

Oxidative Desulfurization in ULSD strategies

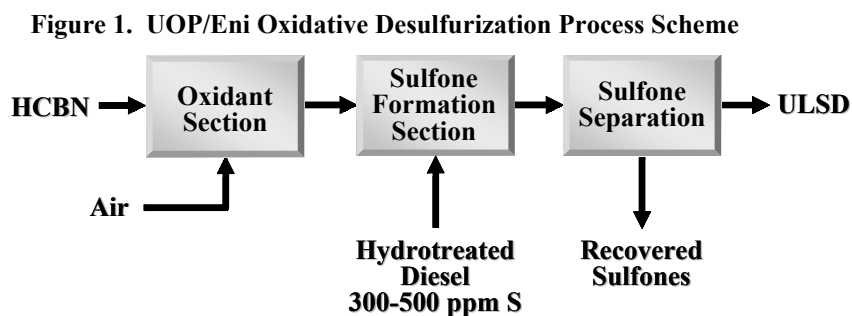
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Fuels regulations continue to tighten worldwide in response to the need for cleaner air. Refiners will meet the Ultra-Low Sulfur Diesel (ULSD) regulations at a significant cost. In most cases, either a new high pressure hydrotreating unit or a major revamp of low/moderate pressure hydrotreating unit is required. In this scenario, alternative desulfurization routes become attractive. Eni S.p.A and UOP LLC have jointly developed a new oxidative desulfurization process as a cost effective solution for ULSD production.

The key feature of the oxidative desulfurization process is the complementary chemistry to hydrodesulfurization. In fact, the most refractory compounds to hydrodesulfurize are the dibenzothiophenes which, on the contrary, show the highest oxidation rate in the oxidative desulfurization. Oxidative desulfurization is a good fit as a finishing process downstream of an existing hydrodesulfurization unit (HDS) producing 300-500 wppm S.

There are several oxidative desulfurization technologies available. A general process consists of three sections: a peroxide supply section, a sulfone generation section and a sulfone separation section. The first section comprises all the peroxide storage and handling facilities. In the second stage the hydrotreated diesel is mixed with the oxidant and the mixture contacted with an oxidation catalyst active for oxidation of sulfur compounds. The oxidation reaction causes physical-chemical properties of the sulfur compounds to significantly change. Taking advantage of this change, it is simple in the final step of the process to separate oxidation products from the diesel stream by using either solvent extraction or adsorption.

In the traditional route a purchased hydroperoxide is used as a source of oxygen for sulfur oxidation. The high cost of either H₂O₂ or organic hydroperoxide make economics comparison with traditional hydrodesulfurization process unfavorable. ENI S.p.A. and UOP LLC have developed a new oxidative desulfurization process in which the hydroperoxide is produced in-situ to reduce ULSD production costs. The process scheme for the UOP/ENI Oxidative Desulfurization Process is shown in Figure 1. In this process, the first step is an oxidation reactor in which a suitable hydrocarbon refinery stream (HCBN) is mixed with atmospheric air to produce hydroperoxide.



The hydroperoxide rich stream is mixed with hydrotreated diesel to prepare the feed stream for the sulfur oxidation section. In the second stage, a proprietary oxidation catalyst oxidizes sulfur compounds at low pressure (P<8 bar) and low temperature (T<180°C). In the third section, all oxidized compounds are separated from the diesel stream producing ULSD. Either oxidized products separation by solvent extraction or by ad-

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sorption are effective. However, extraction is more expensive from both the capital and the operating cost point of view.

Separation of all oxidized compounds results in a diesel yield loss. Hence, the "upgrade" of this oxidized hydrocarbon stream affects the process economics. This stream can be blended into the heating oil pool or treated in either a coking or hydrocracking unit to recover valuable products.

The advantages of the oxidative desulfurization process can be summarized as follows:

- does not use hydrogen to produce ULSD
- mild operating conditions
- complementary chemistry to hydrodesulfurization
- use conventional reaction and separation refinery equipments
- flexibility to process cracked feedstocks