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# Deep desulphurization of gasoline and diesel fuels using non-hydrogen consuming techniques

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## Abstract

Desulphurization of FCC gasoline and diesel fuels has been investigated by chemical oxidation of sulphur containing compounds with hydrogen peroxide in the presence of an acid catalyst such as formic acid and acetic acid, followed by extraction of the oxidized compounds using acetonitrile. Oxidative desulphurization (ODS) of diesel fuel was found to be very promising approach for the reduction of up to 92% of sulphur at low temperature (50 °C) and atmospheric pressure. The direct extraction of diesel oil without any oxidation has resulted in about 45% sulphur removal, however such direct extraction also removed other aromatic hydrocarbons and affected the yield. The ODS is not successful with FCC gasoline due to the high olefinic content that tends to react with hydrogen peroxide to form epoxides. GC–MS technique was used to identify the sulphones during the oxidation of thiophenes. This study recommends that the oxidation extraction technique be used as an additional process to the hydrodesulphurization to enable the refiners to meet the future environmental sulphur regulations. The conventional hydrodesulphurization can be used to lower the sulphur content to few hundreds ppm. Then, the oxidation/extraction approach needs to be used to go for ultra-deep desulphurization as it may provide better mean and cost effective way in order to meet the future sulphur environmental requirements.

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## 1. Introduction

The sulphur content in the motor and diesel fuels is continuously reduced by regulations to lower levels. The current specification in Europe and the USA calls for a maximum sulphur content of 50 ppm in gasoline and diesel by 2005 [1,2], and this level will be reduced to below 10 ppm by the year 2010 [1]. The current industrial method for removal of sulphur from fuels is hydrodesulphurization (HDS), which requires high temperature and high pressure, making HDS a very costly option for deep desulphurization. Moreover, HDS is not effective for removing heterocyclic sulphur compounds such as dibenzothiophene (DBT) and its derivatives especially 4,6-dimethyldibenzothiophene (4,6-DMDBT). There are many research and development efforts both on the conventional hydrodesulphurization and on alternative methods such as

selective adsorption, biodesulphurization, oxidation/extraction (oxidative desulphurization) etc. for removing these refractory sulphur compounds from petroleum products [3–12].

Oxidative desulphurization (ODS) has been given much attention as an alternative technology for deep desulphurization. The ODS is basically a two-stage process, oxidation, followed by liquid extraction. In the ODS process, the sulphur-containing compounds are oxidized using appropriate oxidants to convert these compounds to their corresponding sulphoxides and sulphones. These are preferentially extracted from light oil due to their increased relative polarity [7,9,13,14]. Any unused oxidant that remains in the light oil can be removed by water washing and extracting. The oxidized compounds can be extracted from the light oil by using a non-miscible solvent.

Depending on the solvents used for extraction, the oxidized compounds and solvent are separated from the light oil by gravity separation or centrifugation. The light oil is water washed to recover any traces of dissolved extraction solvent and polished using other methods, such as absorption using silica gel and aluminum oxide. The solvent is separated from the mixture of solvent and oxidized compounds by a simple distillation for recycling and re-use. By using this process,

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the maximum sulphur removal is achieved with minimum impact on the fuel quality [14–18]. Many oxidants have been investigated which include peroxy organic acids, catalyzed hydroperoxides, inorganic oxidants such as inorganic peroxy acids, peroxy salts, ozone, etc. [14,16].

The development and application of oxidation/extraction method (ODS) are considered among the most desired options because they can lower the sulphur without negative impacts on capital investment. However, there are two major problems associated with ODS. First, the oxidants chosen do not always perform selectively. Some oxidants cause unwanted side reactions that reduce the quantity and quality of the light oil. The second problem is the selection of a suitable solvent for the extraction of the sulphur compounds. Using the wrong solvent may result in removing desirable aromatic/olefinic compounds from the fuel or extracting less than a desired amount of the sulphur compounds from the fuel, in either case, the consequences can be costly.

There is also no detailed work to define the appropriate conditions in terms of the optimum temperature, oxidants, catalysts, solvents/fuel ratio for extraction, and the impact of such solvents extraction on fuel quality. So the ODS approach still needs further research, especially in the area of designing the appropriate selective catalysts. The objective of this study is to address such concerns and provide a detailed mechanism of the above mild oxidation/extraction method.

## 2. Experimental work

### 2.1. Fuels

A sample of hydrotreated diesel was obtained from Saudi Rabigh Refinery and a FCC gasoline sample was obtained from Saudi Jeddah refinery.

### 2.2. Chemicals and solvents

Dibenzothiophene (DBT), formic acid 85%, hydrogen peroxide 30%, hydrochloric acid 47%, acetic acid 98%, HPLC grade hexane and toluene, 1-hexene 97%, and Sulphur standards were purchased commercially.

### 2.3. Preparation of the model compound and hydrogen peroxide mixture

A mixture of 0.5 g of DBT, 40 g of toluene and 59.5 g of hexane was prepared. Hydrogen peroxide and formic acid mixtures for all experiments were freshly prepared each time. A mixture of 11 g of 98% hydrogen peroxide and 21.6 g of 30% formic acid was prepared. Oxidation of the model compound was carried out at room temperature, 50 and 80 °C. The reaction of the DBT model was conducted initially at 50 °C using formic acid and hydrogen peroxide for about 2 h whilst stirring. Then, during the cooling process a white precipitate was formed. After washing and drying, the product was analyzed to determine the composition and structure of the product.

### 2.4. Acid selectivity

Three experiments using HCl, formic acid and acetic acid were conducted at 50 °C. In these experiments, acids were prepared and premixed in a 1:1 mole ratio, then immediately added to 50 ml of the DBT model compound and heated at 50 °C with continuous stirring. Samples were collected at different time intervals and analyzed by GC–MS. The DBT consumption was used to monitor the oxidation process.

### 2.5. Solvent selectivity

A 2.6 g of a mixture of 11 g of 30% hydrogen peroxide (wt%), and 21.6 g of 98% formic acid (wt%) was added to two samples of 100 ml of hydrotreated diesel. These amounts were used to obtain 1:1 mole ratio of each and 0.19 mole of each of them were used in the reaction process. The two samples were heated at 50 °C for 90 min. Then both samples were extracted with 15 ml of distilled water. The upper layer was submitted for total sulphur determination. Then, the top layer of each sample was separated. One sample was washed again with acetonitrile and one with methanol and the diesel layer of both samples were submitted to total sulphur determination.

### 2.6. Sulphones speciation in diesel

Hundred millilitres of hydrotreated gas oil (diesel) was treated with 2.6 g of a mixture containing 21 g of 98% formic acid and 11g of 30% hydrogen peroxide. The mixture was stirred and heated at 50 °C for 120 min. The aqueous acid phase was separated in a 150 ml separatory funnel and discarded. The oil phase was extracted with 100 ml of acetonitrile. The acetonitrile extract was washed twice with 50 ml of reagent grade hexane, and the washings discarded. The washed 100 ml extract was evaporated overnight in a stream of nitrogen.

### 2.7. The effect of acetonitrile on diesel quality

About 10, 20 and 50 ml of acetonitrile were added to three 50 ml samples of hydrotreated diesel separately. All were mixed well and left at room temperature for settling down for 1 h. The samples were separated and the volume of each layer was determined. The same experiments were repeated and left for settling down overnight and the volume for each layer was measured again.

## 3. Results and discussion

### 3.1. Physical–chemical properties of the fuels

Some of the general properties of FCC gasoline are given in Table 1. Sulphur speciation of FCC gasoline has been completed using gas chromatography–atomic emission detector (GC–AED) and gas chromatography–mass spectrometry (GC–MS), and by analyzing reference materials and standards including mercaptans, sulphides, thiophene, 2-methyl and 3-methyl thiophenes, benzothiophene, and methyl

Table 1  
Some chemical and physical properties of typical FCC gasoline

Test description	Test method	FCC gasoline
Total acidity (mg KOH/g)	D3242 or D974	0.051
Aromatics (FIA) (V%)	D-5134 M	16.9
Olefins (FIA) (V%)	D-5134 M	38.4
Mercaptan sulphur (W%)	D-3227	0.0009
Total sulphur (W%)	D-5453	0.1045
Distillation, (°C IBP)	D-2887	31.1
10% Recovery	D-2887	52.1
50% Recovery	D-2887	112.0
90% Recovery	D-2887	178.9
End point	D-2887	218.2
Residue, (vol%)	D-2887	1.5
Loss, (vol%)	D-2887	2.0
Gravity API at 60 °F	D-4052	58.9
Vapor pressure (kPa)	D-5191	9.0
Water by Karl Fisher ppm	D-1744	122
Octane rating research	D-2699	95.2

Table 2  
Some properties of hydrotreated diesel

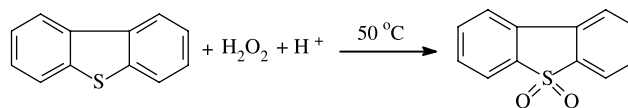
Test description	Test method	Hydrotreated diesel
Color	D-1500	0.5
Total sulphur (wt%)	D-5453	0.1045
Distillation, (°C IBP)	D-2887	216
10% Recovery	D-2887	253
50% Recovery	D-2887	314.0
90% Recovery	D-2887	391
End point	D-2887	401
Specific gravity at 60 °F	D-4052	0.8530
Pour point	D-97	12
Cloud point	D-2500	15
Flash point (°C)	D-93	67
Copper corrosion	D-130	1a

benzothiophenes. The chromatograph in Fig. 1 demonstrates the sulphur compounds that have been identified in the FCC gasoline. Table 2 shows some properties of diesel used in this study. The chromatograph in Fig. 2 illustrates existing derivatives, the majority of them being alkyl dibenzothiophenes. Some of these isomers are co-eluted and it became very difficult to separate them for identification. Another problem is that the diesel includes high concentrations of aromatic hydrocarbons in relation to their sulphur concentrations. This represented a challenge to devise a method that could separate the sulphur aromatics from the remaining hydrocarbon aromatics.

### 3.2. The oxidation of model compounds

In order to understand the oxidation/extraction process, a model compound was prepared simulating the overall compositions of gasoline and diesel fuel. The reaction of the model DBT conducted at 50 °C using formic acid and hydrogen peroxide resulted in a white precipitate. The reaction

was followed by different analytical techniques, e.g. differential scanning calorimetry (DSC), infrared (IR), nuclear magnetic resonance (NMR) and elemental analysis. The results indicate that the following compound was formed during the oxidation process.



The reaction was repeated at room temperature and at 80 °C. The rate of oxidation reaction of DBT was found to increase with an increase in temperature. At room temperature the remaining non-reacted DBT was about 70% after 90 min, whereas about 20 and 6% remained at 50 and 80 °C, respectively, for the same period. The temperatures above 80 °C are not recommended as it may lead to oxidation of other useful compounds present in fuels. The effect of using stronger acids (HCl) and weaker (acetic acid) than formic acids was also studied. Formic acid was found to have better oxidation effect than both HCl and acetic acid. The results are shown in Fig. 3. The HCl shown some oxidative effects but it was insignificant compared to the reaction with formic acid. In the case of acetic acid, the reaction rate is very slow and requires a longer period of time to produce satisfactory results.

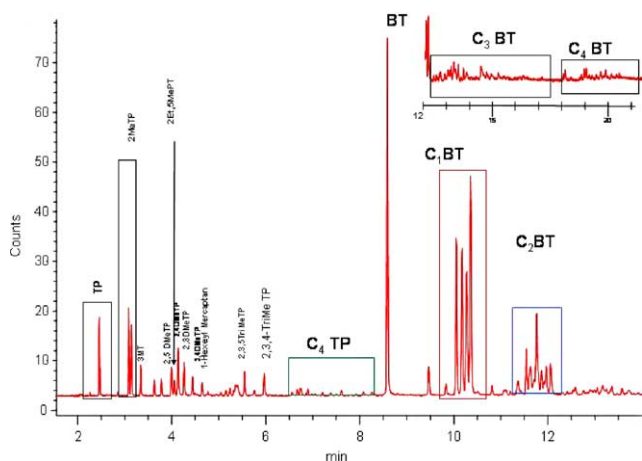


Fig. 1. Sulfur speciation in FCC gasoline.

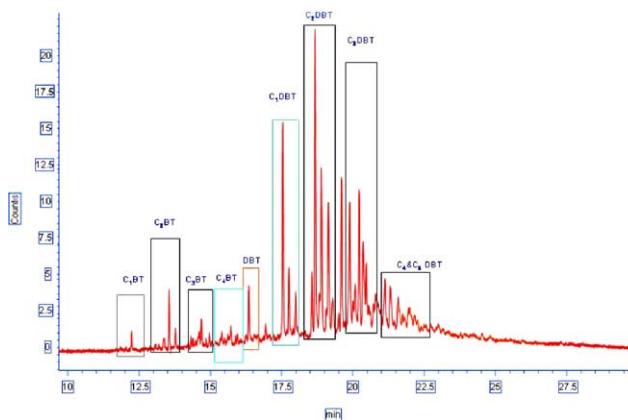


Fig. 2. Sulfur compounds in hydrotreated diesel.

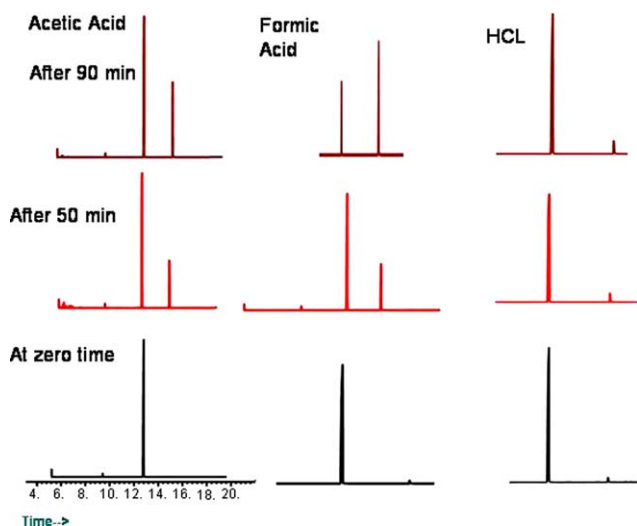


Fig. 3. GC–MS Spectra of DBT oxidation in presence of different acids.

### 3.3. Oxidation of FCC gasoline

The oxidation process using hydrogen peroxide and formic acid was not successfully accomplished on FCC gasoline Fig. 4. This was thought to be due to the high olefin contents of FCC gasoline. The effect of olefin content was studied by substituting 1-hexene instead of *n*-hexane in the model

compound. The oxidized DBT yield was found to be much lower for 1-hexene sample as compared to the *n* hexane Fig. 5. There appears to be a competing reaction between epoxidation of olefins and oxidation of sulphur compounds making the process ineffective.

### 3.4. Oxidation of hydrotreated diesel

Hydrotreated diesel was submitted to several experimental approaches to study the oxidation process. GC–AED spectra of diesel fuel before and after oxidation are shown in Fig. 6. The formation of sulphoxides and sulphones is evident from the spectra. These results are further supported by our earlier oxidation reactions using model compounds. It may be concluded that all hindered sulphur compounds can undergo the oxidation process leading to the corresponding sulphoxide and sulphones. Further, in the presence of excess of acid/H<sub>2</sub>O<sub>2</sub>, the oxidation reaction will go to completion forming final sulphones products.

Another point worth mentioning here is the reactivity of different sulphur compounds in the diesel samples. Fig. 7 shows the sulphur compounds in both original diesel and the treated sample. Looking at the sulphur speciation of these samples in term of their peak heights, the following observations can be drawn: the reactivity of sulphur compounds depends on the position of alkyl groups on the

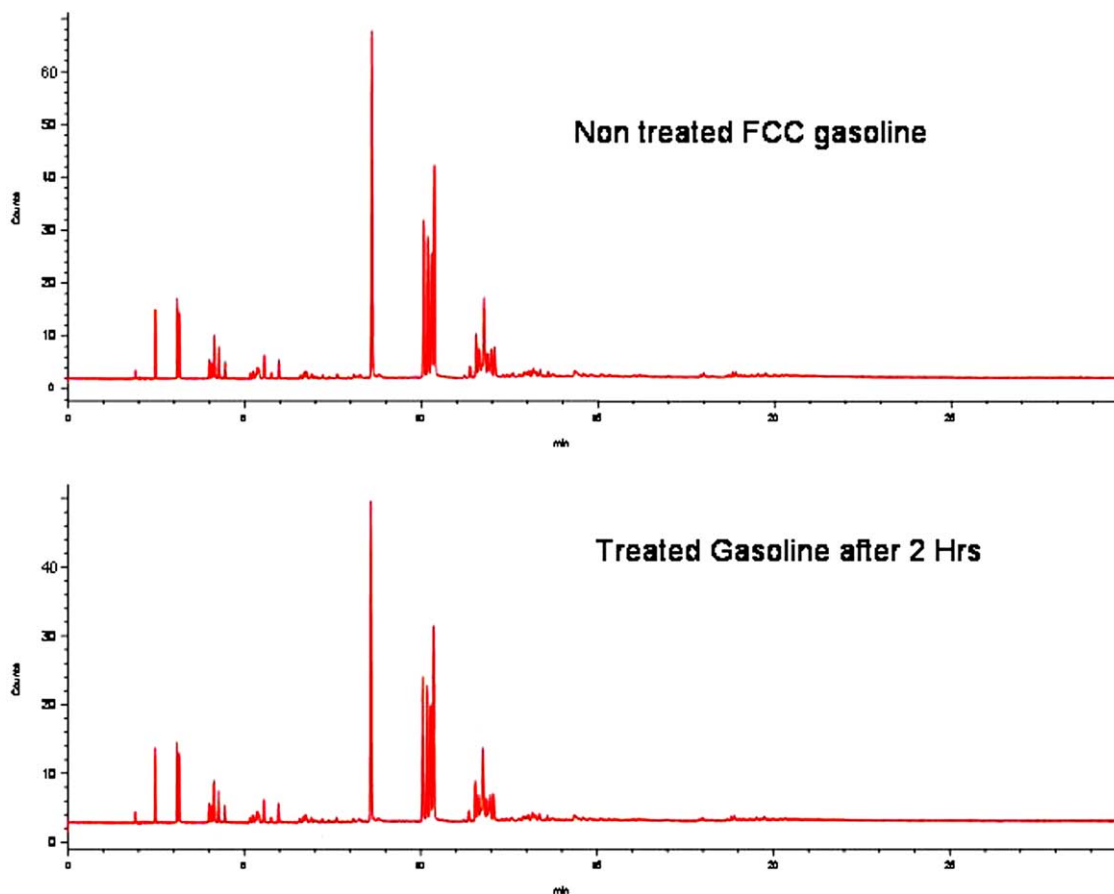


Fig. 4. GC–AED spectra of gasoline before and after oxidation.

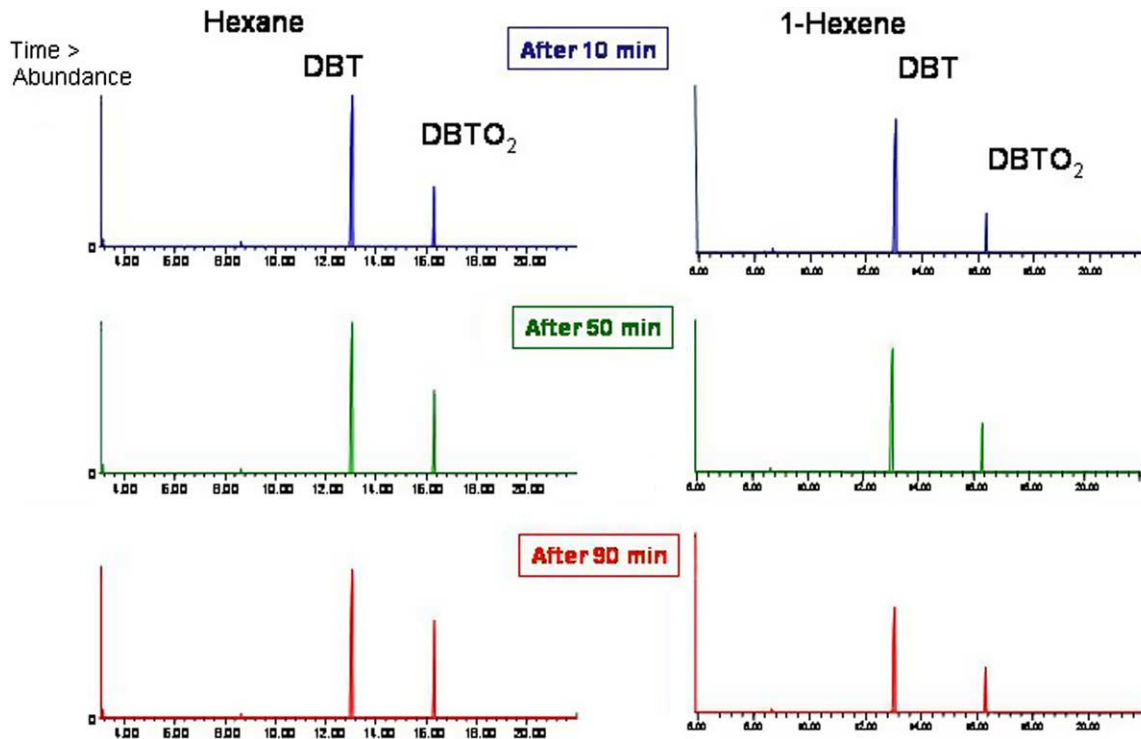
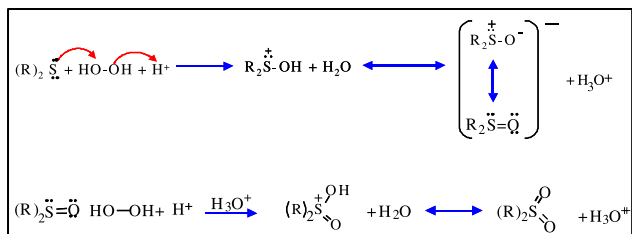


Fig. 5. GC–MS spectra of DBT and oxidized DBT in hexane and 1-hexene at 50 °C.

DBT. The peaks of C<sub>4</sub>DBT, C<sub>3</sub>DBT, C<sub>4</sub>BT, C<sub>3</sub>BT almost disappeared, while the peaks of C<sub>1</sub>BT, C<sub>2</sub>BT, DBT, C<sub>1</sub>DBT, C<sub>2</sub>DBT compounds did not react completely. This can be explained by the reactivity of the sulphur DBT as a result of the electron density of the alkyl group contributions. The following proposed mechanism has helped to explain the reaction requirements for the oxidation of hindered compounds that exist in fuels like diesel and gasoline. The first step of the reaction depends on attacking the hydrogen peroxide by the sulphur atom. Therefore, the higher electron density as a result of donating electron groups will play a significant role on the rate of the oxidation reaction. In addition, the position of alkyl groups and the chain length would also have some effect on the electron density of DBTs, which has been already reported [19].



### 3.5. The effect of acetonitrile extraction in diesel quality

This experiment was conducted to study the effect of direct acetonitrile extraction on the quality of diesel in terms of quantity lost. The diesel sample was submitted to

direct acetonitrile extraction without any oxidation. The GC–MS data confirmed that some aromatic hydrocarbons are removed along with sulphones during the acetonitrile extraction. The results of these experiments revealed some useful information about the extraction process. First, the experiment with 10 ml acetonitrile required overnight to produce a better separation. The volume of this experiment after 1 h showed that there is about 0.5 ml of acetonitrile stayed in the diesel layer; while overnight 0.5 ml of diesel was found in the acetonitrile portion. The experiments using 20 and 50 ml of acetonitrile gave the same results after 1 h and overnight. This probably has to do with the solubility and phase separation of different hydrocarbons in diesel, which may depend on the volume ratio of solvent to solute. The smaller the ratio of acetonitrile to the diesel the more

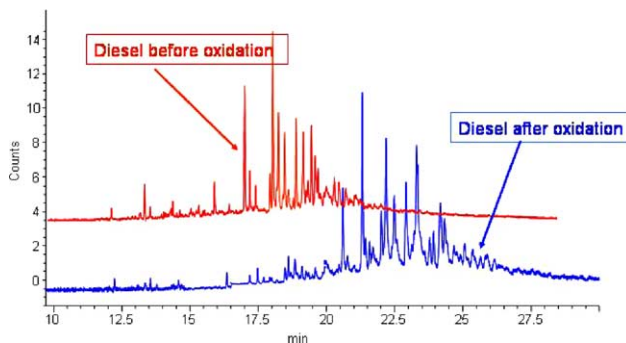


Fig. 6. GC–AED spectra of diesel before and after oxidation.



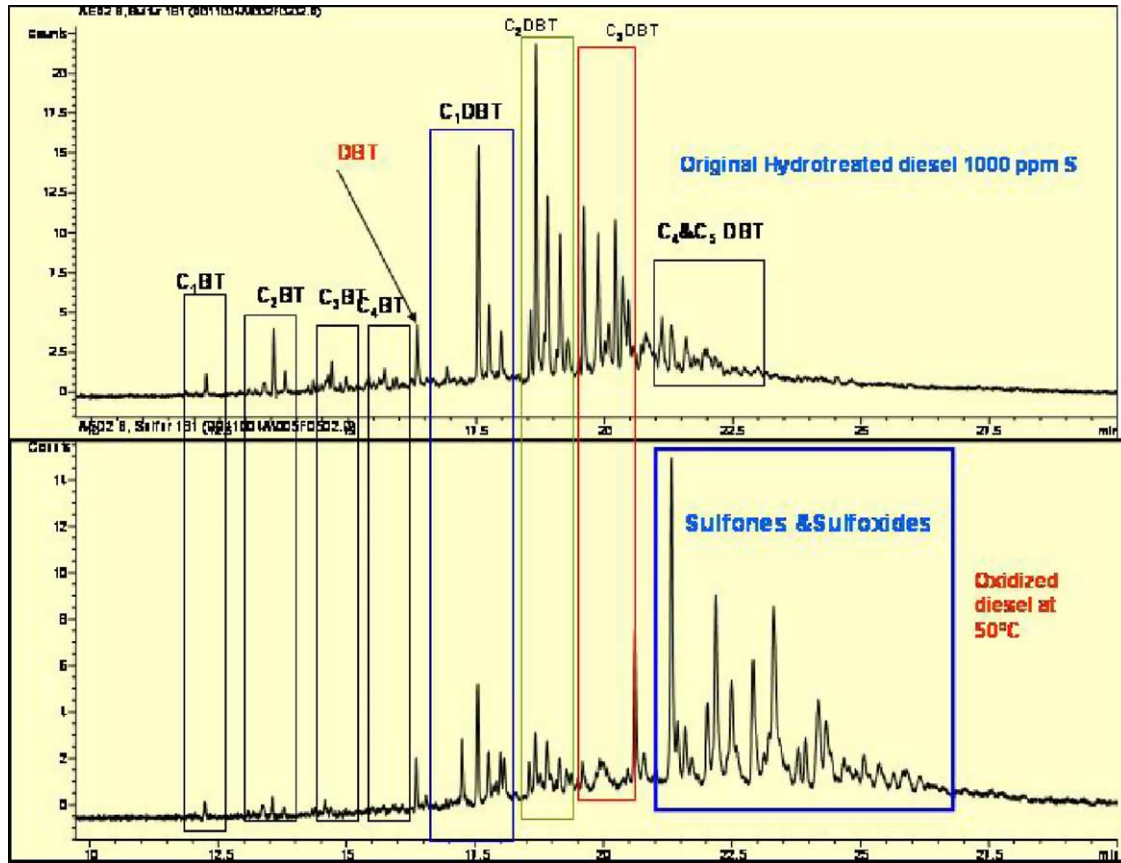


Fig. 7. GC–AED spectra of hydrotreated diesel showing sulfur compounds before and after oxidation.

difficult and longer time is required to have a good separation. However, a greater volume of acetonitrile means a higher cost in term of the extraction and recovery process. In addition, the diesel lost increases with increasing volume of acetonitrile. Table 3 summarizes the results of these experiments. The effect of acetonitrile extraction showed the same result at overnight, however the different time required to have an efficient separation depends on the amount used.

The acetonitrile alone has a great effect on sulphur removal without any pretreatment process. The sulphur content was reduced from its original value of about 1041–563 ppm after the second extraction of 50 ml of acetonitrile. Table 4 demonstrates such effect.

Fig. 8 demonstrates the effect of acetonitrile extraction on diesel with and without oxidation process. Direct extraction resulted in some sulphur removal in addition to other aromatic hydrocarbon species. This is probably due to the small polarity differences between the sulphur-containing compounds and other aromatic hydrocarbons. The oxidation of sulphur compounds resulted in formation of sulphoxides and sulphones products that are relatively polar comparing to the original sulphur species. This gives preferences to sulphur compounds to be easily separated with minimum impact on removing other aromatic hydrocarbons.

Table 3  
The effect of acetonitrile extraction in diesel quality

Diesel (ml)	Acetonitrile, added (ml)	Diesel recovered, (ml)	Acetonitrile, recovered (ml)	Diesel lost (ml)	Diesel lost (%)
<i>After 1 h</i>					
50	10	50.5	9.5	–0.5	–1
50	20	49	21	1	2
50	50	48	52	2	4
<i>Overnight</i>					
50	10	50.5	9.5	0.5	1
50	20	49	21	1	2
50	50	48	52	2	4

Table 4  
The effect of direct acetonitrile extraction sulphur removal

Amount of acetonitrile	Sulphur content (ppm)	
	First extraction	Second extraction
0	1041	1041
10	902	801
20	858	738
50	714	563

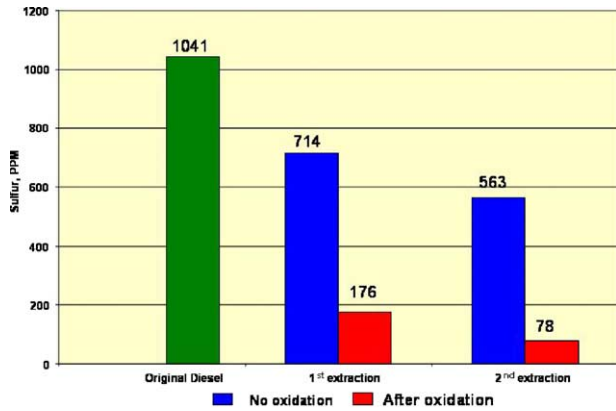


Fig. 8. Effect of acetonitrile extraction on sulfur removal, with and without oxidation.

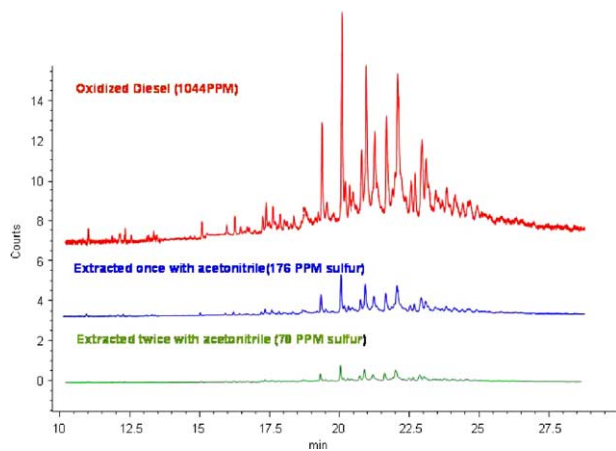


Fig. 9. GC–AED spectra of oxidized diesel and extracts.

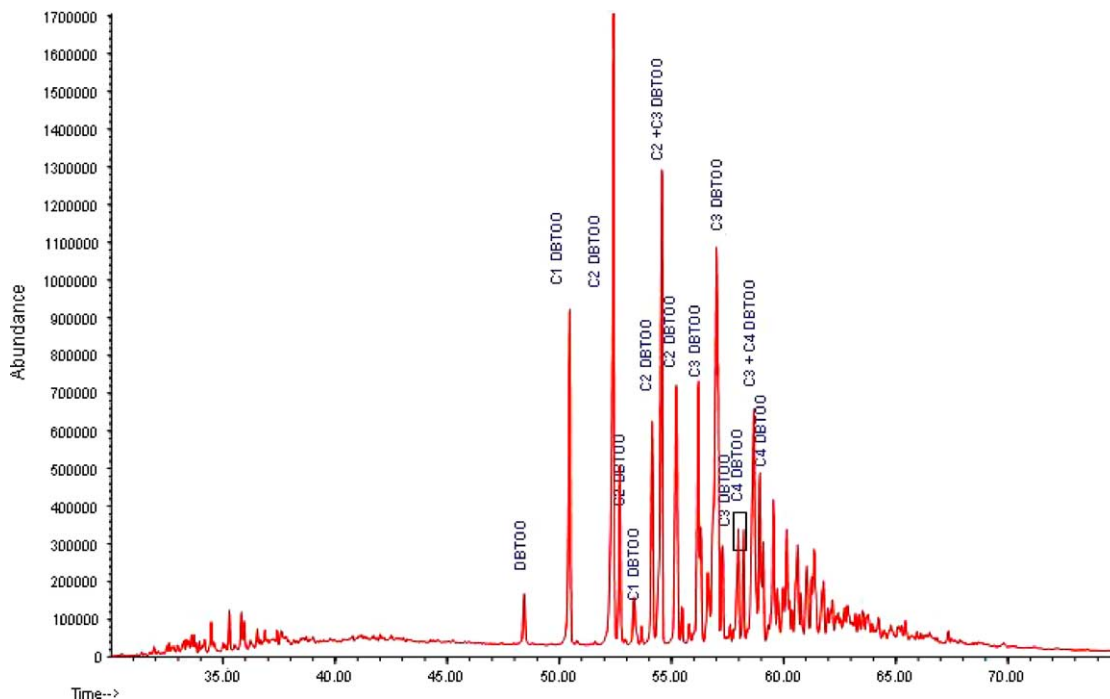


Fig. 10. MS spectra of sulfones.

### 3.6. Sulphones speciation separated from diesel after oxidation

GC–AED chromatograms of the diesel, oxidized diesel, and extracted diesel appear in Fig. 9, which also indicated the sulphur removal of these compounds after first and second extraction with acetonitrile. Selected ion mass chromatograms appear in Fig. 10. Mass spectrometry was used to characterize the components in the range 20–600 amu. Ions pertaining to calculated sulphones moieties were extracted for convenience. Mass spectra were also depicted for verifications. Assignment of sulphone molecules are also done and displayed on top of each spectrum. It has to be noted that there were elution of sulphone homologies in many instances and these are marked by a solid arrow heading toward the molecular ion of the sulphone molecule. Fig. 11 demonstrate some of these compounds and Figs. 12 and 13 show examples of extracted ion for two of these compounds. DMDBT generally follows the hydrogenation route shown in Fig. 1. It is easier to break the sterically hindered C–S bond if one of the aromatic rings is first saturated. After the aromatic ring is hydrogenated, the S atom can be removed via hydrogenolysis at higher pressures using NiMo type catalyst. However, in the absence of hydrogen in ODS process the S removal mostly depends on the strength of oxidizing agent. In mild acidity indirect DS via isomerization may be taking place leading to the formation of 3,6 or 2,6 DMDBT and then removal of S atom as sulfones. In high acidity, the reaction proceeds through dealkylation route followed by desulphurization.

It is worth noting that this is the first time that GC–MS of sulphones is reported in such detail. The mass spectra were

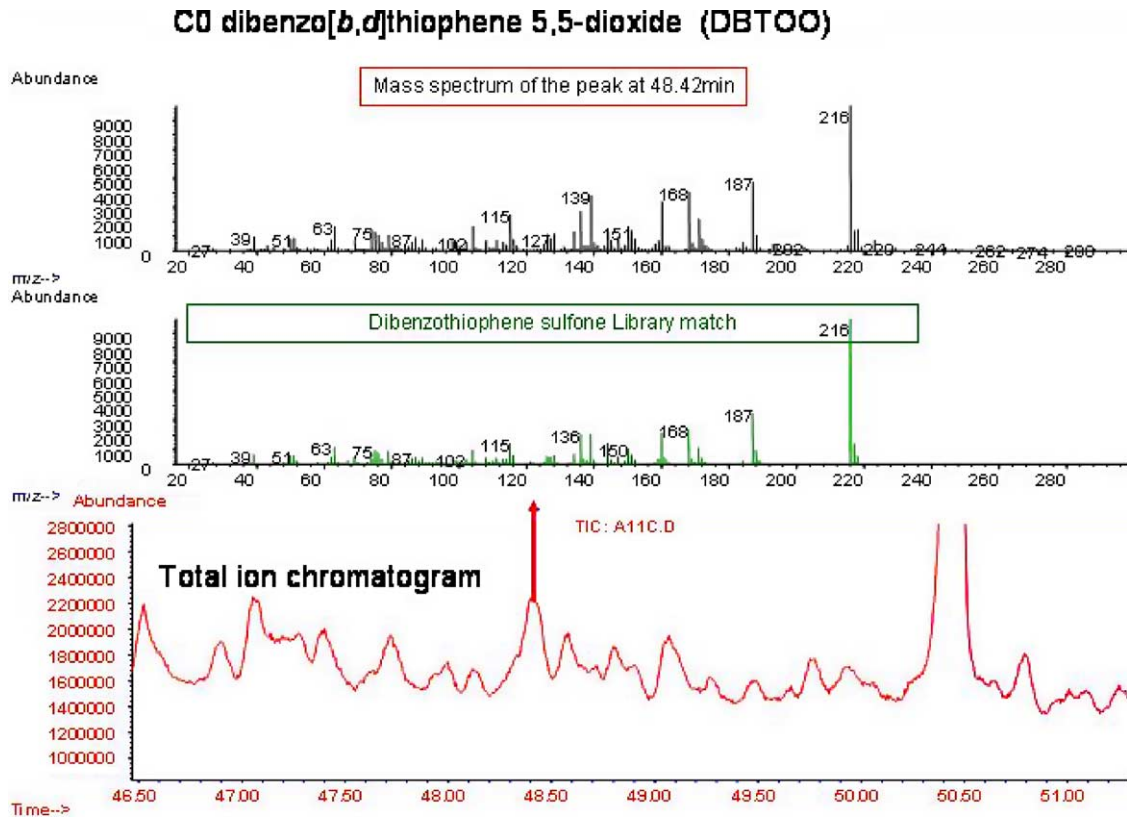


Fig. 11. Mass spectrum of extracted ion for DBT-O<sub>2</sub>.

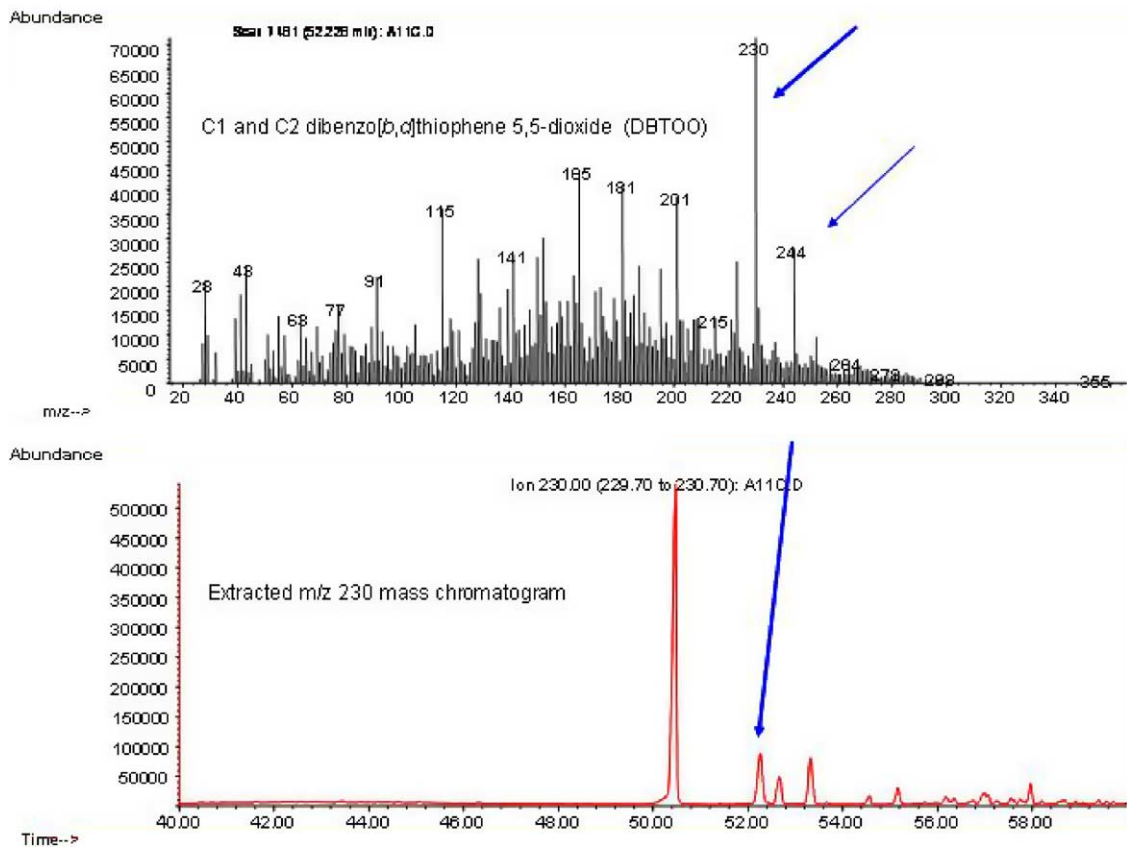


Fig. 12. Mass spectrum of extracted ion for DBT-O<sub>2</sub>.



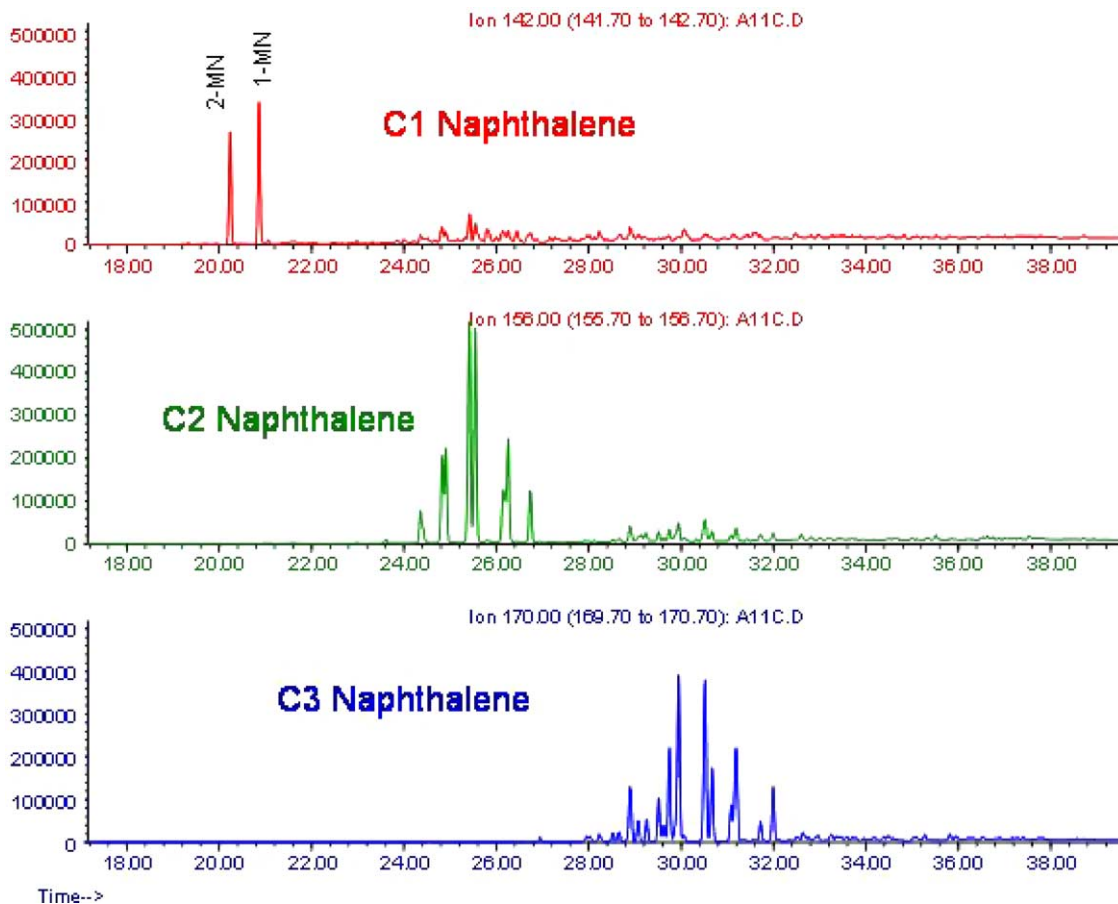


Fig. 13. GC spectra for some naphthalenes isomers.

used to identify these peaks. No library compounds are available for comparison purpose; however the result from the model compound DBT-O<sub>2</sub>, discussed earlier, was used as a key to identify some of these compounds. The mass of the oxidized DBT has resulted in the following named compound, dibenzo[b,d]thiophene 5,5-dioxide with total mass of 216.03 represented in the following formula C<sub>12</sub>H<sub>8</sub>SO<sub>2</sub>. From the previous work and the results of this study, it became clear that most of the untreated sulphur compounds in hydrotreated diesel are thiophene hindered types. We also know that during the oxidation process the sulphur compounds that undergo this process can be separated from the remaining part of the fuel. By knowing all of this, it may be concluded that the only groups that will contribute to the total mass of the resulting sulphones are those with attached alkyl groups, which already exist in the original sulphur compounds. Therefore, the scanning of certain mass that represents the methyl molecular mass and their multiple mass will give various isomers of the sulphones products.

Fragment ions appearing in selected ion chromatograms corresponding with the elution times of heavier molecules arise from the loss of methyl groups (−15 mass) from the P+1 isotopes, which have approximately 10% abundance relative to the parent ion. Table 5 demonstrates the possible sulphones compounds that resulted from the oxidation of

hydrotreated diesel. Such approach can be used to identify more sulphur compounds that exist in the whole diesel or even in the high boiling rang fractions of crude oil. Although the acetonitrile portion was washed twice with normal hexane, the samples showed some remaining aromatic hydrocarbons as shown by GC–MS result in Fig. 12.

#### 4. Conclusions

The oxidation/extraction technique was found to be a promising approach for the reduction of sulphur to less than 100 ppm from the original value of 1044 ppm, with total removal of 92%. This was achieved at low temperature, 50 °C and atmospheric pressure. The direct extraction of diesel fuel without any oxidation has resulted in about 45% sulphur removal, however, such direct extraction has a great impact on removing significant amount of other aromatic hydrocarbons species. The oxidation extraction technique is not applicable to FCC gasoline due to the high olefin content that tends to react with hydrogen peroxide to form epoxide products. The new approach of identifying the sulphones produced, which is based on GC–MS technique will play an important role in the future to help identify more sulphur compounds in different petroleum products. The sulphones identified can be included

Table 5  
Sulphone speciation in hydrotreated diesel

RT	Mass	Name
48.42	216	DBTO2
50.435	230	C1DBTO2
52.228	230+244	C1+C2DBTO2
52.406	244	C2DBTO2
52.695	230+244	C1+C2DBTO2
53.338	230	C1DBTO <sub>2</sub>
54.488	244+258	C2+C3DBTO2
54.514	244+258	C2+C3DBTO2
55.158	244+258	C2+C3DBTO2
55.189	258	C3DBTO2
55.453	244+272	C2+C4DBTO2
55.467	244+272	C2+C4DBTO2
56.583	258+272	C3+C4+DBTO2
56.846	244+272	C2+C4DBTO2
56.912	244+258+272	C2+C3+C4DBTO2
57.989	272	C4DBTO2
58.206	258+272	C3+C4DBTO2
58.705	258+272	C3+C4+DBTO2
58.895	272	C4DBTO2
58.941	272	C4DBTO2
59.02	258+272	C3+C4+DBTO2
59.033	258+272	C3+C4+DBTO2
59.513	272+286	C4+C5 DBTO2
59.559	244+258+272+286	C2+C3+C4+C5DBTO2
59.66	244+258+272+287	C2+C3+C4+C5DBTO2
60.117	258+272+286	C2+C4+C5 DBTO2
60.163	258+272+286	C2+C4+C5 DBTO2
60.617	272+286	C4+C5DBTO2
60.761	258+272+286+300	C2+C4+C5+C6 DBTO2
61.017	244+258+272+286+300	C2+C3+C4+C5+C6DBTO2
61.333	244+258+272+286+300	C2+C3+C4+C5+C6DBTO2
61.424	272+286	C4+C5DBTO2
62.902	258+272+286+300	C3+C4+C5+C6DBTO2

in the GC–MS database as good references for future studies. The technique basically depends on oxidation of fuels in presence of excess H<sub>2</sub>O<sub>2</sub> for sufficient time. Then, the oxidized products are separated and submitted to GC–MS for sulphur identification using selected mass ions. This process creates a petroleum and water emulsion in which H<sub>2</sub>O<sub>2</sub> or another oxidizer is used to convert S in S-containing compounds to sulfones. Most of the peroxide can be recovered and recycled. Commercial viability of oxidative desulphurization (ODS) process depends on the efficient recovery of peroxide and the solvent. Construction of a pilot plant is planned, without a pilot plant study it is not possible to estimate cost of the process and feasibility. The ODS process is still under study by various

refiners and there has been no real-world demonstration of the process.

In summary, the study recommends that the oxidation extraction technique be used as an additional process to the hydrodesulphurization to enable the refineries to meet the future environmental sulphur regulations. Conventional hydrodesulphurization can be used to lower the sulphur content to few hundreds parts per million sulphur. Then, the oxidation/extraction approach needs to be used to go for ultra deep desulphurization as it may provide better mean and cost effective way in order to meet the future sulphur environmental requirements.

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