Predicting pollutant emissions in complex burners using Analytically Reduced Chemistry

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P. Pepiot. Cornell University

MUSAF III - 27-29 September 2016 - ONERA Toulouse
Challenge of pollutant prediction in gas turbines

- Stringent pollutant emissions standards
- Find the best compromise!

→ Development of new combustor technologies at higher pressure and temperature
→ Experiments rare and expensive at these operating points
→ Need for predictive numerical tool: Large Eddy Simulations (LES)
Context

Challenge of pollutant prediction in gas turbines

Flame and Pollutant chemistry

- Complex chemical processes
- Multiple Timescales

Combustor architecture

- Multiple combustion regime
- Complex flame structure

Combustor physics

- Thermal radiation
- Wall heat transfer

From Gas Turbine Emissions, 2013

Bauerheim et al. 2016

Wall radiative heat flux in an industrial combustor

Amaya PhD 2010
Challenge of pollutant prediction in gas turbines

Flame and Pollutant chemistry

- Complex chemical processes
- Multiple Timescales

Combustor architecture
- Multiple combustion regime
- Complex flame structure

Combustor physics
- Thermal radiation
- Wall heat transfer

→ Need for predictive tool: Large Eddy Simulations (LES) + accurate chemistry description

✓ Affordable CPU cost!

From Gas Turbine Emissions, 2013

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Wall radiative heat flux in an industrial combustor

Amaya PhD 2010
Real fuels are composed of dozens of compounds.

**Detailed real fuel chemistry**

- 100s of species + 1000s of elementary reactions

- Accurate predictions of flame propagation, quenching, auto-ignition, pyrolysis ...

- Large range of operating conditions

→ Too expensive for LES!
Real fuels are composed of dozens of compounds

Detailed real fuel chemistry

= 100s of species + 1000s of elementary reactions

- Accurate predictions of flame propagation, quenching, auto-ignition, pyrolysis ...
- Large range of operating conditions

- Too expensive for LES!

State-of-the Art in LES:

<table>
<thead>
<tr>
<th>Global fitted schemes</th>
<th>Tabulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Westbrook &amp; Dryer, 1981]</td>
<td>[FPI Gicquel, 2000]</td>
</tr>
<tr>
<td>« Global reactions » + Fitted Arrhenius</td>
<td>Store all chemistry information in tables</td>
</tr>
<tr>
<td>- From 5 to 7 species</td>
<td>- From 2 to 4 variables</td>
</tr>
</tbody>
</table>

- Global quantities ($S_i$, $T_{ad}$, ...)
- Easy to implement
- Small CPU requirements

- Small operating range
- Additional modelling efforts (dilution, ...)
- Only major species (Global schemes)
- Choice of representative flame (Tabulation)
Introduction of ARC

- Approach chosen at CERFACS: **Analytically Reduced Chemistry (ARC)**
  - Keep relevant chemical pathways, **no coefficient fitting**
  - Reduction from a detailed mechanism + a set of targets (species, HR, ...) :
    - **Two steps** using the reduction tool YARC (P. Pepiot, PhD thesis, Stanford University, 2008):

  1. **Skeletal reduction** = Elimination of unimportant species and reactions
     - DRGEP [Pepiot, C&F, 2008]
  2. **Analytical reduction** = Quasi Steady State (QSS) assumption \(\rightarrow\) elimination of species and stiffness
     - Level Of Importance [Lovas, PCI, 2000]
Approach chosen at CERFACS: **Analytically Reduced Chemistry (ARC)**

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- Access to quantities of interest
- No modelisation required
- Broad operating range
- Easy derivation
- Error control

→ CPU requirements?
Introduction of ARC

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→ ARC is dedicated to specific prediction purposes (pollutants, ignition/extinction, etc),
  defining the derivation targets
  → ARC cannot be taken from literature
  → It is necessary to have a methodology and a reduction tool
Specificity of NOx and CO chemistry

**NOx chemistry**

- « Prompt » NO
  - Fast formation
  - Strong interaction with radicals from the fuel oxidation chemistry
    \[ \text{N}_2 + \text{CH} \rightleftharpoons \text{NCN} + \text{H} \]
  - Significant in rich reactive regions

**CO chemistry**

- Fast formation in the flame
- Highly reactive precursors (HCO)
  \[ \text{HCO} + \text{M} \rightleftharpoons \text{H} + \text{CO} + \text{M} \]
Specificity of NOx and CO chemistry

**NOx chemistry**

- **Prompt NO**
  - Fast formation
  - Strong interaction with radicals from the fuel oxidation chemistry

\[
\text{N}_2 + \text{CH} \leftrightarrow \text{NCN} + \text{H}
\]

- Significant in rich reactive regions

- **Thermal NO**
  - Slow formation
  - Exponentially dependent on temperature

\[
\text{N}_2 + \text{O} \leftrightarrow \text{NO} + \text{N}
\]

- Significant in hot regions

- \( \text{N}_2\text{O} \) pathway etc.

**CO chemistry**

- Fast formation in the flame

- Highly reactive precursors (HCO)

\[
\text{HCO} + \text{M} \leftrightarrow \text{H} + \text{CO} + \text{M}
\]

- Relatively slower destruction by oxidation into CO\(_2\) in the post-flame region

\[
\text{OH} + \text{CO} \leftrightarrow \text{H} + \text{CO}_2
\]

MUSAF III - 27-29 September - ONERA, Toulouse
• Example of ARC derivation and validation: methane-air canonical flames

• Application to the prediction of NOx and CO in a labscale flame: the turbulent SANDIA-D jet flame

• Application to the prediction of NOx and CO in a labscale combustor: the methane-air SGT-100 configuration

• Application to the prediction of soot precursors in a labscale combustor: the ethylene-air ISF3¹ configuration

• Towards heavy and complex fuels
Example of ARC derivation and validation: methane-air canonical flames

- Objective: build a scheme for methane-air able to accurately reproduce NO and CO formation

- Target problem
  - Premixed flame: $\varphi=0.6 \rightarrow 1.4$
  - Target conditions: 1 bar, 300K

- Target quantities:
  - Global quantities: flame speed
  - Local quantities: Heat release, CO and NO concentrations

Detailed Chemistry
GRI-2.11

ARC_22_GRI211
(22 transported species + 18 QSS species)
**Example of ARC derivation and validation: methane-air canonical flames**

- **Objective:** build a scheme for methane-air able to accurately reproduce NO and CO formation

  → Major **chemical pathways** are included in the **ARC_22_GRI211**

**Example for NOx chemistry:**

<table>
<thead>
<tr>
<th>Transported</th>
<th>NOx chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO NO2 HCN N2O</td>
<td></td>
</tr>
</tbody>
</table>

| QSS           | N NH NNH HNO NH2 NCO HCNO HNCO HOCN |

- **Thermal pathway**
- **Prompt pathway**
- **N2O pathway**

**Detailed Chemistry**

**GRI-2.11**

**YARC**

**ARC_22_GRI211**

(22 transported species + 18 QSS species)
Example of ARC derivation and validation: Unstrained methane-air premixed flames

**300 K, 1 bar (Scheme derivation conditions)**

![Graphs showing temperature profiles](image)
Example of ARC derivation and validation: Unstrained methane-air premixed flames

300 K, 1 bar (Scheme derivation conditions)

680 K, 3-6 bars (Gas turbine conditions)

GRI2.11: 3 bars (—) and 6 bars (---)
ARC_22_GRI211: 3 bars (O) and 6 bars (□)

Accurate description far beyond the range of derivation
Example of ARC derivation and validation: Strained non-premixed methane-air flames

Rich air-fuel mixture ($\phi=3.2$, $T=300$ K)

Air ($\phi=0$, $T=300$ K)

Accurate response to strain although it is not part of the target canonical case
Application to the prediction of NOx and CO in a labscale flame: the turbulent SANDIA-D jet flame

Configuration

- Highly resolved LES of the Sandia D flame
  - Turbulent non-premixed flame (Barlow, PCI 1998)
- 3 coaxial jets:
  - Main: methane-air mixture, \( \varphi = 3.2, T = 300 \) K
  - Pilot: burnt gases, \( \varphi = 0.77, T = 1900 \) K
  - Co-Flow: fresh air, \( T = 300 \) K

Numerical setup

- AVBP solver
- Numerical grid: 375 million elements
- Direct resolution on the grid using ARC_22_GRI211
Application to the prediction of NOx and CO in a labscale flame: the turbulent SANDIA-D jet flame
Application to the prediction of NOx and CO in a labscale combustor: the methane-air SGT-100

Experimental data available:
- PIV
- 1D Raman
- OH PLIF
- Exhaust pollutant concentrations

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>Case A</th>
<th>Case B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>3 bars</td>
<td>6 bars</td>
</tr>
<tr>
<td>Temperature</td>
<td>680 K</td>
<td>680 K</td>
</tr>
<tr>
<td>Air mass flow rate</td>
<td>183.8 g/s</td>
<td>338 g/s</td>
</tr>
<tr>
<td>Fuel mass flow rate</td>
<td>6.24 g/s</td>
<td>12.8 g/s</td>
</tr>
<tr>
<td>Global equivalence ratio</td>
<td>0.52</td>
<td>0.59</td>
</tr>
</tbody>
</table>

- Siemens burner studied experimentally in high pressure DLR test-rig (Stopper et al. CF 2013)
- Previous LES study by Bulat et al. CF 2014
Application to the prediction of NOx and CO in a labscale combustor: the methane-air SGT-100

Reactive flow topology:

- Mean axial velocity [m/s]
- RMS axial velocity
- Mean temperature [K]
- RMS temperature

CERFACS

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Application to the prediction of NOx and CO in a labscale combustor: the methane-air SGT-100

- Flame structure
  
  **Exp: OH PLIF**  **LES: OH Concentration**  **LES: Heat release rate**

  **Case A**
  
  Outer flame branch:
  - Case A: intermittent burning
  - Case B: no burning

  **Case B**
  
  Inner flame branch:
  - Higher intensity in Case B closer to injector
Application to the prediction of NOx and CO in a labscale combustor: the methane-air SGT-100

- Comparison of exhaust pollutant concentrations with measurements

**NO**
- Satisfactory prediction
- Slight under-prediction
- Trend correctly recovered

**CO**
- Significant over-prediction
- Trend correctly recovered
Application to the prediction of NOx and CO in a labscale combustor: the methane-air SGT-100

- Comparison of exhaust pollutant concentrations with measurements

- Easy implementation and combination with turbulent combustion model (DTFLES) for LES of complex geometries
- Capacity to reproduce complex flame structure and change in operating conditions
- Strong potential to predict pollutant emissions
Application to the prediction of soot precursors in a labscale combustor: the ethylene-air ISF3

- Pressurised test rig installed at DLR (Germany) part of the ISF test cases [Geigle et al., J. Eng. Gas Turb. and Power, 2013]:
  - Ethylene (C\textsubscript{2}H\textsubscript{4}) combustion
  - Non-premixed complex injection system: two co-rotating swirlers
  - Very thin fuel injection nozzle (0.4 mm)
  - 4 dilution holes after 2/3 of the chamber’s length
  - Large quartz optical access

- Experimental data available:
  - PIV (FoV and SoC)
  - Planar-LIF on OH
  - CARS (temperature)
  - Soot volume fraction
Application to the prediction of soot precursors in a labscale combustor: the ethylene-air ISF3

- ARC derivation
  - Objective: build a scheme for ethylene-air able to accurately reproduce **C2H2** intermediate (soot precursor)

- Target problem
  - Premixed flame: \( \varphi = 0.5-1.5 \)
  - Target conditions: 3 bar, 300K

- Target quantities:
  - Global quantities: flame speed
  - Local quantities: Heat release, \( \text{CO}_2 \), \( \text{CO} \), \( \text{OH} \), \( \text{C2H2} \) concentrations

**Detailed Chemistry**
K. Narayanaswamy *et al.* [C&F, 2010]
(158 species & 1049 reactions)

**YARC**

**ARC_14_C2H4NARA**
(14 transported species)
Application to the prediction of soot precursors in a labscale combustor: the ethylene-air ISF3

- ARC derivation
  → Objective: build a scheme for ethylene-air able to accurately reproduce \( \text{C}_2\text{H}_2 \) intermediate (soot precursor)

- Target problem
  → Premixed flame: \( \varphi = 0.5 - 1.5 \)
  → Target conditions: 3 bar, 300K

- Target quantities:
  → Global quantities: flame speed
  → Local quantities: Heat release, \( \text{CO}_2, \text{CO}, \text{OH}, \text{C}_2\text{H}_2 \) concentrations

✓ A posteriori validation in canonical cases:
  ✓ 300 – 700 K, 1-3 bar, Phi 0.5 – 2.0
  ✓ Premixed unstrained flames
  ✓ Non-premixed strained flames

Detailed Chemistry
K. Narayanaswamy et al. [C&F, 2010] (158 species & 1049 reactions)

ARC_14_C2H4NARA
(14 transported species +6 QSS species)

<table>
<thead>
<tr>
<th>Transported species</th>
<th>QSS species</th>
</tr>
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<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>( \text{HCO} )</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>( \text{CH}_2 )</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>( \text{C}_2\text{H}_5 )</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>( \text{C}_2\text{H}_3\text{HO}_2 )</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>( \text{H}_2\text{O}_2 )</td>
</tr>
<tr>
<td>( \text{OH} )</td>
<td>( \text{CH}_3 )</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>( \text{CH}_3 )</td>
</tr>
<tr>
<td>( \text{CH}_3\text{O} )</td>
<td>( \text{CH}_3\text{O}_2 )</td>
</tr>
</tbody>
</table>
Application to the prediction of soot precursors in a labscale combustor: the ethylene-air ISF3

- Temperature field:

![Image of temperature field]

- **Temperature vs. Axial position**:
  - Z=12 mm
  - Z=18 mm

- **Experiment**
  - Tmean=1358K, Sigma=483K, Temp=795K

- **Expe**
  - 2S_C2H4_BFER
  - ARC_14_C2H4ANA

- ✓ 2S_C2H4_BFER flame is shorter → consistent with 1-D laminar predictions [Franzelli, CRM, 2010]
- ✓ Overall good agreement with experiments
Application to the prediction of soot precursors in a labscale combustor: the ethylene-air ISF3

- OH and C2H2 species using ARC_14_C2H4NARA

→ **OH**: similar structures and levels to OH-PLIF measurements:
  - High levels in flame fronts
  - Flame fronts signature due to secondary air injection throughout the chamber

→ **C2H2**: included in the ARC_14_C2H4NARA, directly usable as precursor for soot formation and transport
Conclusions

• **ARC is flexible** → control of maximum error on targeted quantities
• **ARC shows an excellent behavior** in canonical configurations (1-D) even out of derivation range
• **ARC is easy to implement** and to combine with turbulent combustion model (DTFLES) → no further modelling required, no stiffness
• **ARC has a strong potential for pollutant prediction** (NOx, CO, soot precursors)
• **ARC keeps a limited number of species** which does not increase too much with the fuel hydrocarbon size:
  → CH4 including NOx: 22 / C12H26 including NOx = 26
  → CPU overcost does not exceed 2.5 times the CPU required using global two-step schemes

➔ **Toward “real” fuel blends ?**
Toward real fuel blends

- Collaboration with Stanford University and Cornell university
  [Felden et al., Proc. of the CTR, 2016]

<table>
<thead>
<tr>
<th></th>
<th>3 COMP surrogate approach</th>
<th>HYCHEMA approach (Pr H. Wang, Stanford)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jet-A fuel surrogate</td>
<td>• 30.3% ndodecane</td>
<td>Single component surrogate POSF10325</td>
</tr>
<tr>
<td></td>
<td>• 21.2% Mxylene</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• 48.5% iso-octane</td>
<td></td>
</tr>
<tr>
<td>Detailed mechanism</td>
<td>261 species</td>
<td>112 species</td>
</tr>
<tr>
<td>Model type</td>
<td>Chemistry-based</td>
<td>Physics-based</td>
</tr>
<tr>
<td></td>
<td>Represent the major</td>
<td>Developed from shock-</td>
</tr>
<tr>
<td></td>
<td>hydrocarbon classes</td>
<td>tube experiments</td>
</tr>
<tr>
<td>Resulting reduced</td>
<td>50 species (still too</td>
<td>27 species, no stiffness</td>
</tr>
<tr>
<td>mechanism</td>
<td>large for LES...)</td>
<td>(affordable for LES!)</td>
</tr>
</tbody>
</table>

→ HYCHEMA mechanism **much** easier to reduce than multi-component surrogate approach!
Toward real fuel blends

- **LDI (NASA) configuration:**
  - Operating conditions:
    - Atmospheric
    - Liquid Jet A2
    - $T_g, T_p = 300K$
  - Measurements available:
    - Temperature
    - CO / CO2 / H2O
    - Velocity

- **Preliminary results:**
  - [Graphs showing temperature, water mass fraction, and CO mass fraction]

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Thanks for your attention!
Perspectives: application to real fuels

- Applicable and not costly to monocomponent surrogate fuels

→ Example: Do-decane (nC12H26) used as jet fuel surrogate
  
  → Derivation from JetSurf -1.0 -l [1] kinetics scheme:
    
    27 transported species in the resulting mechanism: $ARC_27_JETSURF$

- Comparison one 1D premixed flame in LEMCOTEC conditions (high pressure and temperature)

![Graphs showing comparisons between DAGAUT, LUCHE, JetSurf, and ARC_27_JETSURF](image)

Isolated pockets of high CO concentrations

More significant in corners

Perspectives: application to real fuels

Isovolume of CO mass fraction
inside the LEMCOTEC combustor and at the exit plane

Radially **staged multipoint injector**

Experimental campaign performed on a mono-sector test rig at ONERA [1]

- Large range of operating conditions
- Pressure, fuel-staging