# OXIDATIVE DEHYDROGENATION OF ETHANE TO ETHYLENE USING MICROTECHNOLOGY

Georgios D. Stefanidis[1,2] and Dion G. Vlachos[2,*],

*[1]Process & Energy Department, Mechanical, maritime & Materials Engineering Faculty, Delft University of Technology, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands*

*[2]Department of Chemical Engineering and Center for Catalytic Science and Technology (CCST), University of Delaware, 150 Academy Street, Newark, DE 19716, USA*

*Summary*

We most likely present the first extended CFD-based analysis of ethane oxidative dehydrogenation (using overall kinetics) in small scale reactors to investigate the effects of important reactor parameters (wall materials and size) and operating conditions (velocity, feed composition) and to propose design principles. In addition, to overall kinetics, a comprehensive first-principle based microkinetic model on $Pt/Al_2O_3$ is developed to provide insights into the coupling of gas and surface reactions and in methods to tune product yield.

*Keywords*

Oxidative dehydrogenation, ethylene, CFD, microkinetic model

## Introduction

Ethylene, one of the most important building blocks for the production of many chemicals, is presently produced via steam cracking of light or heavy hydrocarbon distillates. It is essentially a homogeneous hydrocarbon pyrolysis process taking place in multi-pass coils heated up by means of gas/liquid-fired flames in large furnaces. The high energy demand, the low thermal efficiency, NOx formation and the need for frequent shut downs for tube decoking are some of the important drawbacks of this process. On the other hand, the self-sustained (autothermal) oxidative dehydrogenation (ODH) of hydrocarbons appears as a promising alternative to improve the economics of ethylene production. Furthermore, one may envision downscaling of ODH in the future to take advantage of the microreactor technology. The latter is hailed as an upcoming technology for various processes in the fine chemistry, pharma, petrochemical and energy production sectors. Due to the excellent heat and mass transfer properties, micro(milli) scale reactors can substantially intensify a process (more than one order of magnitude) in terms of yield/throughput as well in terms of improved selectivity, product quality and minimal waste production via more efficient temperature control. Aside from the typical challenges that need to be met when downscaling a process, a critical issue germane to ODH is the presence of competitive gas and catalytic chemistries. Ideally, the reactor should suppress homogeneous chemistry in the upstream zone, where catalytic combustion of ethane and/or co-fed hydrogen occurs and promote the endothermic homogeneous dehydrogenation chemistry downstream. The chemical and thermal coupling of the two zones is critical for yield/selectivity optimization.

## Methods

In this work we perform an extensive parametric study of the ODH process in a catalytic plate microreactor using Computational Fluid Dynamics (FLUENT software[1]) and the recently developed kinetic model of Yang et al.[2] consisting of seven gas-phase reaction steps and one catalyzed (Pt-alloy) hydrogen oxidation reaction. The effect of important operating and design parameters, such as the flow velocity, ethane and hydrogen concentrations in the feed, reactor gap size and material are discussed; the flow-chemistry interplay is explained and the optimal operating regimes are delineated.

## Results and discussion

Figure 1, shows how the amount of ethane in the three-component feed (ethane, hydrogen, oxygen) affects ethane conversion, ethylene selectivity and maximum and outlet temperatures. It is shown that increase in the feed ethane concentration can substantially improve ethylene selectivity, as the rate of the ethane dehydrogenation step increases drastically compared to other side reactions. However, this comes at the expense of reduced temperatures and reduced ethane conversion, as the heat release due to hydrogen oxidation does not suffice to convert the increasing amount of ethane.

---

[*] To whom all correspondence should be addressed

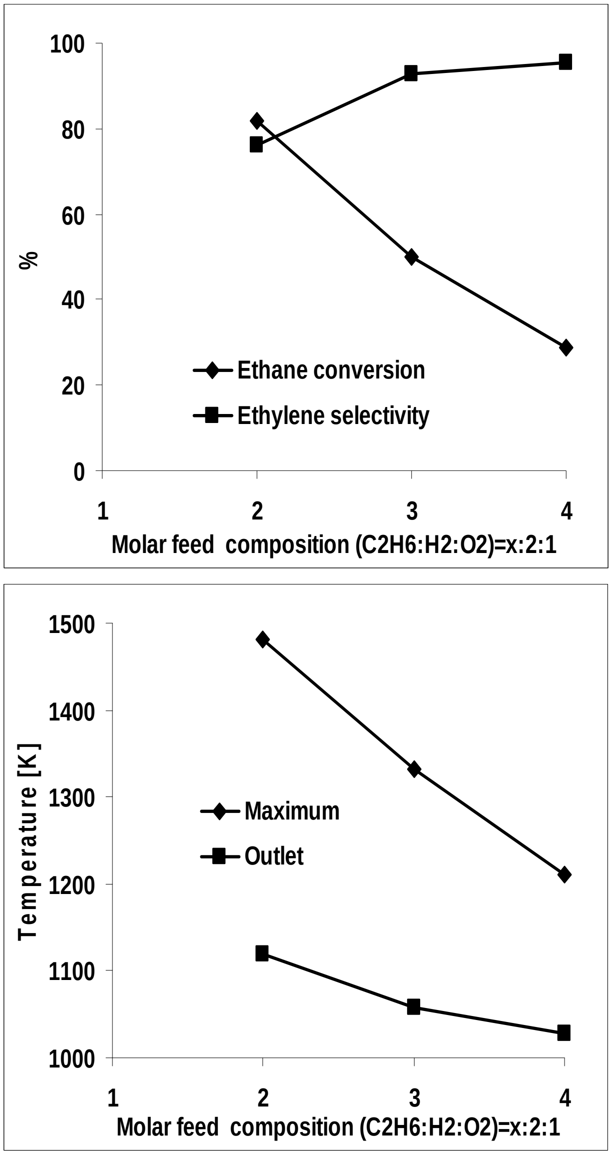

Figure 1: Ethane conversion, ethylene selectivity, maximum temperature and outlet temperature for different amounts of ethane in the feed (C2H6:H2:O2=2:2:1, 3:2:1, 4:2:1). The ethlylene selectivity is defined as the mass fraction of ethylene in the outlet stream over the sum of mass fractions of the carbon based products in the outlet stream.

# Conclusions

We most likely present the first extended CFD-based analysis of ethane ODH in small scale reactors. Although previous studies of the process in short contact time reactors with more detailed kinetics do exist, they were performed with oversimplified reactor models (e.g. plug flow, 2D boundary layer). In this work, the effects of reactor parameters, such as wall materials and size are addressed and design principles are proposed. In addition, to the overall kinetics, a comprehensive first-principle based microkinetic model on Pt/$Al_2O_3$ is developed to provide insights into the coupling of gas and surface reactions and in methods to tune product yield.

# References

(1) Law, C. K.; Sivashinsky, G. I. Catalytic extension of extinction limits of stretched premixed flames. *Combustion Science and Technology* **1982,** *29*, 277.
(2) Yang B., Yuschak T., Mazanec T., Tonkovich A. L., Perry S. “Multiscale modeling of microstructured reactors for the oxidative dehydrogenation of ethane to ethylene”. *Chemical Engineering Journal*, 135S (2008) S147-S152.