# Modeling interactions between chemistry and turbulence for simulations of partial oxidation processes

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## ABSTRACT

Methane Autothermal Reforming (ATR) and non-catalytic partial oxidation (POX) are two industrial processes used to produce syngas, a mixture of hydrogen and carbon monoxide. In those reactors, methane is burnt with oxygen in fuel-rich conditions. Downstream of the flame, the gaseous combustion products further react with steam and remaining methane in the turbulent "post-flame" region. In order to perform Reynolds Average Navier–Stokes (RANS) simulations of the reactor, accurate modeling strategies are required to compute the average chemical source terms in this post-flame region. In the present study, a DNS numerical experiment has been performed to reproduce the properties of the flow in this part of the reactor. Results are used as a reference to a priori assess the performances of different modeling strategies derived from three turbulent combustion models. The results of this analysis show that, among the three selected models, only the two models based on tabulated chemistry description are able to properly recover the right values of the average chemical source term. The PCM-FPI approach, based on a one-point statistic description using a Beta density probability function, appears as the most accurate approach compared to the two others.

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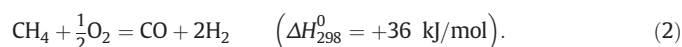
## 1. Introduction

A growing part of the petrochemical industry relies on the use of *syngas*, a gaseous mixture mainly composed of carbon monoxide (CO) and dihydrogen ($H_2$). This gas is an efficient intermediate in many processes for the production of chemicals like methanol, ammonia or dihydrogen, and is at the heart of attractive approaches for converting natural gas into liquid fuels, the so-called gas-to-liquids route.

A comprehensive survey of the major industrial processes used to obtain syngas from natural gas is proposed by Aasberg-Petersen et al. [1]. At the present time, the production of syngas from natural gas is primarily based on methane steam reforming (SMR) process. This mature technology, that produces a $H_2$-rich syngas, has benefited from many improvements since it was developed in the 1930s [2,3]. The endothermic global reaction for this approach is given by Eq. (1):

$$CH_4 + H_2O = CO + 3H_2 \qquad \left( \Delta H^0_{298} = -206 \ kJ/mol \right). \qquad (1)$$
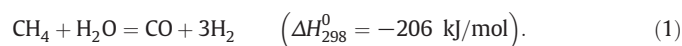
Gasification is an alternative strategy. As explained by Higman and van der Burgt [4], it primarily refers to a partial oxidation process that is used to produce syngas from any carbonaceous fuel, which can be either solid, liquid, or gaseous. When methane is used as the feedstock, non-catalytic partial oxidation (POX) consists of burning methane with pure oxygen at elevated pressure under rich conditions, according to Eq. (2):

$$CH_4 + \frac{1}{2}O_2 = CO + 2H_2 \qquad \left( \Delta H^0_{298} = +36 \ kJ/mol \right). \qquad (2)$$

Autothermal reforming (ATR) is a third process which turns out to be economically particularly attractive, especially for large scale production of syngas dedicated to methanol and GTL applications [1,5,6]. This approach combines both POX and SMR processes in a single reactor, in order to use the energy released by (exothermic) partial oxidation to perform (endothermic) steam reforming. As an example, a schematic illustration of an ATR reactor is given in Fig. 1.

In processes based on partial oxidation (i.e., fuel-rich oxidation processes, like POX, ATR, and other gasification processes based on liquid or solid feedstock), reactants are usually injected separately in the reactor. Combustion takes place in a diffusion flame. Burnt gases that correspond to stoichiometric conditions (mainly $CO_2$ and $H_2O$) and remaining methane react further downstream in the so-called *Post-oxidation* zone, to produce CO and $H_2$. In the present paper, the results are not specific to a particular type of partial oxidation process. However, the case of ATR is of particular interest, because of the especially high water steam content in the post-oxidation region, which enhances reforming reactions. The
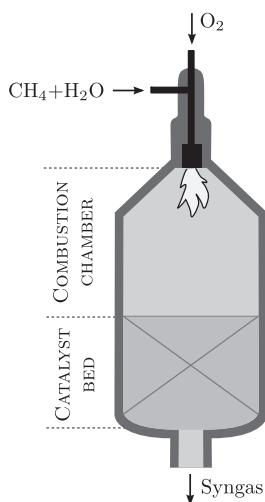
**Fig. 1.** Schematic illustration of an ATR reactor.

ATR process has therefore been selected to conduct the study and illustrate the reasoning.

In order to reduce the operation costs of the partial oxidation process and to increase its global efficiency, a better understanding of the flow structure and properties in the gas-phase turbulent reaction zone is required. For instance, in the ATR process, a wrong estimation of the interactions between the flame and the reactor walls could lead to a reduced lifetime of the catalyst bed and of the other equipments.

Since well-instrumented experiments are difficult to conduct on such high-pressure industrial scale reactors, numerical simulation appears as an efficient tool to address these challenges. The most accurate approach, called Direct Numerical Simulation (DNS), consists of directly solving reactive Navier–Stokes equations. However, because of the extremely high CPU cost of such simulations, DNS remains unaffordable in the case of industrial reactors. For the same reasons, Large Eddy Simulation (LES), although cheaper than DNS, is still limited to experimental studies or at best to small size pilot reactors. For large scale industrial reactors, most of the modeling works therefore rely on Reynolds Average Numerical Simulations (RANS). In this approach, the reactive flow is only described by its largest turbulent structures, and the flow balance equation is closed using numerical models.

Among these models, the turbulence/chemistry interactions (TCI) model aims at evaluating the average chemical source term. In the case of fuel-lean oxidation processes (classic combustion applications), TCI models are usually referred to as "turbulent combustion models". For partial oxidation processes, since similarities are observed with combustion processes, strategies followed up to now have been to use existing turbulent combustion models. Rehm et al. [7] modeled the interactions between chemistry and turbulence in a POX reactor using the Eddy-Dissipation Concept (EDC) developed by Magnussen [8,9]. The Eddy-Dissipation Model (EDM) [10] was also used by Amirshaghaghi et al. [11] to model chemistry evolution in the upper gaseous phase of an ATR reactor. For their part, Vegendla et al. [12] used a TCI model that relies on the use of a flamelet description, Finally, Vegendla et al. [13] and Wu et al. [14] use statistical approaches based on probability density functions (PDF) that are respectively transported [15,16] or presumed [17–19].

Among the possible modeling strategies, EDC/EDM models and presumed-PDF approaches with tabulated chemistry are low CPU time demanding. Then, these methods appear as the ablest strategies for the simulation of large-scale industrial reactors. However, Aasberg-Petersen et al. [1] pointed out that TCI models used in POX simulations often "either overestimate or underestimate the chemical reaction". This observation is also confirmed by Rehm et al. [7], who show that EDC model is extremely sensitive to its own parameters and can lead

to strong errors in the evaluation of the chemical source term. Current CFD models initially developed for turbulent combustion therefore remain to be tested for POX process simulations.

The objective of the present paper is to assess, in the context of POX simulations, the performance of a selection of TCI models that were initially developed and validated for turbulent flames. Two routes for chemistry modeling are explored: detailed chemistry and tabulated chemistry. To tackle flame–turbulence interactions, detailed chemistry is coupled with the turbulent flow using EDC whereas tabulated chemistry is combined with the presumed PDF of the progress variable. The tabulated chemistry method retained here relies on the Flame Prolongation of ILDM (FPI) formalism [20]. The coupling of presumed PDF formalism (also called Presumed Conditional Moment (PCM) in the literature [19]) with FPI is noted PCM-FPI. The mathematical functions retained to presume the PDF are the Dirac and Beta functions. To summarize, three modeling combinations are tested:

- Detailed chemistry with EDC.
- PCM-FPI, with a Dirac function presumed PDF (i.e., no particular modeling of flame and turbulence interactions).
- PCM-FPI, with a Beta function presumed PDF.

Since large scale experiments on real reactors are too difficult to set up because of the severe operating conditions, the present paper proposes to evaluate the above mentioned TCI models using the results obtained in a highly resolved DNS of a 2-D representative domain.

Section 2 describes the context of RANS simulation and the strategy to compare the selected TCI models. Section 3 is dedicated to the description of the DNS simulation designed to reproduce the main properties of a POX reactor post-oxidation zone. The results obtained from this simulation are then presented in Section 4 to evaluate the ability of the selected turbulent combustion models to reproduce the expected average chemical source terms. Section 5 is dedicated to the physical analysis of the obtained results. Finally, in Section 6, a 1-D RANS simulation of the post-oxidation zone is performed to validate the results given by the a priori analysis.

## 2. Context and strategy of the present work

### 2.1. Brief overview of RANS formalism

RANS approach consists in solving averaged Navier–Stokes equations. In particular, species transport equation can be written in compressible form as following:

$$\frac{\partial \overline{\rho} \widetilde{Y}_k}{\partial t} + \frac{\partial}{\partial x_j}\left(\overline{\rho} \widetilde{Y}_k \widetilde{u}_j\right) = -\frac{\partial}{\partial x_j}\left(\overline{\rho Y_k V_{k,j}}\right)$$
$$-\frac{\partial}{\partial x_j}\left(\overline{\rho u_j'' Y_k''}\right) + \overline{\dot{\omega}}_k W_k \quad (3)$$

where $\bar{A}$ and $\tilde{A}$ respectively denote Reynolds- and Favre-average of $A$ quantity. $\overline{\rho}$ represents the average density and $\tilde{u}_j$ the $j$th averaged component of the velocity vector ($j = 1, ..., 3$). For a given species $k$, $\tilde{Y}_k$ refers to the averaged mass fraction, $W_k$ to the molar mass, $\overline{\dot{\omega}}_k$ to the averaged molar chemical source term and $V_{k,j}$ to the diffusion velocity in direction $j$.

Several terms that appear in RANS equations are unresolved and need to be modeled. For instance, in the case of species equation (Eq. (3)), models are required to evaluate the molecular diffusion flux $\overline{\rho Y_k V_{k,j}}$, the species flux $\widetilde{u_j'' Y_k''}$ and the average chemical source term $\overline{\dot{\omega}}_k$. Many approaches have already been proposed for each of these models in the context of turbulent flames [21,22].

However, these strategies may not be valid for RANS simulations of POX processes. In particular, chemical reactions are expected to be very slow in POX post-oxidation zone, compared to oxidation reactions