

The Lower it Goes, The Tougher it Gets!

The Practical Implications of Producing Ultra-Low Sulfur Diesel (ULSD)



Our Technology Touches the World

UOP 4080C-1

***Sulfur, How &
How Low?***

***Cetane?
Aromatics?
Distillation?***

***What About
Fuel Oil?***

***Grade
Segregation?***

***Fuel Cells?
Hybrids?***

***Off-Road
Diesel Specs?***

***Alternative
Diesel Fuels?***

The Lower It Goes, The Tougher It Gets!



- What is ULSD and why is it so difficult to produce?
- Can you revamp your existing unit?
- What are the operational and refinery issues?
- What are the capacity and flexibility issues?

What Is Ultra-Low Sulfur Diesel?



WILL DIESEL ENGINES POWER
TOMORROW'S SUVs?

- 500 wppm S has been a common world specification.
- The EU spec will be likely be 10 ppm at the refinery gate
- The Swedish class one limit is 10 ppm S
- In the US, most refiners are designing for 5 to 8 ppm out of their hydrotreaters

Hydroprocessing Solutions to Clean Fuels

- **ULSD Fundamentals: Feed issues**
- **Revamp issues**
- **New unit design considerations**
- **Other issues**

Sulfur Species Reactivity

Sulfur Species

Thiophenes

Benzothiophenes

Non-Thiophenes

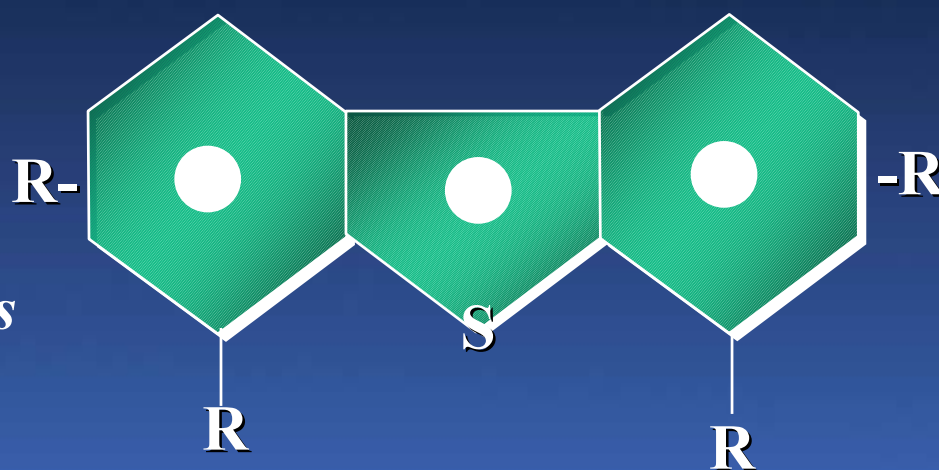
Dibenzothiophenes

Mono-Beta-Dibenzothiophenes

Di-Beta-Dibenzothiophenes

Reactivity

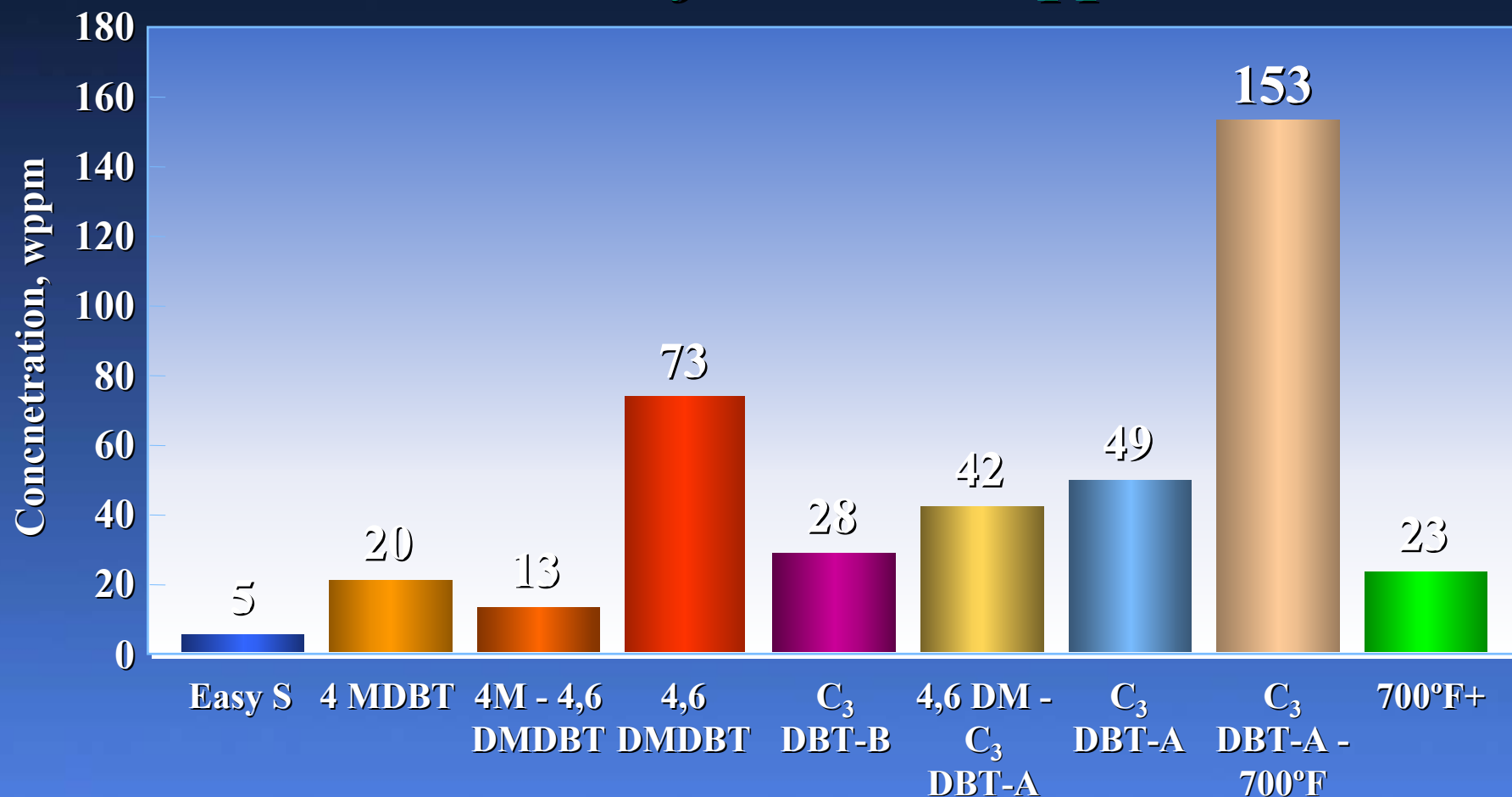
Most Difficult Species



Beta substituted-Dibenzothiophene Family

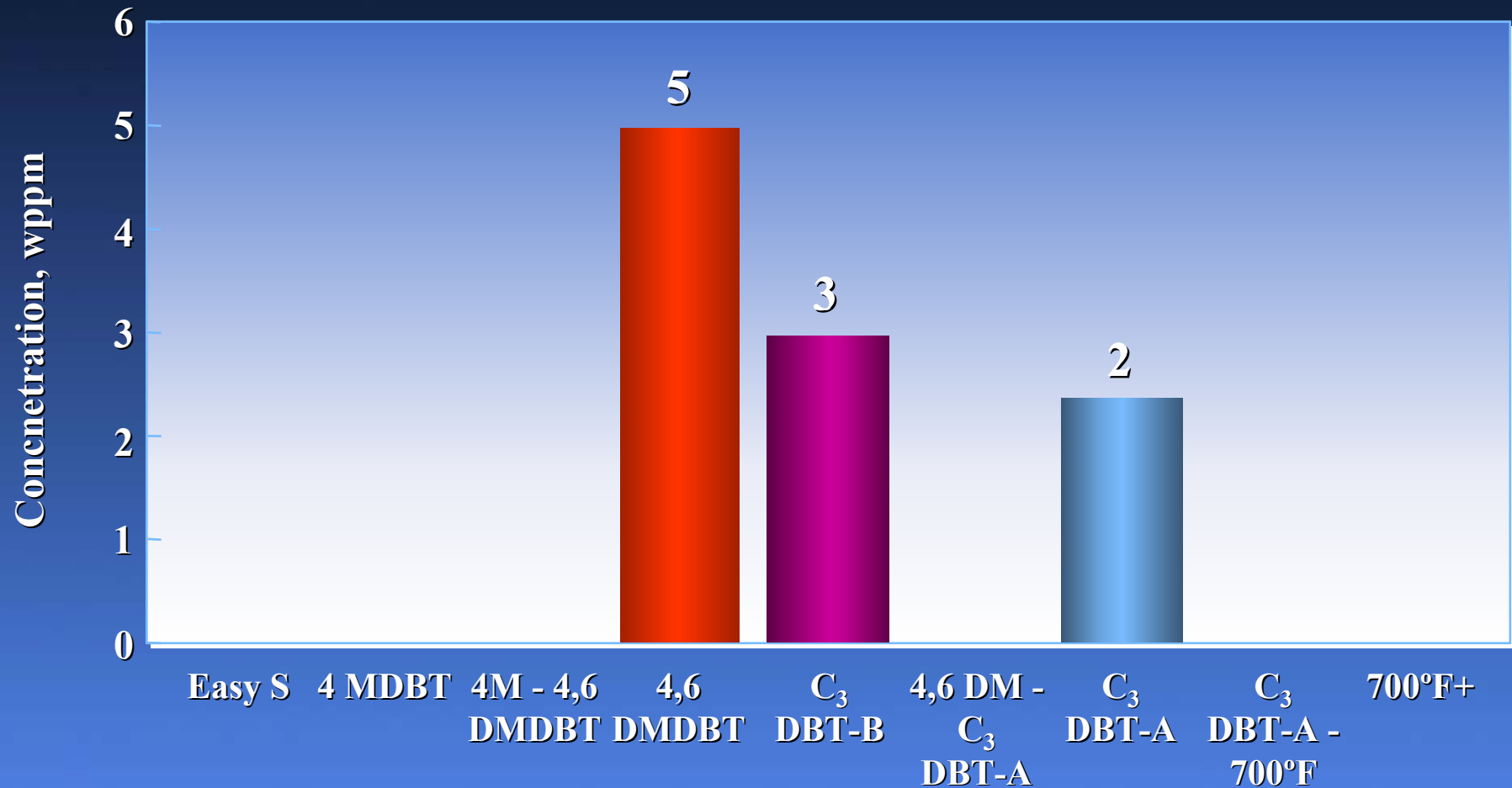
Concentration of Sulfur Species

Total Sulfur = 405 wppm



Concentration of Sulfur Species

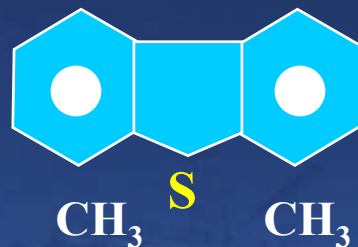
Total Sulfur = 10 wppm



Speciation Study Conclusion

At 10 wppm S, only three species remain:

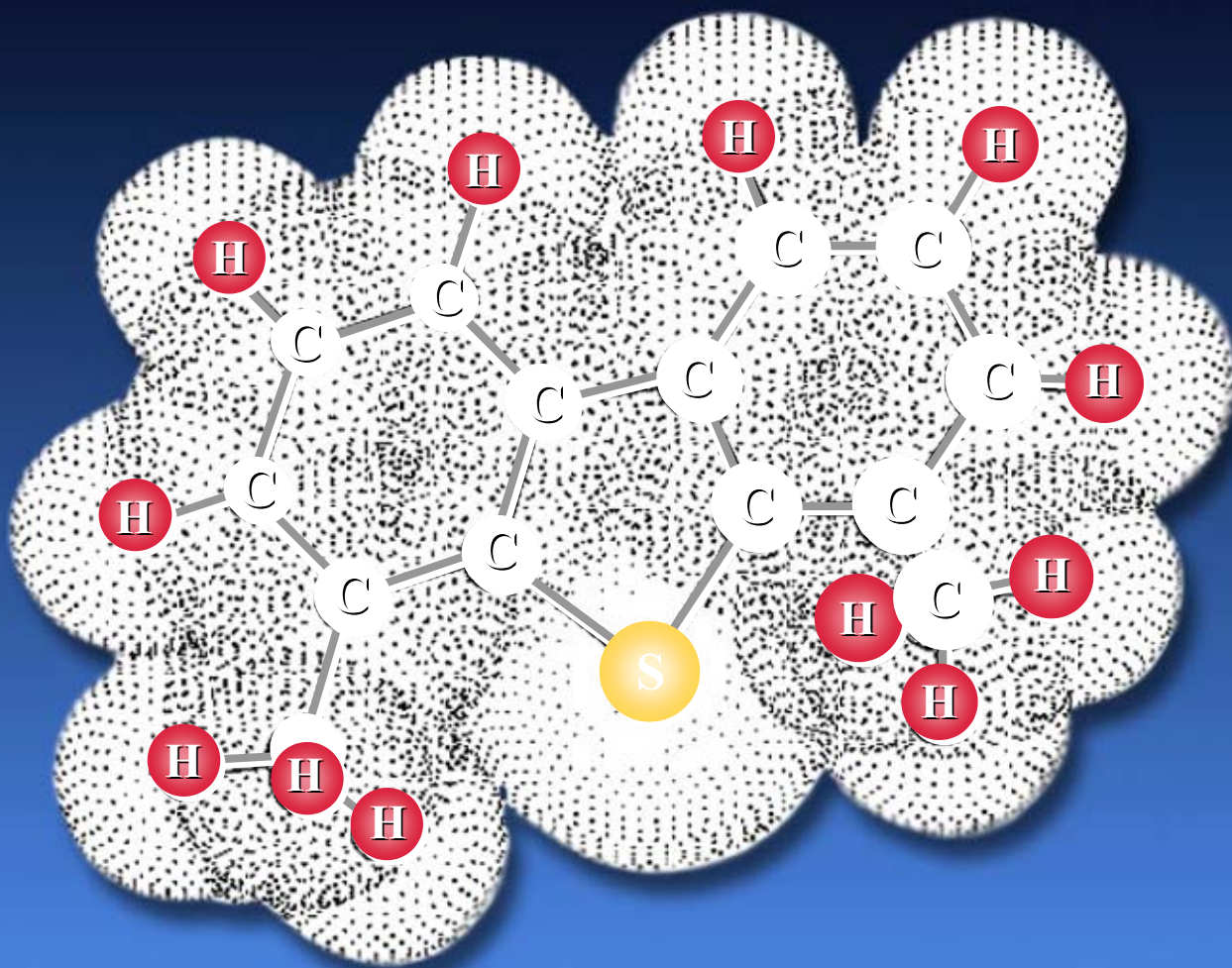
4,6 Dimethyl Dibenzothiophene



C₃ DBT-B - C₃ Dibenzothiophene

C₃ DBT-A - C₃ Dibenzothiophene

4,6-Dimethyl-Dibenzothiophene



Impact of Other Feedstock Components

Feedstock

LCO

SR Gasoil

Density

0.945

0.878

Nitrogen, wppm

549

954

Distillation, °C, IBP / EP

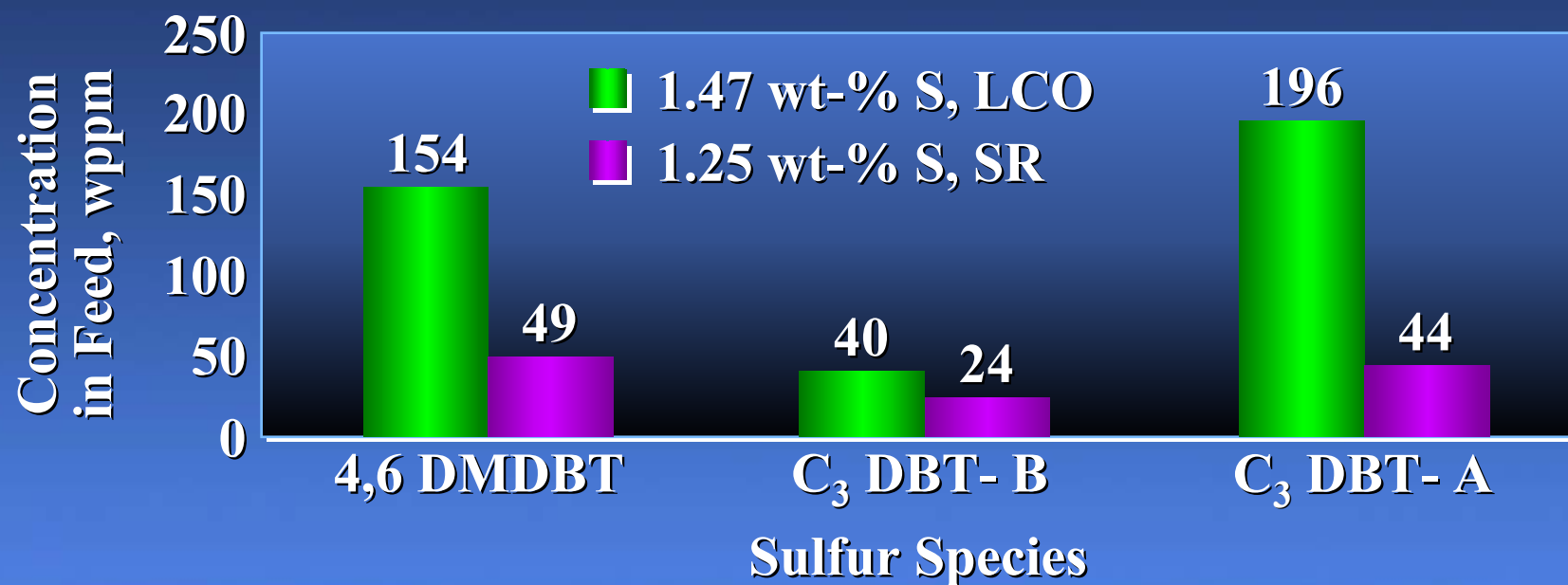
134 / 390

174 / 386

Sulfur, wt-%

1.47

1.25



Impact of Other Feedstock Components

Feedstock

Density

LCO

0.945

SR Gasoil

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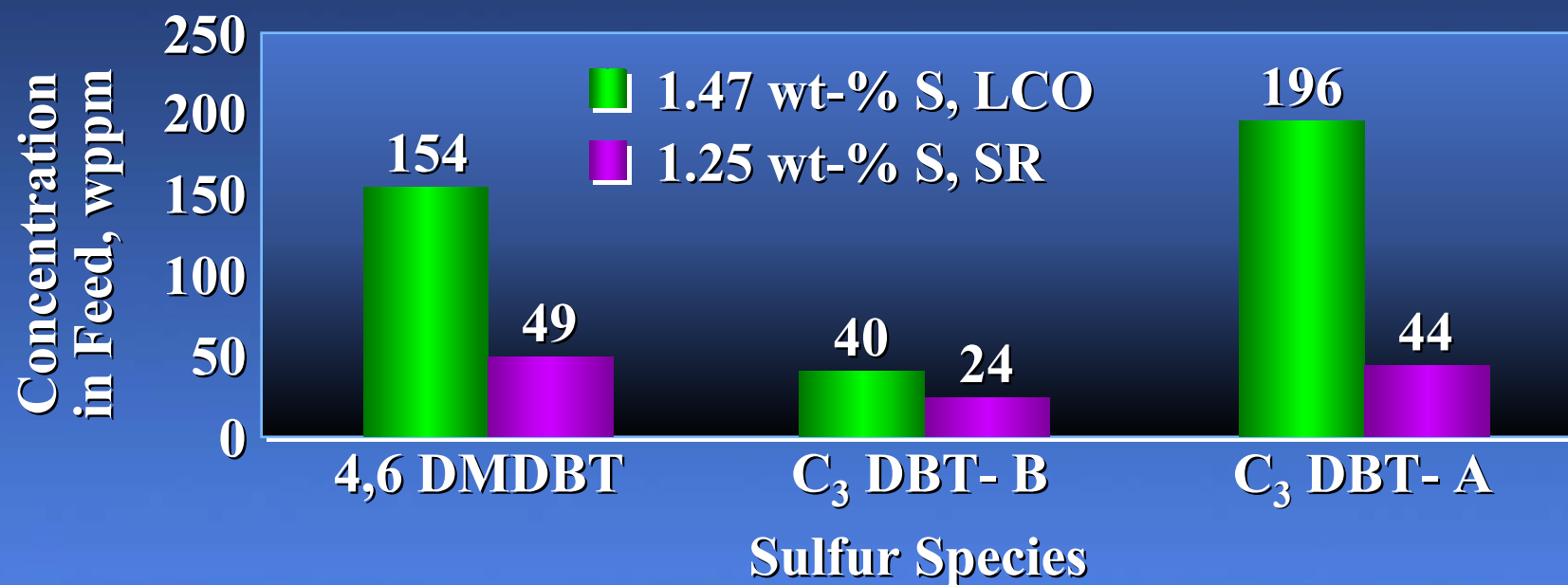
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Sulfur, wt-%

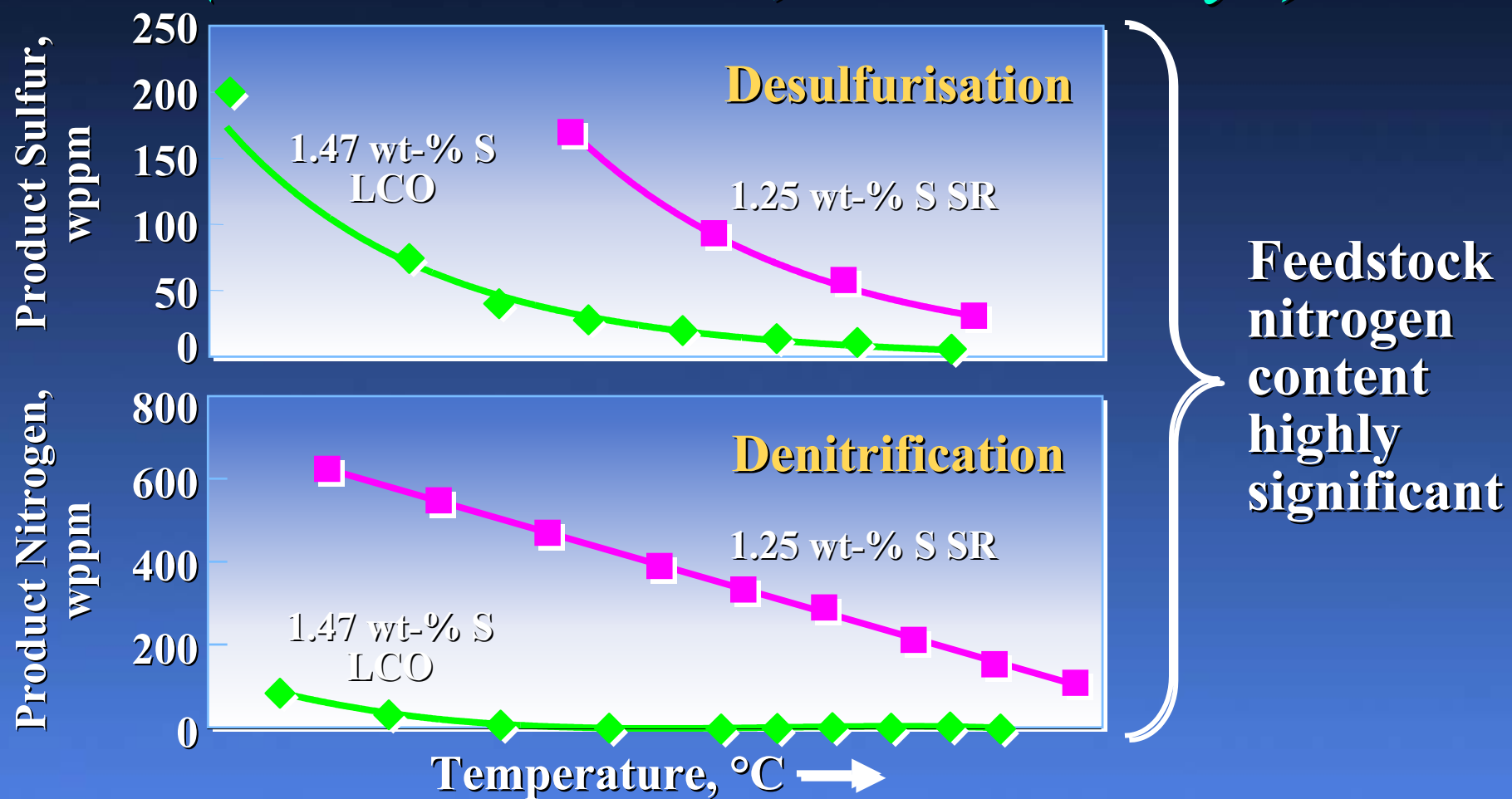
1.47

1.25



Desulfurisation/Denitrification Test Data

(Moderate Pressure, Ni / Mo Catalyst)



Nitrogen Species Reactivity

117°C b.p.



N

Pyridine

1

238°C b.p.



N

Quinoline

2.2

346°C b.p.



N

Acridine

6.6

446°C b.p.



N

Benz [α] acridine

21

Relative Difficulty

*Difficulty of Removal Increases as
Molecules Become More Complex*



ULSD Fundamentals

Feed Issues

- Understanding sulfur species in feed is essential
- Feed nitrogen content is a critical parameter
- *Reactivity of nitrogen compounds must be considered*
- Desulfurization and Denitrogenation are inter-related:
HDN and HDS can not be treated independently

Hydroprocessing Solutions to Clean Fuels

- **ULSD Fundamentals: Feed issues**
- **Revamp issues**
- **New unit design considerations**
- **Other issues**

Process Objectives

Consistent Performance

- Need robust design to produce ULSD day in and day out

Reliability is Key

- At <10 ppm S, off spec. products can not be blended off & need to be re-processed

No By-passing

- A small degree of by-passing or mal-distribution in the reactor will lead to off-spec. materials



*Need best designed and well run
unit to produce ULSD*

Revamp Issues

- **The “Heart” of the unit: The Reactor**

Factors affecting Reactor Performance

Internals

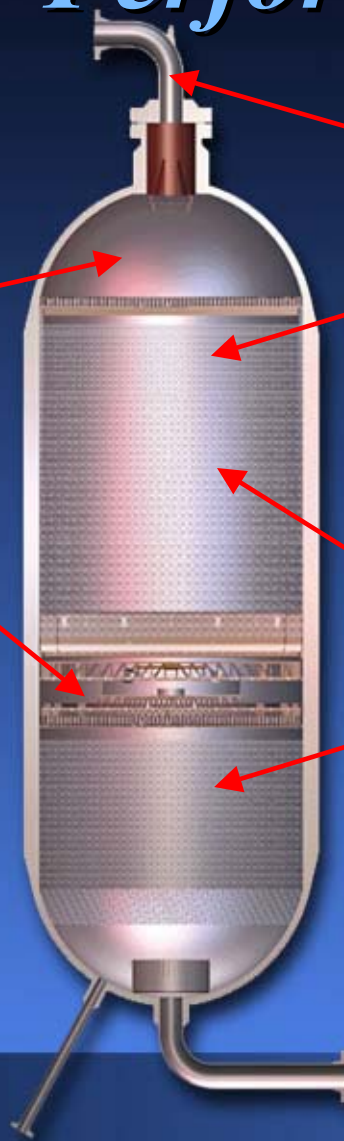
Vapor-liquid
distribution
Thermal mixing
Maintenance

Operations

Liquid and gas rates
Poor startup
Fouling
Upsets
Runaway

Loading

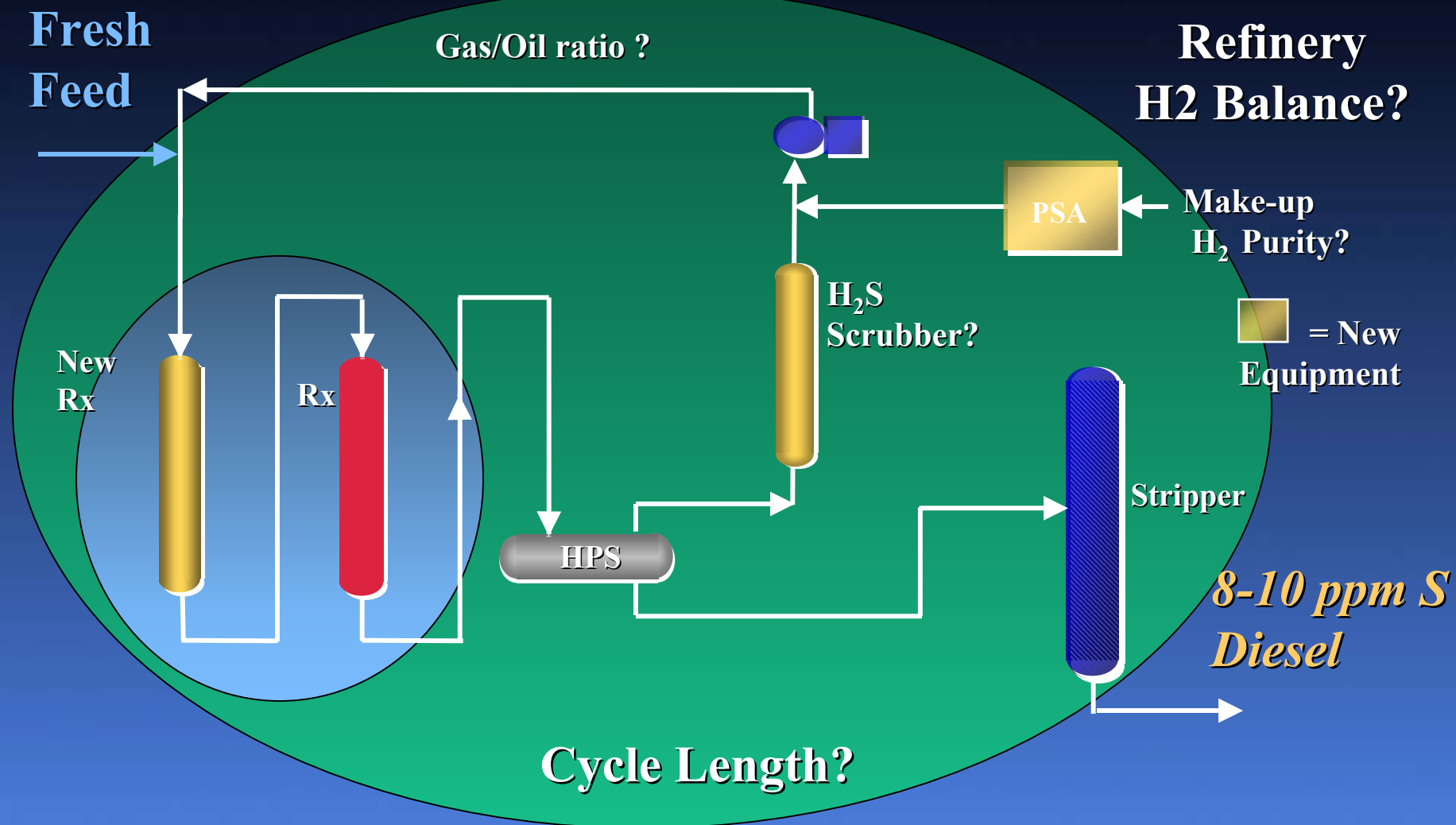
Sock vs. dense
Catalyst handling
Loading profile



Revamp Issues

- **The “Heart” of the unit: The Reactor**
- **The Rest of the unit**

REVAMP ISSUES



Hydroprocessing Solutions to Clean Fuels

- ULSD Fundamentals: Feed issues
- Revamp issues
- New unit design considerations
- Other issues



Technology Options for Hydroprocessing Units

LP	HP	VGO HTU	MHC	HC	HC
U	U	+	+	+	
L	L	U	U	U	
S	S	L	L	L	
D	D	S	S	S	
		D	D	D	



Compliance
No ROI

Compliance
Potential
ROI

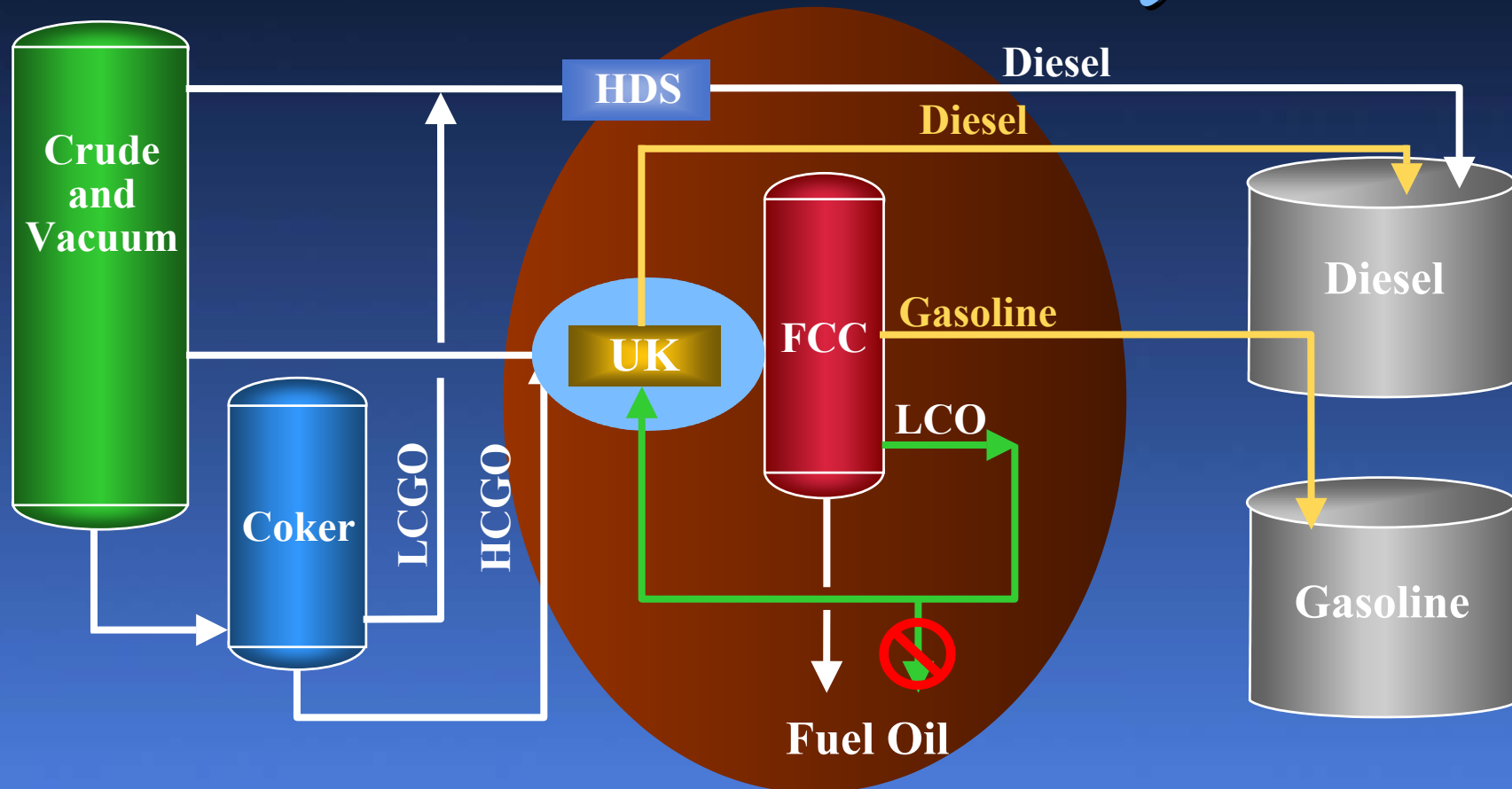
Compliance
Potential
ROI
Flexibility

Compliance
Good ROI
Flexibility

One Example

Partial Conversion Unicracking

Increases Flexibility



What Are the Implications?

**Operating
Issues?**

**Revamp
or New Unit?**



A New Set of Operating Issues



- Is it reliable enough?
- You can't run at 5 wppm S
 - Feed changes
 - Compliance margins
- Feed bypassing
 - Reactor maldistribution
 - Leaking heat exchangers

What Are the Implications?

**Operating
Issues?**

**Revamp
or New Unit?**

**Refinery
Issues?**

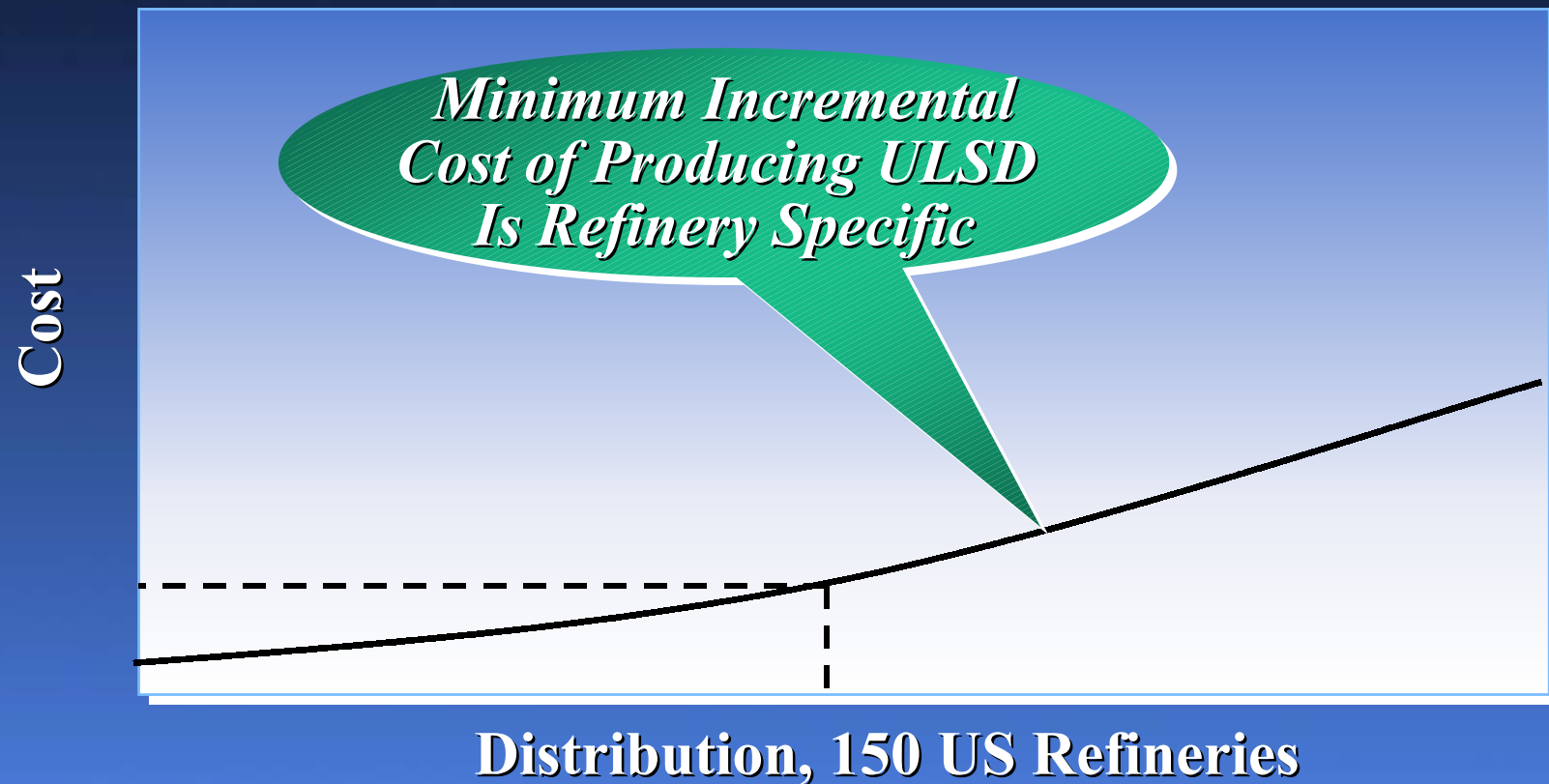


Refinery Implications



- Requirements for system cleanup
- Product segregation costs
 - Manifolding
 - Proof tanks
- Increased hydrogen demand
- Product distribution

Median Cost of Producing ULSD



What Are the Implications?

**Operating
Issues?**

**Revamp
or New Unit?**

**Refinery
Issues?**

**Diesel
Volume?**

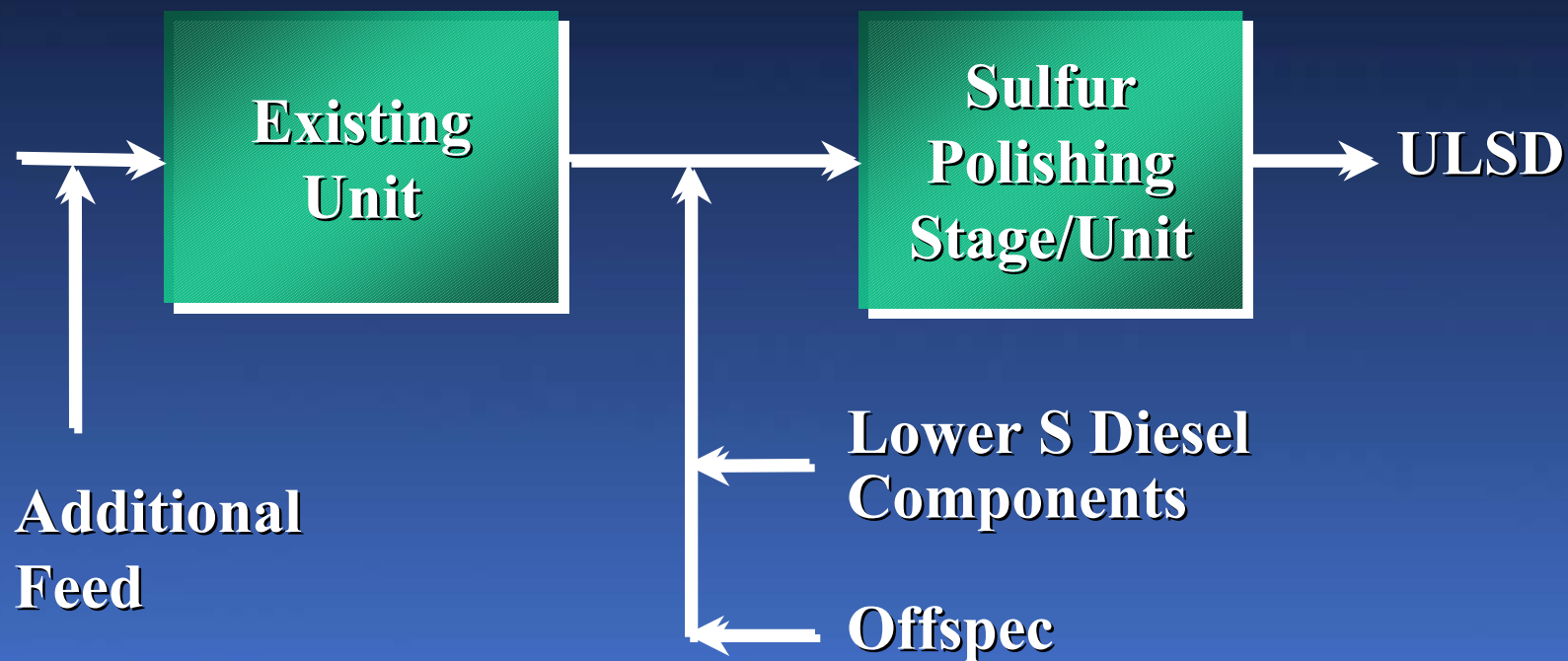


Capacity Implications of ULSD

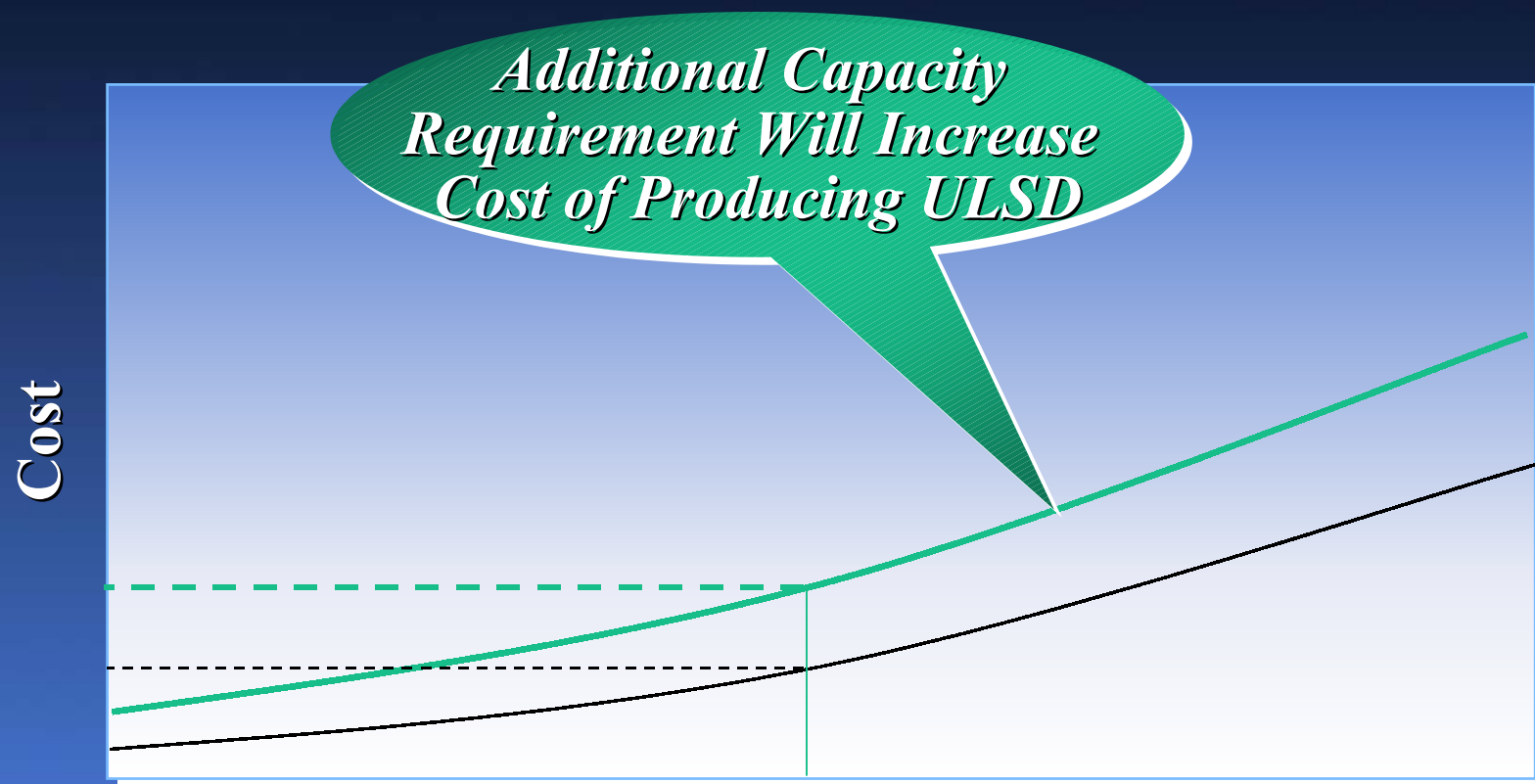


- **Yield loss**
- **Must process materials that were previously high quality blend stocks**
 - Hydrocracked diesel
 - Merox treated kerosene
- **Reprocessing flexibility**
 - Startup, shutdown and emergency procedures
 - Routing of offspec material

Capacity Implications of ULSD



Median Cost of Producing ULSD



Distribution, 150 US Refineries

What Are the Implications?



Flexibility for the Future

Bus Fleets



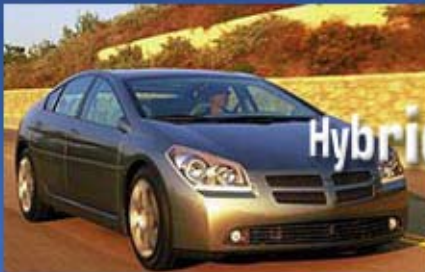
Heavy Duty Trucks



Light Duty Trucks



Hybrid



Passenger Cars

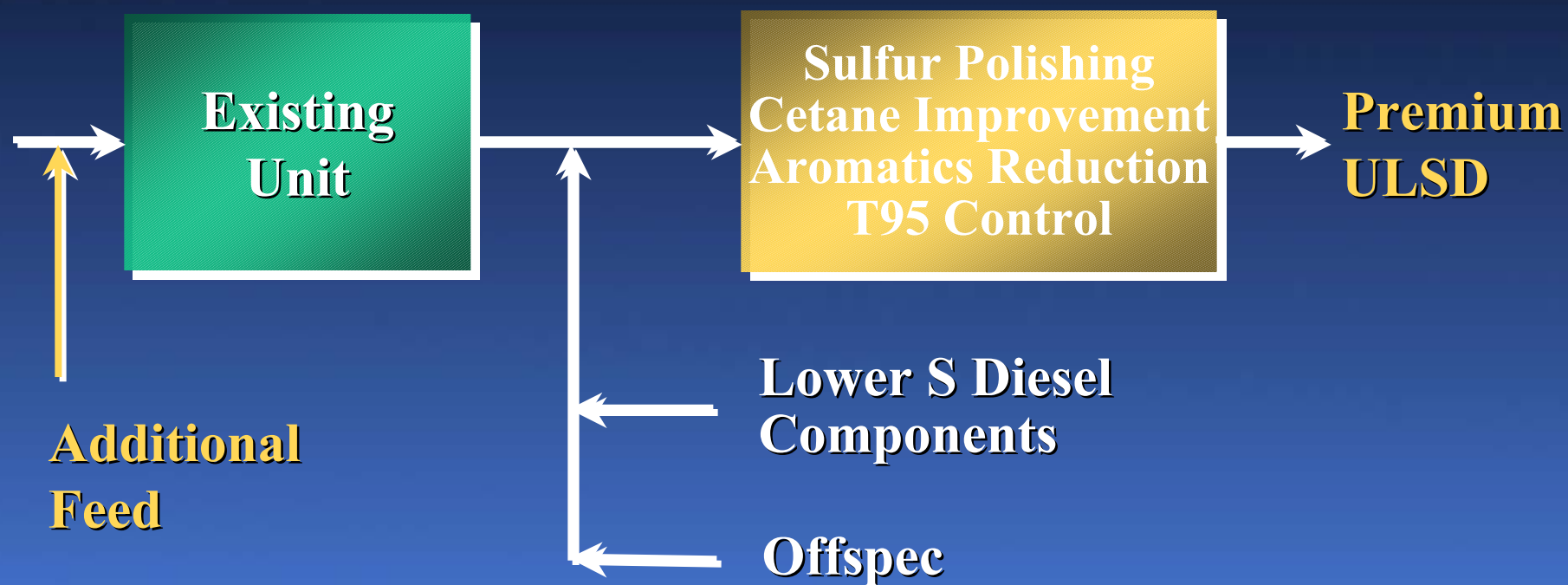


Fuel Cell

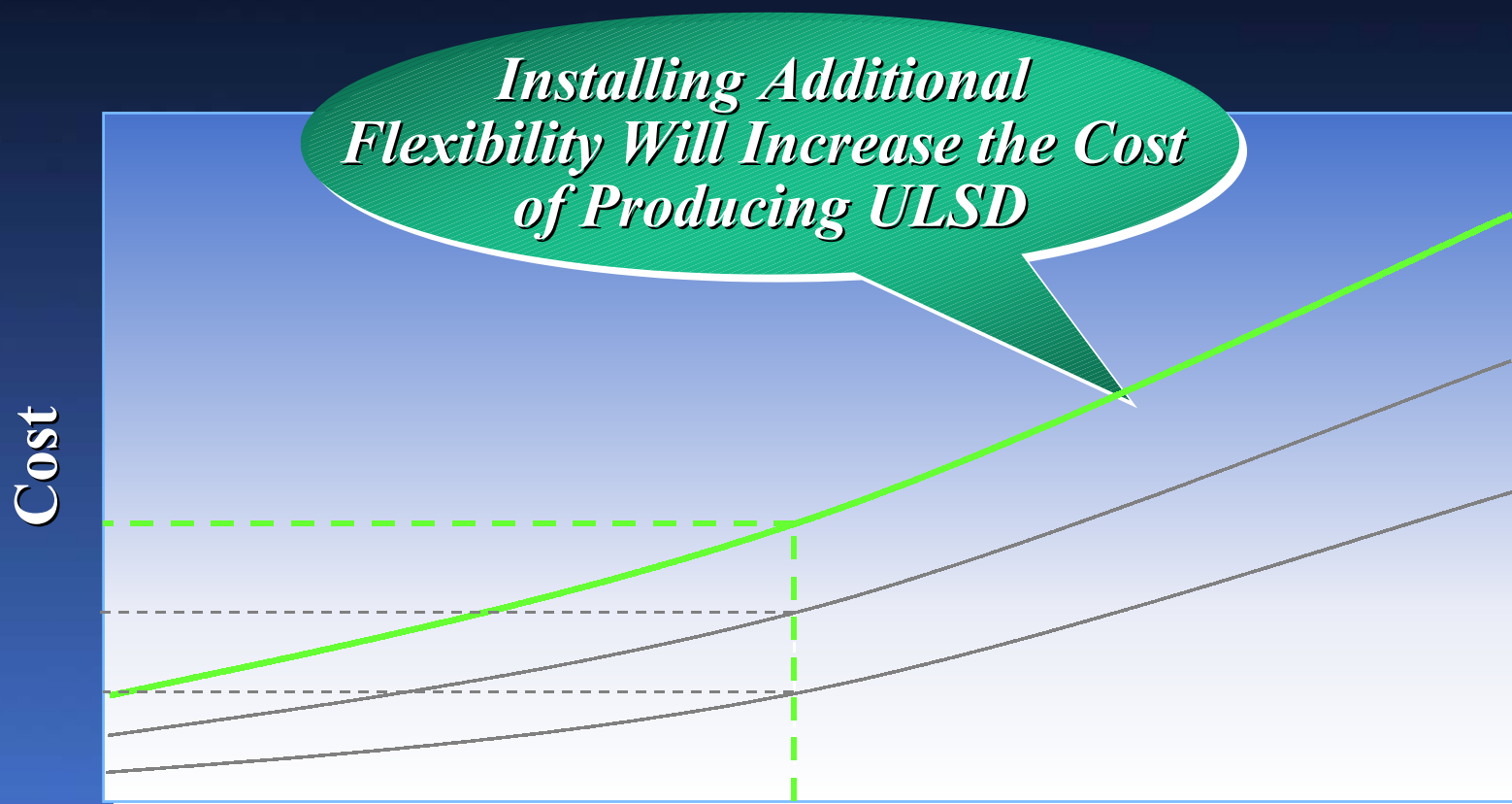


- Expansion of diesel fuel market
- Off road diesel
- Evolving diesel specifications
 - Cetane?
 - Aromatics?
 - T95 distillation?
- More difficult feeds

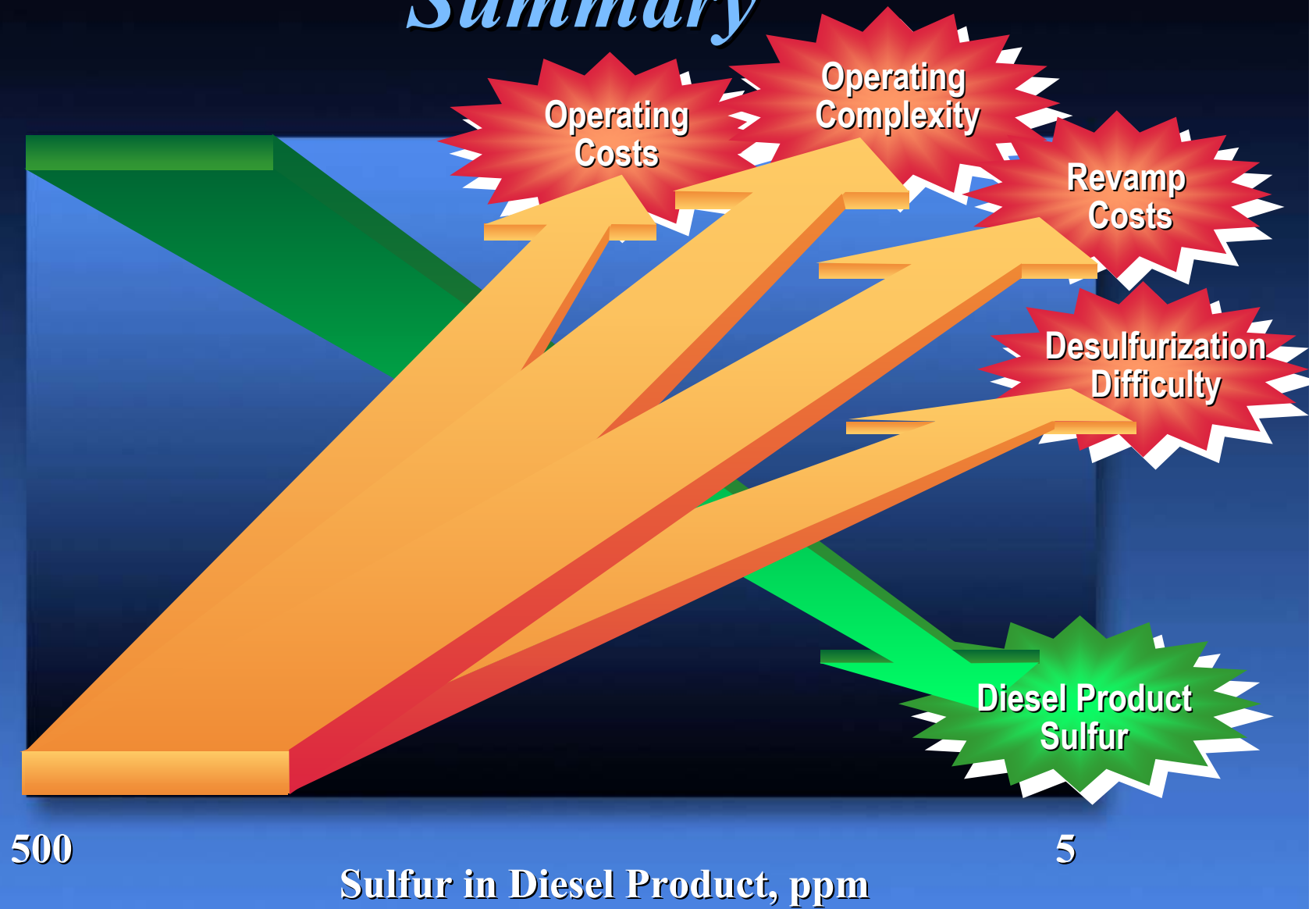
Flexibility Implications of ULSD



Median Cost of Producing ULSD



Summary



Conclusions



- Making ULSD is similar to making a high purity chemical
- Unit operations and product distribution will be more complex and more expensive
- Simple unit revamps may not be enough
- Couple short term plans for ULSD with strategies for diesel product flexibility to achieve the most cost effective, long term solution

Q & A



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