

Combinational Unit Operation Strategies for Sulfur Removal

Bio feedstock derived diesel is produced by esterification, transesterification and hydrogenation reactions and sold as either biodiesel which meets the ASTM 6751 fuel specification or as green diesel which meets the petroleum feedstock derived diesel ASTM 975 fuel specification. Both specifications have a limit of no greater than 15 ppm sulfur be present in the fuel. Repurposed waste bio derived feedstocks have higher levels of sulfur than the more common and higher cost virgin bio based feedstocks.

Sulfur is present in many forms.

Large petrochemical refinery operations use hydrodesulfurization as the primary unit operation. This has been traditionally economical at a large scale. The 15 ppm sulfur limit in diesel fuel has presented even the long established refinery operations a challenge as with any separation as the permitted levels reduce, the amount of effort for further reductions increases.

Many of the unit operations in the process of converting feedstocks to fuel have equipment and conditions that can be modified to progressively remove sulfur in each of the steps. Typically the repurposed waste has additional process steps to make the material suitable for the downstream unit operations. The most useful removal steps that might be present in the current systems are the physical and chemical separations and the conversion reactions themselves. These could include filtration, centrifugation, adsorption, and distillation. In the case of green diesel production, the hydrogen reaction step not only produces the fuel components, but also reacts with the sulfur to allow it to be separated in downstream unit operations.

Sulfur Speciation

Sulfur can be present both as inorganic species and as organic species. The inorganic species can be associated with components of the feedstock that are removed with the initial gross physical separations usually associated with repurposed waste. Some of the organic species are also removed with the physical separations. Primarily the physical separations carry components that contain sulfur species that are associated with the separated component rather than reacting or separating the sulfur species themselves.

The organic sulfur can be present in many different species. Some are light end molecules that will exit with the overhead flash of various separation cuts, and some remain in the feedstock or fuel as heavy cut species.

Species present could include: thiols, sulfides, disulfides, thiophenes, benzo thiophenes, and dibenzothiophenes. The more difficult species to remove from the various process streams include the alkylated dibenzothiophenes. Most cases require a reaction and separation step and these species are usually the last removed in the sulfur mass balance to allow the fuel to meet sulfur specification limits.

Sulfur Removal Strategy

Typically sulfur can be removed from various process streams by adding unit operations such as solvent extraction, thermal decomposition, adsorption, reactive selective adsorption, acid base neutralization, and oxidation reduction.

Commonly biodiesel and green diesel systems make use of a series of reaction and separation unit operations. The order of unit operations can be arranged so that the desulfurization steps make use of the stream conditions available at various boundary limits of each unit.

The removal of sulfur species present may require more than one desulfurization step and technology installed as a series of desulfurization steps to meet the 15 ppm limit.

Use of combinational technologies have also been successful in the industry. Some examples include active filter aides, reactive adsorption and reactive intensification.

Slurry Adsorption and Filtration

Many feedstocks are preprocessed prior to reaction systems. Filtration or an oil/water/solid physical separation is most likely already present. Settling tanks, decanters, centrifuges and filters remove the various constituents detrimental to downstream operations. Filter aides, coagulants or flocculants are sometimes added if small particles or emulsified particulates are present and are difficult to remove. Adsorptive particles could be added to the filter aide mixing systems prior to the separation steps to target the removal of sulfur.

Bentonite, kaolin, montmorillonite, bleaching clays, mixtures of proprietary clays, specific and mixtures of proprietary particles, some silicas, some aluminas, some volcanic derived particles, granulated activated carbon (GAC) and powdered activated carbon (PAC) have had some success in removing a portion of the sulfur containing species in various systems. However, many applications have limited success. An interesting development with active particles is the specific effects of constituent removal based upon particle shape. Many particles clump and agglomerate in many applications and specific shape and size are important in the application. A mix tank is placed ahead of the separation step similar to many solids/liquids operations in industry. The amount of clay, active particles, GAC or PAC is dependent upon the level of sulfur and the type of sulfur species present. A good feedstock characterization and sulfur speciation is required to insure the adsorbent particles selectively remove the sulfur and do not also remove desired components or form other byproducts in the feedstock. Typically mix tanks

installed with a high shear mixing criteria to insure that the particles have sufficient surface area contact with the low concentration sulfur species. The balance here is to not disintegrate the particles due to the high shear mixing rendering the downstream separation step difficult. Porosity and the shape factor become the parameters to focus upon once the smallest size particle allowing effective separation is determined. Success in reduction from 1000 ppm to the low 100s of ppm is possible depending upon the speciation. The residence time in the mix tank with a high shear regime is on the order of 3 – 6 hours. The residence time can be reduced by an increase in temperature, but not because of a reaction kinetics effect, but most likely from the fluid dynamic and interface properties enhancement of an increase in temperature.

Selective Adsorption and Reaction

Many catalytic particles have been developed for different unit operations in refining technology whether the feedstock is bio derived or petro derived. Green diesel has an advantage as its hydrodeoxygenation reaction that converts feedstock to fuel requires hydrogen. Hydrodesulfurization reactions also require hydrogen. Hydrodesulfurization catalysts can easily be added to the reaction unit operations to remove the sulfur from the feedstock since hydrogen is available. Catalysts are usually poisoned by sulfur, so the order of the reactions and the subsequent removal effectiveness is important.

Hydrodesulfurization catalytic systems can also use oxygen sources to break the sulfur species and remove the sulfur as hydrogen sulfide or have it adsorb onto a particle in a packed bed reactor. Hydrogen peroxide is used in conjunction with a series of desulfurization catalysts. Almost all catalysts are proprietary, but the following active species can be found in literature which form the basis of the proprietary development. Many companies have been working on desulfurization catalysts as the fuel sulfur specifications were anticipated and promulgated to the levels to where they are now in effect.

Sodium hypochlorite is recognized as a good oxidizer, but the details of handling the chlorine species and the hydrogen chloride created in the reactions usually discounts its use. There are many other proprietary compounds and base chemical oxidizers being investigated for this type of application.

Selective adsorbents are active particles that have a capacity for selectively retaining certain constituents up to a certain capacity. The sulfur removal application commonly combines a reactivity with selective adsorption. An oxidizer is the commonly part of the reaction strategy. The sulfur selective adsorbents are of interest. Adsorbent performance is determined by its selectivity and its adsorption capacity. The system is usually a packed bed column with certain engineering features. Commonly a column is designed for a superficial velocity of approximately 5 gpm/ft². The pressure drop generated by the flowing liquid across the packed bed is usually no greater than 20 psig. The distribution and collection of the various influent and effluents across the packed bed is critical to performance. Channeling and dead flow zones are detrimental to the removal capacity of the column. The regeneration strategy is usually the factor that determines the economics of the system. The shape factor and the binding agents used to build the agglomerated active species is critical to the survival and effectiveness of the particle. All these factors are critical in designing as sulfur adsorption column. The basis for

many of these factors is lab and pilot scale work. The equilibrium of the system must also be determined through the careful determination of isotherms for the system.

Some adsorbent particles that have shown success in sulfur removal applications include many nickel based particles. Nickel metal on various base alumina, zeolite and silica particles have shown good capacity and selectivity for sulfur. Many other metal oxides also show good performance, but none better than the various nickel particles developed. Cerium oxide also has shown good capacity and selectivity for sulfur removal.

Reactive Intensification

The sulfur removal technology development has been adopting the techniques used in various process systems intensification technologies. Usually the practical application of these intensification technologies has been to increase the surface area of the various reacting or contacting species so as to promote greater probability of the reaction constituent interaction. The high shear mixing application of the slurry reaction and filtration method describes uses this approach. A way to avoid the disintegration of the particles is to use various liquid extraction techniques or to use the intensification techniques in a way that the particles are not disintegrated. Ultrasonic mixing and ultrasonic energy application to the various reacting systems has shown increased reactivity in some applications. Much of the energy of intensification can be added to the system in many different ways. Heating and high shear mixing also are forms of process intensification event though not usually considered as part of the emerging application of the descriptions for the technology.

Distillation and Fractionation

Biofuels production facilities include distillation and fractionation systems. If not for the fuel itself, then the recovery of reagents used to produce the fuel are flashed or distilled out of the fuel keys. In an example biodiesel system the methanol recovery system requires the FAME, methanol, glycerin produce from the esterification or transesterification reactors to be flashed so as to recover the methanol. It has been shown that a small fraction of the light sulfur species present will go overhead in this flash. The sulfur species will continue to reside in the light key of the subsequent methanol fractionation and will require scrubbing from the ultimate noncondensable gas discharge from the fractionation train. The heavier sulfur containing species remain in the fuel cut.

If the fuel is distilled, it is usually completed using a vacuum distillation method. The sulfur containing species will partition themselves in the noncondensable, the condensable overhead and the bottoms. The control of the vacuum will determine the mid cut sulfur containing species that remain in the fuel cut. Usually, most of the heavy sulfur containing constituents remain in the bottoms residue. This residue can be blended with bunker fuel as there is significant BTU value and its addition to other bunker fuel burning operations usually does not render any sulfur containing overhead from those system out of specification due the usually installed sulfur abatement systems. The specific control of the cut at the vacuum distillation is the balance between the amounts of sulfur removed versus the amount of fuel product left in the bottoms. Many proprietary techniques and control algorithms have been developed to economize this control decision. Usually, the fuel cut lowers the sulfur from the low 100s ppm to the below 30 ppm. The fuel does not yet meet the ASTM sulfur specification, but to get a 15

ppm, the amount of fuel lost in the bottoms would not be economical. Interestingly enough, even the historical hydrodesulfurization technology of the refiners from history have had to re-examine the economics of the critical control points of those processes with the new 15 ppm sulfur specification.

To reach the specification limit, an adsorption technique described above has been used as the final polishing step. The adsorption onto nickel sorbents is more effective at higher temperature, so the use of waste heat in the process, or the installation of an economizer becomes part of the needed economic evaluation.

Combinational System Unit Operations

The biodiesel example outlined above was one successful and economical method of using multiple unit operations that already were in existence to manage the sulfur in the system. These in combination with the adsorptive particle and the various physical separation techniques can progressively reduce the sulfur in the feedstock to levels that can be controlled in the conversion processes.

Desulfurization of Feedstock Without Downstream Conversion Operations

There is great bit of activity in creating “clean feedstocks” from repurposed waste for sale to the refiners without having to be combinationally locked into the downstream operation modifications. Many systems cannot tolerate sulfur in their front ends and usually the desulfurization steps are at the front end of any large refinery. To remove sulfur from feedstock would require the same combinational approach as described in the techniques above. The addition of unit operations uniquely to the feedstock only may present challenges in the heat and energy balance and economization techniques will play a significant part in the economics.