obtained in an adiabatic PFR, CSTR and LTR for OCM with Sn-Li/MgO catalyst (Vandewalle et al., 2018a).

Limited species backmixing and good thermal backmixing are also the characteristics that the most promising advanced reactor types for OCM have in common (Vandewalle et al., 2018b). In this work the focus is on the gas-solid vortex reactor (GSVR), where gas is injected tangentially in a reactor chamber**Error! Reference source not found.**, transferring its angular momentum to a bed of particles which in turn starts rotating, see **Error! Reference source not found.** The GSVR can work at very high gas throughput compared to conventional fluidized beds, resulting in high gas-solid slip velocities. The high slip velocity and rapid rotation of the particle bed results in improved heat transfer between the gas and the particles and an effective thermal conductivity much larger than the one that can be obtained in fixed bed reactors. The GSVR is therefore a perfect candidate for process intensification. As it allows to combine short residence times and narrow residence time distributions with optimal heat transfer characteristics, it is also a reactor technology of choice for OCM.

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Conclusions

Because of the high exothermicity of the OCM process, thermal effects and path dependence are dominating in all OCM reactors of practical importance. Understanding and exploiting ignition and extinction behavior is crucial for the design of novel reactor technologies for OCM. Bifurcation analyses have shown that the most important features required in an ideal OCM reactor are good heat management and narrow residence time distributions. Both these characteristics are obtained in the gas-solid vortex reactor (GSVR), which is therefore a promising reactor concept for OCM. Autothermal operation by intentional operation in the multiple steady state region of the GSVR for OCM is the ultimate way to maximize the process intensification opportunities of this reactor technology.

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