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Ultrasound-Assisted Oxidative Desulfurization

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Abstract: SulphCo's Sonocracking™ technology employs high power ultrasound to accelerate oxidative desulfurization (ODS). For ultra low sulfur applications hydrodesulfurization (HDS) suffers from high hydrogen and energy consumption since severe operating conditions have to be employed to treat the most refractory sulfur compounds. In contrast the high power ultrasound-assisted ODS proceeds under mild reaction conditions resulting in a cost and energy effective alternative to HDS. Preferential reactivity towards different sulfur species can be controlled by the selection of an appropriate catalyst/oxidant system. The low capital cost and small equipment footprint suggest a multitude of potential placement options in a refinery. An attractive deployment of the Sonocracking™ technology exploits the advantages of both HDS and ODS to deliver potentially significant operational, investment avoidance and carbon footprint savings. Similar benefits may be achieved in applications ranging from transmix diesel desulfurization to mercaptan removal to natural gasoline desulfurization.

Introduction

Regulatory specifications for acceptable levels of sulfur compounds in transportation fuels have been introduced in many regions of the world. For example, the upper limit for sulfur in gasoline in the U.S. is currently set at 30 ppm. The maximum concentration of sulfur in diesel fuel in the European Union is already limited to 10 ppm and legislation in the U.S. and Canada requires a 15 ppm limit for on-road diesel produced by large scale refiners. In mid-2010 small scale refiners will also have to comply with the 15 ppm ultra low sulfur diesel (ULSD) standard, while large scale refiners will be required to meet the 15 ppm limit for non-road diesel. According to the Environmental Protection Agency's Non-Road Diesel Fuel Standards[1] all other exceptions are set to expire by 2014. It is expected that current regulatory trends will continue resulting in ULSD as the global standard. In addition, carbon dioxide (CO_2) or carbon footprint considerations come into play via carbon cap and trade and/or carbon tax legislation in an increasing number of countries.

Hydrodesulfurization

The incumbent method of desulfurization of petroleum product streams is HDS. HDS (also referred to as hydrotreating) relies on the energy-intensive reaction of oil-based sulfur compounds with hydrogen (H_2) to form gaseous hydrogen sulfide (H_2S) and a corresponding hydrocarbon fragment. Stringent new environmental limits on sulfur content require the removal of even the most refractory sulfur compounds. In practice, HDS of these refractory species involves a step-change in hydrogen and energy consumption, due to side reactions such as the competitive aromatic saturation in both sulfur-bearing and non sulfur-bearing species. Likewise, substantial utility costs are incurred that stem from the higher reactor operating temperatures (650-750 °F) and pressures (700-1000 psi) required to hydrogenate these refractory species. Figure 1 illustrates the drastic increase of hydrogen consumption as ULSD hydrodesulfurization conditions are reached. Only about 60% of the total hydrogen is used to remove 99% of the sulfur, while the remaining 40% of hydrogen is consumed to convert the remaining 1% of sulfur. In addition, the

HDS process has a significant carbon footprint due to the high energy consumption and the extensive use of hydrogen since the production of hydrogen is energy-intensive and results in the formation of CO_2.

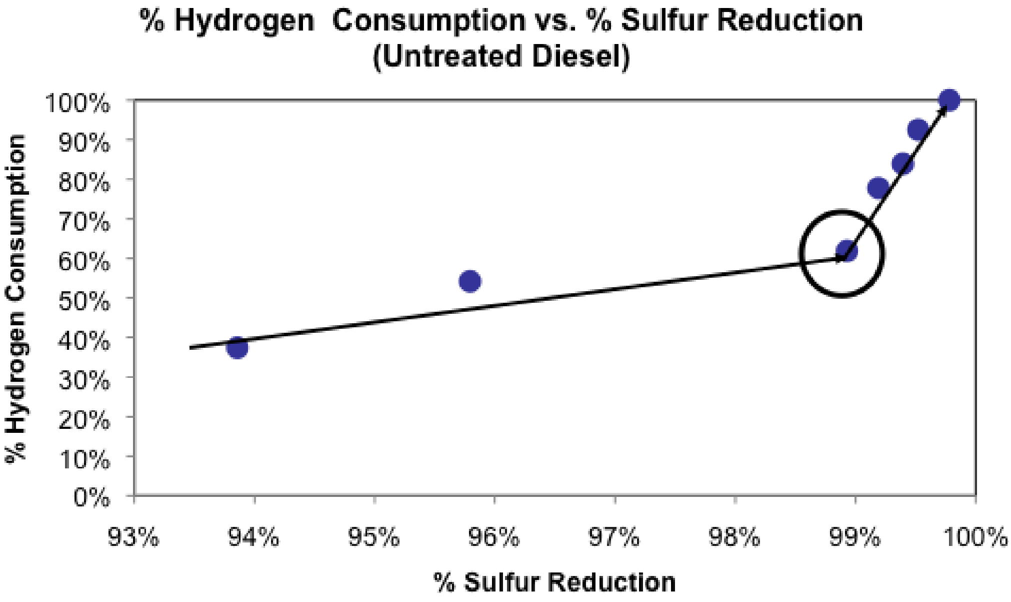

Figure 1. Hydrogen consumption as a function of sulfur removal during hydrodesulfurization. Removal of the last 1% of sulfur requires 40% of total hydrogen. Feed was a straight run diesel containing 3200 ppm sulfur. Experiments were conducted at constant pressure (700 psi) with temperature and space velocity as variables.

SulphCo's Sonocracking^{TM} Process

SulphCo's Sonocracking^{TM} technology is based on the ultrasound-assisted ODS of petroleum product based streams.[2,3] ODS encompasses the selective oxidation (Figure 2) and subsequent removal of sulfur compounds in a hydrocarbon based stream. An attractive oxidant is hydrogen peroxide (H_2O_2) as it yields water as the only byproduct.

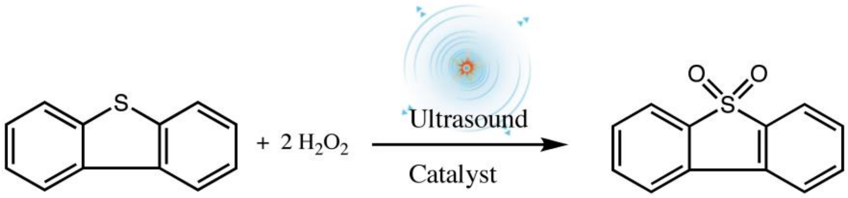

Figure 2. Ultrasound-assisted oxidative desulfurization.

In contrast to ODS reaction conditions described in the scientific and patent literature, SulphCo's Sonocracking^{TM} operating conditions allow the oxidation reaction to occur at comparably mild temperatures (ambient temperature to ~ 100 °C) and pressures (typically 20-40 psi). Despite these mild operating conditions, chemical transformation occurs at very low residence times of only 500 milliseconds or less. The key to this extraordinary reactivity under mild conditions lies in the utilization of high-power ultrasound.

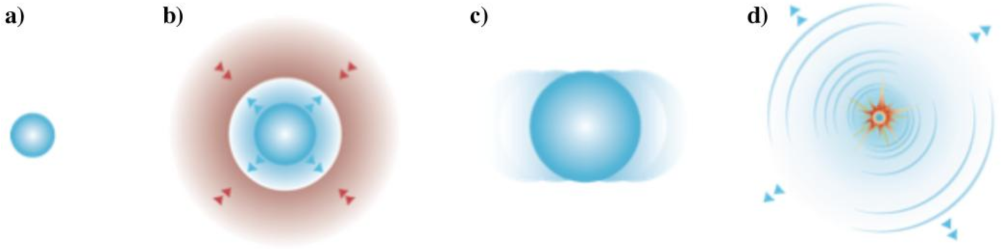

Figure 3. Ultrasound induced cavitation proceeds from the generation of a bubble (**a**) through its growth to an unstable regime (**b** and **c**) and finally to its implosion (**d**) resulting in the release of localized energy.

Ultrasound is used to induce a large, stable field of cavitation in the process fluid. Through exposure to cavitation, the ODS process is dramatically accelerated due to intense mixing of the hydrocarbon phase and an aqueous phase containing hydrogen peroxide and a suitable catalyst. The cavitation field is produced using a specially designed bar of metal, the ultrasound probe, that is pulsed in the process fluid at ultrasonic frequencies of 18-20 kHz and zero-to-peak amplitudes of 30-100 μm. As the ultrasound probe is pulsed in the process fluid, intense compression waves are formed. These waves propagate through the fluid creating regions of high fluid compression and rarefaction. When the amplitude of probe vibration is high enough, the wave rarefaction induces localized pressures that fall below the vapor pressure of the process fluid. In these areas cavities form as shown in Figure 3a. In subsequent exposure to compression waves, the bubbles oscillate and grow in size (Figure 3b and Figure 3c). At a critical bubble size, the wave compression causes the bubble to collapse and implode. During bubble implosion, the bubble wall collapses faster than its contents can diffuse into the process fluid, generating localized heat[4] and pressure both inside and immediately surrounding the collapsing bubble (Figure 3d). Collapse of cavitation bubbles results in intense mixing, high shear and mass transport between aqueous and oil phase enabling the oxidation reaction to occur at comparably mild bulk process conditions.

The resulting oxidized sulfur species – typically sulfoxides and sulfones – have significantly increased boiling points and polarity compared to their parent sulfidic species enabling the use of alternative sulfur removal techniques such as absorption, extraction, distillation and in the case of water soluble oxidized sulfur species a simple water wash.

Reaction Control

Different petroleum product streams exhibit different sulfur speciation profiles. It is therefore important to understand the reactivity of various sulfur compound families with H_2O_2 as a function of the catalyst system employed. A wide range of catalysts including polyoxometalates,[5-7] titanosilicates[8] and organic acids[9] have been employed in the ODS reaction. Surprisingly few papers have investigated relative rates of reaction of typical classes of sulfur compounds with H_2O_2 in the presence of such catalysts.[9,10] It was shown that within a class of sulfur compounds, relative rates of reaction depend on the amount and nature of the substitution pattern (e.g. unsubstituted, mono-alkylated, etc.).

In order to ultimately control the reactivity in the ultrasound-assisted ODS process, relative rates of reaction of three different catalyst/oxidant systems were investigated (Table 1). System A consists of a sterically undemanding Catalyst A and sterically undemanding H_2O_2 as oxidant. System B is based on a sterically demanding Catalyst B, with sterically undemanding H_2O_2. Finally, System C has a sterically demanding Catalyst C, as well as a sterically demanding oxidant, *t*-butyl hydroperoxide (*t*-BuO_2H).[11] ULSD diesel was spiked with a series of thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) derivatives (Figure 4) at 25 ppm S each. Thiophenes are not present in the diesel boiling point range, but we were interested in the relative reactivities between these three classes of sulfur compounds.

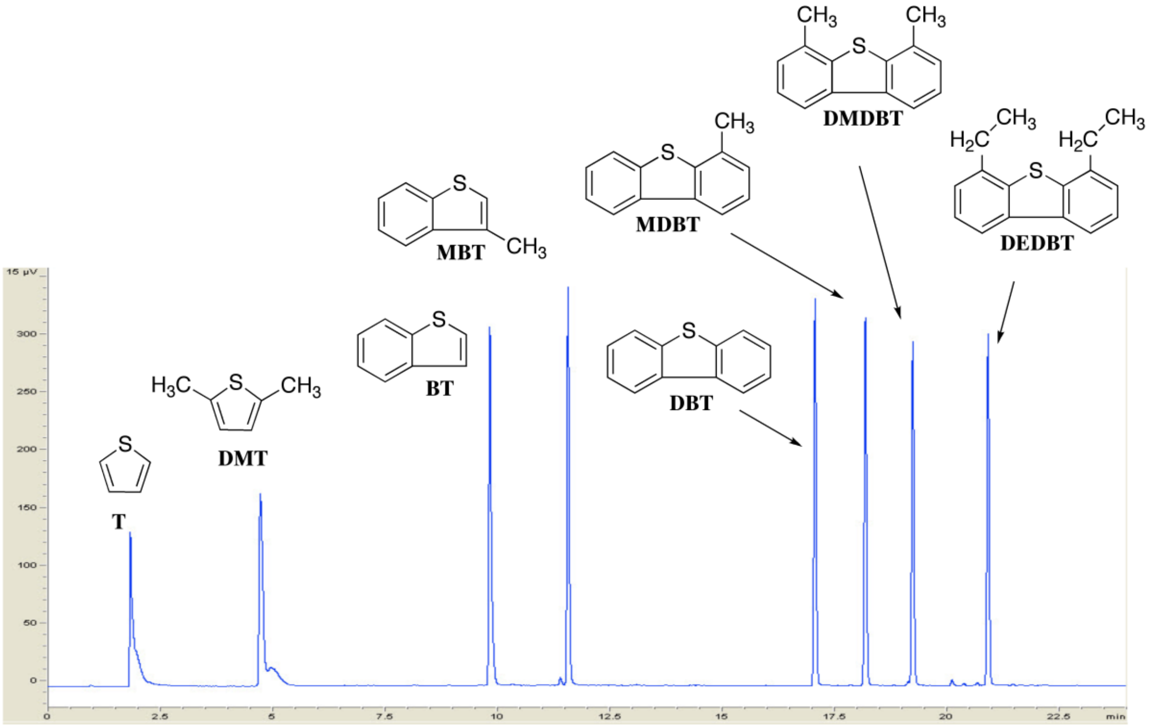

Figure 4. Sulfur speciation of model diesel using a gas chromatograph with a sulfur specific chemiluminescence detector (GC-SCD).

System	Catalyst	Oxidant	Total BTs	BT	MBT	Total DBTs	DBT	MDBT, DMDBT, DEDBT
A	Catalyst A	H_2O_2	33	26	41	85	64	92
B	Catalyst B	H_2O_2	46	46	47	45	58	40
C	Catalyst C	*t*-BuOOH	94	89	98	77	100	69

Table 1. Relative reactivities (in %; 100% = total conversion) of different BT and DBT derivatives in the ultrasound-assisted ODS using three distinctly different catalyst/oxidant combinations. System A shows higher reactivity towards substituted BTs and DBTs, while system C shows bias towards the parent BT and DBT**.**

Figure 5 shows the chromatographic region where peaks due to DBT derivatives elute after reaction of the model diesel with each of the three catalyst/oxidant pairs and subsequent sulfur removal of the oxidized sulfur species. The remaining species are due to DBTs that have not oxidized under the employed conditions. All reactions were run with sufficient catalyst/oxidant to get substantial, but not complete sulfur conversion in order to investigate, which sulfur compounds are oxidized preferentially by a given system. A smaller peak indicates a higher degree of conversion.

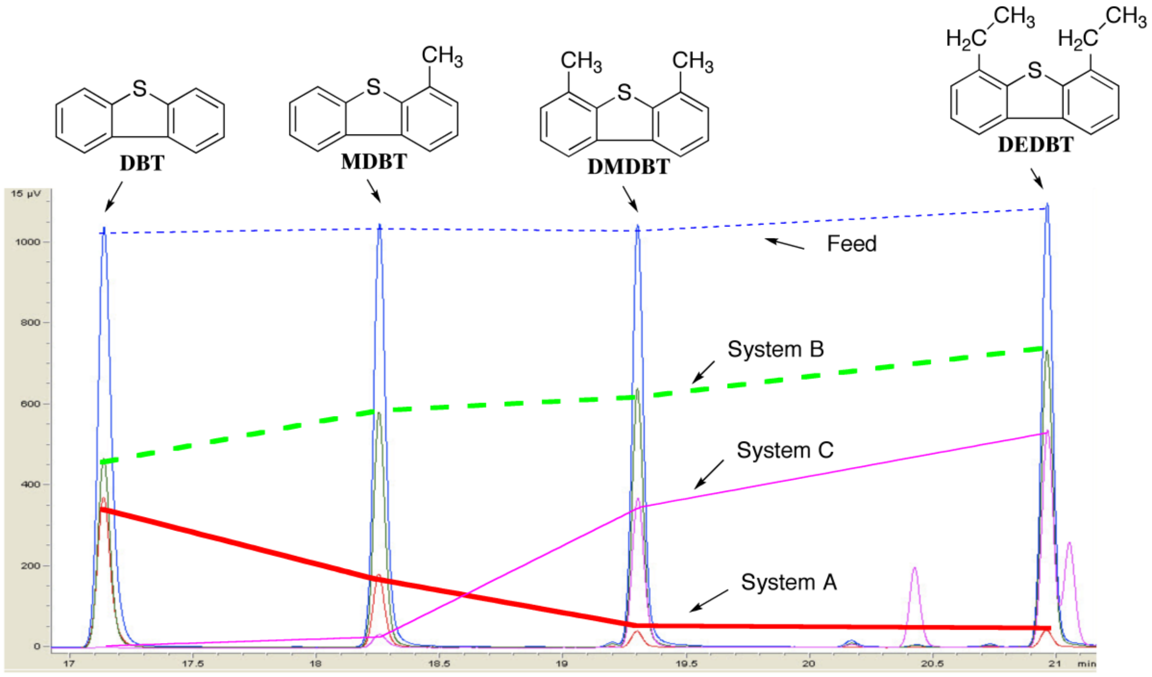

Figure 5. GC trace of the DBT region after the ultrasound-assisted ODS using System A (**red**), System B (**green**) and System C (**magenta**). Lines indicating peaks associated with a given catalyst/oxidant system are added for easier visual reference. The additional smaller peaks (**magenta**) are due to sulfones/sulfoxides that were removed less efficiently when System C was employed.

Although all three catalyst/oxidant systems did not react well with T and DMT, they show markedly different reactivity in the ultrasound-assisted ODS of BTs and DBTs (Table 1). The results can best be explained by taking a closer look at steric versus electronic control during the oxidation reaction. In general, a higher electron density at the sulfur atom results in higher reactivity towards oxidation reactions. When examining the relative rate of reaction for catalyst/oxidant system A, a lower rate of reaction is found for BT and DBT compared to the alkyl substituted derivatives. Since alkyl substituents add electron density to the thiophene based molecules, higher reactivity is expected for alkyl substituted BTs and DBTs versus the unsubstituted analogs. Since the catalyst and the oxidant in System A are small molecules, there are no spatial constraints to substantially affect this electronic preference. The other extreme, System C, consists of a sterically much more demanding catalyst and oxidant. All the electronic arguments still apply, but now the reactants run into spatial constraints during the oxidation step. The more spatial constraints, the lower the reactivity. In the sterically more crowded DBTs case, steric control dominates and reactivity towards the less substituted sulfur compounds is preferred even if the electronic driving force is lower. This trend is reversed in the case of BTs since they are small enough that electronic control starts to dominate. For catalyst system B with a large catalyst, but small oxidant, steric and electronic control offset each other and the result is significantly reduced selectivity.

The fact that different catalyst/oxidant systems exhibit different types of selectivity in the oxidation of petroleum based sulfur compounds has implications for the applicability of the Sonocracking^{TM} process. The selection of the catalyst and the oxidant allows preferential reactivity towards different types of sulfur species contained in petroleum product streams.

Basic Process Flow

A basic process block flow block diagram of SulphCo's Sonocracking^{TM} process is shown in Figure 6. This process distinguishes itself by its relative simplicity and flexibility. There are two primary steps in the Sonocracking^{TM} process – the conversion of the sulfur compounds of the hydrocarbon stream to their oxidized analogs in a continuous process and the subsequent removal of the oxidized sulfur species from the hydrocarbon stream.

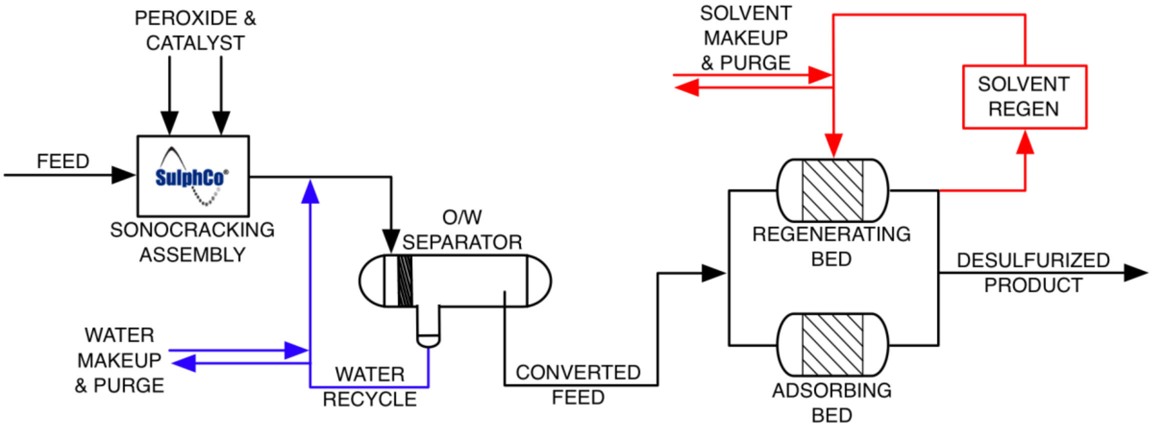

Figure 6. Basic process block flow diagram for SulphCo's Sonocracking^{TM} process. In a mercaptan removal application, the adsorption and solvent regeneration process steps may not be required.

In the first step of the process – the ultrasound-assisted oxidation of sulfur compounds – a 35 wt% H_2O_2 solution and the catalyst are separately injected into the petroleum product feed stream. The combined stream is passed through a static mixer located before the ultrasonic reactor in order to ensure sufficient premix of the hydrocarbon and the aqueous phase. The combined stream enters the reaction chamber and is forced through the ultrasound-induced cavitation zone. In this cavitation zone, oxidation reactions occur at low residence times under comparably mild reaction conditions.

After exiting the ultrasound reactor, the reaction mixture is allowed to phase separate in an oil/water separator. The reacted petroleum product stream is passed through an adsorption bed to remove the oxidized sulfur species due to their increased polarity. The adsorption bed can be regenerated using a desorption solvent such as methanol or ethanol. The desorption solvent can then be regenerated by several means that depend on the scale and the scope of the application. In some applications such as the removal of mercaptans, the oxidized sulfur species become water soluble and a simple water wash efficiently removes the oxidized sulfur species rendering the adsorbent scheme unnecessary.

Applications, Process Economics & Benefits

SulphCo's ultrasound-assisted ODS technology is economically applicable to a range of applications such as diesel finishing, transmix desulfurization, mercaptan removal and natural gasoline desulfurization. Some of the most promising applications in regards to benefits and economics are discussed below.

Diesel Finishing. When paired with SulphCo's Sonocracking^{TM} technology, the previously discussed excessive energy and hydrogen consumptions of HDS can be avoided since the HDS unit can be operated under less severe operating conditions. As shown before, a significant amount of hydrogen is consumed in the hydrotreating process to remove the most refractory sulfur compounds to meet ULSD specifications. These compounds almost exclusively belong to one class of sulfur compounds, alkyl-substituted DBTs. In contrast to the HDS process, these DBTs have shown high reactivity towards the ODS process. In that sense, ODS represents a complementary technology to HDS. Figure 7 shows the nearly quantitative oxidation and desulfurization of a low sulfur diesel (500 ppm sulfur content) to ULSD (5 ppm) using ultrasound-assisted ODS.

Primary benefits in this application are significant hydrogen consumption savings and milder operating conditions of the HDS unit. These benefits also translate to a lower carbon footprint, an important issue for customers in the European Union and a growing concern in the U.S. For refineries that face investment in a new HDS unit or have to upgrade from a low-pressure to a high-pressure hydrotreater in order to produce USLD, SulphCo's Sonocracking^{TM} process may be an attractive alternative due to its comparatively low capital investment cost. Estimates of net benefits range between $0.60-1.00/barrel depending on many factors such as stream volumes and qualities, availability of hydrogen and location. Main contributors to the operational costs are chemical consumables, utilities, replacement ultrasound probes and maintenance.

Transmix. For transmix and similar smaller volume operators HDS capacity is typically not accessible and a new investment in a HDS unit is cost prohibitive. Estimated net benefits are generally higher and range from $1-3/barrel depending on location, stream qualities and volumes, tax structure etc. Reduction in sulfur content to less than 10 ppm has been routinely achieved for a variety of transmix diesel streams using the Sonocracking^{TM} process.

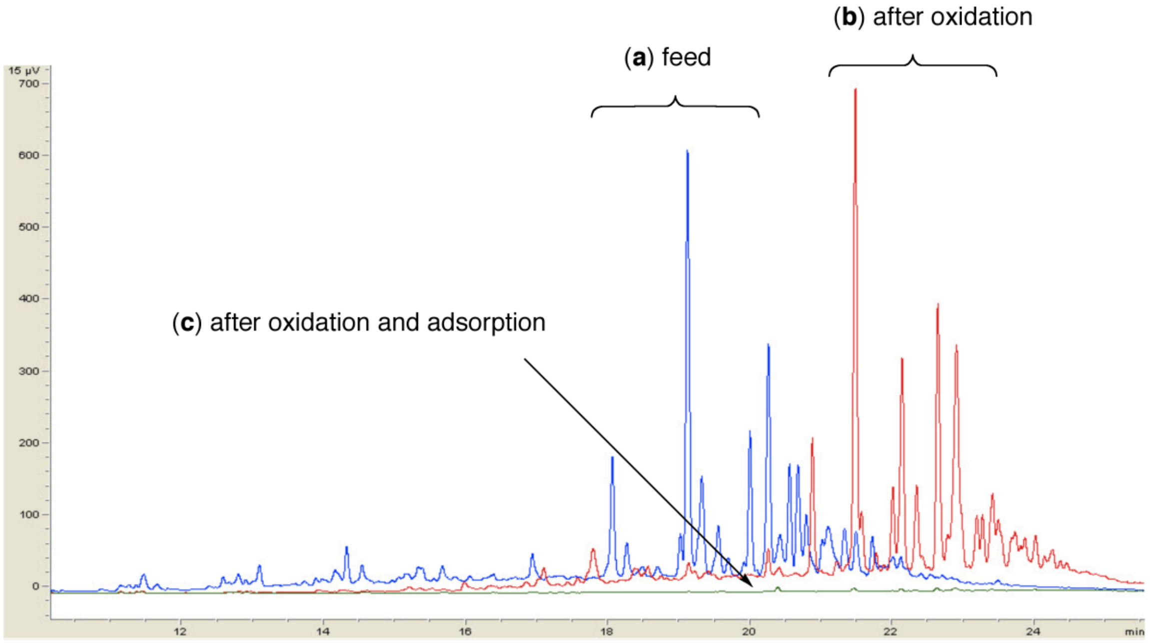

Figure 7. Sulfur speciation of (**a**) a low sulfur diesel (500 ppm sulfur content), (**b**) after oxidation using catalyst/oxidant system A and (**c**) after subsequent adsorption. The desulfurized sample contains 5 ppm sulfur representing a 99% reduction in sulfur content.

Mercaptan Removal. SulphCo's Sonocracking^{TM} process represents an attractive option to remove undesired mercaptans from a hydrocarbon stream. A fundamental advantage of ultrasound-assisted ODS technology over existing options is the ability to tune the chemistry. Depending on the amount of oxidant available, different degrees of oxidation can be achieved in the presence of an appropriate catalyst. Efficient oxidation of mercaptans can be achieved with disulfides as the primary product (Figure 8a), when substoichiometric amounts of H_2O_2 are employed. The use of ultrasound allows the process to proceed at very low residence times. There is typically no effect on total sulfur content as the resulting disulfides are still part of the hydrocarbon stream.

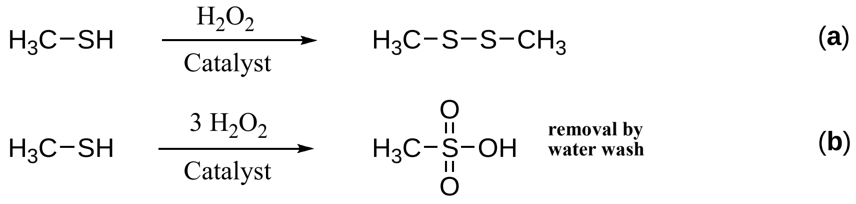

Figure 8. Reaction pathways for mercaptans with hydrogen peroxide depending on the amount of H_2O_2 added.

In contrast, by using an excess of H_2O_2 further oxidation to the respective sulfonic acids can easily achieved (Figure 8b). Especially in the case of low molecular mercaptans the respective sulfonic acids are highly water soluble and are easily removed during the water wash. The result is effective mercaptan removal combined with reduction of total sulfur. By controlling H_2O_2 feed rates in conjunction with the appropriate catalyst choice, this catalyst/oxidant system is tunable and provides considerable flexibility to deal with streams that are off specification in regard to mercaptan and total sulfur level. It is important to point out that mercaptan removal does not require a secondary sulfur removal step such as adsorption, a fundamental advantage. A simple water wash is sufficient. Capital and operational costs for mercaptan removal depend on the sulfur content of the feed. The capital cost compares favorably to existing mercaptan reduction technologies due to the reaction enhancing properties of high power ultrasound and since the adsorption step is not required. Operational costs are stream specific, but are competitive with competing sweetening technologies with the added flexibility to reduce total sulfur.

Other Applications. SulphCo's Sonocracking™ process can be employed in a series of other applications, most notably natural gasoline and natural condensate desulfurization. Almost quantitative oxidation and removal of sulfur species has been achieved in a variety of natural gasoline and condensate streams. The Sonocracking™ process can easily be adapted to stream specific needs and may represent an attractive desulfurization option in regard to capital and operational costs.

Summary

SulphCo's ODS based Sonocracking™ process represents a viable alternative to HDS as a means to remove sulfur from petroleum product streams. The process distinguishes itself through relative simplicity, efficiency and broad applicability. A closer look at the chemistry behind both technologies reveal complementary characteristics of the ODS and HDS technologies. Significant benefits may be realized in applications ranging from diesel finishing and transmix diesel desulfurization to mercaptan removal to the desulfurization of natural gasoline. Benefits may include substantial operational, material and carbon footprint savings and the opportunity to avoid or defer large-scale capital investments.

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