NO\textsubscript{x} EMISSIONS REDUCTION OF A NATURAL GAS SI ENGINE UNDER LEAN CONDITIONS: COMPARISON OF THE EGR AND RGR CONCEPTS.

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ABSTRACT
In natural gas SI engines under lean conditions, NO\textsubscript{x} emissions reduction can be realized by injecting an additional mass flow rate to inlet gases. It can be easily done in situ using two techniques: EGR (Exhaust Gas Recirculation) or RGR (Reformed Gas Recirculation) which is an improvement of the usual EGR configuration. Exhaust gases are catalyzed before being reintroduced at the engine inlet. Reformed gases contain carbon monoxide and hydrogen in addition to carbon dioxide, steam and nitrogen dioxide that compose usual recirculated gases. In order to compare EGR and RGR concepts, the study is divided in three stages. Firstly, a “two-zone” thermodynamic model has been developed and validated on a large open chamber SI engine (18 L CHP plant engine, fuelled by natural gas and equipped with data acquisition). Both in-cylinder pressure and nitrous oxide emissions have been compared between numerical results and experimental data. A good agreement is obtained, the error is less than 0.5%. Secondly, a widespread model of steam reforming on a Ni/MgOAl\textsubscript{2}O\textsubscript{3} catalyst has been used to compute in particular CO and H\textsubscript{2} concentrations. Numerical results lead to a good concordance with experimental data from literature. Finally, SI engine and reformer models have been linked. RGR and EGR configurations have been numerically compared considering the same recirculation mass flow rate. According to the results, RGR is the best way to decrease significantly nitrous oxide emissions, keeping good engine performances.

INTRODUCTION
Compared to others prime movers, Combined Heat and Power (CHP) plants based on SI engines and fuelled by natural gas have a good thermal efficiency and lead to a smaller impact on global warming. Moreover, the high H/C ratio limits the CO\textsubscript{2} emission level.

Nevertheless, Sogaard et al [1] bring to the fore one serious drawback of those CHP plants: the high emission level of unburned hydrocarbon (UHC), mainly methane, present in exhaust gases. Indeed methane has 21 times the GWP of carbon dioxide. Authors have also noticed that an addition of hydrogen in natural gas reduces the UHC emissions. Tsolakis and Megaritis [2] summarise the main advantages of a hydrocarbon and hydrogen blend as a fuel for IC engines: it increases thermal efficiency and reduces UHC, CO, CO\textsubscript{2} emissions. On the other hand, the higher hydrogen flame speed increases in-cylinder peak pressure and temperature. It raises NO\textsubscript{x} emissions except under lean conditions.

Hydrogen is often proposed as the fuel for future since its combustion leads to a limited impact on environment compared to hydrocarbon fuels. Unfortunately, hydrogen production and storage are difficult for both stationary and mobile applications, cf. Hoekstra et al. [3]. Storage can be avoided by an in-situ production, using reformed fuels that are rich in hydrogen, like natural gas. From a chemical point of view, natural gas reforming process aims to crack hydrocarbon molecules like methane to obtain hydrogen and carbon monoxide.

Natural gas reforming is an endothermic operation that requires steam and a catalyst. Consequently, using exhaust gases to bring steam and recover thermal energy, seems to be an efficient solution, especially for CHP plants. The reforming device (see figure 1) is able to mix a fraction of exhaust gases and natural gas to provide heat and steam in presence of catalyst materials. Chemical reaction products are reintroduced (particularly hydrogen) towards engine inlet. Technologically,
this technique can be applied to IC engines incorporating the reforming reactor into the conventional EGR system.

Figure 1. S.I. engine equipped with reformed gas recirculation inspired from Zheng et al. [4]

According to Tsolakis and Megaritis [5] or Jamal et al. [6], the first engines applications of such reformers were available on compression ignited engines running under lean combustion. Similarly, CHP engines exhaust gases contain also a significant amount of oxygen and steam.

The aim of this paper is to predict numerically engine performances and emissions using a steam reformer to crack methane on a Ni/MgOAl2O3 catalyst. To achieve this goal, a SI engine thermodynamic model is developed. As it distinguishes burned and fresh gases in combustion chamber, it is often called a “two-zones” model. It has been validated on an experimental test bench. As the fuel is a hydrogen and natural gas mixture, a specific laminar speed mode is required to characterise in-cylinder rate of heat release. In a second part, a chemical reactive flow is proposed to describe the operations of the steam reformer. In the third part, both engine and reformer models are coupled. The completed model has been used to achieve numerical investigations to predict NOx emissions.

1. S.I. ENGINE MODEL

1.1 S/I ENGINE THERMODYNAMIC MODELS: STATE OF THE ART

For more than 40 years, combustion chamber thermodynamic descriptions are developed to analyse or to predict internal combustion engines performances. In this paper, a “two-zones” model has been developed. Its mathematical foundations are presented in the reference books written by Fergusson [7], Heywood [8] and Ramos [9]. Five assumptions are mainly retained:

1. Combustion chamber is divided in two zones: the first for fresh gases and the second for burned gases. Both are separated by a flame front.
2. In-cylinder temperature for each zone is assumed to be uniform. This hypothesis is realistic for fresh gases but debatable for burned gases considering the temperature gradient that exists inside the burned gases core.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Exponential pre-factor</td>
</tr>
<tr>
<td>Aff</td>
<td>Front flame area</td>
</tr>
<tr>
<td>AFR</td>
<td>Air Fuel Ratio</td>
</tr>
<tr>
<td>B</td>
<td>Bore</td>
</tr>
<tr>
<td>BTDC</td>
<td>Before Top Dead Center</td>
</tr>
<tr>
<td>CA</td>
<td>Crank angle</td>
</tr>
<tr>
<td>CHP</td>
<td>Combined Heat and Power</td>
</tr>
<tr>
<td>CV</td>
<td>Volumic capacity [J/K kg]</td>
</tr>
<tr>
<td>DEN</td>
<td>Denominator</td>
</tr>
<tr>
<td>E</td>
<td>Activation energy</td>
</tr>
<tr>
<td>EGR</td>
<td>Exhaust gas recirculation</td>
</tr>
<tr>
<td>FAR</td>
<td>Fuel Air Ratio</td>
</tr>
<tr>
<td>h</td>
<td>Specific enthalpy [J/kg]</td>
</tr>
</tbody>
</table>

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3. Pressure is assumed to be homogeneous in the whole combustion chamber.
4. Heat transfer between the two zones is usually neglected.
5. Leakage and blow-by can also be neglected, see Gatowski et al. [10].

The first thermodynamic law gives one energy equation for each zone. Ideal gas law supplies another one. In-cylinder global volume is computed knowing engine mechanical design. Heat transfer from each zone towards cylinder walls is evaluated by Hohenberg correlation [11]. Combustion progress is usually modelled using the burned fraction associated to the concept of heat release rate. There are two ways to evaluate the burned fraction. Firstly, behaviour models have been developed to predict burned fraction. The well-known Wiebe’s function [12-19], cosine [12,20] or polynomial approaches [12,21] are mathematical functions which fit experimental data in a satisfying way. Nevertheless such models do not take into account physical and chemical phenomenon that occur during the combustion process. Consequently, specific characteristics of the hydrocarbon and hydrogen mixture are taken into account with correlations. Secondly, phenomenological models are based on physical considerations of the combustion process. In S.I. engines, burned gases zone is usually considered as a half-sphere centred on spark plug enclosed by a flame surface $\text{AFF}$. The flame front propagation through fresh gases, of specific mass $\rho_f$, is governed by turbulent speed $s_T$. Modelling the front flame with a half-sphere is a simple hypothesis. Indeed, because of in-cylinder turbulent motions, the front flame is crumpled. Consequently, the front flame surface is higher than the hemispherical one. To be more realistic, in the smooth hemispherical front flame, turbulent motion effects are taken into account in the turbulent flame speed. This model gives good general results and particularly at high engine loads and small air-excess. For very lean conditions and low loads (i.e. very close to ignition limit), this model does not reproduce correctly experimental results. Hence, Chmela and al. [22] have proposed a new description of combustion in gas engines with large chamber. It is better adapted to CHP plants under lean conditions. In our approach, laminar speed is a combination of the expression proposed by Rousseau [12] for hydrocarbon and the expression proposed by Shahad Al-Janabi and Sadi Al-Baghadi [23] for hydrogen. The set of equations is given in appendix A.

### 1.2 TEST BENCH

In order to validate the previous combustion model, a stationary SI gas engine connected to a 210 kW electric generator has been used (see figure 2) with a test bench. Technical specifications of the engine are gathered in Table 1.

The acquisition system of in-cylinder pressure is composed of:
- A piezo electric cylinder pressure sensor – AVL QH32D, gain 25.28pC/bar, range 0-200 bar
- A charge amplifier - AVL 3066A0
- A shaft position encoder – AVL 364C
- A piezo resistive pressure sensor inside the inlet manifold with its amplifier – range 0-2.5 bar

Experimental curves of cylinder pressure versus crank angle (resolution of 0.1 CA) are averaged over 100 cycles.

### 1.3 VALIDATION OF THE TWO ZONES MODEL

The engine operation point of the test is characterised by the following parameters:
- full load (100% WOT: Wide Opening Throttle),
- FAR: 0.67,
- spark advance: 16°BTDC,
- engine revolution speed: 1500rpm.
Natural gas composition is given in Table 2.

Comparison is performed on the in-cylinder pressure since this is the only available in-cylinder data, see Figure 3.
Figure 2. CHP engine fuelled by natural gas

In-cylinder fresh, burned and adiabatic flame temperatures are plotted on Figure 4. Cause of the dissociation-recombination reactions, the amount energy can be endothermic and the consequence is the flame temperature is under the burnt gas temperature, this is also reported by Leide [24]. In-cylinder mass is represented on Figure 5.

To extend the validation, different running conditions were investigated: $0.59 \leq FAR \leq 0.74$, $8 \leq SA \leq 18^\circ BTDC$, $50\% \leq Load \leq 100\% WOT$.

In the context of this paper, two criteria are analysed: the first one is the in-cylinder peak pressure and the second one is NOx emissions. A very good agreement is obtained for the in-cylinder peak pressure for all the engine conditions, see Figure 6. A good match is obtained for the nitrogen oxide too, see Figure 7.

The thermodynamic two-zones model is validated with a good match on the experimental device (SI engine with large open chamber, natural gas fuelled, under lean conditions).

2. STEAM-REFORMER

Steam reforming has already been studied for furnace applications. The process carries out is conversion of natural gas (mainly considered as methane) and steam mixture to carbon monoxide and hydrogen. Details about kinetic reactions can be found in the original paper by Xu and Froment [25].

<table>
<thead>
<tr>
<th>Designation</th>
<th>Testing Bench</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement Volume</td>
<td>$17,964,cm^3$</td>
</tr>
<tr>
<td>Number of cylinders</td>
<td>6</td>
</tr>
<tr>
<td>Bore $B$</td>
<td>$152,mm$</td>
</tr>
<tr>
<td>Con. Rod length $L$</td>
<td>$300,mm$</td>
</tr>
<tr>
<td>Stroke $S$</td>
<td>$165,mm$</td>
</tr>
<tr>
<td>Intake opens</td>
<td>$25^\circ BTC$</td>
</tr>
<tr>
<td>Intake closes</td>
<td>$45^\circ ABC$</td>
</tr>
<tr>
<td>Exhaust opens</td>
<td>$60^\circ BBC$</td>
</tr>
<tr>
<td>Exhaust closes</td>
<td>$15^\circ ATC$</td>
</tr>
<tr>
<td>Spark timing</td>
<td>$12^\circ BTC$</td>
</tr>
<tr>
<td>Engine Speed</td>
<td>$1500,RPM$</td>
</tr>
</tbody>
</table>

Table 1: Engine data

<table>
<thead>
<tr>
<th>$CH_4$</th>
<th>$C_2H_6$</th>
<th>$C_3H_8$</th>
<th>$C_4H_{10}$</th>
<th>$C_5H_{12}$</th>
<th>$N_2$</th>
<th>$CO_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>87.1</td>
<td>8.8</td>
<td>2.5</td>
<td>0.8</td>
<td>0</td>
<td>0.8</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2: Natural gas composition (in volume)

Figure 3. In-cylinder pressure comparison between measurement and simulation

Figure 4. Estimated in-cylinder temperatures
2.1 STATE OF ART

Nielsen et al. [26] resumed the seven common assumptions of steam reformer models:

1. A one-dimensional heterogeneous approach is used, see Froment and Bischoff [27].
2. The reactor type is assumed to be a fixed bed plug flow reactor.
3. The reformer geometry is assumed to be a pipe shaped as a straight hollow cylinder.
4. The model does not consider axial mixing.
5. All reactants are considered in the gas phase and obey the ideal gas equation of state.
6. Rather than attempt to use the actual pellet geometry, we will approximate it by a slab geometry.
7. One will only consider internal mass transport limitations, and not any heat transfer limitations, so there will be no energy balance inside the particle. This is an assumption that can often be justified, since heat transfer within the particle occurs primarily by conduction through the solid parts, while mass transfer occurs only in the pores.

2.2 MODEL AT EQUILIBRIUM

The intrinsic reaction kinetics on the surface can be represented by three reactions with Langmuir-Hinshelwood style rate expressions, see Xu and Froment [25]:

**Reforming kinetic**

\[
\text{Co-production from } CH_4 \\
CH_4 + H_2O = CO + 3H_2
\]

\[
R_1 = \frac{k_1}{D^2} \left( \frac{p_{CH_4}}{p_{H_2O}} - \frac{p_{H_2}^3}{K_1} \right)
\]

**Water-gas shift**

\[
CO + H_2O = CO_2 + H_2
\]

\[
R_2 = \frac{k_2}{D^2} \left( \frac{p_{CO}}{p_{H_2O}} - \frac{p_{H_2}p_{CO}}{K_2} \right)
\]

**Production of CO2 from CH4**

\[
CH_4 + 2H_2O = CO_2 + 4H_2
\]

\[
R_3 = \frac{k_3}{D^2} \left( \frac{p_{CH_4}}{p_{H_2O}^2} - \frac{p_{H_2}^2}{K_3} \right)
\]

With:

\[
D^2 = 1 + K_{CO} \frac{p_{CO}}{p_{H_2}} + K_{H_2} \frac{p_{H_2}}{p_{H_2O}} + K_{CH_4} \frac{p_{CH_4}}{p_{H_2O}} + \left( \frac{K_{H_2O} \frac{p_{H_2O}}{p_{H_2}}}{p_{H_2}} \right)
\]

The water gas shift is exothermic, the two other are endothermic. The rate of disappearance of methane is calculated from: \( R_{CH_4} = R_1 + R_3 \). Both the absorption constants and the rate constants are found using a Arrhenius type equation:
changes with on efficiency factor for the kinetic set, and the second one is the wall heat transfer flux. The pressure losses are based on Bernoulli equation with a main correction with a friction factor.

### Fluid phase

**Continuity equation**
\[
\frac{d x_{CH_4}}{dz} = \frac{\Omega \left( \eta_1 r_1 + \eta_3 r_3 \right)}{F_{CH_4}^a}
\]
\[
\frac{d x_{CO_2}}{dz} = \frac{\Omega \left( \eta_2 r_2 + \eta_3 r_3 \right)}{F_{CH_4}^a}
\]

**Energy equation**
\[
\rho_g C_p u_s \frac{dT}{dz} = \rho_B \sum_1^3 \eta_i \left( -\Delta H_i \right) - 4 \frac{h_r}{d_r} (T - T_r)
\]

**Momentum equation**
\[
\frac{d p_s}{dz} = -f \frac{\rho_B u_s^2}{d_p}
\]

**Inlet conditions**
\[
x_{CH_4}^0, x_{CO_2}^0, T^0, p_t^0
\]

- The viscosity of water is obtained from the Chapman-Enskog theory [29].
- The overall heat transfer coefficient \( h_r \) is obtained from the Froment and Bischoff book (pp 404-405 [27]). It takes into account the effective thermal conductivity of the bed with no flow, see Kuni and Smith [30].
- The friction factor \( f \) is calculated from the Ergun’s equation [31].
- The average speed \( u_s \) is calculated from the total flow-rate:
\[
u_s = \frac{RT}{\rho_t} \frac{F_{total}}{\Omega}
\]

where \( \Omega \) is the reactor cross-sectional area.

Since the partial pressure gradients are limited to a very thin layer near the surface, planar geometry is studied. The reaction rates in the equations for solid phase are evaluated at the local partial pressures within the catalyst slab. Given the partial pressures of \( CH_4 \) and \( CO_2 \), all of the other concentrations can be found from the stoichiometry. The boundary conditions link the fluid phase and the solid phase.

### Solid phase

**Mass balance**
\[
D_{e,CH_4} \frac{d^2 p_{CH_4}}{dr^2} = \rho_s \frac{RT}{\Omega} (r_1 + r_3)
\]
\[
D_{e,CO_2} \frac{d^2 p_{CO_2}}{dr^2} = -\rho_s \frac{RT}{\Omega} (r_2 + r_3)
\]

**Boundary condition**
\[
\begin{align*}
\text{at } r = 0 & \quad \frac{d p_{CH_4}}{dr} = \frac{d p_{CO_2}}{dr} = 0 \\
\text{at } r = R_p & \quad p_{CH_4} = p_{CH_4,B} \quad p_{CO_2} = p_{CO_2,B}
\end{align*}
\]
Since effective diffusion coefficients \( D_{e,CH_4}, D_{e,CO_2} \) are not constant (given in appendix B), the classical analytical solution is not correct, see Levent et al [34]. Consequently, second derivative terms are evaluated by a classical centred scheme. New iterate is obtain by an application of the classical Taylor polynomial formula. Many numerical tests were done and 161 nodes to discretise mass balance are required to obtain a numerical stable solution (i.e. independent of the number of nodes).

2.3 STEAM REFORMER MODEL VALIDATION

By definition of the methane conversion variable, a unitary value means that the conversion is achieved for a length of the catalyst bed of 30 cm. The main parameters used in the simulation of the steam reformer are given in Table 3. As previously detailed, the conversion variables are plotted on figure 9.

Reformer data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of reformer tube</td>
<td>0.3 m</td>
</tr>
<tr>
<td>Inside diameter of reformer tube</td>
<td>0.10 m</td>
</tr>
<tr>
<td>Outside diameter of reformer tube</td>
<td>0.13 m</td>
</tr>
</tbody>
</table>

Catalyst data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst Pellet dimension</td>
<td>17 x 8 x 10 mm</td>
</tr>
<tr>
<td>Pellet porosity</td>
<td>0.5</td>
</tr>
<tr>
<td>Pellet equivalent diameter</td>
<td>7.5 mm</td>
</tr>
<tr>
<td>Pellet tortuosity</td>
<td>3.54</td>
</tr>
<tr>
<td>Solid catalyst density</td>
<td>2355 kg/m³</td>
</tr>
<tr>
<td>Catalyst bed density</td>
<td>1170 kg/m³</td>
</tr>
</tbody>
</table>

Table 3: Steam Reformer data

At the reformer exhaust, the mole fraction of hydrogen is near to 15% and carbon monoxide 4%. Figure 10 correspond to the 2D representation (length of catalyst bed and Pellet coordinate) of mole fraction of fuel (hydrogen and carbon monoxide) and inert gases (carbon dioxide and steam). This representation clearly shows that the dimensions of the catalyst Pellet are correct since an established state is obtained.

Figure 9. Evolution of molar fraction along catalyst bed

Figure 10. 2D-plot mole fraction versus length of catalyst bed \( z \) and radial grid \( r \) (pellet coordinate)

Allenby et al. [35] have achieved this system for natural gas fuelled engine with a length of catalyst bed of approximately 10 cm) and the reformer inlet temperature of 1000K. They tested three reactors and gave the measured outlet volumetric composition from the reformer. The presented model gives a good tendencies for each specie, see Figure 11.
3. RGR PREDICTION ON S.I. PERFORMANCES

The reformer gas recirculation is evaluated by successive numerical simulations. SI engine initial simulation is calculated on a fuel taken as natural gas. Those exhaust emissions are the inlet conditions for the fluid phase of steam reformer. The steam reformer exhaust is blended to natural gas for a new simulation of SI engine performance. This loop is stopped for two consecutive steam reformer exhaust compositions have a difference lesser than 0.5%. This stop criteria is commonly reached in 3 loops. The considered engine conditions are, weaker lean FAR (avoiding combustion defaults), Best Efficiency Spark Advance, 100% WOT.

Having of model for SI engine and reformer, it is possible to predict the interest of the steam reforming compared to other solution to decrease nitrous oxide in exhaust gas.

To add exhaust gas recirculation (i.e. a major blend of CO₂, H₂O and N₂) has an effect of dilution and then the in-cylinder temperature is globally lesser than without. As the mechanism of nitrous oxide depends on the formation temperature, less NOx are produced with an adding flowrate. Nevertheless, the reformer recirculation is of other nature since this gas is partially a fuel. Considering 20% of RGR volume flowrate as a limit, NOx decreasing is about 30% compared to the same EGR flowrate, see Figure 12. In-cylinder peak pressure is a common indicator to get an idea of SI performances. EGR and RGR concepts provide a significant NOx reduction with quasi-constant SI performances. Greater the RGR, greater the interest in comparison with classical EGR, see Figure 13.

CONCLUSIONS

Utilisation of reformed gas recirculation as a complement to natural gas is an opportunity to optimise the CHP engines in term of emissions.
“motoring cycle”. Tsolakis and Megaritis [5] reported that the high flame speed of hydrogen stabilise the propagation and consequently improve the performance. Secondly, using RGR the in-cylinder cycle to cycle dispersions are decreased (see Apostolescu and Chiriac [36]), this phenomena has its source from hydrogen use. Thirdly, to burn hydrogen must be implicated a decreasing of carbon dioxide emissions. One potential major negative aspect was not mentioned : the “knock combustion”. But, lean conditions are not favourable one. Although it is difficult to test in real conditions the RGR on a CHP plant for insurance aspect in a laboratory, more numerical studies could demonstrated the real interest of this concept.

REFERENCES


APPENDIX A: Two-zones thermodynamic model

The set of equations is summarised through the following 8 points, see Caton [37].

1/ Volume evolution

\[
V(\theta) = V_c + \frac{\pi B^2}{4} \left[ 1 + a(1 - \cos \theta) - \sqrt{1 - a^2 \sin^2 \theta} \right]
\]

2/ Inlet-Outlet Phase

\[
\frac{dm}{d\theta} = \delta_{valve} \frac{C_d A_{valve} P_{ust}}{\omega} \sqrt{\left( \frac{2\gamma}{(\gamma - 1)R T_{ust}} \right) R_p^{\gamma/\gamma} - R_p^{\gamma+1/\gamma}}
\]

3/ State equation

Unburnt gas: \( p V_u = m_u r_u T_u \)
Burnt gas: \( p V_b = m_b r_b T_b \)

4/ First law of thermodynamic

Unburnt gas:

\[
m_u C_v \frac{dT_u}{d\theta} = -p \frac{dV_u}{d\theta} - \frac{dQ_{p,u}}{d\theta} - u_u \frac{dm_u}{d\theta} - h_u \frac{dm_c}{d\theta}
\]

Burnt gas:

\[
m_b C_v \frac{dT_b}{d\theta} = -p \frac{dV_b}{d\theta} - \frac{dQ_{p,b}}{d\theta} - u_b \frac{dm_b}{d\theta} + h_u \frac{dm_c}{d\theta}
\]

5/ Mass burning rate:

Mass fraction of burnt gas, from Chmela et al [22]:

\[
\frac{dx_b}{d\theta} = \frac{\kappa}{1 + \lambda AFR \rho_b S_L} \left( \frac{\theta}{\omega} \right)^2 (1 - x_b)
\]

Laminar Speed from Rousseau [12] and Shahad Al-Janabi and Sadi Al-Baghadi [23]

\[
S_L = 965\eta_0 \frac{p_0}{\rho_0} ^{-0.623} e^{14.75} \left[ \frac{H_2}{air} \right]^{0.623} \left[ \frac{H_2}{air} \right]^{0.2145} \left[ \frac{H_2}{air} \right]^2 + \left[ \frac{H_2}{air} \right]^{1.4}
\]

6/ Lean burn combustion [12,38,39]

\[
\phi \text{ FAR } C_n H_\phi O_N + (0.79 N_2 + 0.21 O_2) \rightarrow \sum Y_j
\]

\[Y_j \in \{CO_2, H_2O, N_2, O_2, CO, H_2, H, O, OH, NO, N\}\]

Coupled with Extended Zeldovich Mechanism and Prompt Nox Model

7/ Physical properties [40]: Chemkin


APPENDIX B: Effective Diffusion Coefficient

The molecular diffusion coefficient of the species must be calculated, which depends on temperature and have both a molecular and a Knudsen diffusion component. In one hand, Knudsen diffusion coefficients are from the standard kinetic theory.

\[
D^K = \frac{d_p}{3} \sqrt{\frac{8 RT}{\pi M}}
\]

where \( d_p \) is the pore diameter. In other hand, molecular diffusion coefficients are from Cussler’s book [32] and are binary diffusion coefficients for CO2 in H2O and CH4 in H2O.

\[
D_{CH4}^m = 0.292 \left( \frac{T}{307.7} \right)^{1.5} \quad \text{and} \quad D_{CO2}^m = 0.202 \left( \frac{T}{307.5} \right)^{1.5}
\]

Composite diffusion coefficients \( D^B \) for each size range are obtained from geometric mean (called “Bosanquet formula”, see Zalc et al [33] of the ordinary and Knudsen diffusion coefficients.

\[
D_{CH4}^B = \left( \frac{1}{D_{CH4}^K} - \frac{1}{D_{CH4}^m} \right)^{-1}
\]

\[
D_{CO2}^B = \left( \frac{1}{D_{CO2}^K} - \frac{1}{D_{CO2}^m} \right)^{-1}
\]

for methane, respectively for carbon dioxide.

By introducing the porosity, or internal void fraction \( \varepsilon \), and the tortuosity \( \tau \), one gets the effective diffusion coefficient for each species, \( D_{e,CH4} \) and \( D_{e,CO2} \).

\[
D_{e,CH4} = D_{CH4}^B \frac{\varepsilon}{\tau} \quad \text{and} \quad D_{e,CO2} = D_{CO2}^B \frac{\varepsilon}{\tau}
\]