



# Fuel-rich methane oxidation in a high-pressure flow reactor studied by optical-fiber laser-induced fluorescence, multi-species sampling profile measurements and detailed kinetic simulations



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## ABSTRACT

A versatile flow-reactor design is presented that permits multi-species profile measurements under industrially relevant temperatures and pressures. The reactor combines a capillary sampling technique with a novel fiber-optic Laser-Induced Fluorescence (LIF) method. The gas sampling provides quantitative analysis of stable species by means of gas chromatography (i.e. CH<sub>4</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>), and the fiber-optic probe enables in situ detection of transient LIF-active species, demonstrated here for CH<sub>2</sub>O. A thorough analysis of the LIF correction terms for the temperature-dependent Boltzmann fraction and collisional quenching are presented. The laminar flow reactor is modeled by solving the two-dimensional Navier–Stokes equations in conjunction with a detailed kinetic mechanism. Experimental and simulated profiles are compared. The experimental profiles provide much needed data for the continued validation of the kinetic mechanism with respect to C<sub>1</sub> and C<sub>2</sub> chemistry; additionally, the results provide mechanistic insight into the reaction network of fuel-rich gas-phase methane oxidation, thus allowing optimization of the industrial process.

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## 1. Introduction

Owing to the predicted depletion of petroleum reserves, the transformation of natural gas (i.e. methane) into value-added chemical products is of growing interest for the chemical industry. Conventional approaches rely on indirect conversion via synthesis gas production (from steam reforming, CO<sub>2</sub> reforming or partial oxidation), followed by a gas-to-liquid process, but these multi-step processes are particularly capital intensive. Therefore, the direct conversion of methane to ethylene, methanol or formaldehyde is economically more favorable [1,2].

Oxidative Coupling of Methane (OCM) could be a desirable direct conversion route in which methane is transformed into ethylene under fuel-rich conditions (CH<sub>4</sub>/O<sub>2</sub> = 2–8, or an equivalence ratio  $\phi$  = 4–16) at temperatures around 1000 K and pressures up to 30 bar. It has been suggested in the literature that the OCM reaction proceeds via a homogeneous/heterogeneous coupled mechanism [3,4]. According to this model, methane is first activated on the catalyst, and the resulting methyl radical desorbs. Two gas-phase methyl radicals combine to form ethane, which is

subsequently dehydrogenated to ethylene. In fact, OCM can occur even without a catalysts, albeit with very low selectivity [5–8]. Although the exact role of oxygen in the homogeneous/heterogeneous mechanism is unclear, it is known that small concentrations of oxygen are necessary for OCM. If the concentration of oxygen is too high, however, the C<sub>2</sub> products will be oxidized, thereby decreasing the yield. Computational engineering will play a key role in the optimization of the reactor design, catalyst choice, and operating conditions. An essential component of this approach includes detailed models that describe the coupling between fluid mechanics and the kinetics of elementary surface and gas phase reactions. The predictive utility of these models depends upon the accuracy of the underlying rate coefficients for the elementary reactions. These kinetic<sup>1</sup> mechanisms are often tested against experimental data taken under low-pressure and/or highly dilute conditions. A more desirable approach would be to validate the mechanisms against data taken under industrially relevant conditions, since it requires less extrapolation, but this approach can work only if the flow field and chemistry can be modeled

<sup>1</sup> Mechanisms of elementary rate constants are commonly referred to as “microkinetic” in the catalysis community, whereas the preferred term in gas-phase chemistry is “detailed kinetics” or “elementary kinetics”.

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simultaneously in a rigorous yet computationally efficient manner. This manuscript presents an experimental apparatus designed precisely for this purpose and the accompanying kinetic simulations.

Gas-phase Oxidative Coupling of Methane was studied in a novel, versatile flow reactor designed for spatially resolved kinetic profile measurements under homogeneous (and/or catalytic) conditions, with temperatures up to 1300 K and pressures up to 45 bar [9]. The reactor features a sampling capillary through which a small fraction of the reacting gas mixture is transferred to quantitative gas analytics, e.g., a mass spectrometer (MS) or a gas chromatograph (GC). Complementarily, a recently developed fiber-optic Laser-Induced Fluorescence (LIF) method [10] was applied for in situ detection of  $\text{CH}_2\text{O}$ , which is an important intermediate in the oxidation process. It is worth emphasizing that the reactor does not require optical viewports; optical access is provided only via the novel fiber-optic LIF probe. This technique is of particular interest for applications where optical access is limited (e.g., high-pressure reactors or internal combustion engines).

Section 2.1 describes the experimental design of the profile reactor, in particular the sampling process as well as the temperature and species analysis. Section 2.2 outlines the optical setup of the fiber-endoscopic LIF method, and Section 2.3 details the corrections necessary to derive relative concentration measurement from the LIF data, including collisional quenching and the temperature-dependence of the excited state populations. Section 3 describes the reactor modeling using Computational Fluid Dynamics (CFD) and the required reduction procedure of the kinetic mechanism. In Section 4 the results of experiment and simulation are presented and discussed, followed by a kinetic description of the elementary reaction steps.

## 2. Experimental methods

### 2.1. Profile reactor measurements

A detailed description of the reactor design is given in [9]; the essential features of the profile reactor are schematically summarized in Fig. 1. The flow reactor consists of a cylindrical fused-silica tube of 18 mm inner diameter and 10 mm thick walls. It is enclosed by an electrical furnace (not shown in the drawing), the temperature of which is monitored using a thermocouple. The gas flow is regulated by calibrated mass-flow controllers for  $\text{CH}_4$ ,  $\text{O}_2$ , and Ar/He mixture (8 vol-% He in Ar, serving as internal standard and carrier gas for the analytics).

Sampling of the reacting gas mixture is accomplished by means of a fused-silica capillary (outer diameter 652  $\mu\text{m}$ ). The capillary is translated along the reactor axis allowing continuous sampling of the reacting gas mixture and thus a determination of the chemical composition as a function of position. A K-type thermocouple can be inserted in the capillary void, additionally providing information about the axial temperature profile. An  $\alpha$ -alumina foam (80 pores per linear inch) provides mechanical stability for the sampling capillary and allows efficient preheating of the gas stream prior to entering the free gas-phase region. The sampling rates ( $\sim 10$  ml/min) are adjusted such that they are considerably smaller than the total flow rate, so that (i) the flow remains largely unaffected from the sampling and (ii) the sampling volume remains small. It was verified experimentally and numerically (i.e. by CFD simulations of the sampling process) that the spatial resolution is on the order of several hundreds of microns so that profile gradients are not limited by the spatial resolution of the technique.

When probing a reacting gas mixture one has to ensure rapid quenching of the chemical reaction in order to achieve an unbiased measurement at the probing position. This may be assured if either

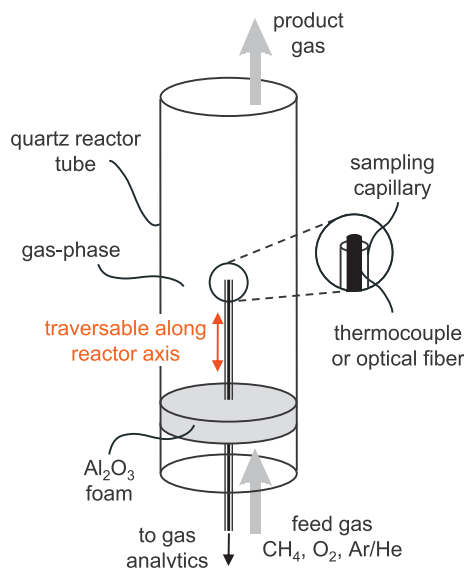


Fig. 1. Reactor design. The electrical furnace enclosing the reactor is omitted for clarity.

(i) the sampling time is short compared to changes in chemical composition (i.e. rapid extraction), or if (ii) heat or radical removal by collisional wall-quenching inhibits reaction progress. In our experiments, the reaction timescale is on the order of 0.1 s while sampling occurs on a slightly shorter timescale, so that the first condition may not suffice to justify unbiased sampling. However, quenching distances of  $\sim 1$  mm between silica walls, even when maintained at 1000 K, are generally sufficient to suppress a reaction [11]. Since in the present experiment the wall distance inside the capillary is much smaller ( $\sim 100$   $\mu\text{m}$ ) it can be assumed that thanks to wall-quenching (i.e. by radical recombination) an unbiased composition of the reaction gas is analyzed.

The sampled gas is transferred to a mass spectrometer for online monitoring of the reaction. Additionally, quantitative detection of the stable gas-phase species is attained by a micro gas-chromatograph (Varian, model CP-4900). The micro-GC consists of two columns: a Molsieve 5 A column for the permanent gases He,  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{H}_2$ , and CO using Ar as carrier, and a PPU column for  $\text{CO}_2$  as well as the three  $\text{C}_2$  compounds –  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  – with He as carrier.  $\text{H}_2\text{O}$  was removed from the gas stream before entering the gas chromatograph with a membrane particulate/water filter (Genie 170 from A+ corporation), since the micro-GC has to be operated below 100  $^\circ\text{C}$  in order to separate He and  $\text{H}_2$ . Consequently, water has to be calculated from the oxygen balance. All gases were calibrated against the internal standard prior to the experiment. On yet another column,  $\text{C}_3\text{H}_8$  and  $\text{C}_3\text{H}_6$  were detected but these gases were not calibrated. The experimental error originates mainly from the mass flow controllers with approximately 2% per gas species for a typical flow rate used (0.1% of max. value +0.5% of current value). The overall error of the gas-chromatograph is better than 1%. The carbon and hydrogen balances close to more than 95%, although minor species such as oxygenates were not calibrated.

### 2.2. Fiber-optic LIF detection of $\text{CH}_2\text{O}$

Formaldehyde ( $\text{CH}_2\text{O}$ ) is an important reaction intermediate in hydrocarbon oxidation. In combustion environments it can be observed in the preheating zone upstream the flame front. Under partial oxidation conditions, it is a major intermediate in the

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