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

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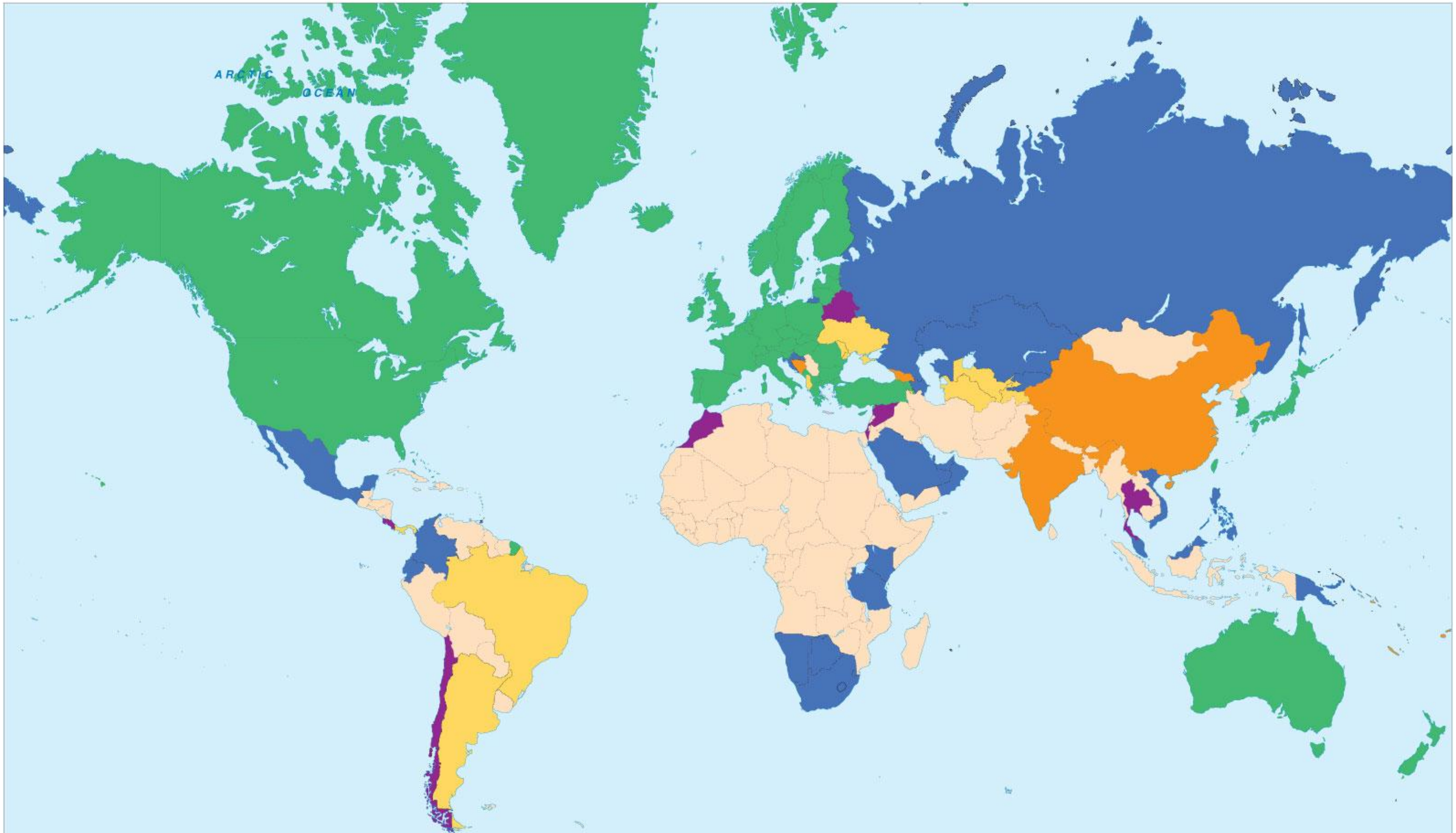
AGENDA

- ULSD Model Development - Motivation
- ULSD Model Formulation
- Model Performance
- Model Application Examples
- Conclusions

WORLDWIDE DIESEL SULFUR SPECIFICATIONS

Maximum On-Road Diesel Sulfur Limits



Source: Hart Energy's International Fuel Quality Center, May 2012

10 - 15 ppm | **16 - 50 ppm** | **51 - 350 ppm** | **351 - 500 ppm** | **501 - 2000 ppm** | **> 2000 ppm**

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 MODEL DEVELOPMENT – MOTIVATION (2)

- 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

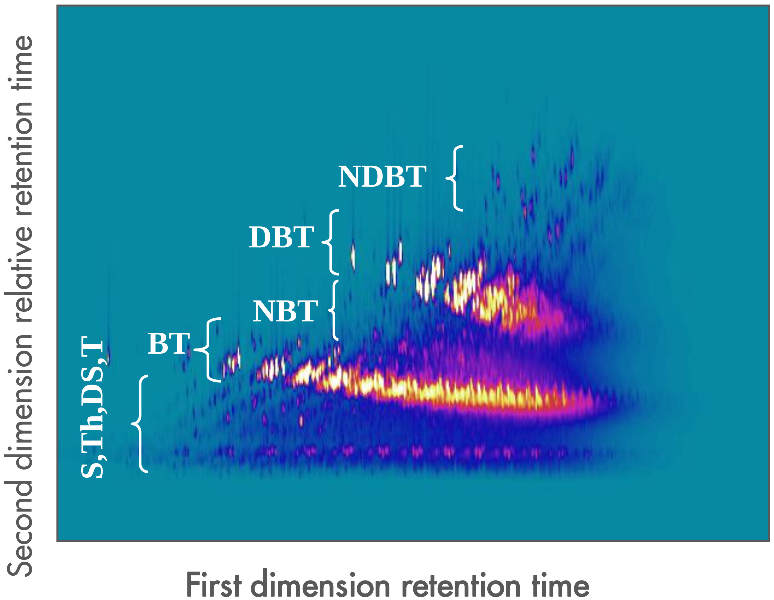
MODEL OBJECTIVE AND FORMULATION

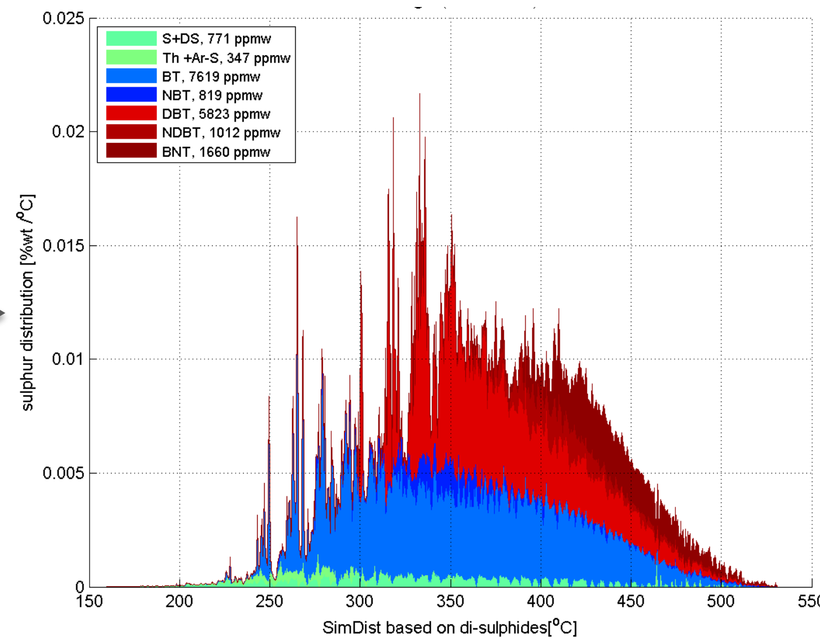
Simulate ULSD kinetic reactions to predict product properties and catalyst life with reasonable accuracy under steady state conditions

Formulation

- Five Sulphur lumps and four Nitrogen lumps, accounting for varying reactivity & equilibrium limitations
- Pseudo components → allows to calculate products slates
- Pseudo components properties describing paraffin, naphthenic, aromatic and Sulphur content → allows calculating product properties such as density, aromatic content, smoke point, cold flow …
- Engineering calculations → delta T/delta P across beds
- Correlation for calculating deactivation kinetics

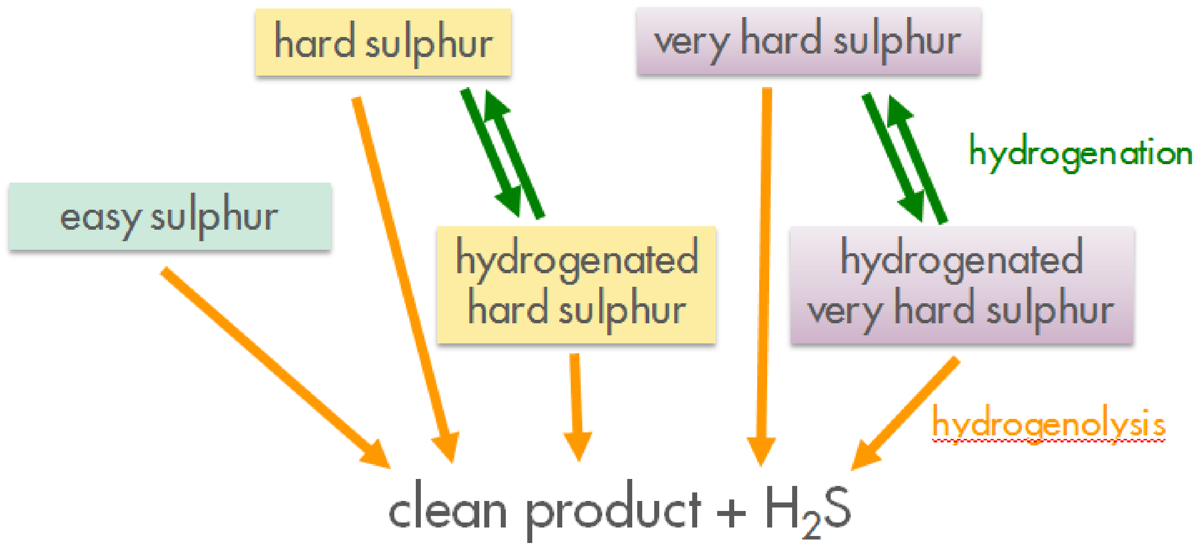
FEED CHARACTERISATION - 2 DIMENSIONAL SULPHUR GC





Collapsing GCxGC data to a single dimension allows quantifying the amount of sulphur species with respect to boiling point

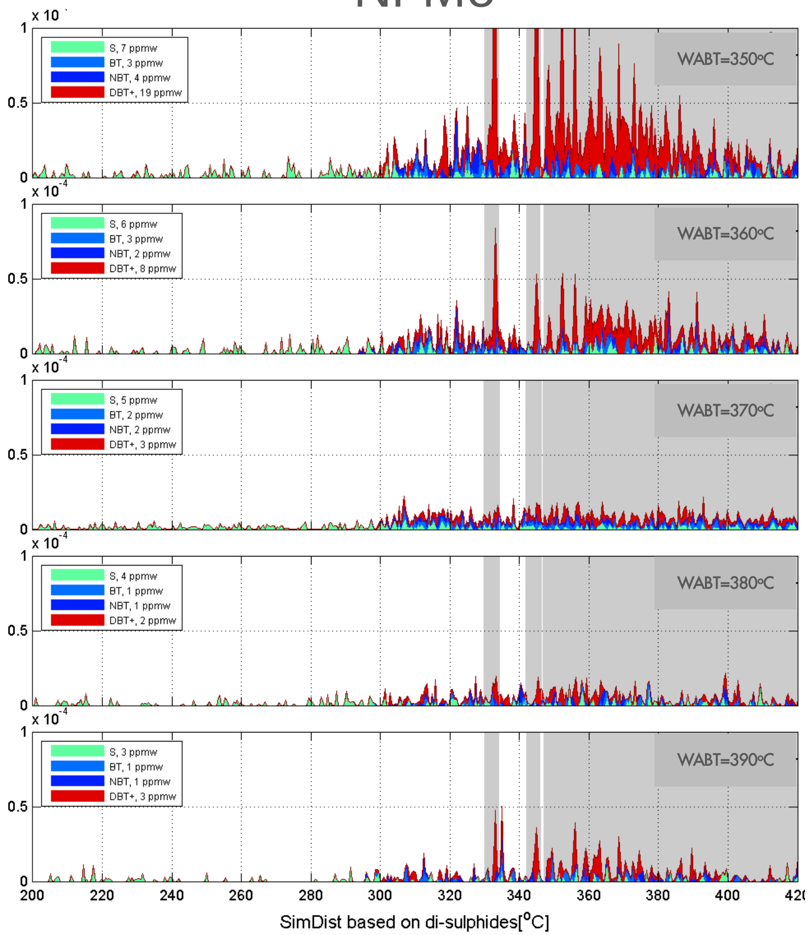
HDS REACTION NETWORK



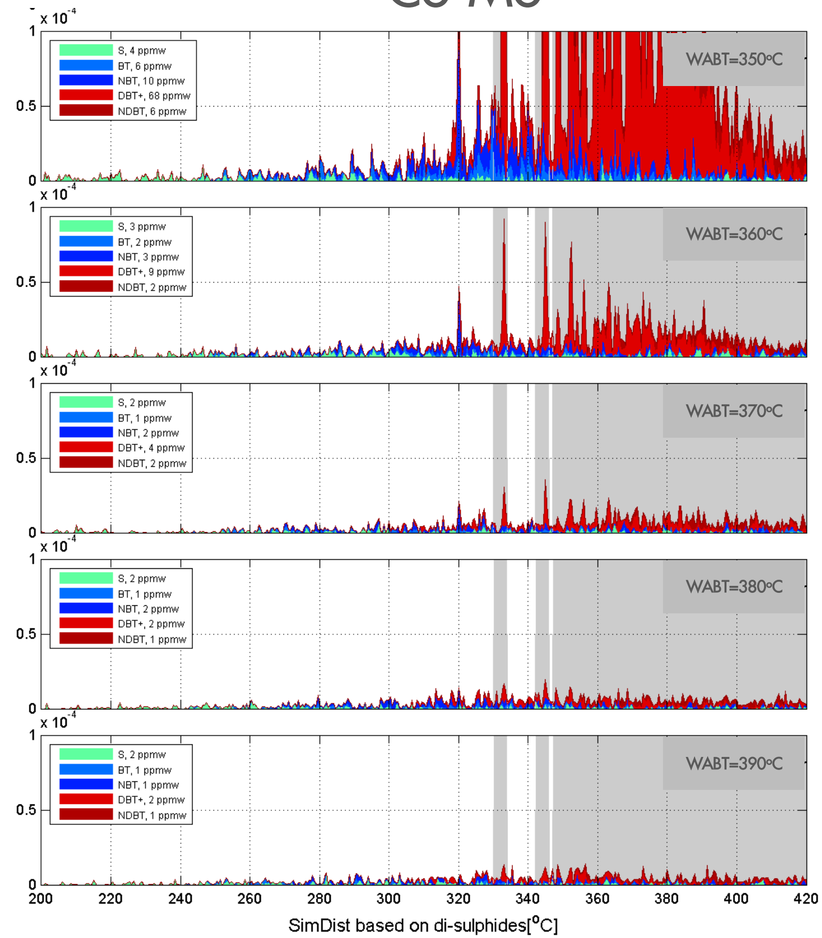
- GCxGC Sulphur speciation technique is used to group Sulphur species into lumps with different reactivates and reaction paths
- An algorithm using a GCxGC data base of over 30 crudes is used to initialize the lumps and estimate the refractory sulphur species
- Langmuir-Hinshelwood kinetics is used to describe the impact of inhibitors such as nitrogen, H_2S and aromatics

EXAMPLE OF APPLICATION OF S SPECIATION TECHNIQUE

Ni-Mo



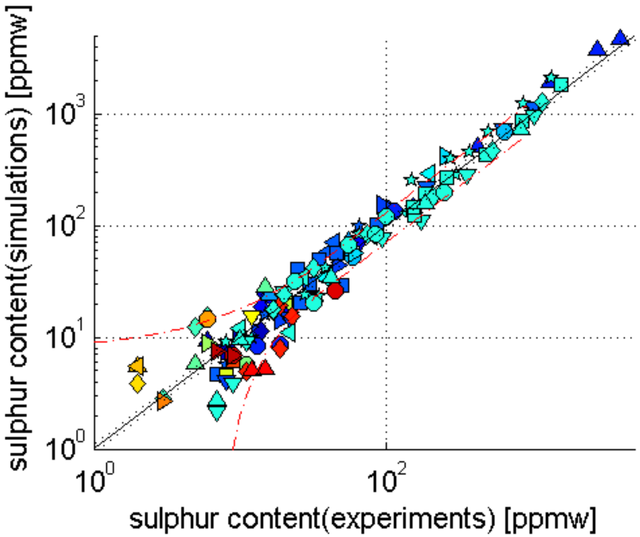
Co-Mo



GC x GC visualizes the predominant reaction paths and helps in identifying refractory sulphur

MODEL VALIDATION AGAINST PILOT PLANTS (I)

The model has been validated on 130+ selected conditions with over 30 different feeds (LCO, CGO, TC, HT & SR)

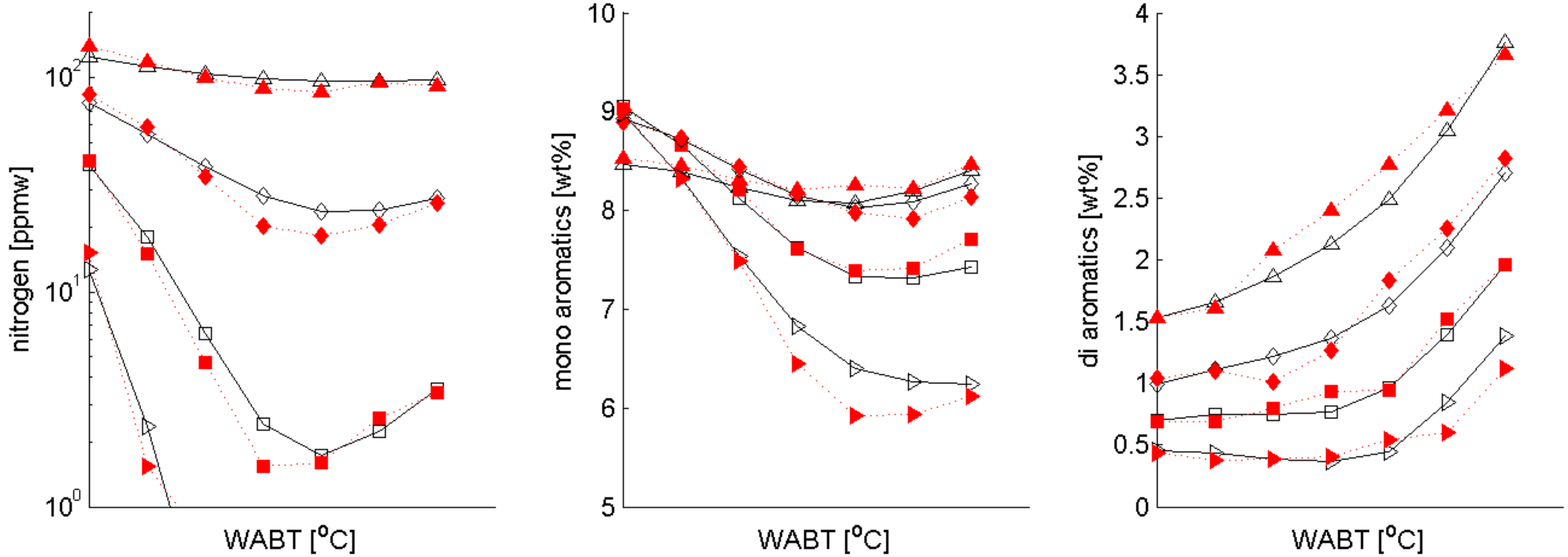


Excellent match in most of the cases inspite of the potential pitfalls in any pilot plant data base:

- Indistinct definition of SOR (WABT)
- Deactivation/ repeatability of tests.
- Measurement of low sulphur slips (2 ppmw)
- Sulphur recombination reactions

MODEL VALIDATION AGAINST PILOT PLANTS (II)

Product Nitrogen and Aromatics at four levels of H_2 partial pressures



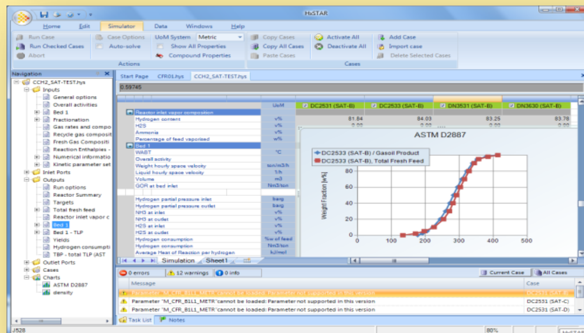
Model accurately predicts onset of equilibrium limitations for entire operating range

APPLICATIONS OF IN-HOUSE PROCESS MODELS

Performance monitoring & optimization

Refinery wide optimization Modeling

Catalyst selection: New & existing units



Real time Optimization

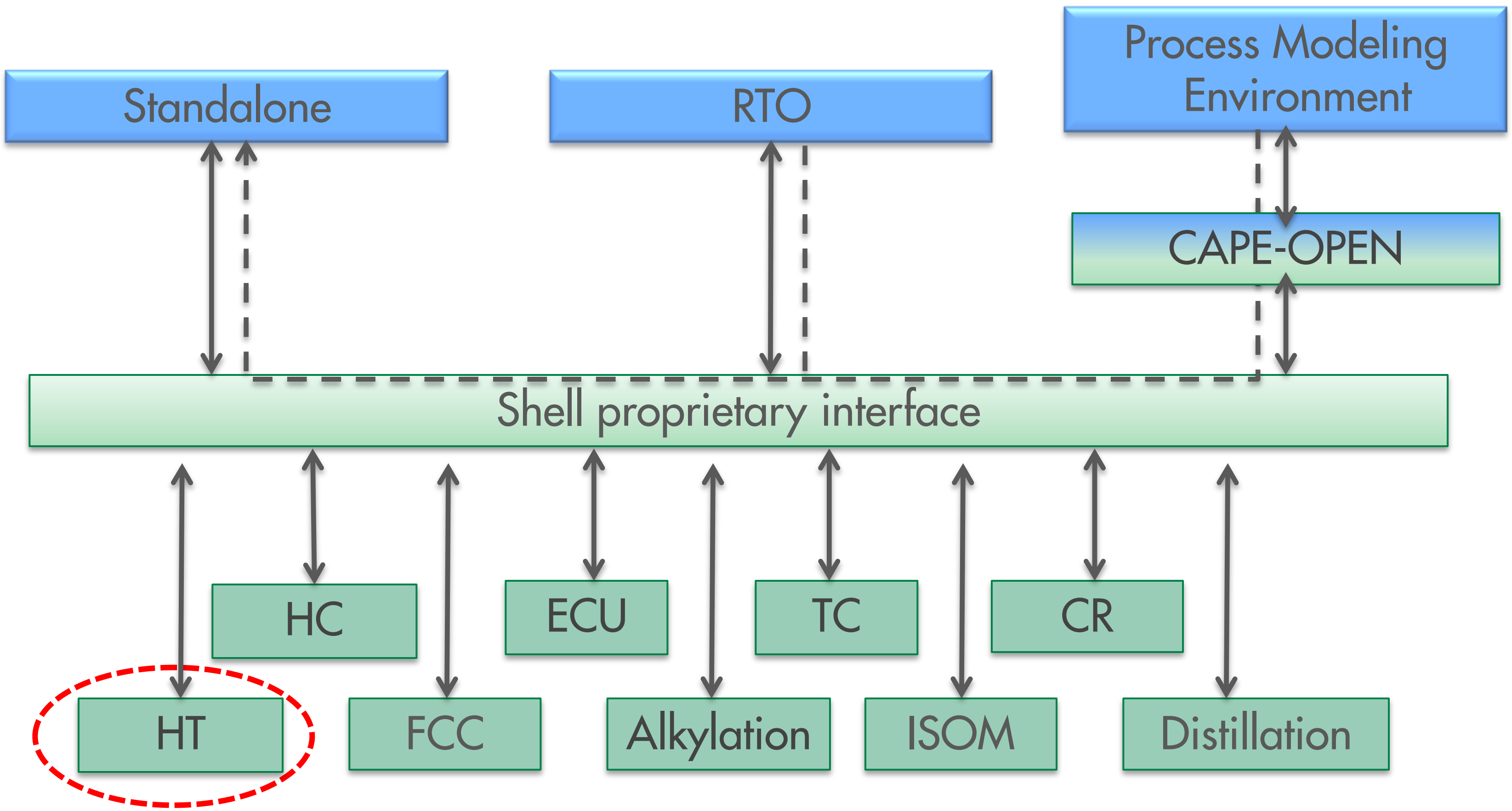
Catalyst cycle management

Operator training

Product predictions for design & revamp studies

Applications require detailed modeling of the heart of the process, the catalysts

PROCESS MODELING FRAMEWORK



CASE STUDY: PERFORMANCE MONITORING OF UNITS

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

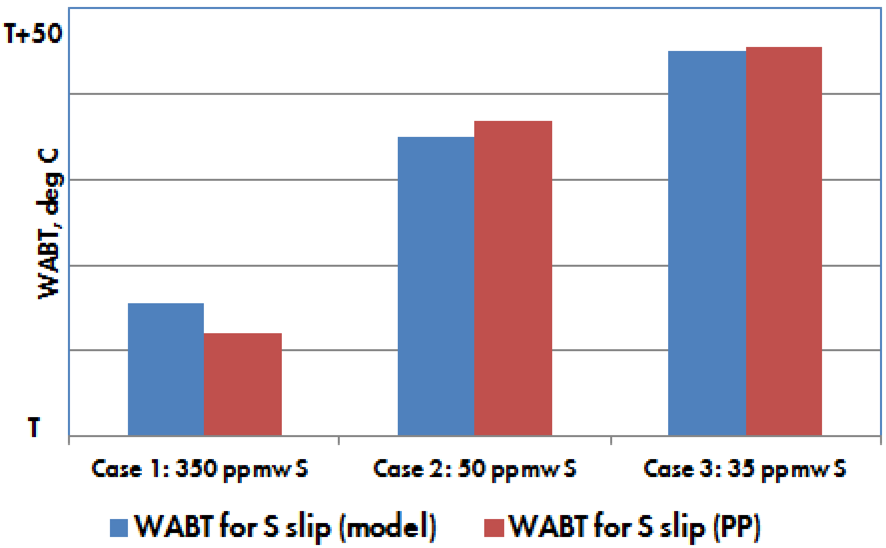
		Refinery A ●	Refinery B ●	Refinery C ●	Refinery D ●	Refinery E ●	Refinery F ●
Average WABT	°C	362	337	364	360	353	307
Pressure	barg	78	67	55	50	48	31
Liquid hourly space velocity	1/h	2.62	0.91	1.09	1.17	1.32	0.93
Sulphur	ppm w	7	3	9	45	8	7
Predicted Sulphur	ppm w	11	2	9	44	10	7

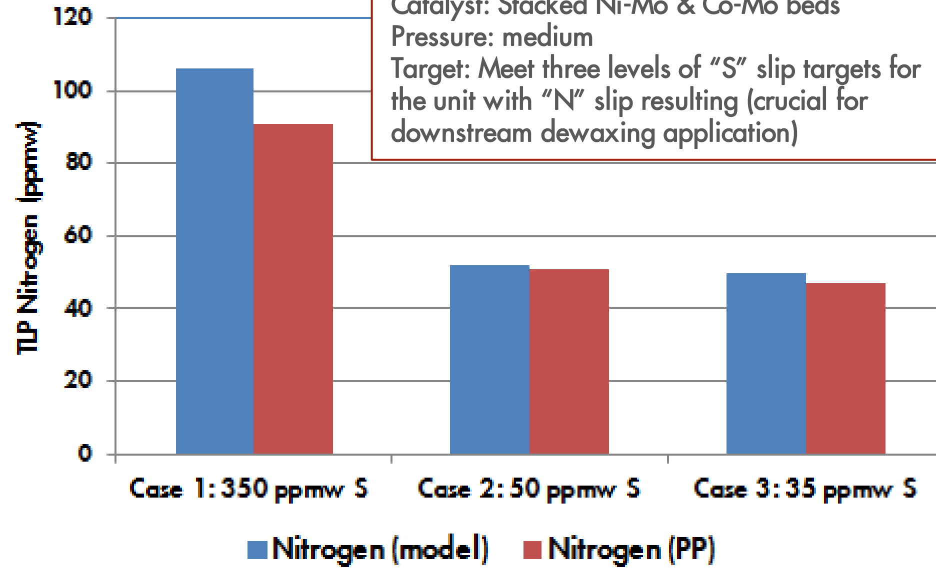
- ● (red) Cracked material
- ● (blue) Predominantly straight run gasoil
- ● (green) Lighter blend containing kerosene

Model applied for regular performance monitoring and what-if studies by the sites

CASE STUDY: CATALYST SELECTION FOR NEW UNITS

Feedstock: Mixture of SR & cracked GO feed
Catalyst: Stacked Ni-Mo & Co-Mo beds
Pressure: medium
Target: Meet three levels of "S" slip targets for the unit with "N" slip resulting (crucial for downstream dewaxing application)





- 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:

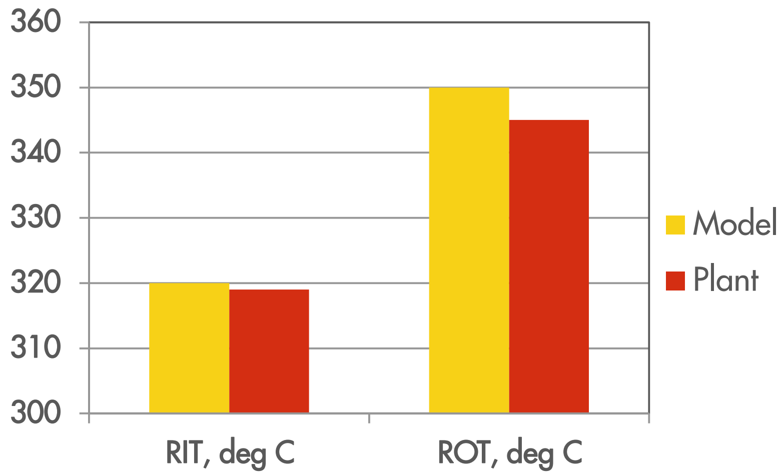
- Capacity increase: 4,560 mtsd to 5,928 mtsd (30%)
- Feed stock: SR feed to SR + cracked stocks (FCC LCO & VN)
- Product diesel specs: 10 ppmw S (max), winter grade (CP: -28°C)
- Catalyst cycle length: 2 years

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.

Q & A