SIMULATION OF DIESEL SCR AFTERTREATMENT WITH CFD USING DETAILED CHEMISTRY

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* REACTION DESIGN

Fourth DOE Crosscut Workshop on Lean Emissions Reduction
Simulation: Selective Catalytic Reduction of NOx with Urea/Ammonia
DIESEL EXHAUST AFERTREATMENT

- Increasingly stringent limits are being placed on diesel emissions.
- In order to meet these limits, it is generally agreed that a combination of aftertreatment devices will be required, including perhaps:
  - Catalyzed Soot Filters (CSF).
  - Selective Catalytic Reduction (SCR).
  - Lean NOx Traps (LNT).
- Most of these approaches use catalysts – thus, a means of using detailed surface chemistry in analyzing these systems may be desired.

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THE CHEMKIN COLLECTION

- A SET OF TOOLS DESIGNED TO MODEL COMPLEX CHEMICAL KINETIC PROCESSES.
- CHEMKIN APPLICATIONS ARE PROGRAMS BUILT FROM THESE TOOLS TO REPRESENT SPECIFIC REACTOR TYPES, E.G., PSR (AURORA).
- THE CHEMKIN COLLECTION IS A PRODUCT OF REACTION DESIGN.

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STAR-CD + CHEMKIN

While very useful for many situations, the idealized reactor models in the CHEMKIN collection do not allow complex geometries to be simulated and are unable to treat many physical processes of interest, e.g., sprays, in aftertreatment problems.

The solution: combine CHEMKIN-derived coupled chemistry solvers with STAR-CD, a general-purpose commercial CFD package.
WHAT IS STAR-CD?

- STAR-CD IS A GENERAL PURPOSE COMMERCIAL CFD CODE FOR FLOWS INCLUDING TURBULENCE, SPRAYS, AND CHEMISTRY:
  - STAR-CD HAS A VARIETY OF BUILT-IN CHEMISTRY OPTIONS, INCLUDING EDDY BREAK-UP, PRESUMED PDF, AND FLAME AREA MODELS – WITH CHEMKIN, DETAILED SURFACE AND GAS PHASE CHEMISTRY AS WELL.
  - SPRAYS CAN BE TREATED WITH EULERIAN OR LAGRANGIAN METHODOLOGIES WITH SUB-MODELS FOR BREAK-UP, COLLISION, TURBULENT DISPERSION, WALL IMPINGEMENT/FILM, ETC.
  - TURBULENCE CAN BE TREATED WITH MODELS FROM $k$-, TO LES.
- AUTOMATED GENERATION OF FULLY UNSTRUCTURED MESHES – TETS TO CLIPPED HEXS – WITH ARBITRARY MATCHING, ETC.
STAR-CD + CHEMKIN

- THE CD-ADAPCO GROUP HAS TEAMED WITH REACTION DESIGN TO COMBINE CHEMKIN AND SURFACE CHEMKIN COUPLED CHEMISTRY TECHNOLOGY WITH STAR-CD.

- STAR-CD + CHEMKIN FEATURES:
  - TRANSIENT AND STEADY STATE CHEMKIN-DERIVED SOLVERS FOR:
    - GAS PHASE CHEMISTRY.
    - SURFACE CHEMISTRY.
  - CHEMKIN-BASED THERMAL AND TRANSPORT PROPERTIES

- BETA TESTING AND PRODUCTION ANALYSES BY INTERNAL AND EXTERNAL USERS UNDERWAY.

- GENERAL RELEASE SCHEDULED FOR LATER THIS YEAR.
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Simulation: Selective Catalytic Reduction of NOx with Urea/Ammonia
THREE-WAY CATALYTIC CONVERTER

MODELING SINGLE CHANNEL IN MONOLITH

SURFACE CHEMISTRY MECHANISM INCLUDES:
- 9 GAS-PHASE SPECIES
- 22 SURFACE-SITE SPECIES
- 53 SURFACE REACTIONS

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# THREE-WAY CATALYTIC CONVERTER

## SURFACE MECHANISM ON Pt

### 1. ADSORPTION

\[
\begin{align*}
O_2 + Pt(S) + Pt(S) &\rightarrow O(S) + O(S) \\
C_3H_6 + Pt(S) + Pt(S) &\rightarrow C_3H_6(S) \\
H_2 + Pt(S) + Pt(S) &\rightarrow H(S) + H(S) \\
H_2O + Pt(S) &\rightarrow H_2O(S) \\
CO_2 + Pt(S) &\rightarrow CO_2(S) \\
CO + Pt(S) &\rightarrow CO(S) \\
NO + Pt(S) &\rightarrow NO(S) \\
NO_2 + Pt(S) &\rightarrow NO_2(S)
\end{align*}
\]

### 2. DESORPTION

\[
\begin{align*}
O(S) + O(S) &\rightarrow Pt(S) + Pt(S) + O_2 \\
C_3H_6(S) &\rightarrow C_3H_6 + Pt(S) + Pt(S) \\
H(S) + H(S) &\rightarrow H_2 + Pt(S) + Pt(S) \\
H_2O(S) &\rightarrow Pt(S) + H_2O \\
CO(S) &\rightarrow CO + Pt(S)
\end{align*}
\]

### 3. SURFACE REACTIONS

\[
\begin{align*}
CO_2(S) &\rightarrow CO_2 + Pt(S) \\
NO(S) &\rightarrow NO + Pt(S) \\
NO_2(S) &\rightarrow NO_2 + Pt(S) \\
N(S) + N(S) &\rightarrow N_2 + Pt(S) + Pt(S) \\
C_3H_6(S) &\rightarrow C_3H_6(S) + H(S) \\
C_3H_5(S) + H(S) &\rightarrow C_3H_6(S) \\
C_2H_5(S) + Pt(S) &\rightarrow C_2H_3(S) + CH_2(S) \\
C_2H_3(S) + CH_2(S) &\rightarrow C_3H_5(S) + Pt(S) \\
C_2H_3(S) + Pt(S) &\rightarrow CH_3(S) + CH_2(S) \\
CH_3(S) + C(S) &\rightarrow C_2H_3(S) + Pt(S) \\
CH_3(S) + O(S) &\rightarrow CH_2(S) + OH(S) \\
CH_2(S) + CH_2(S) &\rightarrow CH_3(S) + O(S) \\
CH_2(S) + OH(S) &\rightarrow CH_3(S) + O(S) \\
CH(S) + OH(S) &\rightarrow CH_2(S) + O(S) \\
CH(S) + O(S) &\rightarrow C(S) + OH(S) \\
C(S) + OH(S) &\rightarrow CH(S) + O(S) \\
CH_3(S) + OH(S) &\rightarrow CH_2(S) + H_2O(S) \\
CH_2(S) + H_2O(S) &\rightarrow CH_3(S) + OH(S) \\
CH_2(S) + OH(S) &\rightarrow CH(S) + H_2O(S) \\
CH(S) + H_2O(S) &\rightarrow CH_2(S) + OH(S) \\
CH(S) + OH(S) &\rightarrow C(S) + H_2O(S) \\
C(S) + H_2O(S) &\rightarrow CH(S) + OH(S) \\
O(S) + H(S) &\rightarrow OH(S) + Pt(S) \\
OH(S) + Pt(S) &\rightarrow O(S) + H(S) \\
H(S) + OH(S) &\rightarrow H_2O(S) + Pt(S) \\
H_2O(S) + Pt(S) &\rightarrow H(S) + OH(S) \\
OH(S) + OH(S) &\rightarrow H_2O(S) + O(S) \\
H_2O(S) + O(S) &\rightarrow OH(S) + OH(S) \\
CO(S) + O(S) &\rightarrow CO_2(S) + Pt(S) \\
CO_2(S) + Pt(S) &\rightarrow CO(S) + O(S) \\
C(S) + O(S) &\rightarrow CO(S) + Pt(S) \\
CO(S) + Pt(S) &\rightarrow C(S) + O(S) \\
NO(S) + Pt(S) &\rightarrow N(S) + O(S) \\
N(S) + O(S) &\rightarrow NO(S) + Pt(S)
\end{align*}
\]
THREE-WAY CATALYTIC CONVERTER

SURFACE MECHANISM ON Rh

1. ADSORPTION

O₂ + Rh(S) + Rh(S) → O(S) + O(S)
CO + Rh(S) → CO(S)
NO + Rh(S) → NO(S)

2. DESORPTION

O(S) + O(S) → O₂ + Rh(S) + Rh(S)
CO(S) → CO + Rh(S)

3. NO(Rh) SURFACE REACTIONS

NO(S) → NO + Rh(S)
N(S) + N(S) → N₂ + Rh(S) + Rh(S)
CO(S) + O(S) → CO₂ + Rh(S) + Rh(S)

NO(S) + Rh(S) → N(S) + O(S)


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Simulation: Selective Catalytic Reduction of NOx with Urea/Ammonia
THREE-WAY CATALYTIC CONVERTER

STAR-CD + CHEMKIN RESULTS

C₃H₆ MASS FRACTION

CO MASS FRACTION

NO MASS FRACTION

POLLUTANT MASS FRACTIONS

NOTE: IMAGES ARE SHOWN GREATLY FORESHORTENED. ACTUAL L/D OF TUBE IS ~15:1.
THREE-WAY CATALYTIC CONVERTER

STAR-CD + CHEMKIN RESULTS

O₂ MASS FRACTION

H₂O MASS FRACTION

CO₂ MASS FRACTION

OXYGEN AND PRODUCT MASS FRACTIONS

NOTE: IMAGES ARE SHOWN GREATLY FOreshortened ACTUAL L/D OF TUBE IS ~15:1.

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THREE-WAY CATALYTIC CONVERTER

OF COURSE, THE GOAL IS TO SIMULATE THE ENTIRE CONVERTER....

TEMPERATURE EVOLUTION

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THREE-WAY CATALYTIC CONVERTER

INCREASING MODELING COMPLEXITY

3D MODELING OF ALL CELLS
2D MODELING OF ALL CELLS
3D MODELING OF SELECTED CELLS

INCREASING COMPUTATIONAL COST

Fourth DOE Crosscut Workshop on Lean Emissions Reduction Simulation: Selective Catalytic Reduction of NOx with Urea/Ammonia
REPRESENTATIVE CHANNEL COUPLING

- PRESSURE AND OTHER FLOW VARIABLES CONTINUOUSLY COUPLED – CONJUGATE HEAT TRANSFER TO SOLID.
- COUPLING METHOD ALLOWS ARBITRARY ASSOCIATIONS BETWEEN ALL DOMAINS.
- IN THIS EXAMPLE, EACH CHANNEL IS ASSOCIATED WITH A DIFFERENT RADIAL ZONE OF THE INLET AND OUTLET TUBES.

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REPRESENTATIVE CHANNEL COUPLING

PRESSURE B.C.

REPRESENTATIVE CHANNEL (ONE OF MANY)

POSDAT.F

“AVERAGE.F”

ASSOCIATE.DAT

SORENT.F

BCDEFLI.F

BCDEFP.F

SOLID CELLS (MONOLITH)

CONVERTER OUTLET DUCT

INLET B.C.

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REPRESENTATIVE CHANNEL COUPLING

Fourth DOE Crosscut Workshop on Lean Emissions Reduction Simulation: Selective Catalytic Reduction of NOx with Urea/Ammonia
PARALLEL COMPUTING MAKES IT POSSIBLE

- PARALLEL COMPUTING AND COMPUTER ADVANCES MAKE ANALYSES WITH DETAILED CHEMISTRY POSSIBLE.

- MILLION+ CELL STAR-CD GE COMBUSTOR ANALYSIS TOOK 75 CPU HOURS IN 1997 ON 4 SP2 NODES – LESS THAN A DAY ON WINTERHAWK II TODAY.

- DAIMLER PERFORMS FULL CYCLE ENGINE SIMULATIONS (INCLUDING SPRAYS AND COMBUSTION) OVERNIGHT WITH 64 CPU SGI ORIGIN.
SELECTIVE CATALYTIC REDUCTION (SCR)

ANALYSIS OF SELECTIVE CATALYTIC REDUCTION (SCR) SYSTEMS REQUIRES CONSIDERATION OF AQUEOUS UREA SOLUTION SPRAYS AND A VARIETY OF THERMAL AND CATALYTIC PROCESSES TO ACCURATELY TREAT THE NO\textsubscript{x} CONVERSION PROCESS. STAR-CD COUPLES ITS EXTENSIVE SPRAY HANDLING CAPABILITIES WITH ITS NEW CHEMKIN-BASED SURFACE CHEMISTRY METHODOLOGY TO MODEL THESE SYSTEMS.
SELECTIVE CATALYTIC REDUCTION (SCR)

- INJECTION CAPTURED WITH STAR-CD’S LAGRANGIAN SPRAY MODEL.
- COMPOSITION MODELED WITH STAR-CD’S MULTI-COMPONENT SPRAY FEATURE.
- THERMOLYSIS AND HYDROLYSIS OF UREA TREATED TOO:
  \[ \text{CO(NH}_2\text{)}_2 \rightarrow \text{NH}_3 + \text{HNCO} \]
  \[ \text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2 \]
SELECTIVE CATALYTIC REDUCTION (SCR)

SURFACE CHEMISTRY MECHANISM INCLUDES:

- 6 GAS-PHASE SPECIES (7 WITH NO₂)
- 7 SURFACE-SITE SPECIES
- 10 SURFACE REACTIONS

MODELING SINGLE CHANNEL IN MONOLITH

MONOLITH TUBE

VANADIA/TITANIA CATALYST

80 mm

1 mm

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Simulation: Selective Catalytic Reduction of NOx with Urea/Ammonia
## SELECTIVE CATALYTIC REDUCTION (SCR)

1. **NH₃ ADSORPTION ON ACID SITES**

\[
\text{NH}_3 + V^{5+} + \text{OH} \rightarrow \text{V--ONH}_4 \\
\text{V--ONH}_4 \rightarrow \text{NH}_3 + V^{5+} + \text{OH}
\]

2. **ACTIVATION OF SURFACE NH₃ WITH REDOX SITES**

\[
\text{V--ONH}_4 + V = O \rightarrow \text{V--ONH}_3 -- V^{4+} -- \text{OH} \\
\text{V--ONH}_3 -- V^{4+} -- \text{OH} \rightarrow \text{V--ONH}_4 + V = O
\]

3. **NO REMOVAL STEP**

\[
\text{NO} + \text{V--ONH}_3 -- V^{4+} -- \text{OH} \rightarrow \text{N}_2 + \text{H}_2\text{O} + V^{5+} -- \text{OH} + V^{4+} -- \text{OH}
\]

4. **REMOVAL OF SURFACE OH TO FORM H₂O**

\[
2V^{4+} -- \text{OH} \rightarrow \text{H}_2\text{O} + V^{3+} + V = O \\
\text{H}_2\text{O} + V^{3+} + V = O \rightarrow 2V^{4+} -- \text{OH}
\]

5. **REOXIDATION OF CATALYST BY O₂**

\[
\text{O}_2 + 2V^{3+} \rightarrow 2V = O
\]

6. **H₂O ADSORPTION ON ACID SITES**

\[
\text{H}_2\text{O} + V^{5+} -- \text{OH} \rightarrow V^{5+} -- \text{OH}_3\text{O} \\
V^{5+} -- \text{OH}_3\text{O} \rightarrow \text{H}_2\text{O} + V^{5+} -- \text{OH}
\]


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*Fourth DOE Crosscut Workshop on Lean Emissions Reduction Simulation: Selective Catalytic Reduction of NOx with Urea/Ammonia*
SELECTIVE CATALYTIC REDUCTION (SCR)

NH$_3$ MASS FRACTION

NO MASS FRACTION

NO$_2$ MASS FRACTION

NOTE: IMAGES ARE SHOWN GREATLY FORESHORTENED ACTUAL L/D OF TUBE IS ~80:1.

WITH SOME ADDITIONAL EFFORT, NO$_2$ CONVERSION CAN ALSO BE PREDICTED...

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Simulation: Selective Catalytic Reduction of NOx with Urea/Ammonia
SUMMARY

- THE COMBINATION OF STAR-CD, CHEMKIN, AND SURFACE CHEMKIN PROVIDES A TOOL TO EXAMINE MANY PROBLEMS INVOLVING COMPLEX GEOMETRIES, DETAILED CHEMISTRY, SPRAYS, ETC. - THIS INCLUDES APPLICATIONS SUCH AS SELECTIVE CATALYTIC REDUCTION AND OTHER DIESEL EXHAUST AFTERTREATMENT TECHNOLOGIES.

- EVEN MORE EFFECTIVE IS A HIERARCHICAL APPROACH COMBINING IDEALIZED REACTOR MODELING WITH THE CHEMKIN COLLECTION WITH CFD MODELING OF MORE COMPLEX PROBLEMS.

- PARALLEL COMPUTING MAKES CFD CALCULATIONS WITH DETAILED CHEMISTRY POSSIBLE.

- THIS METHODOLOGY IS EASILY ADAPTABLE TO NEW CHEMISTRIES, ETC. – WHAT’S NEEDED ARE THE KINETICS, PHYSICAL MODELS, ETC.

- FUTURE DEVELOPMENTS ARE ALREADY UNDERWAY....
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ESTools

BASIS OF ESTools IS CD-ADAPCO GROUP’S Pro*AM PRE-PROCESSING TOOL WHICH BUILDS MESHES FROM CAD SURFACE DATA UTILIZING TRIMMED CELL TECHNOLOGY

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ESTools

Surface Preparation
- Surface Closure Tools
  - Generate New Surface
  - Advanced Surface Wrapping

Automatic Meshing
- Trimmed Cell
  - Tetrahedral
  - Hybrid

Analysis Setup
- Application Specific
  - Analysis Setup

Post Processing
- Application Specific
  - Post Processing