More From the Barrel

On-Line NMR Increases Diesel Production and Quality (Part I)

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Refinery Applications

On-line, high resolution nuclear magnetic resonance spectroscopy (NMR) made its introduction into refinery processes twelve years ago with installation of two units into Texaco's Los Angeles area refinery. From then to now, integration of the proper NMR hardware with the properly designed applications have proven economically and operationally beneficial. Whether the on-line NMR application serves as a preferred multi-parameter analyzer, or, integrated into advanced process control and optimization, the accuracy, reliability, and performance of on-line NMR delivers true value throughout the refining process.

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Advantages and Disadvantages of NMR Applied to Process

Advantages:

Non-Optical Spectroscopy
No Spectral Temperature Dependence
Minimal Sampling Requirements
Spectral Response to Sample Chemistry is Linear
Chemical Regions of NMR Spectra are Orthogonal
Entire Volume is Sampled by the RF Experiment
Water is in Distinct Region and can be digitally removed
Detailed Hydrocarbon information is readily observed.
Fundamental Chemical Information Can be Derived Directly from Spectrum.
Colored/Black Samples Readily Observed

Disadvantages:

Solids Cannot be Observed
Individual Molecular Component Sensitivity Not Observed Directly in the Spectrum.
Low Sensitivity to Impurities – Quantitative > 1000 ppm.
Sensitive to Ferro-magnetics.
Sample Viscosity Causes Resolution Changes
Non-Hydrogen Containing Species are Not Observed

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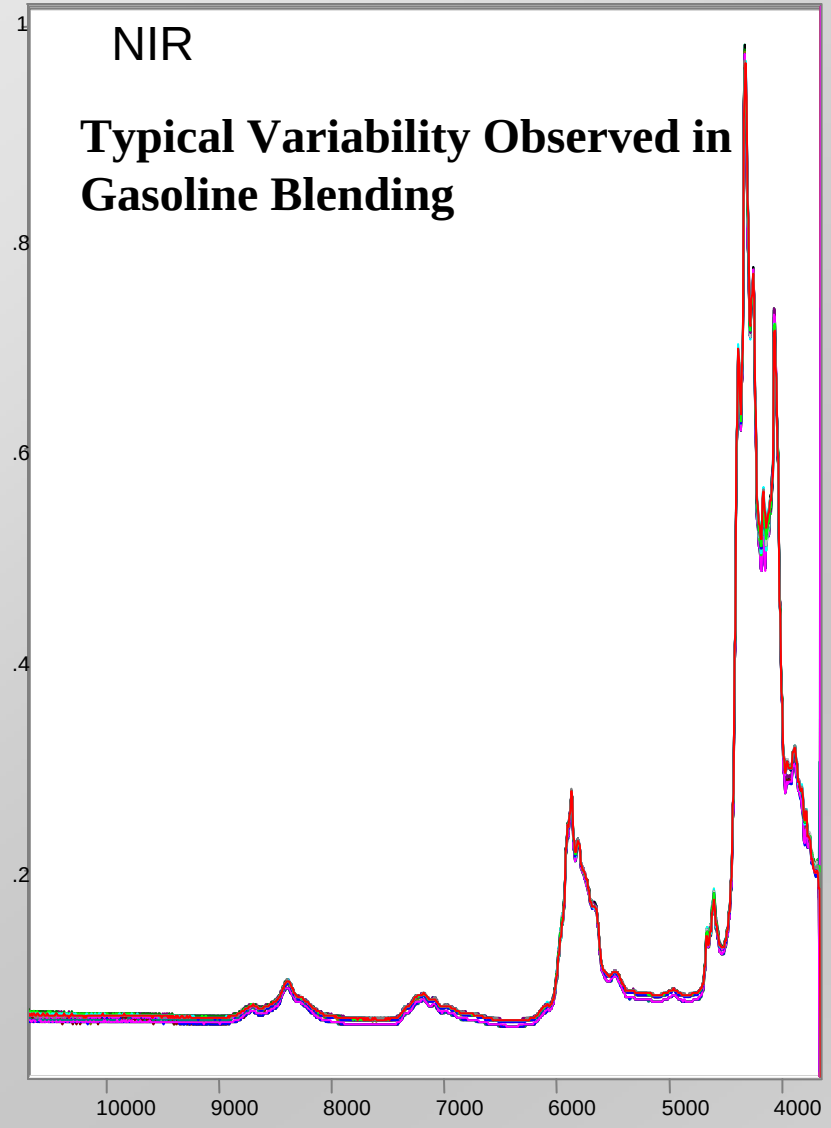

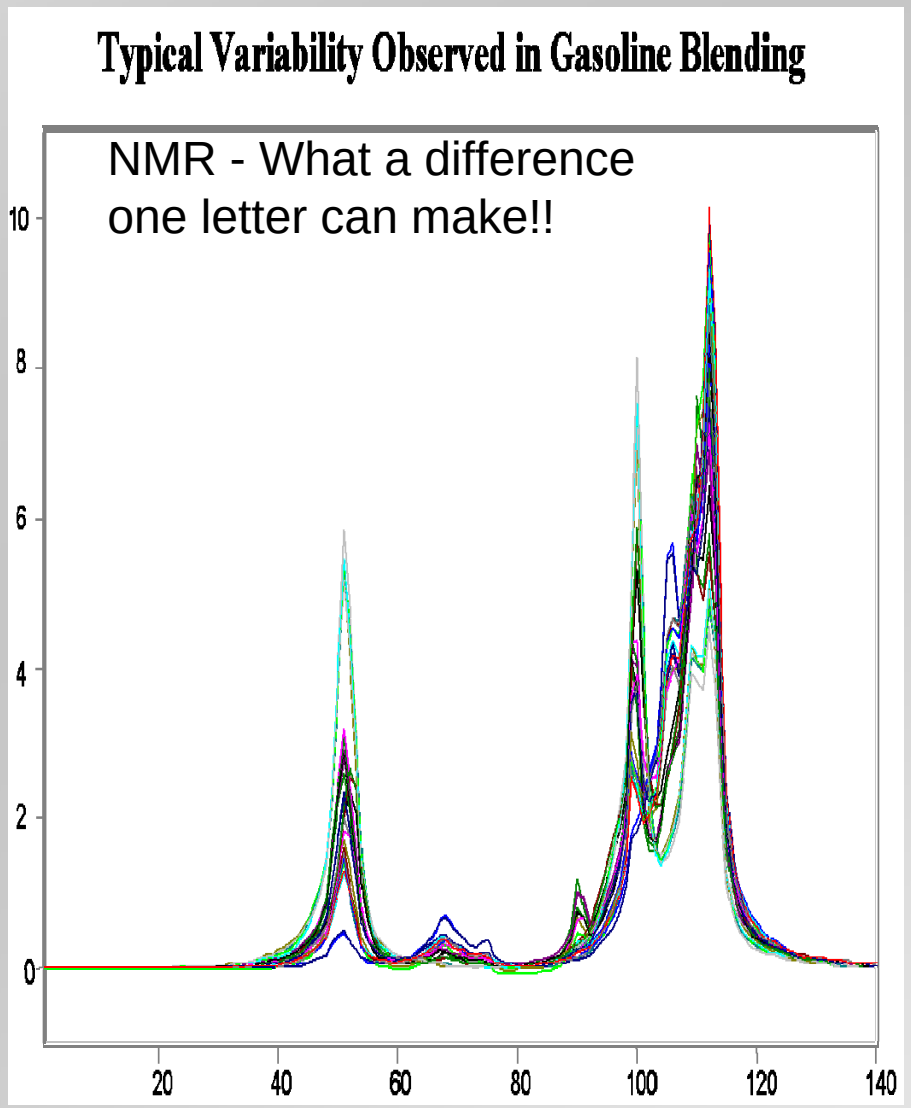

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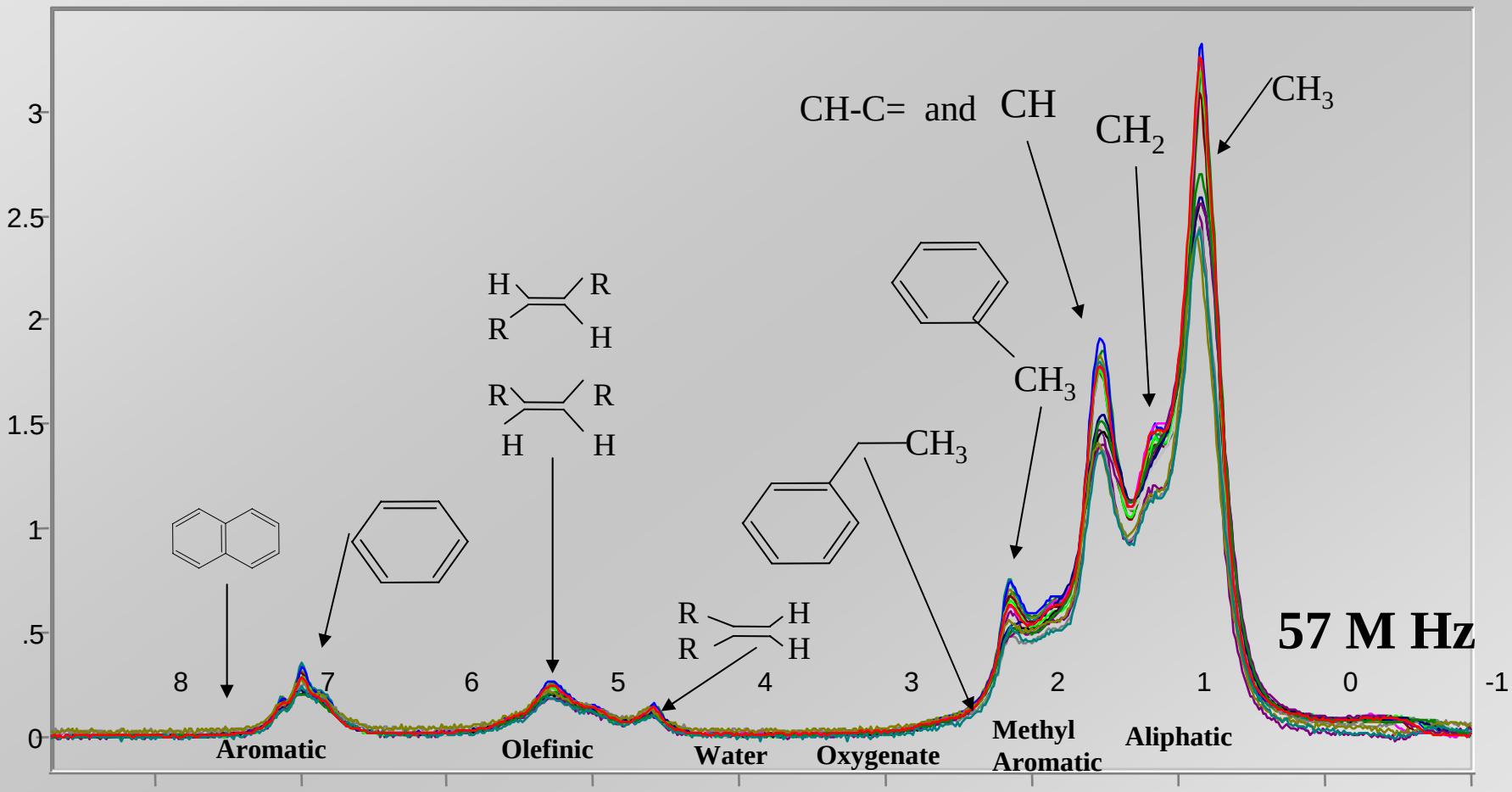
Hydrocarbon Picture



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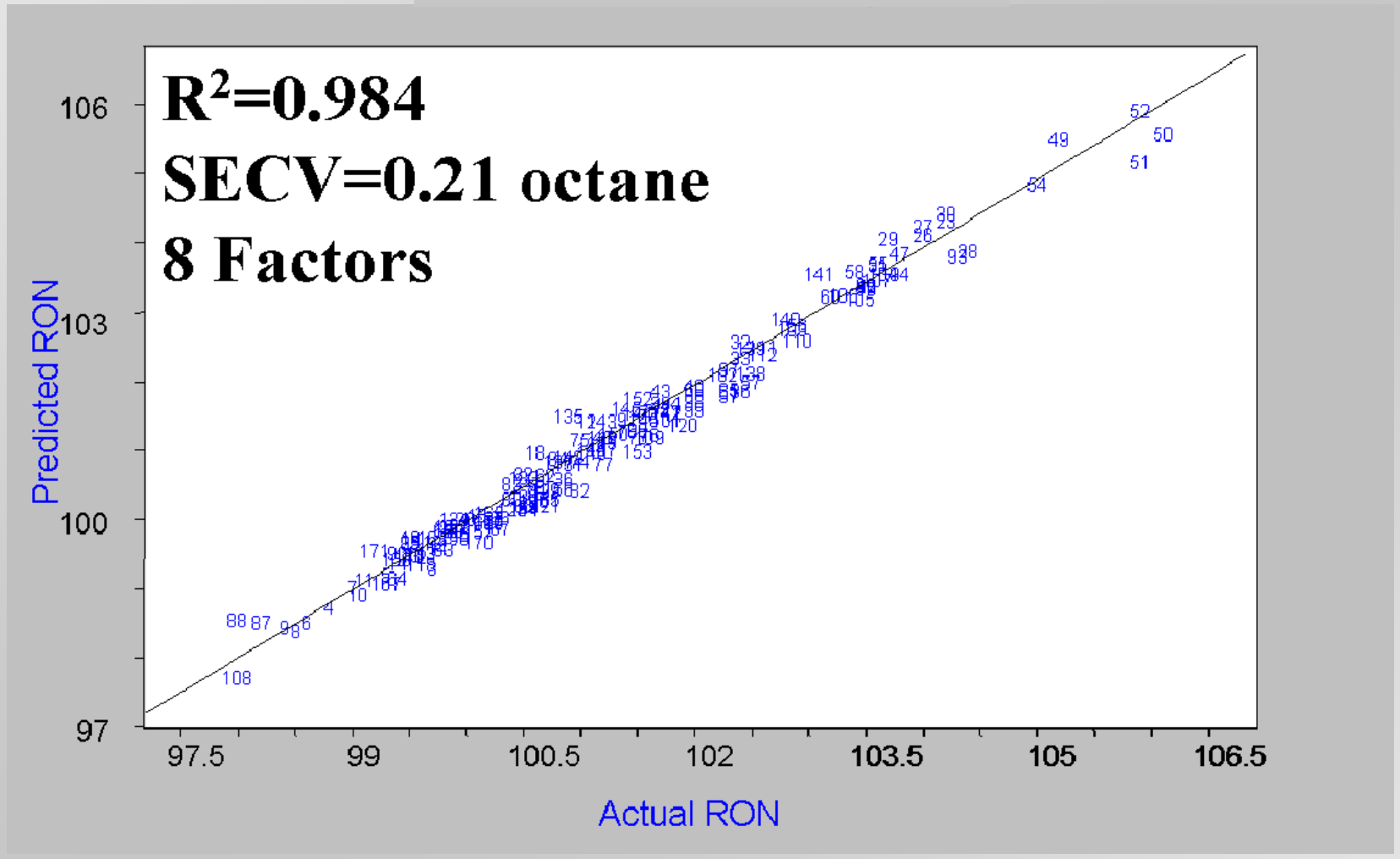

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Parameter Description		ASTM Method Used	ASTM Reproducibility	Engineering Units
Gasoline Blending	RON	D 2699	0.4	Octane
Gasoline Blending	MON	D 2700	0.4	Octane
Gasoline Blending	T10	D 86	9.50	Degrees F
Gasoline Blending	T50	D 86	13.00	Degrees F
Gasoline Blending	T90	D 86	13.50	Degrees F
Gasoline Blending	EBP	D 86	13.50	Degrees F
Gasoline Blending	Aromatics	detailed GC	1.1	Volume %
Gasoline Blending	Benzene	D 3606	0.5	Volume %
Gasoline Blending	RVP		-	information only
Diesel Blending	API	D 4052	1	Degree
Diesel Blending	IBP	D 86	14	Degrees F
Diesel Blending	T10	D 86	14	Degrees F
Diesel Blending	T50	D 86	14	Degrees F
Diesel Blending	T90	D 86	14	Degrees F
Diesel Blending	EBP	D 86	14	Degrees F
Diesel Blending	Viscosity	D 445	-	informational data only
Diesel Blending	Cloud Point	D 5773	7	Degrees C
Diesel Blending	Cetane Index	D 976 - D 4737	2	Index Number
Diesel Blending	Pour Point	D 97	6	Deg C

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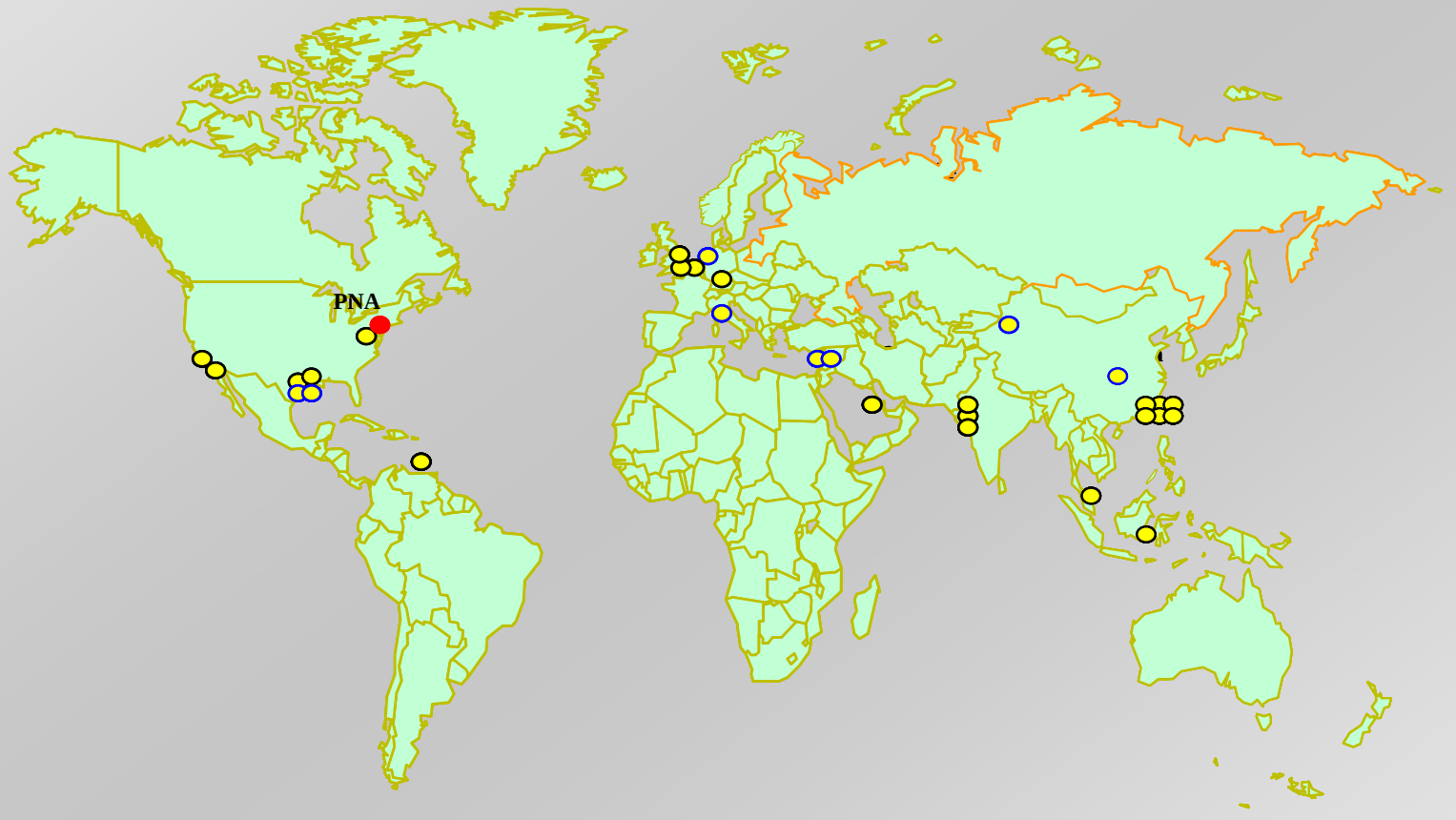
High Resolution Process NMR Installations



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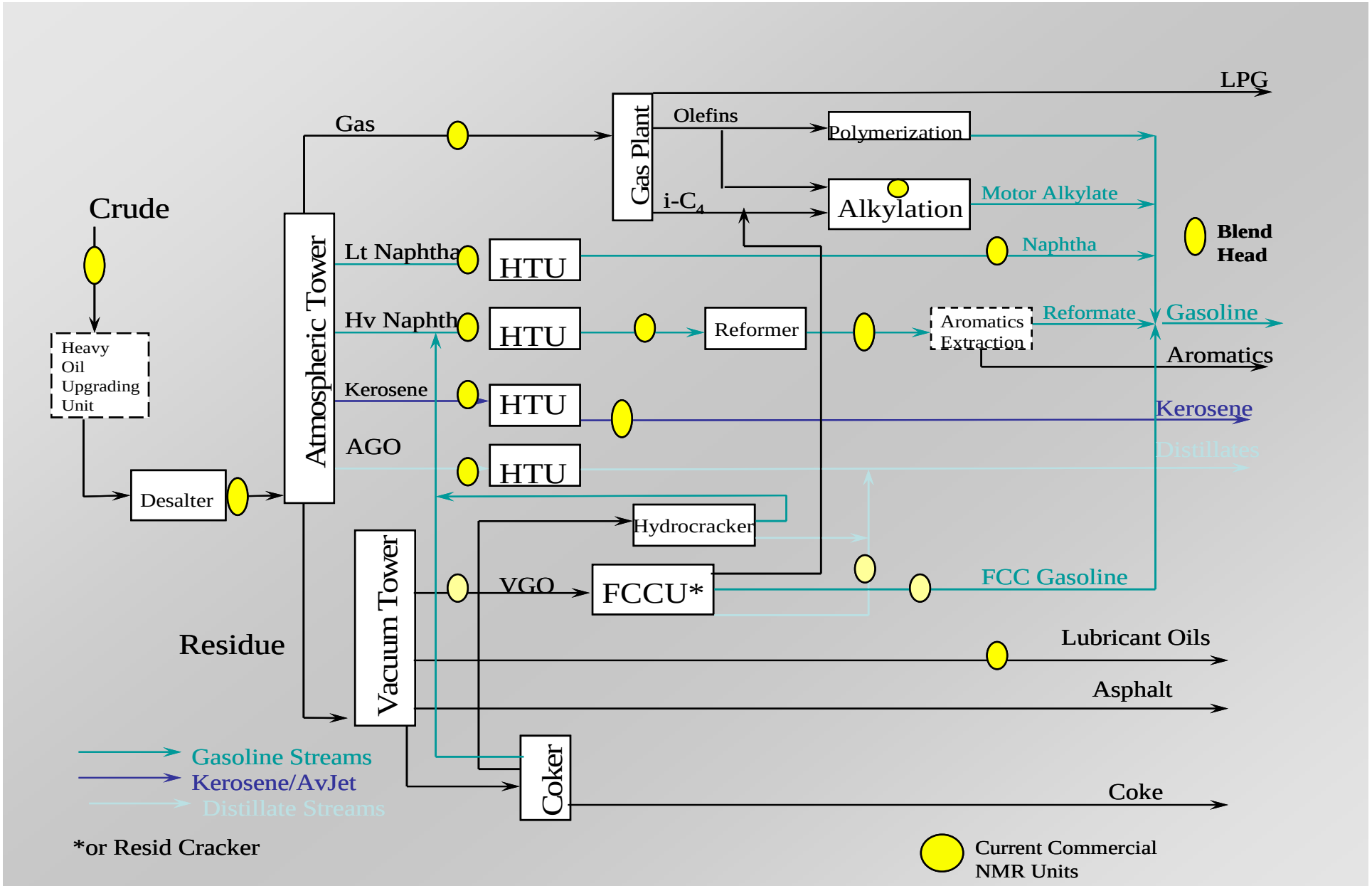

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"Effective feedstock management can save up to 70 cents/barrel for refineries…."

"….modern analytical tools contribute significantly to this …."

Hydrocarbon Processing, September 1998

In 1998 crude was less than $30/barrel.

What about $100+?

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NMR NeSSI: Never expect Small Sample Input!

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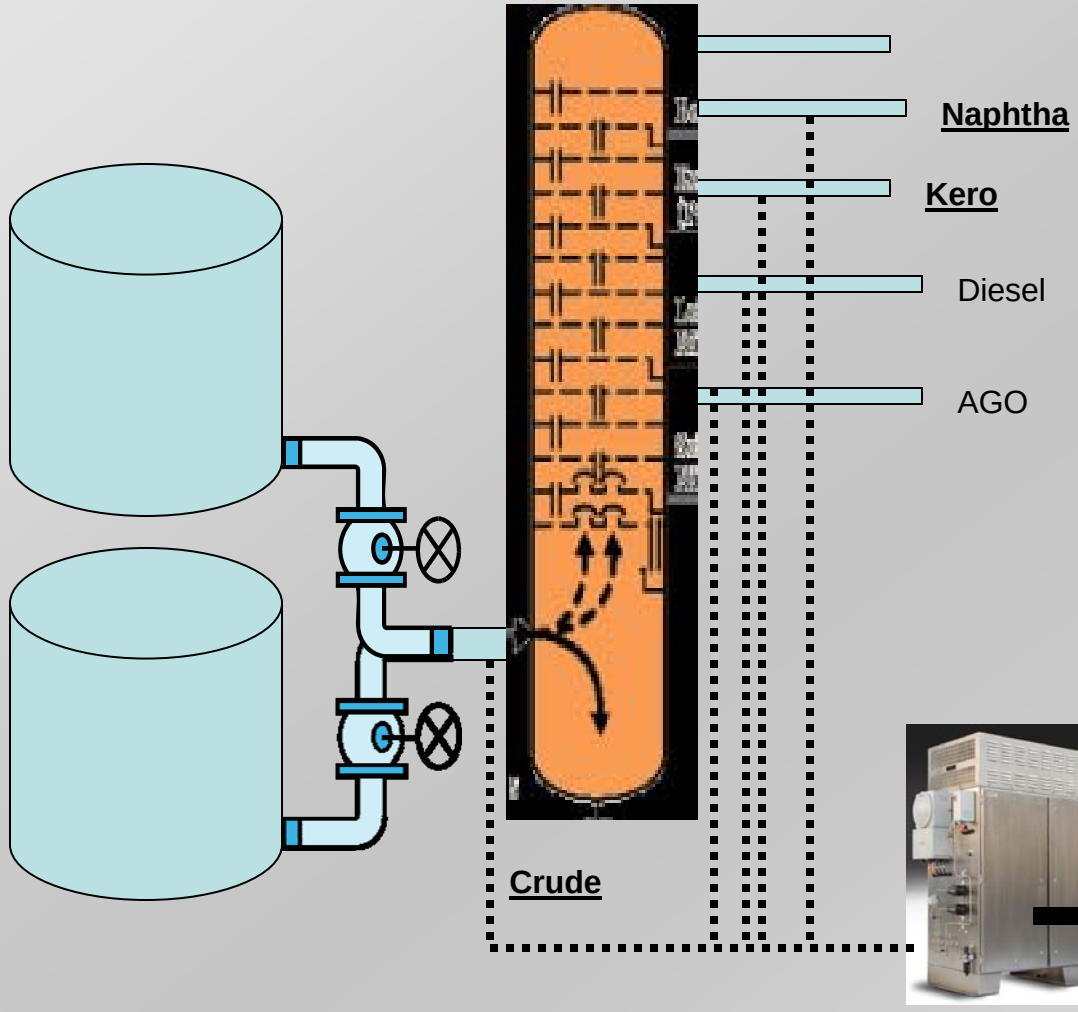
Crude Unit Overview



APC and Optimization

- **Distillation (D86, Sim Dis, TBP)**
- **Flash Point**
- **Cloud Point**
- **Pour Point**
- **Freeze Point**
- **Chemistry (Fa, Fn, Fp, Naphthalene)**
- **PONA/PIONA**
- **API Gravity/Density**
- **Octane/Cetane**

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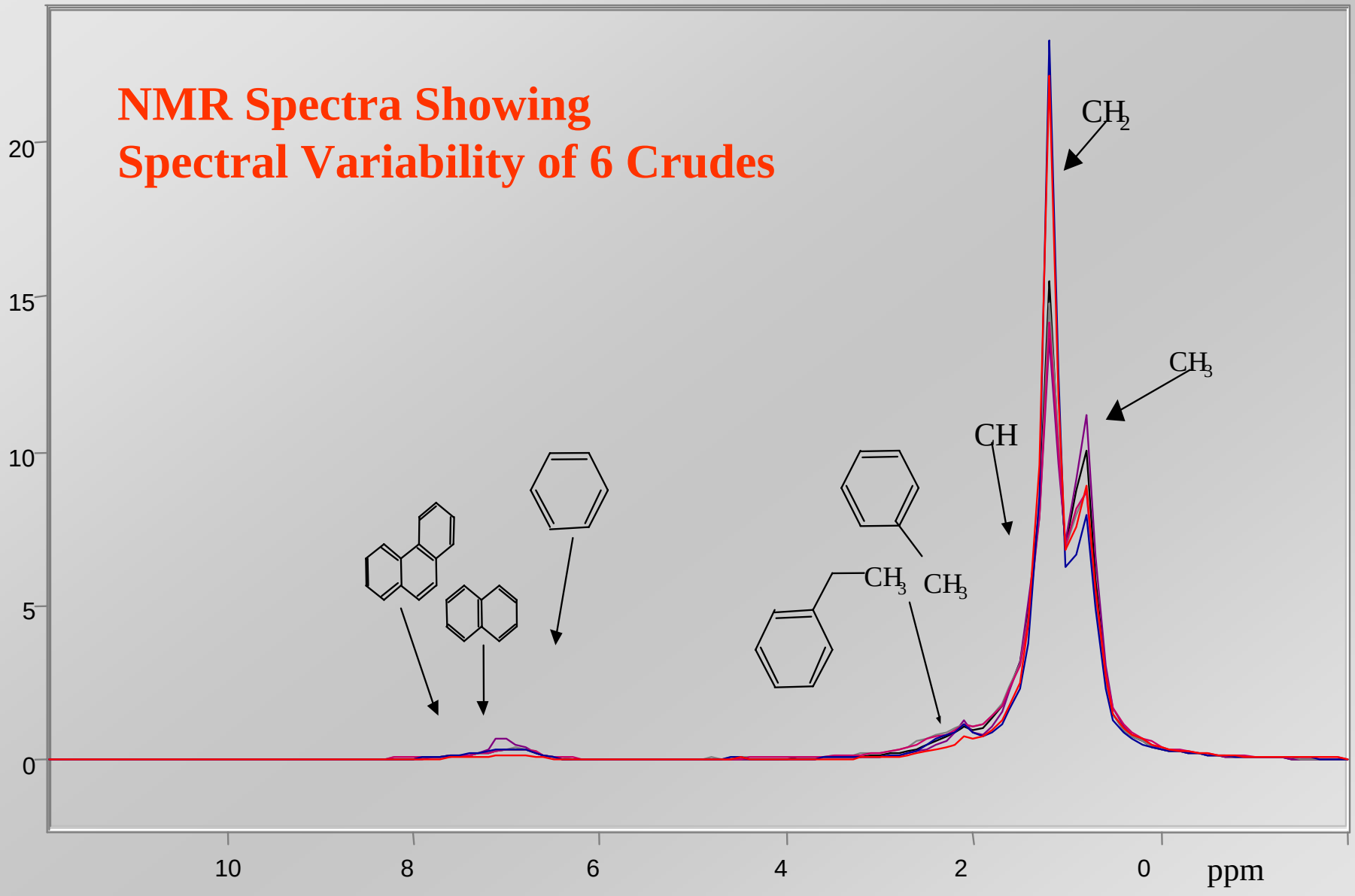
NMR Spectra Showing Spectral Variability of 6 Crudes



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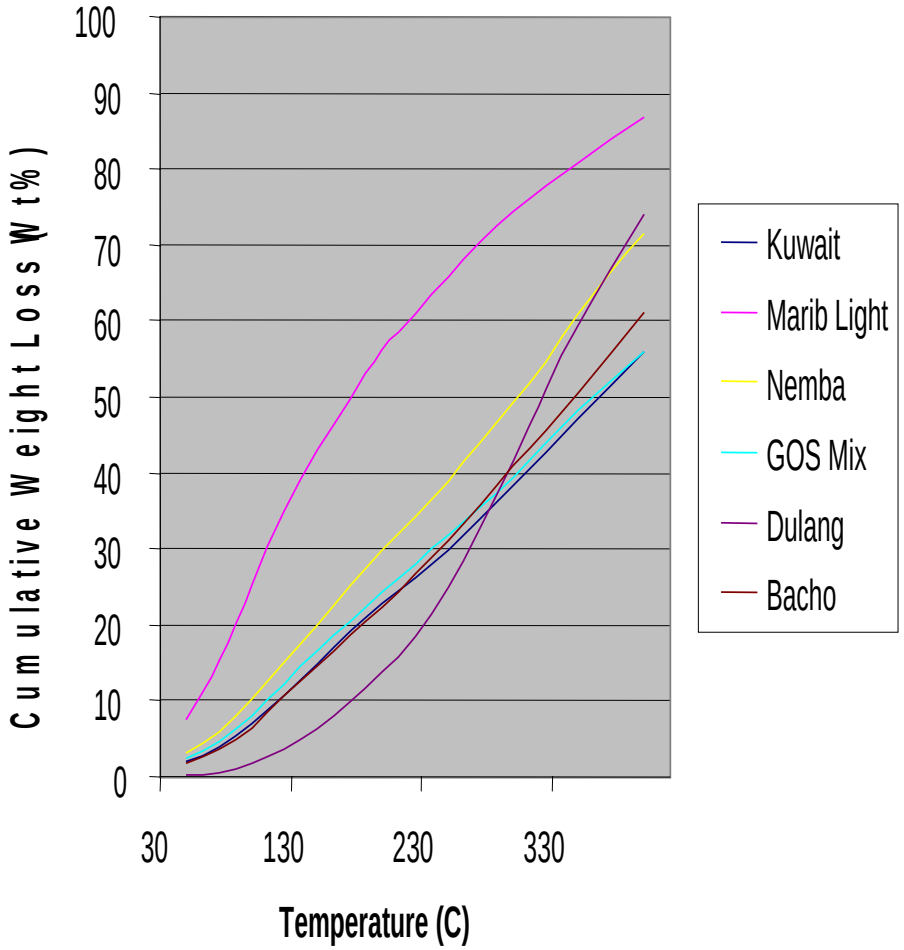
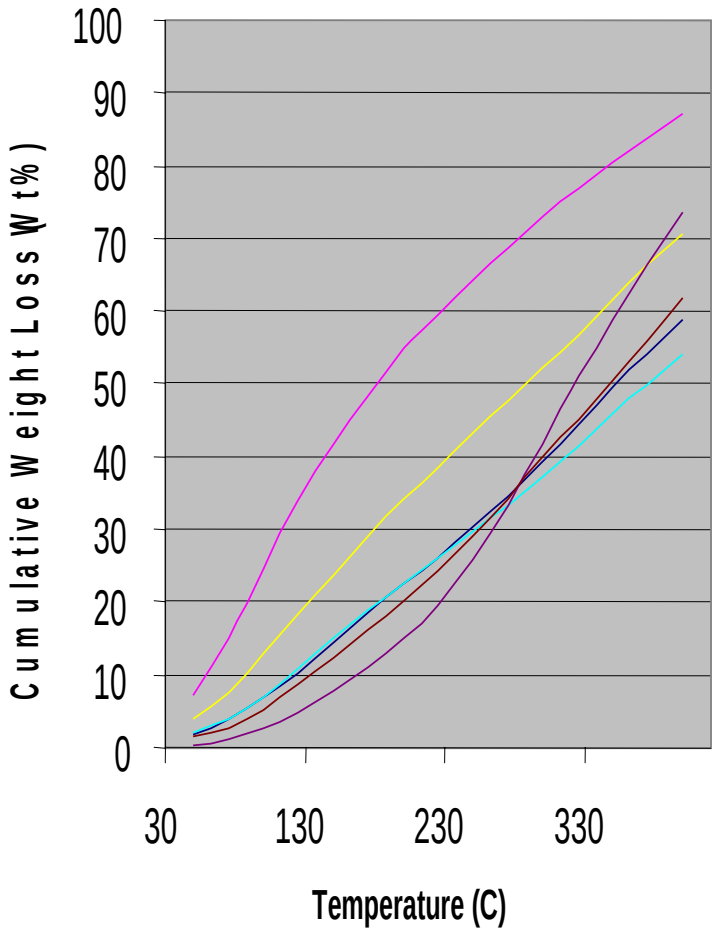
Actual Crude TBP Curves



NMR Predicted TBP Curves for Crudes



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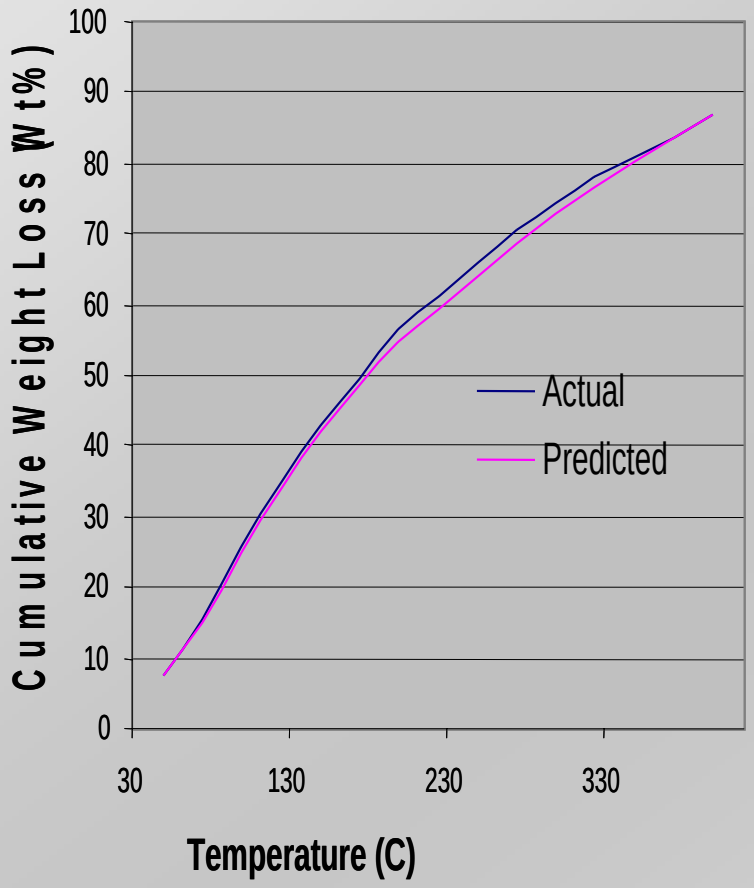
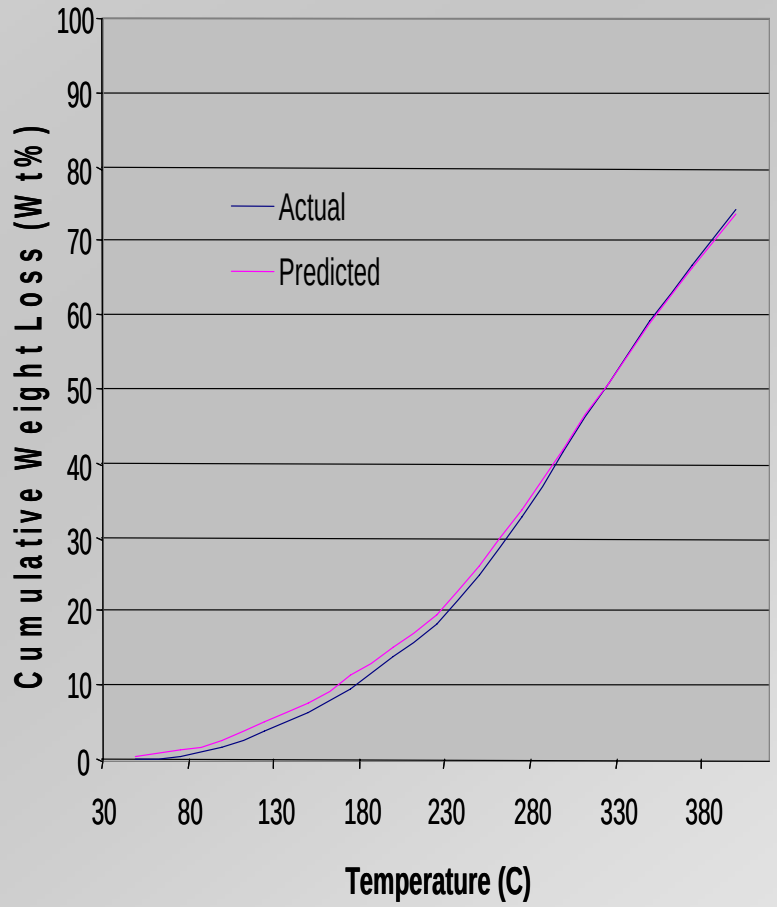
Marib Light Crude TBP Curves

(Actual and NMR Predicted)



Dulang Crude TBP Curves

(Actual and NMR Predicted)



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Parameter Description		Method Used	Reproducibility	Units	
Crude Feed	API	D 4052	1	Degree	
Crude Feed	Sulfur	D 2622 - D 4294	-	Weight %	information only
Crude Feed	TBP wt% 38 C	D 2892	2.2	Weight %	
Crude Feed	TBP wt% 105 C	D 2892	2.2	Weight %	
Crude Feed	TBP wt% 165 C	D 2892	2.2	Weight %	
Crude Feed	TBP wt% 365 C	D 2892	2.2	Weight %	
Crude Feed	TBP wt% 565 C	D 2892	2.2	Weight %	
FCC Feed	API	D 4052	1	Degree	
FCC Feed	Viscosity	D 2161	-		information only
FCC Feed	IBP	D 2887	42	Degrees F	
FCC Feed	T10	D 2887	12	Degrees F	
FCC Feed	T50	D 2887	12	Degrees F	
FCC Feed	T90	D 2887	12	Degrees F	
FCC Feed	EBP	D 2887	25	Degrees F	
FCC Feed	Sulfur	D 2622 - D 4294	-	Weight %	information only
FCC Feed	Carbon Aromaticity	D 5292	2	mole %	
FCC Feed	Carbon Naphthenicity		-	mole %	internal proprietary
FCC Feed	Carbon Parafinicity		-	mole %	internal proprietary
CDU AGO	API	D 4052	1	Degree	
CDU AGO	T10	D 2887	12	Degrees F	
CDU AGO	T50	D 2887	12	Degrees F	
CDU AGO	T90	D 2887	12	Degrees F	
CDU AGO	Sulfur	D 2622 - D 4294	-	Weight %	information only

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Real Time Crude Assays

- On-Line Analysis:
  - Light to Heavy Crude
  - Accurately measured both Actual Crudes and Blends
  - Database of more than 110 Crudes in the Model
  - Does not require exact Crude and/or Blend for an accurate Measurement
- Universal Model
  - Reproducibility
  - Yield Curve < 2 %
  - Broad Range, API Gravity from >9 to 52 deg

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Some Crude Slates and Compositions used in Isla.

Lagomar/Basrah	71/29
GP(Lagotreco/DZO/Boscan)	95/4/1
GP(Lagotreco/DZO/Boscan/Slops)	90/4/1/5
GP(Lagotreco/DZO)	95/5
GP(Lagotreco/Oriente/DZO/Slops)	68/23/4/5
GP(Lagotreco/Oriente/DZO)	92/3/5
GP(Lagotreco/Oriente/mesa/DZO)	74/14/7/5
GP(Lagotreco/Oriente/mesa/DZO/slops)	51/11/28/5/5
GP(Lagotreco/LagotrcoMediano/Oriente/mesa/DZO/Slops)	37/2/24/28/4/5
GP(DZO/MESA/Lagotreco/LagotrcoMediano/Orientae/Slops)	5/27/42/6/12/3

GP = General Purpose Crude. Slops = refinery slop re-blends of unknown composition and quality.

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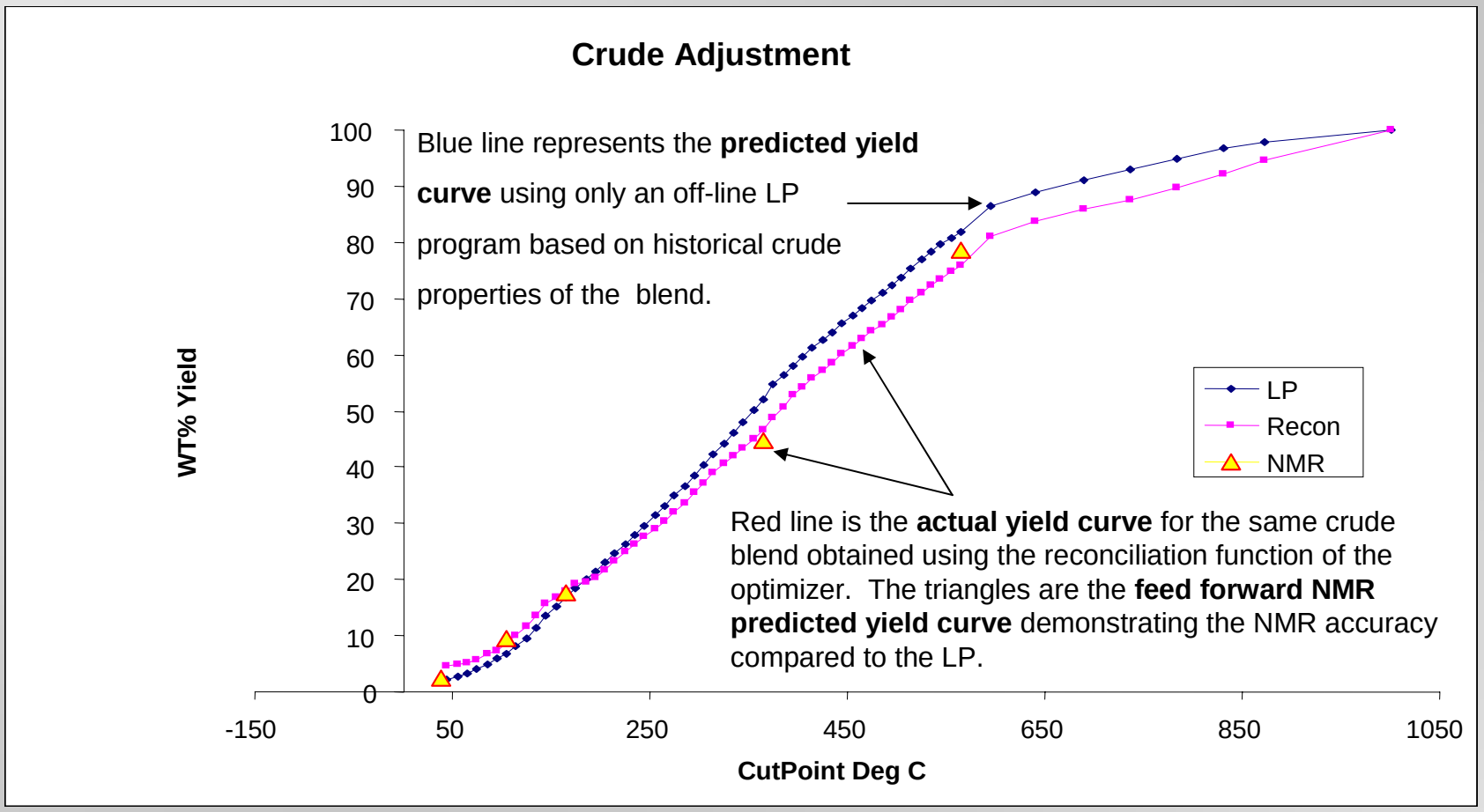

Net Benefit of NMR + Optimization - $3 million/yr.

PDVSA-Curacao implemented their own Romeo Optimization project. The NMR feed forward predictions accurately measured the crude blend properties even though no individual crudes, crude blends, or, on-site lab measurements were used in the NMR crude property models.

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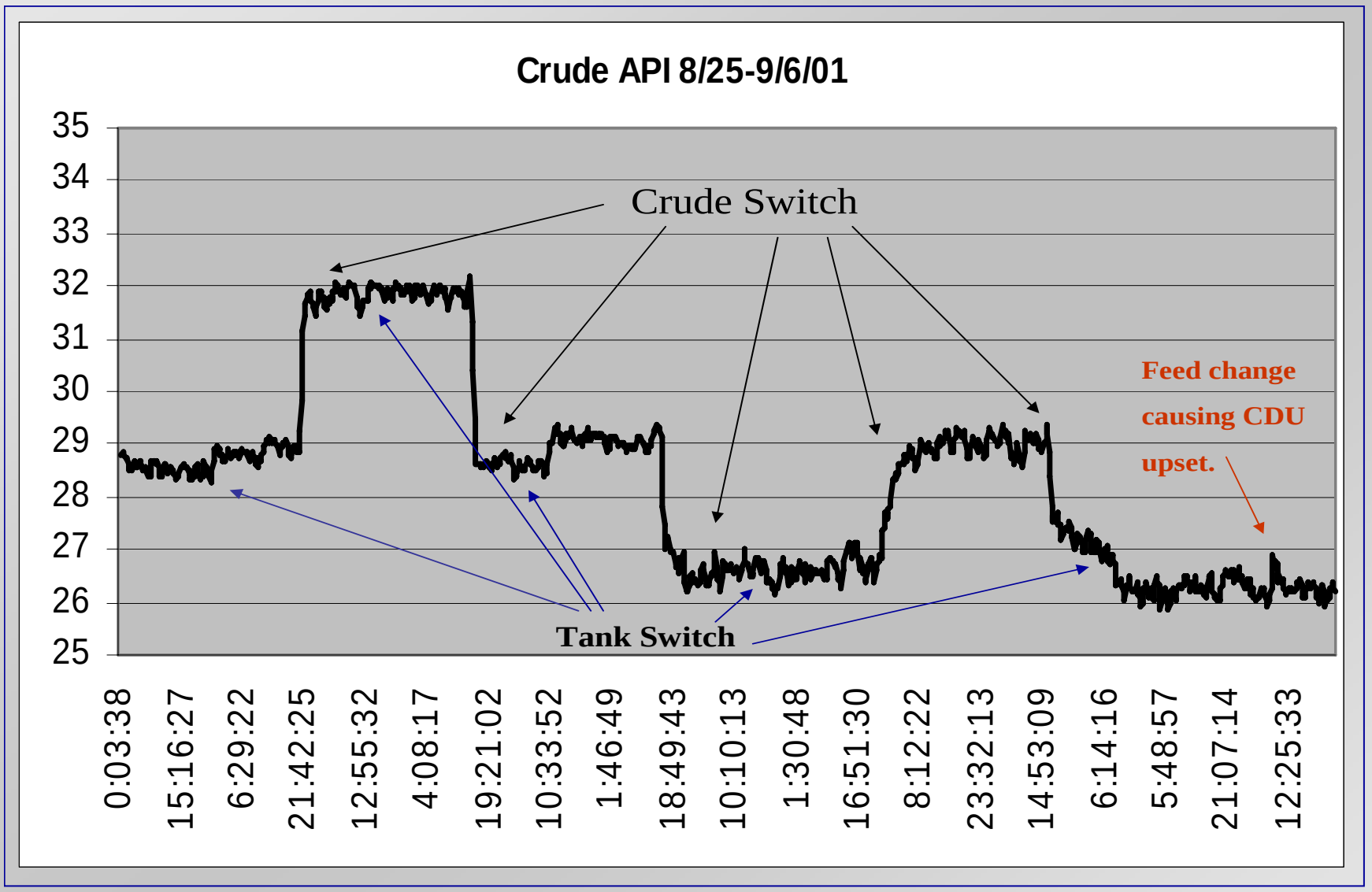

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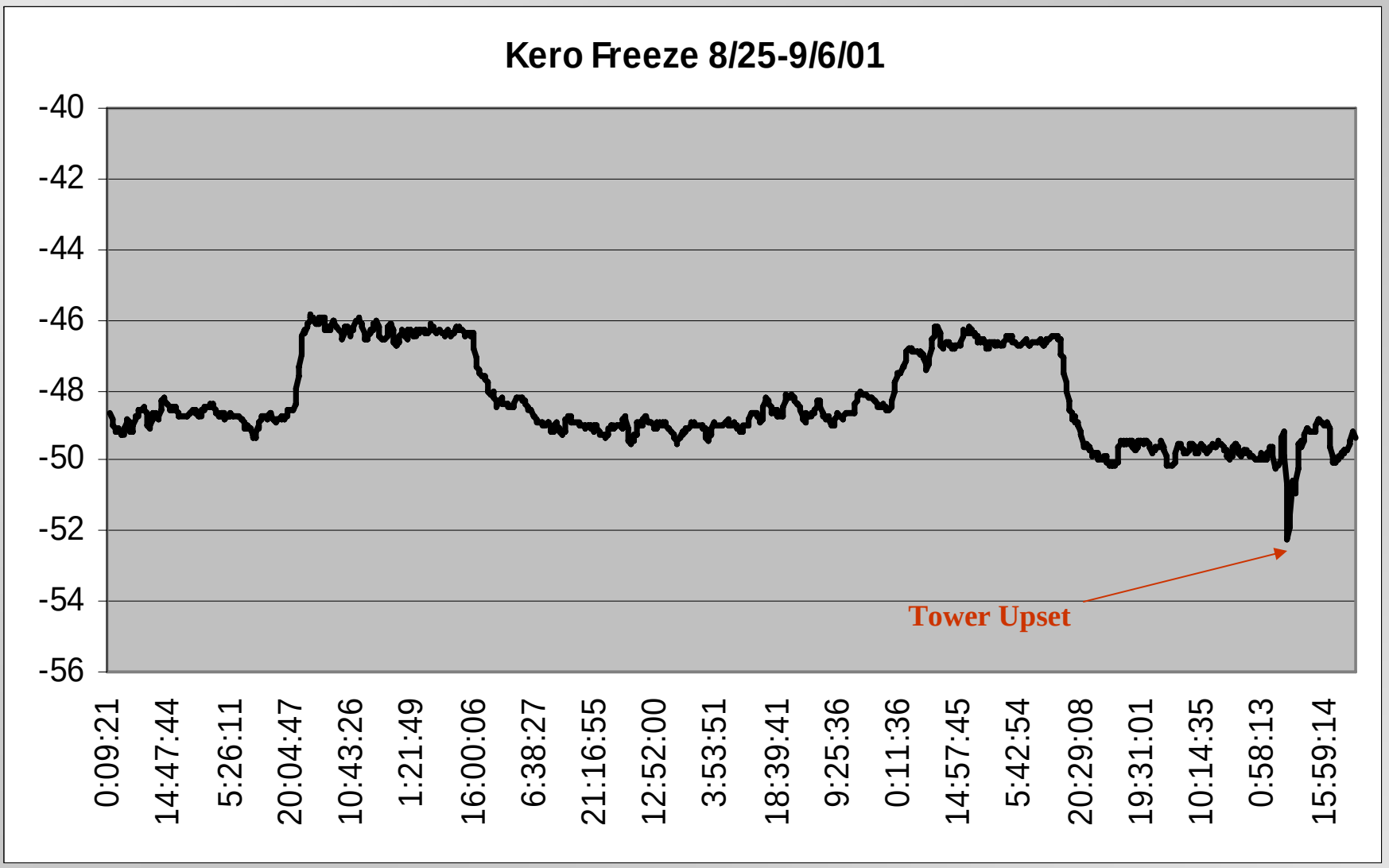

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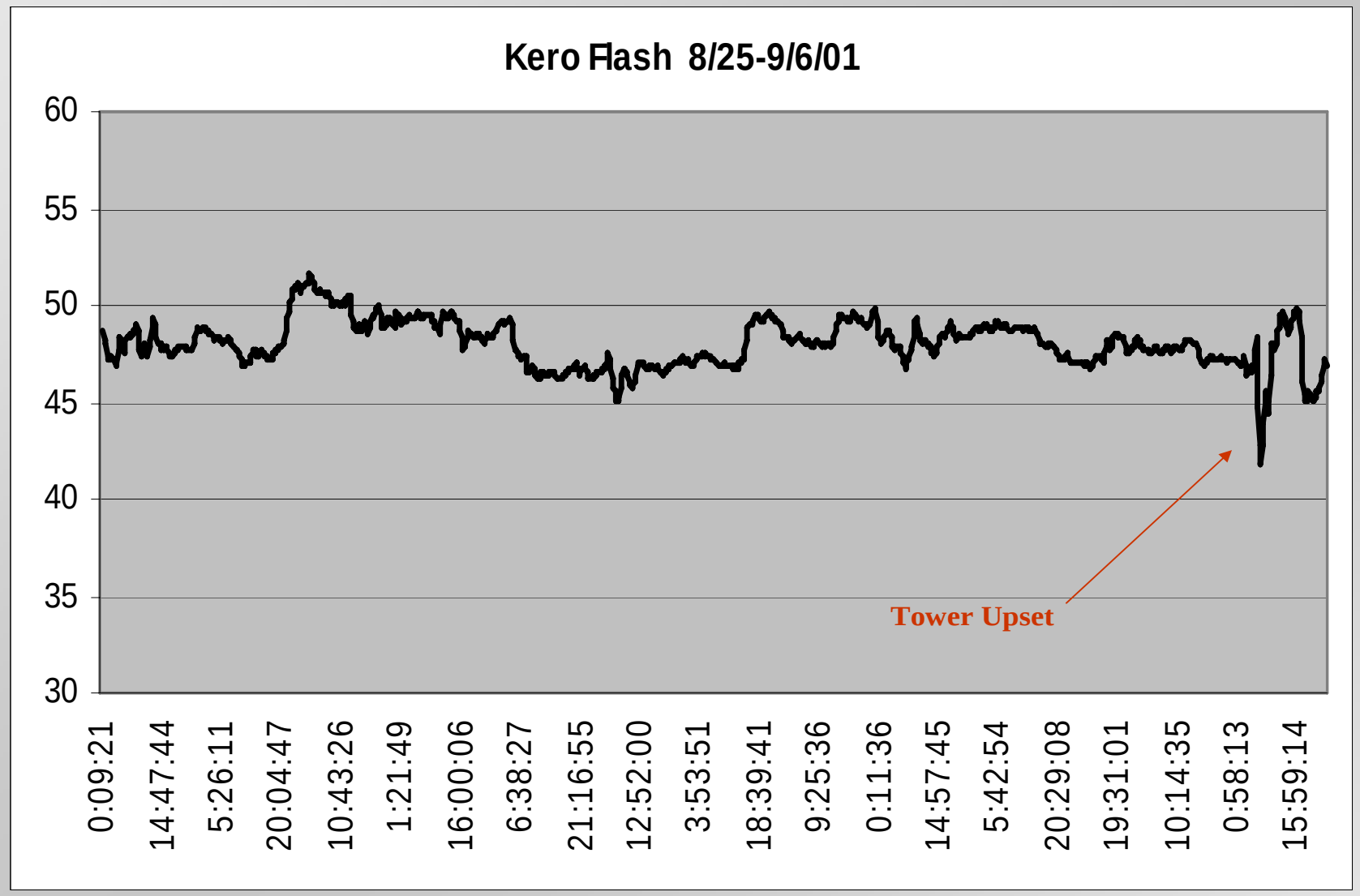

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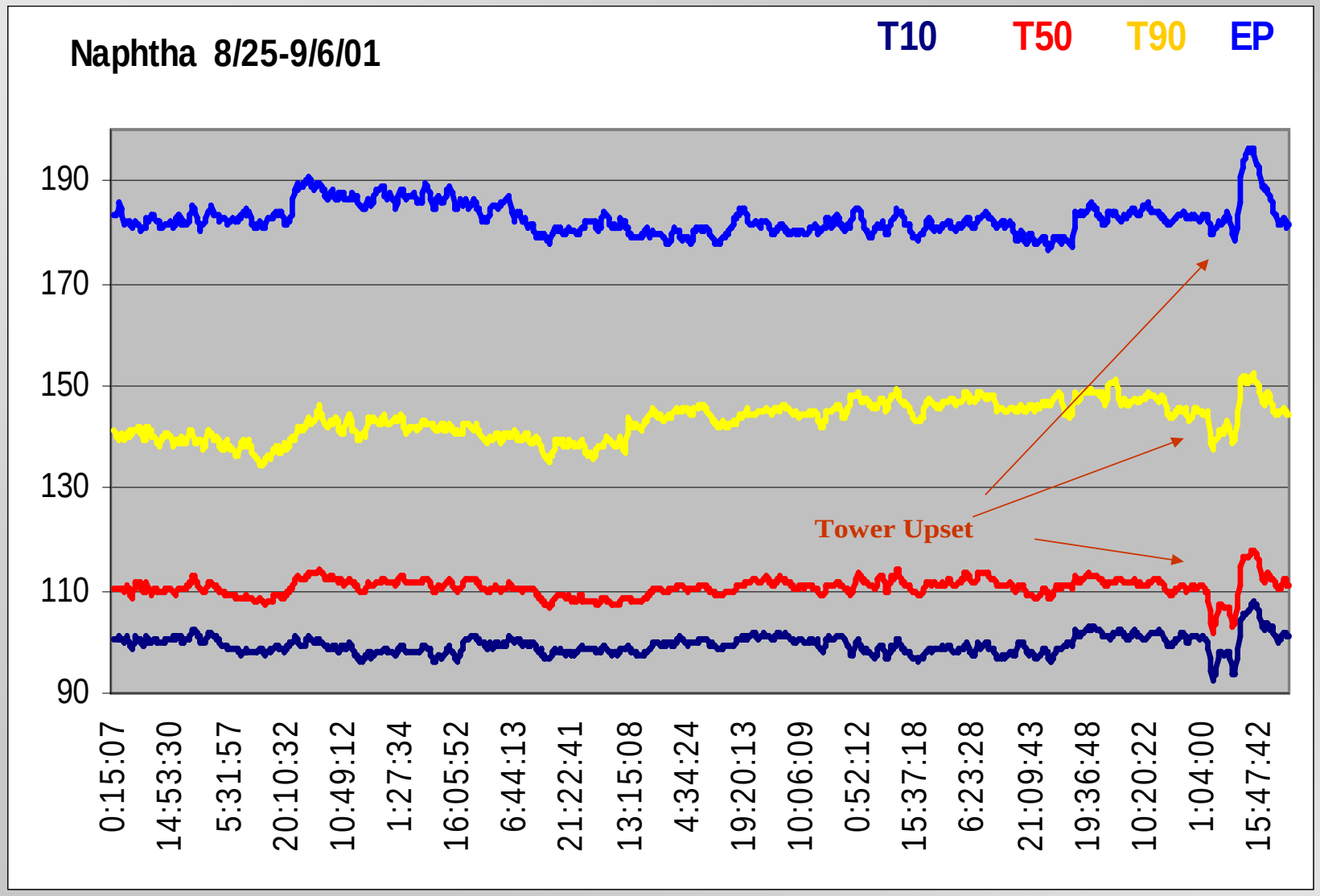

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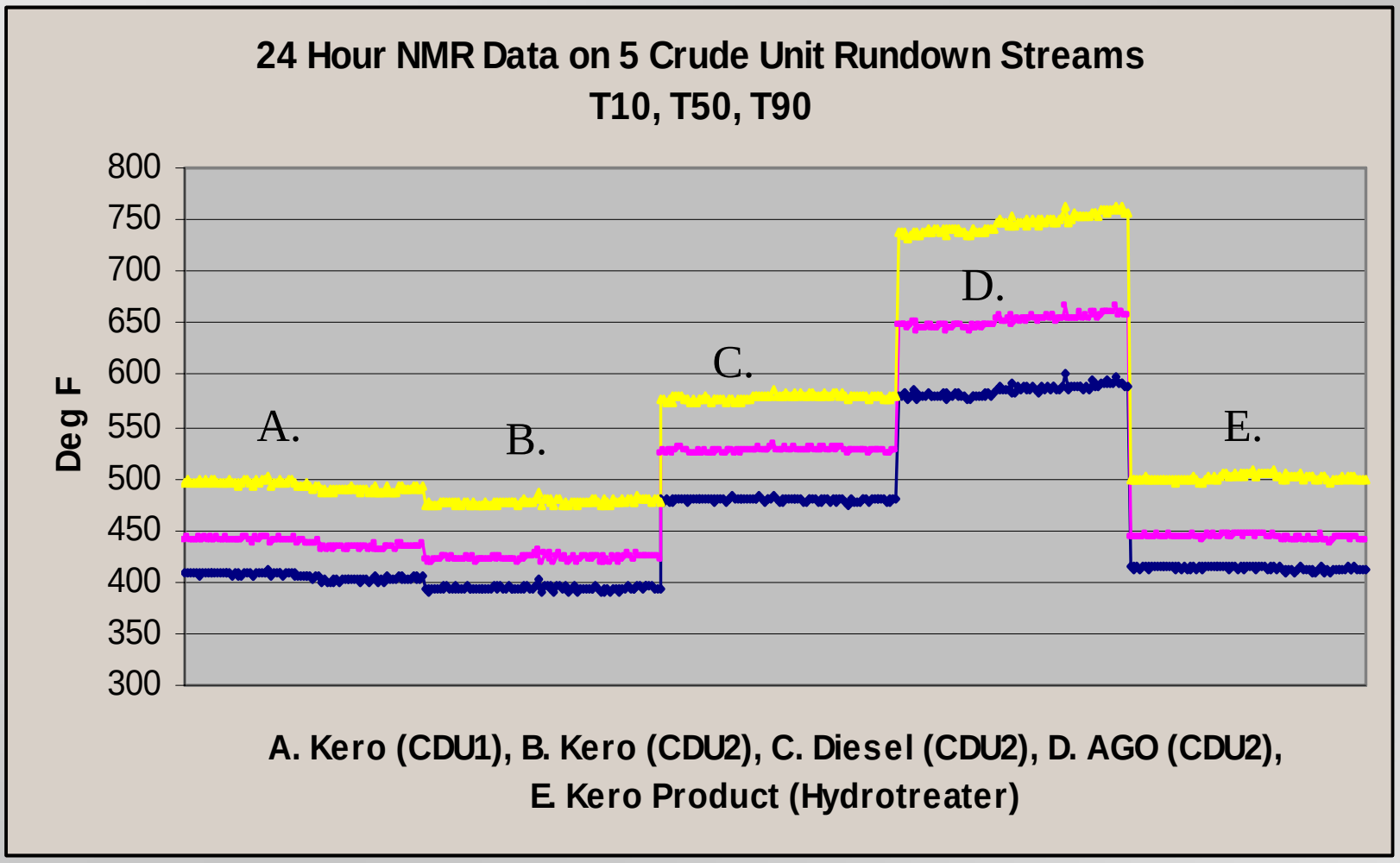
Parameter Description		ASTM Method Used	ASTM Reproducibility	Engineering Units	
Naphtha (med & Hvy)	API	D 4052	1	Degrees F	
Naphtha (med & Hvy)	IBP	D 86	14	Degrees F	
Naphtha (med & Hvy)	T10	D 86	14	Degrees F	
Naphtha (med & Hvy)	T50	D 86	14	Degrees F	
Naphtha (med & Hvy)	T90	D 86	14	Degrees F	
Naphtha (med & Hvy)	EBP	D 86	14	Degrees F	
Naphtha (med & Hvy)	Viscosity	D 445	-	%	informational data only
Naphtha (med & Hvy)	Flash Point	D 93	5	Degrees C	
Kerosene	API	D 4052	1	Degree	
Kerosene	IBP	D 86	14	Degrees F	
Kerosene	T10	D 86	14	Degrees F	
Kerosene	T50	D 86	14	Degrees F	
Kerosene	T90	D 86	14	Degrees F	
Kerosene	EBP	D 86	14	Degrees F	
Kerosene	Viscosity	D 445	-	%	informational data only
Kerosene	Flash Point	D 56	5	Degrees C	
Kerosene	Freeze Point	D 2836	3	Degrees C	
Kerosene	Cloud Point	D 5773	7	Degrees C	
Kerosene	Cetane Index	D 976 - D 4737	2	Index Number	
Diesel	API	D 4052	1	Degree	
Diesel	IBP	D 86	14	Degrees F	
Diesel	T10	D 86	14	Degrees F	
Diesel	T50	D 86	14	Degrees F	
Diesel	T90	D 86	14	Degrees F	
Diesel	EBP	D 86	14	Degrees F	
Diesel	Cloud Point	D 5773	7	Degrees C	
Diesel	Freeze Point	D 2836	3	Degrees C	
Diesel	Viscosity	D 445	-	%	informational data only
Diesel	Cetane Index	D 976 - D 4737	2	Index Number	
Diesel	Flash Point	D 93	5	Degrees C	
Light Cycle Gas Oil	API	D 4052	1	Degrees C	
Light Cycle Gas Oil	IBP	D 86	14	Degrees C	
Light Cycle Gas Oil	T10	D 86	14	Degrees C	
Light Cycle Gas Oil	T50	D 86	14	Degrees C	
Light Cycle Gas Oil	T90	D 86	14	Degrees C	
Light Cycle Gas Oil	EBP	D 86	14	Degrees C	
Light Cycle Gas Oil	Cloud Point	D 5773	7	Degrees C	
Light Cycle Gas Oil	Freeze Point	D 2836	3	Degrees C	
Light Cycle Gas Oil	Viscosity	D 445	-	%	informational data only
Light Cycle Gas Oil	Cetane Index	D 976 - D 4737	2	Index Number	
Light Cycle Gas Oil	Flash Point	D 93	5	Degrees C	
FCC Gasoline	RON	D 2699	1.7	Octane Number	
FCC Gasoline	MON	D 2700	1.7	Octane Number	
FCC Gasoline	T10	D 86	14	Degrees F	
FCC Gasoline	T50	D 86	14	Degrees F	
FCC Gasoline	T90	D 86	14	Degrees F	
FCC Gasoline	Aromatics	detailed GC	1.1	Volume %	
FCC Gasoline	Benzene		0.5	Volume %	



There are a total of 3 models for all 5 streams: One each for T10, T50, and T90.

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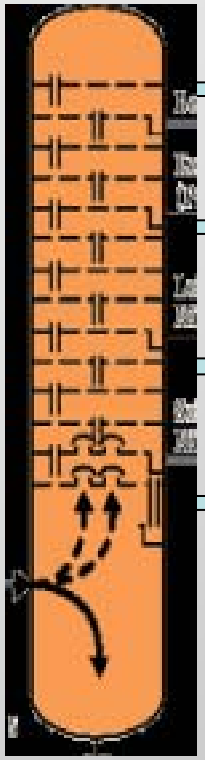
Clean Fuels Project – Bakersfield, CA



Hydrocracker feed

CU diesel

SHS

Clean Fuels

Coker diesel

Density
D-86 distillation
Flash point
Cetane Number
Cloud Point
Pour Point

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Typical NMR Diesel Measurements

Parameter	NMR Model Accuracy	Lab Method Reproducibility	Units
Cloud	1.5	3	deg C
Viscosity	0.085	0.17	%
Density	0.0014	0.0028	g/mL
Flash	2.2	4.4	deg C
D86 FBP	3.7	7.4	deg C
D86 T95	4	8	deg C
D86 T90	4.1	8.2	deg C
D86 T70	4.3	8.6	deg C
D86 T50	3	6	deg C
D86 T30	2.7	5.4	deg C
D86 T10	2.5	5	deg C
D86 T5	3.8	7.6	deg C

Advancements in Advanced Process Analyzer Technology

Who, What, When, Where, Why and How? Or, déjà vu All Over Again!

(Part II)

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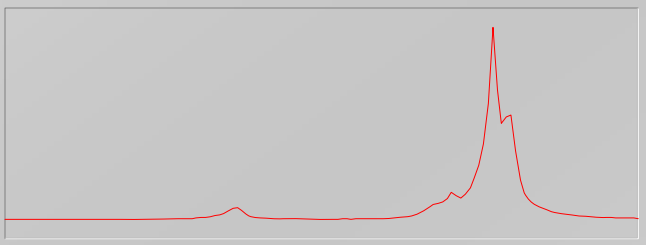
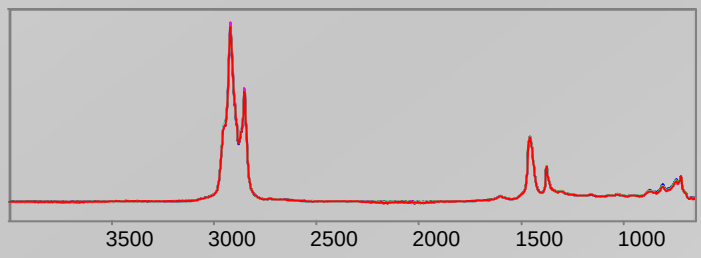
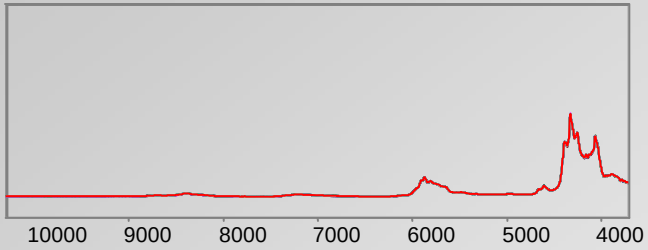


Too many spectroscopic based on-line analyzer projects (FTIR, NIR, NMR, and Raman too) have failed to meet expectations and/or objectives due to:

- **Overselling the measurements**
- **Underestimating the sampling requirements**
- **Trying to replace all traditional analyzers with one technique.**
- **Déjà vu!!**





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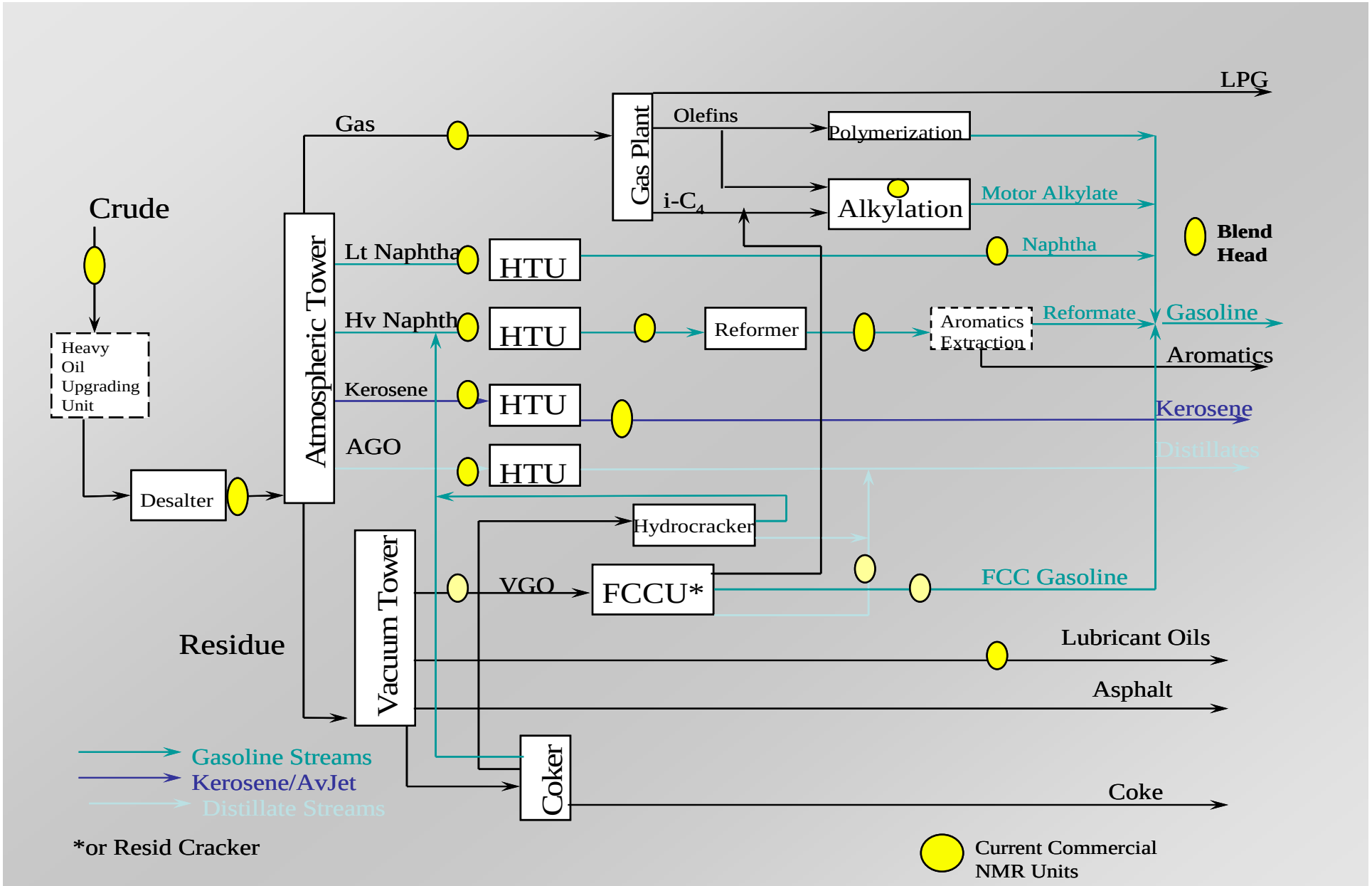

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Who?

- Who's selling it?
- Who wants it?
- Who needs it?
- Who is responsible it?
- Who should be responsible?

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What?

- What is being sold/promised?
- What is the value of the project?
- What is the value of each measurement?
- What will be done with the information?

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When?

- When will the analyzer be delivered?
- When is the project completed?
  - When the site is prepared?
  - When the analyzer completes site acceptance?
  - When the analyzer is connected to the DCS?
  - When the analyzer is retired from service?
- When will I get the benefit?

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Where?

- Where is the money coming from?
- Where is the manpower coming from?
- Where are we going to put it?
- Where are the samples coming from?
- Where is the information going?
  - Control room?
  - Engineer's "desk"?
  - Management/accounting?
  - Nowhere?

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Why?

- Why are we doing this?
  - Replacement and/or update?
  - New measurement/control strategy?
  - Because!!!!!!

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How?

- How will the project be:
  - Budgeted?
  - Implemented?
  - Supported?
  - Integrated?
- How complicated is this?
- How beneficial is it?
- How will my performance review be affected?

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Economic Drivers

Usually:

1. Naphtha is worth more than jet.
2. Jet is worth more than diesel.
3. Diesel is worth more than gas oil.

The problem is pulling product to some limiting property (end point, smoke point, cloud point & freeze point).

Maybe we need better tools in the control room.

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The Real World

Diesel lost to gas oil

- Loss of diesel product
- Tough product properties (cloud)
- Diesel worth more than gasoline
- Poor feed to FCC
  - Loss of diesel product
  - Not much gasoline
  - More coke make
- New Clean Fuels Initiatives – Is 10 ppm sulfur diesel worth an average daily loss of 400 – 500 barrels of diesel production?

Can 200 to 500+ BPD of diesel and gasoline be “found”?

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Current Margin Differentials: Diesel v. Gas Oil

$10 - $30+ / BBL

Big West Refining, Bakersfield, CA

Installation Scheduled for 1st Quarter 2008

- 65,000 Bbl per day
- Conservative estimate leaves 2-300 bbl/day diesel from crude unit and delayed coker.
- $3,000 to $9,000+ in lost profitability
- At 350+ days !!!!!!!!!!!!

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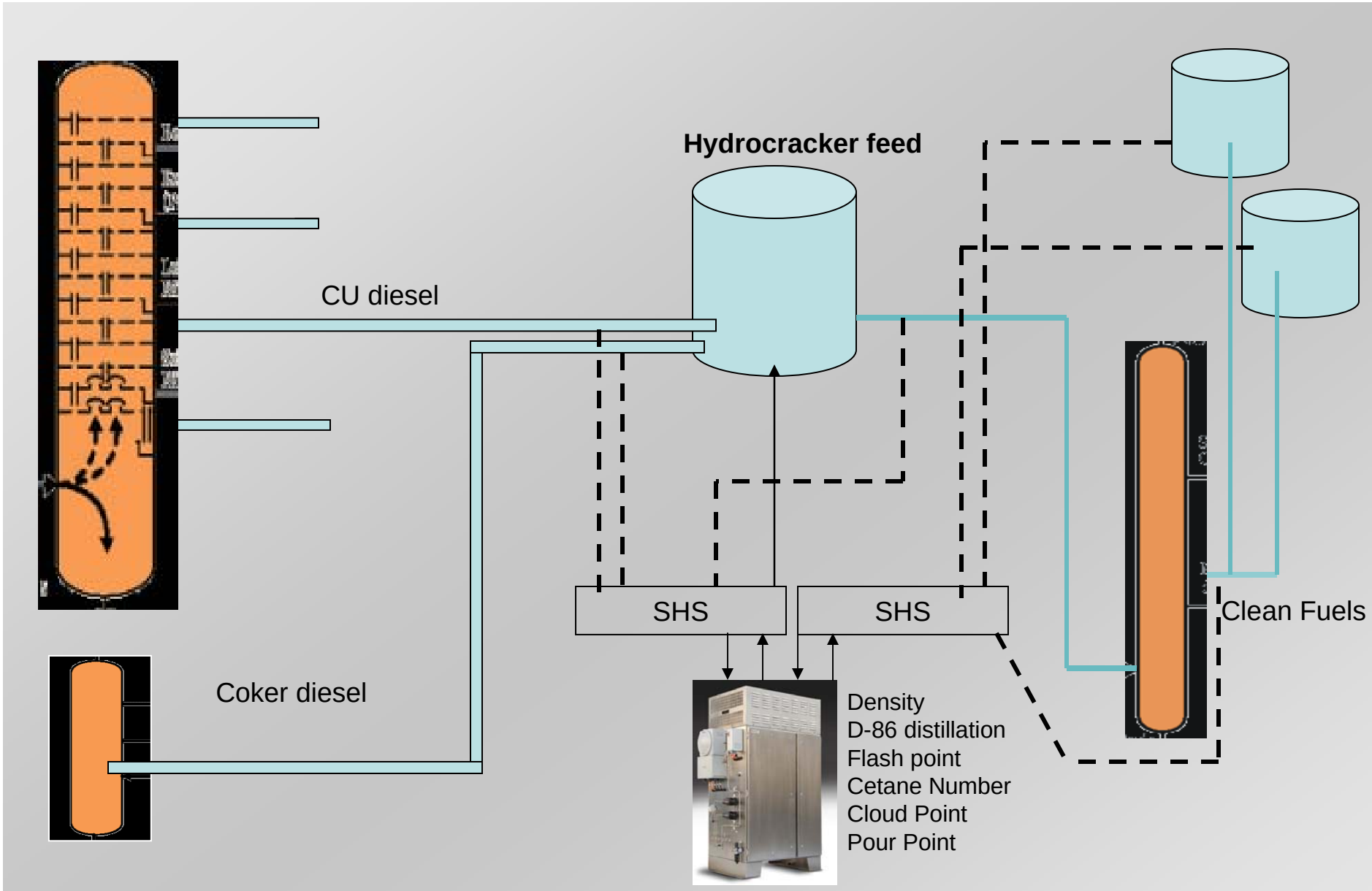

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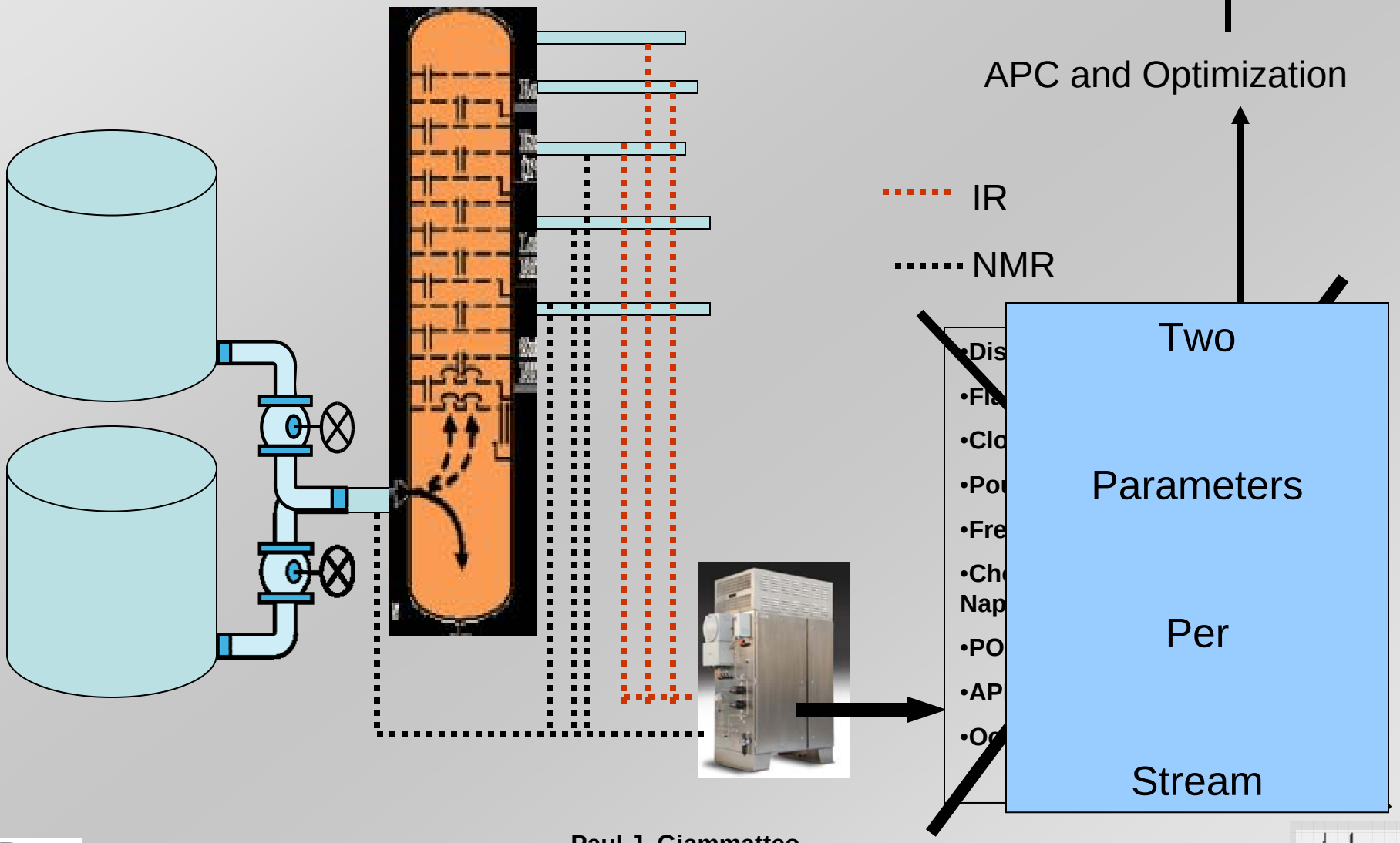
Typical NMR Diesel Measurements

Parameter	NMR Model Accuracy	Lab Method Reproducibility	Units
Cloud	1.5	3	deg C
Viscosity	0.085	0.17	%
Density	0.0014	0.0028	g/mL
Flash	2.2	4.4	deg C
D86 FBP	3.7	7.4	deg C
D86 T95	4	8	deg C
D86 T90	4.1	8.2	deg C
D86 T70	4.3	8.6	deg C
D86 T50	3	6	deg C
D86 T30	2.7	5.4	deg C
D86 T10	2.5	5	deg C
D86 T5	3.8	7.6	deg C

Crude Unit Integrated Solution



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NMR Process Systems, Inc. is a joint venture company between Process NMR Associates, LLC (Danbury CT), and TTC Labs Inc. (Fond du Lac WI). NPS markets, installs and supports process NMR and other technology solutions for control and optimization in the refining, petrochemical, pharmaceutical and food industries.

NPS is now advancing new concepts in process analysis by offering integrated analytical solutions into its product slate. Integrated NMR, NIR and other analyzer solutions offer strategic reliability, sampling, and control benefits to the end user.

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