PRODUCTION OF ULTRA-LOW SULFUR FUELS BY SELECTIVE HYDROPEROXIDE OXIDATION

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Selective Hydroperoxide Oxidative Desulfurization

- Regulatory Drivers
- Why Oxidative Desulfurization
- Lyondell Chemical's

  Oxidative Desulfurization Process
- Process Advantages
- Path To Commercialization
- Summary/Conclusions

Regulatory Drivers

- **Continuing Drive To "Cleaner" Fuels**
  - **Lower Sulfur**
- **U.S. Gasoline: 30 PPM S (2004 – 2007)**
- **U.S. Diesel: 15 PPM S (2006 – 2010)**
- **Europe: 10 PPM S (2009)**
- **Pipelines Will Require Lower Levels**
- **Fuel Specifications Will Continue To Get Tighter**
  - **Lower Sulfur Off-highway/Heating Oil Are Next**
  - **"Zero" S Fuels ?**

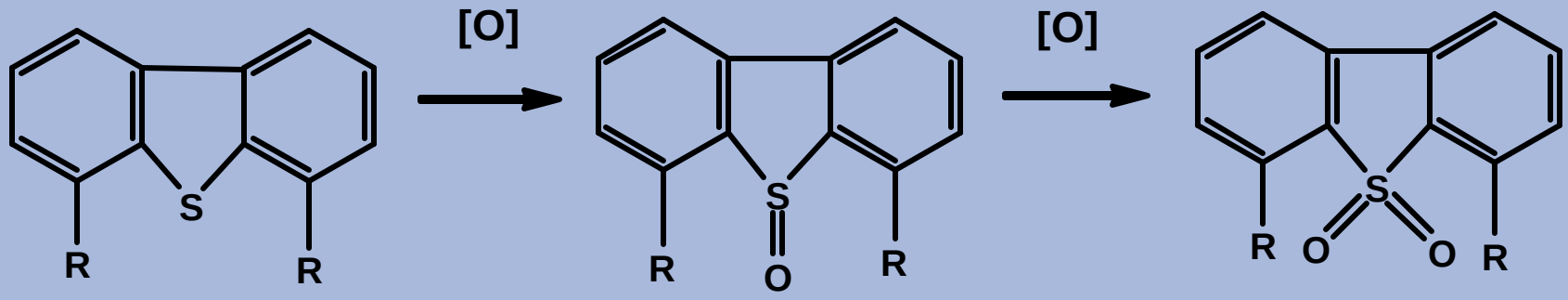
Ultra-low Sulfur Production Alternatives

- **Hydroprocessing**
  - **Proven Technology**
  - **Requires High Temperature & Pressure**
  - **High Capital**
- **Separation**
  - **Adsorption / Extraction / Membrane**
  - **Low Capital**
  - **Poor Efficiencies**
- **Oxidative Desulfurization**
  - **Nearing Commercialization**
  - **Greatly Improves Efficiencies of Standard Separation Technologies**

Why Oxidative Desulfurization

- **Easier To Remove Difficult to HT "S" Species**
  - **Dibenzothiophenes & Substituted Homologs**
- **No Increase in Refinery Hydrogen Demand**
- **"Finishing" Process To Bring Sulfur in Today's Fuels to New Ultra-low Sulfur Levels**
- **Good Fit With Small / Medium Sized Refineries**
  - **Hydrogen & Claus Plants Not Required**
- **Potential For Terminal Desulfurization**
  - **Solution To Sulfur Contamination Due to Commingling**
- **Ability to Achieve "Near-Zero" Sulfur Fuels**

Oxidative Desulfurization



Sulfoxide **Sulfone**

Two Basic Operations

1) **Conversion of Thiophenes to Sulfones**
   - **Increased Polarity**
   - **Increased Molecular Weight / Boiling Point**
2) **Removal of Sulfones From Fuel**
   - **Separation By Adsorption / Extraction**
   - **Separation by Distillation**

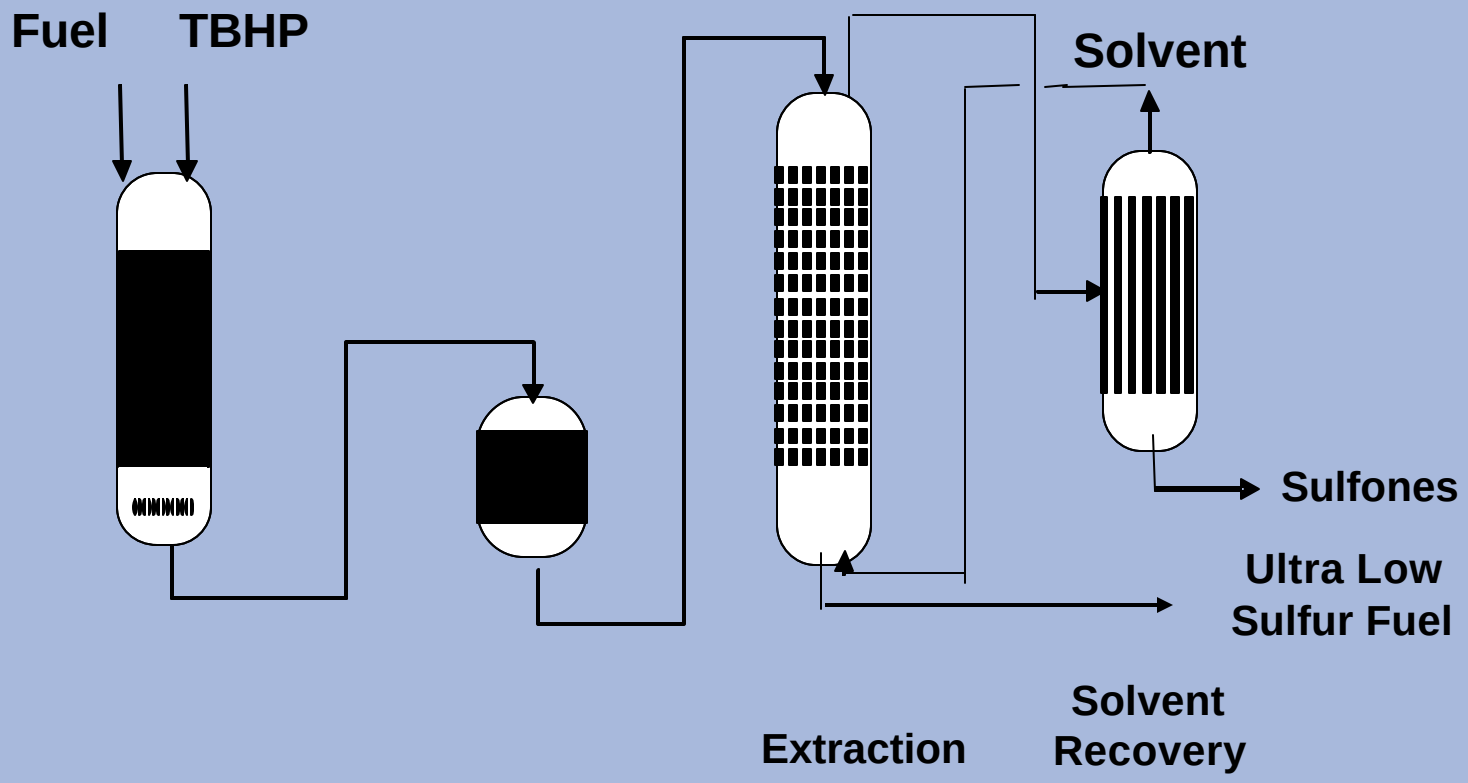
Diesel Desulfurization Process Highlights

- **Hydroperoxide Based Oxidation**
  - **Low Cost Source of "Active Oxygen"**
- **Continuous Oxidation Demonstrated**
  - **Laboratory-scale pilot Unit**
  - **Approaching 3000 Hours Continuous Operation**
  - **Proven Catalyst System**
- **High Conversion to Oxidized Sulfur**
  - **Confirmed For Different Feeds**
- **Several Options For Sulfone Removal Demonstrated**
  - **Focus Cost Optimization**
- **Favorable Economics versus Competitive Options**

t-Butyl Hydroperoxide Oxidant

- **Fuel Soluble**
- **Does Not Require Organic Acid Co-oxidant**
- **Global Production**
  - **Readily Available Supply**
  - **More Than One Potential Supplier**
- **Fuel Oxidation Grade**
  - **Refined Specialty Chemical Grade Is Not Required**
  - **Lowest Cost Source of Active Oxygen**

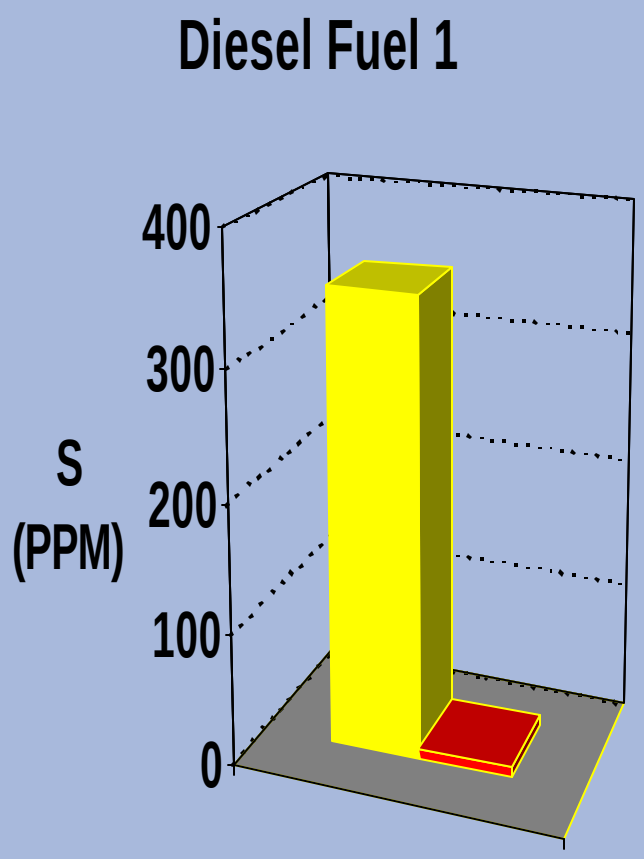
Lyondell's Diesel Oxidative Desulfurization Process

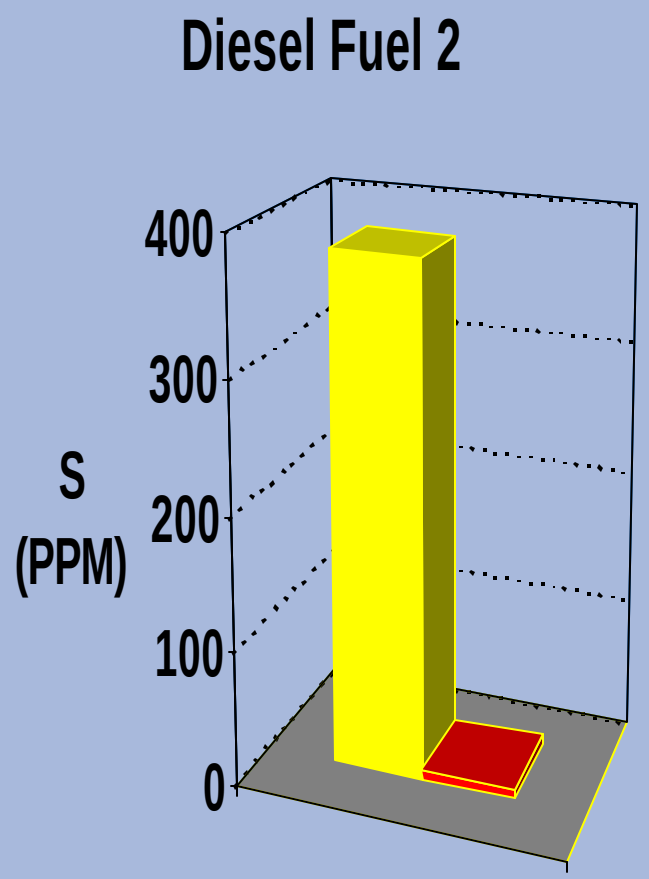


Fuel Appearance

Pretreated Diesel Post-Oxidation Finished Product

Typical Results





Typical Fuel Properties

Test	Diesel (As Received)	Sample 1	Sample 2	ASTM Specifications
Oxidative Stability (D2274 / mg/100 ml)	0.7	0.1	1.1	<1.5
Ramsbottom Carbon (10% Residue, D524)	0.11%	0.08%	0.06%	<0.15%
ASH (D482)	<0.001%	0.002%	N/M	<0.01%
Cetane Number (D613)	48	1 – 2 No. Increase	1 – 2 No. Increase	>40
Viscosity (Kinematic @ 40 C)	2.51 CSt	2.88 CSt	N/M	1.9 to 4.1 CSt
APHA Color	841	366	78	--
Sulfur	375	14	12	15

Advantages of the Lyondell Process

- Low Cost Fuel Soluble Oxidant
- Low Temperatures & Pressures
  - Less Than 200 ^{o}F
  - Slightly Greater Than Ambient Pressure
- No Organic Acids To Recycle
- Carbon Steel Construction For Majority of Unit
- Capable of Producing <10 PPM Diesel Fuel
- Simplicity

Process Economics – Diesel Desulfurization

- Based on Laboratory Pilot Unit
- Base Conditions
  - Feed: Typical 2002 U.S. On-road Diesel
  - Product: 7 – 8 PPM Sulfur
  - Capacity: 30,000 BPD
- Capital: $600 – 750 / BPD-Capacity
  - Installed Cost
  - ISBL & Select OSBL
    - Project Specific Tank age
- Cash Operating Cost:
  - < 2.5¢ per gallon

Oxidative Desulfurization of Gasoline

- **Preliminary Evaluation of Oxidative Desulfurization**
  - **Laboratory Evaluation**
  - **FCC Gasoline**
  - **Heavy Pyrolysis Gasoline**
- **Oxidative Desulfurization Potential Confirmed**
  - **Fuels with LT 30 PPM Sulfur Produced**
- **Requires Development of Modified Process**
- **Focus Remains on Diesel**

Commercialization Pathway

- **Continue Pilot Effort To Optimize Process / Reduce Cost**
  - **Choose Extraction or Adsorption Technology**
  - **Expand Experience with A Wider Range of Distillate Feeds**
- **Scale-up Oxidation to 1 BPD in In-house Pilot Unit**
- **Demo / Semi-Commercial Unit Early in 2004**

Conclusions

- **Oxidative Desulfurization Is Best Suited For Use as a "Finishing" Process**
  - **350 – 500 PPM Sulfur to < 10 PPM Sulfur**
- **Fuels with < 10 PPM of Sulfur Are Obtainable**
- **Process Requires Mild Temperatures & Pressures**
- **t-Butyl Hydroperoxide Is The Oxidant of Choice**
  - **Low Cost & Fuel Soluble**

Conclusions (cont'd)

- **Process Is Well Suited For Hydrogen Limited Refineries and Terminal Installation**

- **Oxidative Desulfurization Offers a Low Capital, Cost Competitive Option to Produce Ultra-low Sulfur Diesel Fuel**