Low Carbon Footprint Adsorptive Technology for ULSD Production

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Desulfurization Of Transport Fuels

- Current practices are hydrodesulfurization based
  - Energy intensive. High capital and operation costs.
  - Associated CO$_2$ emissions are also high

- Need to develop energy efficient, low cost and environment friendly desulfurization technology
# Specifications of Diesel

<table>
<thead>
<tr>
<th>S/N</th>
<th>Characteristics</th>
<th>Unit</th>
<th>BS III</th>
<th>BS IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Density @ 15(^0)C</td>
<td>Kg/m(^3)</td>
<td>820-845</td>
<td>820-845</td>
</tr>
<tr>
<td>2</td>
<td>Cetane no (min)</td>
<td></td>
<td>51</td>
<td>51</td>
</tr>
<tr>
<td>3</td>
<td>Pour point (max)</td>
<td>(^0)C</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>a) Winter (Nov-Feb)</td>
<td>(^0)C</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>b) Summer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Cu strip corrosion for 3 hrs @ 100(^0)C (max)</td>
<td>Rating</td>
<td>Class-1</td>
<td>Class-1</td>
</tr>
<tr>
<td>5</td>
<td>Temp @ 95% vol recovery (max)</td>
<td>(^0)C</td>
<td>360</td>
<td>360</td>
</tr>
<tr>
<td>6</td>
<td>Flash point (Abel), min</td>
<td>(^0)C</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>7</td>
<td>Kin Viscosity @ 40(^0)C</td>
<td>cSt</td>
<td>2.0-4.5</td>
<td>2.0-4.5</td>
</tr>
<tr>
<td>8</td>
<td>Total Sulfur (max)</td>
<td>ppmw</td>
<td>350</td>
<td>50</td>
</tr>
</tbody>
</table>
Global Efforts For Development Of Low Cost Technologies For Diesel Desulfurization

- Focus has been on alternative routes for desulfurization
  - Adsorbents/reactive adsorbents for selective removal of sulfur compounds
  - Catalysts for oxidation of sulfur compounds to sulfones
  - Catalysts for alkylation of sulfur compounds to higher boiling species
  - Membranes for selective permeation of sulfur compounds

- Adsorptive desulfurization promising
- Adsorptive desulfurization has lower hydrogen requirements (and hence lower CO$_2$ emissions) to achieve sulfur reduction.
Capital Cost Estimates And Diesel Cost Impact For Various Sulfur Removal Technologies*

<table>
<thead>
<tr>
<th>Technology</th>
<th>Capital Costs ($/bbl)</th>
<th>H2 Consumption (scf/bbl)</th>
<th>Cost Impact (¢/gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrotreating</td>
<td>1200-1800</td>
<td>1000</td>
<td>6-10</td>
</tr>
<tr>
<td>S Zorb</td>
<td>800-1200</td>
<td>400</td>
<td>4-8</td>
</tr>
<tr>
<td>TReND</td>
<td>500-700</td>
<td>20-100</td>
<td>2-4</td>
</tr>
</tbody>
</table>


*Technologies based on $/bbl costs, HCP, Nov. 2000
Conventional HDT based on $1,250/bbl
Major Sulphur Components In DHDS Feed

- Dibenzothiophenes
- Alkylated benzothiophenes
- Alkylated dibenzothiophenes
Objectives
To develop novel low carbon emitting technologies for production of ultra low Sulphur Gasoline/Diesel Production

Challenges
- To reduce Sulphur levels to below 30 ppm
- To reduce hydrogen requirement
- To minimise overall CO2 emissions
- To reduce process severity compared to existing desulphurisation processes
- To aim for technology with zero emission
Collaborative Development of Adsorptive Desulphurisation

- Adsorptive Desulphurisation Technology Requires Development of Advanced Adsorbent Material and Development of Process Technology Based on this Adsorbent.
- IIP Has Commercialised Several Large Scale Separation Technologies in the Petroleum Refining Sector and Has Expertise in Adsorptive Separation Process Development.
- SINTEF Has World Class Expertise for Advanced Adsorbent and Catalyst Development.
- This Collaborative Development Programme under Indo Norwegian Programme for Institutional Co-operation Was Drawn up Based on Complementarity of Expertises Available With Both Partners.
Adsorbent Development By High Throughput Combinatorial Technique

Develop New HT technology

R&D Using HT Technology
Test procedure – main steps

Pretreatment: 450°C in He for 1 h
Ceramic microplate

- Adsorbent (30mg) + DBT/4,6DMDBT (500mg/l)/n-hexadecane (0.9 ml)
  Rotation for 24 h at RT
Teflon (PTFE) microplate

Dilution of liquid samples
18µl + 900µl n-hexadecane

250µl samples for UV analysis
Polystyrene microplate

Synthesis/characterisation
/screening at mg scale of 48 adsorbent samples at a time
Typical Adsorbents Investigated

- Zeolites (Y, X, clinoptilolite...)
- Mesoporous systems (MCM-41, SBA-15...)
- Oxides (alumina, silica, alumina-silica...)
- Activated carbon

- Metals inserted by ion exchange or impregnation (Cu, Ni, Fe, Zn, Na, Ag, Ga, Ce etc.)
Fixed Bed Adsorption Experiments: Optimisation Of Adsorption Cycle

- Fixed bed experiments carried out with two refinery diesels containing 450 ppm and 150 ppm sulphur.
- Adsorption Temperatures were 350°C and pressure 3 to 10 bar.
- Parameters studied were:
  - Adsorbent type
  - Pressure
  - Feed flow
  - Hydrogen flow
Effect of Feed Sulphur Concentration

- 450 ppm Sulphur Refinery Diesel
- 150 ppm Sulphur Refinery Diesel

Adsorbent: Mesoporous

Adsorption Temperature: 350 °C
Adsorption Pressure: 3 bar (g)

WHSV: 4.8 h⁻¹
Volume of Diesel Treated per gram of Adsorbent up to 50 ppm Sulphur BT Level

Feed: 450 ppm Sulphur Diesel

WHSV = 4.8 h$^{-1}$
Adsorption and Regeneration
Process Steps
Adsorption Cycle

- Air
- Nitrogen
- Knock out drum
- Diesel, <50 ppm sulphur
- Diesel, 450 ppm sulphur
- H₂ gas

C-1, C-2
Nitrogen Purge

H₂ gas

Diesel, 450 ppm sulphur

Air
Nitrogen

Knock out drum

Diesel, <50 ppm sulphur
Diesel, <50 ppm sulphur

Thermal Oxidation

Air
Nitrogen

Knock out drum

C-1
C-2

H₂ gas

Diesel, 450 ppm sulphur

Diesel, <50 ppm sulphur
Air cooling

H₂ gas

Diesel, 450 ppm sulphur

C-1

C-2

Knock out drum

Air

Nitrogen

Diesel, <50 ppm sulphur
Nitrogen Cooling to 350°C

- PSA tail gas/N2/CO2
- Diesel, <50 ppm sulphur
- Diesel, 450 ppm sulphur
- Knock out drum
- Air
- Nitrogen

Diagram details:
- C-1
- C-2
- Cooling to 350°C
- Knockout drum
- Diesel, <50 ppm sulphur
## Process Streams

<table>
<thead>
<tr>
<th>Process Step</th>
<th>Influent to adsorber</th>
<th>Effluent from adsorber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Diesel, 350°C, 3 bar</td>
<td>ULSD product to storage</td>
</tr>
<tr>
<td></td>
<td>H₂ gas, at 350°C, 3 bar</td>
<td>H₂ gas to storage/recycle</td>
</tr>
<tr>
<td>Inert Purge</td>
<td>Nitrogen</td>
<td>Nitrogen to storage/recycle</td>
</tr>
<tr>
<td>Air Oxidation</td>
<td>Air</td>
<td>To Claus unit for sulphur recovery</td>
</tr>
<tr>
<td>Air cooling</td>
<td>Air</td>
<td>To vent</td>
</tr>
<tr>
<td>Inert purge</td>
<td>Nitrogen</td>
<td>To storage/recycle</td>
</tr>
</tbody>
</table>
A vapor phase adsorption process has emerged which is capable of reducing sulphur level from actual refinery diesel from 450ppm to <50 ppm

- Adsorbent is thermally regenerable. Regenerability is strongly dependant on the temperature used.

- Currently the process developed uses H$_2$ to HC ratio of 200 and produces EURO IV diesel

Conventional DHDS process uses pressure of 35 to 40 bar and H$_2$ to HC ratio of 600 to 700 to produce EURO II diesel and requires pressures of 100-105 bar with H$_2$ to HC ratio of 1000 to 1600 to produce EURO III/EURO IV diesel.

- Adsorption process developed uses much lower H$_2$ and therefore will be low carbon emitting compared to conventional DHDS
Integration of Adsorptive Separation Unit (ADSU) with DHDS for Production of Low Sulphur Diesel
Possible Location of ADSU

**Location-1**
51 kg/cm²g
45 °C
1.45 wt% S

**Location-2**
48 kg/cm²g
327 °C
1.45 wt% S

**Location-3**
39 kg/cm²g
300 °C
1.48 wt% H₂S

**Location-4**
35 kg/cm²g
50 °C
1.48 wt% H₂S

**Location-5**
5 kg/cm²g
45 °C
500 ppmw S

PURE H₂

SRGO
LVGO
FILTER

G-1
MUC
K-1
RGC
K-2

LEAK AMINE
P-1
R-1

HP AMINE ABSORBER
C-1

RICH AMINE
C-2

V-7
RICH AMINE
WILD NAPH

Sweet HSD
COALESCER
V-8

SWEET FG

Sweet HSD
## Comparison of diff. ADSU Location

<table>
<thead>
<tr>
<th>Location</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Sulphur Loading</th>
<th>S component</th>
<th>Regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Location-1)</td>
<td>51 kg/cm²g</td>
<td>45°C</td>
<td>1.45 wt% S</td>
<td>Mercaptans, Sulfides, Di-Sulfides, Thiophenes, Benzothiophenes, Di-benzothiophenes etc.</td>
<td>By Solvent</td>
</tr>
<tr>
<td>(Location-2)</td>
<td>48 kg/cm²g</td>
<td>327°C</td>
<td>1.45 wt% S</td>
<td>Mercaptans, Sulfides, Di-Sulfides, Thiophenes, Benzothiophenes, Di-benzothiophenes etc.</td>
<td>By Solvent</td>
</tr>
<tr>
<td>(Location-3)</td>
<td>39 kg/cm²g</td>
<td>300°C</td>
<td>1.48 wt% H₂S</td>
<td>Mainly H₂S. Rest will be mainly unconverted Refractory Sulphur compd.</td>
<td>By Nitrogen purge &amp; controlled oxidation</td>
</tr>
<tr>
<td>(Location-4)</td>
<td>35 kg/cm²g</td>
<td>50°C</td>
<td>1.48 wt% H₂S</td>
<td>Mainly H₂S. Rest will be mainly unconverted Refractory Sulphur compd.</td>
<td>By Nitrogen purge &amp; controlled oxidation</td>
</tr>
<tr>
<td>(Location-5)</td>
<td>5 kg/cm²g</td>
<td>45°C</td>
<td>500 ppmw S</td>
<td>Low S content in feed is favourable for Adsorptive separation.</td>
<td>By solvent</td>
</tr>
</tbody>
</table>

- **Temperature:**
  - Favourable
  - Not Favourable
  - Not Favourable
  - Favourable
  - Favourable

- **Pressure:**
  - No Significant effect
  - No Significant effect
  - No Significant effect
  - No Significant effect
  - No Significant effect

- **Sulphur Loading:**
  - S in feed is too high leading to very large adsorber volume or large cycle time
  - S in feed is too high leading to very large adsorber volume.
  - H₂S content is too high.
  - H₂S content is too high.
  - Low S content in feed is favourable for Adsorptive separation.

- **S component:**
  - Mercaptans, Sulfides, Di-Sulfides, Thiophenes, Benzothiophenes, Di-benzothiophenes etc.
  - Mercaptans, Sulfides, Di-Sulfides, Thiophenes, Benzothiophenes, Di-benzothiophenes etc.
  - Mainly H₂S. Mainly Refractory Sulphur compd.
  - Mainly H₂S. Mainly Refractory Sulphur compd.
  - Mainly Refractory Sulphur component i.e. 4-MDBT, 4,6-DMDBT, 2,4,6-TMDBT etc.

- **Regeneration:**
  - By Solvent
  - By Nitrogen purge & controlled oxidation
  - By Nitrogen purge & controlled oxidation
  - By solvent
  - By Solvent
Conclusion

• Location -3 identified as the possible location for integration among the other options

• ADSU seems to be a viable option for removing refractory Sulphur compounds from Diesel.

• Seamless integration possible due to almost similar operating conditions of DHDS and ADS

• No significant temperature swing envisaged in adsorption and regeneration cycle
Proposed Flow Scheme for Integrated HDS – Adsorption Process for ULS Diesel Production

Make-Up $\text{H}_2$

Recycle $\text{H}_2$

Compressor

Knock Out Drum

Slip Stream to Claus unit

Regeneration Gas Compressor

Treated diesel < 50 ppm Sulphur

Feed Diesel, 450 ppm Sulphur

HDS Reactor-1

Furnace

HP Separator

Amine Treater

Air Condenser

Separator

SW

Treated diesel 50 ppm Sulphur

HDS Reactor

HDS 1

ADS 2

Regenerator Heat Exchanger

TRIM Cooler

Make-Up $\text{N}_2$

Air

Make-Up $\text{H}_2$

Recycle $\text{H}_2$

Compressor

Wash Water

Feed Diesel 450 ppm Sulphur

HDS Reactor

HDS 2

ADS 1

Regenerator Heat Exchanger

TRIM Cooler

Make-Up $\text{N}_2$
Thank You