



Setting the Standard for Automation™

Naphtha Steam Cracking (NSC) Unit Optimization

The Use of Robust On-line Optical
Spectroscopy for the Real-time
Optimization of Steam-cracking Furnace
Operation

Standards
Certification
Education & Training
Publishing
Conferences & Exhibits

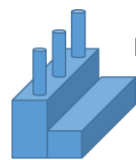
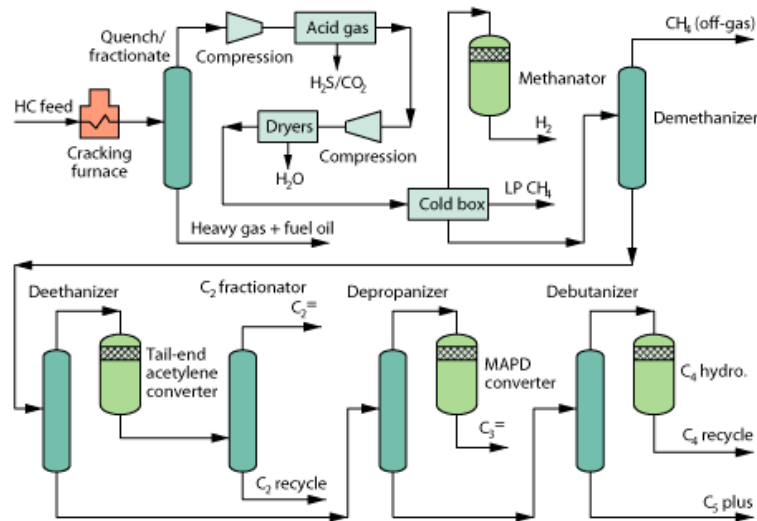
Naphtha Steam Cracking (NSC) Unit Optimization



By

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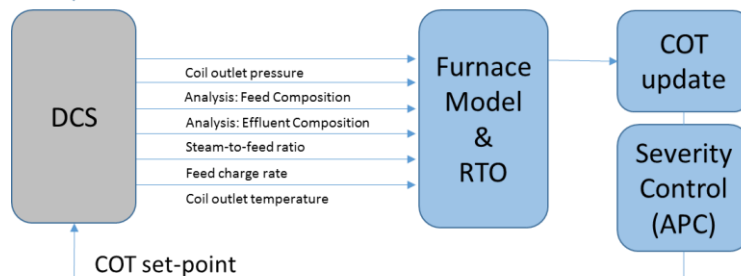
Steam cracker operational constraints



Naphtha Steam Cracker



Furnace CVs, PVs, analyzer stream data



Steam-Cracking Optimisation

- for managing real-time fast analysis of steam cracker naphtha feed
- PIONA, %Distillation and C-number breakdown analyses
- Enables efficient use of SPYRO feed-forward optimiser ment of COT control
- Minimise coil coking, side-products
- Correctly manage cracking severity to match downstream volumetric flow (compressor) constraints
- Maintain optimal P/E ratios in response to feed quality variation
- Ensure safe and efficient acetylene removal in final product olefins

Control and optimization of the steam cracker furnace



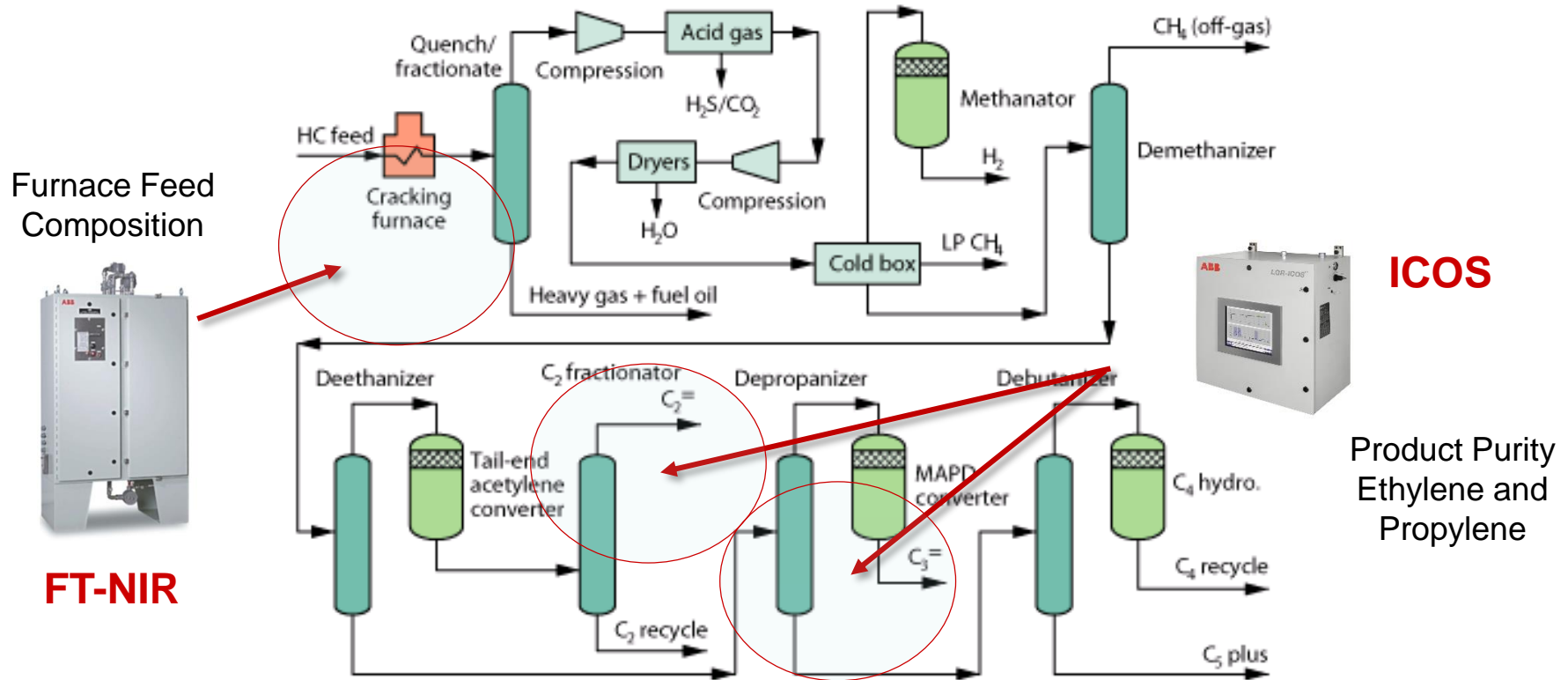
Optimization

- Optimization is normally based on the use of a real-time kinetic furnace model (SPRYO, PYPS+ or similar) for yield estimation
- This is used by the RTO to calculate, and update, the COT (coil outlet temperature) set-point point based on inputs such as cracking targets and feed quality – it aims to achieve constant constant cracking conditions over the furnace run-length
- It will include yield predictions (to help manage downstream volumetric constraints) and an an updated run-time estimate for the furnace

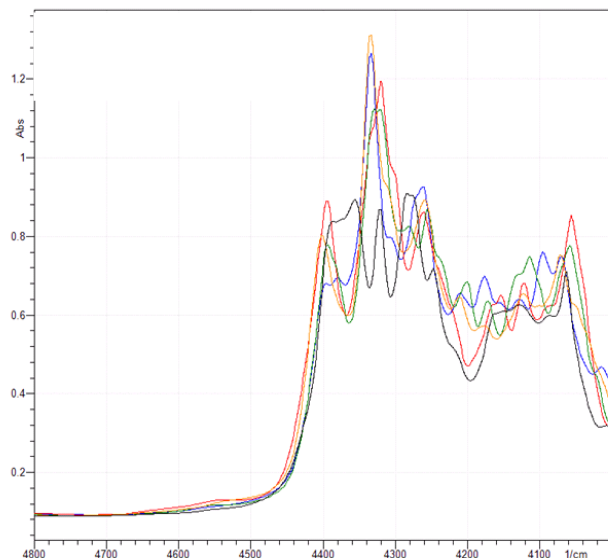
COT set-point calculation in RTO

- The RTO updates as required (frequently during transitions) and sets the COT and makes yield yield estimations using SPYRO which require accurate and timely naphtha feed qualities as as input.
- Key role of on-line FT-NIR which is able to measure multiple naphtha feed qualities dynamically during transitions.

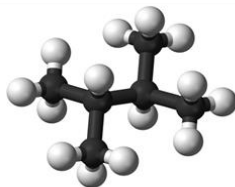
Process optical spectroscopy



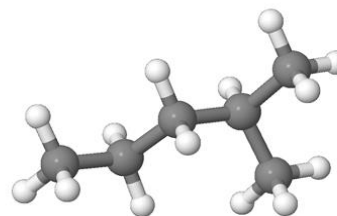
Can NIR distinguish naphtha isomers ?



2,3-dimethylbutane

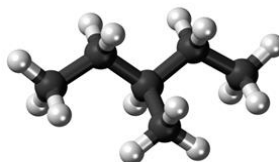


2-methylpentane

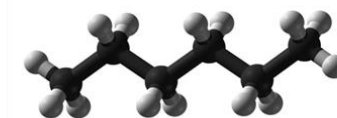


C6 isomers

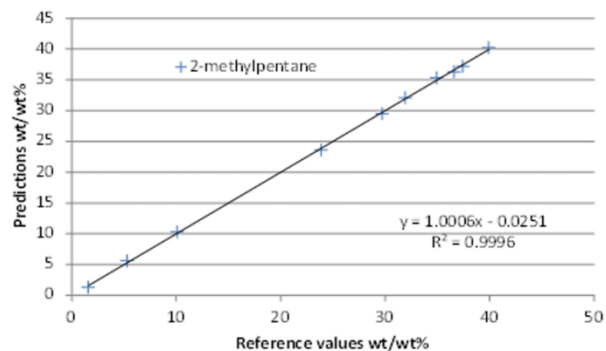
3-methylpentane



n-hexane



methylcyclopentane



Compounds	Range (wt/wt %)	R ²	Uncertainty (wt/wt%)	Repeatability (wt/wt %)
2,3-Dimethylbutane	1 - 15	0.9992	0.13	0.006
2-Methylpentane	1 - 40	0.9996	0.28	0.045
3-Methylpentane	1 - 40	0.9988	0.46	0.118
n-Hexane	1 - 30	0.9979	0.43	0.019
Methyl-cyclopentane	0.5 - 26	0.9997	0.16	0.098

Is it feasible to measure low levels?

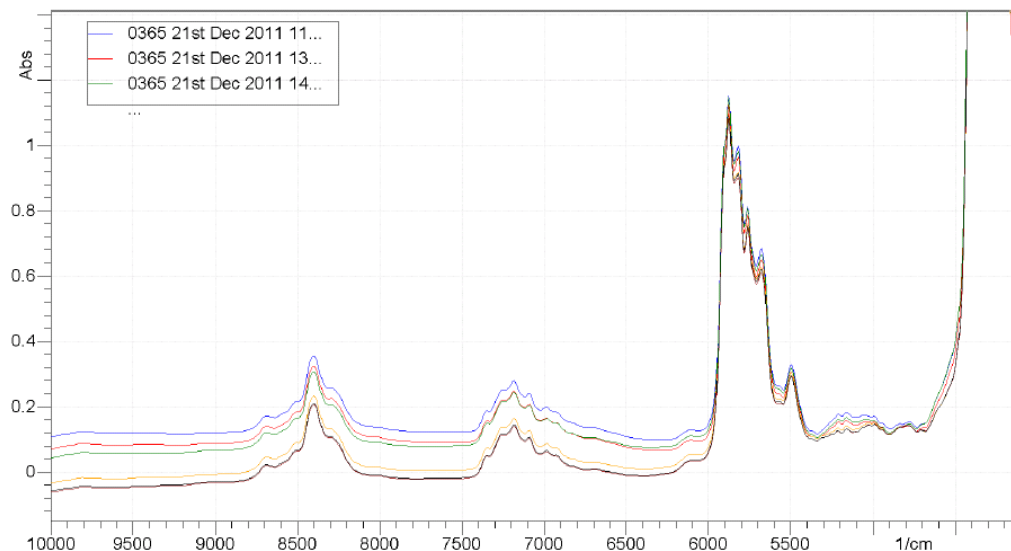


Figure 2: Typical NIR spectra of the LPG samples collected at COP Seal Sands.

Table 1: Performance data for the isopentane in LPG calibration.

Property	Range %	Factors	Uncertainty % (1 x σ)	R ²	Repeatability % (1 x σ)
isopentane	0 - 7.64	7	0.09	0.997	0.05

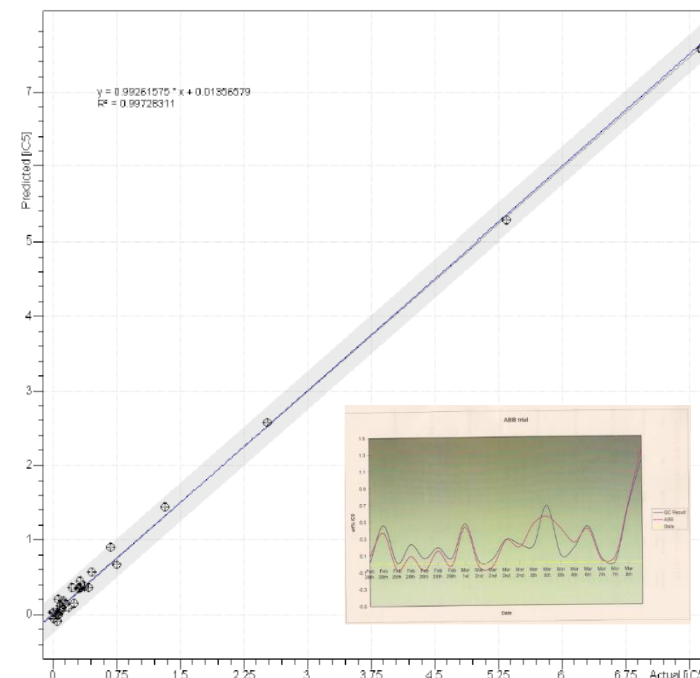


Figure 4: Actual vs. Predicted isopentane concentration in LPG samples collected at COP Seal Sands.

Component	Min	Normal	Max	Range	Units
Methane	0	0.2629	1.7	-	WT%
Ethane	2.7	5.2449	14.9	-	WT%
Propane	26.4	40.2375	57.6	-	WT%
iso-Butane	10	13.8973	17.7	-	WT%
n-Butane	19.2	39.9566	50	0 - 50	WT%
iso-Pentane	0	0.3836	9.3	0 - 2	WT%
n-Pentane	0	0.0172	1.8	-	WT%

FT-NIR vs PGC for PIONA analysis



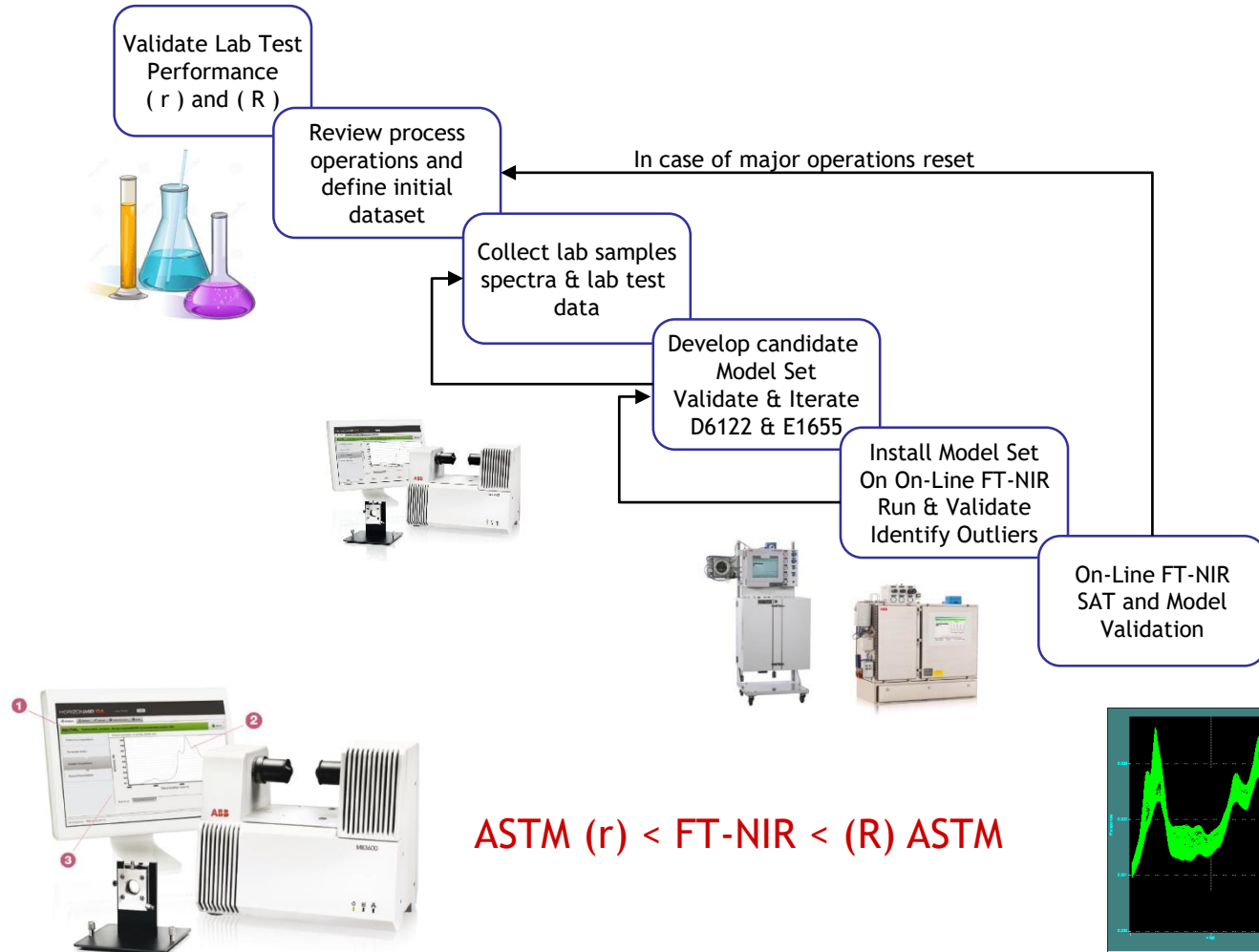
FT-NIR

- No separation of sample
- Fast measurement – 1 minute for all properties
- Flexible measurement, PIONA, T05, T95, RVP, Density
- Very low maintenance
- Low cost of ownership
- Requires calibration model based on lab test data
- Requires routine validation, but but no calibration standards

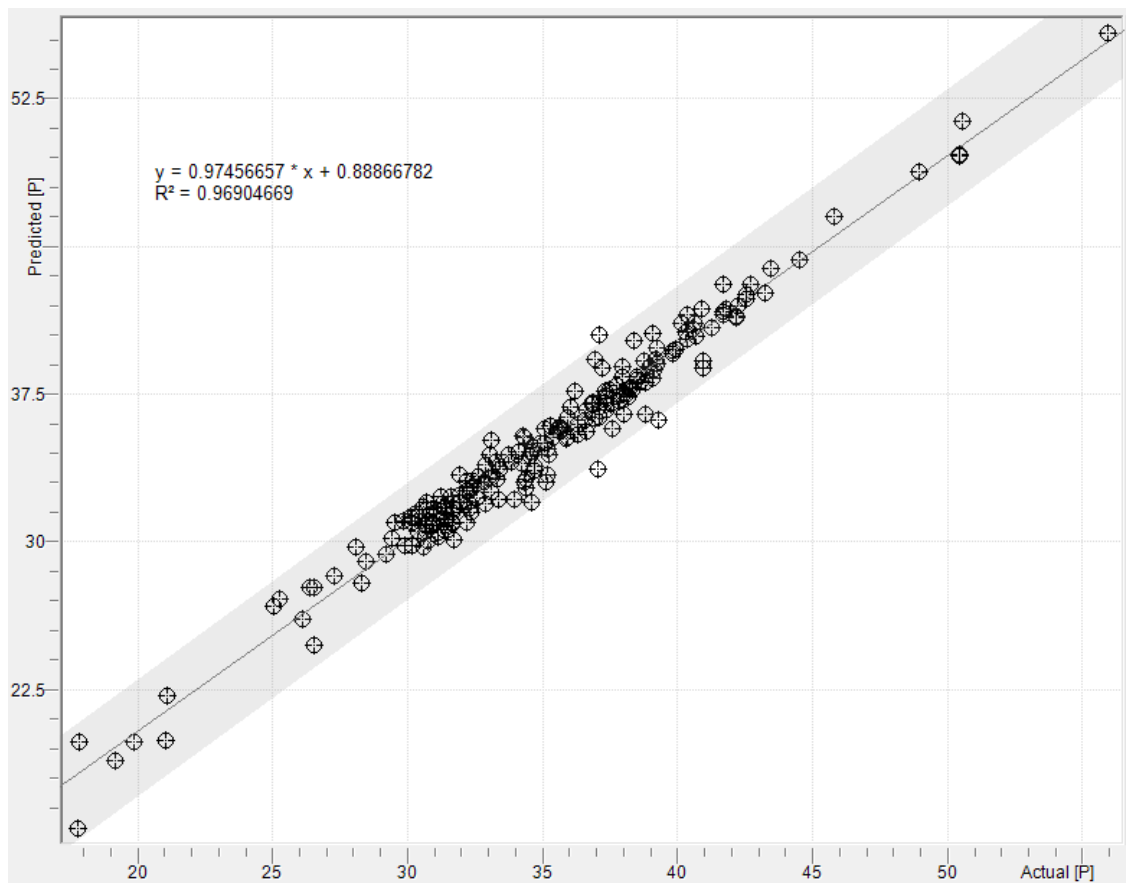
PGC

- Uses column to physically separate all chemical components
- Long cycle time (up to 45 minutes)
- Difficult application for PIONA and cannot directly measure distillation or density
- Maintenance intensive
- Consumables requirement
- Requires routine calibration but no modelling

Calibration workflow and modeling

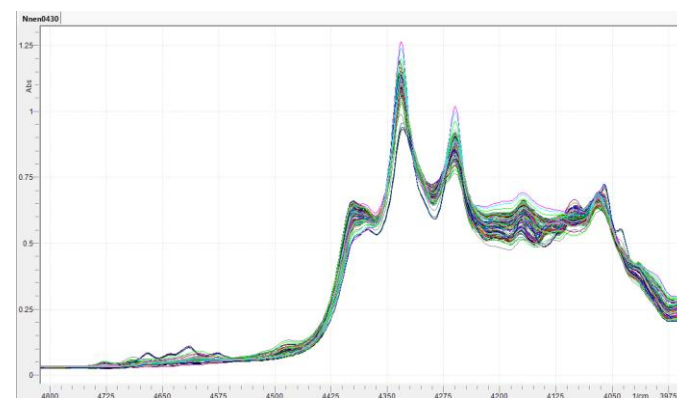


n-paraffins in naphtha

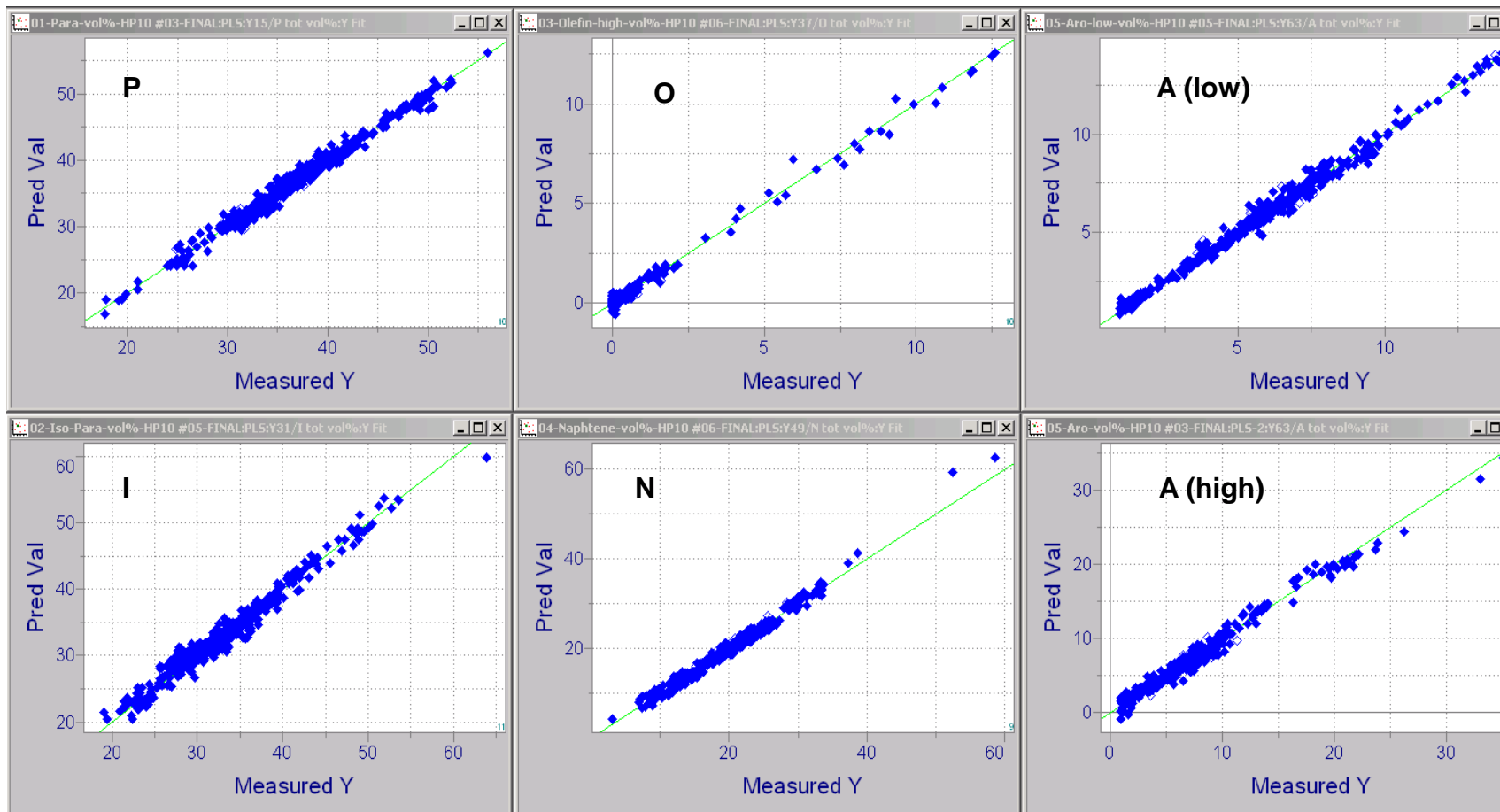


Quantitative Model Statistics

R	0.98
R2	0.97
SECV	0.97
RMSECV	0.97
Mean	34.93
Variance	30.46



FT-NIR calibration models for PIONA%

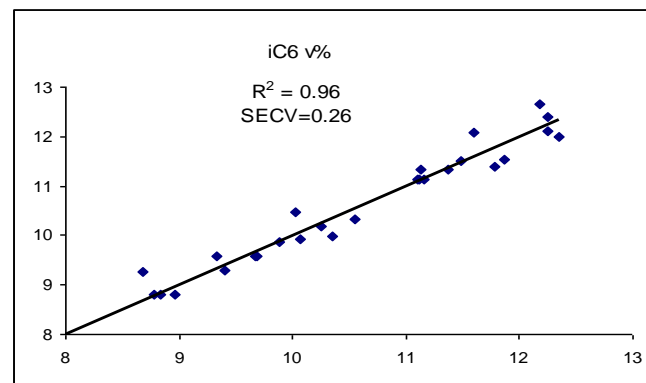
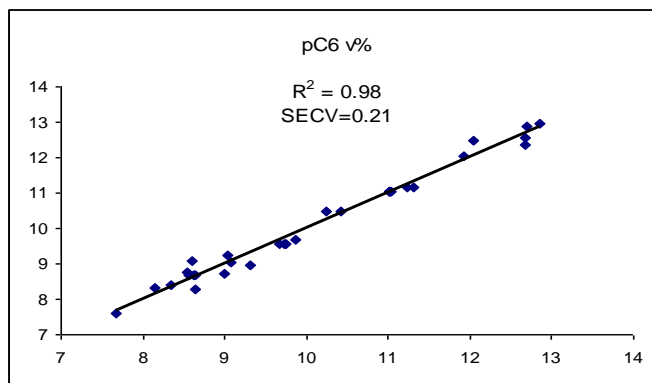
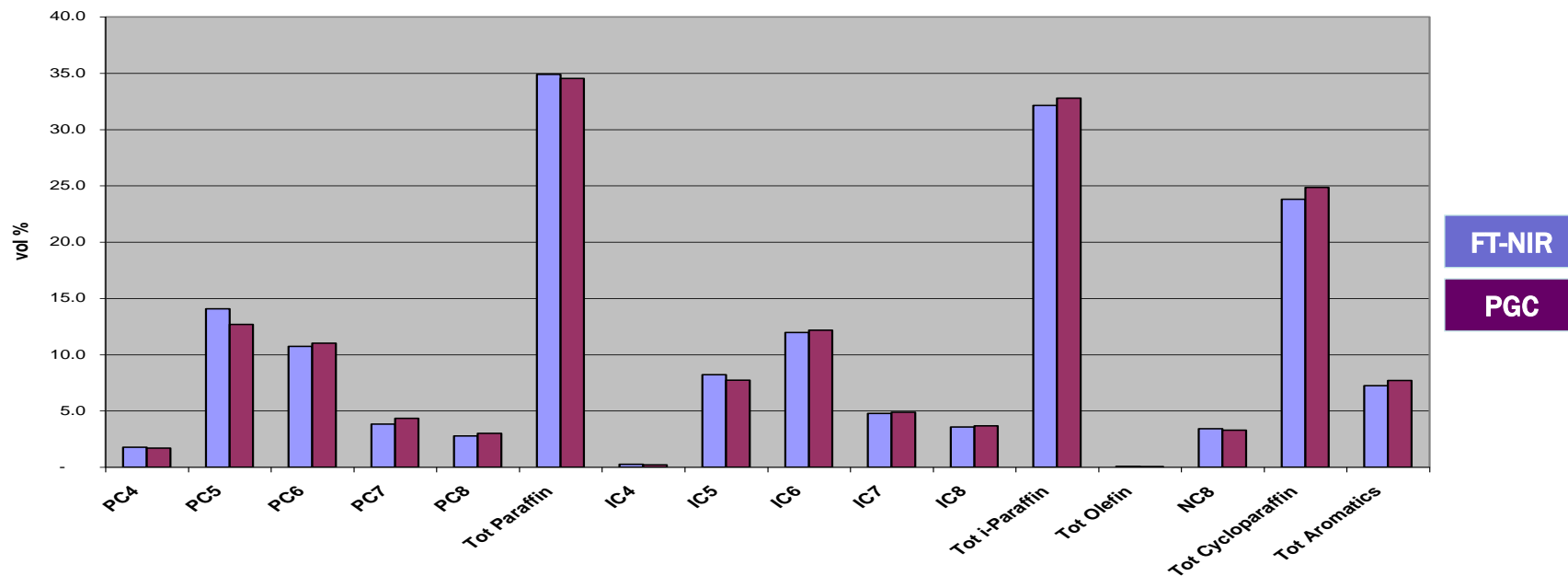


Typical FT-NIR model performances



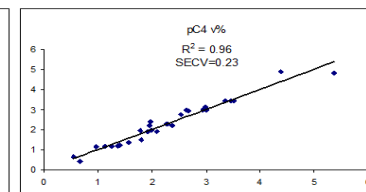
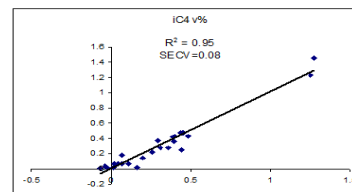
Example Naphtha Feed Calibration Data							
Property	FTIR R	FTIR r	Range vol%	Property	FTIR R	FTIR r	Range degC
P%	0.74	0.14	18 - 53	IBP	2.1	0.26	21 - 105
I%	0.98	0.11	20 - 55	T10	1.2	0.17	35 - 81
O%(hi)	0.17	0.03	0 - 12	T30	1.7	0.16	44 - 93
O%(lo)	0.08	0.03	0 - 1.6	T50	2.4	0.2	50 - 125
N%	0.83	0.13	8 - 40	T70	3.3	0.31	54 - 143
A%(lo)	0.26	0.08	1 - 15	T90	4.9	0.32	67 - 165
A%(hi)	0.57	0.08	0 - 35	T95	7.7	0.48	69 - 185
C4 Total	0.17	0.09	1 - 6	FBP	10.9	0.73	76 - 225

Is C-number detail feasible?

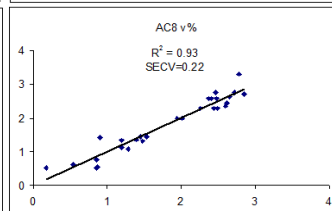
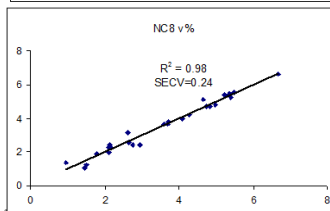
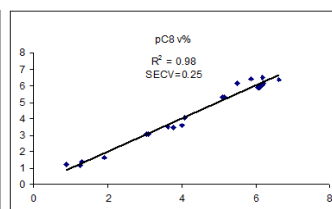
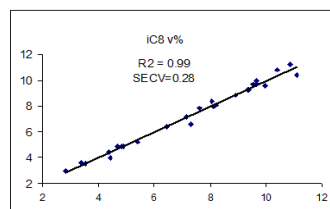


C-number breakdown for naphtha

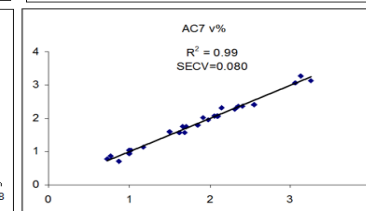
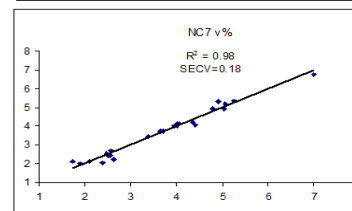
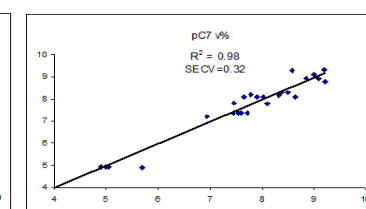
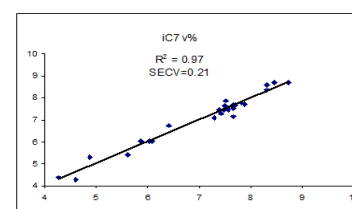
C4



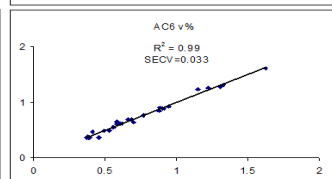
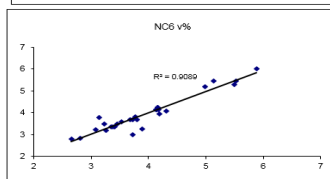
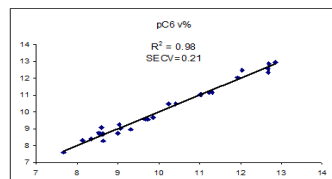
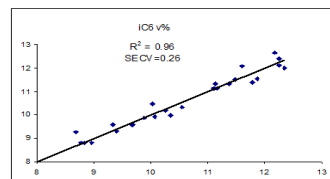
C8



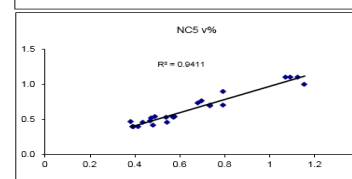
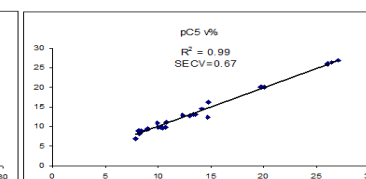
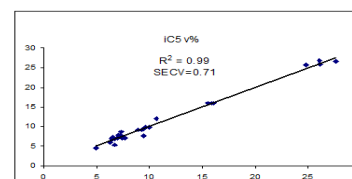
C7



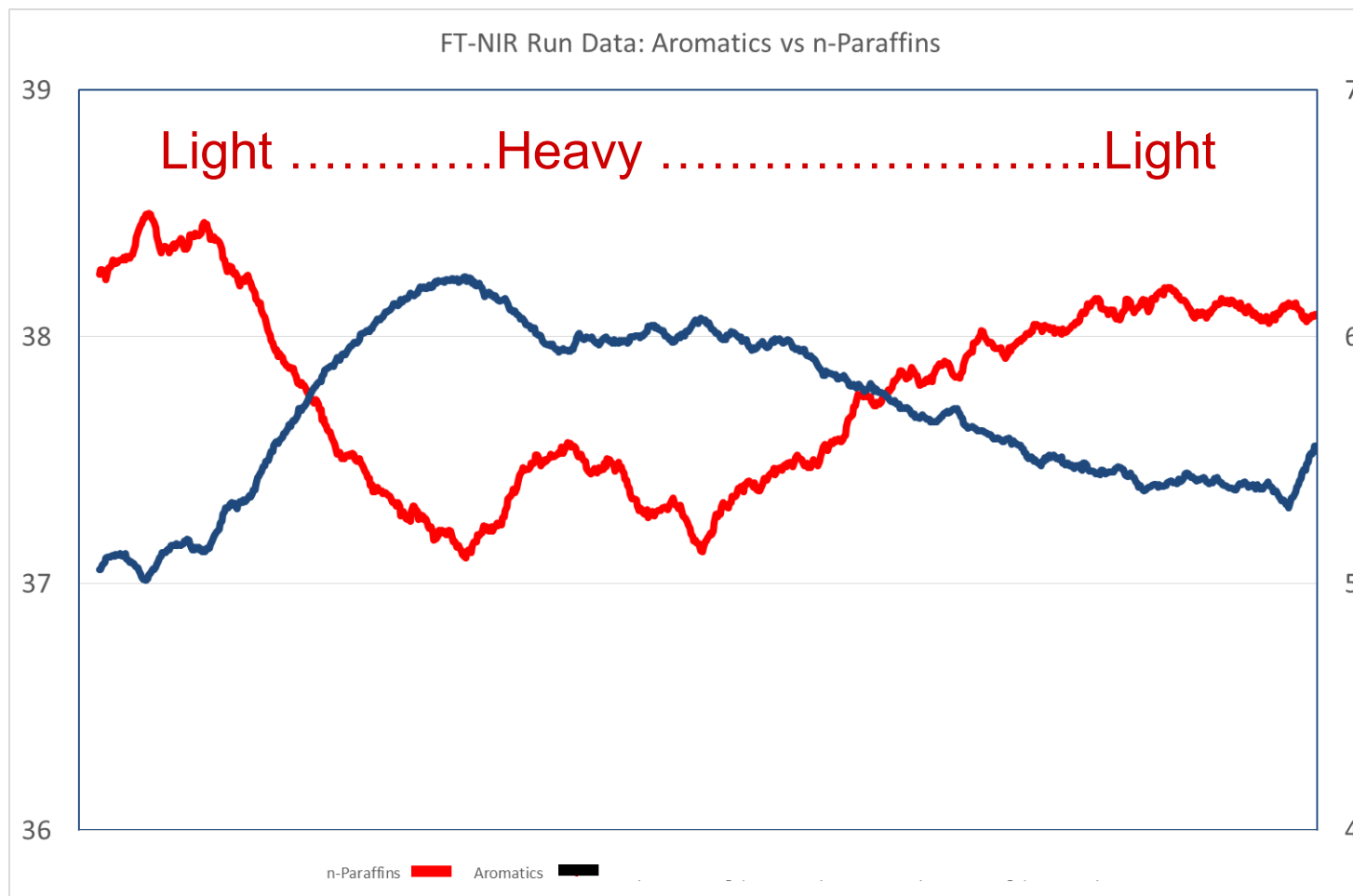
C6



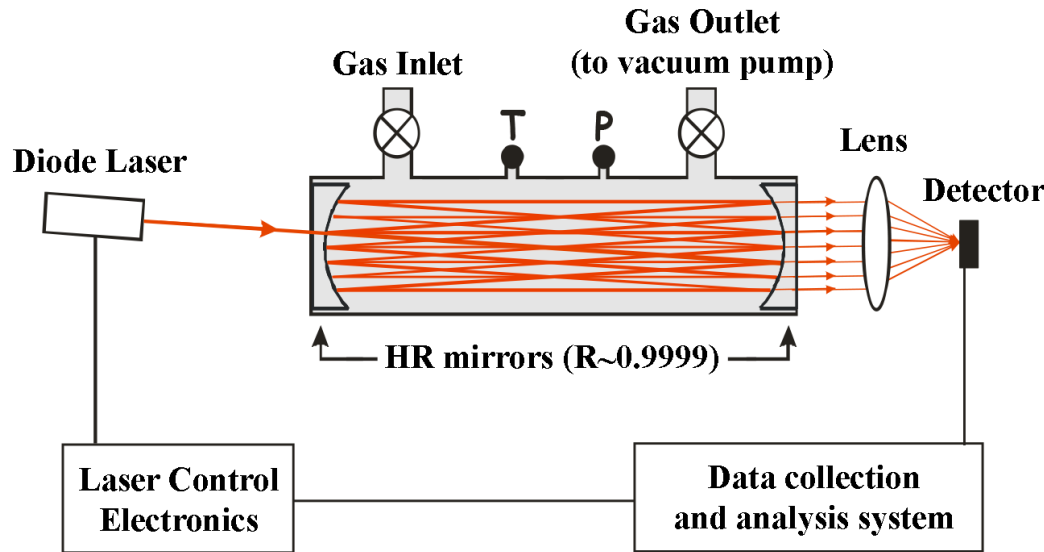
C5



Feed transitions

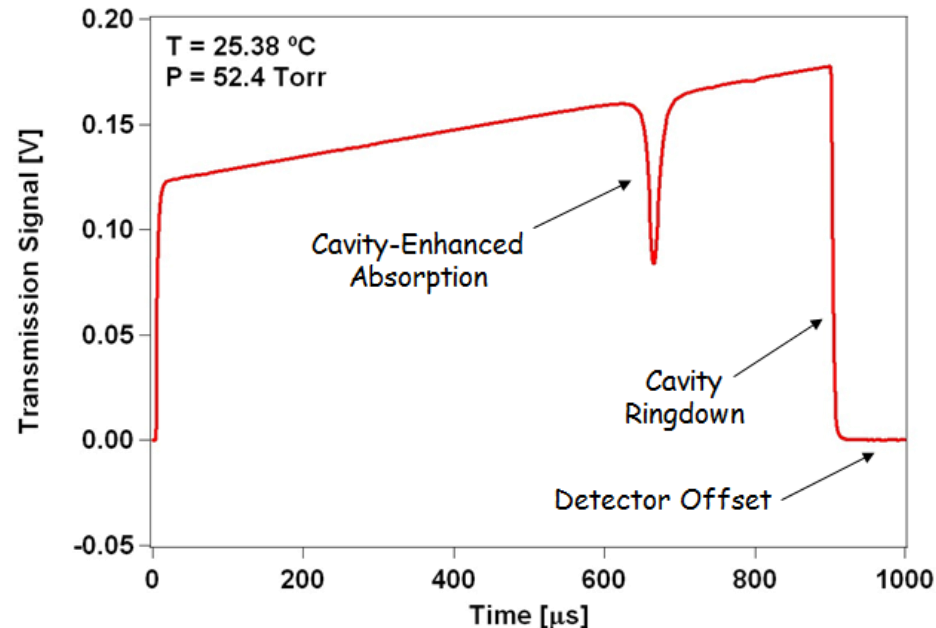


Off-Axis Integrated Cavity Output Spectroscopy (ICOS)



- Small portion of laser power transmits through the front mirror
- Optical cavity provides an effective pathlength of 1 – 10 kilometers
 - Allows for detection of very low concentrations → ppb-level sensitivity
- Off-Axis – prevents optical interference within the cavity and feedback to laser from mirrors
- Very robust - exact alignment, gas pressure, and gas temperature are not critical
 - Significant improvement over multipass cells where precise alignment is critical
- Mirrors can be cleaned in the field by minimally-trained personnel in < 20 minutes

Off-Axis ICOS: Measured Data



- Measure baseline, absorption, ringdown, detector offset, T and P every sweep
- Operate at low pressure to narrow lineshapes and improve selectivity
- Scan laser at 100–1000 Hz to provide complete measurement every 1–10 ms
- User-selectable data rate allows for averaging to improve precision
- Large linear dynamic range (10,000:1) – effective pathlength decreases with absorption increase

Refinery Process Units

Naphtha Steam Cracker – Olefins Unit



Ethylene purity (steam cracker product) analyzer configurations

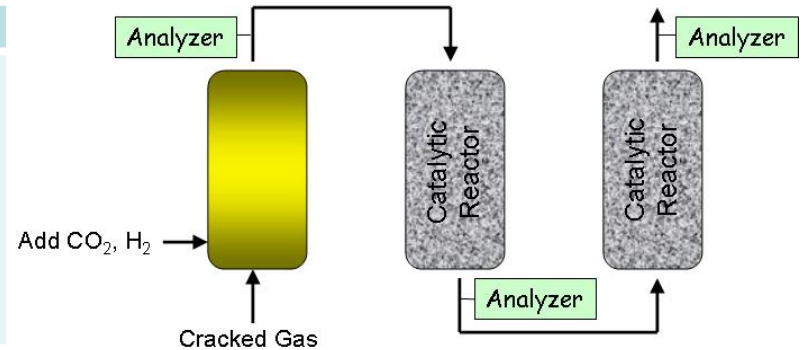
Analyzers	# Laser	C ₂ H ₂ (ppm)	NH ₃ (ppm)
C ₂ H ₂	1	0.002-20	
C ₂ H ₂ /NH ₃	1	0.002-20	0.01-100

LGR-ICOS 950 Series

Steam Cracker Product Ethylene



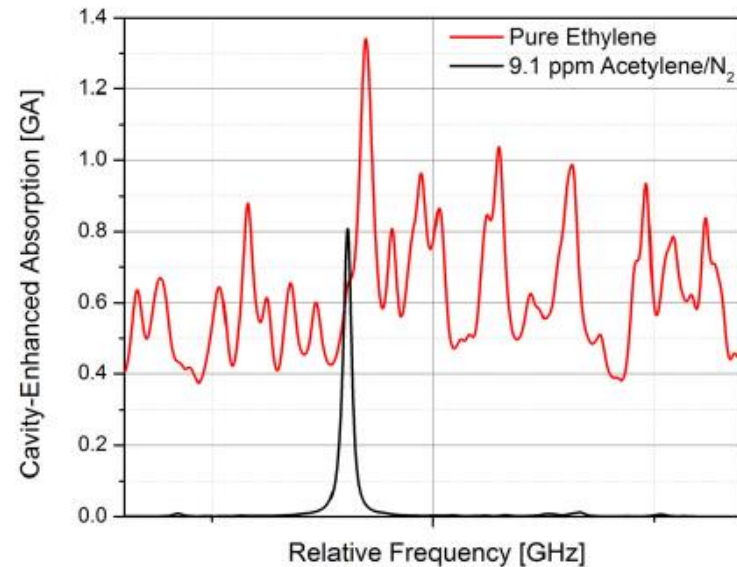
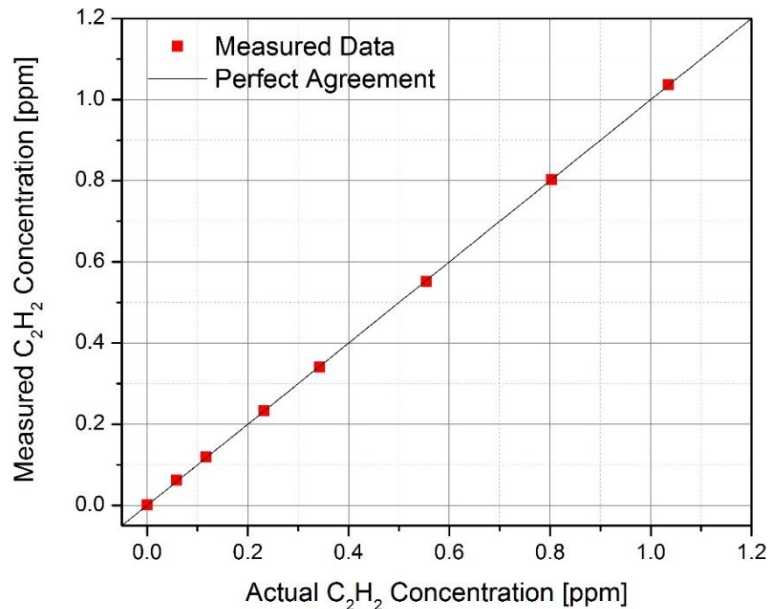
Process	What?	Why?
DOWNSTREAM Steam Cracking Olefins Unit	Steam Cracker Ethylene - Product Purity C_2H_2 2 ppb – 20 ppm NH_3 10 ppb – 100 ppm	Ethylene / Propylene purity to meet critical product specification



Minimize acetylene contamination

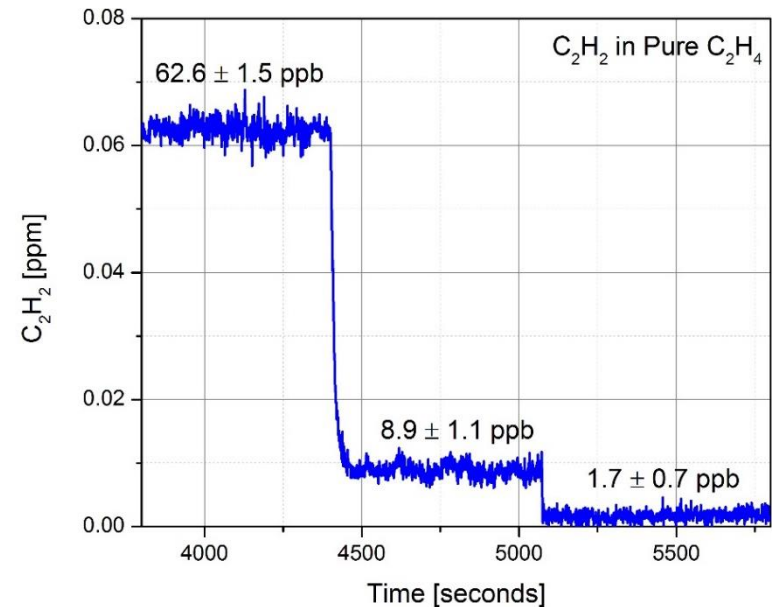
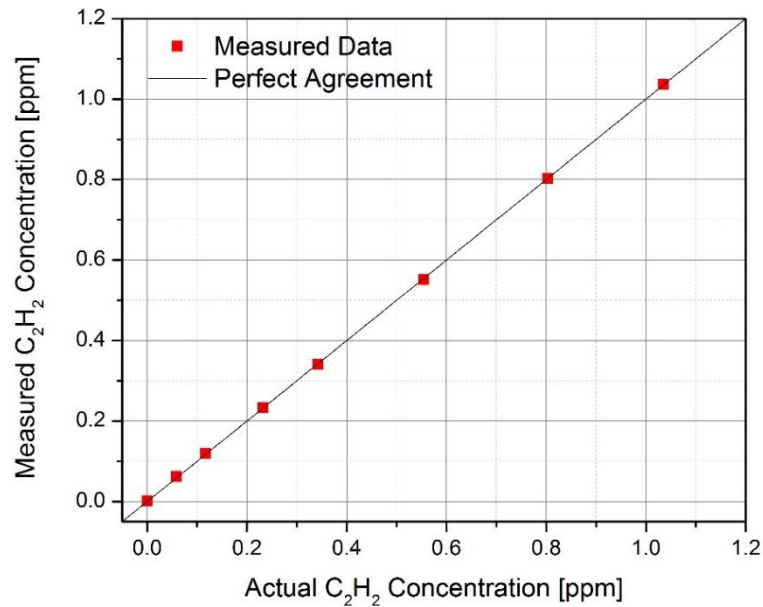
- Must contain < 10 ppmv acetylene
- Actively control hydrogenation
- Divert stream if a plant upset occurs
 - Protect stored product
 - Protect catalysts

Contaminants in Ethylene – Sample Data



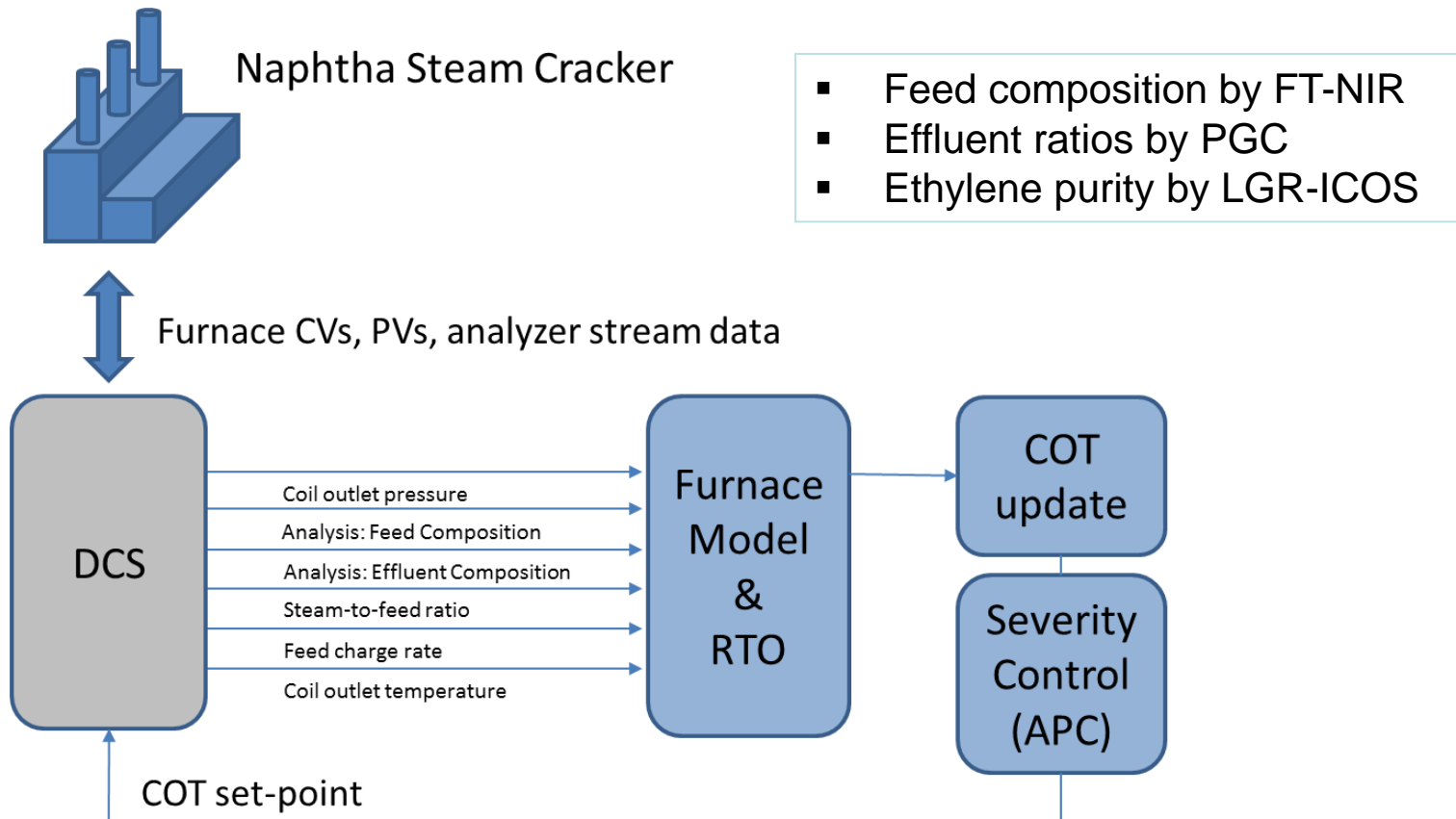
- Measure C_2H_2 with a low LDL (< 20 ppb), high precision (< 2 ppb, 1s, 1sec), and good accuracy
- Simultaneously measure NH_3
- Used for both end-product verification as well as process control

Contaminants in Ethylene – Sample Data



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- Simultaneously measure NH_3
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Feed analysis for furnace RTO



Thank you

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