Process intensification of oxidative coupling of methane

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Abstract

The chemical industry is faced with a dual challenge: the need for more renewable energy input and less CO_2 emissions. The combination of population growth and the increasing prosperity are consistently driving the production of chemicals, with plastics being the fastest growing group of bulk chemical products. Steam cracking of crude oil fractions, the leading production technology for the light olefins that are the key building blocks for all kinds of plastics, is very energy intensive and responsible for a large amount of CO_2 emissions, which are directly linked to the natural gas combustion in the furnace to produce the required heat input. Furthermore, on top of the natural gas that is nowadays burnt for energy and electricity generation, about 140 billion cubic meters of associated natural gas are annually flared at remote oil drilling locations around the world, accounting for 1 % of global CO_2 emissions, and this without any energy benefits. Clearly, there is an urgent need to develop economically viable processes for converting methane into more easily transportable high-value products, such as olefins and higher hydrocarbons.

Oxidative coupling of methane (OCM) is currently considered the most promising direct process for valorizing methane in the form of ethylene. OCM is initiated at the catalyst surface by the generation of methyl radicals. Methyl radicals recombine in the gas phase into ethane, which then dehydrogenates to ethylene. However, 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. Reactors with low space times and narrow residence time distribution are required to avoid oxidation of the C_2 products in secondary reactions. A second important challenge for OCM is the extreme exothermicity of the process, which makes cooling of an industrial-scale OCM reactor infeasible. To tackle these two challenges, namely the low C_2 yields due to the conversion-selectivity tradeoff and the high exothermicity, a novel intensified OCM reactor is needed. In this work, the gas-solid vortex reactor (GSVR), developed at the Laboratory for Chemical Technology (LCT) at Ghent University, is proposed for this purpose.

LCT has a cold flow, hot flow and reactive setup which provide new insights in different effects occurring at every stage of the OCM process. In combination with modeling, valuable experimental studies can be carried out for different operating conditions. Nevertheless, these time intensive experimental studies can be drastically reduced by focusing on high level computational fluid dynamics (CFD) simulations. These simulations allow to optimize the reactor geometry and operating conditions for OCM and to easily investigate alternative

processes benefitting from this technology. In this project, both reactive and non-reactive CFD simulations of the GSVR are performed using the open-source CFD package OpenFOAM. The newly developed reactive CFD model takes into account a detailed OCM microkinetic model consisting of both homogeneous and heterogeneous reactions. The use of detailed kinetics is an important improvement compared to our earlier CFD work on the GSVR for OCM (presented at the EPC conference in San Antonio in 2017), where only a global 10-step mechanism was used.

CFD simulations with this newly developed framework show that the GSVR is indeed characterized by short gas-phase residence times and narrow residence time distributions. Furthermore, it is shown that the GSVR exhibits a high degree of thermal backmixing, which in adiabatic operation results in steady-state multiplicity, which in turn allows autothermal operation of the reactor. In autothermal operation the exothermic reaction heat of the OCM process is used in the best possible way, i.e., to heat the feed. Previously, autothermal operation of the GSVR for OCM was not considered, while in fact it presents the ultimate opportunity for process intensification of OCM.