Abstract:

The numerical prediction of pollutant emissions or bio-fuel flame structure in industrial combustors such as aeronautical engines, ground-based gas turbines or furnaces, requires an accurate description of combustion chemistry. Such precision may be achieved with detailed chemical kinetics mechanisms which have been developed in order to accurately capture all the details of the combustion process over a wide range of thermodynamic conditions. However, these mechanisms involve many species and reactions, making them too expensive for numerical simulation of 3D industrial cases. One solution to this problem is to reduce the complexity by targeting a specific operating range of temperature, pressure, and equivalence ratio, representative of the real case, as well as specific species that are of importance if one wants to account for NOx or soot production for example. Such reduced mechanisms have been successfully derived using the multi-stage reduction code YARC [1] with the following procedure. First, Direct Relation Graph with Error Propagation (DRGEP) [2] is applied on species and reactions with specified species as targets (typically fuel, oxidizer, and pollutants of interest), followed by chemical lumping, resulting in a skeletal mechanism accounting for the relevant species and reactions only. Finally, a timescale analysis along with DRGEP is used to identify species that can be set in Quasi-Steady State (QSS) in order to further speed up the calculation.

In collaboration with Pr. P. Pepiot, a new automatic reduction tool called ARCANE has been developed to make it more efficient, more flexible and easier to use. ARCANE relies on the Cantera chemistry solver [3] and is written in Python language. ARCANE tool has been benchmarked against YARC on canonical cases validating it.

This talk will first present the main features of ARCANE. Then, an example of reduction for methane-air combustion will be presented. Analytically Reduced Chemistries (ARC) first compared to detailed mechanisms on 0D reactor and 1D flame configurations in the target operating range, and confirm that the error induced by the reduction is small enough to correctly capture important features such as intermediate species profiles, ignition delay time and laminar flame speed. Finally, several strategies to model complex fuels such as kerosene in the scope of Large Eddy Simulation (LES) will be presented: n-decane (C_{10}H_{22}) as a mono-component surrogate of kerosene, the HyChem mono-component model [4,5] but accounting for the full composition of kerosene, and finally the multi-component approach. This latter is necessary to study the impact of alternative fuel addition to Jet A1 on the operability of an aeronautical combustor, which is one main objective of the H2020 JETSCREEN European project.

Development of an automatic tool for the reduction of complex fuels chemical kinetics

Quentin Cazères, 2nd year PhD
CERFACS

Advisors : Eléonore Riber, Bénédicte Cuenot
Why do we need complex chemistry?

L'impact de l'aéroport sur la pollution de l'air
Part des activités aéroportuaires sur les émissions de polluants atmosphériques et de gaz à effet de serre sur le territoire

<table>
<thead>
<tr>
<th>Émissions</th>
<th>Toulouse Métropole</th>
<th>Aéroport</th>
<th>Aéronefs</th>
<th>Activités au sol</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>95%</td>
<td>87%</td>
<td>13%</td>
<td>5%</td>
</tr>
<tr>
<td>PM10</td>
<td>98%</td>
<td>89%</td>
<td>11%</td>
<td>2%</td>
</tr>
<tr>
<td>PM2.5</td>
<td>98%</td>
<td>86%</td>
<td>14%</td>
<td>2%</td>
</tr>
<tr>
<td>GES</td>
<td>97%</td>
<td>86%</td>
<td>14%</td>
<td>3%</td>
</tr>
</tbody>
</table>

5% des émissions de NOx
2% des PM10 et des PM2.5
3% des émissions de GES

Sur Toulouse Métropole, l'activité aéroportuaire représente

Aéroport de Toulouse Blagnac

Can only be predicted if complex chemistry is accounted for in CFD solvers

Source : Atmo-occitanie (modélisation sur un an à partir de mesures effectuées en 2013)
Why do we reduce chemistry?

Number of equations to solve = \(5 + N_S\) Chemistry

Mass \((\rho)\), Momentum \((\rho u, \rho v, \rho w)\), Energy \((\rho E)\)

Simplest detailed mechanism: \(\text{H}_2 + \text{air} \rightarrow N_S = 12\)

\[\text{H}_2 \quad \text{H} \quad \text{O}_2 \quad \text{OH} \quad \text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O}_2 \quad \text{N}_2\]

Intensively used mechanism GRI Mech 3.0: Methane + air \(\rightarrow N_S = 53\)

\[\text{H}_2 \quad \text{H} \quad \text{O}_2 \quad \text{OH} \quad \text{O}_2 \quad \text{H}_2\text{O}_2 \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \quad \text{CH}_2(\text{S}) \quad \text{CH}_3 \quad \text{CH}_4 \quad \text{CO} \quad \text{CO}_2 \quad \text{HCO} \quad \text{CH}_2\text{O} \quad \text{CH}_2\text{OH} \quad \text{CH}_3\text{O} \quad \text{CH}_3\text{OH} \quad \text{C}_2\text{H}_2 \quad \text{C}_2\text{H}_3 \quad \text{C}_2\text{H}_4 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_6 \quad \text{HCCO} \quad \text{CH}_2\text{O} \quad \text{HCCOH} \quad \text{N} \quad \text{NH} \quad \text{NH}_2 \quad \text{NH}_3 \quad \text{NNH} \quad \text{NO} \quad \text{NO}_2 \quad \text{N}_2\text{O} \quad \text{HNO} \quad \text{CN} \quad \text{HCN} \quad \text{H}_2\text{CN} \quad \text{HCN}\text{N} \quad \text{HCNO} \quad \text{HOCN} \quad \text{HNCO} \quad \text{NCO} \quad \text{N}_2 \quad \text{AR} \quad \text{C}_3\text{H}_7\]

Mechanism for biodiesel + air \(\rightarrow N_S = 3299\)

Not going to show that!
ARC methodology

ARCANE: new reduction tool
- Presentation
- Examples

ARC for kerosene modelling

Conclusion and PhD continuation
**Detailed mechanism**

> 100 species, 1000 reactions

- Does everything
  - You can study species you never knew existed
  - Too expensive for most people

**ARC**

~ 20 species, 200 reactions

- Tailored for your needs
  - Basic combustion features
  - Pollutants ($CO, NO_x, soot$)
  - Affordable

**Global**

6 species, 2 reactions

- Does the job
  - Laminar flame speed
  - Adiabatic flame temperature
  - Cheap
3 main reduction techniques:

Direct Relation Graph (DRG):

Contribution of A to the production of B

Chemical lumping:

\[ [S_1] + [S_2] = [S_{lumped}] \]

\[ [S_1] \xrightarrow{k_1} [S_3] \]

\[ [S_2] \xrightarrow{k_2} [S_4] \]

Quasi-Steady State Assumption (QSSA):

\[ \frac{d[S_{QSS}]}{dt} \approx 0 \]

Set of linear equations to compute \( [S_{QSS}] \)
\( \rightarrow S_{QSS} \) is no longer transported and its equation is no longer solved
All reductions at CERFACS were performed with the YARC reduction tool (P. Pepiot’s PhD thesis)

In Collaboration with Pr. Perrine Pepiot (Cornell University)

→ New reduction tool:

**ARCANE**

Analytically Reduced Chemistry: Automatic, Nice and Efficient

Relying on Cantera chemistry solver and written in Python:

- Compatible with CERFACS version of Cantera tailored for its needs
- User friendly language (python) for feature implementation
ARCANE: Presentation

ARCANE structure

detailed mechanism

reduced mechanism 1

...  

Cantera  

reduced mechanism n

0D and 1D data

0D and 1D data

0D and 1D data

% error ($S_l, T_{ad}, Y_k, ...$)

if error < tolerance

if error > tolerance

ARCANE

reduced mechanism 1

reduced mechanism 2

...  

ARC = reduced mechanism n - 1
Same reduction methods as YARC based on FlameMaster

+ Functions used for the reduction process can be used independently for deep kinetics insight

+ Use through python allowing direct pre/post-processing

+ The full reduction process is made automatic

+ Reduction possible on every case that you can create on Cantera (complex reactor Network with valves and flow controllers)

+ Output f90 files for AVBP use
Target cases:
- 0D isochoric reactor $T = 1000$ K, $P = 1$ bar, $\phi = 1$
- 1D premixed freely propagating flame $T = 400$ K, $P = 1$ bar, $\phi = 0.6, 1, 1.6$

Reduction targets: $CH_4, CO_2, CO$, Heat Release

Error evaluation:
- ignition delay time for 0D case
- laminar flame speed for 1D cases

Initial mechanism: GRI Mech 3.0: 53 species, 325 reactions

ARC: 22 transported species, 7 QSS species, 165 reactions
ARCANE : Example

Methane-air combustion case

Derivation configuration
+ operational conditions of derivation

Same configuration BUT
High pressure

ARC chemistry is robust to operational conditions
ARCANE: Example

Methane combustion case

ARC chemistry robust to configuration
Time spent between pressing “enter” and results = 15 minutes
Sandia Flame D (methane + air)
*Thomas Jaravel’s PhD thesis*

KIAI burner ignition (n-heptane + air)
Kerosene is a complex blend of many hydrocarbon species

Adapted from http://www.dlr.de/
Chemical Analytics Group
Pericles study (for SAFRAN)

Fuel: Decane (C10H22) as kerosene surrogate

<table>
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<tr>
<th>Designation</th>
<th>Pressure [Pa]</th>
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<tr>
<td>LowP</td>
<td>338 000</td>
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<td>HighP</td>
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Transported species

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<th>Species</th>
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<th>QSS</th>
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<td>680</td>
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<tr>
<td>ARC</td>
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<td>255</td>
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Designation: LowP, HighP

Temperature [K]
- LowP: 0, 500, 1000, 1500, 2000, 2500
- HighP: 20, 15, 10, 5, 0

Position [m]
- LowP: 0, 0.05, 0.1, 0.15, 0.2
- HighP: 0, 5x10^-3, 8, 6, 4, 2

Mass fraction [-]
- LowP: 0, 5x10^-3
- HighP: 0, 5x10^-3

---

Pericles study (for SAFRAN)

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ARC for kerosene modelling

Single component fuel

Temperature [K] vs. Equivalence ratio [-] for different models:
- Skeletal_Luche
- ARC_LP
- ARC_HP
- ARC_ALLP

Laminar flame speed [m/s] vs. Equivalence ratio [-] for different models:
- Skeletal_Luche
- ARC_LP
- ARC_HP
- ARC_ALLP

[Graphs showing temperature and laminar flame speed for different equivalence ratios and models.]
HyChem model for Jet-A POSF10325:

Assumption: Any fuel would first decompose into a handful of small molecules → Radical build-up and heat release rate ~ distribution of those pyrolysis products

Transported species:
- POSF10325: H, H2, O, OH, O2, H2O, H2O2, HO2, CO, CH2O, C2H2, CH3, CO2, CH4, C2H4, C2H6, CH2CO, C3H6, I-C4H8, C5H6, C6H6, C7H8, C6H5O, C6H4O2, NO, HCN, NO2

QSS species:
- CH, HCO, CH2, CH2*, CH3O, C2H5, C2H3, HCCO, A-C3H5, CH2CHO, C6H5, N, NCO, H2CN, CN, NH, HNO

* from Anne Felden’s PhD thesis
ARC for kerosene modelling

HyChem model

* from Anne Felden’s PhD thesis
In literature, Jet A best represented by a three component surrogate [1]

- n-dodecane
- Methylcyclohexane
- Xylene

- The HyChem model requires pyrolysis data and cannot account for multi-components evaporation.

- This model was used because YARC was not able to reduce enough the multi-component fuel to a “LES-friendly” size (< 60 species in the skeletal mechanism)

→ **Better results expected with ARCANE** because its flexibility will allow more complex reductions
  - easier analysis of kinetics data
  - new reduction algorithms can be implemented (PCA, CSP, ...)
  - more accurate error assessment
My PhD:

PhD financed by the JETSCREEN European project (CERFACS, DLR, Safran AE, Safran Tech, ...)

This project aims at creating a platform comparing alternative jet fuels at classical ones on many aspects (Ignition, Lean Blow Out and Thermo-acoustic instabilities).

Alternative fuels addition:

Jet A1 + $C_x H_y O_z$ $\rightarrow$ more difficult because pyrolysis step will no be similar

Multi-component approach will be needed as no single component surrogate is possible
Conclusions and PhD continuation

**Improved reduction tool, ARCANE**

- No need for advanced chemical kinetics knowledge for reducing simple fuels
- Easier reduction of complex multi-component fuels
- Better control of the error metric
- More insight on the reduction process
- Reduction on non-classical cases (Complex reactor networks)

**Multi-component ARC is the next step in complex chemistry modelling**
In the following of my PhD:

- Study of chemistry modelling effects on two-phase flames (1D cases) with AVBP
- Study of ignition in the MERCATO configuration (ONERA) with ARC chemistry of alternative fuels
CERFACS Chemistry website [https://chemistry.cerfacs.fr/en/](https://chemistry.cerfacs.fr/en/)


Chemical kinetics mechanisms database available

Still work in progress for the tutorials and scripts sharing
Mechanisms list

Here is a list of every mechanism available on this website

**Detailed mechanisms:**

- GRI-Mech 3.0 (53 species and 325 reactions)
- GRI-Mech 2.11 (49 species and 279 reactions)
- San Diego (57 species in 268 reactions)
- USC II (111 species and 784 reactions)
- Wang (75 species and 529 reactions)
- Curran (1034 species and 8453 reactions)
- Anderhor (536 species and 3000 reactions)
- Jerzembeck (203 species and 1001 reactions)
- Dagaut (225 species and 1800 reactions)
- JetSurf (348 species and 2163 reactions)
- Narayanaswamy (362 species and 1861 reactions)

**Skeletal mechanisms:**

- Bovin (9 species and 12 reactions)
- Frassoldati (10 species and 6 reactions)
- Lu methane (30 species, 184 reactions)
- Sankaran (17 species, 73 reactions)
- Lu ethylene (32 species and 206 reactions)
- Peters propane (31 species and 107 reactions)
- C3H8_34_173_FC (34 transported species, 173 reactions)
Thank you,

Do you have any questions?

Acknowledgements:

Jonathan Wirtz, Lucas Esclapez for the Pericles configuration