DEVELOPMENT AND APPLICATION OF RIGOROUS KINETIC MODEL FOR PREDICTING ULTRA LOW SULPHUR DIESEL (ULSD) UNIT PERFORMANCE

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AGENDA

• ULSD Model Development - Motivation
• ULSD Model Formulation
• Model Performance
• Model Application Examples
• Conclusions
WORLDWIDE DIESEL SULFUR SPECIFICATIONS

Maximum On-Road Diesel Sulfur Limits


Countries may apply lower limits for different grades, regions/cities, or based on average content. Detailed information on limits and regulations can be found at www.ifqc.org
ULSD MODEL DEVELOPMENT – MOTIVATION (1)

• ULSD “Economic” Drivers:
  • Meet Diesel Sulfur Specifications
    • Produce Saleable Product
    • Minimize Cost
  • Maximize Asset Utilization
    • “Beyond ULSD”
    • Reduce Hydrotreating Catalyst Requirements
    • Maintain ULSD Cycle Length
    • Make Reactor Volume Available – Upgrading Catalysts
    • Improve Product Properties (Cetane, Cold Flow Properties, Aromatics Content)

• Project Development
  • Unit Design/Optimization
  • Capital Cost Minimization
• ULSD Kinetic Modeling Uses/Benefits
  • Optimize Catalyst Loads
    • Desulfurization
    • Product Property Improvement
  • Improve Hydrotreating Asset Utilization
    • Feed Management
    • Increase Throughput
    • Manage Cycle length
  • Beyond ULSD

• ULSD Modeling Requirements
  • Accurate HDS Prediction
    • Broad Feed Property & Process Condition Ranges
  • Accurate Product Property Estimates
  • “Cold” Calculation Capabilities
Simulate ULSD kinetic reactions to predict product properties and catalyst life with reasonable accuracy under steady state conditions

Formulation
- Five Sulphur lumps and four Nitrogen lumps, accounting for varying reactivity & equilibrium limitations
- Pseudo components $\rightarrow$ allows to calculate products slates
- Pseudo components properties describing paraffin, naphthenic, aromatic and Sulphur content $\rightarrow$ allows calculating product properties such as density, aromatic content, smoke point, cold flow …
- Engineering calculations $\rightarrow$ delta T/delta P across beds
- Correlation for calculating deactivation kinetics
Collapsing GCxGC data to a single dimension allows quantifying the amount of sulphur species with respect to boiling point.
GCxGC Sulphur speciation technique is used to group Sulphur species into lumps with different reactivates and reaction paths.

An algorithm using a GCxGC data base of over 30 crudes is used to initialize the lumps and estimate the refractory sulphur species.

Langmuir-Hinshelwood kinetics is used to describe the impact of inhibitors such as nitrogen, H₂S and aromatics.
EXAMPLE OF APPLICATION OF S SPECIATION TECHNIQUE

Ni-Mo

Co-Mo

GC x GC visualizes the predominant reaction paths and helps in identifying refractory sulphur
The model has been validated on 130+ selected conditions with over 30 different feeds (LCO, CGO, TC, HT & SR).

Excellent match in most of the cases inspite of the potential pitfalls in any pilot plant data base:

- Indistinct definition of SOR (WABT)
- Deactivation/ repeatability of tests.
- Measurement of low sulphur slips (2 ppmw)
- Sulphur recombination reactions
Product Nitrogen and Aromatics at four levels of H$_2$ partial pressures

Model accurately predicts onset of equilibrium limitations for entire operating range
Applications require detailed modeling of the heart of the process, the catalysts.
PROCESS MODELING FRAMEWORK

Standalone

RTO

Process Modeling Environment

CAPE-OPEN

Shell proprietary interface

HC
ECU
TC
CR

HT
FCC
Alkylation
ISOM
Distillation

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Example: Start of run (SOR) predictions for commercial units

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<th>Refinery A</th>
<th>Refinery B</th>
<th>Refinery C</th>
<th>Refinery D</th>
<th>Refinery E</th>
<th>Refinery F</th>
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<td>337</td>
<td>364</td>
<td>360</td>
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<td>Pressure barg</td>
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<tr>
<td>Sulphur ppm w</td>
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<td>3</td>
<td>9</td>
<td>45</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Predicted Sulphur ppm w</td>
<td>11</td>
<td>2</td>
<td>9</td>
<td>44</td>
<td>10</td>
<td>7</td>
</tr>
</tbody>
</table>

- ● Cracked material
- ○ Predominantly straight run gasoil
- ● Lighter blend containing kerosene

Model applied for regular performance monitoring and what-if studies by the sites
Excellent match between pilot plant and model at three levels of “S” slip targets for a difficult feed using stacked catalyst bed system

- HDN, aromatics and ccH2 predictions also match very well
- Model predictions used for fine-tuning the catalyst conditions for proposal

Criterion uses the model as a tool for technical proposals
CASE STUDY: CATALYST SELECTION FOR REVAMP (1)

Revamp study for a 3P licensed DHT in a 3P refinery

Objectives:

• Capacity increase: 4,560 mtsd to 5,928 mtsd (30%)
• Feed stock: SR feed to SR + cracked stocks (FCC LCO & VN)
• Product diesel specs: 10 ppmw S (max), winter grade (CP: -28°C)
• Catalyst cycle length: 2 years

Revamp scope:

• New catalyst system (Co-Mo, Ni-Mo, HDW)
• New reactor internals
• New equipment and revamp of certain existing equipment
• New hydrodewaxing (HDW) section
CASE STUDY: CATALYST SELECTION FOR REVAMP (2)

- ULSD model used for
  - Catalyst selection
  - Generation of kinetic data (for applying in commercial flowsheet simulation to design the downstream equipment changes)
  - Product property and chemical hydrogen estimation

All design criteria could be met successfully during test run (2012)
CONCLUSIONS

• Steady state kinetic model developed for in-house HDS/ HDT applications
• Rigorous kinetics, tuned with dedicated pilot plant data, and validated with a combination of pilot plant and commercial data replicates real-life performance quite well.
• Model applications include performance monitoring, optimization, catalyst cycle management, design and revamp, catalyst selection, licensing, and technical training, etc.