# Simplified kinetic schemes for oxy-fuel combustion

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**ABSTRACT**

This work presents simplified kinetic schemes to be adopted in the CFD modeling of oxy-fuel combustion.

Oxy-fuel combustion is an important technology to control $CO_2$ emissions. The reduction of nitrogen content during combustion makes easier the $CO_2$ capture for its successive storage. Flue gas recirculation can be adopted for the eventual temperature control. Moreover, oxygen rich combustion finds several applications where high temperatures are required, like iron and steel industry, or when the plants undergo frequent startups and shutdowns, to minimize the transient times.

Computational Fluid Dynamics (CFD) is also increasing its importance as a tool for industrial design and optimization. In many cases (for example oxy-fuel combustion), very simplified approaches, like *'mixed is burned'*, which do not need any kinetic information, are completely meaningless, because the high temperatures promote dissociation reactions. For such systems it is necessary to use more detailed and complex approaches, which usually require the adoption of a finite rate chemistry. As an example, the Eddy Dissipation Concept Model (EDC), proposed by Magnussen [1, 2], is largely used for the numerical simulation of combustion devices for industrial applications. However, one of the main problems when using CFD in the full scale geometry and with a finite rate chemistry is represented by the dimension of the computational grid and then the large memory and CPU required. For this reason the level of description of combustion chemistry has to be drastically reduced down to a few species and a few reactions. The adoption of detailed chemistry for the CFD simulation of combustion devices is possible only for very simple geometries and fuels (like hydrogen and syngas) whose chemistry involves a small number of species. In general, simplified kinetic mechanisms are required to manage complex geometries and complex fuels.

In the typical air combustion cases, when CO profiles are of interest or when temperature estimations have to be improved, a large number of simplified mechanisms is available, especially for methane. Typical and well known examples are the schemes of Westbrook and Dryer [3] and Jones and Lindstedt [4].

Unfortunately, the temperature peaks of oxy-fuel combustion limit the validity of such mechanisms in these conditions. At temperatures higher than 2500 K, not only $CO$-$CO_2$ equilibrium is in favor of CO and $H_2$-$H_2O$ equilibrium foresees a significant amount of $H_2$, but also the radical pool has a significant impact in limiting the heat release. The simplified mechanisms do not always account for the dissociation reactions [3] and none of them include radicals. Therefore, it is necessary to revise simplified mechanisms already available in the literature or to formulate new mechanisms, specifically conceived for their direct

application in the numerical simulation of oxy-fuel combustion systems.

This paper presents new estimations of the parameters of multistep oxidation mechanisms, optimized for oxy-fuel applications. These evaluations are based on a regression of data with a very effective numerical algorithm [5]. The main novelty is the definition of the set of comparison measures. In order to take into account the quite broad temperature and stoichiometry ranges of a turbulent diffusive flame, the regression analysis is performed over data obtained by a detailed kinetic scheme [6] in laminar counter-flow diffusion flames. These flames are assumed as a good representation of the real flame, still maintaining a simple solution, compatible with the numerical effort required by the regression algorithm.

The validity of the proposed approach and the reliability of the new simplified kinetic mechanism are tested on a set of counter flow diffusion flames fed with methane and oxygen, experimentally studied by Naik *et al.* [7].

## INTRODUCTION

Oxy-fuel combustion is an important technology to control $CO_2$ emissions. The reduction of nitrogen content during combustion makes easier the $CO_2$ capture for its successive storage. Flue gas recirculation can be adopted for the eventual temperature control [8]. Moreover, oxygen rich combustion finds several applications where high temperatures are required, like iron and steel industry, or when the plants undergo frequent startups and shutdowns, to minimize the transient times. In particular, the conversion of natural-gas-fired furnaces from air to oxygen in the glass industry has reduced fuel consumption by 15% to 50% and simultaneously decreased NOx emissions by 50% to 90%. Other advantages of oxygen-enriched combustion include reduced particulate emissions, greater flame stability, reduced exhaust gas volume and better heat transfer characteristics.

Turbulent non premixed flames are largely used in many practical combustion devices to convert chemical energy into work, due to the high efficiency, large heat releases and safety reasons. This explains the increasing demand for computational tools capable of characterizing the combustion systems in a reliable, accurate way, also in terms of pollutant species. Therefore, Computational Fluid Dynamics (CFD) is increasing its importance as a tool for industrial design and optimization of combustion devices. In particular, the oxy-fuel combustion technology can be greatly improved by CFD and numerical tools more in general, since the experimental activities are very expensive and involve a high number of risks. However, one of the main problems when using CFD in the full scale geometry is the dimension of the computational grid and consequently the large memory and CPU required. Even with the continuous increase of computer power and speed, the direct coupling of detailed kinetics (which is usually required to obtain accurate predictions of most pollutant species) and complex CFD is not possible. Since the computational cost of a CFD simulation significantly increases with the number of cells ($N_C$) of the computational grid and with the second or third power of the number of reacting species ($N_S$), the combustion chemistry has to be drastically reduced down to a few species (and a few reactions). This explains the great attention devoted to the development of reliable global mechanisms for the combustion of hydrocarbons, especially during the '80 [3, 4, 9, 10]. Despite the increasing power of modern PCs, there is still nowadays the need of simplified kinetic mechanisms to be coupled with CFD codes. Several reasons explain this need.

✓ First of all, the increasing detail of fluid dynamics description. RANS approaches are replaced by more accurate Large Eddy Simulation, computationally very expensive. In the next future, the scientists are sighting the Direct Numerical Simulations. In these last contexts it is still impossible to perform fluid dynamics simulations of reactive systems with detailed chemistry.

✓ While the global kinetic mechanisms available in literature usually refers to methane or single-component fuels, today liquid fuels, like diesel or jet fuels, are investigated because of their importance in several applications like engines. Therefore it is pretty evident that a further push to revise actual available global mechanisms is the presence of mixtures, where the synergistic effects of the most reactive components have to be taken into account.

✓ Non conventional combustion conditions can limit the validity of global mechanisms available in the literature. Oxy-combustion is an important example. At temperatures higher than 2500 K, not only $CO$-$CO_2$ equilibrium is in favor of $CO$ and $H_2$-$H_2O$ equilibrium foresees a significant amount of $H_2$, but also the radical pool has a significant impact in limiting the heat release. The simplified mechanisms do not always account for the dissociation reactions [3] and none of them include radicals. As better shown in the following sections, this makes impossible to use them for the simulation of oxy-combustion systems.

Literature about single or multi-step oxidation mechanisms refers the evaluation of kinetic parameters and reaction orders to some 'regression approaches'. Results carried out in Plug Flow Reactors (PFR) or flame speed measures are used to adjust the kinetic parameters. Starting points are chemical analyses of the reaction pathways. More recently data from non adiabatic Perfectly Stirred Reactors (PSR) were also used to identify the rate constants [11].

This paper presents new estimations of the parameters of multistep oxidation mechanisms, specifically conceived for oxy-fuel applications. These evaluations are based on a regression of data with a very effective numerical algorithm [5]. The main novelty is the definition of the set of comparison measures. In order to take into account the quite broad temperature and stoichiometry ranges of a turbulent diffusive flame, the regression analysis is performed over data obtained by a detailed kinetic scheme [6] in laminar counter-flow diffusion flames. These flames are assumed as a good representation of the real flame, still maintaining a simple solution, compatible with the numerical effort required by the regression algorithm.

After a short introduction about some numerical issues related to the application of simplified mechanisms for the simulation of laminar and turbulent flames, the importance of revising the actual simplified mechanisms for their application in oxy-fuel combustion conditions is demonstrated and discussed through several examples. Then, the regression procedure for obtaining the *"best"* kinetic parameters (i.e. which are optimized for specific conditions) is briefly presented and applied to an existing simplified mechanism for the combustion of methane. In the last part, the new kinetic mechanism, *"optimized"* for oxy-fuel combustion conditions, is applied for the numerical simulation of several counter flow diffusion flames fed with methane and oxygen (for which experimental measurements are available) in order to show its validity and accuracy.

## DETAILED KINETIC MECHANISM

The source of data to be regressed comes from a detailed kinetic mechanism (DKM), already developed and validated for hydrocarbons up to 16 C atoms [6], freely available on the web at the following address: www.chem.polim.it/creckmodeling. The model showed to be accurate in predicting the pyrolysis, oxidation and combustion of pure components and mixtures in wide ranges of conditions (in terms of pressures, temperatures, stoichiometries and residence times). On these bases, the results coming from this kinetic model are assumed as *'correct measures'*.

## SIMPLIFIED MECHANISMS

As mentioned, several global mechanisms are available in the literature. In principle, the present approach allows to consider any of them or to propose new schemes.

In the typical case of methane combustion in air, when CO profiles are of interest or when temperature estimations have to be improved, the most used simplified schemes are those proposed by Westbrook and Dryer (WD) [3] and Jones and Lindstedt (JL) [4], which are summarized in Table 1 and Table 2 respectively. The WD three-step hydrocarbon oxidation mechanism is selected because this it is available as default in many commercial CFD codes and it is largely applied for the numerical simulation of turbulent flames. The JL scheme is a little bit more complex, but has a higher degree of accuracy than the WD scheme and is used regularly in CFD modelling of industrial applications.

When using simplified kinetic mechanisms for the numerical simulation of reacting system, particular attention must be devoted to two aspects: the thermodynamic consistency of reversible reactions and the existence of reaction orders lower than unity.

*Thermodynamic consistency*

The reverse rate constants of non elementary reactions have to be carefully derived and in particular the reaction orders (see for example reaction JL3). Generally speaking, assuming the following non elementary equilibrium reaction:

$$aA + bB \rightleftharpoons cC + dD \qquad\qquad r_f = k_f(T)\prod_{i=1}^{NS} C_i^{\upsilon_{f,i}} \qquad\qquad (1)$$
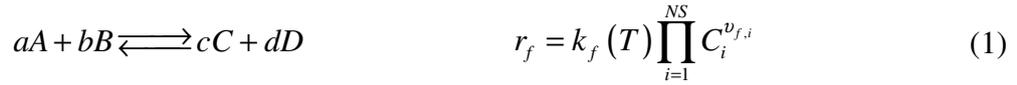
where $\upsilon_{f,i}$ is the order in the forward reaction of each of *NS* species and $C_i$ its concentration, the reverse reaction expression is:

$$r_b = \frac{k_f}{K_{eq}\cdot(RT)^{-\sum_{i=1}^{NS} n_i}}\prod_{i=1}^{NS} C_i^{\upsilon_{b,i}} \qquad\qquad (2)$$

where $n_i$ is the stoichiometric coefficient $(a,b,c,d)$ of each species $(A,B,C,D)$ and $\upsilon_{b,i}$ its order in the reverse reaction. $\upsilon_{b,i}$ can be simply derived from the order of the forward reaction and from the stoichiometric coefficient: $\upsilon_{b,i} = \upsilon_{f,i} + n_i$.

*Reaction orders lower than unity*

The global kinetics typically includes non elementary reactions with real reaction orders. These results might cause numerical problems when orders lower than 1 are proposed, because of possible negative values of the concentration. A solution is a linearization of the

| | Reaction | Reaction rate |
|---|---|---|
| 1 | $CH_4 + \frac{3}{2}O_2 \longrightarrow CO + 2H_2O$ | $r_1 = 5\cdot10^{11} e^{-\frac{47800}{RT}}[CH_4]^{0.70}[O_2]^{0.80}$ |
| 2 | $CO + 0.5O_2 \longrightarrow CO_2$ | $r_2 = 2.24\cdot10^{12} e^{-\frac{40700}{RT}}[CO][H_2O]$ |
| 3 | $CO_2 \longrightarrow CO + 0.5O_2$ | $r_3 = 5\cdot10^8 e^{-\frac{40700}{RT}}[CO_2]$ |

*Units of reaction parameters are: cal, mol, l, s.*

*Table 1. Westbrook-Dryer mechanism (WD).*

| | Reaction | Reaction rate |
|---|---|---|
| **1** | $CH_4 + \frac{1}{2}O_2 \longrightarrow CO + 2H_2$ | $r_1 = 4.4 \cdot 10^{11} e^{-\frac{30000}{RT}} [CH_4]^{0.50} [O_2]^{1.25}$ |
| **2** | $CH_4 + H_2O \longrightarrow CO + 3H_2$ | $r_2 = 3 \cdot 10^8 e^{-\frac{30000}{RT}} [CH_4][H_2O]$ |
| **3** | $CO + H_2O \rightleftharpoons CO_2 + H_2$ | $r_3 = 2.75 \cdot 10^9 e^{-\frac{20000}{RT}} [CO][H_2O]$ |
| **4** | $H_2 + 0.5O_2 \rightleftharpoons H_2O$ | $r_4 = 6.80 \cdot 10^{15} T^{-1} e^{-\frac{40000}{RT}} [H_2]^{0.25} [O_2]^{1.50}$ |

*Units of reaction parameters are: cal, mol, l, s.*

*Table 2. Jones-Lindstedt mechanism (JL).*

rate expression when the concentration of the reactants becomes lower than a certain specified value.

A simple example can show this approach. The species $A$ is consumed with a reaction rate $r = kC_A^\alpha$, where $\alpha$ is less than one. The mass balance can be then written as:

$$dC_A/dt = -kC_A^\alpha \qquad (3)$$

whose solution is:

$$C_A = \left[ C_{A0}^{1-\alpha} - (1-\alpha)kt \right]^{1/(1-\alpha)} \qquad (4)$$

being $C_{A0}$ the initial $A$ concentration. When the time is higher than:

$$t = C_{A0}^{1-\alpha} / \left[ (1-\alpha)k \right] \qquad (5)$$

$C_A$ becomes lower than zero with several problems arising if a numerical solution is adopted. To overcome these difficulties it is possible identify a small threshold value $(C_{AT})$ of $C_A$, below which an order one reaction is assumed: $r = \tilde{k}C_A^\alpha$, where $\tilde{k}$ is estimated making equal the two reaction rates for $C_A = C_{AT}$: $kC_{AT}^\alpha = \tilde{k}C_{AT} \Rightarrow \tilde{k} = kC_{AT}^{\alpha-1}$. The transition between the two reaction rates is obtained through an expression, able to avoid discontinuities in the function and in its derivatives. The final rate constant expression covering the whole time range is then:

$$r = \xi kC_A^\alpha + (1-\xi)kC_{AT}^{\alpha-1}C_A \qquad (6)$$

where $\xi$ is a proper function based on hyperbolic tangent, which allow the continuous transition:

$$\xi = \frac{1}{2}\left[ \tanh\left( \sigma \frac{C_A}{C_{AT}} - \tau \right) + 1 \right] \qquad (7)$$

where $\sigma$ and $\tau$ are two constants. Figure 1 shows the impact of this approach on the solution. The two results are very similar and only zooming at very low concentrations, it is possible to observe the correction introduced.
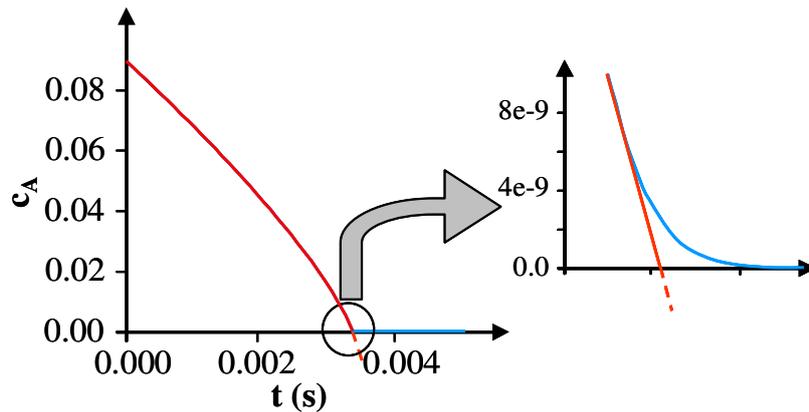
*Figure 1. Concentration of A with (blue line) and without (red line) the linearization ($C_{A0}$=0.09 mol/l; α=-0.3; k=10 mol$^{0.3}$/l$^{0.3}$/s). Small figure zooms the zone where the functions approach zero. The constants σ and τ are chosen equal to 23 and 17 respectively.*

## APPLICATION OF SIMPLIFIED MECHANISMS IN OXY-FUEL COMBUSTION

The WD and JL simplified kinetic mechanisms cannot be expected to work as well under oxy-fuel combustion conditions as they do for conventional combustion. As mentioned before, the temperature peaks of oxy-fuel combustion limit the validity of such simplified mechanisms. At temperatures higher than 2500 K (which are very common in oxy-fuel combustion), the $CO$-$CO_2$ equilibrium is in favor of CO and $H_2$-$H_2O$ equilibrium foresees a significant amount of $H_2$. In these conditions the importance of some of the elementary reactions governing the combustion can dramatically change with respect to the more conventional conditions of air combustion. This requires a modification of the WD and JL simplified mechanisms, whose kinetic parameters need to be re-fitted by taking into account oxy-fuel combustion conditions. Moreover, in oxy-combustion the radical pool has a significant impact in limiting the heat release, but the WD and JL mechanisms do not account for the dissociation reactions and do not include radicals. Therefore, the modification of these mechanisms requires also the introduction of radical species and dissociation reactions; otherwise it remains impossible to correctly describe oxy-fuel combustion conditions.

*Adiabatic flame temperature*

In order to better understand the importance of dissociation reactions and radical species for a $CH_4$/$O_2$ system, it is possible to compare the adiabatic temperature calculated neglecting the presence of radical species with the adiabatic temperature of the same system evaluated considering the most important species (molecular and radicals) for the combustion of methane, corresponding to the species included in the detailed kinetic mechanism (DKM). As reported in Figure 2, if we account only for the main molecular species ($CH_4$, $O_2$, $CO_2$, CO, $H_2O$, $H_2$ and $N_2$), like in the JL mechanism, the adiabatic temperature is largely over-estimated. In order to improve the agreement, it is necessary to introduce radicals, which accounts for dissociation reactions. In particular, if we introduce the H and OH radicals (corresponding to the dissociation of $H_2O$), the adiabatic temperature (JL + H/OH) is again over-estimated, but the agreement with the DKM curve greatly improves. Only if we add the O radiacal too (corresponding to the dissociation of $O_2$), the adiabatic temperature can be predicted with great accuracy (JL + H/OH/O).

This means that if we use a global kinetic mechanism like the JL (which contains only the main molecular species previously mentioned) to perform the numerical simulation of a reacting system in oxy-fuel combustion conditions, a large over-prediction of the temperature
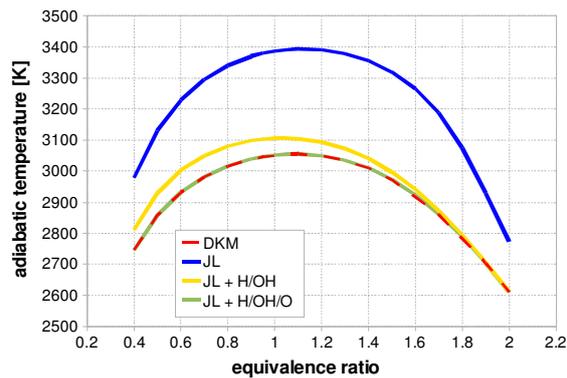
*Figure 2. Calculated adiabatic flame temperature for a CH<sub>4</sub>/O<sub>2</sub> system.*
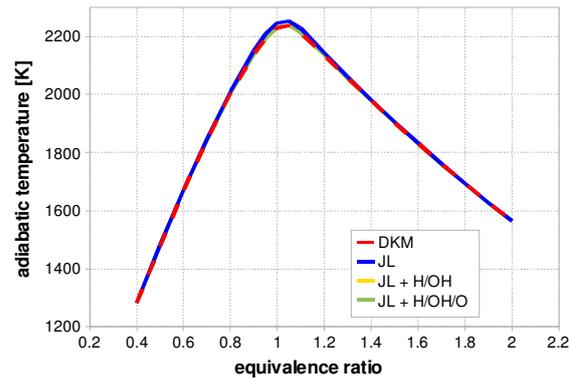
*Figure 3. Calculated adiabatic flame temperature for a CH<sub>4</sub>/air system.*

field must be expected. Dissociation reactions of $H_2O$ and $O_2$ have to be absolutely introduced in simplified mechanisms, otherwise the temperature field cannot be correctly predicted.

Of course the importance of dissociation reactions is more evident if we refer to the WD kinetic mechanism, which relies on a smaller number of molecular species than the JL mechanism (since the $H_2$ is not included). In this case the estimated adiabatic flame temperature reaches unrealistic values larger than 5000 K.

The dissociation reactions play a minor role in conventional air combustion conditions, as reported in Figure 3. In this case the main molecular species ($CH_4$, $O_2$, $CO_2$, $CO$, $H_2O$, $H_2$ and $N_2$) are sufficient to correctly describe the adiabatic flame temperature. This means that the WD and JL mechanisms do not necessarily requires the introduction of dissociation reactions to give a reasonable prediction of the temperature filed. However, as we will better see in the next section, this does not mean that in a non-equilibrium reacting system the same degree of accuracy can be reached.

*Counter-flow diffusion flames*

The absence of dissociation reactions in the WD and JL mechanisms lead to a poor prediction of the temperature field when these schemes are used in oxy-fuel combustion, both in diffusive and premixed systems. As an example, we can compare the numerical predictions of WD and JL mechanisms with the numerical results obtained using the detailed kinetic mechanism (DKM) in a simple reacting system, like a laminar counter flow diffusion flame, in which fuel and oxidizer streams are fed separately.

Figure 4 and Figure 5 show the temperature profiles of a $CH_4$/air and $CH_4$/$O_2$ counter flow diffusion flames respectively (with strain rate equal to 100 Hz). For the $CH_4$/air system the WD and JL mechanisms tend to over-predict the temperature, especially in the fuel-rich region. In particular, the peak temperature is over-predicted by ~200 K. The JL predictions are in better agreement, in particular in the fuel-lean side. Even if the species involved in the WD and JL mechanisms are sufficient to correctly predict the adiabatic temperature (see Figure 3), their application in this counter flow diffusion flame results in a poor agreement in the main reaction zone.

As expected, the results are still worse for oxy-fuel combustion (Figure 5). The WD mechanism over-predicts in a non realistic way the temperature field, leading to a peak temperature larger than 5000 K, which has no physical meaning. The JL mechanism performs better, but it tends to over-estimate the peak temperature of at least ~350 K. These results can be easily understood if we refer to the adiabatic temperatures discussed in the previous section (see Figure 2). The WD mechanism involves only molecular species ($CH_4$, $O_2$, $CO_2$, $CO$, $H_2O$ and $N_2$), which are not sufficient to properly describe the system in conditions close to the chemical equilibrium. The JL mechanism, because of the inclusion of $H_2$, leads to a
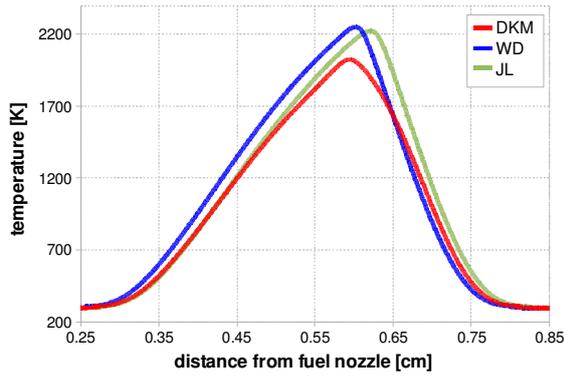
*Figure 4. Calculated temperature profiles for a counter flow diffusion flame fed with $CH_4$ and air (strain rate equal to 100 Hz): comparison between detailed and global mechanisms.*
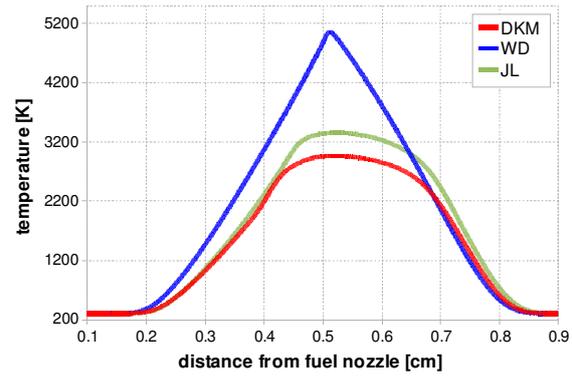
*Figure 5. Calculated temperature profiles for a counter flow diffusion flame fed with $CH_4$ and $O_2$ (strain rate equal to 100 Hz): comparison between detailed and global mechanisms.*

significant reduction of the temperature with respect the WD scheme. However, the lack of dissociation reactions (and therefore radicals) makes impossible, also for the JL mechanism, to match the results from the detailed kinetic mechanism.

*Flame speeds*

The absence of dissociation reactions in the WD and JL mechanisms can be used to explain the poor agreement between flame speeds calculated with detailed kinetic schemes and global mechanisms in oxy-combustion conditions.

Figure 6 shows the flame speed of a mixture of $CH_4$ and air at several equivalence rations as obtained using a detailed kinetic mechanism (DKM) and the JL and WD kinetic mechanisms. It is pretty evident that the JL mechanism tends to overestimate the flame speed, but it is able to catch the bell-shape of the curve corresponding to the detailed kinetic mechanism. The WD mechanism under-predicts the flame speed in the fuel-lean region, but for equivalence ratios larger than 1 the flame speed is largely over-predicted and the mixture reactivity always over-estimated.

In oxy-combustion the differences increase, as reported in Figure 7. In this case the WD mechanism leads to a result which is completely inacceptable for practical applications: the over-estimation is too large, both in fuel-lean and fuel-rich regions. The JL mechanism performs better, but the agreement is poor also in this case. The explanation is always the same: as we previously saw, the WD and JL mechanisms largely over-predict the temperature in oxy-combustion and this leads to a larger flame speed.
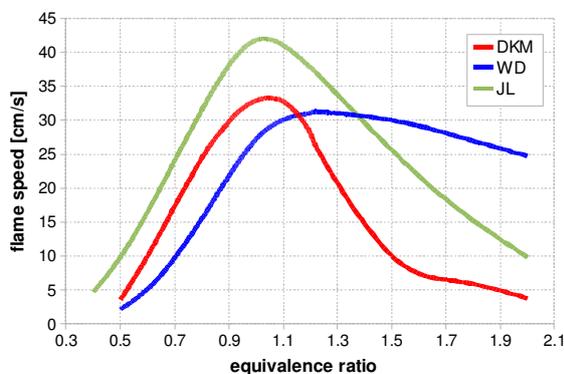


*Figure 6. Calculated flame speed velocities for a mixture of $CH_4$ and air at several equivalence ratios: comparison between detailed and global mechanisms.*
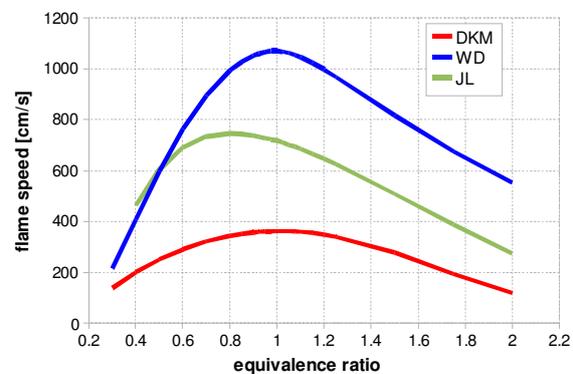
*Figure 7. Calculated flame speed velocities for a mixture of $CH_4$ and $O_2$ at several equivalence ratios: comparison between detailed and global mechanisms.*

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| | Reaction | Reaction rate |
|---|---|---|
| **1** | $CH_4 + \frac{1}{2}O_2 \longrightarrow CO + 2H_2$ | $r_1 = 4.4 \cdot 10^{11} e^{-\frac{30000}{RT}} [CH_4]^{0.50} [O_2]^{1.25}$ |
| **2** | $CH_4 + H_2O \longrightarrow CO + 3H_2$ | $r_2 = 3 \cdot 10^8 e^{-\frac{30000}{RT}} [CH_4][H_2O]$ |
| **3** | $CO + H_2O \rightleftarrows CO_2 + H_2$ | $r_3 = 2.75 \cdot 10^9 e^{-\frac{20000}{RT}} [CO][H_2O]$ |
| **4** | $H_2 + 0.5O_2 \rightleftarrows H_2O$ | $r_4 = 6.80 \cdot 10^{15} T^{-1} e^{-\frac{40000}{RT}} [H_2]^{0.25} [O_2]^{1.50}$ |
| **5** | $O_2 \rightleftarrows 2O$ | $r_5 = 1.5 \cdot 10^9 e^{-\frac{113000}{RT}} [O_2]$ |
| **6** | $H_2O \rightleftarrows H + OH$ | $r_6 = 2.3 \cdot 10^{22} T^{-3} e^{-\frac{120000}{RT}} [H_2O]$ |

*Units of reaction parameters are: cal, mol, l, s.*

*Table 3. Jones-Lindstedt mechanism with dissociation reactions (JL-R).*

*JL mechanism with dissociation reactions*

The results discussed above clearly show the higher accuracy of JL mechanism over the WD mechanism in oxy-fuel combustion and, above all, are a clear indication that it is necessary to add at least the dissociation reactions of water and oxygen to the JL mechanism. This leads to the formulation of a new mechanism reported in Table 3 (which will be called in the following the JL-R mechanism). The kinetic parameters of dissociation reactions of O2 and H2O (respectively reaction 5 and 6) are taken from the detailed kinetic model [6].

The JL-R mechanism needs to be adapted (or optimized) to better describe the oxy-fuel combustion conditions. This means that the kinetic parameters (pre-exponential factors, activation energies and reaction orders) of reactions in Table 3 have to be modified on the basis of a large set of data referring to experimental measurements and/or obtained through the adoption of a detailed kinetic mechanism.

## TUNING PROCEDURE

The procedure to determine the kinetic parameters of a global mechanism and the reaction orders is based on the *'experimental measures'* generated by the detailed kinetic model [6]. Since the turbulent diffusive flames can be thought as the results of laminar flamelets, the selection of laminar counter-flow diffusion flames results particularly convenient as regression device.

A sensitivity analysis showed that the best operative conditions where the temperature and composition profiles are affected by the rate parameters are those close to the flame extinction. It is quite obvious that the chemistry plays a fundamental role when the residence times are short, i.e. at high strain rates. The use of data obtained also for lower strain rates did not significantly modify either the values of the estimated parameters or the accuracy of the global model coming from the regression of just the flame close to extension. On the contrary, different feed compositions allowed to improve the performances. In particular, partially premixed flames were adopted. The introduction of the oxidizer in the fuel feed allows to enlarge the reaction zone and to better characterize the chemical phenomena in the rich side close to the flame front.

It has to be noted that typical kinetic regressions are challenging problems. As a matter of facts, kinetic models are typically strongly nonlinear and, consequently, algorithms adopted for parameter estimation must be both robust and flexible enough to deal with constraints that are not always analytically definable. In this case the function evaluations are quite time consuming and then the algorithm has also to be effective. This work applies a numerical

| Reaction | Parameter | Original Value | Optimized Value |
|----------|-----------|----------------|-----------------|
| 1 | $A$ | $4.4 \cdot 10^9$ | $3.06 \cdot 10^{10}$ |
| 1 | $v_{f,O_2}$ | 1.25 | 1.30 |
| 2 | $A$ | $3.80 \cdot 10^8$ | $3.84 \cdot 10^9$ |
| 3 | $A$ | $2.75 \cdot 10^9$ | $2.01 \cdot 10^9$ |
| 4 | $A$ | $6.80 \cdot 10^{15}$ | $8.03 \cdot 10^{16}$ |
| 4 | $v_{f,H_2}$ | 0.25 | 0.30 |
| 4 | $v_{f,O_2}$ | 1.50 | 1.55 |

*Table 4. Modified Jones-Lindstedt mechanism for oxy-fuel combustion.*

algorithm specifically conceived for kinetic regression: '*BzzNonLinearRegression*' class [5, 12], which is a free software for non commercial use.

The large differences in the predicted temperature profiles justify the need and the possibility to revise the original simplified mechanisms to obtain a better agreement with the detailed kinetic scheme. The first step in the 'optimization' procedure consists in finding the kinetic parameters which are more suitable for the non linear regression. In other words, the regression cannot be performed using all the available kinetic parameters, because their number is usually too large. It is better to choose only the parameters to which the flame is more sensitive. These parameters are chosen following the indications suggested by a sensitivity analysis, with respect to every kinetic parameter in the global kinetic scheme. Following this simple procedure, it is possible to select a relatively small number of parameters (usually less than 10), in order to reduce the computational time and the dimensions of the overall regression problem. The most significant parameters for the problem under investigation were found using this approach and are reported in Table 4.

The regression was performed on different sets of '*experimental data*', obtained through different combinations of counter flow diffusion flames. As previously mentioned, the numerical results suggest that it is better to use flames with large strain rates, because in these conditions the effects of the chemistry are more important and therefore the regression is performed on experimental data more sensitive to the kinetic parameters. For example, this means that the parameters obtained from the regression a flame with a large strain rate work pretty well also for a flame with low strain rate, but the opposite is not true. Therefore, if it is necessary to reduce the number of '*experimental flames*' for reasons related to the excessive computational time, it is more convenient to work on flames with a large strain rate.

The kinetic parameters obtained from the regression are summarized in Table 4. These parameters describe pretty well the counter flow diffusion flames in a large range of strain rates, as shown in the next section.

## NO FORMATION IN OXY-FUEL COMBUSTION

In order to show the validity of the proposed approach from one side and to check the effective improvement deriving from the introduction of dissociation reactions in the JL mechanism and from the optimization procedure from the other side, the modified JL-R mechanism (see Table 4) was applied to a set of counter flow diffusion flames fed with methane and oxygen, experimentally studied by Naik *et al.* [7]. Six different flames were investigated, containing 1%, 3% and 10% of $N_2$ in either the oxidizer (Flames A) or fuel

| Flame | Fuel | Oxidizer |
|-------|------|----------|
| **A01** | *100% CH₄* | *99% O₂ + 1% N₂* |
| **A03** | *100% CH₄* | *97% O₂ + 3% N₂* |
| **A10** | *100% CH₄* | *90% O₂ + 10% N₂* |
| **B01** | *99% CH₄ + 1% N₂* | *100% O₂* |
| **B03** | *97% CH₄ + 3% N₂* | *100% O₂* |
| **B10** | *90% CH₄ + 10% N₂* | *100% O₂* |

*Table 5. Composition (%Vol.) and strain rates of counter flow diffusion flames experimentally studied by Naik et al. [7].*

streams (Flames B) at a global strain rate of ~20 1/s (Table 5). The calculations are performed using a specifically conceived software for the simulation of counter flow diffusion flames with detailed chemistry [13, 14].

Figure 8 shows the predicted temperature profiles obtained using the detailed kinetic mechanism [6], the JL and the modified JL-R mechanisms for Flame A10. As expected the JL mechanism over-predicts the temperature by more than 300 K. On the contrary, the modified JL-R mechanism, which was fitted in oxy-fuel combustion conditions, agree pretty well with the detailed kinetic mechanisms. The temperature is slightly over-predicted, but the difference is very small and can be neglected. Figure 9 shows the calculated profiles of $CO_2$ mole fraction for the same flame. Of course, the results mirror those proposed in Figure 8. The JL mechanism predicts a smaller amount of $CO_2$ with respect to the detailed mechanism, mainly because of the temperature over-estimation. In other words, the larger temperature tends to shift the CO-$CO_2$ equilibrium towards the formation of CO, decreasing the amount of $CO_2$. On the contrary, the modified JL-R mechanism is in good agreement with the detailed kinetic mechanism, not only in terms of peak value, but also for the shape of the numerical profile.

Similar results, which are not here reported because of lack of space, were obtained for all the flames studied by Naik *et al.* [7]. The improvement given by the modified kinetic scheme was found to be very strong, especially for flames A01 and B01, which are the flames closest to the pure oxy-fuel conditions. This result is not so surprising if we take into account that the tuning of the JL-R mechanism was performed in oxy-fuel conditions.
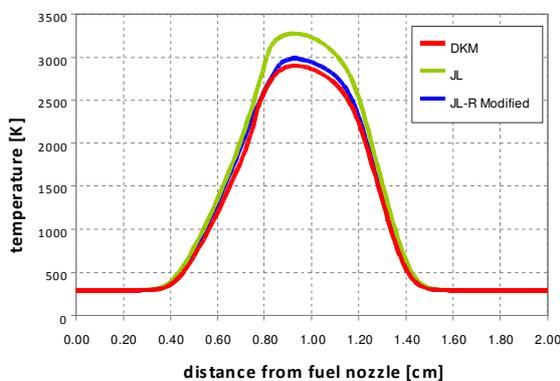


*Figure 8. Calculated temperature profiles Flame A10 (10% N₂ in oxidizer stream): comparison between detailed and global kinetic mechanisms.*
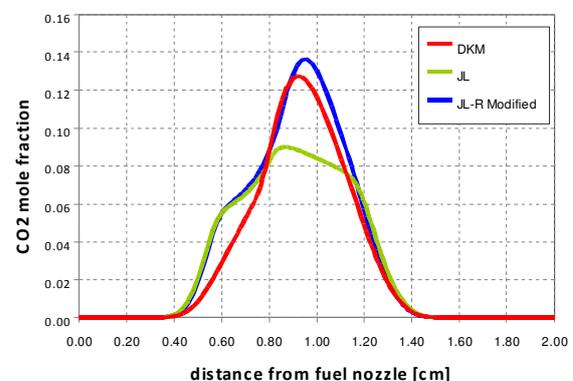
*Figure 9. Calculated CO₂ mole fraction profiles Flame A10 (10% N₂ in oxidizer stream): comparison between detailed and global kinetic mechanisms.*
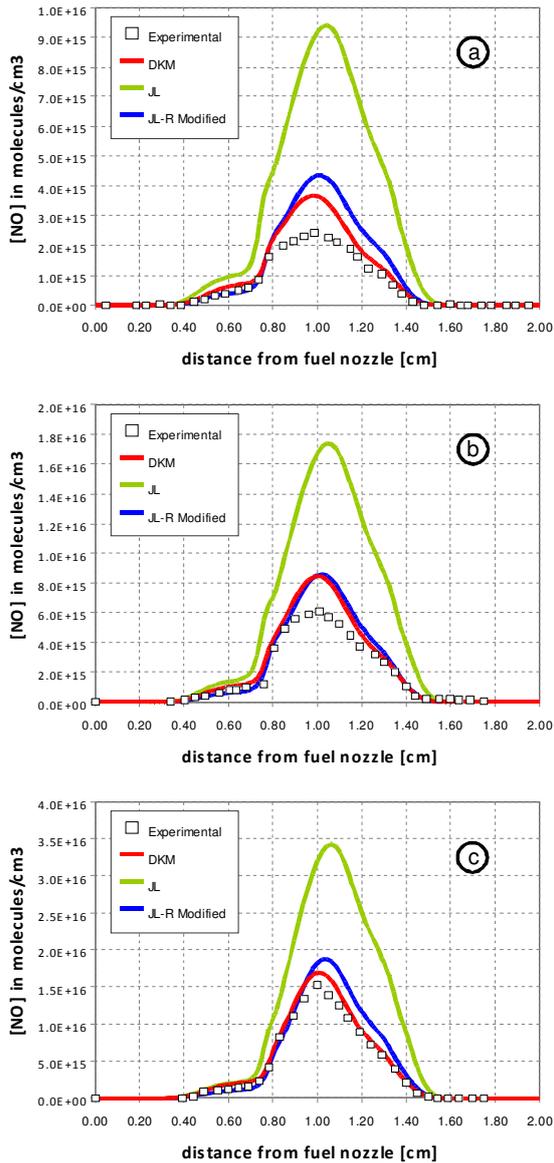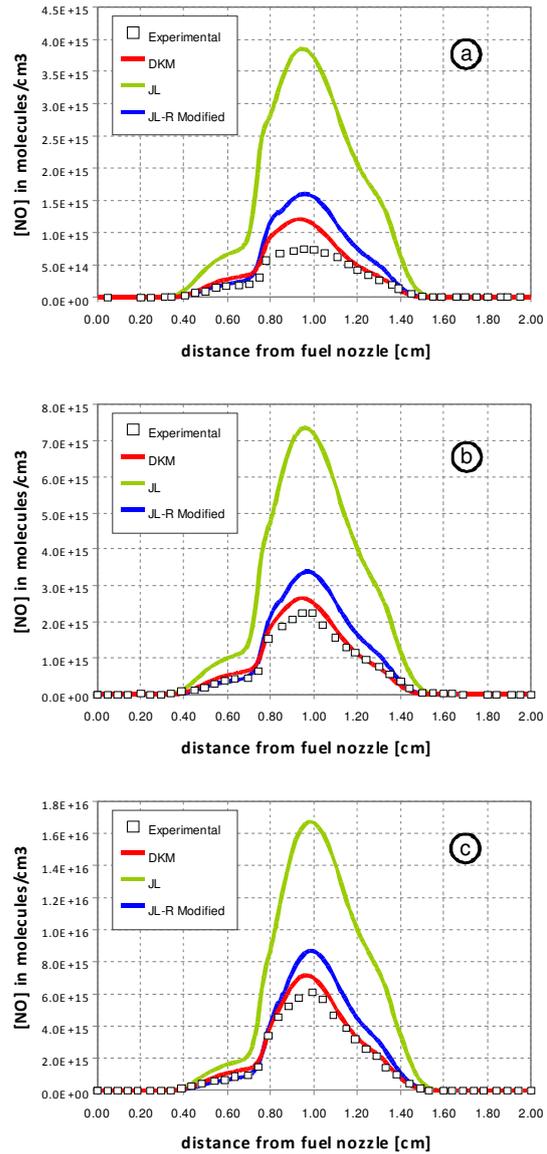
*Figure 10. NO concentration profiles in counter-flow diffusion flames: comparison between experimental [7] and numerical results. (a) 1% $N_2$ in oxidizer stream; (b) 3% $N_2$ in oxidizer stream; (c) 10% $N_2$ in oxidizer stream.*

*Figure 11. NO concentration profiles in counter-flow diffusion flames: comparison between experimental [7] and numerical results. (a) 1% $N_2$ in fuel stream; (b) 3% $N_2$ in fuel stream; (c) 10% $N_2$ in fuel stream.*

Unfortunately no experimental measurements of temperature are available for a direct comparison with calculated profiles. The only experimental information is the concentration of nitrogen oxide (NO). Because of the high temperatures which are reached in oxy-fuel combustion, NO is mainly produced by the thermal mechanism. As a consequence, a good agreement between experimental and calculated NO profiles is an indication of a good prediction of the thermal field.

Figure 10 and Figure 11 show a comparison between the experimental and calculated NO concentration profiles for all the six flames [7]. It is quite evident that the detailed kinetic mechanism agrees pretty well with the experimental measurements, especially when the amount of added $N_2$ to the fuel or oxidizer stream is large (Flames A10 and B10). As we saw in Figure 8, the JL mechanism over-estimates the temperature field by more than 300 K. If we use the temperature field predicted by the JL mechanism to calculate the NO formation through a post-processing technique (using the same NOx formation sub-mechanism adopted

in the detailed kinetic mechanism), we obtain a non negligible over-prediction of NO concentration (Figure 10 and Figure 11). This is a direct consequence of the temperature over-estimation. On the contrary, the simulation performed using the modified JL-R mechanism (optimized for oxy-combustion conditions) leads to a satisfactory agreement with the DKM. The amount of NO is only slightly larger than the amount corresponding to the detailed kinetic mechanism, showing a strong improvement with respect the original JL mechanism. From one side this confirms the importance of revising the actual global mechanisms for their application in oxy-fuel combustion conditions. From the other side, this is a good indication of the ability of the proposed optimization procedure to adapt a global mechanism to conditions different from those in which it was obtained.

In Figure 12 and Figure 13 the peak values of NO concentration for the investigated flames are reported versus the amount of $N_2$ in the oxidizer and fuel streams respectively, in order to better show the ability of the modified JL-R mechanism to agree with the experimental measurements.
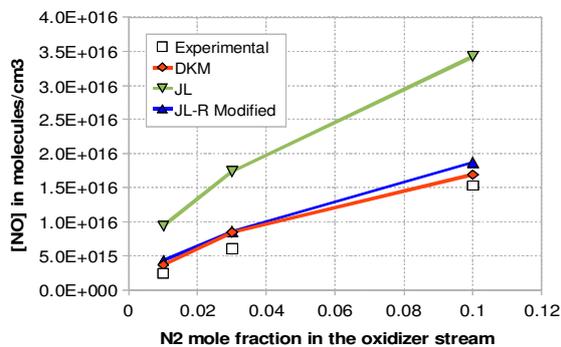


*Figure 12. NO concentration peak values in counter-flow diffusion flames: comparison between experimental [7] and numerical results at several amount of $N_2$ in oxidizer stream.*
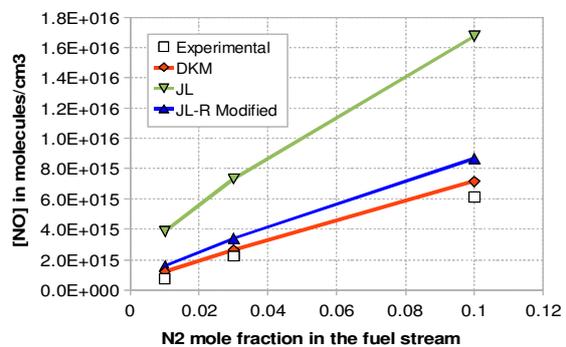
*Figure 13. NO concentration peak values in counter-flow diffusion flames: comparison between experimental [7] and numerical results at several amount of $N_2$ in fuel stream.*

## CONCLUSIONS

In this work the need and the possibility to improve the existing simplified mechanisms describing the combustion of methane were demonstrated and applied to oxy-fuel conditions. A procedure based on non linear regression was used to improve two simplified mechanisms, available in the literature and largely adopted by the combustion community. The novelty of the proposed approach is represented by the choice of *'experimental data'*, which correspond to an appropriate set of counter flow diffusion flames. The *'optimized mechanism'* was applied to a set of counter flow diffusion flames fed with methane and oxygen, for which experimental measurements were available. The results showed a strong improvement of numerical predictions with respect to the original mechanism.

It is expected that a similar improvement could be also observed in a turbulent system burning $CH_4$ in oxygen, considering that the counter-flow diffusion flames are a physical system representative of a turbulent flame.

Further investigations and improvements are needed to confirm the feasibility of this procedure. In particular, the choice of the counter flow diffusion flames to adopt for the optimization must be better defined. However, the results reported in this work appear promising, especially for the formulation of new kinetic schemes for fuel mixtures or for non conventional applications.

## ACKNOWLEDGMENTS

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