Fuel Ethanol: Economically Removing Sulfate and Sodium

The Challenge – Removing Sulfate and Sodium from Fuel Ethanol

Ethanol is ever growing as a renewable energy source to supplement automobile fuel needs. The US Government has mandated use of 7.5 billion gallons of fuel ethanol by 2012. Trace contaminants can be present in fuel ethanol and that is a concern for engine life and performance, as well as pollution issues. These contaminants can be removed from fuel ethanol for a few cents per 1,000 gallons of fuel.

Government Limits

In order to control sulfur emissions, the US Government is studying limits on sulfate in fuel ethanol to meet emissions limits in some areas. While current limits are set at 10 ppm, lower levels of sulfate can be achieved with ion exchange removal processes.

Other salts such as Sodium are an emerging concern

In addition to sulfate, fuel ethanol can contain ppm levels of metals such as sodium, iron, or calcium and organic acids. These contaminants are a potential concern as deposits form in automobiles.

The Solution – DOWEX™ Resins for Sulfate and Sodium Removal

A Cost-Effective, Selective Solution

Ion exchange resins are widely accepted as the preferred treatment for low-level contaminant removal because they offer several advantages compared with other technologies:

- Ion exchange resins act as “chemical sponges,” efficiently removing greater than 99 percent of trace contaminants.
- Ion exchange resins have a high loading capacity. One cubic foot of DOWEX™ ion exchange resin will treat hundreds of thousands of gallons of fuel ethanol before exhaustion (depending on the sodium and sulfate levels).
- Ion exchange resins offer great flexibility. They are incorporated in modular tanks, so systems can be expanded incrementally to meet demand. Systems can be skid-mounted mobile units or permanent installations.
- Ion exchange resins act quickly, allowing high flow rates with lower equipment costs.

DOWEX™ ion exchange resins are the ideal choice for fuel ethanol contaminant removal needs because they offer unique performance benefits:

- Unsurpassed loading capacity in each class of product.
- Guaranteed specifications, with every resin batch tested.
- Manufactured in the U.S., with exacting production methods.
- Greater durability than other ion exchange resins, with less physical attrition, so the media will remain in the vessel.

Choosing the Right Resin for your System

Sodium and sulfate removal from Fuel Ethanol

In many cases, sulfate is present in fuel ethanol as salt of sulfuric acid and common ions such as sodium. Both components are of concern; the sodium is of concern for deposits that can form in engines and sulfate as a contributor to sulfur emissions and air pollution. The most direct approach to removing both of these contaminants is with a deashing resin pair consisting of DOWEX™ 88 and DOWEX™ 66 ion exchange resins. The DOWEX 88 resin is used in the lead position to remove cations such as sodium, calcium or iron, and to prepare the sulfate for removal by the DOWEX 66 weak base anion exchange resin. In addition, the DOWEX 66 resin will remove organic acids.
Choosing the Right Resin for your System (cont.)

Sulfate removal as sulfuric acid
When sulfate is present as sulfuric acid, it can be removed by ion exchange with DOWEX™ 66 ion exchange resin alone. DOWEX 66 is a high capacity weak base anion exchange resin that can very efficiently remove acids such as sulfuric acid from fuel ethanol.

Sulfate removal only
Sulfate alone can be removed even when it is present as a salt with DOWEX™ 22 strong base anion exchange resin. This ion exchange resin is capable of splitting the sulfate salts that are present for complete removal of sulfate that is present as an acid or a salt.

Operating conditions
When a deashing pair of DOWEX™ 88 resin followed by DOWEX™ 66 resin are used to treat fuel ethanol, >95% removal of all cations and anions can be achieved. Flow rates of up to 12.75 bed volumes per hour treatment rates were used with up to 99.8% salt removal.

Volume changes of the media must be considered in systems design
Fuel ethanol of +99% purity will cause the DOWEX™ 66 and DOWEX™ 88 resins to undergo significant volume changes. When DOWEX 88 is cycled from the H form in water to the exhausted form in ethanol, it will shrink by as much as 13%. DOWEX 66 will swell from the free base form in water to the acid exhausted from in ethanol by as much as 25%. Fortunately, these DOWEX™ resins have been used extensively in the high fructose corn syrup (HFCS) industry for decades where they have been perfected to tolerate these substantial volume changes that could destroy other ion exchange resins. When these products are used in equipment designed by knowledgeable engineers, they can be expected to give a long service life.

Operating Costs

Cost of operations
Major contributors to the operating cost of an ion exchange system are the initial cost of the ion exchange resins, chemical regenerants, rinse water, waste water treatment costs, lost ethanol during sweetening off and on and capital cost for the vessels to hold the resin. Gallons of fuel ethanol treated will depend on the level of contaminants to be removed. The range of values listed below are for contaminants in the few ppm to tens of ppm levels. Since hundreds of operating cycles are expected, resin cost is averaged over many gallons of fuel ethanol treated. Regenerant chemicals are typically <1 to 1 cent per 1,000 gal of fuel ethanol (again depending on the level of contaminant). Waste water treatment costs, lost fuel value and equipment cost will vary widely for individual facilities but are not significant costs since they will be averaged over many years of service.

Table 1 – DOWEX™ Resins for Removing Sulfate and Salts from Fuel Ethanol

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Typical Treatment Volumes* and Costs*</th>
<th>Comments</th>
<th>Cost per 1,000 gal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOWEX™ 88 &amp; 66 resins Paired</td>
<td>50,000 to 200,000</td>
<td>Best choice for removal of all ions</td>
<td>&lt;1 to 2 cents per 1,000 gal</td>
</tr>
<tr>
<td>DOWEX™ 66 resin only</td>
<td>100,000 to 200,000</td>
<td>Removes only sulfate when present as an acid</td>
<td>&lt;1 cent per 1,000 gal</td>
</tr>
<tr>
<td>DOWEX™ 22 resin only</td>
<td>100,000 to 200,000</td>
<td>Removes only sulfate and other anions</td>
<td>About 1 cent per 1,000 gal</td>
</tr>
</tbody>
</table>

*Typical Treatment Volumes and costs vary greatly, based on feedwater concentrations, flow rate, end point selected for exhaustion and system configuration.
Regenerable Systems for Salt Removal
DOWEX™ ion exchange resins have proven themselves to be rugged and long lasting performers for deashing HFCS. Once the fuel ethanol is displaced, they can be regenerated with conventional acids and bases for many, many operating cycles.

DOWEX 66 resin is regenerated with 5 to 6 lbs of 4% NaOH per cf of resin. DOWEX 88 resin is regenerated with 5 to 7 lbs of 7% HCl. DOWEX 22 resin is regenerated with 6 to 7 lbs of 4% NaOH per cf of resin. See published data sheets for these products for more details.

References
See literature for these products at www.dowex.com.

1 "World Fuel Ethanol Analysis and Outlook" by Christoph Berg, April 2004