Oxidative desulphurisation of oils via hydrogen peroxide and heteropolyanion catalysis

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Abstract

Oxidation of dibenzothiophene with hydrogen peroxide using phosphotungstic acid as catalyst and tetraoctylammonium bromide as phase transfer agent in a mixture of water and toluene has been studied. Catalysed decomposition of hydrogen peroxide competes with dibenzothiophene oxidation but by choice of suitable conditions yields of dibenzothiophene sulphone approaching 100% may be obtained. Treatment of gas oils with this technology shows that all the sulphur compounds present are oxidised by this catalyst system and highly substituted dibenzothiophenes are the most readily oxidised of species containing a thiophene nucleus. Oxidised sulphur compounds can be separated from the oil by adsorption on silica gel. The use of oxidation and adsorption in a process for desulphurisation of gas oils is discussed.

Keywords: Catalysis; Desulphurisation; Dibenzothiophene; Oxidation; Phase transfer

1. Introduction

Petroleum oils used as feedstocks for diesel oils are middle distillates in the 180–400°C boiling range. They include straight run gas oils, largely paraffinic, ranging from light gas oils to heavy gas oils that usually contain from 1 to 3 wt% sulphur. Various processes are used to upgrade heavier petroleum fractions to highly aromatic oils also in the middle distillate boiling range, containing up to 3 wt% sulphur. The sulphur compounds present in the various oils are mostly aliphatic sulphides, benzothiophenes and dibenzothiophenes.

Sulphur compounds in fuels are a major source of pollution. On combustion they are converted to sulphur oxides which, in turn, give rise to sulphur oxyacids that contribute to acid rain. Recently, legislation has been introduced to reduce the levels of permitted sulphur in diesel fuel. Table 1 shows that this is a world-wide trend.

The requirement to produce diesel fuels with very low levels of sulphur has stimulated much work in the area of hydrodesulphurisation (HDS). Possible ways of increasing the effectiveness of HDS at producing low sulphur prod-

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Table 1
Legislation on sulphur in diesel

Country	Date	Sulphur wt% (max)
Europe	1993	0.3
Europe	1994	0.2
Europe	1996	0.05
USA	1993	0.3
USA	1996	0.05
Japan	1996	0.2
Japan	1997	0.05
Sweden	1996	0.001 (class 1)
Sweden	1996	0.005 (class 2)

uct include use of higher temperatures, higher pressures, more active catalysts, longer residence times or the use of alternative technologies such as mild hydrocracking. All of these methods incur a cost penalty and this stimulated our interest in alternative forms of desulphurisation.

Oxidation of petroleum oils has a long history. Many different types of oxidants have been used, including $HNO_3/AcOH$ [1–3], NO/NO_2 [4], NO_2 [5], HNO_3 [6], H_2O_2/H_2SO_4 [7], Bu^tOOH [8] and O_3 [9]. The objectives of oxidation have been varied in that some have been aimed at desulphurisation while others have been aimed at cetane number enhancement. Use of nitrogen oxides as oxidising agent can have the double effect of oxidising the sulphur compounds and nitrating the aromatic compounds present in the oil: nitroaromatics are thought to have high cetane numbers. All of the oxidation methods used to date have drawbacks of one form or another, e.g. poor activity, poor selectivity, loss of catalyst or cost of catalyst [2].

The aim of the present work was to produce a highly selective, inexpensive and/or recoverable catalyst for the oxidation of sulphur compounds present in oil. The oxidant had to be inexpensive and give by-products that would not adversely affect the product or cause environmental problems. Further, a process for removal of sulphur compounds from the oxidised oil was sought.

2. Experimental

All chemicals were commercial products used as supplied. H_2O_2 (30 vol%) was diluted with water as necessary. Silica gel adsorbent was Merck Silica Gel 60, totally mesoporous (surface area = 475 m^2/g; pore volume = 0.77 cm^3/g).

Oxidation of dibenzothiophene was monitored by gas chromatography on a GP 10% SP 2300 on 80/100 Supelcoport column on a Pye Unicam PU4500 chromatograph equipped with a flame ionisation detector. Consumption of H_2O_2 was followed by titrimetric analysis with $Ce(IV)(SO_4)_2$ (0.1 M in 7 wt% sulphuric acid) as the titrant and ferroin as the indicator [10].

Sulphur concentration in diesel samples was determined by ICP or XRF analysis. Sulphur-specific gas chromatography was carried out using capillary gc in combination with a Hewlett Packard atomic emission detector.

2.1. Typical procedure for the oxidation of dibenzothiophene

A glass reactor vessel fitted with an overhead stirrer was charged with a solution of dibenzothiophene (1 g, 5.43 mmol) and tetraoctylammonium bromide (2 g, 0.366 mmol) in toluene (40 g). Hydrogen peroxide (100 g 30 vol% solution) was added and the mixture stirred at 500 rpm and heated to 50°C. Phosphotungstic acid (0.2 g, 0.07 mmol) was added to initiate the reaction and the progress of the reaction was monitored by at intervals sampling and analysing the organic phase. The reaction was continued until > 90% of the dibenzothiophene had been oxidised. Upon cooling, a white solid which was identified as dibenzothiophene sulphone precipitated from solution.

The reaction order and activation energy for decomposition of hydrogen peroxide were determined by experiments in which the substrate (dibenzothiophene) was absent. Plots of $([H_2O_2]_{initial} - [H_2O_2])$ versus time to > 90% completion showed zero order kinetics with all regression coefficients > 0.998. Activation en-

ergy was determined by experiments within the temperature range 40–75°C.

2.2. Oxidation of gas oil

A two litre glass reactor was charged with 776.8 g of diesel oil (UK winter grade from BP's Grangemouth refinery, 0.23 wt% S, essentially straight run, non-hydrotreated gas oil), phosphotungstic acid (2.5 g in 15 g water), 'Aliquat 336' (tri-n-octylmethylammonium chloride, 4.15 g) and a solution of H_2O_2 (49.8 g of 100% equivalent in 388.9 g water). The contents were heated to 60°C and stirred at that temperature for four hours, then cooled to 20°C. The bulk diesel phase was separated from the aqueous phase and a small precipitate of dark brown oil (5 g). The bulk phase and the precipitate were found to contain 0.255 and 1.87 wt% S respectively.

2.3. Distillation of oxidised gas oil

Distillation of oxidised gas oil was carried out using a column packed with stainless steel gauze (Porapak) giving an efficiency of about 15 theoretical plates. The method used was as described in ASTM D2892 although smaller scale equipment was used.

2.4. Silica adsorption of oxidised gas oil

A glass column (1 × 30 cm) was filled with silica (5 g) that had been dried in a vacuum oven overnight. Oxidised diesel (75 g) was loaded onto the column and fractions (2 g) of the effluent were collected. The column was run under a slight pressure of nitrogen to achieve a flow rate of about 25 g/h. Thirty three fractions were collected and also a further fraction (2.7 g) by allowing the column to run dry, leaving 6.3 g of diesel entrained in the silica.

3. Results and discussion

It was thought that the problem of catalyst loss during the treatment of oils could be mitigated by the use of two-phase catalysis, especially if most of the catalyst resided in the non-oil phase. Since a number of epoxidation systems employing biphasic catalysis have recently been developed, it was decided to employ similar catalysts for attempted oxidation of sulphur compounds in oil. The system of choice proved to be similar to the Venturello epoxidation system, employing a phase transfer agent, aqueous hydrogen peroxide as the oxidant and phosphotungstic acid as the catalyst [11].

3.1. Dibenzothiophene oxidation

Dibenzothiophene was selected as a sulphur compound representative of those present in gas oils. A series of model reactions was carried out to optimise the reaction and in particular to minimise the consumption of hydrogen peroxide. Fig. 1 shows a typical reaction profile of
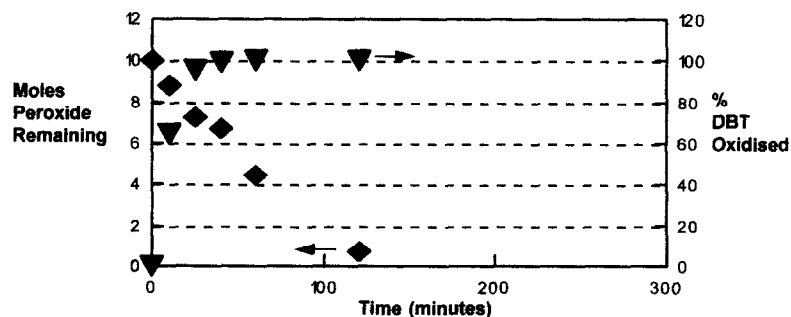

Fig. 1. Oxidation of dibenzothiophene.

hydrogen peroxide consumption and dibenzothiophene oxidation against time.

The results show that there appear to be two competing reactions: the oxidation of dibenzothiophene and the non-productive decomposition of hydrogen peroxide. This was confirmed by carrying out the reaction in the absence of dibenzothiophene substrate, when it was found that the decomposition of substrate was zero order in hydrogen peroxide, and non-linearly dependent on catalyst and phase transfer agent concentration. These results suggest that there is a fast reaction between the hydrogen peroxide and the catalyst to give a new species with a concentration independent of the hydrogen peroxide concentration and that the rate of peroxide decomposition is proportional to the concentration of the new species. A plot of $\log k$ versus $1/T$ for the decomposition reaction gave a straight line and the activation energy was calculated to be 50 kJ mol^{-1}, comparable with 71–76 kJ mol^{-1} for the uncatalysed reaction [12] and 42 kJ mol^{-1} for decomposition catalysed by ferrous ions [13].

The rate of oxidation of dibenzothiophene showed good second order kinetics, first order in hydrogen peroxide and dibenzothiophene: the second order rate constant at 293 K was found to be 9×10^{-5} 1 mol^{-1} s^{-1}. In the presence of a large excess of hydrogen peroxide the reaction followed pseudo first order kinetics and the rate constant followed the Arrhenius equation with an activation energy of 38 kJ mol^{-1}.

Overall, it may be seen that under suitable conditions the oxidation is effectively quantitative with virtually 100% selectivity based both on hydrogen peroxide and on dibenzothiophene.

3.2. Oxidation of diesel oils

The oxidation of diesel oils with nitric acid in glacial acetic acid was studied in detail by Eldridge et al. [1,3], who concluded that sulphur removal by oxidation is due to the formation of high-sulphur-containing residue, which results from the accelerated sedimentation of the oil from instability induced by nitric acid. Residues amounting to 6–13 wt% of the feed gas oil were precipitated, containing around 3% sulphur. Sulphur-specific gas chromatography showed that there were three classes of sulphur compound present, characterised by the different rates at which they oxidised and precipitated. Extraction of the bulk of the oxidised oil with γ-butyrolac-
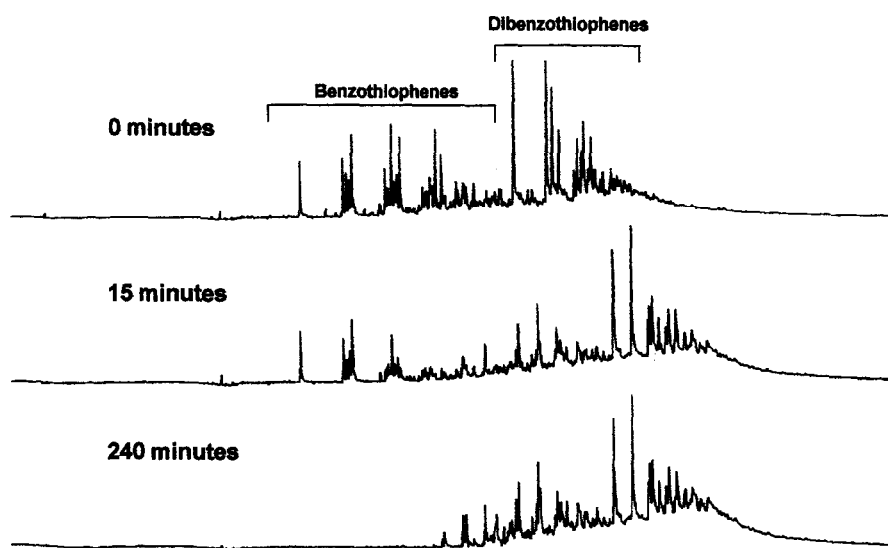

Fig. 2. Sulphur-specific GC of oxidative desulphurisation.

tone showed that the sulphur content could be reduced by up to 70% with a 90% yield of extracted oil.

In contrast, the oxidation with hydrogen peroxide and phosphotungstic acid catalyst in a biphasic system gave very little residue: less than 1% of the feed oil and containing just 1.9 wt% sulphur. The reaction was monitored using sulphur-specific gas chromatography. At the end of the reaction all the original sulphur compounds had reacted, to be replaced by new sulphur-containing compounds. During the reaction course there was no noticeable diminution in the amounts of sulphur compounds present (Fig. 2). The compounds present were identified as falling into two main groups, benzothiophenes and dibenzothiophenes, and the dibenzothiophenes reacted the faster. For both benzothiophenes and dibenzothiophenes it was observed that the more highly substituted species reacted the faster. These results are consistent with a number of studies that have been carried out on the oxidation of organic sulphur compound. For peracetic acid the ease of oxidation is RSR > RSAr > ArSAr > dibenzothiophene [14]. Studies on oxidation of dibenzothiophene with peroxybenzoic acid showed that oxidation to the sulphoxide is slower than oxidation of the sulphoxide to the sulphone [15]. Peracetic acid

oxidation of alkyl-substituted thiophenes showed that the relative reaction rates were thiophene (1), 2-methylthiophene (6.8), 2,5-dimethylthiophene (31) and 2,3,4,5-tetramethylthiophene (613) [16].

The reactivity of sulphur compounds in the oxidation of gas oil contrasts to the behaviour seen in hydrodesulphurisation. Fig. 3 shows a sulphur-specific chromatogram of a gas oil before and after hydrodesulphurisation. It can be seen that the benzothiophenes react more quickly than the dibenzothiophenes, and that increasing substitution increases resistance to reaction.

These results show that hydrodesulphurisation and oxidative desulphurisation are complementary processes in their reactivity. Those sulphur compounds that are hard to treat by hydrodesulphurisation are readily oxidised, and vice versa.

3.3. Distillation of oxidised oils

Sulphones have higher boiling points than the parent sulphide or thiophene compounds. A way of producing a cut of very low sulphur oil is, therefore, to oxidise an oil with a wide boiling range and then distil it and collect only the lower boiling fractions. Table 2 shows that this works well in practice, with the disadvantage
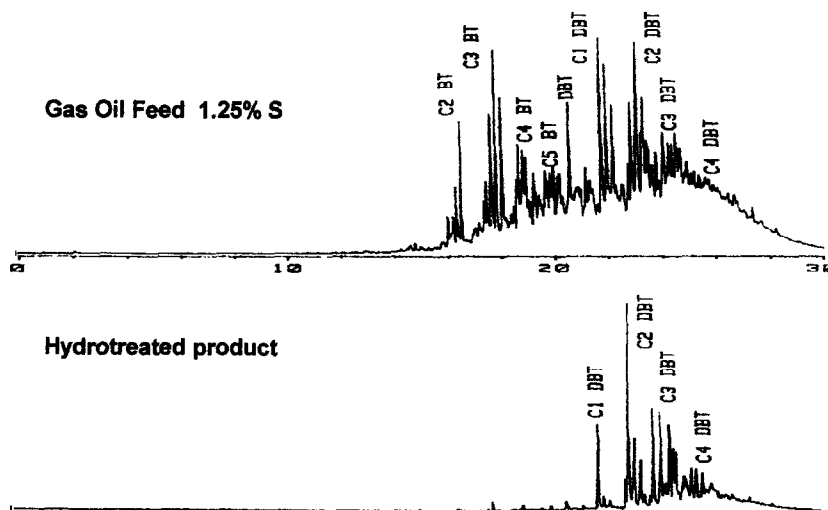

Fig. 3. Sulphur-specific GC of HDS.

Table 2
Distillation of straight run and oxidised gas oils

Fraction °C	Gas oil		Oxidised gas oil	
	yield (wt%)	sulphur (wt%)	yield (wt%)	sulphur (wt%)
IBP–210°C	14.10	0.025	14.25	0.005
210°C–300°C	46.15	0.187	43.75	0.041
300°C–330°C	18.60	0.319	19.00	0.18
330°C–342°C	6.45	0.460	7.05	0.25
342°C–FBP	14.50	0.497	15.35	0.86
IBP–210°C	14.10	0.025	14.25	0.005
IBP–300°C	60.25	0.149	58.00	0.032
IBP–330°C	78.85	0.189	77.00	0.069
IBP–342°C	85.30	0.210	84.05	0.084

IBP = initial boiling point. FBP = final boiling point.

Table 3
Hydrotreatment of gas oils

Residence time	0	1	2	3	4
% S in product	1	0.1	0.03	0.01	0.005
Desulphurisation	0	90	97	99	99.5

that a significant fraction of the oil is recovered as high boiling fractions high in sulphur.

3.4. Silica adsorption of oxidised oils

Sulphones are generally more polar materials than thiophenes and are likely to bond strongly to adsorbents like silica or alumina. It was found that column chromatography of untreated gas oils had negligible effect on the composition of the oils. However, chromatography of an oxidised oil containing 0.25 wt% sulphur showed that the oxidised sulphur compounds were strongly adsorbed to the silica and the eluate contained only 0.005 wt% sulphur until the column was saturated. (Fig. 4).

3.5. Utilisation of oxidative desulphurisation

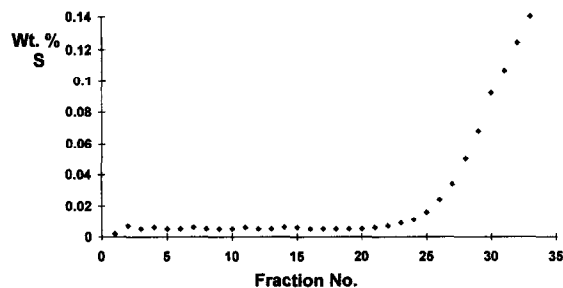The greatest cost involved in treating most gas oils by oxidative desulphurisation is the cost of the hydrogen peroxide. It was found in the oxidation of gas oils that four moles of hydrogen peroxide were consumed for every mole of sulphur oxidised (i.e. 50% selectivity based on hydrogen peroxide) which, at $1130/t for 100% equivalent hydrogen peroxide (price in 1980 [17]) equates to $4.5 to oxidise 0.1 wt% sulphur in one tonne of gas oil. Thus to oxidise all the sulphur compounds in an oil with 0.23 wt% sulphur would incur an oxidant cost of $10.4/t whereas, in contrast, a 1984 study showed that the average *total* cost to refineries to treat an oil with 0.23 wt% sulphur to a product with 0.05 wt% sulphur by non-oxidative methods was only $8/t [18].

Deep hydrodesulphurisation of gas oils (to less than 0.5 wt% sulphur) is difficult because the compounds remaining after conventional hydrodesulphurisation are resistant to reaction. This is reflected in the increased residence times needed to achieve deep desulphurisation, as shown in Table 3. Since the compounds remaining after HDS are particularly reactive towards oxidation, and the cost of hydrogen peroxide for oxidation is proportional to the amount of sulphur to be oxidised, sequential HDS and ODS treatments should be very effective. Fig. 5 shows a scheme for combining the two processes on

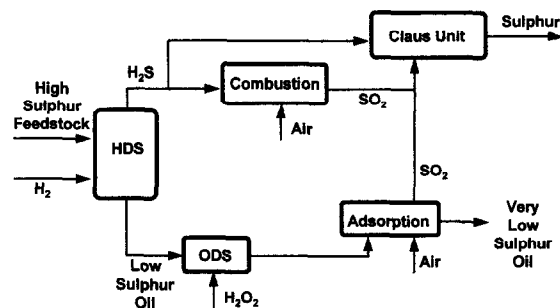Fig. 4. Adsorption of S compounds on silica.

Fig. 5. Integrated HDS-ODS plant.

one site. Two silica adsorbent columns are used: whilst one is treated with oxidised oils the other is regenerated by burning off the sulphur residues in a stream of air. The sulphur dioxide formed is sent to a Claus unit to react with hydrogen sulphide (formed from HDS) to produce elemental sulphur.

In summary, gas oils may be treated by oxidative desulphurisation to give product oils containing as little as 0.005 wt% sulphur. This process complements conventional hydrodesulphurisation and presents an alternative to the use of deep hydrodesulphurisation.

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