

Simulation of partial oxidation process by using flamelet/progress variable approach

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Abstract

Partial oxidation of a carbonaceous material (natural gas, coal, biomass among others) is widely used for producing gas for power generation or as feedstock in the chemical industry. In partial oxidation processes two significant reactions regimes can be observed. In the flame zone, the fast oxidation reactions are mainly governed by the mixing of the fuel with the reactants, similarly to conventional lean diffusion flames. In the post-flame zone, the reforming reactions take place, slowly approaching to the chemical equilibrium conditions. In order to describe both regimes, the flamelet/progress variable (FPV) approach was successfully applied to model a pilot scale High Pressure Partial Oxidation (HP-POX) reactor fired with CH₄. The chemistry was precomputed using premixed freely propagating flames in and stored in a look-up table, after the PDF-averaging of the laminar solution. The laminar solutions were converted from physical space to a progress variable space, which was defined combining different chemical species in order to have a unique mapping. Additionally, the PV should be accurately defined for resolving the slow reactions in the post-flame zone. Finally, the PDF look-up table was coupled to the CFD solution of the turbulent flow in the HP-POX reactor. The numerical results show that the FPV allows to describe both the fast oxidation and the slow reforming reactions, giving a reasonable agreement with the experiments. In addition to the precise predictive capabilities, the computational cost by using the FPV approach is significantly reduced due to the efficient lookup of the precomputed flamelet solutions.

Introduction

Partial oxidation is a process in which a solid, liquid or gaseous hydrocarbon feed in a fuel rich mixture is converted into a synthesis gas (syngas), primarily composed of hydrogen and carbon monoxide. Such mixtures represent the intermediary step from hydrocarbons to bulk chemicals (methanol, DME, ammonia, acetic acid, oxo-alcohols, isocyanates) and synthetic fuels (synthetic Diesel) [1].

CFD simulations of a High pressure Partial Oxidation (HP-POX) pilot-scale reactor were performed using the Eddy Dissipation Concept (EDC) [2] with a detailed mechanism reduced from GRI-mech [3]. EDC is very computationally expensive, especially in combination with the large kinetic mechanism required for describing the slow reforming process. To reduce the computing effort for simulating the turbulence-chemistry interaction reduction techniques are usually applied. The chemistry is separated from the solution of the turbulent flow and modeled using simplified reduced approach, such as homogeneous reactors, 1D diffusion and premixed flames, generally referred as flamelets. Results of the reduced chemistry models are pre-calculated and stored in a flamelet look-up table (FLUT). The tables are commonly parametrized using global scalar variables, such as mixture fraction Z and progress variable Y_c , etc.. FLUTs are coupled to the CFD solutions through the same input variables, which are solved together with the turbulent flow. The turbulence-chemistry interaction is captured with the PDF integration based on the mean/filtered values and its variance of mixture fraction (and progress variable). The

steady laminar diffusion flamelet (SLDF) approach [4] was used for modeling the HP-POX reactor [5]. However, different reaction regimes can be identified in the HP-POX. On one hand, the flame zone is generally characterized by fast oxidation reactions, which is correctly described by the SLDF approach. On the other hand, the reforming zone is dominated by slow reactions converting the combustion products with excess fuel into CO and H₂. This zone mainly occurs in premixed regime and with larger time- and length-scale than the oxidation zone, and it cannot be properly described by the SLDF [5, 6].

The flamelet/progress variable (FPV) [7] model is a suitable choice to capture slower processes as demonstrated for local extinction, NO_x emission and radiation [8, 9]. The FPV model was derived from the SLDF approach, as well as the flamelet generated manifolds (FGM) approach [10]. The FPV model use the idea of the progress variable as the parameter describing the progress in the reacting mixture.

In this work the FPV approach is used for describing the turbulence-chemistry interaction in the HP-POX reactor [2]. The chemistry is modeled by means of freely propagating premixed 1D flames and stored in premixed flamelet look-up tables (P-FLUT). The use of a P-FLUT is justified by the fact that the large part of the HP-POX reactor is dominated by the slow reforming reactions, which mainly occur in premixed regime.

Numerical models

The turbulent reacting flow in the HP-POX reactor is simulated using the 2D axisymmetric version of the commercial CFD solver Ansys-Fluent [11], using the pressure-velocity coupled algorithm. Convective fluxes in all transport equations are discretized with a second-order upwind scheme and the pressure gradients are discretized with

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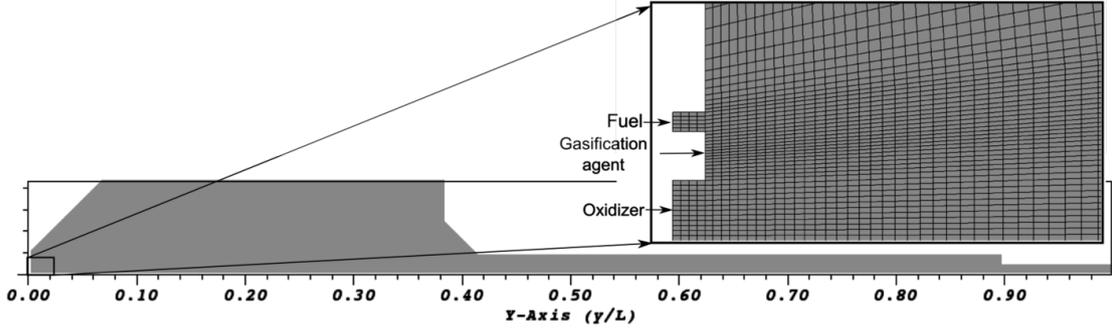


Figure 1: Schematic view of HP-POX reactor.

a second-order accurate scheme. Turbulence is modeled using the realizable $k - \varepsilon$ approach [12], and radiation with the P-1 model [13]. The radiating properties of the gas were modeled assuming a gray-band model, based on the Weighted Sum of Gray Gases (WSGG) model [14].

The FPV approach is implemented in Ansys-Fluent using the UDF capabilities of the software and coupled to the pre-calculated FLUT. The look-up and interpolation was performed with a multi-dimensional interpolation procedure and a subsidiary memory abstraction layer [15].

Governing equation for the turbulent reacting flow

In the FPV approach the transport equations for the mean (\tilde{Z}) and the variance ($\overline{Z'^2}$) of the mixture fraction and for the mean progress variable (\tilde{Y}_c) are solved in addition to the transport equations for the momentum, pressure, total enthalpy, turbulent kinetic energy and its dissipation:

$$\nabla \cdot (\bar{\rho} \mathbf{u} \tilde{Z}) = \nabla \cdot [\bar{\rho} (D + D_t) \nabla \tilde{Z}] \quad (1)$$

$$\nabla \cdot (\bar{\rho} \mathbf{u} \overline{Z'^2}) = \nabla \cdot (\bar{\rho} (D + D_t) \nabla \overline{Z'^2}) + C_g \nu_t \bar{\rho} (\nabla \tilde{Z})^2 - C_d \bar{\rho} \frac{\varepsilon}{k} \overline{Z'^2} \quad (2)$$

$$\nabla \cdot (\bar{\rho} \mathbf{u} \tilde{Y}_c) = \nabla \cdot [\bar{\rho} (D + D_t) \nabla \tilde{Y}_c] + \tilde{\omega}_c, \quad (3)$$

Where \mathbf{u} is the velocity vector, D the molecular diffusivity and D_t the turbulent diffusivity. For all the transport equations the turbulent diffusivity was calculated with the turbulent Schmidt-number being $Sc_t = \frac{\nu_t}{D_t} = 0.7$, where ν_t is the turbulent viscosity. For all molecular diffusion coefficients, a unity Lewis-number approach $Le = \frac{\lambda}{\rho c_p D}$ was assumed. The constants terms in Eq. 2 are $C_g = 2.86$ and $C_d = 2.0$ [16]. The density ρ , the progress variable source term $\tilde{\omega}_{Y_c}$, the temperature \tilde{T} and the species mass fractions \tilde{Y}_i are looked-up from the FLUT table using \tilde{Z} , $\overline{Z'^2}$ and \tilde{Y}_c as input parameters. The adiabatic temperature and density from the FLUT are corrected accounting for the enthalpy defect due to the radiative heat flux inside the reactor.

Chemistry

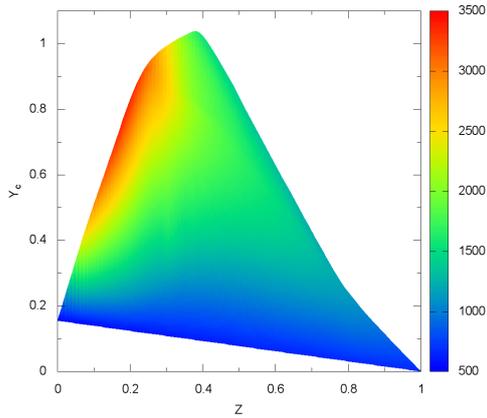
The Cantera software package was used to model one-dimensional adiabatic steady laminar freely propagating premixed flames in order to generate the FLUT required by the CFD simulation. The transport properties were

evaluated assuming $Le = 1$, similarly to the CFD solution. Furthermore, an adaptive grid refinement was used with an average of over 1000 grid points on a domain up to 5 m to ensure a chemical equilibrium state in the burned gas, especially for fuel rich mixture fraction, where the slow reforming reactions requires a very long domain for achieving chemical equilibrium. The chemical mechanism developed at the Deutsches Zentrum für Luft- und Raumfahrt (DLR) [17] is used for solving the 1D flames. The DLR mechanism was originally developed to account for the PAH gas phase growth in methane, ethylene and ethane flames. Modifications to the gas phase chemical mechanism are proposed in order to increase the quality of the prediction of soot precursors. These changes in the mechanism were also tested on premixed methane, ethane and ethylene flames with oxygen to ensure that the changes in the mechanism do not corrupt the application to C_2 fuels. The proposed modifications improve the agreement of the premixed laminar flame simulations when compared to the experimental results. The used version of the DLR mechanism consists of 43 species and 319 reactions. For each mixture fraction the premix flame is converted from physical space to progress variable Y_c space. The progress variable is defined as linear combination of species concentrations:

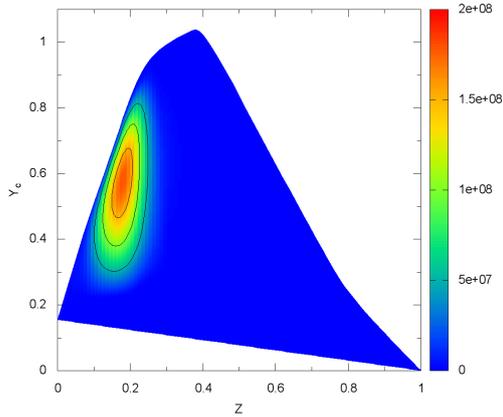
$$Y_c = \sum_{i=0}^n \alpha_i Y_i. \quad (4)$$

A suitable choice of the progress variable is crucial. Attention has been paid to this topic in [18, 19, 20, 21]. Some requirements for the progress variable can be defined according to [19]: (i) the transport equation is conveniently solved in a combustion simulation. (ii) The parameter setup characterize uniquely each point in the thermo-chemical state space, hence it has to be strictly monotonically decreasing or increasing. (iii) Process controls quantity and projection of the trend of the combustion (flame region, slow conversion reactions). (iv) Appropriate mapping with respect to the species and temperature is required. For complex flame structures and detailed chemistry identifying a suitable progress variable can become more complicated.

Furthermore, turbulent effect are accounted by a PDF-integration of the laminar flame database, which considers the mean mixture fraction and its variance to capture the



(a) T , K



(b) ω_c , kg/(m³ s)

Figure 2: Temperature and progress variable source term in mixture fraction/progress variable space from P-FLUT.

turbulence-chemistry interactions. The PDF for the mixture fraction is a presumed β -PDF. For convenience, the mixture fraction and progress variable were assumed to be statistically independent and the progress variable PDF was assumed to be a δ -PDF. After the integration, the progress variable is normalized with $c = \frac{Y_c - Y_{c,min}}{Y_{c,max} - Y_{c,min}}$ and the P-FLUT was constructed with \tilde{Z} , \tilde{Z}''^2 and \tilde{C} being the look-up parameters.

High Pressure Partial Oxidation (HP-POX) pilot-scale reactor

Detailed description of the HP-POX pilot-scale reactors was reported by Rehm et al. [2]. Figure 1 reports the schematic view of the reactor. Three input streams are considered in the reactor, as illustrated from the enlarged view of the burner: the oxidizer stream, composed by a mixture of O₂ and H₂O, enters from the central inlet,

	Oxidizer	Gasification Agent	Fuel
\dot{m} , kg/s	0.1452	0.1491	0.1014
T , K		506.8	657
CH ₄		0	1
O ₂		0.837	0
H ₂ O		0.155	0
N ₂		0.008	0
Z	0.0		1.0
Y_c	0.155		0

Table 1: Input conditions of the HP-POX reactor. Concentrations are given as mass fractions.

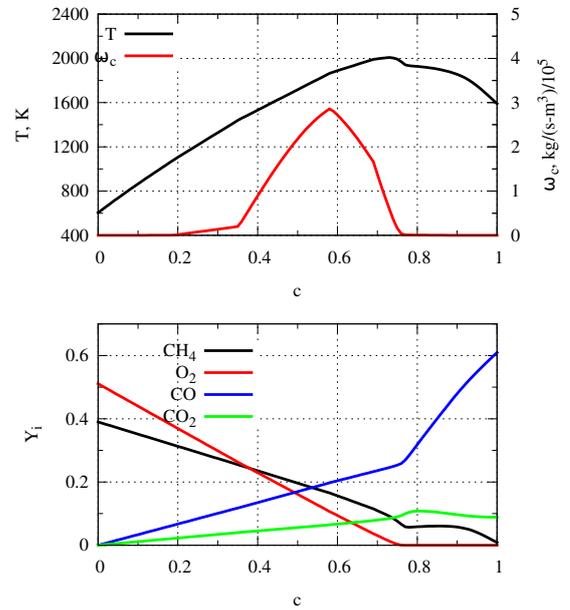


Figure 3: Temperature, progress variable source term and mass fraction of the main species as a function of the normalized progress variable c at $Z = 0.388$ from P-FLUT.

the gasification stream, composed by water enters from the intermediate annular section, and the fuel, composed by CH₄ from the external annular section. In order to simplify the FPV approach only two streams are considered for the calculation: the fuel stream with $Z = 1$ and the oxidizer stream with $Z = 0$, which corresponds to the mixing of the oxidizer and the gasification streams. The mass flow rates, composition and temperature of the input streams are reported in Tab. 1. Reactor walls are assumed adiabatic. For the simulations, a 2D axisymmetric mesh with 14 000 hexahedral cells was used after grid independence could be ensured.

Results

Analysis of the P-FLUT

The P-FLUT was generated using freely propagating premix flames as previously described. The progress variable is defined as follows: $Y_c = 2Y_{H_2} + Y_{H_2O} + 0.6Y_{CO_2} +$

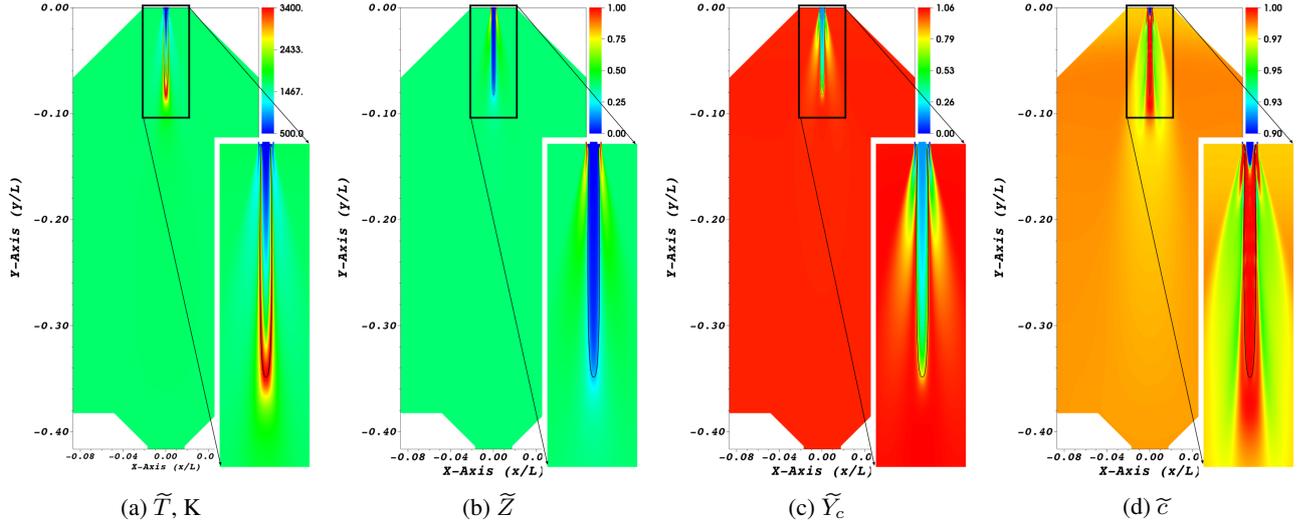


Figure 4: Temperature (a), mixture fraction (b), progress variable (c) and normalized progress variable (d) distributions on the HP-POX axial section obtained from the CFD FPV simulation. The black lines show the stoichiometric conditions ($Z_{st} = 0.192$)

Y_{CO} . Y_c is chosen in order to satisfy the requirements described above, and particular attention was given for accurately resolving the partial oxidation process close to the outlet mixture fraction ($Z_{out} = 0.388$), which is the main goal of the work.

The temperature and the progress variable source term obtained from the laminar 1D premix flames are shown in the Z - Y_c space in Fig. 2. The lower limit in the plots represent the minimum values of Y_c for a given mixture Z , corresponding to $c = 0$. This condition represents the pure mixing between the reactants without reactions. The non-normalized progress variable is set to zero for the fuel inlet ($Z = 1$), while is set to 0.155 for the oxidizer inlet ($Z = 0$), corresponding to the mass fraction of H_2O in the oxidizer. The upper limit represents the maximum values of Y_c , which correspond to the equilibrium condition reached by the premix manifold for every mixture. Here the normalized progress variable c assume a value of one. The maximum value of $Y_c = 1.039$ is obtained close to the outlet mixture ($Z_{out} = 0.388$), optimizing the resolution of the progress variable in the reforming zone of the HP-POX reactor. The solutions of the 1D premixed flames are obtained for several mixture fractions going 0.07 to 0.92. Outside of this range the results of the extreme solutions are extrapolated to the minimum and maximum values of the mixture fraction space.

Very high temperatures (Fig. 2a) above 3000 K are achieved around the stoichiometric mixture fraction ($Z_{st} = 0.192$), corresponding to extremely high values of the progress variable source term (Fig. 2b). Such high temperatures and source terms mainly depend on the very high O_2 content of the oxidizer streams (84 wt% see Tab. 1). It means that equilibrium conditions are quickly reached for values of mixture fractions close to the stoichiometric conditions. Richer mixtures are characterized by slower reaction rates and temperatures. For this reason T , ω_c and the main Y_i from the P-FLUT are also reported in Fig. 3

for the outlet mixture fraction. The source term ω_c is about three orders of magnitude lower than the ones at the stoichiometric conditions (Fig. 2). Consequently the time and the length scales of the reforming zone are much respect to the flame zone. The temperature increases almost linearly with the progress variable up to 0.67, which corresponds to the point where the O_2 is almost completely consumed. Once O_2 is fully consumed, the endothermic reforming reactions proceed extremely slowly, reducing the temperature and almost completely consuming the remaining CH_4 . Additionally CO increases during the reforming.

Analysis of the CFD results

The results of the HP-POX reactor simulation using the FPV approach with a P-FLUT are reported in this section. Figure 4 shows the contour plots of the mean temperature, mixture fraction, non-normalized and normalized progress variable on the axial section of the HP-POX reactor. The stoichiometric conditions are also reported in the plots ($Z_{st} = 0.192$). The normalized progress variable \tilde{c} (Fig. 4d) is also reported in addition to the non-normalized \tilde{Y}_c for highlighting the deviation from the equilibrium conditions inside the reactors. A scale between 0.9 to 1 is used for \tilde{c} for underlining the conversion in the reforming zone. The largest gradients can be observed in the oxidation region close to the reactor burner, while the remaining reforming part is characterized by extremely low variations of the flow properties. A zoomed view of the oxidation region is therefore reported for every scalar for highlighting gradients in the oxidation zone. The \tilde{Z} plot shows that the mixing between the fuel and the oxidizer occurs in about 1/10 of the total length of the reactor. However the flame is much longer than the size of the burner, due to the high velocities of the input streams. The external fuel stream is also mixed to the recirculating syngas. The extremely high reaction rates, related to the oxyfuel conditions in the

reactor, quickly push the reactions towards the chemical equilibrium, as it may be observed from Figs. 4(c)-(d).

Externally to the mixing zone, which is bounded by the stoichiometric conditions, the mixture fraction quickly reaches the outlet condition ($\tilde{Z} = 0.388$), behaving like a premixed reforming reactor. In the reforming zone the temperature and the other scalars are characterized by an uniform distributions. The Y_c distribution (Fig. 4c) shows values close to 0.8 along the stoichiometric conditions, which corresponds to the maximum Y_c for Z_{st} . In the reforming zone the progress variable shows an almost uniform distribution, due to the slow advancement of the reforming reactions. For clearly highlighting the slow advancement of the reforming reaction, the normalized progress variable is also shown (Fig. 4d). In fact, in the oxidation zone, c quickly reaches the equilibrium conditions ($c = 1$), as previously discussed. Downstream of stoichiometric conditions, the normalized progress variable decreases from one to values between 0.94 to 0.98. The decrease of the normalized progress variable depends on the mixing with richer mixtures with $c < 1$. These mixtures are characterized by higher values of the maximum non-normalized progress variable, as it can be observed from Fig. 2 moving from Z_{st} to $Z = 0.388$.

The numerical results of the CFD simulation of the HP-POX are also reported along the centerline in Fig. 5. As already observed from the contour plots in Fig. 4, the mixture fraction Z at first gradually increases, then rapidly increases at $y/L = 0.1$ crossing the flame, and remains nearly constant in the reforming zone for $y/L > 10$. Similar behavior can be observed for the non-normalized progress variable Y_c , which reaches the maximum values $Y_c = 1.022$ approximately at $y/L = 0.1$ for $Z = 0.365$. After this point Y_c slightly decreases and then increases again. The plot also reports the maximum progress variable $Y_{c,max}$ for the given mixture fraction. For $y/L < 0.1$ the progress variable corresponds to its maximum value, and only in the reforming zone becomes lower than $Y_{c,max}$. The difference between Y_c and $Y_{c,max}$ can be more clearly observed looking at the normalized progress variable c plot. In fact, c rapidly tend to 1 in the oxidation zone, because of the high oxidation rates, while in the reforming zone at first decreases to 0.967, because of the mixing. Then it begins slowly to increase until the exit of the reactor without reaching the equilibrium conditions.

The main chemical species concentrations are also reported as mass fractions. In the oxidation region, O_2 is completely consumed as soon as the stoichiometric conditions are reached at $y/L = 0.1$. CO follows the opposite trend, quickly increasing in the flame and then slowly in the reforming zone. CO_2 reaches its maximum for the stoichiometric conditions and then it slowly decreases in the reforming zone. Small fractions of CH_4 can be observed after the stoichiometric conditions from the mixing of the burned products with the recirculated syngas.

Finally, Fig. 6 shows the comparison between the experimental outlet composition in mass fraction [2] and the numerical results for the HP-POX reactor. The CFD results

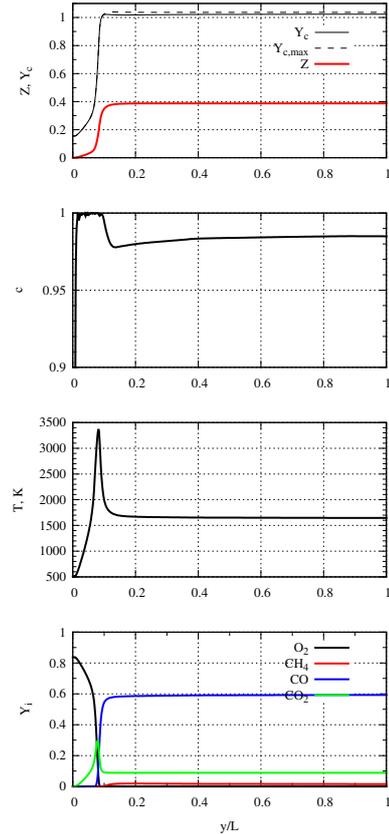


Figure 5: Mixture fraction, progress variable, temperature and species mass fractions along the centerline of the HP-POX reactor.

show generally a good agreement with differences lower than 2.8% by weight. CO, which is the most abundant species, is correctly predicted with a deviation of 0.3%. The largest deviations exist for CO_2 and CH_4 . In particular the numerical simulation predicts 1.06% of CH_4 , while only 0.5% was measured. The comparison of the progress variable Y_c shows a very good agreement with a difference of 0.1%, which confirms the validity of the approach used for describing the slow reforming reaction rates.

Conclusion

A pilot-scale high pressure partial oxidation reactor (HP-POX) was numerically investigated using the flamelet progress variable (FPV) approach coupled with a premix laminar flamelet look-up table (P-FLUT). The HP-POX is characterized by an oxidation zone, which is mainly governed by the diffusion of the reactants, and by a reforming zone, where the slow chemical reactions take place in premixed regime. For this reason, the FPV approach, which was originally developed for partially premixed flames, allows to describe the different reaction regimes existing in the reactor. Since the main focus of this work is too accurately describe the slow reforming process, the CFD solution of the reactor is obtained coupling the FPV approach to a look-up FLUT table generated using 1D laminar freely propagating premix flames. The choice of

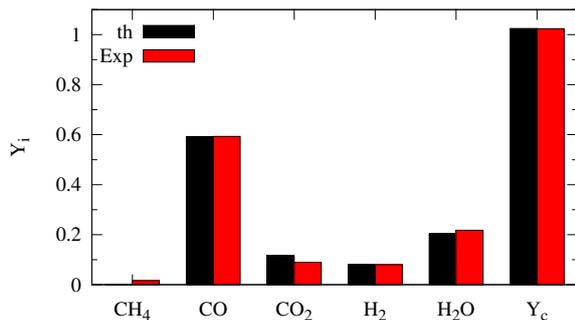


Figure 6: Comparison between the measured and calculated syngas outlet composition for the HP-POX reactor reported as mass fraction.

the progress variable is one the most delicate challenge for using the FPV in partial oxidation flames. In fact, the progress variable should allow to describe the reforming reactions with a sufficient resolution, beside to be always strictly monotonic for all the mixture fractions.

The analysis of the P-FLUT shows that chemical reactions in proximity of the stoichiometric conditions are extremely fast, because the fuel reacts with almost pure oxygen. Therefore the oxidation reactions occur at extremely smaller time and length scales compared to the reforming. In fact, the CFD analysis of the HP-POX reactor using the FPV approach in combination with the premix look-up table shows that a large reactor volume is required for completing the reforming process. The oxidation zone takes up only a minor part of the reactor, where the mixing of the reactants occur.

The FPV approach in combination with a look-up table generated using 1D freely propagating laminar flames gives an excellent agreement with the measurements of the outlet syngas composition, showing differences of the mass fractions of the main species below 2.7% by weight. In particular the outlet progress variable shows an excellent agreement with the experimental one, demonstrating that the partial oxidation processes can be accurately modelled using the flamelet/progress variable.

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