SpinTek, Inc. has developed a non-oxidized desulfurization process which is based on Direct Extraction of Sulfur (DXs). The new process is efficient and cost effective for removal of middle distillate sulfur hydrocarbons: Gasoline, Transmix, and Diesel No. 2.

The technology uses a cyclic process of an adsorbent to adsorb and desorb. After the adsorbent is fully loaded with sulfur compounds, the adsorbent bed is regenerated by using a simple process to detach sulfur from adsorbent surfaces using recyclable strip solution. Thus, the adsorbent bed can be changed from operating mode into regenerating mode.

The DXs process has undergone 3 years of exhaustive testing, consistently yielding successful results as seen in Figure 1. The Polanyi potential theory (Dubinin–Radushkevich Model) is further derived to calculate reactor sizes.

The SpinTek DXs process is scalable from pilot size systems up to 200,000 barrels per day (bpd) systems.
ADVANTAGES

Direct Extraction of Sulfur
- No hydrogenation & no oxidation process requiring hazardous oxidation agents, e.g., peroxide
- No sodium hydroxide treatment
- No sulfones created; no difficult to process byproducts
- Low operating temperature <150 °C
- Low pressure <100 psi
- Stand-alone operation or a concentrator of sulfur distillates for more efficient HDS operation
- Extraction efficiency does not depend upon molecule size or structure of sulfur middle distillate (e.g., thiophene to larger than dibenzothiophenes)
- Production of Ultra Low Sulfur Diesel (ULSD)

PROCESS

SpinTek’s Direct Extraction Process
- Simple system of packed columns; regenerable with low cost recyclable strip solution
- Closed loop strip process
- Low temperature and pressure
- High sulfur middle distillate enters system; continuous cycle; two streams exit:
  - Low sulfur stream
  - Concentrated sulfur stream

PROCESS IMPLEMENTATION
- Sample Testing
- Technical Report/Analysis
- Lab Scale Plant
- Field Pilot Plant

Figure 1. Example Applications

<table>
<thead>
<tr>
<th>Application #1</th>
<th>Application #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>Inlet</td>
</tr>
<tr>
<td>≈300 mg/kg, 10,000 bpd</td>
<td>≈1,500 mg/kg, 10,000 bpd</td>
</tr>
<tr>
<td>SpinTek Direct Extraction Process</td>
<td>SpinTek Direct Extraction Process</td>
</tr>
<tr>
<td>Ultra Low Sulfur Diesel &lt; 10 mg/kg, 9,425 bpd</td>
<td>Low Sulfur Diesel ≈500 mg/kg, 7,500 bpd</td>
</tr>
<tr>
<td>Outlet 1</td>
<td>Outlet 1</td>
</tr>
<tr>
<td>High Sulfur Concentrate &gt; 5,000 mg/kg, 575 bpd</td>
<td>High Sulfur Concentrate &gt; 2,500 mg/kg, 2,500 bpd</td>
</tr>
<tr>
<td>Outlet 2</td>
<td>Outlet 2</td>
</tr>
</tbody>
</table>

PROCESS VALIDATION
- Analyze sterically hindered molecules and removal efficiency
  - Agilent sulfur chemoluminescence device (SCD) with gas chromatograph for characterization of sulfur molecule removal
  - Horiba X-ray fluorescence analysis (XRF) for removal efficiency

Figure 2. Typical Packed Bed Column
To the right are test results illustrating how SpinTek's desulfurization process reduces the sulfur content in an untreated (non-oxidized) diesel from about 4900 to 10 ppm. Chart 1 shows that the SpinTek process removes the same species of organosulfur compounds from the highly concentrated 4900 ppm sulfur diesel to the same extent as from the less concentrated 300 ppm sulfur diesel.

**Table 1. Process Comparison**

<table>
<thead>
<tr>
<th>Process Method</th>
<th>Need Catalyst/Adsorbent</th>
<th>Process Parameters</th>
<th>Safety Hazard</th>
</tr>
</thead>
</table>
| Hydrodesulfurization (HDS)   | Noble Metal Stability and Regenerable | 1. Pressure Stage 1-300°C at 650psig.  
2. Pressure Stage 2-400°C at 850psig.  
3. High maintenance equipment and reactors.  
4. Requires Hydrogen gas and noble metal catalysts. | Hydrogen  
High Pressure  
High Temperature                         |
| Oxidation (ODS)              | Phase Transfer Catalyst Stability and Regenerable | 1. Pressure ambient.  
2. Varying temperatures contingent on oxidizing agents e.g., peroxide  
3. High maintenance equipment and reactors.  
4. Requires peroxide and expensive phase transfer catalysts. | Peroxide  
High Pressure  
High Temperature                         |
| SpinTek's Direct Extraction (DX₅) | Very stable Regenerable | 1. Pressure ambient <100psi.  
2. Temperature between 60°C and 150°C.  
3. Regenerated adsorbent bed using recyclable strip solution.  
4. Low maintenance equipment and reactors.  
5. No dangerous chemical agent involved.  
6. Produces diesel suitable for fuel cell technology. | Minimal |

**Figure 3. Regeneration Mode**

**S P I N T E K ‘ S  D X S**  
**P R O C E S S O N  H I G H  S U L F U R  D I E S E L**

To the right are test results illustrating how SpinTek's desulfurization process reduces the sulfur content in an untreated (non-oxidized) diesel from about 4900 to 10 ppm. Chart 1 shows that the SpinTek process removes the same species of organosulfur compounds from the highly concentrated 4900 ppm sulfur diesel to the same extent as from the less concentrated 300 ppm sulfur diesel.
DE SUL F U R I Z A T I O N  P R O C E S S E S

1. Hydrodesulfurization
   The standard desulfurization process in the oil industry is hydrodesulfurization (HDS). In this process, middle distillates with high sulfur content go through two consecutive stages of hydrogen treatment: the first stage removes smaller sulfur compound molecules and the second stage removes larger molecules. The first stage operates at a temperature of about 300°C and a pressure of about 650 psi. This high temperature and pressure is needed to reduce the wetting barrier between solid, diesel and hydrogen. The second stage operates at a temperature of about 400°C and a pressure of about 850 psi. The higher temperature in the second stage is required to mitigate the higher resistance to mass transfer of the more sterically hindered sulfur compounds such as benzothiophene, dibenzothiophene, etc.

2. Oxidative Desulfurization
   Another desulfurization process, still in development, is Oxidative Desulfurization (ODS), in which the sulfur compounds are oxidized to sulfoxides using an oxidizing agent that is usually an organic peroxide or ozone. The sulfoxides are more polar than the organosulfur compounds, enabling easy separation by liquid-liquid extraction or adsorption. The catalysts used are composed of phosphate derivatives, tungsten derivatives, etc., and in general are non-regenerable. The sulfoxide created by ODS cannot be treated by HDS.

3. SpinTek Direct Extraction of Sulfur
   The SpinTek technology is based on Direct Extraction of Sulfur (DX₈) to adsorb and desorb sulfur compounds in diesel. As the GC-SCD analysis demonstrates, the SpinTek DX₈ process removes all of the sulfur compounds in diesel nonselectively. In contrast to ODS, the adsorption requires no oxidation or chemical addition and any concentrated sulfur compounds can be sent, if necessary, to HDS. Because the HDS process is more cost effective at higher sulfur concentrations, the SpinTek DX₈ process enables use of smaller HDS reactors for a given sulfur throughput, or alternatively, higher throughput capacity in an existing HDS unit (debottlenecking), and lower energy/operating costs and hydrogen usage.

As a stand-alone system, the SpinTek DX₈ process produces a concentrate of sulfur hydrocarbons and an ultra low sulfur diesel (ULSD). While ULSD is discussed here, the technology works the same on gasoline and transmix.

Figure 4. DX₈ - Before and After

![Diesel with 10 weight ppm of sulfur -- product of SpinTek's DX₈ technology on diesel with 4900 ppm and 2900 ppm of sulfur.](image)