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Production of Ultra-Low Sulfur Fuels by Selective Hydroperoxide Oxidation

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Abstract

The majority of technology available today for the production of ultra-low sulfur fuels relies on the use of hydrogen and high pressure, and therefore uses capital-intensive equipment.

Oxidative desulfurization offers a lower capital alternative to hydrodesulfurization (HDS). Several other oxidative desulfurization technologies have been introduced based on hydrogen peroxide and require the recycle of an organic acid co-oxidant. Lyondell Chemical Company's oxidative desulfurization (ODS) process uses a hydroperoxide oxidant, eliminating the need to recycle the co-oxidant acid. The company has demonstrated this process in a small continuous pilot unit for several refinery streams, with our focus being predominately on diesel fuel. This process has the capability to produce a clear, colorless diesel with less than 10 ppm of sulfur. Progress has also been made on extending this technology to treat heavy pyrolysis gasoline and FCC gasoline.

Introduction

Over the last two decades, regulations in developed countries have driven the sulfur levels in fuels to lower and lower levels. As the drive to even lower sulfur fuels continues in the developed countries and spreads to developing countries, alternatives to hydrodesulfurization are needed. The vast majority of the commercially available desulfurization options involve hydrotreating, putting an ever increasing strain on the available hydrogen supply. The production of ultra-low sulfur fuels, less than 10 ppm, by hydrodesulfurization, both conventional and the newer selective processes, requires high temperature, high pressure equipment, representing a significantly higher capital expenditure than that required to produce low sulfur, 500 ppm, fuel.

The non-hydrogen consuming desulfurization processes can be grouped into three categories; biodesulfurization, separation, and oxidative desulfurization. While progress continues to be made on biodesulfurization, the technology is not advanced to the stage for it to contribute to meeting the current regulations taking effect before the end of the decade in the U.S. and Europe. The physical separation processes of adsorption and solvent extraction, while potentially offering a lower capital cost that hydrodesulfurization, suffer from inefficiencies due to the very limited polarity difference between the sulfur containing compounds and the remainder of the fuel.

Of the alternatives to hydroprocessing, oxidative desulfurization has advanced to the state were it is nearing commercialization. Oxidative desulfurization functions by altering the polarity of the sulfur species. Through the increased polarity of the oxidized of the sulfur species, separation of the sulfur containing species by conventional means becomes feasible.

Why Oxidative Desulfurization

Oxidative desulfurization offers clear advantages over both conventional and selective hydrodesulfurization technologies. Firstly, the refractory compounds, predominantly, 4, 6-disubstituted dibenzothiophenes, which require severe conditions, high temperatures and pressures, to hydrotreat can be oxidized under mild temperatures and pressures. Secondly, the process does not require hydrogen, supply of which is becoming more limited with the changes in refinery operation required to reduce the aromatics in gasoline. With the exception of those refineries located on a hydrogen pipeline, increased hydrogen demand may require a refinery to add a hydrogen plant.

Since oxidative desulfurization does not require hydrogen and the capital costs scale down favorably compared to the alternatives, it is well suited for use in the small and medium size refinery, especially those that are isolated and not located on a hydrogen pipeline. Oxidative desulfurization is typically conducted at temperatures and pressures far lower than those required for deep hydrodesulfurization, thus the capital required to install an oxidative desulfurization unit is significantly less than that required for deep hydrodesulfurization.

Oxidative desulfurization is best suited as a finishing process for taking today's low sulfur fuels, less than 500 ppm, to ultra-low sulfur fuels. The scale and scope of equipment required for using oxidative desulfurization as a finishing step make it well suited for modularization.

Technology Overview

Oxidative desulfurization is not new. It was reported in the literature as early as 1954.[1] However, before the current regulations requiring the production of ultra-low sulfur fuels the benefits of this technology were unable to be realized. The introduction of regulations requiring ultra-low sulfur fuel brought a renewed interest in oxidative desulfurization. At least two companies are promoting technology using peracids to oxidize the sulfur.[2] A third technology uses ultrasound to drive the oxidation.[3] All of these technologies including the Lyondell process convert the sulfur compounds to sulfones as shown in Figure 1 for dimethyl dibenzylthiophene. The conversion of the sulfur species to sulfones requires two equivalents of oxidant, hydrogen peroxide in the peracid technologies or t-butyl hydroperoxide in the Lyondell technology.

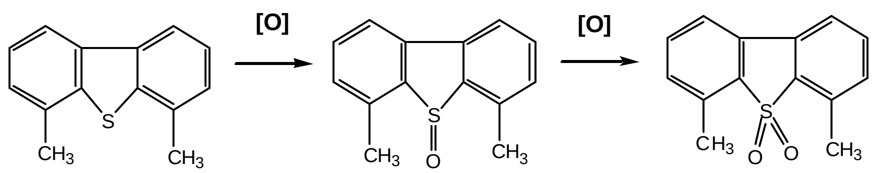

Figure 1

The oxidation is only the first step in the desulfurization process. The sulfones need to be removed from the fuel. This separation process is facilitated by the differential polarity of the sulfones. Capitalizing on the increase polarity, the sulfones can be removed either by solvent extract or by adsorption.

The Lyondell oxidative desulfurization technology uses the organic peroxide t-butyl hydroperoxide, TBHP, as the oxidant. Unlike hydrogen peroxide, TBHP is completely fuel soluble, making it well suited for oxidative desulfurization. Lyondell first demonstrated the use of TBHP for oxidative desulfurization in the early 1970's.[4] TBHP, the highest volume organic peroxide, is produced worldwide. Unlike some of the alternative technologies using hydrogen peroxide, the use of TBHP avoids the need to recycle corrosive organic acid catalysts. The fuel and TBHP are co-feed over a fixed bed catalyst, at mild temperatures and pressures, less than 200 ^{o}F and less than 100 psig. Minimal pressure is required to keep TBHP/fuel mixture in a liquid state and to maintain the hydraulic pressure required to move the fuel stream over the fixed bed catalyst. Lyondell's proprietary catalyst, while not currently used in any commercial process, has been produced on a commercial-scale by a major catalyst vendor. The oxidation takes place in less than 10 minutes with near quantitative conversion of the thiophenes to sulfones. t-Butyl alcohol, which is easily removed from the fuel during post processing, is produced as a coproduct from the oxidation.

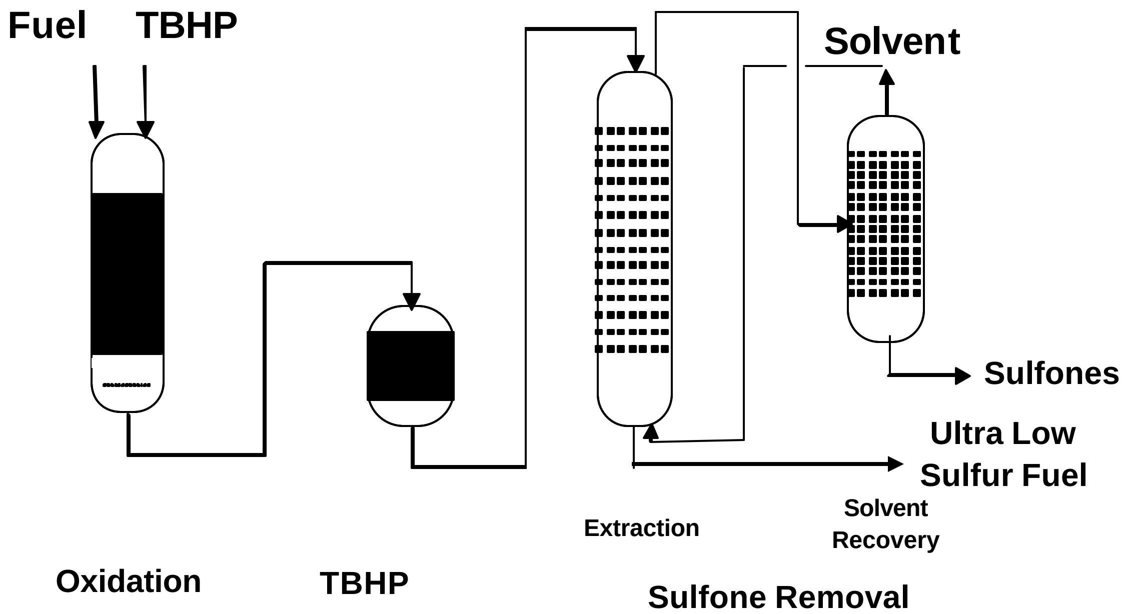

Figure 2

In the second step of the process any unreacted TBHP is decomposed. Hydroperoxides, such as TBHP, are known to decrease the storage stability of fuels. [5] Therefore, it is crucial to maintaining good fuel stability that all unreacted TBHP be either completely decomposed or removed from the fuel. Technology for TBHP decomposition is commercially practiced today by Lyondell Chemical Company. While shown in Figure 2 as a separate reactor, the decomposition will likely be effected in a separate zone in the oxidation reactor.

The removal of the sulfones from the fuel can be affected either through solvent extraction or adsorption. Lyondell has demonstrated both alternatives. For the purposes of this paper, the focus will be on the solvent extraction process. The fuel is extracted using low cost readily available solvent system.

The extraction solvent is recovered by distillation and reused. The solvent is taken overhead and the sulfones are concentrated as a heavy stream. For a typical 30,000 BPD unit processing diesel fuel with a sulfur level of 350 - 500 ppm, this sulfone stream will amount to approximately 50 - 100 BPD. Several options exist for disposition of this low volume sulfone stream, including processing in the coker or sending for bioprocessing. The t-butyl alcohol that is produced as a co-product of the oxidation along with that which serves as a diluent for the TBHP is recovered . (TBHP is diluted with t-butyl alcohol for increased safety during shipment and handling.) For a typical 30,000 BPD unit processing diesel fuel with a sulfur level of 500 ppm, the t-butyl alcohol stream will amount to approximately 150 BPD. Several options for using the t-butyl alcohol exist within the refinery. Depending on the size of this stream and the refinery needs, the t-butyl alcohol can be converted to MTBE or isooctane, or used as fuel within the refinery. Lyondell's Alkylate 100 process consumes t-butyl alcohol in the production of isooctane. In the past, t-butyl alcohol has been added to gasoline to boost octane.

Diesel Desulfurization – Cost and Product Fuel Quality

While Lyondell has been developing oxidation desulfurization for both gasoline and diesel, the focus has been on diesel. With the requirements to produce ultra-low sulfur gasoline rapidly approaching and with most refiners having already selected desulfurization technology, Lyondell has chosen to focus its efforts on diesel desulfurization.

As stated previously, oxidative desulfurization is best suited as a "finishing" process for taking today's low sulfur fuels to ultra-low sulfur fuels. Therefore, Lyondell's efforts have been focus on converting diesel fuel with 350 – 500 ppm of sulfur to ultra-low sulfur fuel with less than 10 ppm of sulfur.

Lyondell has achieved over 3000 hours of continuous operation in a laboratory-scale continuous pilot unit, with near quantitative oxidation of the sulfur to sulfones. Either solvent extraction or adsorption of the oxidized fuel stream produces a fuel with less than 10 ppm of sulfur. Typical sulfur reductions are shown in Figure 3 for two different diesel fuels. Over this period a limited amount of deactivation of the catalyst has been observed. Based on the results obtained thus far in this work and on prior experience with the catalyst, the catalyst life is estimated to be in excess of one year.

The oxidation process results in a darkening of the fuel. While the fuel directly exiting the oxidation reactor has darkened, as shown in Figure 4, the final product is nearly colorless after removal of the sulfones and other polar species.

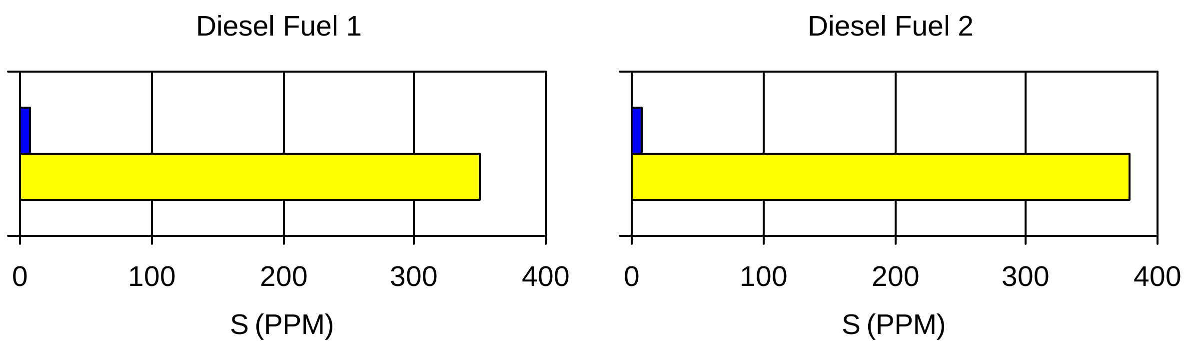

Figure 3

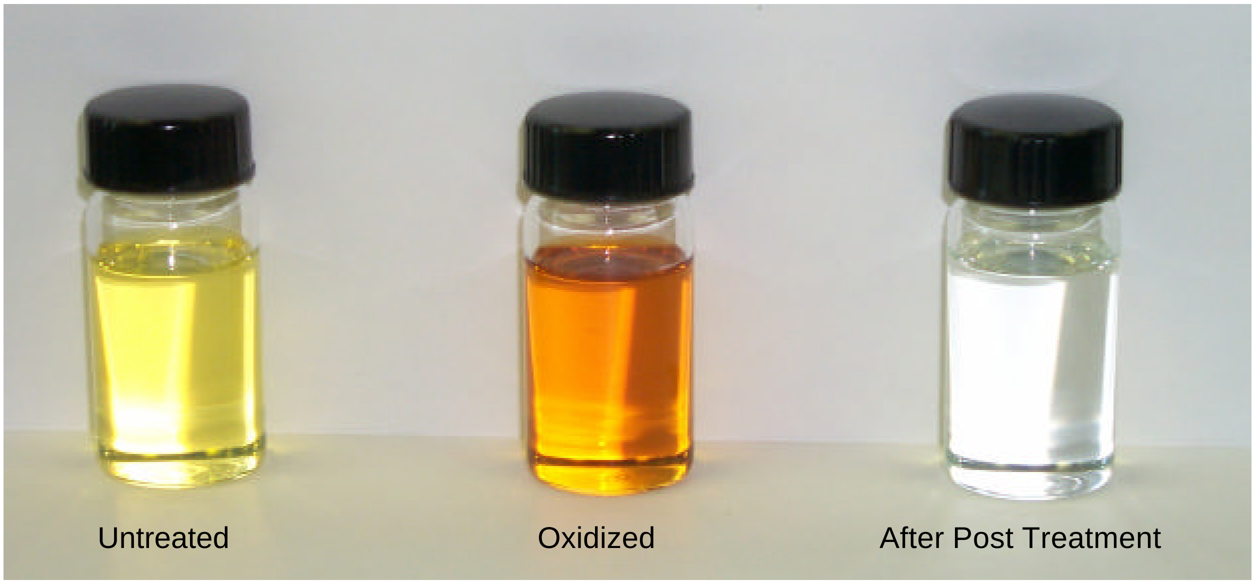

Figure 4

A key requirement of any desulfurization process is that the ultra-low sulfur fuel produced is fungible with the rest of the ultra-low sulfur fuel pool. As shown in Table 1, the Lyondell oxidative desulfurization process has no measurable effect on the oxidative stability, Ramsbottom carbon, ash and viscosity of the fuel when compared with the low sulfur diesel fuel as received. The oxidative stability results confirm that no hydroperoxide remains in the fuel. The decrease in the APHA color is consistent with the removal of the polar species, as previously discussed.

The one to two number increase in cetane number as shown in Table 1 has been confirmed over multiple samples and fuels. This increase, while small, is a valuable secondary benefit. There are several possible effects that could explain this increase, which are under investigation.

The effects of the oxidative desulfurization process on other important fuel properties, including lubricity, cold flow, cloud point, and corrosion are in the process of being determined. We expect that any change in these properties will be no worse that what occurs during hydrodesulfurization. One could expect the cloud point and the cold flow properties to be improved over what is obtained from deep hydrodesulfurization, since in oxidative desulfurization aromatic saturation does not occur.

Test	Diesel (As Received)	Sample 1	Sample 2	ASTM Specifications
Oxidative Stability (D2274 / mg/100 ml)	0.7	0.1	1.1	<1.5
Ramsbottom Carbon (10% Residue, D524)	0.11%	0.08%	0.06%	<0.15%
ASH (D482)	<0.001%	0.002%	N/M	<0.01%
Cetane Number (D613)	48	1 – 2 No. Increase	1 – 2 No. Increase	>40
Viscosity (Kinematic @ 40 C)	2.51 CSt	2.88 CSt	N/M	1.9 to 4.1 CSt
APHA Color	841	366	78	--

Table 1

The Lyondell process has the clear advantages of being conducted at mild temperatures and pressures and does not require the use of special materials of construction. With the exception of equipment used in the solvent extraction to remove the sulfones from the fuel, the major pieces of equipment can be constructed from carbon steel. Should extraction be used to remove the sulfones, it is anticipated that stainless steel may be required for that section of the unit. As a result of the mild process conditions, the capital cost required to install the process in reduced. We estimate that the capital expenditure required for this implement this process is $600 - $750 per BPD of capacity. This estimate assumes that the unit is constructed on a cleared site and includes all ISBL and project specific OSBL, such as TBHP feed tanks. Due to the mild temperature and pressure required for this process it is likely that a refinery would have idle equipment that could be converted to oxidative desulfurization service, further reducing the capital cost.

Based on our current estimates, we expect that the cash operating cost for a unit taking today's low sulfur diesel fuel to ultra-low sulfur diesel with less than 10 ppm of sulfur to be less than 2.5¢ per gallon. Included in this estimate is the cost of the t-butyl hydroperoxide oxidant, all utilities, labor, and taxes and insurance. In this estimate the by-product t-butyl alcohol is valued at its BTU value, assuming that it is used as fuel within the refinery. Utilization of the by-product t-butyl alcohol in a higher value application, such as in the production of isooctane or MTBE, will reduce the net cash cost. One option is to use the t-butyl alcohol in an Alkylate 100 unit to produce isooctane. The choice of either solvent extraction or adsorption will affect the final cost. Our current efforts are focused on cost optimization of the two possible sulfone removal processes.

Gasoline Desulfurization

While lower olefin composition of diesel fuel is better suited for oxidative desulfurization, ultra-low sulfur gasoline can also be prepared using oxidative desulfurization. We have demonstrated the ability to take a 260 ppm sulfur heavy pyrolysis gas stream to less than 10 ppm in a batch laboratory process. Scoping experiments to evaluate the oxidative desulfurization of FCC gasoline have indicated the potential to develop a process to produce ultra-low sulfur gasoline. Due to the nature of the sulfur species present in gasoline, the oxidative desulfurization process developed for diesel using t-explore investigate process and catalyst modifications for the oxidative desulfurization of gasoline. However, with the regulations requiring the production of 30 ppm gasoline rapidly approaching, our efforts will remain focused on diesel fuel.

Future Development

Over the coming months, efforts to optimize the oxidation process conditions will continue. The continuous laboratory pilot oxidation unit, which has been in operation with the current catalyst for over five months, will continue to be operated to demonstrate the expected catalyst life of over one year.

As discussed previously, two sulfone removal technologies have been demonstrated, solvent extraction, described in this paper, and adsorption. Over the next several months, both technologies will be optimized and the option that offers the best cost profile will be select for further development and commercialization. Once this selection is made, the sulfone removal process will be integrated with the continuous oxidation unit.

As the efforts to optimize the process continue, we have begun to design a demonstration unit with a capacity of 100 to $1,000^+$ BPD. We plan to begin operation of the demonstration unit in late 2003 or early 2004. Options are also being investigated to move directly to a small commercial unit. We expect to make the technology available for license in the second half of 2003.

Summary

Oxidative desulfurization offers a non-hydrogen consuming, lower capital alternative to hydrodesulfurization. Lyondell Chemical Company has demonstrated a cost effective oxidative desulfurization process, based on t-butyl hydroperoxide. The process is conducted under mild temperatures and pressures, significantly reducing the capital as compared to hydrodesulfurization options. The nature the process makes it well suited to be used as a finishing process to take today's low sulfur fuels to ultra-low sulfur fuels. The process has been in continuous operation for over 5 months, producing diesel with less than 10 ppm of sulfur. Plans are underway to demonstrate the process on a semi-commercial scale by late 2003 or early 2004.

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