Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 116 (2006) 446–460
www.elsevier.com/locate/cattod

On novel processes for removing sulphur from refinery streams

Eri Ito, J.A. Rob van Veen *

Shell Research & Technology Centre, P.O. Box 38000, 1030 BN Amsterdam, The Netherlands

Abstract

This review discusses some of the processes that have been, or are being, developed as an alternative/addition to present-day hydrodesulphurization processes that are based on (selective) heterogeneous catalysis. The technologies applied in these alternatives range from reactive adsorption, oxidative routes (especially for diesel) and other chemical conversion methods, to ‘‘simple’’ physical separation methods (non-destructive adsorption, extraction, *etc.*). It is concluded that it appears that for the time being, as long as sulphur levels of 10 ppmw or slightly below are aimed at, the classical hydrotreating options and their off shoots still hold the field of transportation-fuel desulphurization, although a few of the possible alternatives do have achieved commercial status in the gasoline area. If, on the other hand, S in product levels should be as low as <1 ppmw, then polishing processes will come into their own.

Keywords: Review; Desulphurization; HDS; Hydrodesulphurization; Reactive adsorption; Non-destructive adsorption; Oxidative desulphurization; Membrane; Extraction; FCC gasoline; Diesel; N adsorption; Ionic liquid; Precipitation; Biodesulphurization; Ultrasonic wave; Microwave; X-ray; Sodium desulphurization

1. Introduction

Recent developments in environmental legislation are inexorably moving us to a world of zero-sulphur, *i.e.*, in this respect spectroscopically pure, transportation fuels. For the time being, ‘‘zero-sulphur’’ means <10 ppmw S, but it is not excluded that the upper limit will in time come down even further. It is also to be noted that 10 ppmw is not *de rigueur* everywhere yet, but this is certainly only a question of time.

In the wake of this legislation, especially in the case of gasoline desulphurization, quite a number of novel process options have been created, or revived, both catalytic and non-catalytic ones, some of which have indeed been successfully commercialized. The subject has been ably reviewed by Babich and Moulijn [1], Song and Ma [2,3] and – for gasoline only – Brunet et al. [4]. Since after the first flurry of novelty creation things have quieted down to a certain extent, we will not go over the field *in extenso* again, but try and limit ourselves to a brief overview of ongoing developments.

Even a cursory glance at the list of ideas that have been canvassed to address the zero-sulphur issues will show that most of them have not (yet?) been implemented, *i.e.*, not progressed beyond the pilot-plant stage, if indeed they did reach that stage. This is of course to be expected in this Darwinian world. Indeed, for a given design to be commercialized, it needs to meet quite a stringent set of criteria, some of the more important of which include:

- Capital cost: *e.g.*, the less unit operations (less pieces of equipment) the better, no expensive materials; preferably a single product stream for diesel.
- Operation cost: *e.g.*, minimize the consumption of hydrogen or expensive chemicals, minimize the generation of waste streams (esp. dilute ones).
- Product volume should be high, *e.g.*, >99%.
- Process cycle life should be reasonably long, *e.g.*, four plus years in general, and five plus years for FCC gasoline post treatment units in order to match the FCC cycle length.
- Technical complexity should be avoided as much as possible: *e.g.*, no difficult to operate units (minimizing down time), no difficult catalyst(s) (tolerant of upsets).
- Feed flexibility.
- Overall value to refiner.

To be a possible winner, a particular process design needs to look good on all counts, and this one can easily imagine not being a trivial matter.

---

* Corresponding author. Tel.: +31 20 6303148; fax: +31 20 6303964.
E-mail address: rob.vanveen@shell.com (J.A.R. van Veen).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.06.040

The next two sections will summarize the developments in the areas of gasoline, and diesel desulphurization, respectively, where the emphasis will be on the non-catalytic routes, after which some concluding remarks will be made.

2. Gasoline desulphlurization

Of all the streams that go into the mogas (motor gasoline) pool, it is the fluid catalytic cracking (FCC) derived naphtha, which is by far the highest contributor to its sulphur content. This stream is characterized by a high olefin content, which makes it very suitable for a gasoline product with a high octane number. In the absence of severe sulphur specifications, the stream can therefore usually be directly blended into the mogas pool, after sweetening, in contrast to hydrocracker or straight-run naphtha streams, which should be reformed first to boost the octane number to an appropriate range.

When, however, the sulphur content of the FCC gasoline streams has to be reduced to an extremely low level like 10 ppmw, the challenge is to do this while retaining the octane (RON/MON) number. Selective desulphurization to meet 50 ppmw specification is already quite a challenge, let alone meeting 10 ppmw sulphur specification. In terms of the obvious process choice here, *viz.* hydrodesulphurization (HDS), the challenge takes the form of converting almost all of the sulphur-bearing molecules present while leaving the olefins untouched, *i.e.*, achieving a high hydrogenation of sulphur over hydrogenation of olefin ratio—although one is helped a bit by the fact that the boiling fraction containing the most S is least abundant in olefins and vice versa (Fig. 1). The HDS process faces an additional challenge, *viz.* to prevent the formation of recombination sulphur compounds. Recombination of H_2S and olefin can occur in the downstream part of the gasoline HDS process:

$$R{=} + H_2S \rightarrow R{-}SH$$

This would lead to an increase of mercaptan species in the gasoline product. For realizing the stringent sulphur content like 10 ppmw in gasoline product, a proper management of this recombination mercaptan is essential [4].

One could, in principle, avoid these selectivity issues by applying deep HDS, including the hydrogenation of olefins, and restore octane through reforming. And in fact, this option is being applied in quite some units, especially in Europe (debottlenecking rather new units). But it provides only a solution for the heart-cut gasoline (~85–160 °C). The light- and heavy gasoline cannot be processed in a reformer. Besides, reforming catalysts are extremely sulphur sensitive and the product is relatively high in aromatics content.

Alternatives to reforming have been considered, and some processes based on cracking/isomerization to restore octane have been commercialized (*e.g.*, ExxonMobil's OctGain [5] and UOP's Isal). Inevitably, however, some yield loss occurs, while also the hydrogen consumption is relatively high, and this process option has not been popular.

What has happened is that, to date, the ULS gasoline challenge has mostly been met by implementing selective processes, such as CD TECH's CDHydro/CD HDS [6], Axens' Prime G+ [7] and ExxonMobil's Scanfining [8]. Many units based on these technologies have already been built/licensed, with CDTECH leading in the high sulphur application market.

It is also important to recognize that the very light portion of FCC gasoline can be desulphurized through non-destructive means, such as thioetherification of the light mercaptans, *e.g.*, CDHydro, or, perhaps slightly less efficiently, oxidation of mercaptans to disulphides, *e.g.*, extractive Merox [4], to preserve all of the olefins therein, hence retain its octane value.

It remains the case, however, that the selective catalysis processes entail some, however, slight, loss of octane at high S conversions, and this has served as a motivation for the continued search of alternative processes.

2.1. Reactive adsorption

One idea has been to remove sulphur species by reactive adsorption. The chemistry involved is illustrated in Fig. 2 [1,9]. Adsorbents are usually comprized of transition metals supported on base oxides. Ni on ZnO is the prototypical formulation most often found in literature and patents. As shown in Fig. 2, Ni functions as hydrodesulphurization sites, while ZnO has the crucial role of taking up the resulting H_2S, converting into ZnS in the process. After completion of the ZnO → ZnS conversion, the adsorbent can either be discarded, or regenerated. ConocoPhillips's S-Zorb process is the first real commercial process of importance based on reactive adsorption [10]. The process is schematically illustrated in Fig. 3.

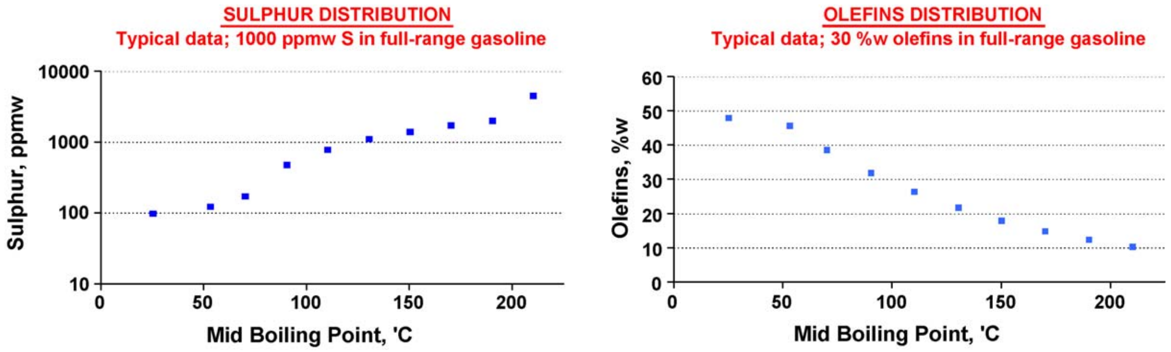


Fig. 1. Sulphur and olefin distribution in gasoline in general.

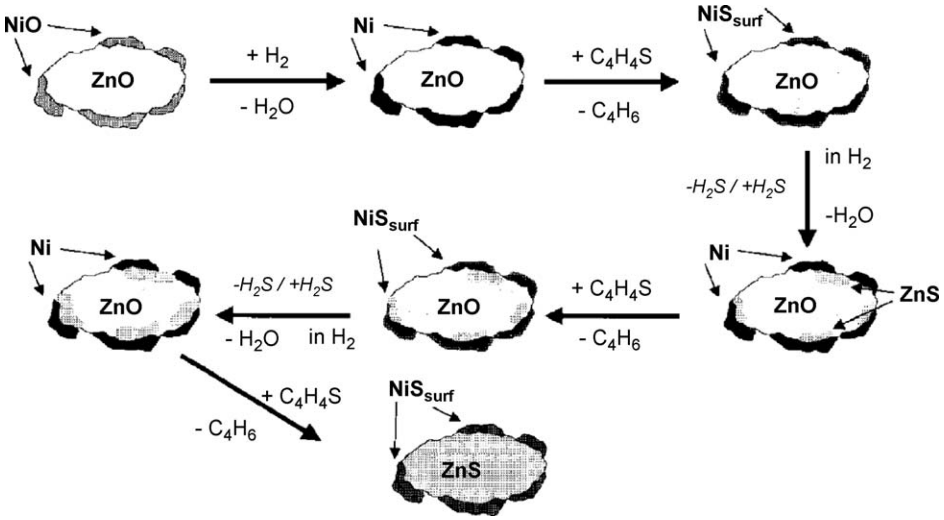


Fig. 2. Schematic illustration of reactive adsorption with NiO–ZnO sorbent.

The process consists of a desulphurization section (reactor on the left) and the sorbent regeneration section (regenerator on the right). It looks quite similar to fluid catalytic cracking in its process scheme, equipped with a reactor and a regenerator section in which fluidized sorbent particles are transported. However, the reactor circulation speed is slow, *viz.* a residence time of a few days, comparable to that in a continuous regeneration reformer. The feed with hydrogen is brought into the reactor to make contact with the sorbent, which is then pushed upwards slowly until it is finally separated into product and sorbent at the separator. The sulphided spent sorbent is then regenerated in the regenerator under a proper oxidative atmosphere. The process is claimed to be able to preserve octane number well, while removing sulphur species effectively [11]. The clue seems to lie in the use of a tuned reaction temperature, probably on the high side, which balances the hydrogenation and dehydrogenation equilibrium, therefore minimizing hydrogen consumption and effectively minimizing olefin hydrogenation. The usual problem of coking on the catalyst is not an issue, since the sorbent is anyway regenerated. They publish an enormous number of patents on sorbent formulation [12].

There are several S-Zorb gasoline units in the ConocoPhillips refineries. Their first demonstration unit in Borger refinery is still in operation (since 2001). They appear to have recently won two non-ConocoPhillips commercial units, one to be installed in Pasadena refinery in Texas owned by Pasadena Refining System and another in a Beijing Yanshan refinery in China owned by Sinopec Corp. It seems fair to conclude that, despite some attractive features, the S-Zorb process has not nearly had the same impact as the selective desulphurization processes mentioned above. This is likely due to the relatively high complexity of the process—there are relatively many pieces of equipment, and the proximity of hydrogen (in the reactor) and oxygen (in the regenerator) in the process could mean some operational complexity, as known in FCC.

The detailed description of the process can be found in reference [10]. Note that there is another pre-commercial reactive adsorption process called TReND reported from the Research Triangle Institute. The process scheme is quite similar

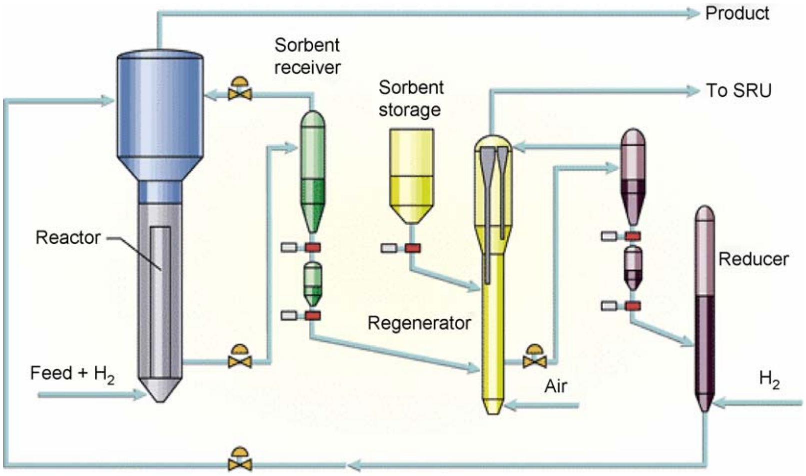


Fig. 3. S-Zorb process scheme.

to S-Zorb and they seem to apply adsorbents of iron or copper promoted Al_2O_3–ZnO [13,14].

2.2. Non-destructive adsorption

An alternative to 'reactive' adsorption could be 'non-destructive' adsorption (or molecular adsortion, *i.e.*, physisorption and some forms of chemisorption) where sulphur species are adsorbed as molecules as such. Of course, this generates an adsorbent loaded with S-bearing molecules that has somehow to be disposed of. In this field, zeolites like 5X and 13A and active carbon have been reported as sorbents for removing mercaptans, sulphides and thiophene under mild conditions already some time ago [15]. Furthermore, some commercial materials like Ni–Al_2O_3 are available for adsorbing thiophene type sulphur species for the purpose of applying it as a guard bed of naphtha reformer platinum catalyst. However, the Irvad process, named after its developer Mr. *Irv*in and sulphur *ad*sorption, could probably be mentioned as one of the first commercially oriented desulphurization processes reported for gasoline sulphur reduction [16,17]. They use an in situ regenerative process with fluidizable sorbent particles like S-Zorb, but then without applying H_2. They have disappeared from the field upon the rise of the S-Zorb process. The adsorbent for the Irvad process was to be supplied by Alcoa and mentioned to be alumina with an inorganic promoter [16]. The fate of the sulphur species is not well described in the publications on Irvad, but they seem to adsorb physically, given the typical reaction conditions of 30 °C, 13 bar without applying hydrogen. The sulphur-loaded adsorbent is then regenerated by 'reactive gas'. After Irvad has disappeared from the commercial field, Alcoa still continued its adsorbent development, as seen in its report on Ag–Al_2O_3 [18,19].

In the academic field, gasoline desulphurization by adsorption is being actively pursued by the group of R.T. Yang (Michigan U.) and by the group of Song (PennSate). Yang et al. have published a review of sulphur adsorption on different sorbents [20]. The group has intensively investigated Cu(I)–Y as a promising sorbent. Among different cations, *e.g.*, Na, Ag, Ni, Cu(II) and Cu(I) in zeolite, Cu(I) showed the highest selectivity to bind thiophenic sulphur species via Π-complexation, more strongly than benzene. In their MO calculation, they show that Π-complexation becomes stronger when an alkyl group is attached or more benzene rings are attached to thiophene molecules. The adsorption strength becomes like 4,6-DMDBT $>$ DBT $>$ BT $>$ 2-methyl thiophene $>$ thiophene [21], which is interestingly the reverse of their HDS propensities. An effort has been made to increase the amount of Cu(I) by incorporating Cu(I) in vapor phase exchange of CuCl instead of usual liquid phase exchange [22], and also to increase the adsorbent capacity of Cu(I)–Y by adding a pre-adsorbent like active carbon [20]. Their system, however, still seems to have several serious technical issues to overcome. Firstly, the uptake capacity of the sulphur in the real gasoline, *e.g.*, ∼1 wt.% sulphur [20,23] is too low. They mention that Cu(I)–Y can typically treat 15 ml desulphurized gasoline with 1 g of Cu(I)–Y adsorbent. Hydrotreating units process hundreds to thousands of tons of feed per day. So, if the adsorbent reactor contains, say, 1–10 t adsorbent, an unrealistically short cycle length results for the process in a fixed bed mode. Interestingly, Cu(I)–Y system actually performs much better with the model gasoline based on thiophene in decane and benzene, showing an uptake capacity of ∼6–7 wt.% [23]. This, therefore, indicates strong competitive adsorption of presumably large aromatics in the real gasoline, which hinders the removal of the target thiophenic sulphur species in gasoline. A decrease of S adsorption as a result of competitive adsorption of aromatics and/or olefins have also been reported by Song and co-workers for their Ce–Y [24] and also by Richardeau et al. for H^+-FAU zeolites [25]. For HFAU, the competitive adsorption turned out to be so strong that they can adsorb thiophene only when no olefinic compounds are present. The use of a pre-adsorbent, or, in other words, a guard bed, to remove aromatics and maybe some of the larger sulphur-bearing molecules, has been suggested for an improvement in the uptake capacity [20b]. One should, however, realize that it requires additional considerations on the life cycle of the pre-adsorbent as well as that of the main adsorbent. The second serious issue to be addressed is the treatment of the adsorbed organic sulphur species as wastes. The third issues is probably the intrinsic instability of Cu(I) to air and moisture leading to the formation of Cu(II). This could limit the feed flexibility in the water and oxygenates contents and demand delicate catalyst handling in the process. The group of Song and co-workers have published an article recently that their Ni/SiO_2–Al_2O_3 adsorbents have much higher uptake capacity than Cu(I)–Y when direct comparison is made with the same commercial gasoline feeds [26]. The uptake capacity reported by them, however, is also still often limited, to something like ∼1%. Besides, the same group has recently published about their Ni based adsorbents for gasoline [27]. They found that the effect of olefin inhibition becomes less when the adsorption temperature is elevated from 25 to 200 °C. Furthermore, interestingly, they observed C–S bond cleavage on their Ni based adsorbent at 25 °C.

2.3. Alkylation

Alkylation chemistry of thiophenic sulphur over acidic catalysts (Fig. 4) can also give an opportunity of reduction of

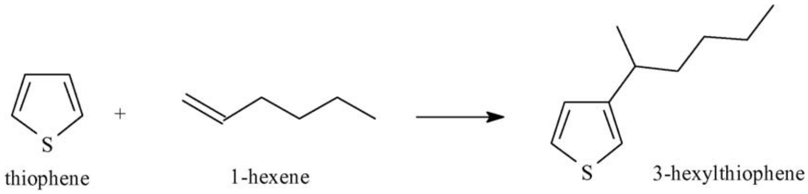


Fig. 4. Alkylation of thiophene.

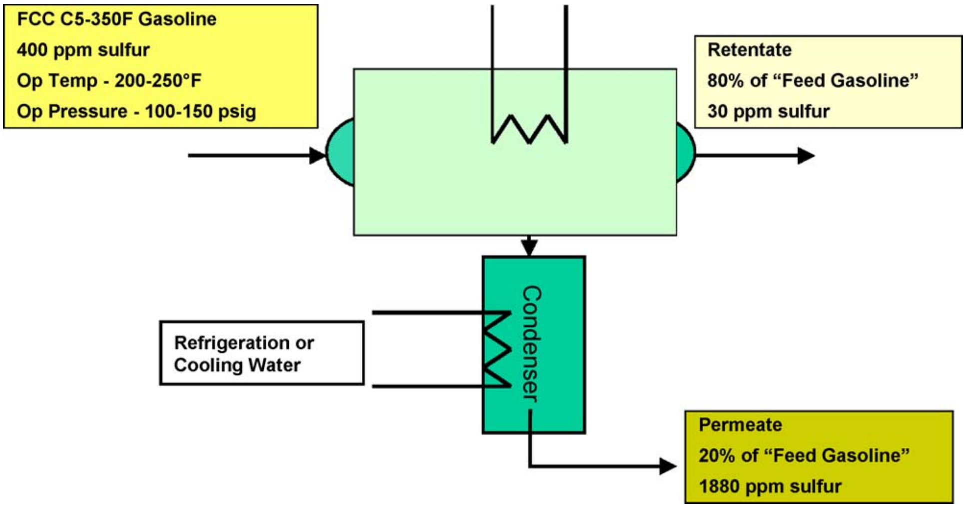


Fig. 5. S-Brane schematic process flow.

sulphur in gasoline as the case in OATS process [28]. Alkylation of thiophenic sulphur leads to a boiling point shift of the resultant sulphur compounds toward a diesel range, thus reducing the sulphur content in the gasoline range product. A recent patent proposed also the possibility of alkylation of sulphur and nitrogen containing compounds in the presence of ionic liquid containing alkylation agency [29]. There are, however, several issues. The most important issue is the fact that it is only applicable for a narrow boiling range fraction, thus a large fraction of the gasoline will still require treatment. Furthermore, the high boiling product should be also further treated.

2.4. Other physical separation methods

Apart from adsorption and alkylation routes, other physical separation methods have been looked into in some detail as well. For example, a membrane-based process, called S-Brane, is offered by Grace Davison and CB&I (Fig. 5). Though it is apparently commercially available, a full commercial unit has not been announced yet, to our knowledge. They reported on their demonstration project of 2003 in the NPRA conference of 2004, announcing that they successfully produced 30 ppmw S stream with their per-vaporation membrane technique [30]. The biggest issue of this process would, however, appear to be the 'stage-cut' (related to the ratio of S-rich to S-poor product) to be applied. The typical stage cut of the present S-Brane process is high at around 30%, which means that only 70% of the stream can be desulphurized to, for instance, 30 ppmw S, while the remaining 30% is the sulphur-rich stream, to be routed to HDS or other processes. Such a high stage cut is possibly also connected with the necessity of retaining the olefins in the low-S stream, selectivity always being a problem. Maybe the process is only suitable to treat certain boiling-range fractions, in which case integration with hydrotreating is still required when full-range FCC gasoline is treated.

An extractive distillation process, GT-DeSulph™, has been reported by GTC in 2002. The process scheme is shown in Fig. 6. The GT-DeSulph™ utilizes a proprietary aromatics selective solvent, which is effective in extracting thiophenic sulphur species and aromatics, and to a limited extent, mercaptans and sulphides as well [31,32]. Since olefin is not extracted, it is indeed a 'selective' desulphurization system. The application is, however, limited to a light and a middle FCC cut, with specified boiling point range up to180 °C [31]. This is probably due to a substantial amount of aromatics present in the heavier FCC fraction, which would make an effective sulphur species separation difficult. This process has been announced in 2002–2003, but nothing much has been heard about it since then. Several drawbacks are apparent. The first is a high volume of the sulphur-rich stream, like 10–30% of the total volume. This should be separately treated in HDS later. Another point of concern is the complexity of the extraction process, *i.e.*, many pieces of equipments, due to the separation and recovery of extractant [32]. That often seems to make such an extraction process a potentially high CAPEX process.

2.5. Miscellaneous

Among other intriguing options to reduce sulphur content in gasoline, precipitation and polymerization can be named. Precipitation of sulphides and thiophenes is realized by alkylating the sulphur atom in such molecules to form S-alkylsulphonium salts, $(R\text{–}S^{+}\text{–}CH_3)\cdot BF_4^{-}$, that precipitate

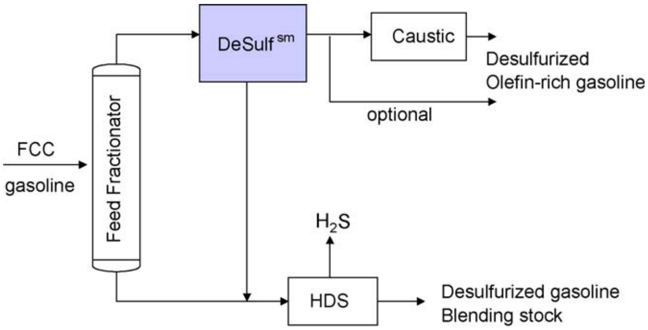


Fig. 6. GT-DeSulph^{sm} schematic process flow.

from the matrix [33]. The desulphurization of FCC gasoline from 100 to less than 30 ppmw has been reported. The problems with this route, however, can be envisaged to be some olefin loss, consumption of expensive chemicals and the waste treatment of alkylsulphonium salts. Another interesting approach is electrochemical polymerization of sulphur compounds [34]. The idea is to electrochemically oxidize thiophene and aniline type species to form dimer/oligomer of them, which can be separated easily from the matrix by gravity or boiling point. This, however, seems to be limited in the type of species that are polymerizable. Furthermore, the cost of electrochemical processing and of ionic liquid should be also considered.

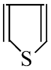
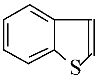
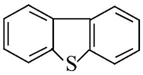
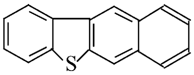
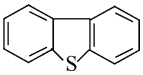
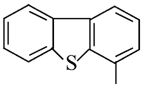
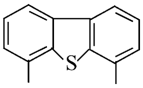
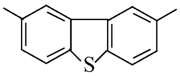
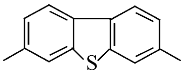
3. Diesel desulphurization

While the challenge in gasoline hydrodesulphurization is achieving a high hydrogenation selectivity of sulphur over olefin, the main issue in diesel HDS is the low reactivity of highly aromatic sulphur species. The issue has already been pointed out in the 1980's [35,36], and nicely reviewed by Girgis and Gates [37], and the reactivity of thiophene (T), benzo-thiophene (BT) and dibenzothiophene (DBT) is shown in Table 1. The hydrodesulphurization reactivity constant k shows a decrease of about an order of magnitude upon the addition of each aromatic ring. Moreover, HDS reactivity further decreases when substituents are present in sterically hindering positions, *e.g.*, the four- and six-positions in the case of DBT [36]. When the diesel sulphur specification becomes something like 10 ppmw, it starts to become a pre-requisite to tackle those highly refractive sulphur compounds. Note that the reactivity of the alkyldibenzothiophene species is further decreased in the presence of other inhibitors like aromatics [39] and organic nitrogen species [40,41], which are generally co-present in the feed. This tends to limit also the application of cracked diesel feeds like LCO and thermally cracked diesel to HDS.

In the event, improvements in catalyst performance have proved to be fully up to the challenge posed by ultra low sulphur diesel (ULSD), such that it appears that to date hydroprocessing remains the only commercially viable option. Of course, the major HDS-catalyst suppliers have been in the lead here [3], but also in academia a search for better catalysts has been going on, with quite interesting results in all areas from alternative catalyst carriers (*e.g.*, mixed oxides), via alternative preparative methods (*e.g.*, sol–gel, mesoporous bulk sulphides), to novel active phases (*e.g.*, TM phosphides) [42,43]. Although also in these latter cases improvements over existing commercial catalysts have been claimed from time to time, these have not often resulted in commercial developments, for reasons that have recently been outlined by Armor [44].

Innovation of the HDS process design has also been attempted. An interesting example is provided by the "Iso-therming' concept developed by Process-Dynamics and Linde,

Table 1
Reference data showing typical reactivity pattern observed in hydrodesulphurization catalysis which is based in the reference [37]

Reactant	Structure	Pseudo-first-order rate k (L/g cat)	Rate constant (min^{-1})***
Thiophene		$1.38 \times 10^{-3*}$	
Benzothiophene		$8.11 \times 10^{-4*}$	>0.20 (CoMo) >0.20 (NiMo)
Dibenzothiophene		$6.11 \times 10^{-5*}$	
Benzo[*b*]naphtho-[2,3-d] thiophene		$1.61 \times 10^{-4*}$	
Dibenzothiophene		$7.38 \times 10^{-5**}$	0.058 (CoMo) 0.057 (NiMo)
4-Methyldibenzothiophene		$6.64 \times 10^{-6**}$	0.018 (CoMo) 0.020 (NiMo)
4,6-Dimethyldibenzothiophene		$4.92 \times 10^{-6**}$	0.006 (CoMo) 0.008 (NiMo)
2,8-Dimethyldibenzothiophene		$6.72 \times 10^{-5**}$	
3,7-Dimehyldibenzothiophene		$3.53 \times 10^{-5**}$	

The original data * are reported in reference [35] and the data ** in reference [36]. The data *** are taken from reference [38].

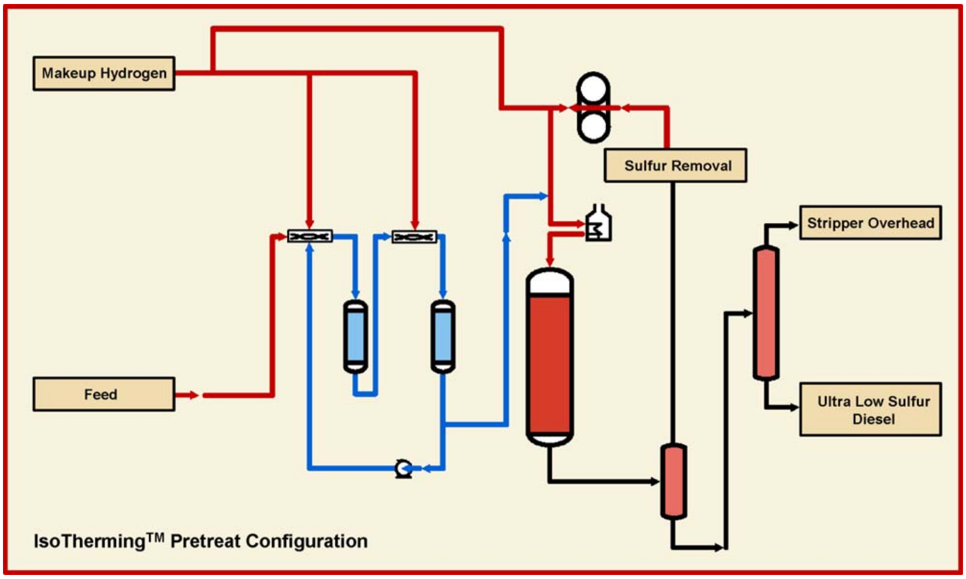


Fig. 7. Schematic process of IsoTherming^{TM}.

and for which the former company has filed a US-patent (6,123,835). They say to offer here a low capital cost process in order to produce <10 ppmw S diesel stream [45]. They have one commercial unit in Ciniza refinery in New Mexico and another one to be built in 2006 in Yorktown, Virginia [46], both owned by Giant Refining.

The so-called ‘‘Iso-therming concept’’ equips an HDS unit with an add-on pre-treat reactor, which is operated under liquid full conditions with a standard HDS catalyst. The pre-treat unit is positioned before the charge furnace and the main HDS reactor, and it is claimed to desulphurize a gas–oil feed to low sulphur and nitrogen levels such that the main HDS reactor can bring the feed to <10 ppmw sulphur levels in a hydro-finishing or polishing step. The process scheme is shown in Fig. 7. The fresh feed is mixed with a part of the recycled product and hydrogen is dissolved in it. The feed then goes through the pre-treater at a high space velocity, in which the low (but not ‘ultra-low’) sulphur product (*e.g.*, 20 ppmw) is produced. In the figure, two such pre-treat reactors are illustrated. The intermediate product is then sent to the main HDS reactor, which produces the final ultra low sulphur product (*e.g.*, 5 ppmw S). It is claimed that the usage of the sufficiently dissolved hydrogen in feed in the liquid phase reactor eliminates the mass transfer problem of H_2 from gas to liquid phase in the usual trickle flow reactor. Interestingly, the data suggest that in the pre-treat reactor the removal of nitrogen species is relatively more important than in the usual HDS process and this could contribute also to the deeper HDS in the main reactor. A recent scientific journal article from the group of Jess describes the kinetics in the ‘Iso-therming’ type process, wherein the H_2 is brought into the system by pre-saturation of the feed/product and the liquid-phase HDS reaction is considered [47].

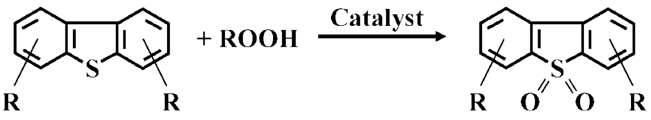
Transferring the downstream hydrogen in the dissolved form in the recycled product stream toward upstream, the process has an interesting large advantage that it can spare an expensive hydrogen compressor. That is therefore the core aspect, making the process low cost.

There are really not sufficient technical data available to date, to be able to judge where this concept stands, compared to advanced HDS processes in general. One potential issue could be some limitation in the feed flexibility, since all published examples involve rather low-sulphur feeds.

Apart from all these efforts to improve HDS catalysts and process, there also has been a lot of work on a variety of possible alternatives. In what follows, the oxidative method, adsorption, extraction and N-compounds removal will be described. The oxidative method is discussed in most detail, reflecting the long history of the field. The adsorption method is categorized into three groups, as will be described later, dependent on the regenerability of the catalyst and the fate of the sulphur molecules. The last item is a typical subject for diesel hydrodesulphurization. HDS of diesel range alkylated DBT like compounds is very much inhibited by organic nitrogen species, hence nitrogen removal prior to HDS can be a potential ‘indirect’ approach to obtain deep desulphurization.

3.1. Oxidative desulphurization (biological route included)

While hydrodesulphurization attempts to reduce sulphur species to form H_2S, the oxidation method aims at promoting a reaction in the opposite direction, to form oxidized sulphur species. With diesel as a feed, aromatic type sulphur species like dibenzothiophene are usually transformed into the corresponding sulphone species.



In order to finally obtain a deeply desulphurized product, the sulphone species should then be removed in a second step.

This is usually achieved by way of adsorption on a solid adsorbent or by solvent extraction. Theoretically, the oxidized sulphur molecules like sulphones have a much higher polarity than the parent sulphide molecules, and thus are substantially easier to separate from the feed. The practice, however, suggests that this separation process also is not without substantial technical and economical issues (*vide infra*). Note that when extraction is applied, an additional issue of yield loss (*e.g.*, ∼10–20%) arises as well. And one must also not forget what should happen with the end product sulphone 'waste'.

The history of the oxidative desulphurization is quite old, starting already from 1920' [48]. The initial attempts involved nitric oxides/acids type oxidants like HNO_3 or NO/NO_2 gases [48,49–52], next to several reports on other oxidants *t*-butyl hypochlorite [53], very toxic RuO_4 [54] or later on persulphate-based oxidant (*i.e.*, $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) [55] or on H_2O_2–H_2SO_4 system [56]. The purpose of the attempts in the initial period was two-fold; one was to oxidize sulphur for desulphurization, and another aimed at nitration of aromatic molecules with use of NO_x oxidants. Nitrated aromatics are thought to have a high cetane number. Tam et al. have, however, pointed that the approach involving nitric acids or nitric oxides tends to lead to formation of a relatively high amount of residues [52]. Later in 1950–1980, the detailed study on the oxidation of thiols and sulphides by hydro peroxides and per acids have been reported in several books, and a couple of patents and publications from different oil companies appeared on the oxidative desulphurization of more aromatic sulphur species, *e.g.*, Anglo Iranian oil (1954) [57], Shell (1964) [58], Esso (1966) [59], BP (1967) [60] and Texaco (1970) [61], mostly reporting the use of hydro peroxides as an oxidant. Since the 1990's, when the sulphur specification in diesel became evidently more stringent, the approach has regained an interest and many reports have appeared in the scientific literature. In the later period (late ∼1990's), hydro peroxides like H_2O_2, TBHP with a catalyst or in situ produced per-acids (*e.g.*, H_2O_2 and formic acids) have been the oxidants of choice. Those oxidants can convert sulphur efficiently to sulphones without forming a substantial amount of residual product.

The oxidative desulphurization seems to offer several advantages, compared to hydrodesulphurization. Firstly, the use of mild reaction conditions and avoiding the use of expensive hydrogen are listed (of course, no H_2 only is an advantage as long as product specifications – density, cetane – are not tightened further). Furthermore, the most attractive intrinsic aspect is the anticipated higher reactivity of more aromatic sulphur species, since the electrophilic attack on the sulphur atom is promoted with the increase of electron density at the sulphur atom by attached electron rich aromatic rings. In addition, alkyl groups attached to the aromatic rings will further increase the electron density at the sulphur atom. Thus, the intrinsic reactivity of molecules like 4,6-dimethylDBT is substantially higher than that of DBT, and in fact the sequence of increasing susceptibility to oxidation is exactly opposite to that to HDS. Whether the higher reactivity is actually observed, however, turns out to be highly dependent on the type of catalysts. With the homogeneous H_2O_2-formic acid system, the reactivity is reported to be well correlated to the electron density of sulphur species, that is, thiols > sulphides > DBT > BT [62,63] (Fig. 8). However, H_2O_2-phosphotungstic acid system (homogeneous system but with a bulky catalyst) reflects already a negative influence of steric hindrance in the sulphur species reactivity, and the reaction order of DBT > 4-methyl,6-ethyl DBT > BT is reported [64]. With heterogeneous catalysts, the order of reaction seems definitely influenced by steric hindrance. Typical example is seen in the report from Wang et al. observing the reaction order of DBT > 4-methyl-DBT > 4,6-dimethyl DBT ≫ BT in the Mo catalysis with use of *t*-butyl hydro peroxide as an oxidant [65].

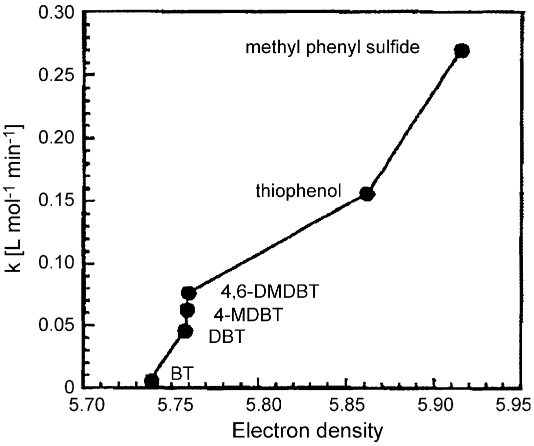


Fig. 8. Correlation between the electron density of sulphur atom in compounds and the reaction constant (*k*) for oxidation of sulphur atom.

Several disadvantages of oxidative processes can be, however, also listed. An important practical issue, to begin with, is the waste management of sulphone compounds at the end of the process. Refiners are not accustomed to handle chemicals wastes. It brings up a negative economic and technical impact, even when it is sent to common options like hydrotreaters or cokers. Another issue is a rise in the operation cost with the increase in the feed sulphur content, due to the stoichiometric or higher consumption of oxidants relative to the sulphur amount (>2:1 = O:S in molar ratio). This could limit the feed flexibility for refineries when targeting a given process economy, or limit the process to a post treatment of already mildly desulphurized diesel. Further, the many 'pots and pans', particularly due to the second step of sulphone separation followed by regeneration of extractant or adsorbent, seem to be an issue, as will be discussed later for the Unipure process. Note also that the decreased oil yield to 80–90% is an additional issue in case that extraction is applied to the sulphone separations [62,66].

Based on the available literature, one can make the following classification:

(1) two liquid-phase system (aqueous H_2O_2 as oxidant);
(2) single liquid phase system (organic hydro peroxides or peroxyacids as oxidants);
(3) gas–liquid phase system (ozone, NO_2, O_2);
(4) biological system (O_2 + bacteria).

The highest number of papers is seen in the first category, *i.e.*, the use of H_2O_2 in the two liquid phase (usually aqueous

H_2O_2 applied to an oil feed) system in the presence of a variety of catalysts, with and without assisting components (*e.g.*, a phase transfer agent [64,67], co-adsorbent like active carbon [68]), co-solvent [64,69] or even application of physical methods like ultrasound [70] or microwave [71]. The type of catalysts varies from organic acids [62,68,72,73], phosphotungstic acids or other heteropolyacids [64,70,75,76], Fe-TAML complex [77], Fenton-like catalysts [78] to heterogeneous catalysts. Examples of the latter include Ti-silica based catalysts [69], W–V–TiO_2-cogerite [79], solid bases like MgLa metal oxides/hydrotalcites [80], Fe oxides [81], oxidation catalyst on monolith [82]. Yu et al. suggested that the co-use of activated carbon apparently helps to obtain a deeper desulphurization in the H_2O_2-formic acid oxidation system [68]. Further, several notes pointed out that the presence of sulphone extracting agent like acetonitrile in the oxidation phase enhances the sulphone oxidation substantially [69,83]. Publications on Fe-TAML (Tetra Amido Macrocyclic Ligand) have also drawn attention in the field of alternative desulphurization. The catalyst seems to be very efficient in sulphide conversion according to their data showing a >95% conversion of DBT and 4,6-dimethyl DBT in a few minutes in reaction with H_2O_2 at 40 °C [77]. Despite those attractive features like a high reactivity under mild reaction conditions and (relatively!) cheap oxidant H_2O_2, the two liquid phase systems have several technical disadvantages. Firstly, reactor engineering is necessary for homogenization in the reaction, for which a continuously stirred tank reactor (CSTR) is most often used. The use of a most simple fixed bed type reactor, therefore, is not possible. Furthermore, producing sulphone compounds (potential surfactant molecules) in the polar–apolar two liquid phases means that emulsion-breaking technology should be also taken into consideration. In addition, when acid catalysts are chosen, an additional disadvantage, like a limited choice of reactor material due to acid corrosion, could arise as well.

Furthest down the road towards commercialization appears to be Unipure with its ASR-2 process [72], which is schematically illustrated in Fig. 9. They have done a demonstration project in 2004. The process is based on H_2O_2 oxidation assisted by formic acid catalysis. The sulphone species formed are then separated by adsorption on an Al_2O_3 bed, which is regenerated by washing with methanol. The methanol is then also regenerated in the scheme. As a result, one can see that the number of 'pots and pans' is quite high. With respect to waste management, Unipure mentions a 1 t/day production of sulphone species for processing 1000 t/day (a feed containing 500 ppmw S). They advocate to send it to hydrotreaters or coker units or to utilize it as surfactants. They recently have published a patent assuring that the oxidized product is much easier to reduce in sulphur content than the one without oxidation [73]. The old BP patent of 1967, interestingly, already claims the same approach of oxidation prior to HDS as well [60]. The intrinsic reactivity of sulphone species in hydrodesulphurization conditions, however, is not expected to be spectacularly higher than the parent sulphide molecules, given the report of Geneste et al. [74]. They suggest a reaction route for sulphones, which involves the reduction to parent sulphide molecules, followed by the usual hydrodesulphurization routes. One possible explanation could be the potential removal of HDS inhibitors like nitrogen species during the first oxidation process. Guth and Diaz [50] suggested oxidation of nitrogen compounds during real diesel oxidation by nitrogen oxide gases, leading to the formation of a variety of amine oxides, like R_1NOH_2, R_2NOH, R_3NO. Those oxidized nitrogen compounds can be separated from the feed together with oxidized sulphur compounds. Unipure, however, has not clearly stated the decrease of nitrogen content in the product. Next to sulphone waste treatment, another disadvantage of the Unipure process is the increased operation cost when processing feeds with a higher sulphur content. They seem to realize this issue as well, since Unipure recently mainly targets the reduction of sulphur in the contaminated ultra low sulphur diesel during transportation towards retails. The reduction of sulphur content in such case could be like from 50–100 ppmw to <10 ppmw, and it could be advantageous for Unipure economy. The oil industry, however, has not yet responded enthusiastically to the process, probably due to many 'pots and pans' and the waste management of the processes, which do not easily fit with retails and depots.

The SulphCo process is another H_2O_2-based potentially commercial process, and it utilizes ultrasound power during H_2O_2 sulphur oxidation in the presence of tungsten phosphoric acid [70,68]. It is mentioned that ultrasound decreases the reaction time by one order of magnitude. Further, other aspects

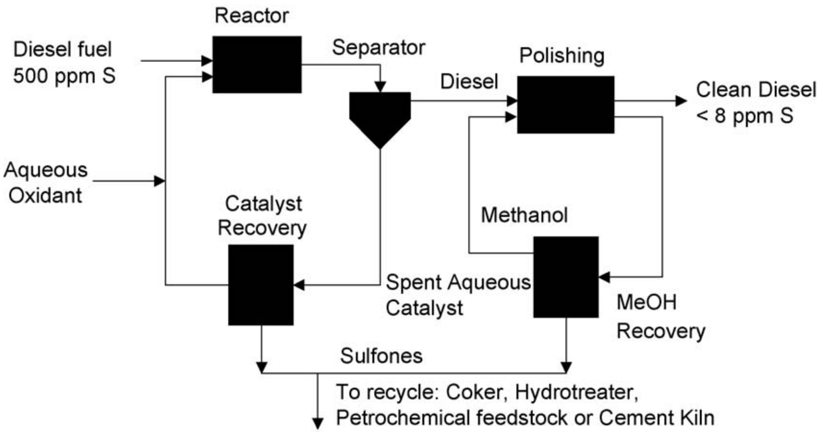


Fig. 9. Schematic illustration of Unipure process.

not mentioned by Unipure, for instance, an increased cetane number and decreased nitrogen contents, are claimed for its ultrasound chemistry, and it will be interesting to see whether this can be confirmed. Technically speaking, they have similar issues as the Unipure process, *i.e.*, a complicated process scheme and the waste treatment of sulphone species. Some reports from academia on the ultrasound approach can also be found [78].

With respect to the second category 'a single liquid phase system', the use of *t*-butyl hydro peroxide (TBHP) and peroxyacids is noted. The biggest advantage of the single liquid system is simple reactor engineering, enabling the application of a fixed bed system. Lyondell Chemicals [84] and EniChem/UOP [85] have announced development of a TBHP based commercial oxidative desulphurization processes. Lyondell process utilizes extraction for sulphone separation (Fig. 10), while EniChem/UOP removes sulphone species by adsorption. Major drawback is the high price of *t*-butylhydroperoxide, and the waste treatment of *t*-butyl alcohol as an accompanied product, as well as sulphone waste treatment. They suggest the use of *t*-butyl alcohol as potential octane boosting compounds for gasoline. Furthermore, in academia, the group of Corma has published a patent utilizing Ti-silica based catalysts to enhance TBHP oxidation chemistry [86]. In addition, an exotic choice of catalyst like silica tethered oxorhenium(V) dithiolate catalyst (*i.e.*, $[–S(CH_3)_3S–]Re(O)(CH_3)(PPh_3)$ in which dithiolate ligand contains silicon atom attached to silica) is also recently pointed out for selective oxidation of sulphide [87]. Conversion/extraction desulphurisation (CED) process of PetroStar is another oxidative process, which utilizes peroxyacid oxidation chemistry, followed by extraction [88]. Not much detailed information is available, however. Some reaction kinetics involving peroxyacetic acid has been reported by others [89], and the reaction rate sequence appears to be similar to H_2O_2-formic acid one, that is sulphides > DBT > BT > thiophene. PetroStar also looked into the involvement of a bio-process for converting sulphones to highly valuable sulphonate surfactants. They have, however, disappeared from the desulphurization scene since 2003, possibly related to the stopped national funding for their research around that time. A very different choice of oxidant is also noticed. First is the use of $HOF{\cdot}CH_3CN$ showed to be very selective oxidant to oxidize sulphide while aromatic rings and other function groups remain untouched [90]. Another report is seen on sulphur oxidation by sodium periodate assisted with ruthenium trichloride as catalyst [91]. Those oxidants, however, seem too expensive to apply in oil industry.

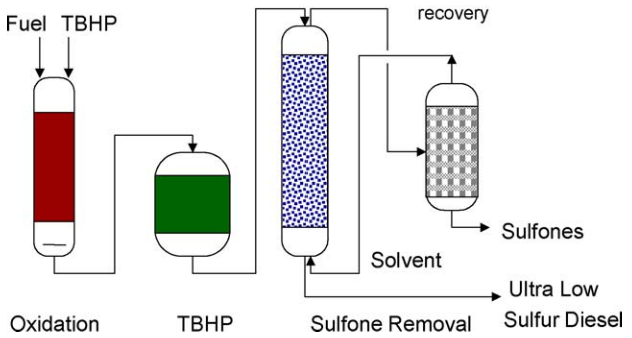


Fig. 10. Schematic illustration of Lyondell Chemicals oxidation process.

In the third category of 'gas–liquid phase system', the use of ozone [92] and O_2 can be noted as well as nitric oxide, which was already mentioned earlier. Ozone is a known powerful oxidant but one might wonder about the reaction selectivity of sulphur species over hydrocarbons in general. With regards to O_2 or air, which indeed are the ultimate oxidants, a reference from 1976 reported the use of RuO_x for oxidation of DBT at 100 °C under the 70 bar of air [93]. A sulphur conversion of 97% is obtained after 12 h. Recently, Murata et al. reported the potential of oxidation of sulphur species in diesel fuel with molecular oxygen in the presence of cobalt catalysts and aldehydes [94]. The homogenous cobalt acetate catalyses air oxidation of aldehydes leading to per acid formation. The per-acid can effectively react with sulphur leading to sulphone formation. They report a reduction of sulphur content from 193 to <5 ppmw with a real diesel feed according to their method. This seems an interesting option, though in this case, the consumption of aldehydes seems to trade off the potential process economy. Recently, the use of cobalt and manganese based catalysts is patented for air oxidation of DBT type aromatic sulphur compounds [95]. They reported ∼80% oxidation conversion of DBT at 120 °C with manganese or cobalt containing catalyst. Another recent patent by Geus et al. [96] reported the use of silica supported iron catalyst for thiophene oxidation. Those could become a potential economical option, when the high oxidation selectivity to sulphur compared to hydrocarbon would be proven. A very different type of air oxidation system is also proposed which is based on $FeBr_3$ [97]. This system can perform oxidation of sulphides to sulphoxides effectively in the presence of air in catalytic cycles, particularly when stabilized in cyclodextrin. This, however, seems to be more appropriate in the field of fine chemicals in view of the expensive catalysts.

A conceptually very attractive, 'green', option is to utilize a biological system to do the oxidation chemistry of sulphur species, as illustrated in Fig. 11. The reaction proceeds in the presence of water and oxygen at ambient temperature and pressure. Interestingly, bacteria converting dibenzothiophene and alkyl sulphides are well investigated, whereas fewer bacteria are found for benzothiophene, and further, only a few bacteria detected for thiophene [98]. Enchira is the one company that reported their activity in development of bio-desulphurization for diesel [99], but it appears to have stopped with its activity. In general, many reports of bio-desulphurization do not show very deep desulphurization, down to 50–200 ppmw sulphur at best. This can be well understood due to the higher bacterial activity in the higher concentration range. In that sense, the potential of biodesulphurization for achieving the 10 ppmw S level might be not so great. Furthermore, another important aspect to consider in the bio-system is the competitive reactions caused by other bacteria. A successful H_2S biological process like the one from ThioPaque [100] has the great advantage that only target type bacteria seem to

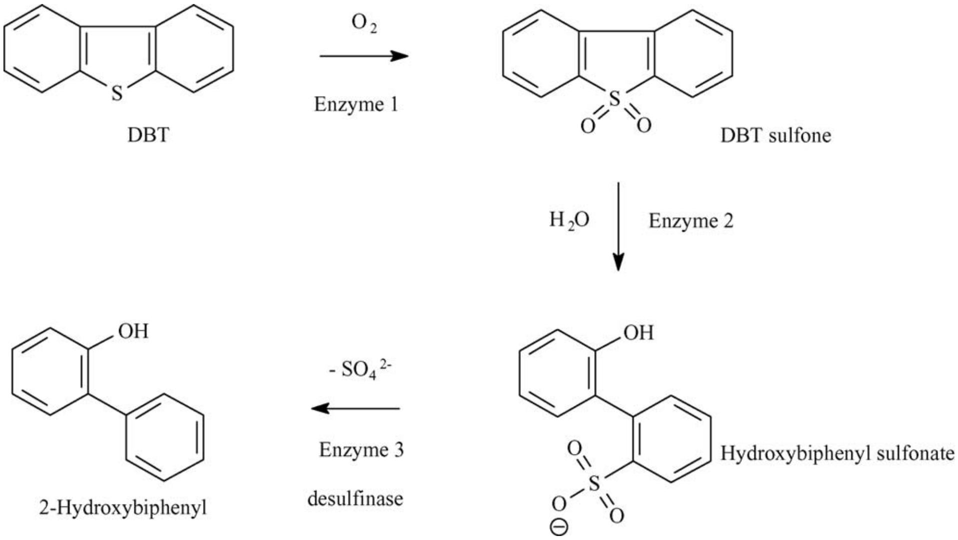


Fig. 11. Schematic figure of biological oxidation reaction by bacteria.

survive in a very poisonous environment of H_2S, converting H_2S to elemental sulphur efficiently. In that respect, crude and diesel desulphurization would need an additional effort to promote the working of target bacteria. Occasionally, reports appear on development of new bacteria for petroleum desulphurization [101–103].

3.2. Reactive adsorption

Like for gasoline, another popular approach in alternative desulphurization of diesel is reactive adsorption. Again, adsorbents promoted with transition metals are applied, which reacts with sulphur molecules in the presence of hydrogen at the temperature of 200–400 °C. Sulphur species are converted into hydrocarbons and H_2S, and H_2S is subsequently absorbed by the sorbent component (Fig. 2). There are two types of processes here, one is continuously regenerative and the other is based on a fixed bed configuration. Example of the former process is S-Zorb work on diesel [104]. They have demonstrated its potential for removing sulphur from diesel feeds, but there would appear to be several important issues. Firstly, the process requires full evaporation of the diesel feed for a proper contact with moving catalyst particles. That would be technically difficult or costly with energy, when diesel feeds of a high final boiling point >380 °C should be treated. Secondly, the reaction conditions would appear to approach those of regular HDS, high temperatures like ~380–420 °C with a limited space velocity (~0.5–1) at 30 bar being mentioned. Given that it stands to reason that the relative reactivity of DBT-type molecules is the same for the S-Zorb and traditional HDS catalysts as well, it becomes difficult to see where the advantage of the former process could come from. As far as we are aware, there has been no recent communication on this subject from ConocoPhillips.

With respect to fixed bed reactive adsorption, the works of Cosmo [9] and other Japanese oil companies [105], and some reports of ExxonMobil [106] can be noted. The focus of the Japanese oil/energy companies is seen to be on very stringent desulphurization of kerosene for fuel cell application. Types of adsorbents reported are ZnO promoted with transition metals like Ni and Cu. Similar to HDS, they apply hydrogen at mild conditions in an attempt to convert sulphur species to H_2S, which is subsequently absorbed by ZnO support. As in the S-Zorb case, the Ni–ZnO is thought to remain working well because ZnO, through its fast uptake of H_2S, reduces the H_2S partial pressure to such low levels that part of the Ni remains unsulphided, thus still acting as catalytic desulphurization sites. This is a simpler process option than S-Zorb, of course, but it will require already low-S feeds, to ensure sufficient on-stream times, and it will suffer from the same reactivity limitations.

3.3. Non-destructive adsorption

In this category, the work of the group of Song and the group of Mochida are prominent. Both groups use adsorbents mainly in the form of fixed beds, and sulphur molecules are adsorbed as such without conversion. The process of Song is named selective adsorption for removing sulphur (SARS), employing mild adsorption conditions (*e.g.*, 80 °C). They work often for the purpose of desulphurization of kerosene for producing a fuel cell grade fuel, but have also published some works in the gasoline area. They employ several types of adsorbents as revealed in their patent [107], *i.e.*, transition metal chlorides on support, activated Ni adsorbent (*e.g.*, Ni–SiO_2), metal ions in zeolite (*e.g.*, CeY, Ni–Y), NiAl layered double hydroxides, NiZnAl layered double hydroxides, Ni–SiO_2/Al_2O_3 and even HDS catalyst like sulphided CoMo/alumina. Their recent article has reviewed the interesting difference in the adsorption selectivity between different adsorbents [108]. The largest issue of this approach is still a low uptake capacity, which has also been pointed out in the gasoline section. The group of Mochida has reported an interesting approach to remove refractive sulphur species, *viz.* applying high surface-area active carbon containing a high amount of oxygen atoms. Such a carbon seems to be selective in removing the more refractive sulphur species. They suggest therefore to apply this adsorption process prior to HDS. The uptake capacity is a point of concern, which should be investigated.

Another important issue in the adsorption approach is the waste treatment of organic sulphur molecules released at the end of the process.

3.4. Extraction

Extraction of organic sulphur compounds from diesel feed by a variety of extractants, from common polar organic solvents to ionic liquids, is discussed in many reports. Most popularly used liquid solvents are acetonitrile, lactones like gamma butyrolactone, DMF, N containing solvents like amines and pyrrolidones, or sulphur containing solvents like DMSO and sulpholane. It appears that a selective extraction of aromatic sulphur compounds from diesel is not straightforward. This comes from the fact that the polarity of such aromatic sulphide type compounds is too close to that of aromatic hydrocarbon molecules of similar structures without a sulphur atom. The experimental results of liquid extraction of organic solvents indeed demonstrate a poor removal of sulphur compounds from the feed ($\sim$50% at most), and also a high amount of co-extraction of aromatic hydrocarbon molecules, leading to a high loss of feed volume.

A better approach to effectively remove sulphur in extraction is to first oxidize sulphur compounds prior to extraction, as already discussed in the previous section ‘oxidative desulphurization’. The polarity of sulphur compounds becomes substantially higher, and thus the partition coefficient of the sulphur molecules in the polar solvent is much increased. Tam and Kitrell have already reported in 1990 that oxidation prior to extraction leads an increased sulphur removal with a better volume retention of the hydrocarbon feed. The extent of co-extraction of the feed is, however, still regarded as high (*e.g.*, 10–20%). That high volume of the diesel feed comes out as a high sulphur product stream containing sulphone molecules, which cannot be directly used as a marketable product. It demands a spare capacity in HDS or coker units.

The use of a very different type of extractant, namely ionic liquid, is reported by the group of Wasserscheid. An ionic liquid is a non-volatile organic liquid salt, which potentially can extract sulphur and also organic nitrogen compounds in fuels by its polarity. Reference [109] gives a good recent overview on the desulphurization with different types of ionic liquids, particularly on the most promising water-stable and less costly [BMIM][$OcSO_4$] (*i.e.*, 1-*n*-butyl-3 methylimidazolium octylsulphate) type. Given the poor extraction of alkylthiols and sulphides, the formation of liquid-clathrates and π–π interaction is assumed to be the main driving force for extraction [109]. Interestingly, they indicated that the extraction of 4-methylDBT and 4,6-dimethylDBT proceed almost as efficiently as that of DBT. Furthermore, nitrogen compounds are found to be more efficiently extracted than sulphur compounds. The problems of the ionic liquid process are the limited extraction efficiency of sulphur compounds, cross-solubility of hydrocarbons and the regeneration of expensive ionic liquid compounds. With respect to the extraction efficiency, they have, for instance, proposed a 10 steps extraction to reduce sulphur content of 300 toward $<$10 ppmw [110]. Another issue is cross-solubility of hydrocarbons, as pointed out for [BMIM][$OcSO_4$] [109]. As expected, the oxidation of sulphur compounds to sulphones is found to improve the extraction selectivity/efficiency of ionic liquids as well [111]. In all, ionic liquids do not at present appear to have the edge over the more traditional extractants (extractant mixtures).

3.5. N adsorption

A totally different approach to achieve deep desulphurization is to remove the HDS inhibitors like organic nitrogen compounds upfront in order to promote the deep desulphurization of subsequent HDS. Such upstream removal of nitrogen compounds has been taken to the pilot-plant stage by SK Corporation in South Korea [112]. They claim that they can remove nitrogen compounds so efficiently that the production of 10 ppmw S diesel becomes relatively easy with the standard HDS units. Their technical data have, however, not been extensively published, and since 2003 no further developments seem to have taken place. For the same approach, Haldor–Topsoe has also published a patent where the use of spent FCC catalyst is named as efficient and economical nitrogen adsorbent [113].

Other types of adsorbents have also been reported for nitrogen removal. Macaud et al. reported the use of tetranitrofluorenone (TENF) on polymer (*e.g.*, polystyrene) as efficient adsorbent for removing nitrogen compounds [114], which group also patented the same with IFP/Total Fina as heterogenized π-acceptor [115]. Furthermore, it is also noticed that adsorbents reported for sulphur removal are reported again for nitrogen removal. In such reports, it is seen that the sulphur removal adsorbents can actually remove nitrogen compounds more efficiently than sulphur compounds. Such cases are seen in the work of Mochida reporting the active carbon type adsorbents first for sulphur removal then later for removal of nitrogen compounds. A similar case is $Cu^{+-}Y$, reported from the group of Hernandez-Maldonado and Yang [116].

Although nitrogen pre-adsorption is conceptually simple enough, there are a few things to be considered. In the first place, there is the question of the uptake capacity of the nitrogen adsorbent, and another is the assumed feed flexibility. Diesel fuels tend to contain a few hundred ppmw of nitrogen compounds. The uptake capacity therefore should be sufficiently high. In addition, some feeds contain more nitrogen than others. It has also to be realised that one has to do something with the spent, N-loaded, adsorbent, which greatly complicates matters. And then there is the issue of how deeply the adsorbent needs to denitrogenize the feed in order to make the production of $<$10 ppmw S effluent in the subsequent process of HDS that much easier. Further complications here are that if [N] becomes very low, the HDS catalyst might start to deeply hydrogenate the feed [117], which is often undesirable because of the consequent high hydrogen consumption, and that if the [N] ex-adsorption column is not steady, the HDS unit may become difficult to operate. These are matters for further investigation, but for the time being it would appear that present-day HDS catalysts can cope quite well without the N pre-removal trick.

3.6. Miscellaneous

Quite a few creative alternative approaches have been proposed to rid diesel of its sulphur. As in the case of gasoline desulphurization, attempts have been made to precipitate the sulphur compounds, which can then be easily separated from the diesel product. One such example is the use of a π-accepter like TENF (2,4,5,7 tetranitrofluorenone), which forms insoluble charge transfer complexes when reacting with sulphur compounds [118]. Although TENF showed an interesting stronger complexation to DBT than to BT, desulphurization ratio is still low like 12% and the complexation efficiency is not high. Note that the same authors have made an effort to support TENF on polymers to apply that as sulphur or nitrogen adsorbents [114]. Another chemical approach is reported by Shiraishi et al. for reacting aromatic sulphur species in diesel with Chloramine T (sodium *N*-chloro-*p*-toluenesulphonamide) to produce *N*-tosylsulphimides (RS=N-Ts) in the presence of methanol [119]. N-tosylsulphimide can be removed in the methanol phase, which can be precipitated when water is added to the methanol phase. The drawback of this method is, however, a side reaction of chlorination of aromatics. And as a general issues of precipitation, the consumption of expensive chemicals and the treatment of organic sulphur waste should be noted.

As mentioned earlier, the low reactivity of highly aromatic sulphur compounds is the core issue in diesel desulphurization. Given this aspect, another possible approach to take is to apply an energy source, which is powerful enough to decompose sulphur compounds. One such approach is the application of microwaves. Several patents describe this methodology [120–122]. Patents of Carnegy Mellon University report hydrocracking and hydrotreating effects, when a hydrocarbon stream containing sulphur species is mixed with catalyst (*e.g.*, Cu, Fe metal), microwave sensitizers (*e.g.*, NiO), desulphurizing additives (*e.g.*, $CaCO_3$) and solid hydrogen sources (*e.g.*, metal hydrides) and exposed to microwave energy. This looks anything but simple, but it would be nice to see further technical results to support the beneficial effect of this approach.

As a more powerful energy source, X-rays, can be also applied [123]. A mixture of a hydrocarbon feed and a homogeneous catalyst, $AgNO_3$, is irradiated with X-rays, and the resulting metal sulphides are collected, and silver is regenerated to reuse it as $AgNO_3$. The process economy and practicality of this method could be important issues.

Another interesting, indeed for an electrochemist seductive, chemical approach is to apply metallic Na to remove sulphur atoms from organic molecules. This can be written as, for instance, $Na + DBT \rightarrow biphenyl + Na_2S_4$. This methodology has actually long been known, *viz.* since 1929 [124], and has been particularly well studied in the Exxon lab [125], but a big issue has been the regeneration of the sodium and the practicality of a Na solution. The new firm Trans Ionics, founded by a former Exxon researcher, Dr. R.C. Schucker, is looking into the possibility of actually applying this process, and they reported recently that they can successfully regenerate the sodium metal electrochemically, in a set-up that reminds one of the Na/S battery of yesteryear (see Fig. 12). It will be interesting to follow the further development of the process. While we are on the subject, another firm, SiGNa, recently reported that they can prepare silica supported Na or K metal, which can be handled easier than alkali metal in solution form [126]. Although the chemical activity seems to be weaker than original Na metal solution, it can possibly offer an important input for the potential growth of this approach.

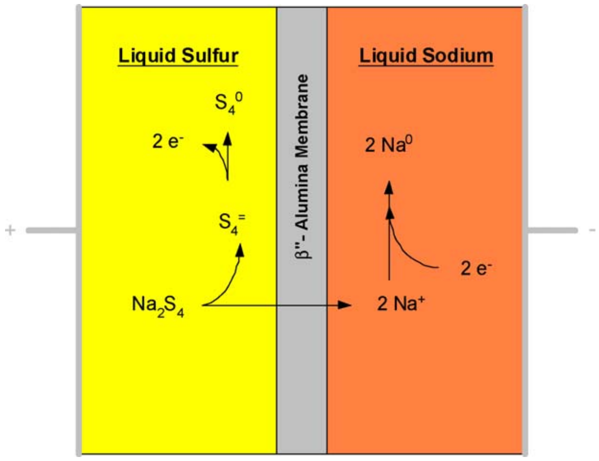


Fig. 12. Electrochemical regeneration of sodium from sodium sulphides.

4. Concluding remarks

It would appear that for the time being the classical hydrotreating options and their offshoots still hold the field of transportation-fuel desulphurization. These processes are relatively simple, robust and flexible, and the corresponding catalysts are still susceptible to improvement. A lot of effort is still being spent on this latter aspect, both in industry and in academia. Nevertheless, in the gasoline area a few of the possible alternatives did achieve commercial status, *e.g.*, S-Zorb, but their popularity does not even approach that of the commercialized desulphurization alternatives, CD-Hydro/CD-HDS(+), PrimeG(+) or Scanfining. In the diesel area, only the oxidative desulphurization method has come anywhere near commercialization, and then only as an after-treatment option. If, however, sulphur specs are going to be much lower than <10 ppmw, *e.g.*, <1 ppmw, then polishing processes may come into their own, either at refineries, or conceivably at depots. Which of the alternative options would then be the most attractive one(s) is an interesting question.

Acknowledgement

Authors acknowledge Dr. Jacques Dirkx for very useful discussions.

References

[1] I.V. Babich, J.A. Moulijn, Fuel 82 (2003) 607.

[2] C. Song, X. Ma, Appl. Catal. B 41 (2003) 207.

[3] C. Song, Catal. Today 86 (2003) 211.

[4] S. Brunet, D. Mey, G. Pérot, C. Bouchy, F. Diehl, Appl. Catal. A 278 (2005) 143.

[5] G.K. Chitnis, J.A. Richter, T.L. Hilbert, M.J. Dabkowski, I.A. Kuwari, N.A. Kuwari, M. Sherif, Commercial Octogain^{sm} unit provides zero sulphur gasoline with higher octane from a heavy cracked naphtha feed, NPRA (2003) AM03-125.

[6] (a) K. Rock, S. Shorey, Long term reliability, Hydrocarbon Eng. (2004) 45;
(b) K. Rock, S. Shorey, Producing low sulphur gasoline reliably, NPRA (2003) AM03-122.

[7] Q. Debuisschert, J.L. Nocca, PrimeG+^{TM} commercial performance of FCC naphtha desulphurization technology, NPRA (2003) AM03-26.

[8] N.H. Sweed, E.S. Ellis, PTQ Autumn (2001) 45.

[9] (a) K. Tawara, T. Nishimura, H. Iwanami, T. Nishimoto, T. Hasuike, Ind. Eng. Chem. Res. 40 (2001) 2367;
(b) K. Tawara, T. Nishimura, H. Iwanami, Sekiyu Gakkaishi 43 (2000) 114.

[10] C. Tucker, E. Sughrue, J. Vanderlaan, Production of ultra-low sulphur fuels: today and tomorrow, NPRA (2003) AM-03-48.

[11] G. Germana, D. Abbott, U. Turuga, Continued innovation, Hydrocarbon Eng. (2004) 35.

[12] For instance, US2003188993, US20040048743, US20040004029, US20030232723, US20030070966, US20030203815, US20030113250, US20030111389, US20030064889, US2003018303, US20040007498, US20040007130 and US2003114299 in 2003–2004 only.

[13] R.P. Gupta, B.S. Turk, Research Triangle Institute, WO2002/22763.

[14] R.P. Gupta, B.S. Turk, US20050098478.

[15] (a) A.B.S.H. Salem, Ind. Eng. Chem. Res. 33 (1994) 336;
(b) J.A. Ali, Ph.D. thesis, The University of Aston, Birmingham, December 1987.

[16] R.L. Irvine, D.M. Varraveto, Adsorption process for removal of nitrogen and sulphur, PTQ Summer (1999) 37.

[17] R.L. Irvine, US5730860, 1998.

[18] D.L. Rehms, Am. Chem. Soc. Fuel Chem. Div. Prepr. 47 (2) (2002) 454.

[19] R.A. Frye, E.M. Mophett, D.L. Rehms, US 6531052, 2002.

[20] R.T. Yang, Catal. Rev. 46 (2004) 111.

[21] F.H. Yang, A.J. Hernandez-Maldonado, R.T. Yang, Sep. Sci. Technol. 39 (2004).

[22] A.J. Hernandez-Maldonado, R.T. Yang, J. Am. Chem. Soc. Commun. 126 (2004) 992.

[23] A.J. Hernandez-Maldonado, R.T. Yang, Ind. Eng. Chem. Res. 42 (2003) 123.

[24] X. Ma, M. Sprague, L. Sun, C. Song, A.C.S. Fuel Chem. Div. Prepr. 47 (2) (2002) 452.

[25] D. Richardeau, G. Joly, C. Canaff, P. Magnoux, M. Guisnet, M. Thomas, A. Nicolaos, Appl. Catal. A 263 (2004) 49.

[26] X. Ma, S. Velu, J.H. Kim, C. Song, Appl. Catal. B 56 (2005) 137.

[27] X. Ma, M. Sprague, C. Song, Ind. Eng. Chem. Res. 44 (2005) 5768.

[28] B.D. Alexander, G.A. Huff, V.R. Pradhan, W.J. Reagan, R.H. Cayton, BP Amoco, US 6024865.

[29] F. Diehl, L. Magna, B.H. Olivier, D. Uzio, French patent, FR 2840916.

[30] X. Zhao, G. Krishnaiah, T. Cartwright, 'S-Brane^{TM} Technology Brings Flexibility to Refiners' Clean Fuel Solutions', NPRA paper, 2004, AM-04-17.

[31] J. Gentry, T. Khanmamedov, R.W. Wytcherley, Profitable desulphurisation, Hydrocarbon Eng. (2002).

[32] S. Kumar, J. Gentry, Hydrocarbon Eng. (2003) 27.

[33] Y. Shiraishi, K. Tachibana, Y. Taki, T. Hirai, I. Komasawa, Ind. Eng. Chem. Res. 40 (2001) 1225.

[34] R.C. Schucker, W.C. Baird, Jr., ExxonMobil, US6274026, 2001.

[35] N.K. Nag, A.V. Sapre, D.H. Broderick, B.C. Gates, J. Catal. 57 (1979) 509.

[36] M. Houalla, D.H. Broderick, A.V. Sapre, N.K. Nag, V.H.J. de Beer, B.C. Gates, H. Kwart, J. Catal. 61 (1980) 523.

[37] M.J. Girgis, B.C. Gates, Ind. Eng. Chem. Res. 30 (1991) 2027.

[38] D.D. Whitehurst, T. Isoda, I. Mochida, Adv. Catal. 42 (1998) 362.

[39] C. Song, C. Hsu, I. Mochida (Eds.), Chemistry of Diesel Fuels, Taylor and Francis, New York, 2000, p. 128.

[40] T. Koltai, M. Macaud, A. Guevara, E. Schulz, M. Lemaire, R. Bacaud, M. Vrinat, Appl. Catal. A 231 (2002) 253.

[41] C. Kwak, J.J. Lee, J.S. Bae, S.H. Moon, Appl. Catal. B 35 (2001) 59.

[42] S.K. Bej, S.K. MaiFy, U.T. Turuga, Energy Fuels 18 (2004) 1227.

[43] (a) D. Genuit, Afanasiev, M. Vrinat, J. Catal. 235 (2005) 302;
(b) J.H. Kim, X. Ma, C. Song, Y. Lee, S.T. Oyama, Energy Fuels 19 (2005) 353.

[44] J.N. Armor, Appl. Catal. A 282 (2005) 1.

[45] R.D. Key, J. Laurent, M.D. Ackerson, J. Hallock, NPRA meeting, San Antonio, 2003, AM-03-11.

[46] Hydrocarbon Process., August 2005, p. 51.

[47] C. Schmitz, L. Datsevitch, A. Jess, Chem. Eng. Sci. 59 (2004) 2821.

[48] J. Williams, Trans. Faraday Soc. 24 (1928) 245.

[49] J.H. Baxendale, M.G. Evans, G.S. Park, Trans. Faraday Soc. 42 (1946) 155.

[50] E.D. Guth, A.F. Diaz, US3847800, 1974.

[51] P.S. Tam, J.R. Kitrell, US 4485007, 1984.

[52] P.S. Tam, J.R. Kitrell, J.W. Eldridge, Ind. Eng. Chem. Res. 29 (1990) 321.

[53] L. Skattebol, B. Oulette, S. Solomon, J. Org. Chem. 32 (1967) 3111.

[54] J.L. Courtney, K.F. Swansborough, Rev. Pure Appl. Chem. 22 (1972) 47.

[55] B.M. Trost, D.P. Curran, Tetrahedron Lett. 22 (1981) 1287.

[56] E. Ahnonkitpanit, P. Prassassarakich, Fuel 68 (1989) 819.

[57] D. Alexander, J. Nobel, Anglo Iranian Oil, British Patent 713740, 1954.

[58] A.B. Webster, R. Righy, Shell Oil company, US patent 3163593, 1964.

[59] B.N. Heimlich, T.J. Wallace, Tetrahedron 22 (1966) 3571.

[60] J.F. Ford, T.A. Rayne, D.G. Adlington, British Petroleum, US patent 3341448, 1967.

[61] E.L. Cole, R.F. Wilson, S. Herbstman, Texaco, US patent 3551328, 1970.

[62] S. Otsuki, T. Nonaka, N. Takashima, W. Quian, A. Ishihara, T. Imai, T. Kabe, Energy Fuels 14 (2000) 1232.

[63] P. De Filippis, M. Scarsella, Energy Fuels 17 (2003) 1452.

[64] J.M. Campos-Martin, M.C. Capel-Sanchez, J.L.G. Fierro, Green Chem. 6 (2004) 557.

[65] D. Wang, E.W. Qian, H. Amano, K. Okata, A. Ishihara, T. Kabe, Appl. Catal. A 253 (2003) 91.

[66] L.F. Ramirez-Verduzco, E. Torres-Garcia, R. Gomez-Quintana, V. Gonzalez-Pena, F. Murrieta-Guevara, Catal. Today 98 (2004) 289.

[67] F.M. Collins, A.R. Lucy, C. Sharp, J. Mol. Catal. A Chem. 117 (1997) 397.

[68] G. Yu, S. Lu, H. Chen, Z. Zhu, Energy Fuels 19 (2005) 447.

[69] V. Hulea, F. Fajula, J. Bousquet, J. Catal. 198 (2001) 179.

[70] (a) T.F. Yen, H. Mei, S.H.M. Lu, WO 02/26916 A1.;
(b) R.W. Gunnerman, WO 02/074884.;
(c) R.W. Gunnerman, P.S. Moote, M.T. Cullen, US 2003/005, 1988.

[71] P. Li, S. Zhao, L. Kong, J. Li, Y. Zhai, China Petro. Proc. Petr. Tech. 3 (2004) 51.

[72] (a) R.E. Levy, A.S. Rappas, F.-M. Lee, V.P. Nero, S.J. DeCanio, AIChE 2002, Spring Meeting, New Orleans, paper number no. 36C, March 2002.;
(b) R.E. Levy, A.S. Rappas, S.J. Decanio, V.P. Nero, NPRA meeting, 2001, AM-01-10.

[73] R.E. Levy, A.S. Rappas, C. Sudhakar, V.P. Nero, S.J. Decanio, WO2003014266.

[74] P. Geneste, P. Amblard, M. Bonnet, P. Graffin, J. Catal. 61 (1980) 115.

[75] F.M. Collins, A.R. Lucy, D.J.H. Smith, British Petroleum, EP 0482841 A1.

[76] H. Mei, W. Mei, T.F. Yen, Fuel 82 (2003) 405.

[77] Y. Hangun, L. Alexandrova, S. Khetan, C. Horwitz, A. Cugini, D.D. Link, B. Howard, T.J. Collins, ACS Petr. Chem. Div. Prepr. 47 (2002) 42.

[78] R. Flores, A. Rodas, W. Chavarria, Prepr. Pap.—Am. Chem. Soc. Div. Fuel Chem. 49 (2004) 341.

[79] M. Ikura, M. Stanciulescu, US20030075483.

[80] J. Palomeque, J.M. Clacens, F. Figueras, J. Catal. 211 (2004) 103.

[81] US2002189975, Petroleo Brasileiro SA.

[82] JP2002363574, Idemitsu Kosan.

[83] K. Yazu, Y. Yamamoto, T. Furuya, K. Miki, K. Ukegawa, Energy Fuels 15 (2001) 1535.

[84] F.J. Liotta, Y.Z. Han, NPRA (2003) AM-03-23.

[85] C. Gosling, R. Gatan, A. Cavana, D. Molinari, NPRA (2004) AM-04-48.

[86] A.C. Corma, M. Domine, C. Martinez Sanchez, EP 1342772 A1.

[87] K.J. Stanger, J.W. Wiench, M. Pruski, J.H. Espenson, G.A. Kraus, R.J. Angelici, J. Mol. Catal. 243 (2006) 158.

[88] D. Chapados, S.E. Bonde, W.L. Gore, G. Dolbear, E. Skov, NPRA annual meeting, San Antonio, March 2000, AM-00-25.

[89] J.F. Ford, V.O. Young, Polym. Prepr. Am. Chem. Soc. Divi. Polym. Chem. 10 (1965) C111.

[90] S. Rozen, Y. Bareket, J. Org. Chem. 62 (1997) 1457.

[91] W. Su, Tetrahedron Lett. 35 (1994) 4955.

[92] J.H. Sherman, US20020079272A1.

[93] M.A. Ledile, T.V. Howell, Tetrahedron Lett. 10 (1976) 785.

[94] (a) S. Murata, K. Murata, K. Kidena, M. Nomura, Energy Fuels 18 (2004) 116;
(b) M. Nomura, S. Murata, JP 2004-168663, 2004.

[95] J. Thirugnanasampanthar, R. Xu, F.M. Dautzenberg, WO2005/116169.

[96] J.W. Gues, C.M.A.M. Mesters, R.J. Schoonebeek, WO2005/030638 A1.

[97] L.I. Rossi, R.H. Rossi, Appl. Catal. A 267 (2004) 267.

[98] D.J. Boron, W.R. Deever, R.M. Atlas, B.L. McFarland, J.A. Meyer, A.R. Johnson, NPRA meeting, San Antonio, 1999, AM-99-54.

[99] C. Song, C.S. Hsu, I. Mochida (Eds.), Chemistry of Diesel Fuels, Taylor and Francis, New York, 2000 , p. 187 (Chapter 9).

[100] W.E. Kleinjan, A. de Keizer, A.J.H Janssen, Biologically produced sulphur, in: R. Steudel (Ed.), Topics in Current Chemistry, vol. 230, 2003, p. 167.

[101] Waseda University, JP2004283120.

[102] L. Mingfang, G. Zhongxuan, X. Jianmin, L. Huizhou, C. Jiayong, J. Chem. Technol. Biotechnol. 78 (2003) 878.

[103] S. Maghsoudi, M. Vossoughi, A. Heirolomoom, E. Tanaka, S. Katoh, Biochem. Eng. J. 8 (2001) 151.

[104] P. Slater, Johnson, D. Kidd, Phillips's S-Zorb Diesel sulphur removal technology, NPRA, 2002, AM-02-46.

[105] For instance, JP2003-268386 (New Nippon Oil), JP2003-253270 (Nippon Oil), JP2004-75778 (Idemitsu Kosan), EP1-224970 (Cosmo).

[106] G.B. McVicker, W.C. Baird Jr., J.J. Schorfheide, M. Daage, D.P. Klein, E.S. Ellis, D.E.W. Vaughan, J. Chen (ExxonMobil), US6193877.

[107] C. Song, X. Ma, M. Spragues, V. Subramani, WO2003068892.

[108] J.H. Kim, X. Na, A. Zhou, C. Song, Catal. Today 111 (2006) 74.

[109] J. Eβer, P. Wasserscheid, A. Jess, Green Chem. 6 (2004) 316.

[110] A. Jess, P. wasserscheid, J. Esser, DGMK-conference, Innovation in the manufacture and use of hydrogen, Dresden, (2003), p. 313.

[111] R.E. Schoonover, US20030085156.

[112] W.S. Min, K.I. Choi, S.Y. Khang, D.S. Min, J.W. Ryu, K.W. Yoo, H. Kim, US patent 6248231, 2001.

[113] Whitehurst et al., EP 1 057879 A2, 2000.

[114] M. Macaud, E. Schulz, M. Vrinat, M. Lamaire, Chem. Commun. (2002) 2040.

[115] R.A. Favre, M. Lambire et al., FR2837212.

[116] A.J. Hernandez-Maldonado, R.T. Yang, Angew. Chem. Int. 43 (2004) 1004.

[117] R. Prins, Adv. Catal. 46 (2001) 399.

[118] T. Koltai, M. Macaud, A. Milenkovic, E. Schulz, M. Lamaire, M. Vrinat, Catal. Lett. 83 (2002) 143.

[119] Y. Shiraishi, T. Naito, T. Hirai, I. Komasawa, Ind. Eng. Chem. Res. 41 (2002) 4376.

[120] D.A. Purta, M.A. Portnoff, F. Pourarian, M.A. Nasta, J. Zhang, US20040077485.

[121] D.A. Purta, M.A. Portnoff, F. Pourarian, M.A. Nasta, J. Zhang, US20040074759.

[122] V. Scharivker, T. Honeycutt, WO02/086022.

[123] Y. Ayukawa, M. Ono, Rigaku, JP2002-338971 or EP1256618.

[124] Hofsass et al., Int. Bergin-Compagnie, US1729943, 1929.

[125] For instance, Bearden et al., US4076613, 1978; Howard et al., US4062762, 1977.

[126] J.L. Dye, K.D. Cram, S.A. Urbin, M.Y. Redko, J.E. Jackson, M. Lefenfeld, J. Am. Chem. Soc. 127 (2005) 9338.