A Look at Gasoline Sulfur Reduction Additives in FCC Operations

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Refcomm Galveston 2016

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Drivers for Low Sulfur Additive

- Worldwide legislative drive for air quality improvements require modifications in fuel quality
- 90% of gasoline sulfur is derived from FCC gasoline
- Tier III coming in 2017-2020
  - 10 ppm gasoline sulfur
- BASF has developed and commercialized - Low Sulfur Additive (LSA) and NaphthaClean® (catalyst formulation) for improved FCC gasoline sulfur reduction

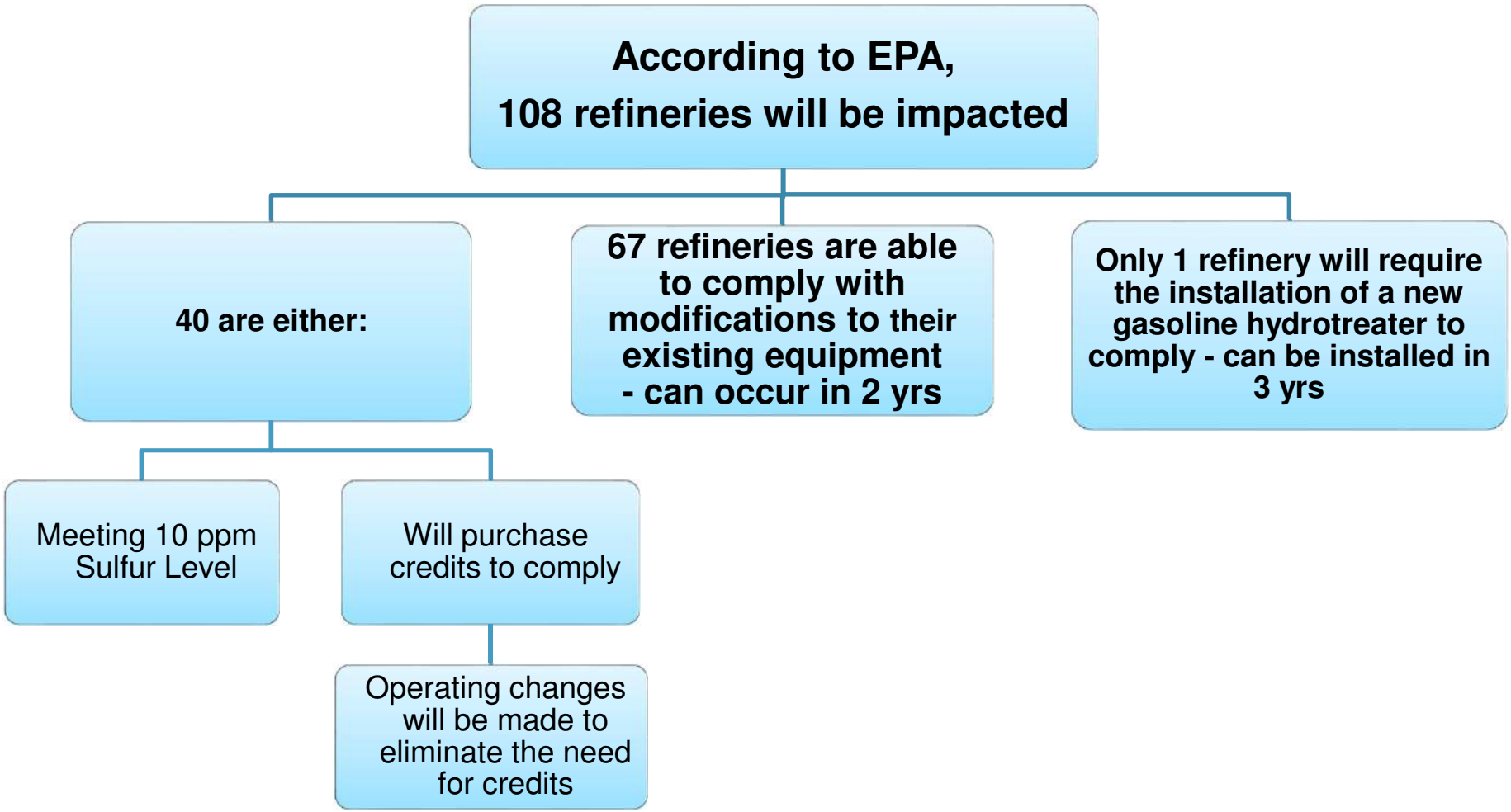
Global Sulfur Standards

10 ppm or less		> 10 ppm
Canada 10 ppm (2017)	Russia 10 ppm (2016)	India 150 ppm (2010)
EU 10 ppm (2009)	China 10 ppm (2018)	Brazil 50 ppm (2014)
Japan 10 ppm (2008)	S. Africa 10 ppm (2017)	Thailand 50 ppm (2012)
US 10 ppm (2017)		

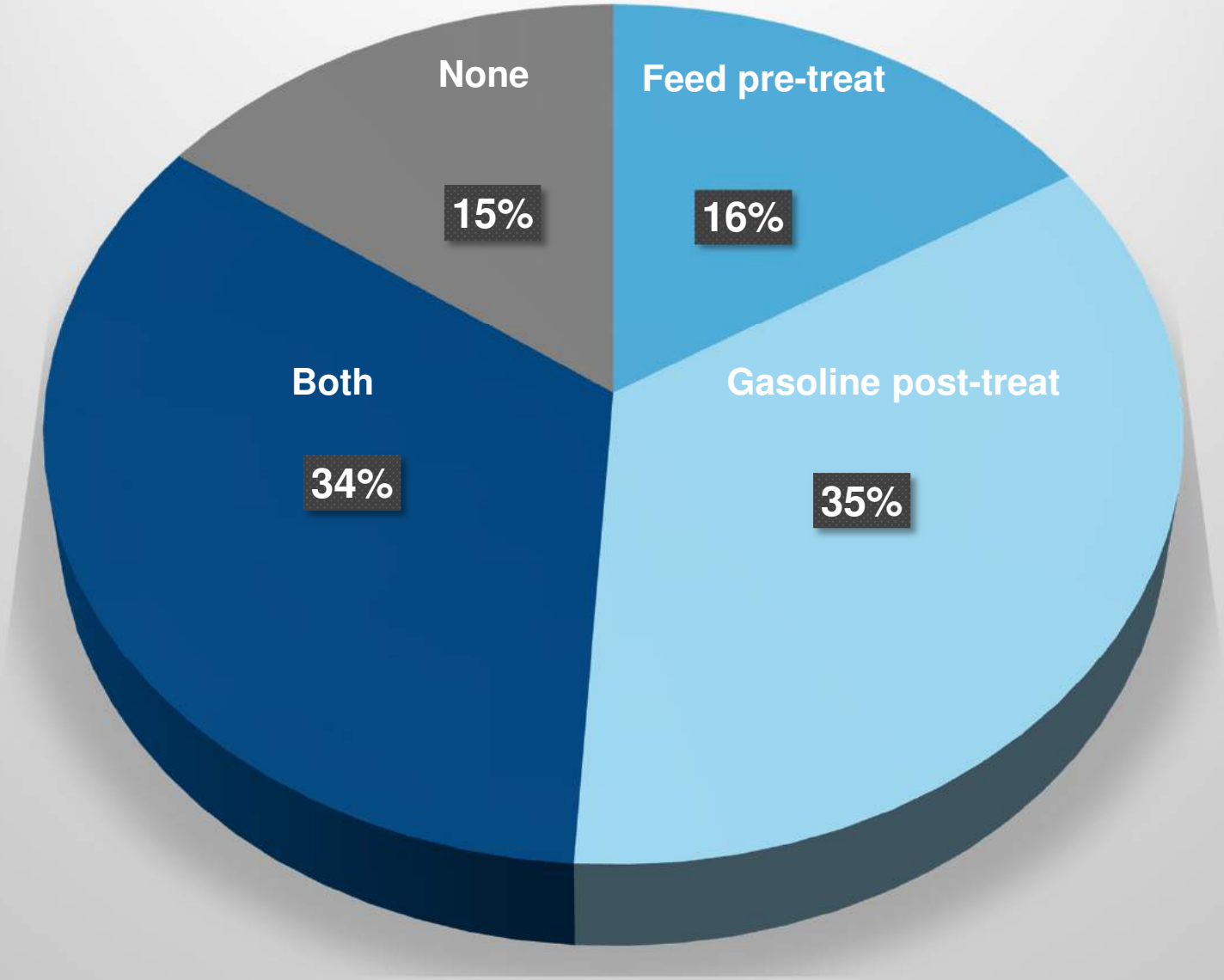
In 2011,

- Two countries/regions at 10 ppm
- US at 30 ppm
- 3 at 150 ppm, 2 at 500 ppm, 1 at 1000 ppm

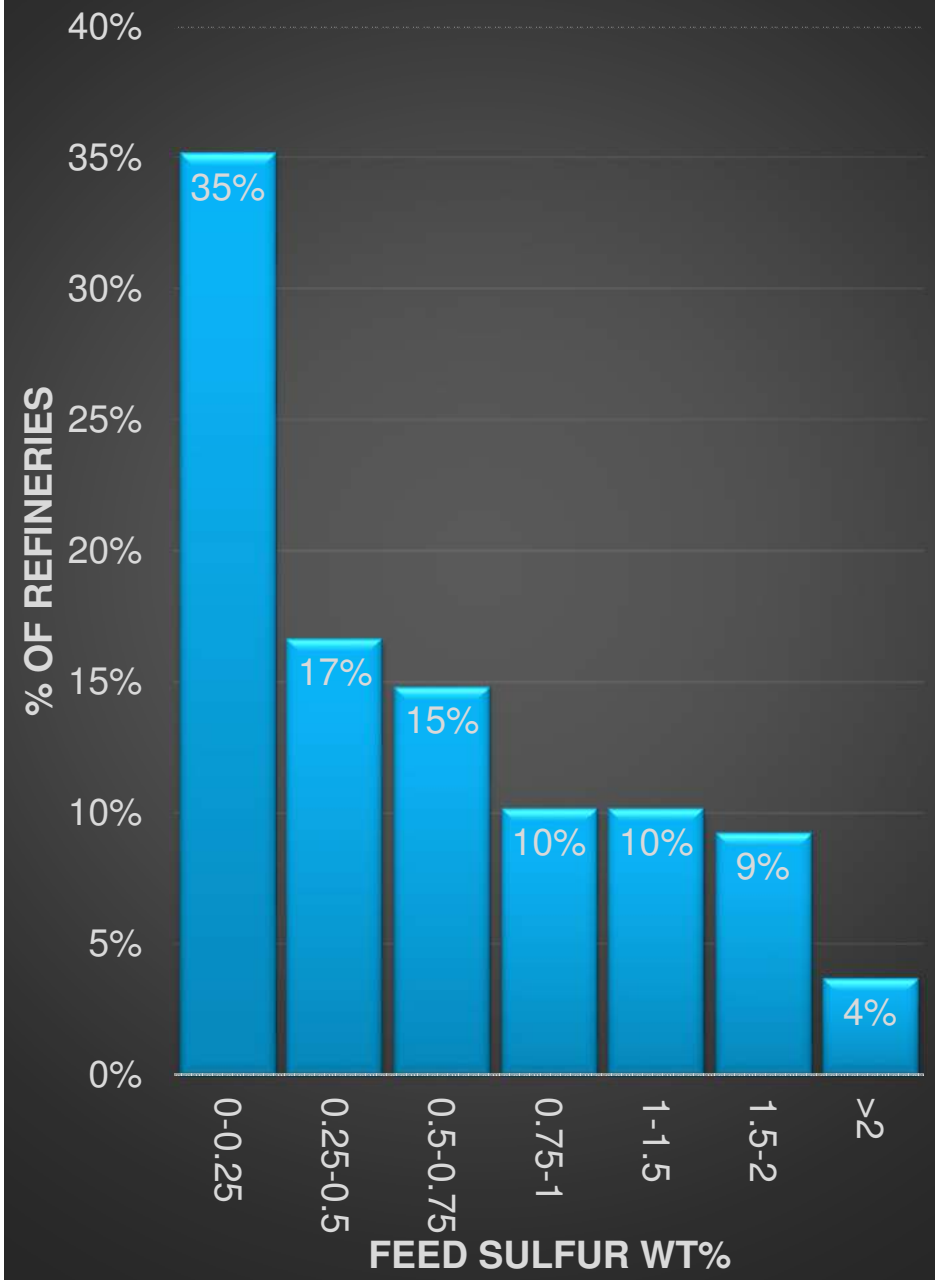
Tier III Impact on Refiners



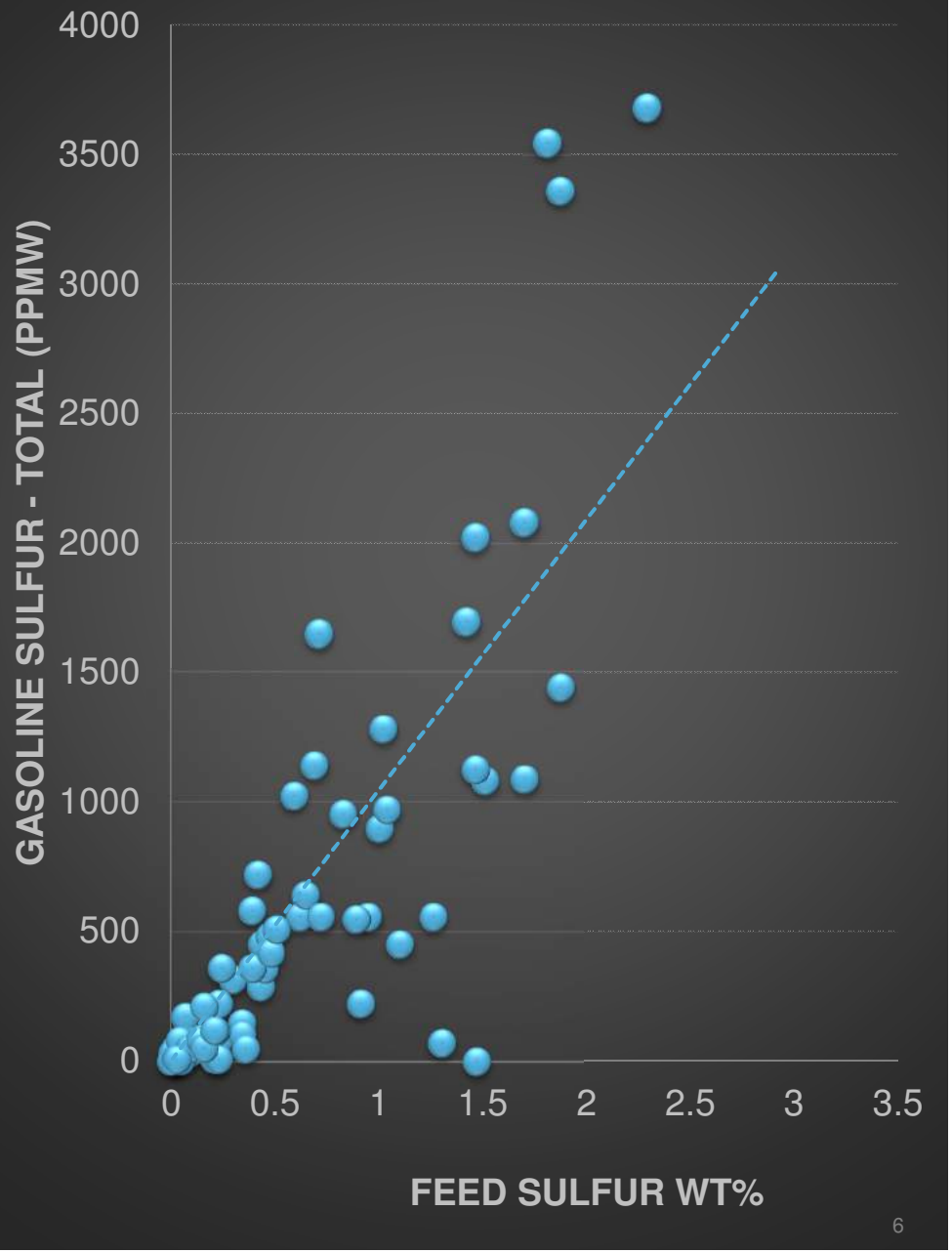
Existing Sulfur Treatment Options
US FCC Units



Refinery Feed S



Feed S vs Gasoline S



Tight Oil Impacts

- Tight oils typically have lower sulfur than conventional crudes, along with other contaminants

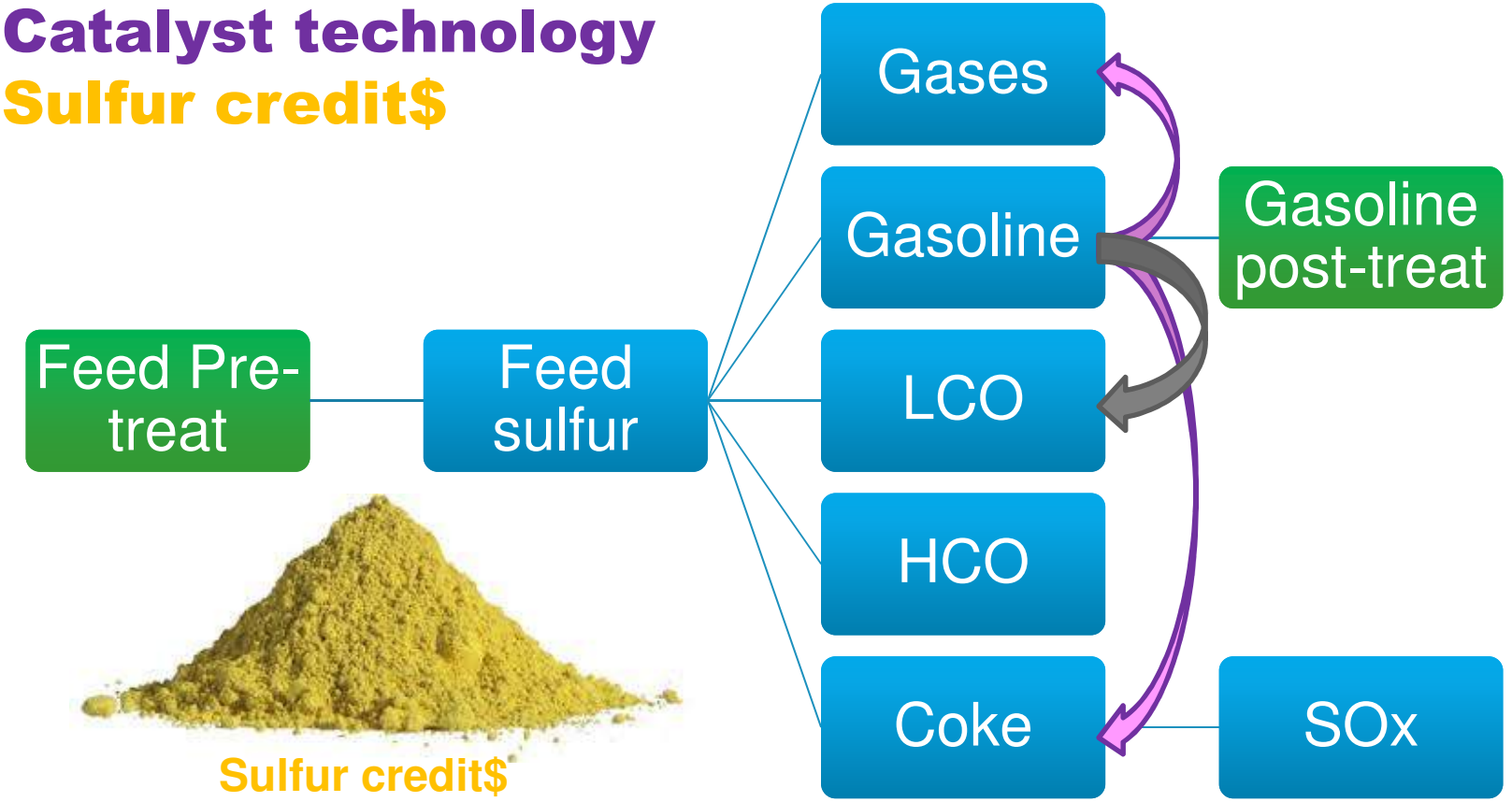
VGO cut properties		TX Shale	Bakken Core	WTI	Maya Blend
API gravity		31.9	24.5	26.3	21
Sulfur	wt%	0.18	0.27	0.46	2.05
Acidity	mg KOH/g	0.049	0.053	0.095	0.085
Nitrogen	wt%	0.01	0.11	0.13	0.18
Refractive index	67C	1.4588	1.4824	1.4759	1.498
Nickel	ppm	0.09	0.47	0	0.64
Vanadium	ppm	0.08	0.14	0	4.48
Con Carbon	wt%	0.03	0.68	0.01	0.47

Source: Shackleford, Hydrocarbon Processing Sept 2014

Sulfur Reduction Technologies Overview

FCC Gasoline Sulfur Reduction Options

- **Hydrotreating**
- **Cutpoint adjustment**
- **Catalyst technology**
- **Sulfur credit$**



FCC Gasoline Sulfur Reduction Options

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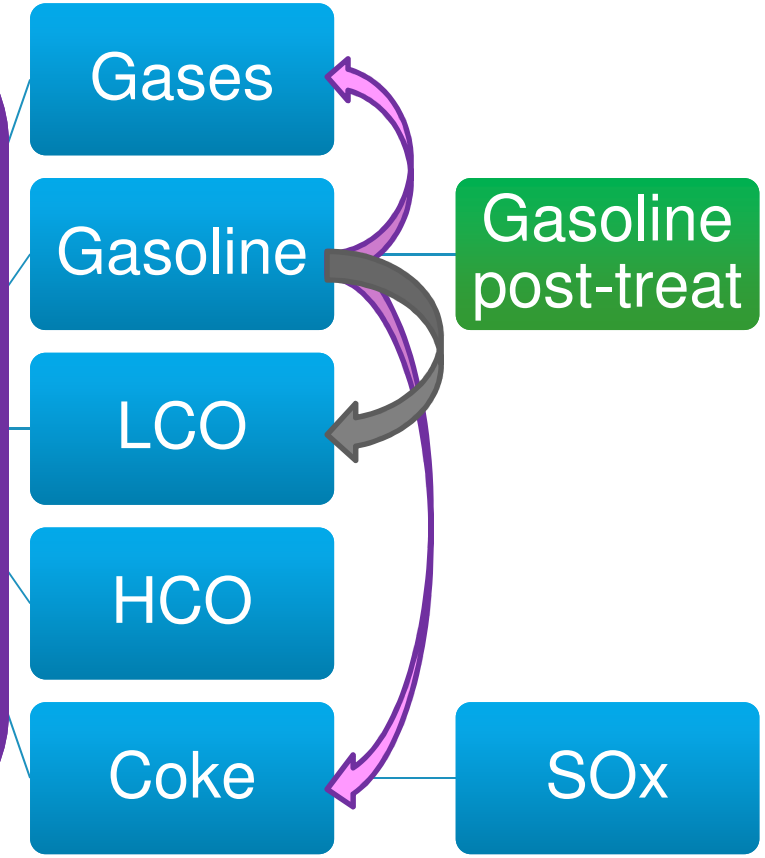
Feed Pre-treat

- CFHTs reduce FCC feed sulfur by 70-90%
- FCC gasoline from CFHT'ed feed is typically 200-500 ppm sulfur
- High severity can reduce this to 75-100 ppm
- Higher severity means operating more in poly nuclear aromatic mode (PNA)
- Removes nitrogen and improves FCC performance
- High severity may mean catalyst life of only 1-2 years

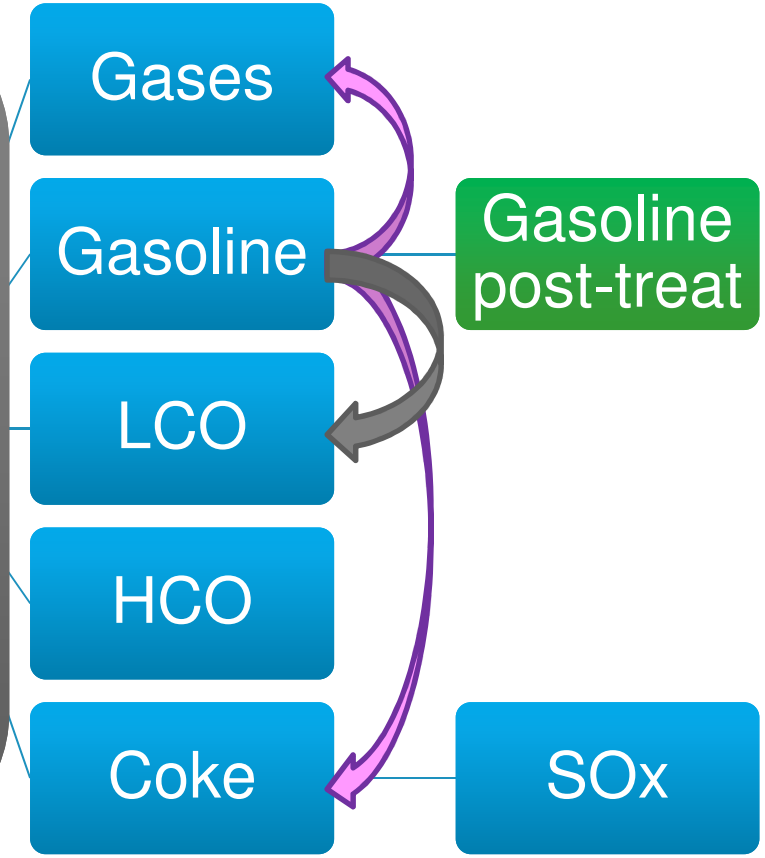
FCC Gasoline Sulfur Reduction Options

- LSA/Naphthaclean may be used on a spot basis or in conjunction with other measures to reduce gasoline sulfur to the post-treater
- Could help avoid a capital investment / octane loss / hydrogen limitations



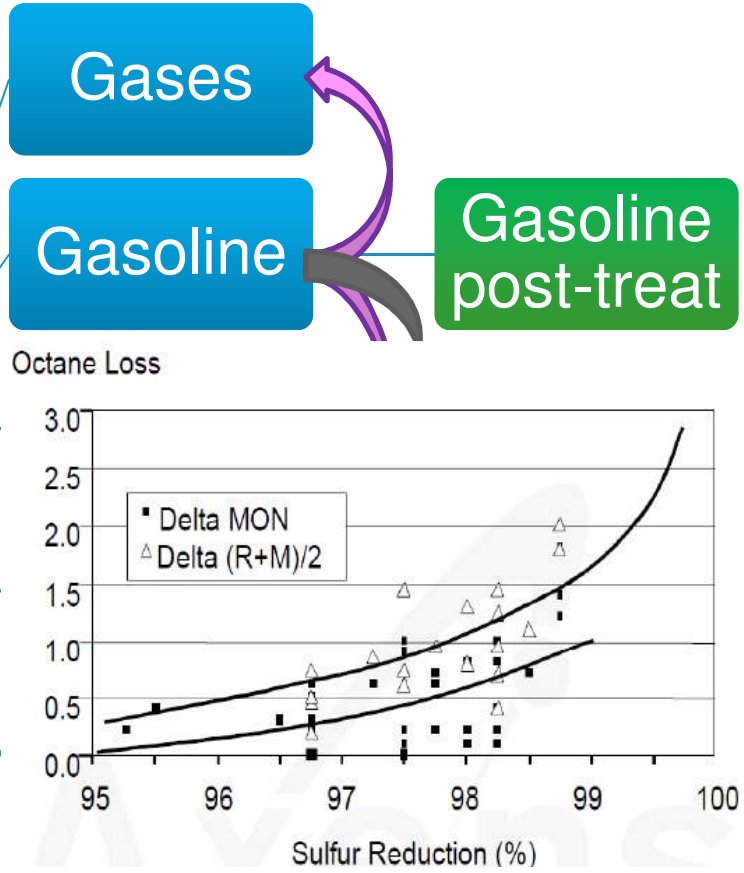
FCC Gasoline Sulfur Reduction Options

- EPA estimates that in 2009, 22% of refineries undercut to distillate
- 2018 estimate is 68% as result of Tier 3
- FCC gasoline volume estimated to drop 16%
- With the benefit of a 50% reduction in FCC gasoline sulfur
- Coincides with predictions for increased diesel demand



FCC Gasoline Sulfur Reduction Options

- Revamps of post-treaters are likely to be the source of most investment meet Tier 3
- Can achieve up to 99% sulfur removal, depending on naptha sulfur content
- In high naphtha sulfur content cases, post-treating might not be enough
- Octane loss can be significant at high severity
- Hydrogen requirements are not linear with sulfur reduction



%FCC feed sulfur re-distributed to products

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Non-hydrotreated feed	
Sulfur Distribution	
Light gases	40-50%
Gasoline	5-15%
Bottoms+LCO	40-50%
Coke	5-10%

Hydrotreated feed	
Sulfur Distribution	
Light gases	30-50%
Gasoline	2-10%
Bottoms+LCO	30-50%
Coke	15-30%

However, 90% of naphtha pool sulfur comes from the FCC

Development of BASF's Low Sulfur Additive

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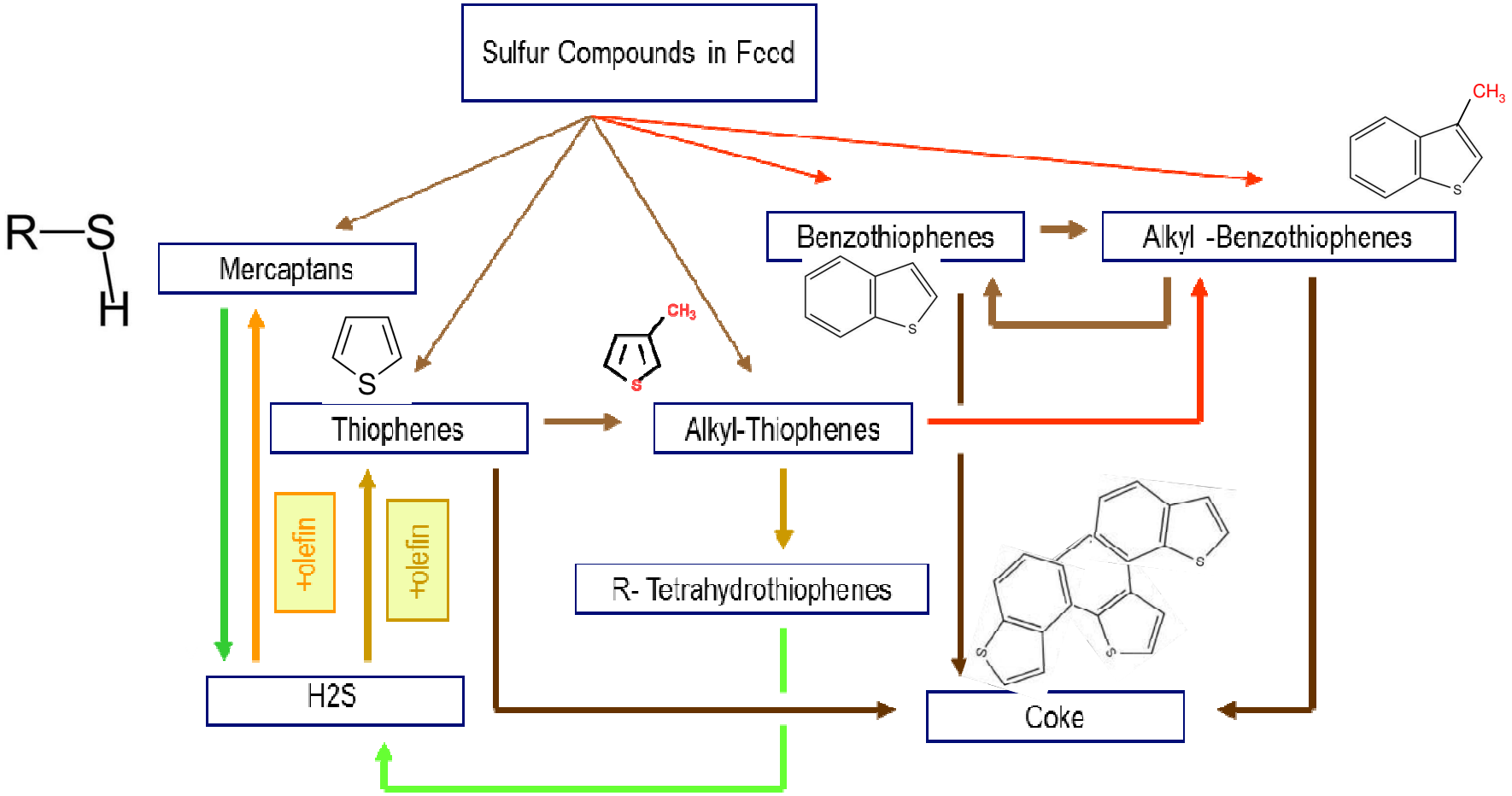
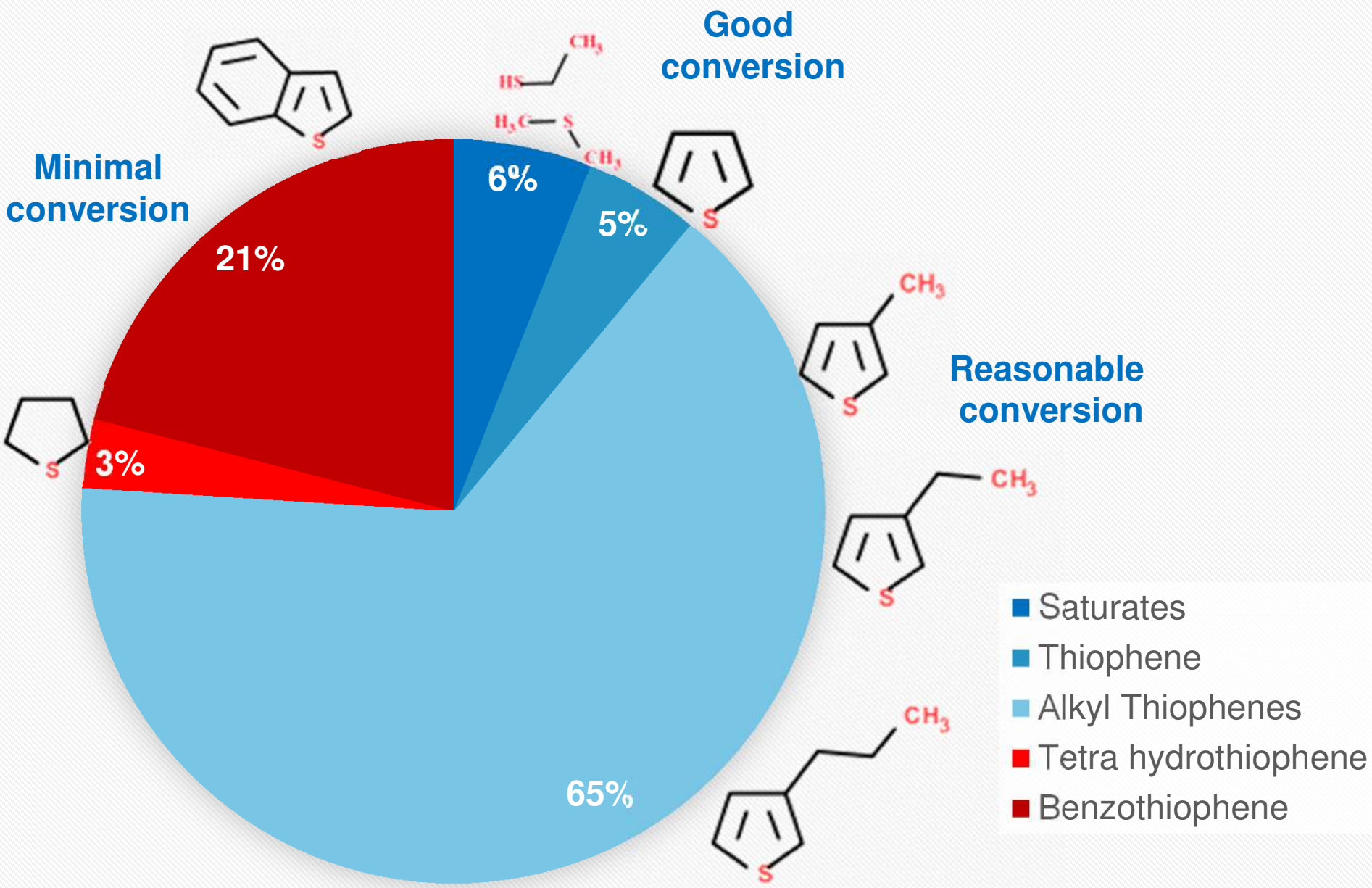
- Sulfur speciation method developed for understanding sulfur reduction chemistry
- Reactive compounds (mercaptans, sulfides, disulfides) are cracked to H_2S
- Refractory compounds (thiophenes, alkyl thiophenes, benzothiophenes) remain in FCC gasoline
- Compounds like dibenzothiophenes (DBT) and substituted DBT's remain in the LCO and bottoms fractions

Feed sulfur compounds

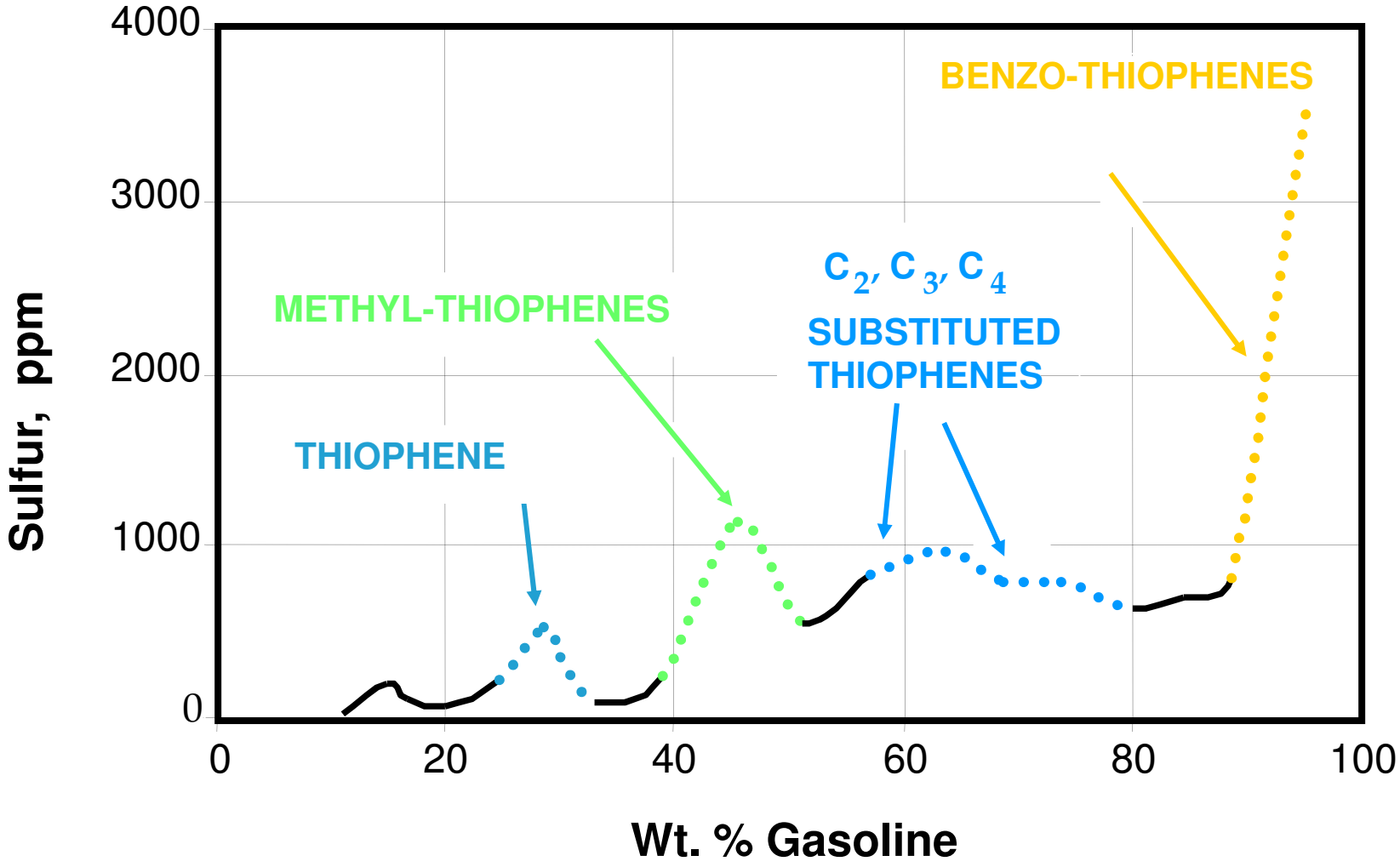


A. Corma et. al., Appl. Catal. A: Gen. 208 (2001) 135

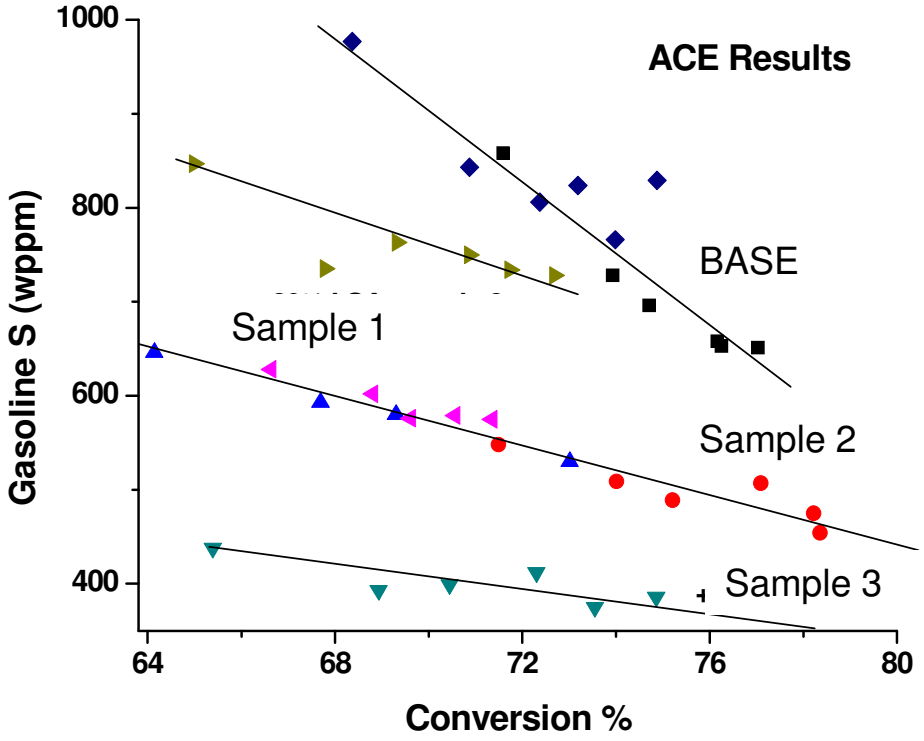
Typical Contribution of S Compounds in Naphtha Cut



Gasoline Sulfur Distribution Concentration in Back End Due to Benzo-thiophenes



R&D Testing to Develop & Improve Gasoline Sulfur Reduction



Develop an additive with best gasoline sulfur reduction performance

Sulfur Speciation Tool Used for Sulfur Reduction Additive Development

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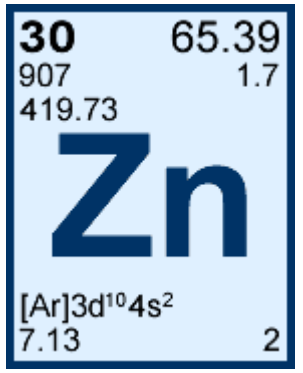
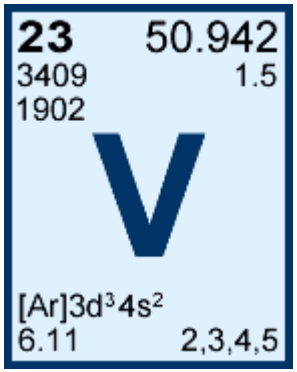
S species	Base ECAT S (wppm)	LSA S (wppm)	S reduction (%)
carbon disulfide	0.8	0.5	38
Ethylmethyl sulfide	0.3	0.0	100
Methyl mercaptan	0.6	0.0	100
n-hexyl mercaptan	0.5	0.3	40
Thiophene	27.0	15.4	43
2-methyl Thiophene	25.8	14.6	43
3-methyl Thiophene	34.7	17.7	49
Tetrahydro Thiophene	12.1	5.4	55
2-methyltetrahydro Thiophene	6.8	2.4	65
2-ethyl Thiophene	6.9	3.8	45
2,5-dimethyl Thiophene	7.9	4.7	40
3-ethyl Thiophene	20.5	10.3	50
2,3-dimethyl Thiophene	18.3	10.0	45
3,4-dimethyl Thiophene	9.6	4.7	51
C3s Thiophene	51.6	26.7	48
C4s Thiophene	40.6	19.1	53
Benzothiophene	133.8	114.3	14
Gasoline S (wppm)	411.3	255.9	38

BASF's Low Sulfur Reduction FCC Catalyst and Additive Technologies

- Two types of technologies for gasoline sulfur technology:
  - Zinc based: focused on coking sulfur containing compounds
  - Vanadium based: focused on cracking sulfur containing compounds
- Both are built upon BASF's in-situ catalyst platforms
- Maximize H-Transfer of additive
- Catalyst base allows BASF technology to achieve maximum volume and value expansion
- Both technologies are available as both:
  - FCC catalyst solution – NaphthaClean
  - FCC additive – LSA (Low Sulfur Additive)
- BASF will work with the refiner to determine the best fit for the individual refiner's needs





Opportunities to use FCC Catalyst and Additive Technologies

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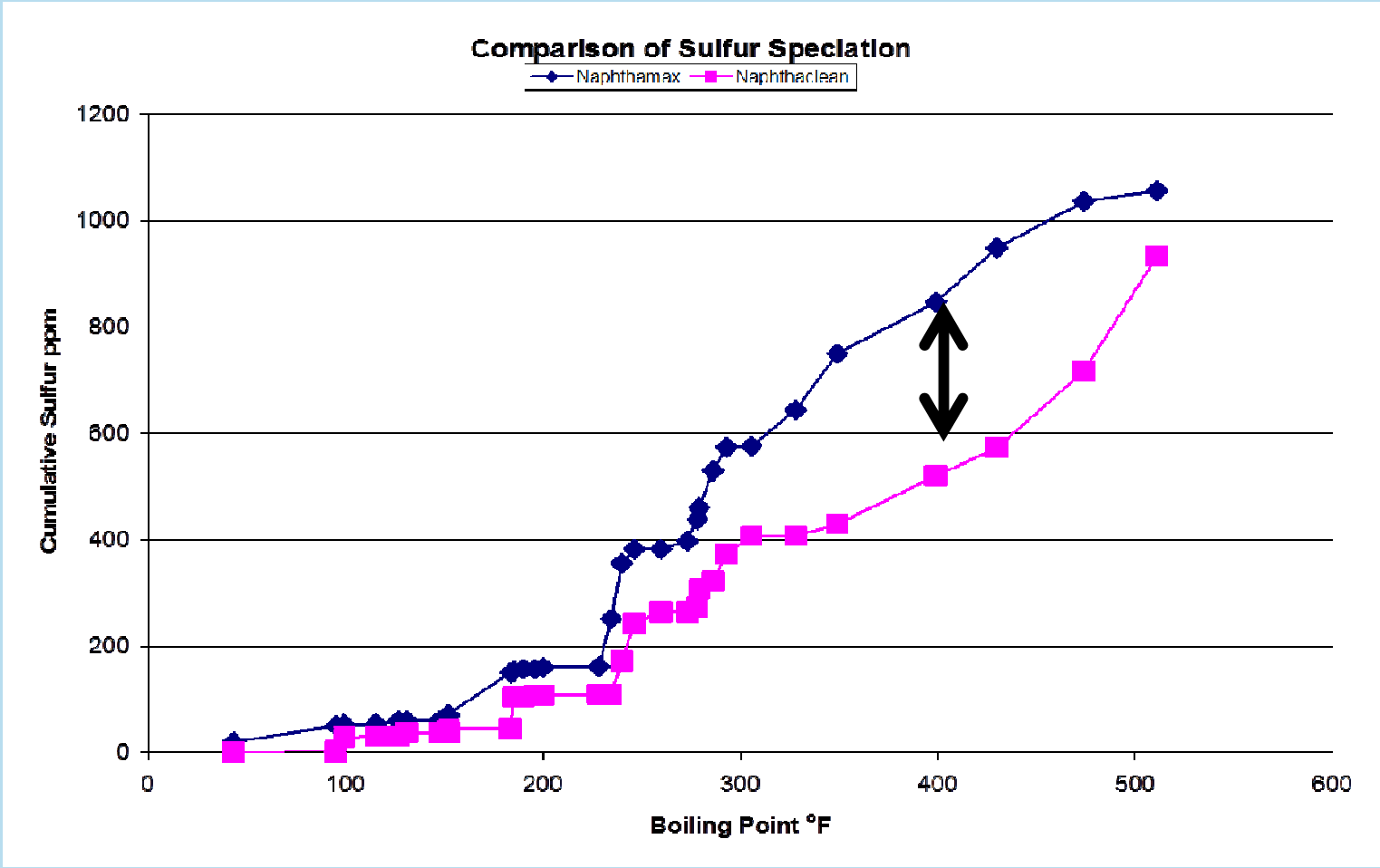
- Octane preservation through by-passing a portion of light gasoline
- During turnaround of Post Treatment or Pre Treatment Unit
- Improved flexibility of crude selection
- Reducing severity of existing equipment
- Reduced hydrogen availability
- Can be used on an ongoing basis or on a spot basis

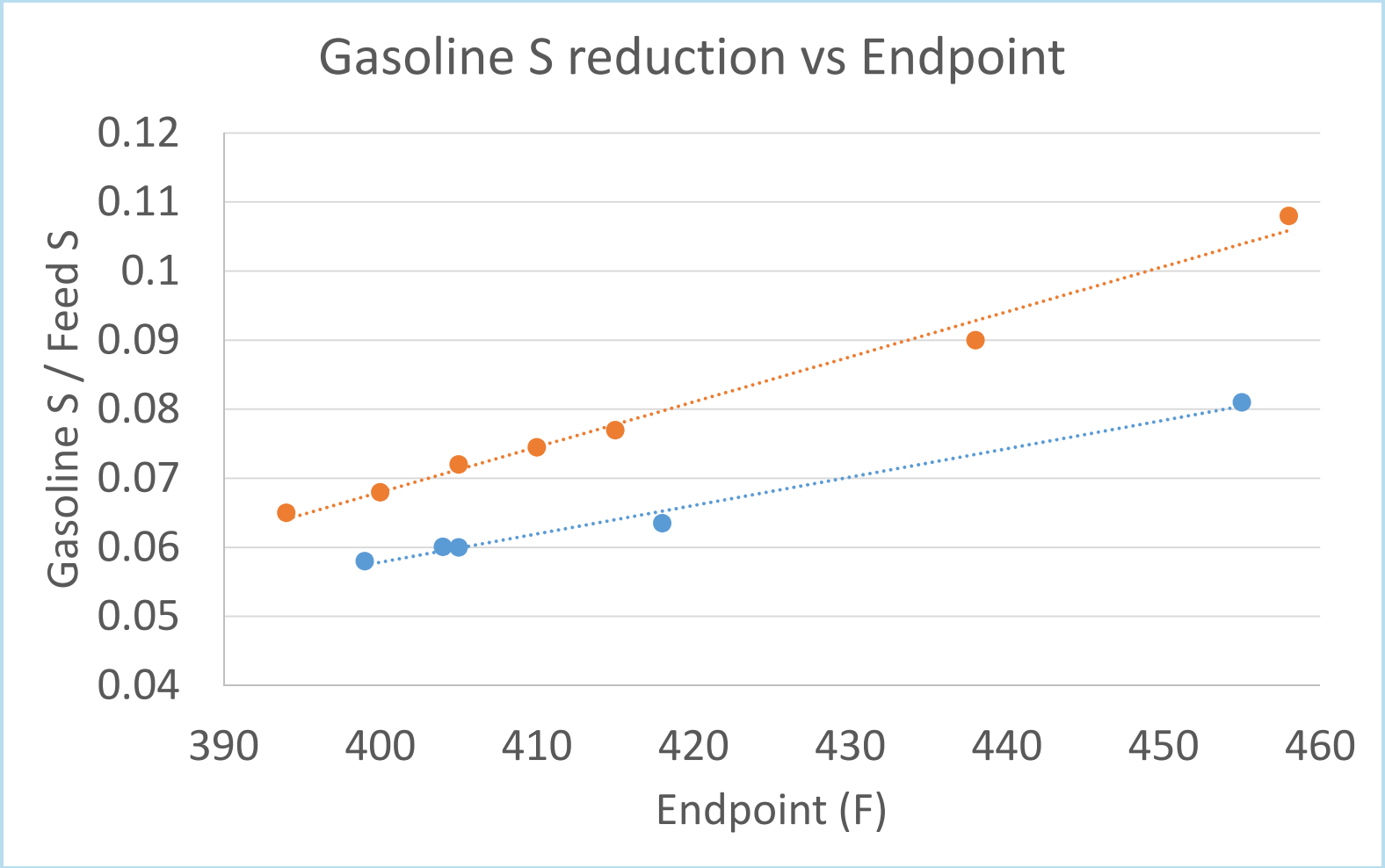
Considerations for using FCC Catalyst and Additive Technologies

- 15-25% of LSA can reduce gasoline sulfur by 20-40%
- Level of gasoline sulfur reduction is impacted by:
  - Sulfur speciation (impacted by feed hydrotreating and crude)
  - Operating conditions
  - FCC catalyst
- Value of sulfur credits
- Effects on H2S and/or SOX emission handling
- Value of octane retention
- Value of turning down severity of hydrotreating equipment

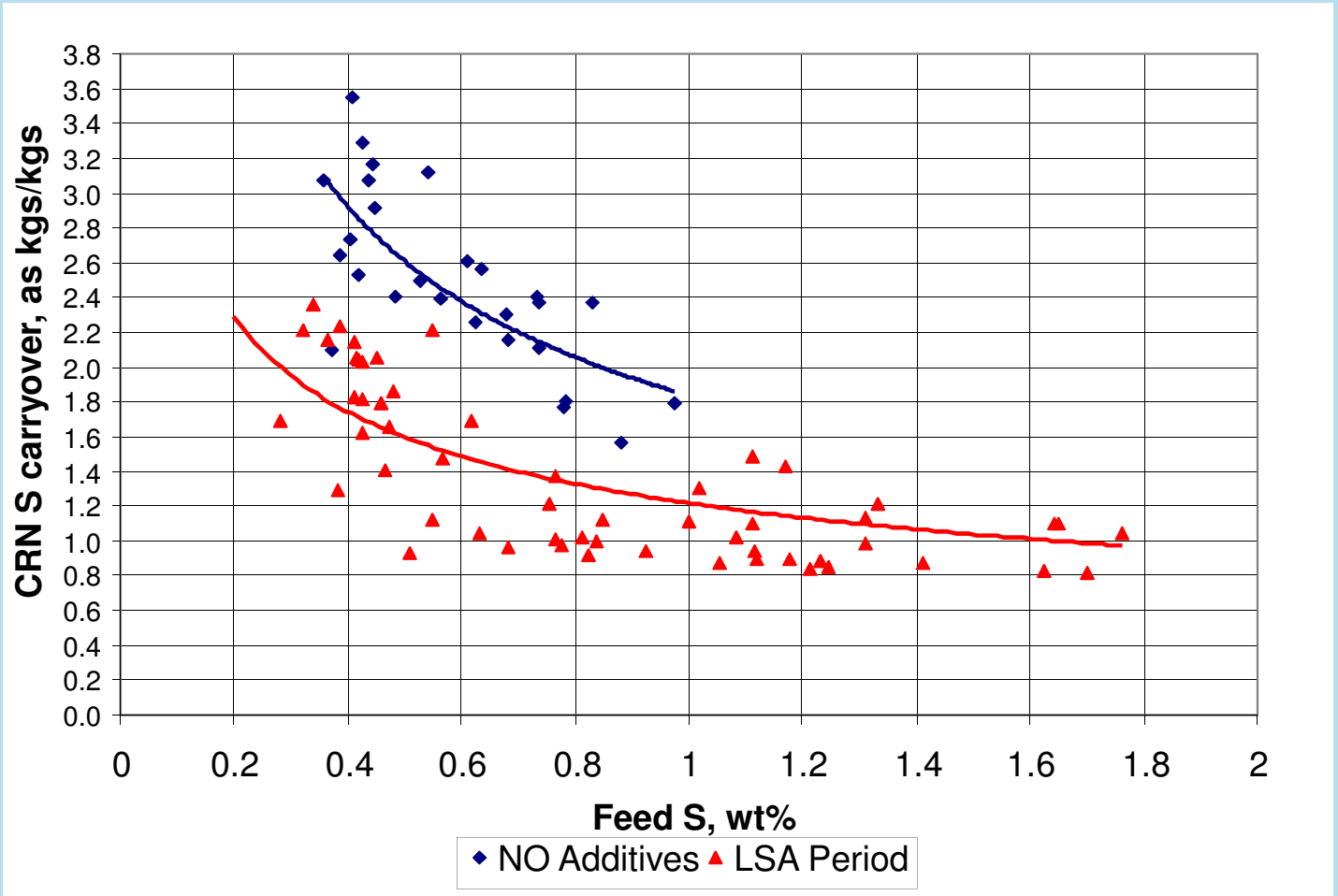
Commercial Example #1: Naphthaclean reduces gasoline sulfur across the range



Commercial Example #1: Naphthaclean reduces gasoline sulfur by >20%



Commercial Example #2: LSA reduces gasoline sulfur by 35%



BASF's NaphthaClean and LSA can cost effectively remove sulfur from gasoline

- Gasoline sulfur reduction strategy based on existing refinery configuration, expectations in capital projects, and existing sulfur credits
- Cutpoint change is a good method for a quick fix, but must take into account product values (diesel vs. gasoline)
- Hydrotreating (pre- and post-) have tremendous benefits, but watch out for octane impacts
- FCC catalyst technology solutions can be tailored based on refinery needs and constraints
  - Expectations for 20-40% reduction in gasoline sulfur
  - LSA maximizes volume expansion as its based on BASF's in-situ based catalyst
  - **Proven, experienced technology for removing sulfur from gasoline**

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