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Sulfur Removal Strategies for Biodiesel

High FFA fats, oils and grease are feedstock for ASTM 6751 biodiesel. These feedstocks contain higher levels of sulfur than traditional feedstocks. Common oil crops contain sulfur species that are water soluble and remain with the meal during oil processing. High FFA feedstocks from cooking and rendering operations contain oil soluble sulfur species that require additional processing steps to produce ASTM 6751 biodiesel that meets the 15 ppm sulfur specification. It all begins with good feedstock characterization.

Traditional Sulfur Removal Technology

Petroleum feedstock uses hydrodesulfurization or HDS technology to remove sulfur. Simply described, hydrogen is added to a Co-Mo or Ni-Mo charged catalytic column at high temperature and pressure liberating the sulfur as hydrogen sulfide, H_2S. The H_2S is converted to elemental sulfur using the classic Claus process. These systems are capital intensive, complex and require significant investment in technology, engineering and operational resources usually only found at large scale petroleum refineries.

Biodiesel Feedstock Species and Sources

Biodiesel feedstock can contain sulfur in many different species. The most prevalent are mercaptans. They can be high molecular weight complex mercaptans with aromatic ring backbones, or simple lower molecular weight species with straight chain backbones. Other more complex sulfur containing products can be found where there is significant animal protein degradation. Characterize each feedstock for sulfur and use a high/low sulfur feedstock blending strategy targeting the average sulfur feedstock levels so the process will output the 15 ppm sulfur limit.

Acid Esterification Using Sulfuric Acid

Sulfuric acid is commonly used to esterify high FFA feedstocks. The residual sulfuric acid stays with the water/glycerol stream, leaving the FAME without significant sulfur levels. If sulfur is high and free glycerin levels are high, take a look at the performance of the glycerin separation.

Additives

There are many mercaptan scavengers on the market. Traditionally they are used for sweetening natural gas but they have had success in removing some of the simple lower molecular weight sulfur species from liquid fuels. There is no additive that will remove all of the sulfur species that could be present in biodiesel feedstocks. If your feedstock characterization shows lower molecular weight mercaptans, the use of an additive may help.

Absorbents

Silica, clays, and other simple absorbents have not been very effective at removing sulfur species. Hydrogen active absorbents have had some success. These absorbents are more like catalysts and must be handled carefully to not poison the functional sites. They require moderate temperatures to activate and high temperature to regenerate. To use these catalysts, a series of columns, a heat economizer, and a regeneration system will be required.

Distillation

Vacuum distillation will separate the methyl esters from the sulfur species. The light end sulfur species, H_2S and SO_2, will flash out of the liquid phase. These will need to be absorbed or scrubbed to meet atmospheric discharge requirements. Vacuum distillation has been successful in delivering significant reduction in sulfur. In most cases, this method allows the fuel to be in spec. In high sulfur feedstock cases a combination of distillation and one of the other techniques above may be required. The trick to this approach is the distillation control as many heavy sulfur species will carry over with the fuel cut. Leaving the heavy sulfur residue behind is also effected by how well the glycerin is removed prior to the vacuum distillation. In vacuum distillation, the glycerin will carry over and will keep some heavy sulfur species in the mid fuel cut. The balance between fuel remaining in the residue phase versus the amount of heavy sulfur species in the fuel distillate must be optimized. The residue can be further distilled in a smaller second step to recover any fuel left in the bottoms.

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