



# Speciation data for fuel-rich methane oxy-combustion and reforming under prototypical partial oxidation conditions



Markus Köhler<sup>a,\*</sup>, Patrick Oßwald<sup>a</sup>, Hongbin Xu<sup>b</sup>, Trupti Kathrotia<sup>a</sup>, Christian Hasse<sup>b</sup>, Uwe Riedel<sup>a</sup>

<sup>a</sup> Institute of Combustion Technology, German Aerospace Center (DLR), Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany

<sup>b</sup> Chair of Numerical Thermo-Fluid Dynamics, ZIK Virtuhcon, Technische Universität Bergakademie Freiberg, D-09599 Freiberg, Germany

## ARTICLE INFO

### Article history:

Received 7 July 2015

Received in revised form

29 September 2015

Accepted 30 September 2015

Available online 13 October 2015

### Keywords:

Gasification

Rich combustion

Partial oxidation

Chemical modeling

Molecular-beam mass spectrometry

(MBMS)

Flow reactor

## ABSTRACT

Non-catalytic partial oxidation (POX) of hydrocarbon fuels is an important process for producing syngas. Quantitative experimental data under the demanding conditions relevant for POX reactions, e.g. long residence times, rich stoichiometries and high temperatures, respectively, are rare in literature. Here, the DLR high-temperature flow reactor setup was used to obtain a unique experimental data set for validation of reaction models and general understanding of fuel-rich hydrocarbon chemistry. A systematic experimental speciation data set for rich methane conditions with relevance to partial oxidation/gasification processes is presented. Both fast oxidation and slow reforming reactions are considered here. Quantitative data is obtained in the DLR high temperature flow reactor setup with coupled molecular beam mass spectrometry (MBMS) detection. Five test case scenarios are investigated, featuring rich methane conditions ( $\phi=2.5$ ) for the temperature range from 1100–1800 K under atmospheric conditions. CO, CO<sub>2</sub> and acetylene in two different amounts is added to the system for systematic analysis for addressing phenomena related to partial oxidation. The new experimental database includes quantitative species profiles of major and intermediate species and is available as [Supplemental material](#). The experimental data is compared with results from a 0D modeling approach using the GRI 3.0, USC-II, Chernov and a reduced model based on the full Chernov mechanism. The comparisons reveal significant differences in the model predictions among themselves and with respect to the experimental data, underlining the relevance of this unique data set for further mechanism development and/or optimization.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Non-catalytic partial oxidation (POX) of hydrocarbon fuels is an important process for producing syngas – an indispensable intermediate product of numerous bulk chemicals such as methanol, ammonia or dimethyl ether and other synthetic fuels. The process is characterized by chemical reactions under fuel-rich or partial oxidation conditions and thus significantly different to stoichiometric and lean air-combustion. Although the overall process is characterized by fuel-rich/partial oxidation conditions, locally both stoichiometric reactions zones as well as under lean reforming zones can be found. For example, close to the burner, the fuel is oxidized – often using pure O<sub>2</sub> as oxidizer leading to maximum flame temperatures around 3000 K – consuming most of the available oxidizer. The hot combustion products then mix with the

remaining fuel in the reforming zone, which is characterized by much longer time scales compared to the combustion zone (Caudal et al., 2013; Prüfert et al., 2014). In fact, non-catalytic partial oxidation processes can be considered similar to fuel-rich combustion, e.g. in premixed flames (Caudal et al., 2013, 2015), having a well-defined fast reaction zone and slow reforming reactions in the post-flame zone. In this study, we especially investigate the slow kinetics in the post-flame/reforming zone.

For design, optimization and control of POX reactors, experimental and numerical investigations are widely used in both research and applications. Zero-dimensional simulations of batch reactors (Al-Hamamre et al., 2009; Berger and Marin, 1999; Cao et al., 2010; Lemke et al., 2005) and one-dimensional simulations of premixed flames (Smith et al., 2013; Turbiez et al., 2004; Watanabe et al., 2013; Zhu et al., 2001) or plug flow reactors (Han et al., 2010; Skjoth-Rasmussen et al., 2004) are used to analyze the thermochemical process and validate the reaction mechanisms with experimental data.

\* Corresponding author. Tel.: +49 711 6862 756.

E-mail address: [m.koehler@dlr.de](mailto:m.koehler@dlr.de) (M. Köhler).

Complementary experimental studies for partial oxidation/rich combustion investigate primarily processes with methane as fuel by using shock tubes (Levy et al., 2006; Lifshitz et al., 1971; Olson and Gardiner, 1978; Petersen et al., 1999), flow reactors (Berger and Marin, 1999; Lemke et al., 2005; Han et al., 2010; Konnov et al., 2004; Rasmussen and Jakobsen, 2008), premixed flames (Smith et al., 2013; Turbiez et al., 2004; Watanabe et al., 2013; Bechtel et al., 1981; Castaldi et al., 1995; Davis and Law, 1998; Egolfopoulos et al., 1989; Langley and Burgess, 1989; Musick et al., 1996), partially premixed flames (Struckmeier et al., 2010) and inverse diffusion flames (Stelzner et al., 2013; Hunger et al., 2013; Stelzner et al., 2013; Garten et al., 2015). A summary of the experimental investigations in simple chemical reactors for partial oxidation of methane can be found in (Li et al., 2013). Only a very limited number of studies looked at higher hydrocarbons including propene for partial oxidation conditions (Alatorre et al., 2001; Atakan et al., 2003; Kohse-Höinghaus et al., 2001; Lamprecht et al., 2000) and recently for reforming conditions with equivalence ratios up to 22 (Sen et al., 2015).

For numerical simulations, detailed chemical mechanisms are required. GRI-MECH 3.0 (Smith et al., 2015) or more generally GRI-MECH-based kinetic models are often used (Smith et al., 2013). Furthermore, the Petersen mechanism (Petersen et al., 1999), the mechanism from the University of Leeds (Hughes et al., 2001), the Konnov mechanism (Konnov et al., 2004), the Glarborg mechanism (Skjoth-Rasmussen et al., 2004), the USC-II mechanism (Wang et al., 2007) and the mechanism from NUI Galway (Bourque et al., 2008), respectively, were commonly employed. A comparison of some of these mechanisms can be found in Cao et al. (2010) and Zhou et al. (2010). Looking specifically at the results of Vascellari et al. (2015) and of Guo et al. (2012), it can be concluded that under POX conditions the concentration of CO can be overestimated, while the CO<sub>2</sub> concentration is underestimated at the outlet of the reactors using the above-mentioned mechanisms. Further, the experimental data from Liu et al. (2011) and Li et al. (2013) show that the C<sub>2</sub>H<sub>2</sub> concentration could not be reproduced accurately indicating another shortcoming of the mechanisms. To investigate the reactions under POX conditions systematically, especially for the influence of the intermediate species, detailed measurements are very much needed to analyze and potentially improve the mechanisms.

Quantitative experimental data to realize the demanding conditions relevant for POX reactions, e.g. long residence times, rich stoichiometries, and high temperatures are rare in literature. Here,

the recently reported DLR high-temperature flow reactor setup (Oßwald and Köhler, 2015) was used to obtain experimental data sets for validation purposes and a general understanding. Therefore, detailed speciation data was obtained from molecular beam sampling mass spectrometry at the reactor exhaust. This technique allows for simultaneous detection of almost all species involved including highly reactive species and has recently been applied successfully for the fundamental investigation of chemical reaction networks (Hansen et al., 2009; Qi, 2013) of e.g. novel biofuels such as alcohols (Sarathy et al., 2014), esters (Yang et al., 2013), or heterocyclic fuels (Liu et al., 2014; Lucassen et al., 2009; Togbé et al., 2014; Tran et al., 2014).

Here this powerful technique was used for the investigation of rich methane oxidation under atmospheric conditions and doped with CO, CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> to address the aforementioned points raised above systematically. As an initial approach towards understanding phenomena related to POX conditions, selected mechanisms with relevance to gasification are compared to the experimental data and discussed.

## 2. Experimental method

### 2.1. Flow reactor experiment

The DLR high-temperature flow reactor has been described elsewhere recently (Oßwald and Köhler, 2015), so only a brief description is given here. A schematic of the reactor setup is shown in Fig. 1. The system consists of the high temperature reactor, including the gas supplies and the coupled gas analyzer i.e. a molecular beam mass spectrometry (MBMS) system. Gases are sampled directly at the reactor outlet and are transferred to the vacuum system of the time-of-flight mass spectrometer.

The reactor consists of an alumina (Al<sub>2</sub>O<sub>3</sub>) ceramic tube with 40 mm inner diameter and a total length of 1497 mm. The pre-mixed gases are fed into the reactor by a tempered flange equipped with a porous bronze plug to create homogeneous flow conditions. The reaction segment has a total length of 1000 mm, heated by a customized high temperature oven (Gero, Typ HTRH 40-1000). The setup is capable to provide temperatures up to 1900 K and heating/cooling rates up to 500 K/h are applicable. Measurement series are performed at constant inlet flow conditions and a monotonically decreasing (−200 K/h) oven temperature ramp is applied. Thus, the

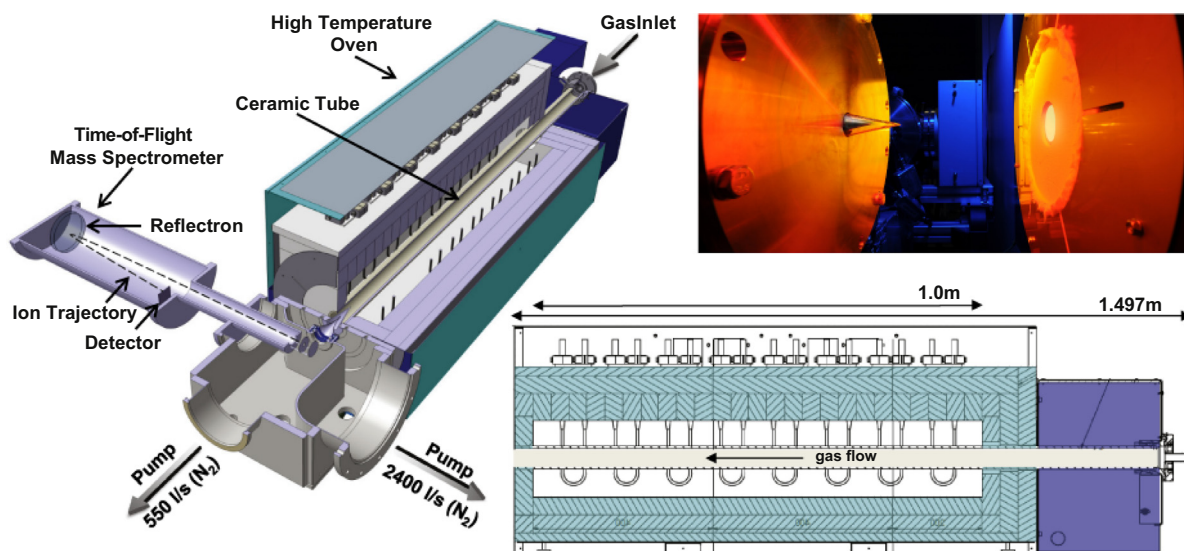


Fig. 1. Schematic DLR high-temperature flow reactor and photograph, details in Oßwald and Köhler (2015). Note that the oven is mounted on rails and sampling is performed about 25 mm inside the tube.

Download English Version:

<https://daneshyari.com/en/article/6589379>

Download Persian Version:

<https://daneshyari.com/article/6589379>

[Daneshyari.com](https://daneshyari.com)