

# The ULSD oxidative desulfurisation option

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Several novel oxidative desulfurisation (ODS) processes have been developed in the past 10 years. At the same time new regulations have been mandated for ultra low sulfur diesel (ULSD) motor fuel in the EU, Japan and the USA, demanding 10 - 15 wppm S by 2006 - 2010. However, a review of ULSD projects completed and under construction worldwide shows that, in spite of the early promise by ODS to produce ULSD without using hydrogen, at lower conversion cost and lower capital investment than required for hydrodesulfurisation (HDS), no ODS projects have been built. In hindsight the explanation may be simple, but there are reasons to believe that ODS will be able to compete directly with HDS, while also supplementing HDS operations. Common acronyms used in the industry are listed in (Table 1).



**Table 1. Acronyms and nomenclature**

BPD	Barrel per day
BT	Benzo-thiophene
DBT	Di-benzo-thiophene
FCC	Fluid cat cracking
Gas oil	Petroleum fraction in the boiling range 235 - 370 °C at 1 ata
GHG	Greenhouse gas emissions
LSD	Low sulfur diesel fuel, 500 wppm S maximum
HC	Hydrocarbon material
HCO	Heavy cycle oil from FCC and coking
HCHP	Hydrocarbon hydroperoxide
HC-O	Oxygen containing hydrocarbons
HC-S	Sulfur containing hydrocarbon
HDS	Catalytic hydrotreating of gas oil for desulfurisation
Hydrotreating	Catalytic process exchanging sulfur for hydrogen
LCO	Light cycle oil from FCC and coking operations
ODS	Oxidative desulfurisation
S	Sulfur contained in various petroleum compounds
ULSD	Ultra low sulfur diesel, below 10 wppm S (EU) and 15 wppm (US)

There are indeed several reasons why ODS has not become commercially successful during the past few years. First, ODS process development was driven by expectations of new low sulfur fuel standards not fully defined regarding sulfur limits and the timeline until 2002. During the same period, hydrotreating catalyst activity improved dramatically and ULSD processing cost declined significantly. Second, the untested new ODS technology had to overcome the experience and demonstrated cost profile of HDS, with insufficient time to do so before deadlines for refinery projects passed. Third, due to inadequate resources supporting ODS process development its merits by and large went untested. There are reasons to believe that this could change as a result of the dramatic increase in the cost of crude oil, hydrogen and plant construction during the past few years. Where some amount of incremental hydrogen capacity could be obtained in the past by process optimisation, recovery from refinery fuel gas and HDS improvements, any future hydrogen demands from ULSD production will require new syngas and hydrogen plant capacity, as well as HDS and Claus sulfur unit capacity expansion.

## ODS market drivers

Oxidative desulfurisation (ODS) can be an attractive alternative to hydrodesulfurisation (HDS) for refinery operations where the cost of hydrogen is prohibitive. ODS processing differs from HDS in several important ways. Firstly, it does not require hydrogen, but instead uses an oxidant such as aqueous hydrogen peroxide. Secondly, in the ODS process the hydrocarbon fraction containing the sulfur compounds is extracted from the feedstock, instead of converting to hydrogen sulfide as in HDS processing. Thirdly, ODS processing operates at near atmospheric pressure and relatively mild temperatures as compared with HDS, and as a result the capital cost for ODS is substantially lower. The market drivers for ODS include regulations demanding near sulfur free motor fuels worldwide, the escalating cost of hydrogen supply for hydrotreating sulfur removal, and increasing capital cost of HDS. Other ODS advantages

relative to HDS include the avoidance of catalyst cost, plant turnaround downtime and GHG emissions.

## ULSD requirements

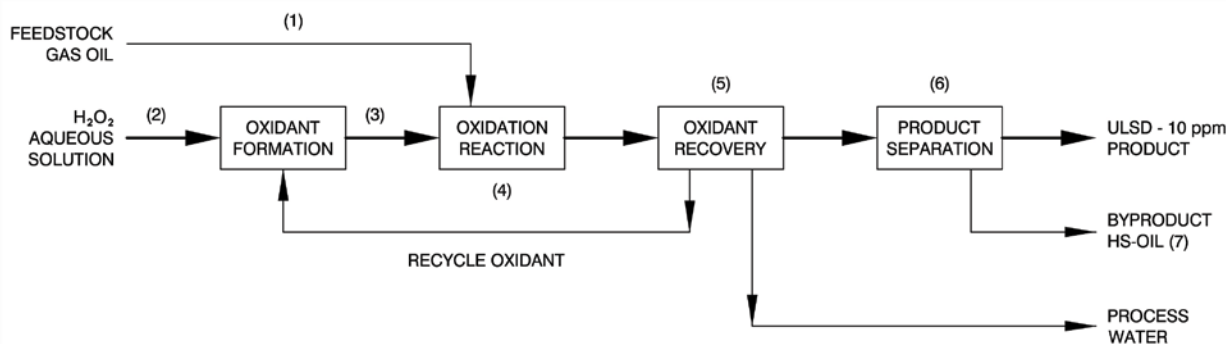
ULSD with less than 15 ppm sulfur has been implemented during the past several years in Europe, Japan and the USA. Most of the rest of the world is expected to adopt similar ULSD regulations during the next 15 years. The production of ULSD was shown to be economically feasible at the turn of this century with the development and demonstration of improved HDS processes, reactor designs and high activity catalysts. Today most major petroleum refineries have implemented HDS processing with expanded hydrogen production and sulfur conversion plants to match. The high sulfur fuel streams that are still left untreated will require desulfurisation during the next phase of refinery development, as will product streams that result from incremental refinery expansion. For these purposes ODS represents an alternative to HDS processing.

## Gas oil sulfur compounds

Refinery distillates boiling higher than the naphtha fraction (gasoline) include the gas oil fractions (diesel fuel product) containing considerable amounts of sulfur compounds. These are predominantly benzo-thiophene (BT) compounds, i.e., a benzene molecule attached to a five member ring containing four carbons and one sulfur atom, and their alkylated derivatives with broad range of molecular weights (134 - 368 Dalton) and boiling points (200 - 350 °C; 390 - 660 °F). These BT compounds are notoriously difficult to hydrogenate to remove the sulfur compared with the sulfides, disulfides and mercaptan compounds found in the lighter naphtha fraction. The family of BT compounds include dibenzo-thiophene (DBT), naphthothiophenes and their mono, di and tri-methyl alkylated derivatives with a broad range of molecular weights and boiling points. The boiling point range of the BT and DBT compounds therefore coincides with gas oil and diesel fuel, and therefore they accumulate in the gas oil and diesel fuel fraction and cannot be separated from the hydrocarbons by distillation. Until recently this has meant that the BT and DBT families of compounds were allowed to remain in the diesel fuel product, in most cases representing 350 - 550 wppm sulfur. Based on the availability of better catalytic HDS processing technology in the late 1990s, the current much stricter ULSD fuel specifications became technically viable just a few years before the enactment of the US regulations last year.

## ODS process history

ODS process development dates back to patents from before 1932 with many well known companies active during the 1960s and 1970s including Shell Oil, Gulf Oil, ESSO, BP and Texaco. In the past 20 years alone more than a dozen companies have been engaged in ODS process technology development issuing more than 30 process patents (Table 2). However, as of 2006 none are in commercial operation.



1. FEEDSTOCK GAS OIL, 50 - 5,000 WPPM SULFUR
2. PRIMARY OXIDANT: HYDROGEN PEROXIDE 50 w % AQUEOUS SOLUTION
3. SECONDARY OXIDANT FORMED FROM ORGANIC ACID AND H<sub>2</sub>O<sub>2</sub>
4. OXIDANT REACTION AT AMBIENT PRESSURE AND 50°-90° C
5. OXIDANT RECOVERY BY SOLVENT EXTRACTION
6. PRODUCT RECOVERY BY SOLVENT EXTRACTION, DISTILLATION, ABSORPTION
7. BYPRODUCT HIGH-SULFUR OIL, 4-8 w % SULFUR

Figure 1. ODS process schematic (typical example): ULSD, 10 ppm S.

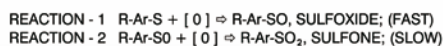
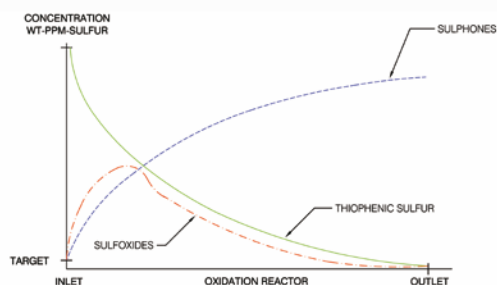


Figure 2. ODS oxidation reaction concentrations. Schematic example: qualitative.

## Process description

ODS processes follow a general process schematic including, as the first step, an oxidation reaction where the BT, DBT and other sulfur containing compounds are converted selectively to the corresponding sulfoxides (R-Ar-SO) and sulfones (R-Ar-SO<sub>2</sub>). At the end of the reaction, the oxidised compounds are predominately sulfones due to the higher reactivity of sulfoxides. Compared with the original thiophenic sulfur compounds, the sulfones are much easier to separate with extraction and adsorption from the hydrocarbons. In the second process step the sulfones are removed, usually with solvent extraction and/or adsorption that separate the polar sulfone compounds from non-polar hydrocarbons. The relative completeness of both the oxidation and separation processes together determines the residual ULSD sulfur content. Recovery of recycle solvent from the ULSD and sulfone products is accomplished with distillation in the third and fourth process steps, in some cases also requiring separation of the solvent from the water of reaction.

ODS process flow sheets are similar for the most part although they may differ significantly in the details. The most frequently used oxidant is hydrogen peroxide in aqueous solution combined with phase transfer agents and catalysts such as formic or acetic acid that convert

reversibly to the corresponding per acid. Other oxidants and phase transfer agents have been evaluated during the past 20 years (Table 2), but the combination of hydrogen peroxide and acetic acid appears to be the least costly and most successful reagent.

The oxidation is followed by several separation process steps that may employ a combination of extraction, adsorption and distillation processes. Several solvents or solvent combinations already well known from aromatics extraction can be used for the separation of alkylated BT and DBT sulfone derivatives from the ULSD. These can be used alone or in combination with solid adsorbents to remove any residual sulfur compounds (Figure 1).

## Conversion challenges

A major process design challenge for ODS is to force the sulfur oxidation reaction to near completion in order not to allow any substantial amount of thiophenic sulfur to slip by, while at the same time keeping the amount of reactant to a minimum. For example, an ODS process designed for ULSD with maximum 5 wppm S and 1200 wppm S feed will require 99.6% sulfur reduction. Assuming that the residual sulfur in the ULSD product is split evenly between non-oxidised thiophenes and unextracted sulfones, then each process step must perform at 99.8% effectiveness. Similarly, an Alaska North Slope 4000 wppm S light atmospheric gas-oil will require 99.94% removal in each process step to achieve 5 wppm S. ODS can in fact achieve these exacting conversion goals. Other major design challenges for the process design include reduction of costly reactants, e.g., hydrogen peroxide, optimisation of solvent recovery and energy efficiency, and low capital cost.

## Oxidation selectivity

The selectivity of the oxidation towards sulfur compounds is also an important consideration in ODS processes due to the cost of oxidant and concern for byproduct formation. It is preferred that all sulfur and nitrogen containing compounds are oxidised, but it is also necessary

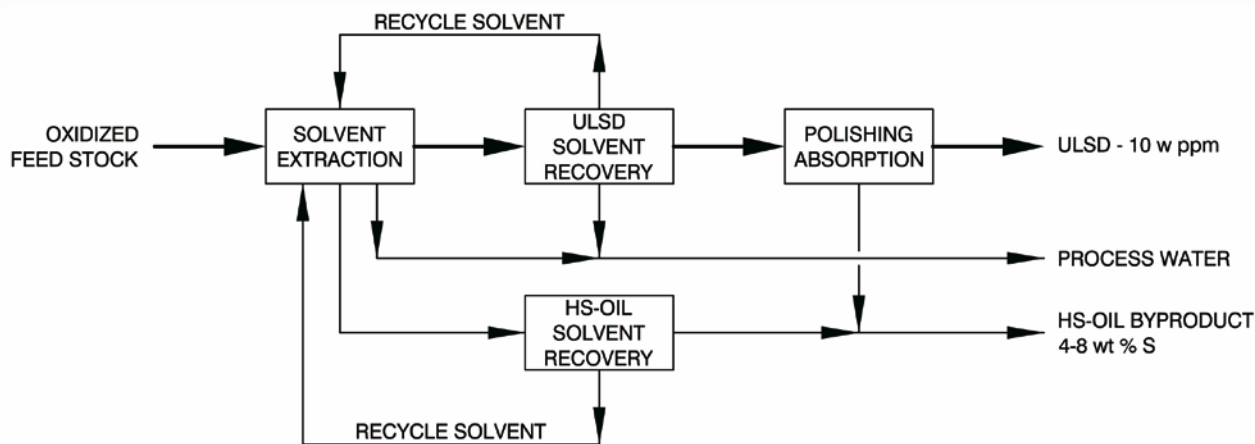


Figure 3. ODS Separation process. Schematic, typical example.

to avoid oxidation of olefins and alkylated aromatic compounds that convert to undesirable compounds such as hydroperoxides, aldehydes, ketones, epoxides and alcohols. These HC-O compounds are relatively polar and therefore will be extracted together with the HC-S material, thereby decreasing the ULSD yield. For this reason ODS processes are not well suited to feedstock rich in olefins such as LCO and HCOs, and the oxidant and operating conditions must be carefully selected to avoid non-selective oxidation of hydrocarbons.

### Byproducts

HDS processing essentially removes the sulfur atoms from the hydrocarbon molecules, producing hydrogen sulfide that is then converted to elemental sulfur in the Claus plant. The ODS processes instead convert the HC-S compounds to HC sulfones and then remove a byproduct mixture containing sulfones and hydrocarbons. The byproduct yield is directly proportional to the concentration of sulfur in the feedstock and inversely with the selectivity of the chosen separation process. Between various proposed ODS solvents and adsorbents there is a wide range of selectivity and the range of HC to sulfone varies from 0.5 - 5 or more. For example, with an average weight ratio of 7.5 HC-S to sulfur that is typical for the BT and DBT mixtures in many gas-oils, and extraction selectivity of 2.5 HC/HC-S, the resulting sulfone byproduct yield is 3.75 wt% for a 2000 wppm S feedstock. Correspondingly, for a 300 wppm S feedstock the byproduct yield will be less than 0.6 wt%. In both cases the concentration of sulfur in the byproduct would be 3.8 wt%. The disposition of the sulfone byproduct in the refinery will depend to a large extent on the capacity of the individual process units; however, possible choices include, from the most to the least desirable, to use it as feedstock for hydrocracking, HDS, FCC, coking or Claus unit cogeneration.

Table 2. Recent ODS process development (companies engaged in ODS process development during the past 20 years; none are in commercial operation)

Company	Country	Oxidant*	Patents
BP Corp., Amoco	USA	H <sub>2</sub> O <sub>2</sub>	2
DS2Tech., Inc.	USA	H <sub>2</sub> O <sub>2</sub>	1
Carnegie-Mellon Univ.	USA	H <sub>2</sub> O <sub>2</sub>	2
Exxon Corp.	USA	H <sub>2</sub> O <sub>2</sub>	1
Gulf Oil Corp. R&D	USA	HNO <sub>3</sub>	1
Lyondell Chem. Comp.	USA	TBHP	2
Oxochem Techn. Inc.	USA	H <sub>2</sub> O <sub>2</sub>	3
Petrobras	Brazil	H <sub>2</sub> O <sub>2</sub>	2
PetroStar Inc.	USA	H <sub>2</sub> O <sub>2</sub>	3
UOP	USA	HCHP	4
Stanciulescu	USA	H <sub>2</sub> O <sub>2</sub>	1
SulphCo	USA	H <sub>2</sub> O <sub>2</sub>	3
TotalFinaElf Corp.	France	H <sub>2</sub> O <sub>2</sub>	2
UniPureEnergy Corp.	USA	H <sub>2</sub> O <sub>2</sub>	4

\* Oxidant: hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), t-butyl hydroperoxide (TBHP), hydrocarbon-hydroperoxide (HCHP)

Table 3. Comparison between ODS and HDS for ULSD

Criteria	ODS processing	HDS, hydrotreating
Feedstock application	Gas oils and HDS product	Gas oil, LCO, HCO
Feedstock sulfur	Cost effective <4500 ppm-S	500 - 9000 ppm-S
Product	ULSD <10 ppm sulfur	ULSD <10 ppm sulfur
Byproduct, yield	High sulfur oil, 1 - 5 wt%	Elemental sulfur, 0.1 - 0.9 wt%
Hydrogen	None required	Hydrogen 450 - 550 ft <sup>3</sup> /bbl
Peroxide, 50 wt%-HP*	5 x sulfur wt%	None required
Operation temperature	Near ambient	280 - 350 °C
Operating pressure	Near ambient	45 - 80 ata
Ancillary units required	None	Syngas and H <sub>2</sub> plant, Claus sulfur plant
Total capital cost (US\$/bpd)	1000 - 1500	2500 - 3500
Feedstock olefin content	Oxidant consumption	Hydrogen consumption
Product volume yield	Reduced due to byproduct. Increased by hydrogenation	

\* Hydrogen peroxide (HP) 50 w% soln.; or others incl., HC-hydroperoxide, tBHP, oxygen

Process	ODS	HDS
Conversion cost*	US\$/bbl	US\$/bbl
Hydrogen peroxide(100 w%), US\$ 1.10/kg	1.75**	-
Hydrogen, US\$ 0.27/Nm <sup>3</sup> (US\$ 7.50/1000 ft <sup>3</sup> , 450 ft <sup>3</sup> /bbl)	-	3.37†
Catalyst cost (purchase and regeneration)	0.05	0.17
Utilities and other operating and maintenance costs	1.65	0.55
Total operating and maintenance conversion cost	3.45	4.09
Capital and related charges	0.65	1.35†
Unrealised benefit due to unit downtime	-	0.15
Total estimated cost	4.10	5.59

\* Examples based on 3500 ppm-S feed, 10 ppm-S ULSD 20 000 bpd capacity. Capital cost based on generic data include assumed cost of hydrogen unit and sulfur processing

\*\* Proportional to feed-sulfur content.

† These costs probably will be higher in most cases

ODS application	Advantages
HDS feed pretreatment	Removes refractory S compounds. Increases HDS capacity. Reduce hydrogen requirement.
HDS post treatment	Extends effective catalyst life. Allows higher throughput, m <sup>3</sup> /m <sup>3</sup> .s. Capacity expansion of HDS unit. Reduce hydrogen requirement. Reduce HDS and refinery downtime.
Parallel with HDS	LSD processing to ULSD. Unloads HDS unit. Lower space velocity for high S feed. Reduce hydrogen requirement.
Substituting HDS	Avoid hydrogen supply. Avoid Claus sulfur plant. Reduce refinery downtime.
Transmix cleanup	Recovery of ULSD from pipeline mixtures.

## Process comparison

It seems useful to compare ODS with HDS processing for ULSD based on design studies and test data extracted from key patents or presented at conferences during the past several years (Table 3). Comparisons between the individual ODS processes is more difficult because relatively little commercial reference data is available, and also because the processes seem to differ considerably from one another with respect to choice of solvents and separation process designs.

## Cost comparison


A true cost comparison between ODS and HDS processing would require a definition of how hydrogen and Claus sulfur plant capital costs are accounted for, and in the future perhaps also considerations for cost associated with carbon dioxide emissions. A simplified evaluation, based on data from various sources and cost estimates reflecting first quarter 2007 levels, suggests that ODS may be competitive in refineries where there is a deficiency of hydrogen supply, but also in direct competition with HDS (Table 4). The key conversion cost differences appear to be between hydrogen and hydrogen peroxide, utility costs and capital charges. Each of these cost parameters would

therefore warrant more critical examination on a refinery project and process specific basis. However, based on this examination it appears that ODS may indeed be competitive with HDS as the ODS/HDS cost ratios fall in the range of 0.3 - 0.6 for capital cost and 0.7 - 0.9 for operating cost.

## ODS applicability

ULSD production based on ODS would seem to become attractive for refineries without access to low cost hydrogen supply for HDS. These would include larger refiners that have exhausted the available hydrogen supply and therefore must confront building of new hydrogen capacity, as well as small refiners in the EU, Japan and USA that still have not provided for ULSD processing. This also would apply worldwide where ULSD regulations may still have several years to be implemented. However, the applicability of ODS is not limited to direct substitution of HDS (Table 5). ODS is well suited to process low sulfur gas oil feeds that may need to be reduced only from 500 wppm S to 10 wppm, including HDS catalyst life extension and post treatment of LSD effluent from HDS units. It can also help expand the effective refinery capacity by enabling higher HDS throughput while still maintaining ULSD specifications. Operating ODS in parallel with HDS would also be useful where the HDS unit could be unloaded and thereby provide longer residence time for more difficult to treat feedstock.

## Conclusion

ODS appears to be technically and economically viable for processing ULSD from gas oil feedstock up to 4500 wppm S. It can be considered in conjunction with or as substitute for HDS processing. Notably, ODS does not require hydrogen for desulfurisation, but instead converts the sulfur compounds to sulfones that are then extracted from the ULSD. A high sulfur byproduct stream results with yields in the range 1 - 6% based on the feed sulfur content and process design. Prospectively, capital cost and operating cost with ODS would be significantly lower than with HDS. A number of ODS processes have been developed during the past 10 years, but none are in commercial operation at this time. Therefore ODS is a developmental process technology and still has to overcome the hurdles of industrial scale-up and commercialisation. 

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