

# Demonstration and scale-up of autothermal oxidative coupling of methane

David West<sup>1\*</sup>, Vemuri Balakotaiah<sup>2</sup>, Tian Gu<sup>1</sup>, Pankaj Gautam<sup>3</sup>, Robert Broekhuis<sup>1</sup>, Jonathan Banke<sup>1</sup>, Hector Perez<sup>1</sup>, Nathon Caton<sup>1</sup>, Hoang Nguyen<sup>1</sup>

*1 SABIC, Corporate R&D, Sugar Land TX; 2 Department of Chemical and Biomolecular Engineering, University of Houston; 3 SABIC, Corporate R&D, Geleen, NL*

*\*Corresponding author: dwest@sabic.com*

## Highlights

- We present theory and experiments for operation of an adiabatic autothermal reactor.
- Emergence of spatial patterns were one difficulty encountered on scale-up.
- We demonstrate stable autothermal operation in a pilot-scale reactor for the first time.
- Remaining challenges for large-scale production are discussed.

## 1. Introduction

Four practical problems must be solved to achieve a commercially viable process for oxidative coupling of methane (OCM): (i) the reaction is so exothermic ( $\Delta T_{ad} \geq 800$  K) that it is impossible to remove the heat generated at practical methane conversion (20%) using a conventional cooled tubular reactor [1]. (ii) long contact times (*e.g.*,  $>0.1$  s) cause steam reforming of the products, and (iii) the sum of methane conversion and C<sub>2</sub>+ hydrocarbon selectivity must be high enough (without diluents) for good economics (*i.e.*, near 100%). (iv) In addition to stability, high productivity per reactor, *e.g.*, 50 kta, is needed to minimize the capex; this requirement makes high pressure operation a necessity. To address the first two problems, we developed an adiabatic autothermal reactor that takes advantage of steady-state multiplicity to achieve high reaction rate and rapid cooling from the incoming feed. It operates on the ignited branch with very short contact time;  $< 50$  ms. The catalyst bed is configured with dimensions that maximize the stability of the ignited state, approaching what we call a lumped thermal reactor (LTR), in which the longitudinal conduction of heat is much faster than the longitudinal diffusion of mass [2]. Bifurcation analysis guided the concept for the reactor and the special start-up procedure required to enable its operation. Through extensive testing (several hundred materials), we developed a catalyst that was active enough to enable stable autothermal operation with ambient feed temperature (maximizing conversion) and selective enough to satisfy condition (iii). In this talk, we will introduce the theoretical principles for the reactor design and present some results of laboratory and pilot plant experiments that demonstrate successful, stable, autothermal operation with near-ambient-temperature feed, and a combination of conversion and selectivity that exceeds all previously published results for autothermal mode of operation.

## 2. Methods

The catalysts used were primarily Sr doped, mixed Lanthanides [3]. Laboratory experiments were performed using granular catalysts (either 50/80 or 20/40 mesh) in a quartz tube, heated by an electric furnace. Tubes with various diameters were used (from 2.3 to 34 mm i.d.). Once ignited, the furnace was turned off and opened in some cases. Pilot plant experiments were performed using (approximately) 0.5 mm catalyst granules. The catalyst bed dimensions (aspect ratio) were optimized to maximize longitudinal dispersion of heat while minimizing longitudinal dispersion of mass [2,4]. Pilot scale catalyst beds with diameter of 70 and 96 mm, and length from 5-20 mm were tested. The largest scale tests were larger than the smallest lab scale by a factor of 3000. All products except water were analyzed by gas chromatography. A wide range of space-times were used (10-300 ms).

## 3. Results and discussion

Achieving stable, autothermal, operation in a laboratory scale reactor (10.5-34 mm i.d.) at atmospheric pressure was relatively easy [1]; see Figure 1. A variety of catalysts gave acceptable methane conversion (20%) and C<sub>2</sub>+ selectivity as high as 84% in laboratory experiments. On scaling up the reactor and

catalyst bed to a suitable pilot plant scale (70 and 96 mm bed diameter), it was difficult to obtain stable operation. Often non-uniform temperature patterns were formed, in which only a fraction of the bed was ignited, giving extremely poor selectivity. Figure 2 shows two photographs of the ceramic catalyst-bed support. The dark regions have some slight carbon deposits. These correspond to regions in which the bed was ignited, with complete oxygen conversion. The catalyst above the white regions was partially extinguished, yielding much lower conversion. This phenomenon is caused by a pattern forming instability [5]. In a highly exothermic gas phase reaction, the increase in viscosity with temperature causes higher pressure drop within the hotter regions of the reactor, making uniform flow unstable. To obtain a uniformly ignited bed and high selectivity requires a catalyst with very high activity and a special start-up procedure [6], and perhaps most-importantly, high thermal conductivity. After solving this problem, we were able to demonstrate stable operation with 17% methane conversion and 70% C2+ selectivity under near adiabatic conditions at near atmospheric pressure; this is the highest ever reported in autothermal operation. Operation at higher pressure (4 bar) caused a drop in selectivity to 65% or less.



**Figure 1.** Ignited bed in 7.5 mm lab reactor



**Figure 2.** Patterns on pilot plant catalyst bed support.

#### 4. Conclusions

We have demonstrated stable operation of OCM in a pilot-plant-scale near-adiabatic autothermal reactor. This solves three main technical problems of OCM. Achieving acceptable values of selectivity and conversion, at high enough productivity/reactor and with moderately high pressure, is still challenging. Obtaining natural gas at a price that is significantly lower than the price of ethane is an additional, non-technical, barrier to commercialization of OCM.

#### References

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#### Keywords

oxidative coupling of methane; autothermal; bifurcation; scale-up.