University of Alberta

Autoxidation for Pre-refining of Oil Sands

by

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ABSTRACT

Oxidative desulfurization of oil sands bitumen as pre-refining methodology to improve bitumen quality in the absence of catalysts was studied. It has potential advantages such as employing a cheap reagent (air) and moderate processing conditions (<180 °C, autogenous pressure). The specific aims of our research were: (a) To establish whether autoxidation followed by aqueous extraction is able to efficiently desulfurize bitumen; (b) To establish whether autoxidation conducted in the presence of a diluent is necessary to limit bitumen hardening as a result of free radical addition reactions; (c) To establish whether autoxidation is selective enough toward organosulfur compounds, because it is undesirable to cause extensive hydrocarbon oxidation; and (d) To establish whether autoxidation reactions are more efficient < 150 ^{o}C or in the temperature range 150-180 ^{o}C, which reportedly results in selective autoxidation. These questions were addressed and best sulphur removal obtained was 46-47 %.

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1. INTRODUCTION

Oil sands are unconventional petroleum resources containing mixtures of sand, clay, water and very viscous and heavy bitumen. Bitumen is very thick and sticky that does not flow unless heated or mixed with lighter hydrocarbons [1-25]. Some countries have large oil sands deposits such as Canada, Venezuela, United States, Russia and various countries in the Middle East. The world's largest oil sands reserves are mainly in Canada.

The heavy feedstocks from different areas of the world have some properties in common. The oils all have high density, high viscosity, and high heteroatom (S, N, metals, etc.) content. At the molecular level, it is difficult to characterize the oils, but in general it can be said that the molecules have high molecular weight, containing large multi-ring structures and is a mixture of compounds containing sulphur, nitrogen and metals. Most of the sulphur is in the form of polycyclic aromatic compounds in such type of heavy crude oils [1].

Oil sands bitumen extraction and processing requires more water and larger amounts of energy in comparison to conventional oil extraction and processing. This is because special methods are required to reduce the viscosity of bitumen (i.e. steam, solvents or hot air injection into the formation). Moreover, such heavy feedstock requires pre-processing or upgrading treatment before it is suitable for conventional refineries (removal of water, sand, physical waste). Also coping with the impurities (S, N, metals) or the heteroatom content of the oil sands derived bitumen while refining is one of the main challenges.

As the need for hydrocarbon-based fuels increases, the need for improved desulfurization methods also increases. Many efforts have been made to improve the parameters of hydrodesulfurization catalysts and develop new alternative desulfurization methods such as various extractive, adsorptive and oxidative desulfurization methods [2-35]. Those methods improve the conversion processes of feedstock such as oil sands bitumen, coal and oil shale into lighter and more valuable fuel products. These methods are reviewed in Chapter 2.

Why is desulphurization important?

Sulphur in petroleum products is highly undesirable and the sulphur content of many products is strictly regulated. Sulphur decreases the quality of the oil needed to produce final products, and by extension the commercial value of the oil. The combustion of fuels with sulphur results in sulphur oxide release which is noxious, corrosive and pollutes the atmosphere. Among other sulphur oxides, SO_2 is more abundant and can cause sulphate aerosol formation in the atmosphere. The aerosol particles have 2.5 μm diameter and can be transported into the lungs [2]. Recent studies show that the sulphur content in the atmosphere is growing and could pose serious health consequences, like respiratory diseases such as emphysema [3]. The sulphur and nitrogen content of the petroleum products contribute to air pollution mainly through exhaust gases from motor vehicles with their NO_x and SO_x emissions [4]. The SO_2 reacts with moisture in the atmosphere and contributes to acid rain or low pH fogs [2, 5]. The acid formed in this way can accelerate the erosion of historical buildings, can be transferred to soil, damage the foliage, depress the pH of lakes with low buffer capacity and endanger the marine life [2].

Sulfate produced by sulphur in the fuel also has a poisoning effect on the exhaust catalyst; in other words, - the SO_x poison the catalysts which converts NO_x, CO and uncombusted hydrocarbons in the exhaust gas. Sulfate is highly thermostable and can saturate the reduction sites on the catalyst. The catalyst loses its efficiency because of decrease in the space available for the reduction of NO_x [2]. Therefore, the government regulations limiting sulphur in fuel is mainly driven by the sulphur-intolerance of the catalytic converters that are responsible to reduce exhaust emissions of vehicles.

Since SO_2 is transported by air streams, it can be produced in one place and show its bad impacts in another place hundreds of miles away. Since 1979 Canada, the United States and the European nations have signed several agreements related to reducing and monitoring SO_2 emissions. The sulphur content in fuels is limited strictly and its allowable limit becomes lower and lower from year to year. This leads some countries to adopt new regulations in order to decrease sulphur content in the fuels; it was 50 ppm in 2005 and less than 10 ppm by 2009[4]. The sulphur level in diesel and gasoline was 10ppm as of November 2001 in Germany [6]. Under *Sulphur in Diesel Fuel Regulations* (SOR/2002-254), the sulphur content of diesel fuel was limited to 15 ppm after 31 May 2006 in Canada. The maximum allowable sulphur level in diesel is targeted at 10 ppm by 2010 in the United States [7].

What is the objective of this study?

Heavy oil and specifically oil sands bitumen has high sulphur content. The sulphur is undesirable in final products and must be removed during refining. However, hydrodesulphurization is challenging due to the high density, high viscosity and high metal content of the bitumen. An alternative method for desulphurization of bitumen was sought.

The ability to pre-refine the bitumen in a low capital process (applicability in current refineries) to improve its refining properties is consequently desirable. This work investigates oxidative desulphurization (ODS) with air as oxidant. The proposed pre-refining methodology has some inherent advantages, namely a cheap reagent (air) and moderate processing conditions (<180 °C, autogenous pressure).

The specific aims of our research were:

- To establish whether autoxidation (using air as an oxidant) followed by aqueous extraction (using water as extractant) is able to efficiently desulfurize bitumen.
- To establish whether autoxidation conducted in the presence of a diluent is necessary to limit bitumen hardening as a result of free radical addition reactions.
- To establish whether autoxidation is selective enough toward organosulfur compounds, because it is undesirable to cause extensive hydrocarbon oxidation.
- To establish whether autoxidation reactions are more efficient < 150 ^{o}C or in the temperature range 150-180 ^{o}C. There is a reported change in the reaction network of autoxidation at around 150 ^{o}C, resulting in less selective autoxidation above 150 ^{o}C.

2. LITERATURE REVIEW

Different approaches can be applied to classify desulfurization methods such as the role of hydrogen in the process, the behaviour of the organosulfur compounds in the process and the nature of the process used [6]. However, all those methods have associated advantages and disadvantages. Depending on the way how sulphur compounds are transformed, processes can be divided into three groups: decomposition, separation without decomposition and decomposition with separation.

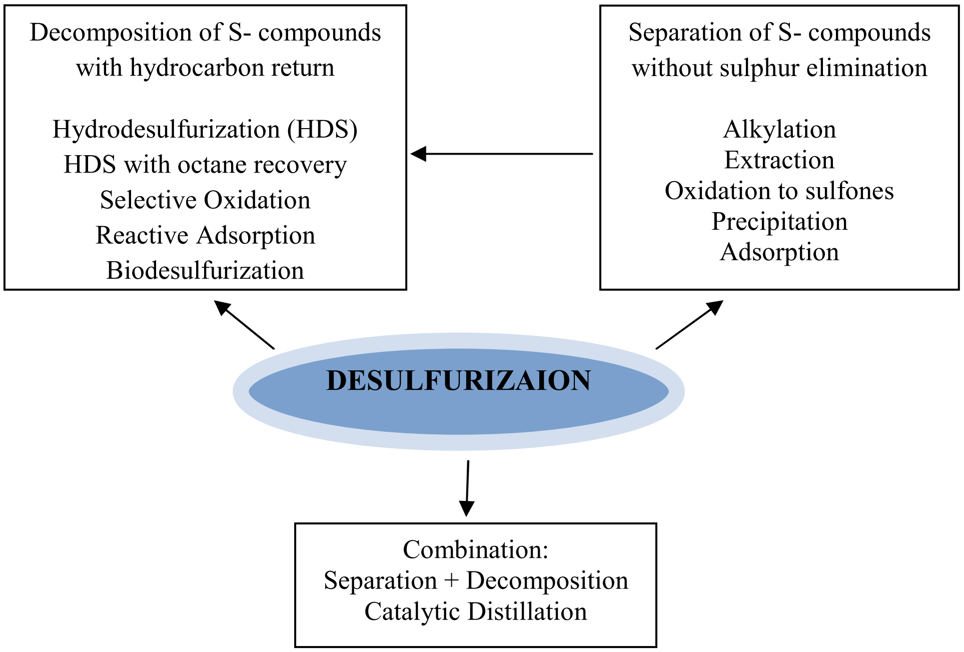


Figure1. Classification based on transformation of sulphur compounds [6].

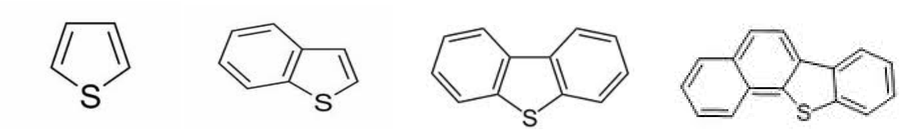
The traditional hydrodesulphurization method can be an example for decomposition in which sulphur is decomposed into gaseous and solid sulphur compounds, then the hydrocarbon part is recovered and remains in the refinery stream. In some processes (i.e. oxidative desulfurization) sulphur compounds are separated or initially transformed into different sulphur containing compounds that are easier to separate (i.e. sulfones).

Desulfurization methods can also be categorized into two groups, “HDS-based” and “non-HDS based” depending on the use of hydrogen for removing sulphur compounds. HDS-based methods require hydrogen to decompose sulphur compounds from the feedstock. For non-HDS-based methods hydrogen is not required to eliminate organosulfur compounds from a refinery stream.

2.1. Sulphur Compounds in Crude Oil

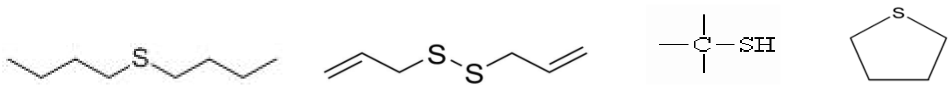
Sulphur is considered the most abundant element in petroleum after carbon and hydrogen. The average sulphur content ranges from 0.03 to 7.89 wt% in crude oil [2]. The sulphur compounds can be found in two main forms in petroleum [8]: inorganic sulphur such as elemental sulphur, H_2S, pyrite and organic sulphur such as an aromatic or saturated form of thiols, thiophenes, heterocyclic sulfides, etc.

Aromatic or Thiophenic Sulphur Compounds



Thiophene Benzothiophene Dibenzothiophene Benzo[b]naphtho[2,3-d]thiophene

Thioethers or Sulphide Sulphur Compounds



Dibutyl Sulphide Diallyl Disulfide Thiol Thiolane

Figure 2. Examples of various types of sulphur compounds present in petroleum products.

Inorganic sulphur compounds can be in both dissolved and suspended forms in petroleum [2]. Crude oil with higher viscosity and density contain higher amounts and more complex sulphur compounds. The aromatic rings such as thiophene and its benzologs or substitutes (benzothiophene, dibenzothiophene, benzonaphthothiophene, etc.) are more resistant to HDS, because they have strong C-S bonds that are not easy to break. On the other hand, aliphatic sulphides or thioethers (organic sulfides) such as cyclic sulphides (thiolanes) are easy to remove sulfur from, since they have only straight chain bonds or non-aromatic cyclic bonds; those bonds do not require high temperature for the bond cleavage and are easy to break in comparison to the bonds of aromatic sulfur compounds, Figure 3 [10].

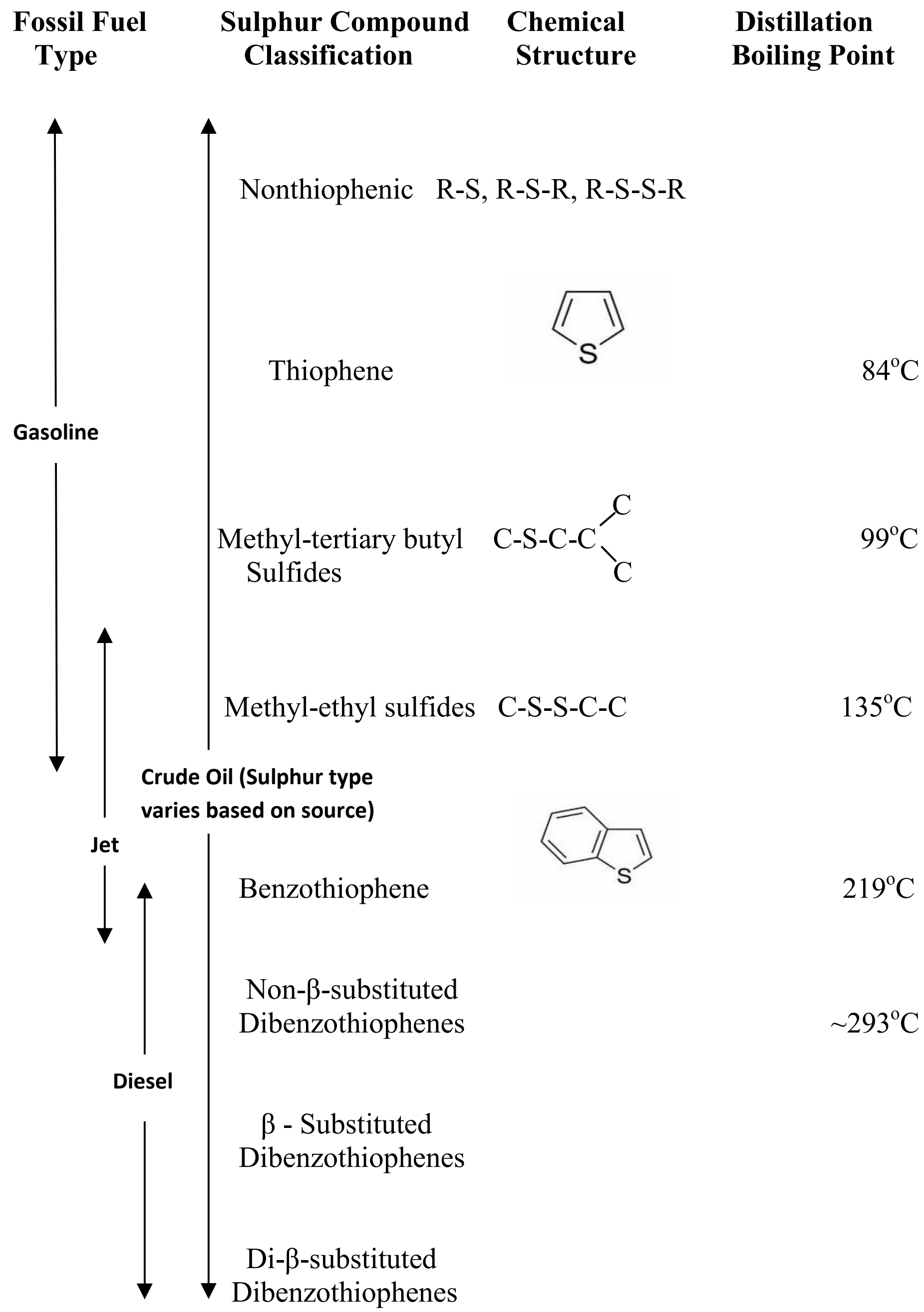


Figure 3. Examples of various organosulfur compounds present in different fractions of fuel [10].

Heavy oils such as bitumen do not have any elemental sulphur/nitrogen and hydrogen sulphide content [9]. Lyapina' s research group have done extraction experiments with acetonitrile and sulfolane to identify different types of sulphur compounds in crude oil from Arkhangel'sko –Tanaiskoe field, Tatarstan, [11].

During catalytic hydrotreatment process thiophenic or aromatic sulphur compounds show high resistance and do not react easily, however, sulphides are reactive and can be removed easily in comparison to thiophenic sulphur impurities. The heteroatom content of heavy petroleum products is contained in big aromatic molecules, which keep sulphur and nitrogen atoms with stronger bonds, so it is not easy to break those bonds during the reactions. Some sulphur compounds are considered recalcitrant which are most stable and need a more invasive desulfurization procedure to remove their sulphur atom. Those are thiophenic compounds such as DBT derivatives with 4 and/or 6 alkyl substituting groups [12]. Substituted dibenzothiophene was identified as the most common type of sulphur product in residual fractions after hydrotreatment [9].

Benzothiophene (BT), non-β, single β and di-β-substituted benzothiophenes (B.P. > 219 ^{o}C) are the typical thiophenic sulphur compounds found in diesel fuel [2]. Thiophenic sulphur compounds can lose their sulphur atoms directly from their aromatic rings via hydrogenolysis which is mainly a catalytic reaction. Thiophenic compounds can convert to sulphides through hydrogenation as well. Sulphides can lose their sulphur content as hydrogen sulphide as a result of thermal and catalytic reactions. Any reduction in the catalyst activity would reduce the conversion rate of the thiophenes to sulphides:

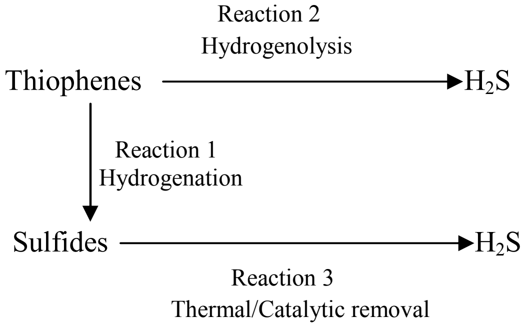


Figure 4. Reaction mechanism of residue fraction during HDS [9]

Commercial gasoline contains fractions coming from reforming, isomerisation and Fluid Catalytic Cracking (FCC) units [4]. The fractions coming from reforming or isomerisation units contain no sulphur since they are coming from distillation cuts after hydrotreatment. About 30-40 wt% of the total commercial gasoline pool come from FCC units, which contributes to 85-95 wt % of the sulphur content of the gasoline. FCC gasoline contains mainly thiophene, thiols, sulphides, alkylthiopenes, tetrahydrothiophene, thiophenols and benzothiophene [4, 13, and 14].

Sudipa' s research group used X-ray Absorption Near-Edge Structure (XANES) spectroscopy to determine naturally occurring sulphur compounds in asphaltenes, resins and oil fractions of two different crude oils (CAL and KUW2) and investigated if there is any *in situ* air oxidation [15]. The XANES results showed that there is the same amount of sulfoxide in all the three fractions of the crude oils. Their study confirmed that the source of sulfoxide is *in situ* oxidation of the sulphide within the crude oil. A stock tank oil was used in the experiments, thus, it is not likely that sulfoxide in CAL was generated by air oxidation after production of crude. They claim that the extreme oxidation of sulphides in CAL occurred within the earth formation due to contact with meteoric water [15].

2.1.1. Sulphur compounds in Canadian Oilsands bitumen

Processing bitumen extracted from oil sands to transportation fuel is challenging due to high viscosity, density and high concentration of heteroatoms. Information related to detailed composition of sulphur compounds in the bitumen feedstock is a main parameter required for catalyst development [18].

S_x Class Compounds in Oilsands Bitumen: Shi' s have determined detailed elemental composition of sulphur compounds in oilsands bitumen by methylation followed by Electrospray Ionization Fourier Transform Ion Cyclotron Mass Spectrometry (ESI/FT-ICR MS) analysis [18]. Oilsands bitumen obtained from the Fort McMurray, AB, Canada area typically has 4.5 and 0.4 wt% sulphur and nitrogen content, respectively. Sulphur compounds in oilsands bitumen were reacted with methyl iodide in the presence of silver tetrafluoroborate and converted to methylsulfonium salts. Initially, in Purcell's study it was supposed that the methylation discriminated against the polar aromatic sulphur hydrocarbons (PASHs) having DBE value (rings plus double bonds) greater than 10 [19]. However, Panda' s recent study showed that methylation does not discriminate against polar aromatic sulphur compounds and variation in the MS (high resolution mass spectrometry) data depends on the ionization technique [20]. Heteroatoms in the oilsands bitumen were classified by their class (number of nitrogen, oxygen and sulphur heteroatoms), type [rings plus double bonds (DBE)] and carbon number distribution [18]. The relative abundance of S_1, S_2 and S_3 type sulphur species were 74 %, 11%, and 1% respectively. The S_1 class sulphur species, especially the ones having DBE value from 2 to 12, were more common. The order of relative abundances of sulphur species were like [18]:

$$S_1 > S_2 > O_1S_1 > O_2S_1 > N_1S_1 \approx O_1S_2 > S_3$$

Benzothiophene were most abundant S_1 species in the samples. The sulphur atoms in S_2 and S_3 class species were in the form of cyclic sulfides or thiophenic compounds. The S_2 type species were most likely to be benzodithiophenes. The S_3 class species were likely conjugated benzothiophenes or dibenzothiophenes with two thiophenes [18].

O_yS_x Class Compounds: Those O_1S_1 type compounds were likely to be two cyclic-ring sulfides with hydroxyl group or/and sulfoxides. Those types of compounds are likely to have molecular structure similar to dibenzofuran flanked on a thiophene [18].

Alan G. Marshall and Ryan P. Rodgers' s have identified higher amount of O_1S_1 compounds in the acid free fraction of Athabasca bitumen derived heavy vacuum gas oil than in bulk vacuum gas oil [22]. This shows that some of the O_1S_1 compounds are not acidic and most of the oxygen atoms are not in a hydroxyl group in the O_1S_1 type compounds. The O_2S_1 type sulphur compounds are acidic and the oxygen atoms are in the carboxyl functional group. The O_2S_1 compounds were likely to be two cyclic-ring sulfides with a carboxyl group and cyclic sulfides or/and thiophene with carboxyl group [18].

This research confirms Sudipa's studies which indicate that source of sulfoxide is in situ oxidation of the sulphide within the crude oil, in other words, there are naturally occurred sulfoxide, sulfone and sulfate compounds within the crude oil [15].

2.2. Hydrodesulfurization

Generally, removal of sulphur from petroleum is difficult which requires breakage of carbon-sulphur chemical bonds at high temperature and pressure [2]. When the n electrons of the sulphur atom resonates with π electrons, then energy of the C-S bonds become identical with C-C bonds and adding hydrogen to the system causes hydrogenation of unsaturated carbon-carbon bonds. During conventional catalytic HDS, the sulphur in organosulfur compounds is mainly converted to H_2S in the presence of $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts [6]. Subsequently during gas cleaning the H_2S is catalytically air oxidized to elemental sulphur [2]. Depending on crude oil type, hydrodesulfurization may occur at 200-425 ^{o}C and as low as 1-1.7 MPa (150–250 psi) H_2. However, to increase the level of desulfurization (<15 mg/kg) higher temperature and pressure are required [2]. The organosulfur compounds are present in almost all fractions of crude oil distillation; however, in different levels e.g. fractions with higher boiling point have more and complex sulphur compounds. Low boiling fractions contain mainly aliphatic compounds: mercaptans, sulfides and disulfides. Those types of sulphur compounds contain approximately 50% of total sulphur in bitumen and asphalts [24]. They are very reactive during thermal reactions or HDS and can be removed completely from the feedstock according to the following reaction mechanisms:

Mercaptans: $R\text{-}S\text{-}H$ $R\text{-}S\text{-}H + H_2 \rightarrow R\text{-}H + H_2S$

Sulphides: $R^1\text{-}S\text{-}R^2$ $R^1\text{-}S\text{-}R^2 + 2H_2 \rightarrow R^1\text{-}H + R^2\text{-}H + H_2S$

Disulphides: $R^1\text{-}S\text{-}S\text{-}R^2$ $R^1\text{-}S\text{-}S\text{-}R^2 + 3H_2 \rightarrow R^1\text{-}H + R^2\text{-}H + 2H_2S$

The fractions with higher boiling point such as thiophenes, dibenzothiophene and their alkylated derivatives have thiophenic rings which are more difficult to remove via hydrotreating in comparison to mercaptans and sulphides. The heaviest fractions; FCC naphtha, coker naphtha contain alkyl benzothiophene, dibenzothiophene, alkyldibenzothiophene and polynuclear sulphur compounds which are the least reactive compounds in the HDS process.

Hydrotreatment is the most common used method in the petroleum industry to reduce heteroatom content of the crude oil in which both feedstock and hydrogen are fed to a fixed bed reactor packed with HDS catalysts. The operating conditions, 315-370 ^{o}C (600-700^{o}F) and 3.5-17 MPa (500-2,500 psig), vary depending on feedstock and sulphur content and level; in other words, more refractory sulphur removal needs more severe operating conditions.

The parameters of HDS vary from study to study so efficiency or reactivity of the different catalysts varies too. NiMo catalysts are more reactive in comparison to CoMo catalysts in continuous flow reactors, whereas CoMo catalysts are more efficient in a batch reactor [26]. Also, NiMo catalysts are more reactive in desulfurization of 4, 6-dimethyldibenzothiophene (DMDBT) [27]. CoMo catalysts tends to be more reactive in the hydrogenolysis reaction pathway in comparison to the hydrogenation pathway, so it results in less hydrogen that is consumed while using CoMo catalyst [28]. So CoMo catalysts are preferred for the HDS of unsaturated hydrocarbon streams like FCC naphtha, in contrast, NiMo catalysts are preferred for fractions requiring extreme hydrogenation.

Even though HDS is a considered cost effective method to desulfurize fossil fuel, the cost of sulphur removal from refractory compounds is high. According to Atlas' s research, the cost of desulfurization to lower the sulphur level from 500 to 200 mg/kg (ppm) is approximately one cent per gallon, but, cost of lowering the sulphur level from 200 to 50 mg/kg is four times higher [29]. Catalytic hydrodesulphurization has been applied for heavy petroleum products as well as vacuum residue, atmospheric residue, bitumen, asphaltenes etc.

It is a fact that benzothiophene and dibenzothiophene content of hydrocarbon can be decreased and it has been applied commercially for a long time. However, HDS has some weaknesses, such as its inefficiency in converting refractory sulphur compounds [2]. Even though hydrodesulphurization is still the main method applied in the petroleum refining industry some disadvantages appears as it is described below [2, 30]:

- Severe reactor conditions; High T and P required to process heavy crude oil; longer residence time.
- Use of expensive catalysts; due to high organometallic content of heavy hydrocarbons the catalyst life shortens as the metal (Nickel, Vanadium and Iron porphyrins) sulphides causes deposit formation on the catalysts. Moreover, due to high tendency for coke and asphaltenes formation while processing heavy feedstock, catalyst life shortens sharply as well.
- Hydrogen; HDS is economically employed for desulphurization of light fractions such as kerosene, naphtha, and diesel fuels. However, hydrotreating of heavy feedstock is not as selective as light fractions; therefore, excessive amounts of hydrogen is necessary for processing heavy feedstock, in other words, a high demand for hydrogen gas under high pressure increases operations costs. The H_2 needed for HDS is limited in the refinery. H_2 is produced by catalytic naphtha reforming, which links it to the motor-gasoline production in the refinery. Additional H_2 can be produced by steam reforming of natural gas, but this is costly, making HDS beyond that which can be supplied by refinery. Furthermore, when you perform HDS, you may also perform hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrodearomatisation (HDA). Although this is not necessarily bad, it adds to the H_2 consumption.
- Mandatory utilization of blocks in the process design to separate hydrocarbon and hydrogen containing gases from hydrogen sulphide;

units for processing hydrogen sulphide into sulphur and sulphuric acid; which complicate the process

- Extraction of compounds with heteroatom content makes protective films on the metal surfaces from distillates, which makes antiwear properties of the fuels worse; e.g. hydrotreated jet fuels has shown increased wear of fuel-pump regulator pistons in the engines [30].
- Some form of sulphur compounds such as 4- and 4,6-substituted DBT, and polyaromatic sulphur heterocycles (PASHs) are resistant during HDS and are the most abundant sulphur species after HDS [2].

2.3. Extractive Desulfurization

Desulfurization via extraction depends on the solubility of the organosulfur compounds in certain solvents. Babich's study describes general process flow of the extractive desulfurization method as below [6]:

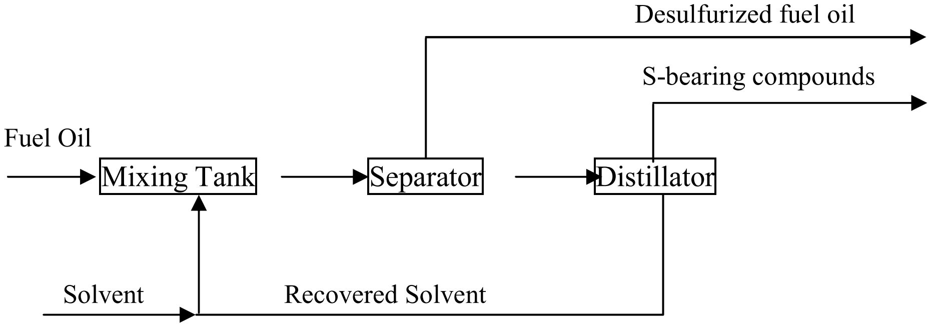


Figure 5. Process flow of the extractive desulfurization [6]

In the mixing tank the feedstock is mixed with the solvent and the organosulfur compounds are extracted into solvent because of their higher solubility in the solvent. Then, in the separator section, hydrocarbon is separated from the solvent. After separation the treated hydrocarbon is blended to final product or transferred to distillation for further transformation or treatments. During distillation organosulfur compounds are separated from the solvent and the recovered solvent is recycled to mixing tank. The extractive desulfurization method is attractive because of its process conditions, low temperature and pressure, and the capability of mixing tank to operate at ambient conditions [6]. As a result, chemical content of the feedstock does not get changed. Also it is not difficult to apply this process in refineries as it is not complex process. The efficiency of the extractive desulfurization method is limited by the solubility of the organosulfur compounds in the solvent. So appropriate solvent selection is very important for efficient desulfurization method e.g. solvent should have different boiling point than sulphur compounds. Furthermore, solvent should be cost effective in order to make it feasible for industrial applications. Different types of solvents have been tried such as acetone, ethanol and polyethylene glycols, which resulted in 50-90% desulfurization depending on the number of extraction cycles of the process [33, 34]. The efficiency of the method can be enhanced if a solvent mixture is prepared by considering the sulphur content and composition of the oil. It can be achieved by preparation a "solvent cocktail" such as acetone –ethanol or a tetraethylene glycol-methoxytri glycol mixture [33, 34].

Solubility of the organosulfur compounds can be increased by transformation of the sulphur compounds in the feedstock. The Conversion/Extraction technology started in 1996 when Petro Star Inc. combined conversion and extraction to eliminate sulphur compounds in the fuel [35, 36]. For example, thiophene, BT, DBT can be converted to sulfones which are easier to separate from the hydrocarbon. For instance, peroxoacetic acid can be used as an oxidant in order to transform sulphur compounds to sulfones. This can be considered oxidative desulfurization as well (Section 8). Liquid/liquid extraction is employed to separate sulphur compounds from the hydrocarbon phase.

2.3.1. Desulfurization with alkali-metal compounds

Siskin's describe the desulfurization process of bitumen and heavy oils at 250-370 ^{o}C and 4-20 MPa (600-3000 psig) via hydrogen containing gas and potassium hydroxide in superheated water in his patent US 2009/0152168 A1. As a result, the sulphur content of heavy oil is decreased at least 35 wt %. Under the superheated conditions the solubility of the hydrogen in aqueous alkali solution increases, as a result, the required hydrogen pressure decreases [1]. Potassium hydroxide breaks the sulphur carbon bonds and hydrogen is substituted for broken sulphur bonds:

$$R\text{-}S\text{-}R + 2KOH + 2H_2 \rightarrow 2RH + K_2S + 2H_2O$$

$$K_2S + R\text{-}S\text{-}R + 2H_2 \rightarrow 2RH + 2KSH$$

$$2R\text{-}S\text{-}R + 2KOH + 4H_2 \rightarrow 4RH + 2KSH + 2H_2O$$

Regeneration of KOH:

$$K_SH + H_2O \xrightarrow{H2} KOH + H_2S$$

$$K_2S + 2H_2O \xrightarrow{H2} 2KOH + H_2S$$

The resulting product will have at least 35wt% lower S content, at least 25% lower kinematic viscosity and 5 points higher API gravity than the feed [1].

2.3.2. Desulfurization of crude oil by chlorinolysis

Chlorinolysis process is done at low temperature (25-80 ^{o}C) and ambient pressure for a short period of time without organic solvent but in the presence of some water. This is followed by aqueous and caustic washes to remove the sulphur and chlorine containing by-products. By chlorinolysis 75-90% of total sulphur can be removed in an hour. This process mainly requires good mixing of oil and the chlorine gas and requires equipment having corrosion resistance to chlorine gas [36].

Breaking C-S bonds by chlorine treatment in the presence of water happens as below [36]:

$$\text{R-S-R`} + \text{Cl}^{+}\text{-Cl}^{-} \xleftrightarrow{\text{H+}} \text{RSCl} + \text{R`}^{+} + \text{Cl}^{-} \longleftrightarrow \text{RSCl} + \text{R`Cl}$$
$$\text{R-S-S-R`} + \text{Cl}^{+}\text{-Cl}^{-} \xleftrightarrow{\text{H+}} \text{RSCl} + \text{R`S}^{+} + \text{Cl`} \longleftrightarrow \text{RSCl} + \text{R`SCl}$$

The chlorinated organo-sulphur compounds are oxidized and hydrolyzed in the presence of chlorine and water at moderate temperature to produce sulphate compounds as follows:

$$\text{RSCl} \xrightarrow{H_2O} \text{RSO}_2\text{Cl} \xrightarrow[\Delta]{H_2O,\ Cl_2} \text{RCl} + \text{SO}_4^{=}$$

Most of the sulphur and chlorine compounds are removed by hydrolysis during water and caustic washing steps. This method is applicable at the well site: oil can be treated by chlorine gas in the presence of water and then treated oil can be washed to remove sulphur and chlorine by products. The desulfurized oil later can be used in the boiler to produce steam [36].

2.3.3. Desulfurization by ionic liquids

The extractive desulfurization of fuels such as diesel oil by ionic liquids has been interesting alternative to provide ultra clean diesel oils. This process does not require hydrogen gas and works at ambient temperature and pressure, which makes it advantageous method; however, due to some drawbacks such as the high cost and water sensitivity of some ionic liquids, it is not used in large scale commercial applications.

Ionic liquids (ILs) are liquid organic salts at temperatures below 100 ^{o}C. Ionic liquids have different properties based on their structure and they are used instead of organic solvents in desulfurization process. Desulfurization by ionic liquids is a mild process and based on extraction theories.

Ionic liquids such as 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), 1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]), 1-Butyl-3-methylimidazolium methyl sulfate ([BMIM][$MeSO_4$]), 1-Butyl-3-methylimidazolium Aluminum tetrachloride ([BMIM][$AlCl_4$]) and 1-Butyl-3-methylimidazolium octylsulfate ([BMIM][$OcSO_4$]) have demonstrated high selective partitioning for heterocyclic organosulfur compounds such as DBT, single β and di-β methylated DBTs [2]. Some of the chlorometallate ionic liquids such as [BMIM][$AlCl_4$] has a high propensity for sulphur removal, however, they are very sensitive to air and moisture and they can cause alkene polymerization in fuel [37]. Ideal ionic liquids have a high distribution coefficient for sulphur compounds, a low cross solubility for the hydrocarbons, a low viscosity, and fast phase separation rate after mixing /extraction [38]. In the literature imidazolium-, pyridinium- or quinolinium based ionic liquids with anions such as alkylsulfates, alkylphosphates or halogen-containing anions are presented as the most appropriate ILs with good extraction characteristics [38]. The halogen free ionic liquid, 1-ethyl-3-methylimidazolium diethylphosphate [EMIM][DEP] is good ionic liquid for practical uses because of its thermal and hydrolytic stability as well as commercial availability and cost; therefore, it was employed in Seeberger's experiments [38].

The size of the anions in the ionic liquids is an important factor, in other words, bigger anions such as $[OcSO_4]^-$ are more effective in extraction of DBT in comparison to smaller anions e.g. $[PF_6]^-$ or $[CF_3SO_3]^-$ [39]. Anions with larger alkyl substitution groups are more effective in DBT removal, however, alkyl groups beyond a certain size decreases selectivity e.g. even though [BMIM][$OcSO_4$] demonstrates high partitioning for DBTs, it dissolves non-sulphur organic molecules such as cycloalkanes and aromatics [40]. Therefore it is not considered as a selective ionic liquid for the removal of DBT compounds.

Although ionic liquids shows high distribution coefficient for model sulphur compounds such as DBT, the distribution coefficient is relatively low for real straight run diesel oils, in other words, ionic liquids are not ideal solvents for extractive desulfurization of real straight run diesel oil. Therefore, the efficiency of extraction process with ILs increases if the organosulfur compounds are previously oxidized to corresponding sulfoxides and sulfones, since they have much higher distribution coefficient [38]. In Seeberger's experiments [EMIM][DEP] did not show high distribution coefficient with real straight run diesel oil, however, with corresponding sulfone compounds extraction was significantly improved. The second drawback is that the recycling and recovery of ionic liquids is difficult and organic solvent extraction methods can be applied to recover or recycle the ionic liquids [38]:

- Direct removal of sulphur compounds from ionic liquids by distillation - The boiling point of organosulfur compounds such as alkylated dibenzothiophenes are high (~340 ^{o}C for 4,6-DMDBT), so high vacuum would be required in case of diesel or heating oil. Thus this method would be applicable mainly for the fractions having sulphur compounds with low boiling point such as gasoline.
- Sulphur compounds can be re-extracted with a low boiling point solvent – It requires an additional separation step though; e.g. separation of sulphur compounds and solvent by distillation.
- Sulphur compounds can be separated from S-loaded ILs by addition of water – The distribution coefficient decreases to almost zero if enough water is added to the system. Then sulphur compounds dissolve or form a second liquid phase in the water together with some light hydrocarbons extracted by ILs, or may even sometimes precipitate. The removal of oxidized sulphur compounds from S-loaded ionic liquids by addition of water leads to displacement of sulphur compounds from the ILs. Thus, separation of water by evaporation is required before re-using ILs. The water evaporation from ionic liquids is crucial step in this process in terms of energy consumption. Seeberger’s have proposed a multi stage evaporation process in order to save energy, which is based on four stage evaporation at different temperature and pressure levels [38]. The energy demand is comparable with the energy demand of traditional hydrotreatment, if multi-stage evaporation is used.

2.4. Adsorptive Desulfurization

Desulfurization by adsorption depends on the ability of a solid sorbent to selectively adsorb organosulfur compounds from the refinery steam. This method can be divided into two pathways: Adsorptive Desulfurization and Reactive Adsorption Desulfurization [6]. Adsorptive desulfurization is based on physical adsorption of organosulfur compounds on the solid sorbent surface whereas during reactive adsorption desulfurization a chemical interaction happens between organosulfur compounds and solid sorbent surface. Sulphur is usually attached to the sorbent as a sulphide. Regeneration of the sorbent can be achieved by flushing spent sorbent with desorbent which results in sulphur removal as H_2S, S or SO_x depending on the process applied and the nature of feedstock [6]. The efficiency of this method depends on the properties of the sorbent: selectivity to organosulfur compounds, adsorption capacity, durability and regenerability.

Adsorption is a non-invasive approach which removes sulphur from refractory hydrocarbons under mild reaction conditions and it in principle has potential for industrial desulfurization [41]. Intensive research has been conducted to develop materials with high desulfurization capacity or efficiency, however, even highest efficiency achieved thus far is still insufficient for industrial applications. To increase the efficiency of adsorptive desulfurization method the adsorption capacity and sorbent regeneration should be further improved. More work is needed in areas such as increasing specific desulfurization activity, hydrocarbon phase tolerance, sulphur removal at higher temperatures and the development of new porous substrates for the desulfurization various types of sulphur compounds [41].

2.4.1. Desulfurization by Zeolite Sorbents and Activated Carbon

Activated carbon, zeolite 5A and zeolite 13X were proposed as solid sorbents by Salem and Hamid for desulfurization of naphtha [42, 43]. Work was conducted with naphtha having 550ppm initial sulphur in a batch reactor. Activated carbon had the highest capacity, but resulted only in low sulphur removal, whereas zeolite X13 was superior for the removal of sulphur compounds at room temperature. Therefore, for industrial applications a two-bed system was proposed. In the first bed activated carbon is used at 80 ^{o}C and 65% of the sulphur can be removed. In the second bed zeolite 13X is used and almost 100% of sulphur is removed at room temperature if sorbent feed ratio is 800 g/l.

Activated carbon, zeolite, CoMo catalysts and silica-alumina sorbents were tested to desulfurize mid-distillate streams with 1200 ppm sulphur content [44]. The aim was desulfurization of 4- and 4, 6-substituted dibenzothiophene which are present after hydrotreatment. Activated carbon showed good desulfurization at 100 ^{o}C for 75 min contact time, even though sorbent capacity was not calculated after the experiments. To regenerate the sorbent, it was flushed with toluene at 100 ^{o}C and after 2 hours, absorptive capacity was completely restored.

Below is the process flow diagram of the adsorptive desulfurization method called IRVAD (Combination of the inventor's name “IRVine” and

“Adsorption”) developed by Black and Veatch Pritchard engineering company [45, 48]: In this method an alumina based solid sorbent is brought into counter-current contact with oil at 240 °C and sorbent to oil weight ratio is around 1.4. Reactivation section of the flow process requires a bit higher temperature where spent sorbent is separated from organosulfur compounds and adsorbed valuable hydrocarbons can be recovered.

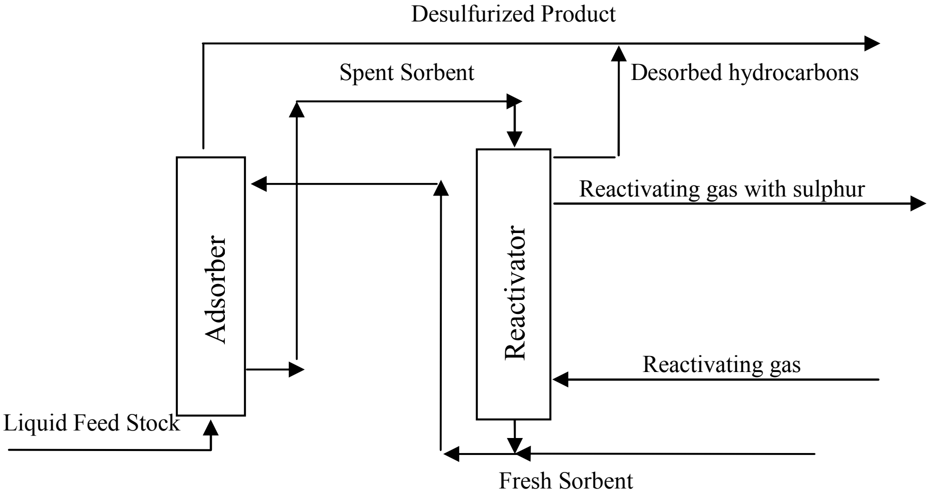


Figure 6. Adsorptive desulfurization flow - IRVAD [6]

This technology was tested in pilot plant experiments in order to desulfurize the FCC feedstock (1276 ppm S) and coker naphtha (2935 ppm S) which resulted in a 90% decrease in sulphur content [45]. The IRVAD method is limited by the sorbent capacity and its selectivity because adsorption of sulphur compounds occur parallel to the surface of the sorbent e.g. dibenzothiophene gets attached parallel to the surface of the catalyst via π-electron of the aromatic ring [47]. So, the sorbent requirement is very high for effective operations.

IRVAD adsorptive desulfurization technology is not applied commercially in large scale industrial refineries because of the following limitations: In the adsorption step organosulfur compounds are concentrated; therefore, later high pressure hydrotreatment is required in order to eliminate sulphur compounds. However, optimization of some properties of adsorbent and process conditions can increase the efficiency and potentially make the process commercially viable e.g. sorbent particle size, reactivation step temperature, number of adsorption-reactivation steps, and weight ratio of hydrocarbon to adsorbent.

2.4.2. Desulfurization by Metal Organic Frameworks (MOF) Sorbents

MOF sorbents are metal cations linked by polyfunctional organic linkers yielding porous three-dimensional networks with large pore volumes and inner surface areas [41]. Due to their large pore volumes and high surface area, there are various types of promising applications, such as gas storage, separation, sensing and catalysis.

Blanco-Brieva's have tested MOF sorbents performance on adsorptive desulfurization of benzothiophene, dibenzothiophene and 4, 6-dimethyldibenzothiophene [41]. Commercial Basolite F300 ($C_9H_3FeO_6$), Basolite A100 ($Al (OH) (C_8H_4O_4)$) and Basolite C300 ($Cu_3(C_9H_3O_6)_2$) metal organic frameworks were employed during the experiments and Y-type zeolite (Conteka) was used as a reference [41].

The metal-organic frameworks (C300, A100 and F300) demonstrated better adsorption for sulphur removal at temperatures close to ambient in comparison to activated carbon and Y-zeolite, in other words, C300 adsorbs approximately 8 times more DBT at 31 ^{o}C compared to Y-zeolite and activated carbon [41].

2.5. Biodesulfurization

Anaerobic path: Sulphate-reducing bacteria were observed to desulfurize model sulphur compounds (Benzothiophenes, Dibenzothiophene and Dibenzothiophene with substitutions) and fossil fuels which resulted in H_2S production [48, 49]. Kim's investigated the desulfurization by *Desulfovibrio desulfuricans* M6 which could degrade 96% of benzothiophene and 42% of dibenzothiophene [50]. Metabolite analysis demonstrates that it can convert dibenzothiophene to biphenyl and H_2S. Some anaerobic microorganisms such as *Desulfomicrobium scambium* and *Desulfovibrio long-reachii* can desulfurize approximately 10% of dibenzothiophene dissolved in kerosene. The advantage of anaerobic desulfurization processes is that oxidation of hydrocarbons to undesired compounds such as colored and gum-forming products is negligible [10]. Armstrong's experiments under well controlled anaerobic conditions did not demonstrate significant desulfurization degree in dibenzothiophene amount or total sulphur content of vacuum gas oil, deasphalted oil or bitumen [51, 52]. Therefore, there is not much evidence related to commercial anaerobic desulfurization of heavier fractions.

Aerobic path: Sharma's studies propose a biodesulfurization method as an alternative desulfurization method to hydrodesulfurization. They tested heavy crude oil with 1.88% S and light crude oil with 0.378% S content respectively. Bio-desulfurization (BDS) of light crude oil by *Pantoea agglomerans* D23W3 resulted in 61.40% sulphur removal whereas heavy crude oil showed 63.29% sulphur removal [8]. Some of the isolated microorganisms such as *Pantoea agglomerans* D23W0033 and *Klebsiella sp* 13T capable of sulphur removal are not effective for commercial uses. They tested the same crude oil with other desulfurization methods such as solvent extraction, oxidative desulfurization with hydrogen peroxide, adsorption and photo-desulfurization in order to compare the efficiencies with biodesulfurization [8]. It was proposed that integrated methods will perform better than single methods. Especially, oxidative desulfurization and biodesulfurization together resulted in 91% sulphur removal from crude oil. Although oxidative desulfurization can be applied as a first step in this process, biodesulfurization can be employed as a first step too, since they both are applied under mild conditions [8].

According to Ranson's experiments, it has been found that members of the genus *Alcaligenes* are highly active in attacking carbon-sulphur-carbon bonds in complex organosulfur compounds leading to inorganic sulphur compounds [53]. They mainly used *Alcaligenes xylosoxidans*, which are very effective in terms of selective transformation under certain conditions, 30-50 ^{o}C [53]. The bioactive materials transform organosulfur compounds into inorganic sulphur compounds, which have affinity toward water, in other words, inorganic sulphur compounds dissolves in the water phase. So when this process is carried out with an emulsion, inorganic sulphur compounds dissolve in the water additionally facilitating separation. This separation happens without removal of valuable constituents of the organic phase.

Microorganisms such as *R. Erythropolis* D-1, *Rhodococcus erythropolis* IGTS8, *Rhodococcus* ECRD-1 ATCC 55301, *Rhodococcus* B1, *Rhodococcus* SY1, *Rhodococcus* UM3 and UM9, *Agrobacterium* MC501, *Mycobacterium* G3, *Gordona* GYKS1, *Klebsiella*, *Xanthomonas*, *Nacordia globelula*, thermophilic *Paenibacillus* and some cytochrome P450 systems can selectively desulfurize benzothiophenes or dibenzothiophenes.

Biodesulfurization of petroleum results in 30-70% sulphur removal for mid-distillates, 40-90% for diesel fuels, 65-70 % for hydrotreated diesel, 20-60% light gas oil, 75-90% for cracked stocks and 20-60% for crude oil [10]. Biodesulfurization mechanism has been proposed for desulfurization of petroleum in production fields and refineries, although no microbes selective to thiophenic sulphur compounds of gasoline are commercially available [54, 55, 56].

Biodesulfurization has potential benefits such as lower operation costs and production of valuable byproducts. Sulphur compounds can be converted into hydroxybiphenyl and its derivatives by biodesulfurization [8]. BDS requires approximately two times less capital cost and 15% less operating costs in compare to traditional HDS. BDS process used to have short biocatalyst life around 1-2 days; however, current design allows the production and regeneration of the biocatalyst within the BDS process which provides 200-400 hours biocatalyst life [57]. Current reactor design led to improvement in the efficiency of BDS, in other words, the affect of mass transport limitations were reduced permitting higher volumetric reaction rates [57]. Current BDS reactors use staging and air sparging with less water-to-oil ratio [57]. Although it decreases reactor size, it requires some modification in the downstream processing for emulsion breakage since the difficulty of separations increases with increased biocatalyst concentration. In addition, BDS has less greenhouse emissions and energy requirements in comparison to HDS. BDS processes for oil field production applications are under development, which will employ microbes that function at 40-65 ^{o}C and remove nitrogen, metals and sulphur, resulting in crude upgrading. Currently, the microbial degradative desulfurization methodology is not commercially employed because of several reasons: the logistics of sanitary handling, shipment, storage and use of living bacterial cells within the production field or refinery environment. Therefore, there is still need to improve this method. The separation of- oil- water-biocatalyst system, byproduct disposition, product quality and reactor design are key engineering issues. Cost effectiveness and the ability of being integrated into existing petrochemical operations as much as possible are important for commercial implementations too [50-57].

2.6. Desulfurization with supercritical water

The effect of supercritical water (SCW) was tested on desulfurization and only a marginal degree of desulfurization as a result of their experiments [58]. However, after adding some conventional hydro treating catalyst some desulfurization was observed, which means super critical water is not a suitable or a convenient medium when it is used alone without any catalyst. The experimental results show that SCW can not remove sulphur alone, nevertheless, in combination with H_2 and conventional HDS catalysts, sulphur and metal impurities can be removed completely [58]. The purpose of using super critical water as catalyst medium is to break carbon – heteroatom bonds. According to the experiments, which were carried out at 400 ^{o}C (673 K) and 25MPa (critical point of water: 374 ^{o}C and 22.1 MPa), aromatic sulphur compounds do not react in SCW as they are very stable compounds. SCW can affect non-aromatic sulphur compounds as they are less stable in comparison to aromatic sulphur compounds.

If supercritical water was good medium for the desulfurization process, it would have some advantages over conventional HDS methods such as; there would not be need for catalyst ($CoMo/\gamma\text{-}Al_2O_3$), SCW would act as a catalyst and reaction medium, hydrogen requirements would be much less than conventional methods [58].

The desulfurization of dibenzothiophene of heavy and light oils was proposed in different mediums such as; H_2-SCW, CO-SCW, CO2-H_2-SCW and HCOOH-SCW at 400 ^{o}C (673 K) and 30MPa with $NiMo/Al_2O_3$ catalyst [59]. Alkylbenzene is one of the main components in the heavy and light oils; therefore, CO formation takes place during its partial oxidation in SCW. They expected doing desulfurization by generating H_2 *in-situ* through the water-gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The water-gas shift reaction does not take place if the catalyst, $NiMo/Al_2O_3$, is not present in the reaction medium. Result of their experimental work demonstrated that less dibenzothiophene conversion was obtained under H_2-SCW atmosphere in comparison to other atmospheres; CO-SCW, CO_2-H_2-SCW and HCOOH-SCW.

Unlike the Makkee's study, Adschiri' s research introduces catalytic desulfurization in SCW environment as a promising new technology in their paper. By introducing oxygen or air with SCW instead of expensive hydrogen, CO can form as a result of partial oxidation of the oil, which can then react by the water-gas shift reaction to produce H_2 *in-situ* in order to provide and effective hydrogenating atmosphere.

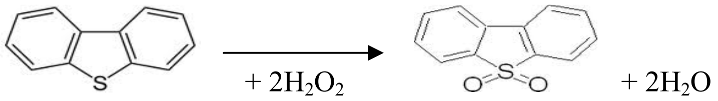
2.7. Oxidative Desulfurization

In recent years petroleum industry started to give more attention to the development of cost effective alternatives instead of relying exclusively on traditional hydrotreating operation. Oxidative desulfurization has been one of the alternative methods proposed, however, intensified research on developing industrial versions of this method began in 1990s [31]. This process, oxidative desulfurization, makes use of air as reagent, instead of H_2. One of the main advantages of oxidative desulfurization is the capability to oxidize and remove thiophenic sulphur compounds at ambient conditions, which cannot be done by HDS process, because of the steric hindrance effect around the sulphur atom in the molecule [31]. For instance, it has been reported that activity of thiophenic sulphur compounds by HDS is in following sequence: DBT (dibenzothiophene) > 4 MDBT (4-methyl dibenzothiophene) > 4, 6 DMDBT (4, 6-dimethyl dibenzothiophene). However, the activity of thiophenic compounds via oxidative treatments is opposite: 4, 6 DMDBT > 4 MDBT > DBT [31]. In other words, oxidative desulfurization methods are complimentary to HDS, because ODS is more effective in removing the sulphur compounds that are the most difficult to remove by HDS from heavy crude oil or hydrotreated oil in order to produce ultra- low sulphur products. Oxidative desulfurization has some advantages over hydrodesulfurization:

- Lower temperature and pressure in compare to HDS
- High selectivity for removal of S compounds, especially, thiophenic sulphur compounds
- Cheaper reactants; molecular oxygen or air

Oxidative desulfurization is based on oxidation of organosulfur compounds and then separation of products of oxidation via various methods such as adsorption, extraction, fractional distillation etc.

It is known that sulphur-carbon bonds of the molecules become weaker when the sulphur is oxidized [60]. When sulphur containing hydrocarbons are treated with an oxidant, some molecules contain oxygen and sulphur at the same time, with the oxygen bonded to the sulphur:



It decreases the strength of the bonds between sulphur and carbon atoms in the molecule. Then by thermal treatment the sulphur - carbon bonds can be ruptured to yield SO2, which is a stable molecule in its own right.

Oxidative desulfurization has some advantages over traditional HDS such as mild reaction conditions (ambient pressure and low temperatures), high selectivity, no use of hydrogen gas, and potential for desulfurization of sterically hindered sulphides such as 4, 6- dimethyldibenzothiophene (DMDBT) and 1, 2-benzodiphenylene sulphide [61]. Oxidative desulphurization is a two step processes: In the first step the oxidation process occurs. Different types of oxidizing agents can be employed, such as organic or inorganic peroxides, hydroperoxides, organic and inorganic peracids, chlorine, oxides of nitrogen, ozone and because of its cheapness preferably molecular oxygen or air [32]. In the second step after oxidation, the oxidized feedstock is thermally treated at 300-400 °C for a period long enough to ensure that all the gaseous products are given off and sulphur is mainly released as SO_2 gas, but also H_2S can be released at high temperatures above 300 °C. The thermal treatment step can be improved with certain compounds having basic or acidic properties such as ferric oxide on alumina, bauxite, thoria on pumice, silica alumina, soda-lime and acid sodium phosphate on carbon [32]. If during thermal treatment step some amount of inert gas, for instance nitrogen, is passed through reaction mixture it can avoid local over-heating and remove the gaseous decomposition products [32]. The desulfurization degree increases significantly, when the oxidative desulfurization process is followed by catalytic HDS.

2.7.1. Photochemical Oxidative Desulfurization

Photochemical oxidative desulfurization is a new technology to decrease the sulphur level in the fuel and it has attracted attention as a new deep desulfurization method for light oil in recent years. The photochemical oxidation seems to be a promising method due to its reportedly high efficiency, mild reaction conditions, simple technological process and low cost [62]. This method has two steps: firstly, sulphur compounds are transferred from light oil into a polar solvent and then this transfer is followed by photooxidation or photodecomposition under UV irridation [63-69]. Some research groups, Zhao Di-Shun’s, Fa-tang Li’s, Shiraishi’s, have developed various photooxidative desulfurization methods for different types of light oil and organosulphur compounds such as thiophene, benzothiophene, dibenzothiophene [63-72].

Photochemical oxidation of thiophene in an *n*-octane/acetonitrile extraction system using O_2 as the oxidant was studied [63-64]. At ambient temperature and pressure, thiophene dissolved in *n*-octane was mixed with acetonitrile (MeCN) and was photodecomposed under UV light. A 500-W high pressure mercury lamp (365nm, 0.22kW m^{-2}) was used as a light source for irridation and air was supplied as O_2 source. The desulfurization degree was 65.2 % after 5 hours of photoirradiation under continuous air flow-150mL/min, in a 1:1 *n*-octane/acetonitrile - solvent. In this method the desulfurization degree was increased up to 96.5% by adding 1.5g/L artificial zeolite (Na-ZSM-5) which is an absorbent for O_2. As a result, the sulphur level can be reduced from 800 ppm to 28 ppm. The main photooxidation products were sulfone, oxalic acid, SO_4^{-2} and CO_2.

Zhao’s research group has investigated the effect of air flow rate, volume ratio of *n*-octane/MeCN and amount of zeolite on the desulfurization degree of thiophene [63, 64].

The desulfurization yield increases as the ratio of *n*-octane/MeCN increases because when the *n*-octane/MeCN ratio is low, the extraction effect of MeCN on the gasoline is bad; however, it is not significant after *n*-octane/MeCN ratio reaches 1:1. Therefore, 1:1 ratio was considered as the appropriate volume ratio for the *n*-octane/MeCN [63-64]. It was found that there was some desulfurization (8.2 %) even in the absence of air flow and photoirradiation because some polar thiophene compounds were transferred from the non-polar *n*-octane phase to the polar acetonitrile (MeCN) phase. When *n*-octane and MeCN were mixed and photoirradiated, thiophene was extracted and photooxidized in the MeCN phase.

If there is no air introduced to the system, the desulfurization degree was only 11.2% because thiophene could not be oxidized by irradiation only. Thiophene needs O_2 dissolved in MeCN for oxidation. Moreover, the desulfurization yield increased as the air flow rate increased at first and then reached a maximum at an air flow rate of 150mL/min. When the air flow rate was above 150mL/min, the desulfurization degree decreased, because of extra volatilization of *n*-octane [63, 64]. Moreover, the desulfurization yield was 6.3 % after 5 hours at 150 mL/min air flow rate without photoirradiation, because the volatilization of *n*-octane was faster than that of thiophene [63, 64].

Thiophene was not oxidized in *n*-octane phase with adequate amount of O_2, because the solubility of O_2 in MeCN solution is limited. In order to increase oxidative desulfurization of thiophene, or in other words, in order to increase the solubility of O_2 in the MeCN the artificial zeolite (Na-ZSM-5) was added to the system. The pore diameters of zeolite is larger than the molecular size of thiophene and oxygen, therefore, O_2 and thiophene could be absorbed in the pores of the zeolite and it led to an increase in the desulfurization yield. Sufficient amount of zeolite (1.5g/L) increased the desulfurization degree up to 96.5%; however, too much zeolite decreased the desulfurization degree, because zeolite scattered the UV light in the solution and blocked the UV absorption of O_2 and thiophene to UV light [63, 64].

Similar experiments were tested related to photooxidative desulfurization of thiophene in *n*-octane/water with the photosensitizer, riboflavin. Photosensitizers are usually expensive products and the cheap photosensitizers are mainly organic dyes which degrade under the photoirradiation. As a result, the photosensitization ability of photosensitizers disappears over time [62]. The riboflavin decomposes under natural sunlight and its photoproduct, lumichrome, still has ability to photosensitize after photolysis of riboflavin. In these experiments the reaction conditions were same as that of the *n*-octane/MeCN study, room temperature and pressure, 150 mL/min air flow rate and a model gasoline-thiophene mixture dissolved in *n*-octane. However, riboflavin dissolved in water was used for extraction purposes instead of acetonitrile with a zeolite. The absorption of UV light by the photosensitizer electronically excites the photosensitizer and then the reactants can be oxidized in two different ways by excited photosensitizers [62]:

$$\begin{tikzcd} & & & \mathrm{Sen}^- \arrow[r] \arrow[d, dash] & \mathrm{Sen} + \mathrm{O}^-_2 \\ \mathrm{Sen} \arrow[r, "hv"] & {}^1\mathrm{Sen}^* \arrow[r] & {}^3\mathrm{Sen}^* \arrow[ur] \arrow[dr] & {} \arrow[d, dash] & \\ & & & \mathrm{Sen} + {}^1\mathrm{O}_2 & \end{tikzcd}$$

In the absence of riboflavin, the desulfurization yield was 40.2% and it increased up to 85.4 % when the riboflavin concentration was increased to 30μmol/L. However, desulfurization yield decreased at higher concentrations of riboflavin, because the extra riboflavin scatters UV lights and hinders absorption of UV by O_2 and thiophene [62].

2.7.2. Photochemical Oxidative Desulfurization - Ionic Liquid Extraction System

D.S. Zhao’s have also tested photochemical oxidative desulfurization with ionic liquids for deep desulfurization of model organosulfur compounds and real straight run light oils [73]. [BMIM][PF_6] was used as the extractant and reaction medium during the photochemical oxidation process, which was at room temperature and atmospheric pressure.

The effect of oxidant amount on the desulfurization of the model light oil was also investigated; when H_2O_2/sulphur mole ratio was < 7 there was not enough H_2O_2 to oxidize dibenzothiophene and when H_2O_2/sulphur mole ratio was > 7, the excess H_2O_2 led to a high reaction rate, but, the H_2O_2 was not used well. When H_2O_2/sulphur mole ratio = 7, almost all DBT (99.5%) was removed from model light oil. A possible reaction mechanism of the DBT in photochemical oxidation process was suggested, Figure 7 [73]:

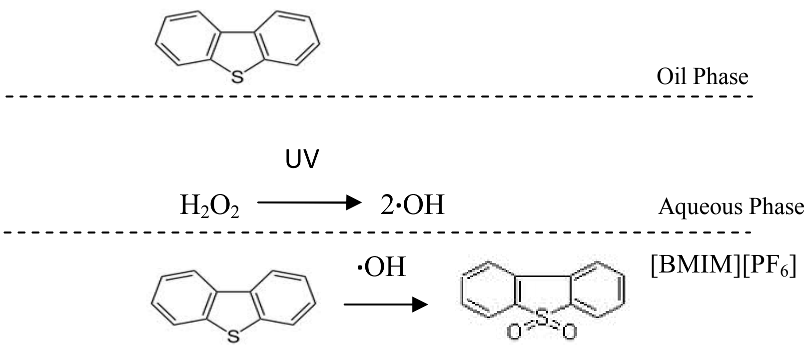


Figure 7. Photochemical oxidation of DBT molecules [73]

Firstly, DBT molecules were extracted from the *n*-octane into the ionic liquid phase, [BMIM][PF_6]. Then the H_2O_2 was decomposed to an oxidizing agent, the hydroxyl radical (· OH). Ionic liquids consist of a cation and anion and have a lower dielectric constant, so the hydroxyl radicals (·OH) transfer into [BMIM][PF_6] easily and oxidize the DBT molecules into dibenzothiophene sulfoxide (DBTO) and dibenzothiophene sulfone ($DBTO_2$) in [BMIM][PF_6] phase.

The sulphur removal degree was 90.6% from the straight run light oil in 10 hours and 99.5% removal of DBT from model light oil was achieved in 8 hours. Ionic liquid, [BMIM][PF_6], was recycled eight times during the process with a slight decrease in desulfurization efficiency of [Bmim]PF_6.

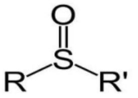
2.7.3. Oxidative desulfurization with strong oxidants in combination with acids

Webster et.al in US Patent 3,163,593 proposes organic peracids, performic or peracetic acid, mixtures of hydrogen peroxide with formic or acetic acid, organic hydroperoxides, inorganic peracids and salts, hypochlorite solutions, nitrogen peroxide or air as suitable oxidizing agents for oxidative desulphurization [60]. However, hydrogen peroxide with lower alkyl mono carboxylic acids, such as formic or acetic acids, are more preferable oxidizing agents, because their selectivity to sulfone formation is higher. Formic and acetic acids are strong organic acids and they are highly active with oxidative agents at low temperatures. Acids do not participate in the reactions themselves as they have catalytic role in the reaction medium. An acetic medium helps oxidants to convert sulphides to sulfoxides which are reaction intermediates for sulfones. In addition, in comparison to long chain carboxylic acids the short chain carboxylic acids (1-5 carbons) are soluble in the water, which means later they can be washed from the reaction medium with water, so they are preferred. The ratios of peroxide to acid and peroxide to sulphur present in the hydrocarbon are important factors during preparation of the oxidizing agents. The oxidation of sulphur containing hydrocarbons should not proceed further than sulfone formation. Otherwise, sulfonic acid derivatives, e.g. sulphuric acid (H_2SO_4), can be formed which is bad for the next step. Sulphuric acid is a very corrosive acid and at high temperature during the thermal treatment it can poses a safety hazard if the process is on large scale. Otherwise it would be separated easily by washing since it is soluble in the water.

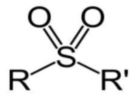
The oxidation products can be removed by acid washing, solvent extraction, fractional distillation, extractive distillation or combination of these methods. The thermal after treatment temperature should not be too high in order not to degrade the hydrocarbons. The temperature should be sufficient enough to break C-S bonds, which are already weakened by the oxidation process. After the oxidation process the hydrocarbon mixture is washed with water in order to separate solvent and excess reagents from treated hydrocarbon. Later thermal treatment breaks carbon-sulphur bonds which have already been weakened by oxidation process and yields the volatile sulphur compounds mainly in SO_2 form, although at high temperatures H_2S can be released as well. This method is applicable to sulphur containing hydrocarbon oils such as, cracked gas oils, residual fuel oils, crude oil after removing the light fractions, vacuum residues and oil from tar sands [60]. Also it is stated that dissolving heavy hydrocarbon oils in a low boiling organic solvent, such as benzene or carbon tetrachloride, improves the oxidation process. The heavy hydrocarbons are soluble in the organic solvents so adding some organic solvent to the reaction medium decreases the viscosity of the heavy hydrocarbons and better mixing can be achieved between oxidizing agents and heavy hydrocarbons, as a result, oxidation degree will be improved.

2.7.4. Oxidative desulphurization with strong oxidants in combination with molten alkali metal hydroxide

Wallace’ s described a method to desulfurize petroleum residue in US Patent 3,505,210 and according to him after treating hydrocarbon with an oxidizing agent like hydrogen peroxide in acidic medium, the hydrocarbons should be treated with molten alkali metal hydroxide to rupture the sulfone ring and form a hydrocarbon fraction with lower sulphur content [3]. So, petroleum residue should be treated with an oxidizing agent in acidic aqueous medium in order to convert bivalent sulphur compounds to sulfoxides or sulfones. Sulfones are preferred, because they can be separated from hydrocarbon more easily in the second step of the process. It is apparent that rupture of sulfone would be easier than sulfoxide, because sulfone has two oxygen atom bonded to sulphur atom; however, sulfoxide has one oxygen atom bonded to sulphur atom. So the sulphur atom in sulfones is bonded with less energy to the carbon atoms in comparison to the sulfoxide, which means less energy is necessary for liberation of sulphur atoms from sulfone compounds.



Sulfoxide



Sulfone

During oxidation of the oil some sulphur gets converted to sulfones and some to sulfoxides, however, it was proposed that there is a specific temperature limit that favors formation of either sulfoxides or sulfones [85].The acid medium acts as a catalyst and it is suggested to use water soluble carboxylic acids such as formic acid, acetic acid, chloroacetic acid etc. for this purpose [3].

However, adding that kind of acids may cause extra cost and is disadvantage for this type of desulfurization process, especially, in oil sand upgrading. The carboxylic acid content of oil sand process affected water will increase since the short chain carboxylic acids are soluble in the water. It will require extra work and cost to eliminate the high carboxylic acid content of the oil sands process affected water. Conversely, if the carboxylic acid content in the process water increases after oxidation process of oils sands, then we can use that water next time without adding extra carboxylic acid. The addition of a little amount of sulphuric acid to acetic acid during first step decreases the need for acetic acid greatly, so it permits the addition larger amount of water to the system [3]. Moreover, it is easier to handle H_2O_2 hazards when it is diluted rather than when it is concentrated. However, Webster’ s study stated that sulphuric acid may also form during the reaction when exceeding temperature limit of sulfone formation.

In the second step the oxidized oil is treated by molten alkali metal hydroxide (NaOH or KOH) at 300-400 °C to rupture the sulphur carbon bonds and dissolve these sulphur compounds in the aqueous medium. Before oxidizing heavy stock it should be dissolved in an inert hydrocarbon medium like benzene as in other methods. Almost in all of these methods operating conditions are the same. Pressure is not an important factor neither in the first or second steps for desulphurization with strong oxidants in combination with molten alkali metal hydroxide.

2.7.5. Oxidative desulfurization with strong oxidants in combination with lower paraffinic hydrocarbon solvents

The method to decrease the sulphur content of the heavy hydrocarbon fractions suggested in 1968 by Edward’s research [74] is similar in principle to the other oxidative desulphurisation methods using strong oxidants. The oxidation step, its conditions and oxidizing agents are very similar depending on the hydrocarbon type being treated [74]. However, after the oxidation step, contacting the heavy fraction with lower paraffinic hydrocarbon solvent to separate the oxidized sulphur compounds was suggested instead of thermal treatment. So the oxidation step oxidizes some sulphur containing hydrocarbon molecules selectively and the solvent treating step precipitates or does phase separation of some oxidized sulphur compounds. The oxidizing agents used in this method are similar to the other methods such as oxygen, air, ozone, organic peroxides, organic hydroperoxides, organic peracids etc. in the presence of metal catalysts (Group IVB, VB, VIB metals). Paraffinic solvents which were suggested for this method are propane, butane, isobutane, pentane, isopentane, hexane, isohexane, heohexane, heptanes, octane and mixtures of them. One can consequently describe this process as oxidation followed by solvent deasphalting.

Lin’s study [31] in the US Patent 7,276,152 B2 proposes an oxidative desulfurization and denitrogenation process with non-aqueous, oil-soluble organic peroxides which takes place at low concentration and substantially lower temperatures in comparison to other methods [31]. Non-aqueous peroxide oxidants are very reactive and fast in oxidation reactions without a catalyst and requires less residence time. Much of the advantage is derived from reducing the mass transfer resistance.

Non-aqueous peroxide oxidants refers to peracids, RCOOOH (R represents hydrogen or an alkyl group) which is soluble in the organic solvent or hydrocarbon feedstock. Desulfurization and denitrogenation take place in a single phase non-aqueous environment, so no phase transfer of the oxidant is required. Besides that there is not any water in the system, which otherwise would cause solids precipitation; indeed, the non-aqueous medium of the oxidant is a good solvent for the sulfones and organic nitrogen oxides.

The peracids employed in this process can be generated *ex situ*. In this method they use organoiron catalysts in order to synthesize peroxide oxidants, in other words, organoiron catalysts help to the oxidation of aldehydes to peroxide by molecular oxygen:

$$RCHO + O_2 \rightarrow RCOOOH$$

Organoiron catalysts include Fe (III) acetylacetonate (FeAA), Fe (III) ethylhexanote (FeEHO), Ferrocenyl methyl ketone (FeMK) etc. Those catalysts are soluble in the organic solvents too. Since it is a non-aqueous medium they use organic solvents in the medium which dissolves sulfones and organic nitrogen oxides such as ketones (R_2O), e.g. acetone, CH_3OCH_3. These types of organic solvents are miscible in the hydrocarbon feedstock as well as in oil [31].

$$CH_3CHO \;+\; O_2 \rightarrow \text{(organoiron catalyst and acetone)} \rightarrow CH_3COOOH$$

When the peroxide is in the aqueous phase, it requires phase transfer agent to carry peroxide from aqueous phase to oil phase where it oxidizes sulphur and nitrogen compounds. The phase transfer step is the rate defining step so it slows down the reaction rate significantly. The presence of water can cause the important portion of the sulfones and organic oxides to precipitate from reactor effluent. The solid precipitation in the critical stages of the process can cause malfunctioning of the valves, pumps and even in the adsorbent bed [31].

2.7.6. Oxidative Desulfurization with strong oxidants and ultrasound system

Ultrasound oxidative desulfurization is a new technology and its mechanism can be described as below: raw materials and oxidants are mixed with surfactants in water in a reactor to make a mixture of water and the organic medium. Under the influence of ultrasound, the mixture is stratified easily into the water and organic phases and local temperature and pressure of the mixture increases rapidly in a short period of time [75]. At the same time, free radicals by activation of oxygen are generated in the mixture; as a result, those substances react and oxidize sulfides to sulfoxides, sulfones and sulfates which are transferred to the water phase. After solvent extraction sulfones and sulfates are removed from the system.

Sun Mingzhu applied this method to remove sulphur compounds from diesel fuel [76]. H_2O_2 was employed as a strong oxidant, ultrasound irradiation was introduced to the system to provide energy for the reaction and phosphoric or acetic acid was used as a catalysts. They achieved optimal desulfurization degree after 10 min at 50 ^{o}C. Yen’ s research group conducted similar experiments to remove sulphur from model oil in which DBT was dissolved in the toluene [77]. DBT was completely oxidized to DBTO after 7 minutes at 73-77 °C.

In 2007 this method, ultra-sound assisted oxidative desulfurization followed by extraction, has been applied for various diesel fuels [78]. The transition metal complex and quaternary ammonium salts were applied as a catalyst with strong oxidants, H_2O_2. The results show that sulphur removal degree can exceed 95 % in a short period of time under ambient temperature and atmospheric pressure.

Although the ultrasound oxidative desulfurization system provides high sulphur removal degree, it has some drawbacks such as employing H_2O_2 as an oxidant and an ultrasound device, which increase the cost of the process, as well as limit the scale of production. Moreover, H_2O_2 can cause emulsification of oil when added to the oil and it requires a long time to mix sufficiently with the oil [75].

2.7.7. Oxidative desulfurization of organic sulphur compounds with air in the presence of catalysts

It was observed that high reactivity while doing oxidative desulfurization with air in an acetone solution in the presence of copper (II) phenolates [79]. C. The ODS experiments have been done with molecular oxygen or air in the presence of Fe(III) salts [Fe(III) nitrate and Fe(III) bromide] to desulfurize thiophenic sulphur compounds into corresponding sulfoxides or sulfone compounds at ambient temperature, 25 °C [5].

Oxidative desulfurization experiments conducted with tertiary butyl hydroperoxide in the presence of a Ni-Mo catalyst and the removal of sulfone compounds was achieved by adsorption on an alumina surface [80]. The rate constant for ODS was higher than the rate constant for traditional hydrodesulphurization process.

Similar oxidative desulfurization experiments have been done to decrease sulphur content of diesel fuel with molecular oxygen in the presence of cobalt salts (acetate, chloride, bromide) and aldehydes in an organic solvent, benzene [61]. In their experiments cobalt salts were used as catalyst and aldehydes as sacrificial material. Transition metal (Cobalt, Nickel, Copper) catalyzes co-oxidation of organic sulphur compounds and aldehydes with molecular oxygen (1), which includes oxidation of aldehydes with molecular oxygen to the corresponding peroxy acids(2) and oxidation of organic sulphur compounds with peroxy acids (3)[61].

$$\mathrm{RCHO + Substrate + O_2 \rightarrow RCO_2H + Product\ (1)}$$
$$\mathrm{RCHO + O_2 \rightarrow RCO_3H\ (2)}$$
$$\mathrm{RCO_3H + Substrate \rightarrow RCO_2H + Product\ (3)}$$

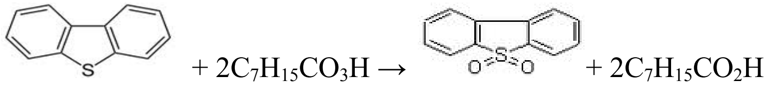
The reaction mechanism can be described in more detail. At first, aldehydes are oxidized by metal salts to give a proton and the corresponding acyl radical (4). Acyl radicals react easily with oxygen to produce acylperoxy radicals (5). Acylperoxy radicals react with aldehydes to produce peracids and regenerate acyl radicals (6). Peracids can oxidize sulphides to sulfones (7-8) [61].

$$\mathrm{RCHO + M^{(n+1)+} \rightarrow RCO\cdot + H^+ + M^{n+}\ (4)}$$
$$\mathrm{RCO\cdot + O2 \rightarrow RCO\cdot_3\ (5)}$$
$$\mathrm{RCO\cdot_3 + RCHO \rightarrow RCO_3H + RCO\cdot (6)}$$
$$\mathrm{RCO_3H + R`SR` \rightarrow RCO_2H + R`SOR`\quad (7)}$$
$$\mathrm{RCO_3H + R`SOR` \rightarrow RCO_2H + R`SO_2R`\ (8)}$$

Aldehydes are known to be oxidized easily to the corresponding peracids by molecular oxygen in the presence of transition metal salts.

$$\mathrm{C_7H_{15}CHO + O_2 \rightarrow C_7H_{15}CO_3H}$$

For example, in the experiments DBT was used as a representative for sulphur compounds in the diesel fuel with the oxygen-cobalt salts-aldehyde system:



$$+\ 2\mathrm{C_7H_{15}CO_3H} \rightarrow \quad +\ 2\mathrm{C_7H_{15}CO_2H}$$

After the oxidation process in the presence of cobalt acetate, aldehydes and molecular oxygen, oxidized compounds were removed by alumina adsorption and/or solvent extraction. Their experiments resulted in 97% reduction in the sulphur content of diesel fuels. The sulphur concentration of commercial diesel fuel with 193 ppm sulphur was reduced to 5 ppm by this method. This method has some advantages in comparison to other oxidative desulfurization methods besides being applied at ambient pressure and low temperature, 40 ^{o}C. It is a fact that peracids or peroxides are attractive oxidants in terms of selectivity, rapidity and conditions of their reactions, however, they are considered dangerous for large scale industrial applications as their large scale storage and application during processes is somewhat dangerous. Therefore, in this method *in situ* generation of peracids is employed, in other words, in this method both aldehydes and molecular oxygen were used instead of peracids, which are not dangerous reagents in general.

In US Patent 3,341,448 it is proposed that oxidative effect of molecular oxygen or air on the hydrocarbons can be improved with certain materials like metals from Group 5A and Group 8 of the Periodic table or their salts and oxides, especially platinum, palladium, nickel and vanadium [32]. They state that those metals can be placed on suitable materials, for instance alumina, soda lime or active carbon. The purpose those metals with molecular oxygen or air are to improve the selective oxidation and also to increase the reaction rate, in other words, the selective oxidation step is completed in a shorter time. In the presence of those metals the required temperature for desulfurization becomes lower because metals catalyze the decomposition of organic hydroperoxides, which are the primary intermediates in autoxidation. This reduces the induction time, which is the time required between the start of autoxidation and when a significant increase in O_2 consumption is seen. Depending on the oxidizing agent and product being treated, the temperature generally should range between 80-180 °C for the oxidation step and the required oxygen amount is 1-6 active oxygen atoms in oxidizing agent per each sulphur atom in feedstock [32]. When air is used as an oxidizing agent, the 130-180 °C temperature range is more suitable.

Thiols are reasonably stable in air and can be oxidized to disulfides via molecular oxygen or air in the presence of various reagents such as metal catalysts, bromine under phase-transfer conditions, iodine and various metal salts such as Fe^{III}, Mn^{IV} and Tl^{III} [81]:

$$\text{R-SH} \xrightarrow{[o]} \text{RS-SR}$$

Thiols oxidation to disulfides:

$$4\text{R-SH} + O_2 \rightarrow 2\text{RS-SR} + 2H_2O$$

The oxidation can be catalyzed by addition of various metal ions such as Cu^{II}, Fe^{III}, Ni^{II} and Co^{II} and their complexes, and more importantly, the addition of those metal catalysts leads to the selective formation of disulfides without any overoxidized products.

2.7.8. Oxidative desulphurization with air or molecular oxygen in the absence of catalyst

Oxidative desulfurization was suggested as an alternative method to HDS, which differs completely from HDS process [83]. This method includes two steps: Firstly, sulphur compounds are oxidized to sulfoxides or sulfones respectively which have 80-150 ^{o}C higher boiling points than the corresponding sulphur compounds [30]. In narrow cuts this would enable separation by distillation:

$$\text{R-S-R'} \xrightarrow{[O]} \underset{\text{[Sulfoxide]}}{\text{R-SO-R'}} \xrightarrow{[O]} \underset{\text{[Sulfone]}}{\text{R-SO}_2\text{-R'}}$$

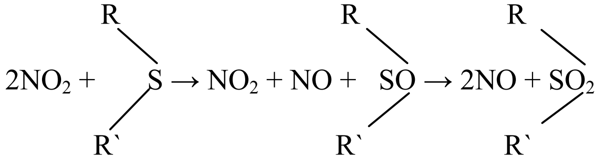
Secondly, the oxidized product is thermally decomposed in the presence or absence of base as it is shown below:

$$R\text{-}SO_2\text{-}R' \xrightarrow{\text{[Heat]}} \text{Hydrocarbons} + SO_2$$

In the industry most economical oxidant is air and it can be applied in two different ways: 1) Direct application of oxygen or air 2) indirect oxidation using an oxygen carrier. Oxygen carriers are molecules which can selectively oxidize the sulphur and can be regenerated by using molecular oxygen. There are two different kinds of carriers: regenerable and nonregenerable carriers. Oxidation of sulphur compounds with regenerable oxygen carriers includes two steps; oxidation and regeneration of the oxygen carrier with molecular oxygen [83]:

1) Oxidation: $UO_2 + R\text{-}S\text{-}R` \rightarrow U + R\text{-}SO_2\text{-}R`$
2) Regeneration of the oxidizer with molecular oxygen: $U + O_2 \rightarrow UO_2$

For example, nitrogen as regenerable oxygen carrier:

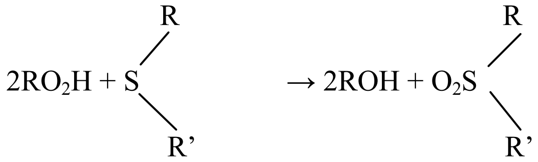


$$2NO + O_2 \rightarrow 2NO_2$$

When sulphur containing fuel is oxidized with molecular oxygen two kinds of reaction happen: firstly, hydrocarbon produces peroxidic species via oxidation [83]:

$$2RH + 2O_2 \rightarrow 2RO_2H$$

Then selective oxidation of organic sulphur happens by the peroxidic species to produce sulfoxides and sulfones:



The reactions demonstrate that even if the *in situ* oxidation of the sulphur is selective, two hydrogen atoms will be oxidized to hydroxy groups for every sulphur atom oxidised to a sulfone group, in other words, optimal oxygen selectivity in this process is 0.5. However, in fact it is usually less than 0.5 since some peroxidic groups decompose thermally and do not oxidize sulphur atoms.

Xu and Makkee's have proposed a solvent system that can promote oxidation of sulphur compounds with air in the absence of a catalyst [84]. The proposed solvents have high polarity to dissolve oxidized products and a boiling point in the range of transportation fuels such as γ-butyraloctone (GBL), γ-valerolactone (GVL), δ-valerolactone (DVL), 1-methyl-2-

pyrrolidinone (NMP), ethyl heptanoate and *n*- tetradecane (C14) as an inert fuel matrix [84].

When nitrogen was used instead of air, no conversion reaction happened in the reactor. This solvent system was applied to hydrodesulfurized diesel fuel having 44ppm sulphur content. There was no sulphur present in the diesel fuel after 4 hours of addition of an equal amount of GBL under continuous air flow at 140 ^{o}C. This process has some advantages over other oxidative desulfurization methods

- No need for catalyst
- Cheaper oxidant – air
- Higher selectivity and conversion rate

However, availability and commercial value of proposed solvents do not make this method feasible for large scale applications in the petroleum refining industry.

Low temperature oxidative desulfurization experiments were conducted without catalysts over the temperature range 100 to 186 ^{o}C for Athabasca bitumen [85]. Oxygen supply for desulfurization was around 2.5 $*10^{-3}$ k-moles O_2/kg bitumen. During the extraction process the temperature was kept below 55 ^{o}C and in order to minimize oxygen exposure nitrogen purge streams was applied at the desired operating pressure 5.5 MPa. It was stated that 150 ^{o}C (423 K) is very important temperature value in terms of affecting sulphur compounds [85]. At 150 ^{o}C, there is chance in reaction order regime- (I) high rate first order regime below 150 ^{o}C, (II) a second order regime at low extents of oxidation at temperature above 150 ^{o}C, (III) a low rate first order regime for extents of reaction greater than $1.7*10^{-3}$ k-moles/kg-bitumen over the entire range of temperature.

Atmospheric oxygen was used to oxidize sulphur compounds to sulfoxides and sulfones. The sulfoxides and sulfones, which have boiling points 80-150 ^{o}C higher than boiling point of corresponding sulphur compounds and are polar compounds that can be separated by distillation, extraction or adsorption [30]. They used a straight run kerosene fraction, SKF, (total S wt % 0.15, mercaptan S wt% 0.0063) in their experiments and applied distillation to separate the oxidized products. Reactions were performed at 120-220 ^{o}C and high pressure, and oxidized products, primarily sulfoxides and sulfones, were obtained in the aqueous phase and were separated after filtration by distillation. The main factors in oxidative treatment that were identified are: temperature, stirring rate in reaction medium, ratio of water to feedstock, oxidant consumption and duration of oxidation [30]. The increase in desulfurization degree with temperature was also confirmed by an increase in the degree of conversion of atmospheric oxygen.

Oxidative desulfurization with atmospheric oxygen is a multi phase process in which two insoluble liquids-straight run kerosene fractions and water, and air participate. P.M. Paniv’s [32] have tested effect of stirring rate of reaction medium on desulfurization degree since it is related to the contact area of the reacting phases. They found that stirring rate increases the degree of conversion of oxygen as a result of breaking air bubbles and an increase in the effective mass transfer area from the air to the reaction medium [32]. The residence time of air in the reaction medium also had an effect. In order to eliminate the effect of process duration on the results, they have conducted experiments at 5 and 20 minutes. Cormack’s have done similar desulfurization experiments via air for Athabasca bitumen and proposed that stirring rate does not have important effect on the desulfurization degree since the duration of their experiments were much longer, about 10 hours [85].

During the oxidative desulfurization process with air, some hydrocarbon molecules are oxidized too and insoluble oxidation products are formed that appear such as gums and sediments.

Bolshakov’s have studied the effect of the structure of organic sulphur compounds on the oxidation processes of jet and diesel fuels demonstrating that all sulphur compounds inhibit the oxidation of hydrocarbons, in other words, the induction period of the hydrocarbon oxidation increases and oxygen uptake decreases [86]. The observed inhibition can probably be accounted for by the formation of species containing sulphur radicals (as inhibitors, represented by In·) that do not chain propagate as readily:

$$RO_2^{\cdot} + InH \rightarrow ROOH + In\bullet$$

The structure of sulphur compounds on the inhibition efficiency is as follows: thiophenes < sulfides < disulfides <thiols [86]. The inhibiting effects of sulphur compounds become obvious at low concentrations (0.01-0.03 wt %). At higher concentrations of the sulphur compounds the oxidation rate of sulphur compounds increases as well, exceeding to a considerable extent the oxidation rate of the pure hydrocarbons [86].

The insoluble oxidation products such as sediments and gums formed in fuels, especially in those in aviation fuels, are extremely undesirable because of their detrimental effect on vehicle operation and reliability [86]. Bolshakov’s have also investigated the effect of the structures of sulphur compounds and of the hydrocarbon medium on the formation of insoluble oxidation products. Chemical analysis of the sediments formed during oxidation show that they contain significant quantities of acids (70-90%) which titrate with a distinct potential jump [86]. The average molecular weight of sediments was between 670 and 810, which were formed from the oxidation of a mixture containing alkanes, cycloalkanes, linear aliphatic and thiophenic sulphur compounds. As the molecular weight of hydrocarbon medium decreased, the molecular weight of sediments decreased too. Sediments with similar elemental composition are formed due to the oxidation of a mixture of hydrocarbon/aliphatic sulphur compounds. The least amount of solid phase or sediment was formed in the case where the structure of carbon skeleton of the hydrocarbon medium is similar to sulphur compounds, e.g. the oxidation of *n*-hexadecane/1-nonanethiol mixture resulted in least amount of solid particle formation [86]. The formation of the solid phase was due to the presence of oxidized sulphur compounds in the mixture, in other words, no sediment was formed after pure alkanes/cycloalkanes oxidation [86]. The compounds formed as a result of oxidation and condensation contains aliphatic chains of considerable length and those compounds should be readily soluble in the alkanes or cycloalkanes. After further condensation, the size of the oxidized molecules increased and a solid precipitates formed.

2.8. Summary table of desulfurization methods

Desulfurization Methods	Advantages	Disadvantages
Hydrodesulfurization (HDS)	• Most common industrial method • Well known process mechanism and chemistry • Feasible for desulfurization of light petroleum fractions or non- refractory sulphur compounds • H_2 is economically employed for desulfurization of light fractions, e.g. kerosene, naphtha and diesel fuels	• High P and T requirements while processing heavy feedstock • Hydrogenation of heavy feedstock is not selective as light fractions; therefore, high demand for H_2 under high pressure • Use of expensive catalysts/Shortened catalyst life while processing heavy feedstock • Not selective for complex sulphur compounds in heavy fractions • Some sulphur compounds such as 4- and 4,6-substituted DBT, and polyaromatic sulphur heterocycles (PASHs) are resistant and form most abundant sulphur species after HDS[2] • Extraction of compounds with heteroatom content makes protective films on the metal surfaces from distillates, which makes antiwear properties of the fuels worse; e.g. hydrotreated jet fuels has shown increased wear of fuel-pump regulator pistons in the engines[30]
Extractive Desulfurization	• Low T and P requirements • Chemical content of the feedstock is not affected • Not difficult to apply in the refineries as it is not complex process • No H2 need • Sulphur compounds can be separated by addition of water from some solvents such as ionic liquids. The distribution coefficient decreases to almost zero if enough water is added to the ionic liquid system, in other words, sulphur compounds dissolve or form second liquid phase in the water together with some light	• Limited by the solubility of organosulphur compounds in solvent • Appropriate solvent selection: Solvent having high distribution coefficient for S compounds, a low cross solubility for the hydrocarbons, a low viscosity, fast phase separation rate after mixing/extraction[38] • High distribution coefficient for model sulphur compounds such as DBT, however, relatively low distribution coefficient for real fuel • More efficient if sulphur compounds pre-oxidized • Recycling and recovery of ionic liquids is difficult

(cont'd) **Extractive Desulfurization**	hydrocarbons extracted by ILs or even sometimes precipitate. The removal of oxidized sulphur compounds from S-loaded ionic liquids by addition of water leads to displacement of sulphur compounds from ILs. • Separation of water from ionic liquids by evaporation is required before re-using ILs. The water evaporation from ionic liquids is crucial step in terms of energy consumption. Multi stage evaporation was proposed to save energy which is based on four stage evaporation at different temperature and pressure levels [38]. The energy demand is comparable with the energy demand of traditional hydrotreatment, if multi-stage evaporation is used.	• Separation of sulphur compounds from solvent by distillation: The boiling point of organosulfur compounds such as alkylated dibenzothiophenes are high (~340 ^{o}C for 4, 6-DMDBT), so high vacuum would be required in case of diesel or heating oil. So it would be applicable for the fractions having sulphur compounds with low boiling point such as gasoline.
Adsorptive Desulfurization	• Mild reaction conditions/Low T and P requirement • Not complex process • Removes sulphur compounds from refractory hydrocarbons • Tested in pilot plants and resulted in 90% sulphur removal	• Limited by selectivity of sorbent to organosulfur compounds • Limited by adsorption , durability and regenerability capacity of sorbent • Highest efficiency achieved so far is not sufficient for industrial applications • Adsorption of sulphur compounds occurs parallel to the surface of the sorbent e.g. dibenzothiophene gets attached parallel to the surface of the catalyst via π-electron of the aromatic ring, so sorbent requirement is very high for effective operations[47]. • In the adsorption step organosulfur compounds are concentrated; therefore, later high pressure hydrotreatment is required in order to eliminate sulphur compounds[47].

Biodesulfurization	• Mild operating conditions • Environmentally friendly • Results in 60-70% sulphur removal when applied by itself • No change in calorific value • Large amount of sulphur ~ 91% can be removed when applied by other desulfurization methods • Production of valuable byproducts/ Sulphur compounds can be converted into hydroxybiphenyl and its derivatives by BDS[8] • BDS requires approximately two times less capital cost and 15% less operating costs in compare to traditional HDS[8] • Current design allows the production and regeneration of the biocatalyst within the BDS process which provides 200-400 hours biocatalyst life[57] • Less greenhouse emission and energy requirement in compare to HDS • BDS process for oil field production applications is under development which will employ biocatalysts that function at 40-65 °C and remove nitrogen, metals and sulphur, resulting in crude upgrading. • BDS process used to have short biocatalyst life around 1-2 days; however, current design allows the production and regeneration of the biocatalyst within the BDS process which provides 200-400 hours biocatalyst life[57]	• Currently, microbial degradative desulfurization method is not commercially usable because of several reasons; the logistics of sanitary handling, shipment, storage and use of living bacterial cells within the production field or refinery environment. • Large amount of carbon gets mineralized during BDS which reduces fuel value[10] • There is still need to improve this method: the separation of- oil-water-biocatalyst system, byproduct disposition, product quality and reactor design are key engineering issues. • Cost effectiveness and the ability of being integrated into existing petrochemical operations as much as possible are important for commercial implementations too.

Desulfurization by Supercritical Water	• Together with H_2 and conventional HDS catalysts sulphur and metal impurities can be removed completely. The purpose of using super critical water as catalyst medium is to break carbon – heteroatom bonds.	• Requires high reaction temperature and pressure • Not suitable or convenient medium when it is used alone without any catalyst: SCW cannot remove sulphur alone • Aromatic sulphur compounds do not react in SCW as they are very stable compounds
Oxidative desulfurization	• Cheap and available oxidant, e.g. air or molecular oxygen • No catalyst requirement depending on oxidant • Higher reaction rate in compare to HDS • No H_2 requirement • More selective to various sulphur compounds in compare to HDS, e.g. desulfurization of sterically hindered sulphides such as 4, 6-dimethyldibenzothiophene (DMDBT) and 1, 2-benzodiphenylene sulphide[61] • Almost nearing commercial application in large scale industrial level • Applicable to cracked gas oils, residual fuel oils, crude oil after removing the light fractions, vacuum residues and bitumen from tar sands[60] • Well known and widely researched method for light fractions, e.g. kerosene, diesel fuel	• The oxidation of sulphur containing hydrocarbons should not proceed further than sulfone formation, otherwise, sulfonic acid derivatives, e.g. sulphuric acid H_2SO_4 formation, can be formed which is bad for the next step, thermal treatment, of the process because sulphuric acid is very corrosive acid and at high temperature during thermal treatment can poses safety hazards if the process is in large scale. • Strong oxidants such as H_2O_2 are not cost effective for large scale industrial applications • Strong oxidants such as H_2O_2 can cause emulsification of oil when added to the oil and it requires a long time to mix sufficiently with the oil • Requires hydrocarbon solvent or catalyst for higher desulfurization degree, in other words, to meet current governmental regulations. • Not sufficient research on heavy crude oil or oil/sands bitumen applications

3. EXPERIMENTAL WORK

3.1 Materials

Air was employed as an oxidant to decrease the sulphur content of oil sands derived bitumen in the absence of catalysts at moderate reaction conditions. The bitumen used for low temperature oxidation experiments was from Cold Lake, Alberta as provided by Imperial Oil Limited. Typical properties of Cold Lake bitumen are given in Table 1.

Table 1. Properties of Cold Lake Bitumen used in our autoxidation experiments

Typical physical and chemical properties of the Cold Lake Bitumen	
Physical State	Liquid
Specific Gravity	1.1
Odour	"Tarry " odour and associated smell of "rotten eggs" due to hydrogen sulphide presence
Appearance	Black Viscous Liquid
Vapour Density	Negligible
Boiling Point	168 ^{o}C (initial)
Freezing/Melting Point	7 - 12 ^{o}C
Viscosity	4400 centistokes at 38 ^{o}C
Solubility	Insoluble
Percent Volatile	~ 73 %
Sulphur content	5.1 wt %

We have conducted our autoxidation experiments in the absence of catalysts at 145 and 170-175 ^{o}C in a batch reactor system. Previous literature shows that bitumen oxidation kinetics and selectivity are different below and above 150 ^{o}C, in other words, oxidation reactions can be in a high rate first order regime or second order regime, respectively [85]. Initially, we conducted our experiments in the absence of catalyst and diluent at 145 and 175^{o}C. Based on the experimental results and observations it was necessary to employ the right diluent or solvent for the autoxidation system due to the increase in bitumen viscosity after autoxidation.

Firstly, we used water as a diluent in autoxidation experiments, as the previous literature shows that water can be beneficial during oxidation of bitumen with air [88]. Moreover, autoxidation of straight –run diesel in the presence of water at low temperature shows that water affects the process selectivity, essentially, decreases the oxidation of valuable hydrocarbon compounds and it does not affect the oxidation rate of sulphur compounds [89].

In our batch reactor experiments (as reported later on), bitumen did not demonstrate similar results like heavy oil in porous media or straight-run diesel in a batch reactor, in other words, bitumen hardening as a result of free radical addition was not avoided [88, 89]. This necessitated a change in diluent.

Secondly, we used organic solvent, heptane, as a diluent in the system to avoid free radical addition reactions after autoxidation.

Due to complex composition of bitumen, it was difficult to determine the selectivity of the autoxidation process, in other words, identification of hydrocarbon oxidation at the same time with oxidation of organosulfur compounds. We used dibenzothiophene as a model organosulfur compound and diluted it with heptane to prepare model oil. Experiments were conducted at 145 and 170 ^{o}C to determine the temperature effect on the organic solvent or hydrocarbon autoxidation and desulfurization degree of aromatic sulphur compounds.

3.2 Equipment and Procedure

Autoxidation of bitumen in the absence of diluent was carried out in the 1 litre glass reactor (Buchi Autoclave, Polyclave glass reactor, 1.0 lt, max 12 bar/200 ^{o}C). In the presence of diluent, pressure requirements are higher in comparison to autoxidation experiments in the absence of diluent, because diluents (water and diluent) should be kept in liquid phase at the temperatures above their boiling point. So 100 mL stainless steel reactor that is capable to operate at high temperatures and pressure was employed for autoxidation experiments in the presence of diluent. A back pressure regulator was attached to stainless steel reactor to keep the pressure high enough, in other words, to keep the solvent or diluent in liquid phase at the temperatures above their boiling point. A Julabo external heater was employed to heat the system. Auxiliary equipments on the autoclave included a pressure gauge, thermometer, safety valve, and a gas entraining stirrer. The air injection flow rate was controlled by Supelco flow controller. Outgoing gases such as hydrogen sulphide, sulphur oxides, carbon dioxide, etc. were transferred to a fume exhaust hood and the end of the pipe carrying those gases was left inside a water trap. As a result, outgoing sulphur oxides (i.e. SO_2) are converted into a dissolved acid in the trap water. The features of the reactor are shown schematically below in Figure 8.

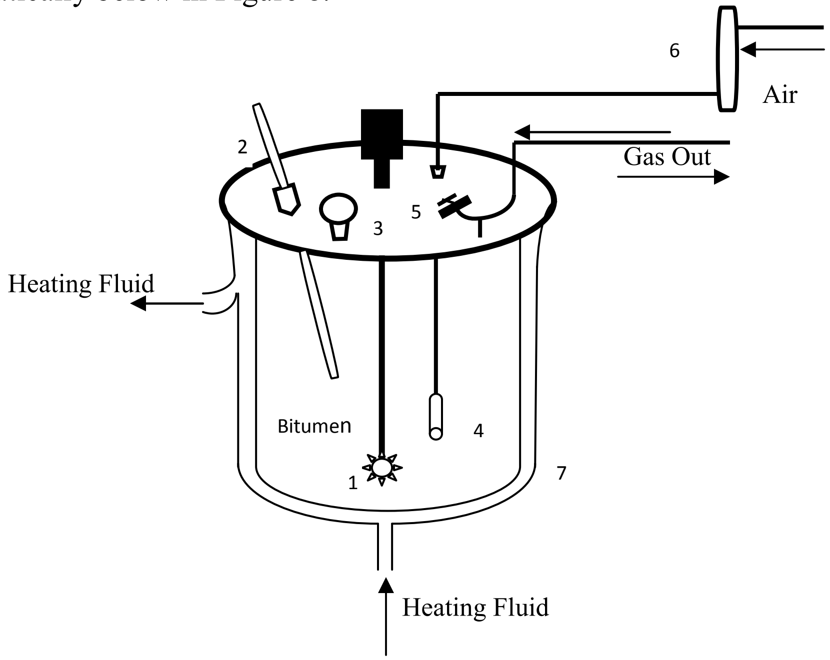


Figure 8 Reactor used in autoxidation experiments: 1.Stirrer 2.Thermometer 3.Pressure Gauge 4.Filter 5.Safety Valve 6.Flow Controller 7.Glass Reactor

The following equipments were employed for analysis of bitumen before and after autoxidation, as well as solvents, precipitated sediments and model organosulphur compounds: Antek Sulfur Analyzer (Antek 9000 NS), The HAAKE viscometer (ViscoTester VT550), Brookfield Cone/Plate Viscometer (HBDV-III UCP), IR Spectrometer (Nicolet Magna 750 FTIR), Elemental analyser (Carlo Erba EA 1108 Elemental analyser for CHNS and Oxygen), Gas Chromatograph (Hewlett Packard 5890 Gas Chromatograph-MS-FID-TCD).

Some details of the employed equipments:

- GC-MS and GC-FID: The instrument was configured with a 1:1 flow splitter post-column that enables the column eluent to be directed to the MS and FID for simultaneous detection.
  Make: Agilent
  Model: HP5890
  Column: DB-5MS 15 meter x 0.25 mm, 0.25 micron film thickness.

Carrier gas: Helium 2 ml/min, split post column 1:1: 1mL to MSD, 1 mL to FID
Temperature program: Initial T = 50C, hold 0.5 min; Ramp = 10C/min, Final T = 280C, MS Interface T = 280C, FID Temp = 330C, Inj T = 280C

- IR (used for precipitated sediment analyses after autoxidation with heptane at 145 ^{o}C)
  Make: Thermo Nicolet
  Model: 8700
  Resolution: 4 wavenumbers
  Spectra: 128 scans

- Sulfur Analyzer
  Make: Antek
  Model: 9000 NS

- Brookfield Cone/Plate Viscometer (used for bitumen autoxidised in the presence of water and heptane)
  Make: Brookfield
  Model: Brookfield Cone/Plate Viscometer
  Model number: HBDV-III UCP
  Cone Spindle: CPE-41
  Sample Volume: 2mL
  Shear rate (sec^{-1}): 2.0 N

- The HAAKE Viscometer (used for original bitumen and bitumen autoxidised in the absence of diluent)
  Make: HAAKE
  Model: ViscoTester 550
  Coaxial cylinder geometry: MV/DIN, ISO ASTM Spindle
  Sample Volume: 40 mL

- Elemental analyser (used to analyze the precipitants formed while autoxidation of model oil)
  Make: Carlo Erba
  Model: EA 1108 (Elemental Analyser for CHNS and Oxygen)

3.2.1 Autoxidation of bitumen in the absence of diluent

During autoxidation of bitumen in the absence of diluent and catalysts, 600-700 mL bitumen was placed in the reactor and heated to the target temperatures; 145 and 175 ^oC. After reaching the temperatures of interest, air injection and stirring were commenced at 1000 mL/min flow rate and 200 rpm respectively and continued for 6 hours. Reactor pressure was kept at atmospheric pressure during the experiments. More severe reactions were observed in the reactor during the autoxidation at 175 ^oC. This temperature is slightly above the initial boiling point temperature of the Cold Lake bitumen, 168 ^oC. After autoxidation experiments a severe increase in the viscosity value of bitumen was observed. Autoxidised bitumen samples were heated and stirred with water at 60 ^oC for 1 hour to extract the oxidised sulphur compounds from the system. Mass loss was negligible after autoxidation in the absence a diluent. Free gas, carbon dioxide, sulphur dioxide, hydrogen sulphide was removed from the system. The Antek sulphur analyser was used to identify the sulphur content after autoxidation and extraction with water. The viscosity of the autoxidised bitumen was measured with the HAAKE VT550 viscometer at 45 and 60 ^oC.

3.2.2 Autoxidation of bitumen in the presence of water

Reactions were carried in the 100mL stainless steel reactors at 145 and 170 ^oC. A 1:1 volume ratio of bitumen to water was employed, in other words, 40mL of bitumen was mixed with same volume amount of water. Auxiliary parts of the experimental setup were same as the system that was applied for autoxidation in the absence of water. However, a back pressure regulator was installed on reactor to keep the pressure above the vapor pressure of water at 145 and 170 ^oC (above 417 kPa and 893 kPa), respectively. The air flow rate was 350mL/min and the mixture was not stirred during reaction period (3 hours), due to smaller size of reactor and relatively low amount of bitumen in the system (40mL). Agitation occurred by air flow only. After the autoxidation experiments a single phase liquid (bitumen + water) was present in the reactor, which had a much higher viscosity in comparison to the original bitumen. Some color change in some parts of the bitumen was also observed; especially, a dark grey color was coming out while stirring the bitumen after the experiments. A small amount of water 5-7mL was retained inside the bitumen like an emulsion. Autoxidised bitumen samples were heated and stirred with water at 60 ^oC for 1 hour to extract the oxidised sulphur compounds from the system. The viscosity of the bitumen was measured at 45 and 60 ^{o}C by a Brookfield Cone/Plate Viscometer which provides direct dynamic viscosity. Sulphur removal degree was determined by Antek sulphur analyser after autoxidation and extraction process with water.

3.2.3 Autoxidation of model oil

Due to the complex composition of bitumen, it was difficult to analyze the autoxidised bitumen samples to determine the hydrocarbon oxidation level, in other words, our purpose was to identify what happens to hydrocarbons while trying to remove sulphur by autoxidation at low temperatures. Was the autoxidation selectivity efficient enough in the absence of catalysts? We used dibenzothiophene as a model organosulfur compound and diluted it with heptane to prepare the model oil. Dibenzothiophene (98 % pure) contains 17.4% sulphur. 0.9715 grams of dibenzothiophene was diluted to 225mL with heptane.

$$G = \frac{(0.9715g)\left(\frac{0.1740g}{1g}\right)\left(\frac{1\times 10^{9}ng}{1g}\right)\left(\frac{0.98g}{1g}\right)}{(225mL)\left(\frac{1000mL}{1mL}\right)} = 736.267ng/\mu L$$

50mL from the model oil with 736.267 ng/µL (0.11 wt % S) sulphur content was autoxidised at 145 and 170 ^{o}C to determine temperature effect on the organic solvent (hydrocarbon autoxidation). In addition, desulfurization degree of aromatic sulphur compounds was measured at each temperature. After the autoxidation experiments, precipitated sediments was observed in the bottom of the reactor. The amount of precipitated sediment was much higher at 145^{o}C in comparison to 170^{o}C. Autoxidised model oils were analysed with the Antek sulphur analyser, GC-MS and GC-FID to determine the desulfurization degree of the process and oxidation degree of hydrocarbon (selectivity of the process).

The experimental setup was similar to previous ones described above. The back pressure regulator was installed on the reactor to keep the pressure above the vapor pressure of heptane at 145 and 170 ^{o}C, (~ 300 kPa and ~ 570 kPa) respectively. The air flow rate was 350mL/min and the mixture was not mechanically stirred during reaction period (3 hours), due to smaller size of the reactor and relatively low concentration of sulphur in the model oil. Agitation was by air flow only.

3.2.4 Autoxidation of bitumen in the presence of organic solvent

These experiments were conducted because bitumen hardening after autoxidation was still challenge for us. The experimental setup and conditions were similar to previous ones described above. Reactions were conducted at only 145 °C based on the results achieved from the model oil autoxidation at 145 and 170 °C. We used heptane as an organic solvent and the volume ratio of heptane to bitumen was 0.8:1, in other words, 32mL of heptane was added to 40mL of bitumen. Air flow rate was 350mL/min and the mixture was not stirred during reaction period (3 hours), due to smaller size of the reactor and relatively low amount of bitumen in the system (40mL).

After the autoxidation experiments a single phase liquid (bitumen dissolved in organic solvent) was present in the reactor and the viscosity was very close to the viscosity of water. Bitumen was completely dissolved in the solvent and the precipitated sediments were apparent in the bottom of the reactor. Antek Sulphur Analyser and IR were used to determine the desulfurization degree and the composition of the precipitated sediments, respectively. The Brookfield Cone/Plate viscometer was used to measure the viscosity of bitumen and heptane mixture before and after autoxidation.

4. RESULTS

4.1. Viscosity Measurements

After autoxidation in the absence of diluent we observed a severe viscosity increase, or bitumen hardening, which was due to free radical addition reactions. Initially we tried water as a diluent in the system to avoid free radical addition based on the previous literature [88, 89]. However, it did not result in what we expected. Organic solvent, heptane, was used in the system to avoid bitumen hardening while performing autoxidation. Organic solvents such has benzene have been used for a long time in the oil and gas industry as a diluent or moderator while processing heavy oils [31, 60]. However, benzene is known as carcinogen and has poor hydrogen donor properties.

The HAAKE viscometer (*Model: ViscoTester 550, 115-230V/50-60Hz, Coaxial cylinder geometry: MV/DIN, ISO/ASTM Spindle, Sample Volume: 40 mL*) was used to measure the viscosity at 45 and 60 ^{o}C of unoxidised and autoxidised bitumen (in the absence of diluent) before and after extraction with water. Based on viscometer software output (Time vs. Torque vs. RPM), the shear stress (Pa) and shear rate (1/s) were calculated based on formulas below:

$$\textit{Shear Rate}, 1/s \qquad \dot{\gamma} = 4 \cdot 3.14 \cdot \left(\frac{RPM, \left(\frac{1}{min}\right) \quad \Omega}{60} \right) \cdot \frac{1}{\left(1 - (20.04/21)^2\right)}$$

$$\textit{Shear Stress}, Pa \qquad \tau = \frac{Torque, nM \quad M}{(2 \cdot 3.14 \cdot 0.06 \cdot 0.02004^2)}$$

$$\textit{Viscosity}, Pa \cdot s \qquad \mu = {}^{\tau}/_{\dot{\gamma}}$$

A Brookfield Viscometer (*Brookfield Cone/Plate Viscometer, Model HBDV-III UCP, Cone Spindle: CPE-41, Sample Volume: 2 mL, Shear rate (sec^{-1}): 2.0 N*) was used to measure the viscosity of autoxidised bitumen (in the presence of diluent) before and after extraction with water at 45 and 60 ^{o}C. Both of these viscometers provide dynamic viscosity and due to equipment availability in the labs two different viscometers were used for measurements.

Viscosity measurements of original raw bitumen at 45 °C

Table 2. Viscosity of original bitumen at 45 °C

t, s	Ω, 1/min	M, Nm	T, °C	Shear Rate, 1/s	Shear Stress, Pa
36	0.12	0.0021	45	0.27	14
66	0.16	0.0031	45	0.40	20
96	0.21	0.0040	45	0.49	26
126	0.26	0.0049	45	0.60	32
156	0.33	0.0061	45	0.76	40
189	0.33	0.0061	45	0.76	40
219	0.26	0.0051	45	0.60	33
249	0.21	0.0041	45	0.49	27
279	0.16	0.0032	45	0.38	21
308	0.12	0.0022	45	0.27	15

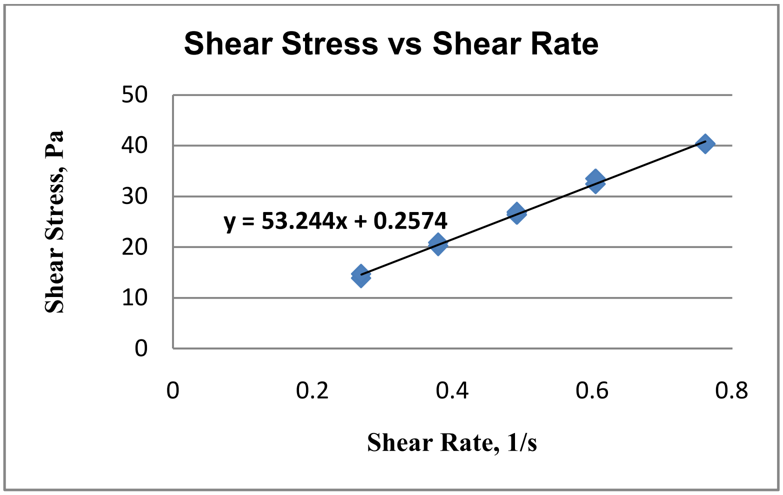
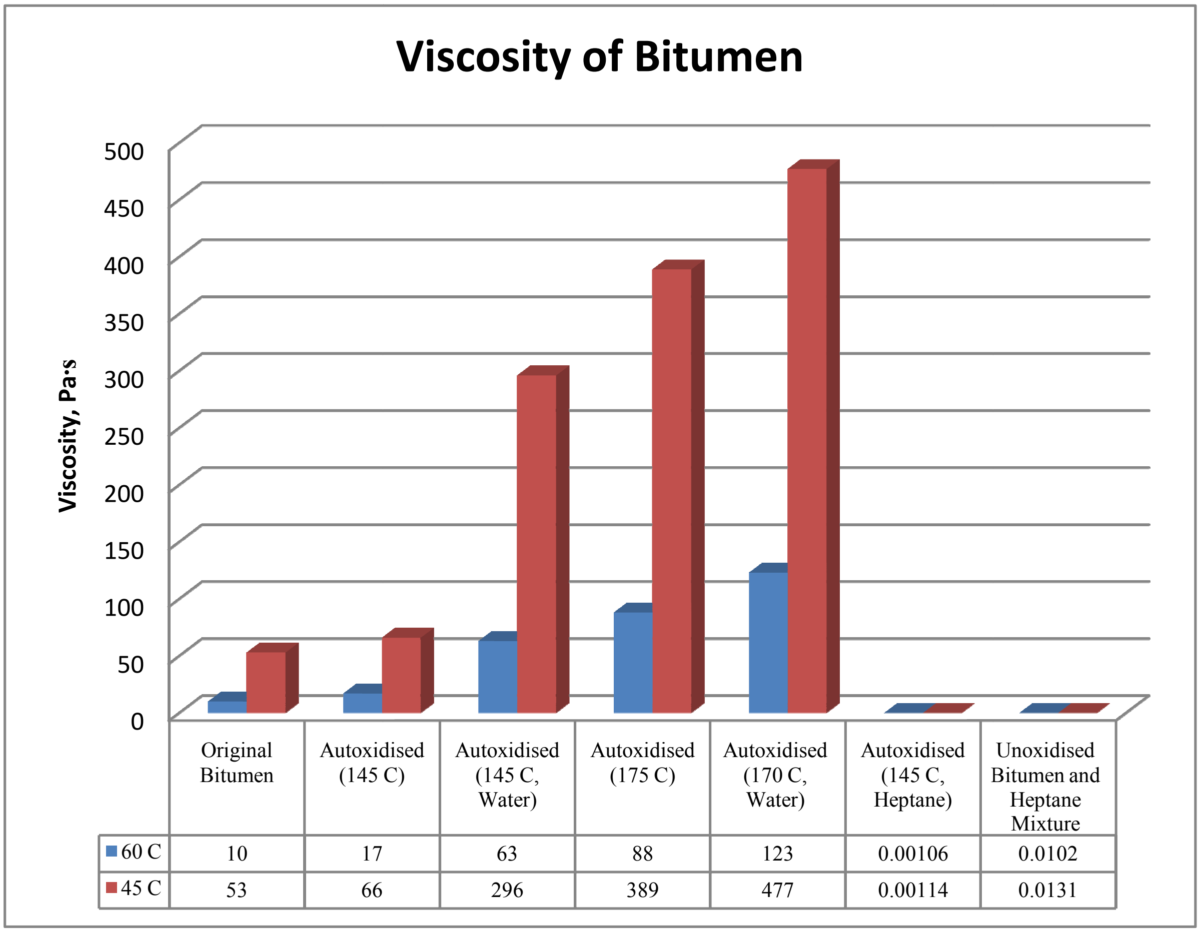


Figure 9. Original bitumen - shear stress vs. shear rate at 45 °C

$$\mathbf{k = \mu = 88\ Pa\cdot s}$$

Details of the viscosity measurements are in detail in Appendix A. Figure 10 below is the summary of the viscosity measurement



	Original Bitumen	Autoxidised (145 C)	Autoxidised (145 C, Water)	Autoxidised (175 C)	Autoxidised (170 C, Water)	Autoxidised (145 C, Heptane)	Unoxidised Bitumen and Heptane Mixture
🟦 60 C	10	17	63	88	123	0.00106	0.0102
🟥 45 C	53	66	296	389	477	0.00114	0.0131

Figure 10. Viscosity of original and autoxidised bitumen (in the absence and presence of diluent) at 45 and 60 ^{o}C

From the Figure 10 above, it is clear that when there is no diluent in the system while autoxidation viscosity increases tremendously. We can also see the effect of temperature on the viscosity (in the absence of diluent), in other words, higher temperature results in more viscous bitumen. Free radical addition reactions after autoxidation at 175 ^{o}C result in more complex and large molecules which contribute to bitumen hardening. Viscosity of autoxidised (in the absence of diluent) bitumen samples were measured after 11 months again. The viscosity of bitumen samples autoxidised at 145 ^{o}C (in the absence of diluent) decreased approximately 4 %. The viscosity of bitumen autoxidised at 175 ^{o}C (in the absence of diluent) decreased approximately 3 %. Thus, if viscosity can be used as an indication of the storage stability of bitumen after autoxidation, the lack of change indicates that there was not continued free radical addition; in other words, viscosity of autoxidised bitumen (in the absence of diluent) does not decrease or increase after a long period of time.

Firstly, water was used as a diluent to avoid bitumen hardening while autoxidation, however, the viscosity of bitumen increased more than the bitumen autoxidised in the absence of diluent, Figure 10. It is very clear that bitumen becomes less viscous when autoxidised in the presence of organic solvent, heptane (0:8:1 heptane: bitumen). Bitumen was completely dissolved in the heptane during autoxidation and after the experiments its viscosity value was very close to viscosity of water, Figure 10. In industry, for commercial applications, a lower ratio of organic solvent to bitumen would be more efficient in terms of economics.

4.2 Desulfurization Degree Analysis

Due to equipment availability in the labs, Antek Sulphur Analyzer (Model 9000 NS Nitrogen/Sulfur Analyzer) was used to determine the sulphur content of the original and autoxidised bitumen samples before and after extraction with water. As mentioned before, the extraction process was done by mixing and stirring autoxidised bitumen with same volume amount of water (1:1 volume ratio) at 60 ^{o}C.

Antek Sulphur Analyzer was calibrated with dibenzothiophene dissolved in toluene at various concentrations. Original and autoxidised bitumen samples were dissolved in toluene to make 20 mL solutions. Concentrations of samples were calculated with the following formula:

$$\frac{(a)(b)(c)(d)}{(e)(f)} = G$$

a: actual weight of bitumen or dibenzothiophene in the calibration sample
b: sulphur content in compound (g/g)
c: ng conversion (ng/g)
d: purity of compound (g/g)
e: volume of dilution (mL)
f: µL conversion (µL/mL)
G: standard concentration (ng/µL)

Example: Dibenzothiophene (98 % pure) contains 17.4% sulphur. 0.1106 grams of dibenzothiophene was diluted to 20mL with toluene.

$$G = \frac{(0.1106g)\left(\frac{0.1740g}{1g}\right)\left(\frac{1 \times 10^9 ng}{1g}\right)\left(\frac{0.98g}{1g}\right)}{(20mL)\left(\frac{1000mL}{1mL}\right)} = 942.9756 ng/\mu L$$

Analysis of the sulphur content of Original Bitumen

Table 3. Original raw bitumen sulphur concentration analysis data

Original Cold Lake Bitumen Samples	**Average Sulphur Concentrations, ng/µL**
Sample 1	861
Sample 2	870
Sample 3	863
Sample 4	869
Sample 5	870
Average	**866.6**
Standard Deviation	**4.3**

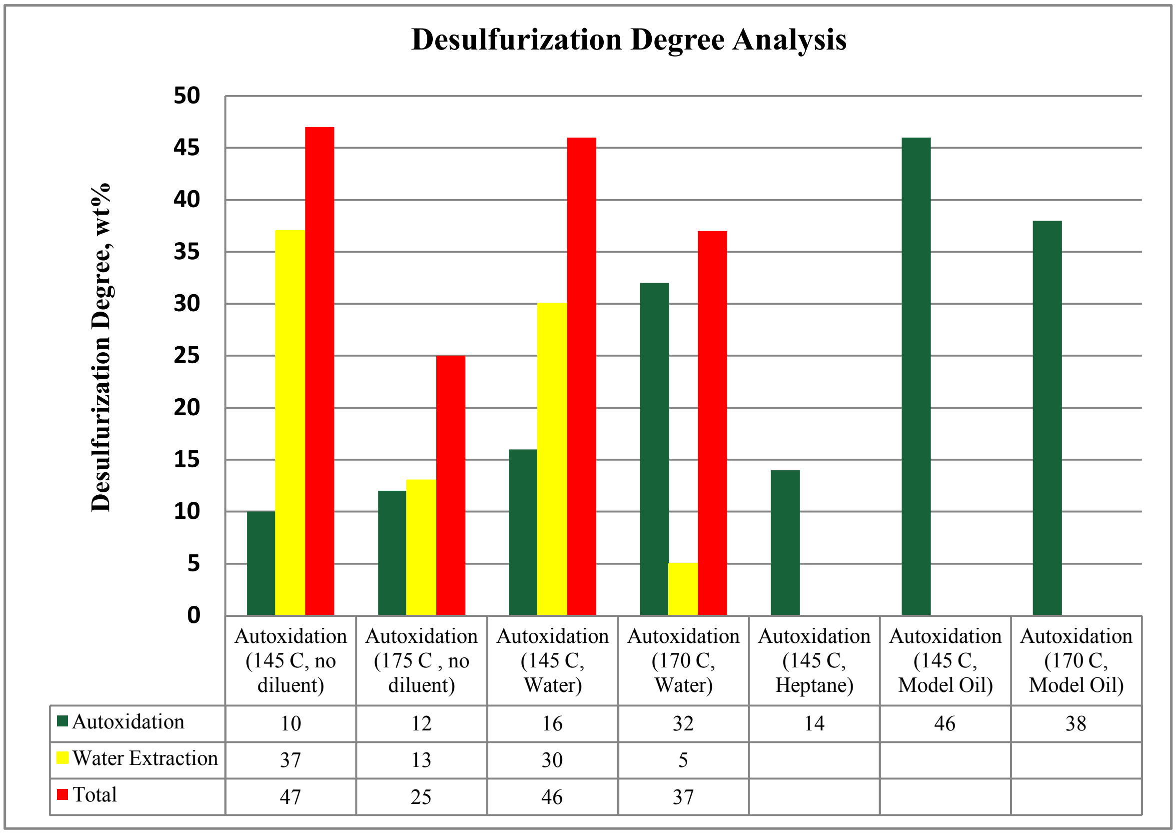
Example, 4th Sample:

$$Sulphur\ Content, g/g = \frac{869\frac{ng}{\mu L} \times 20mL \times 1000\frac{\mu L}{mL}}{0.3449g \times \frac{1\times10^9 ng}{1g} \times \frac{0.98g}{1g}} = 0.05142$$

Solution Volume: 20mL
Bitumen weight in solution: 0.3449g
Purity or error % in sample preparation measurements (volume, weight: 98%)

Sulphur Content of Original Cold Lake Bitumen ≈ 5.1 wt%

Details of the sulfur analyses data are in Appendix B. Summary of the desulfurization degree analyses is shown below in Figure 11.



	Autoxidation (145 C, no diluent)	Autoxidation (175 C , no diluent)	Autoxidation (145 C, Water)	Autoxidation (170 C, Water)	Autoxidation (145 C, Heptane)	Autoxidation (145 C, Model Oil)	Autoxidation (170 C, Model Oil)
🟩 Autoxidation	10	12	16	32	14	46	38
🟨 Water Extraction	37	13	30	5			
🟥 Total	47	25	46	37			

Figure 11. Summary of desulfurization degree analyses

Figure 11 above shows that higher temperature does not mean higher desulfurization degree. In the absence and presence of water, more sulphur is removed during autoxidation at 145 ^{o}C than autoxidation at 170 ^{o}C. Because at higher temperatures more C-S bond cleavage occurs, however, less extractible oxidised sulphur compounds form. During extraction with water at 60 ^{o}C, more oxidised sulphur compounds are removed from the bitumen autoxidised at 145 ^{o}C in comparison to the bitumen autoxidised at 170-175 ^{o}C.

Addition of water to the bitumen as a moderator does not improve the desulfurization degree significantly. On the other hand, total desulfurization degree is higher in the absence of water at 145 ^{o}C. In the presence of water, more sulphur is removed from the bitumen while autoxidation at 170 ^{o}C. However, we compare the effect of temperature on desulfurization degree, 145 ^{o}C is more efficient in comparison to 170 ^{o}C both in the absence and presence of water.

Autoxidation of bitumen in the presence of heptane removes approximately same amount of sulphur from bitumen with autoxidation in the absence and presence of water (14%). Based on the experiments conducted before, only 145 ^{o}C was selected for autoxidation of bitumen in the presence of the organic solvent, heptane. Bitumen was completely dissolved in the heptane during autoxidation and some precipitated sediments formed in the bottom of reactor which was analysed by IR. Since autoxidised bitumen was dissolved in heptane, it was difficult to extract oxidised sulphur compounds with water from bitumen that is dissolved in heptane. Organic solvent (heptane) should be separated from bitumen and then oxidised sulfur compounds can be extracted with water.

Due to precipitated particles, autoxidised solutions of the model oil were filtered and then analyzed with the Antek Sulfur Analyzer to determine the desulfurization degree. As it shown in Figure 11, more aromatic sulphur compounds are desulfurized while autoxidation at 145 ^{o}C in comparison to 170 ^{o}C. The amount of precipitated sediments was much higher after autoxidation at 145 ^{o}C than after autoxidation at 170 ^{o}C. The autoxidised model oil was also analyzed by GC-MS and GC- FID (results reported separately). Elemental analyser was used to determine the elemental composition of precipitated sediments.

4.3. GC-MS and GC- FID Analysis

The model oil, which is a mixture of heptane and dibenzothiophene, was analyzed by GC-MS and GC-FID (Hewlett Packard 5890 Gas Chromatograph) before and after autoxidation at 145 and 170 ^{o}C. Autoxidised solutions were analyzed after filtration to remove the precipitated matter.

GC-MS and GC-FID analyses were mainly conducted to identify selectivity of the process. We used Antek Sulfur Analyzer only to determine desulfurization degrees after autoxidation and extraction with water, whereas GC analyses were mainly conducted for qualitative analysis. In other words, purpose was to identify how much and what kinds of oxidized hydrocarbon and sulphur compounds were formed after autoxidation in the model oil.

Carboxylic acids, alcohols, sulfoxide, sulfone and etc., were formed after autoxidation of mixtures. However, valuable hydrocarbon oxidation that is not desirable is three times more at 170 ^{o}C in comparison to 145 ^{o}C. Also sulfoxide and sulfone formation is more at 170 ^{o}C than 145 ^{o}C. Details of the GC-MS-FID analyses are in Appendix C.

Quantification by GC-FID relies on the use of appropriate response factors. In the case of heptane the response factor is 1. The area values for the other compounds should strictly speaking be corrected, since the response factors are not 1. This was not done and there is consequently a slight bias in the results.

4.4. Elemental Analysis

Elemental Analyzer for CHNS and Oxygen (Carlo Erba EA 1108) was used to determine the elemental composition of the oxidised model oil and the precipitated matter. It was conducted for confirmation purposes, in other words, to check the results with GC-MS, GC-FID and Antek Sulfur Analyzer. The S column in the Table 4 shows zero level sulphur content for autoxidised model oil; however, they are not logical results and do not correspond to the results from GC and Antek Sulfur Analyzer.

Table 4. Elemental analysis of autoxidised model oil and precipitated sediments

Sample	**C**	**H**	**S**	**O**
Sediments #1 (145 °C)	67.9	3.8	15.3	12.3
Sediments #2 (145 °C)	67.7	3.7	15.4	12.3
Sediments #1 (170 °C)	65.6	4.3	12.4	15.7
Sediments #2 (170 °C)	65.8	4.6	12.1	15.9
Autoxidised mixture #1 at 145 °C	76.7	14.2	0.6	1.1
Autoxidised mixture #2 at 145 °C	79.8	14.8	0	1.2
Autoxidised mixture #1 at 170°C	79.3	13.8	0	5.6
Autoxidised mixture #2 at 170 °C	77.6	13.8	0	6.1

50 mL model oil was autoxidised at 145 and 170 °C having same feed concentration of DBT in heptane. However, the amount of sediments formed was much higher at 145 °C in comparison to 170 °C.

Table 5. Sediments amount after autoxidation of model oil

Sample	**Weight , mg**
Sediments from autoxidation at 145 °C	122.9
Sediments from autoxidation at 170 °C	5.2

4.5 Analysis with IR

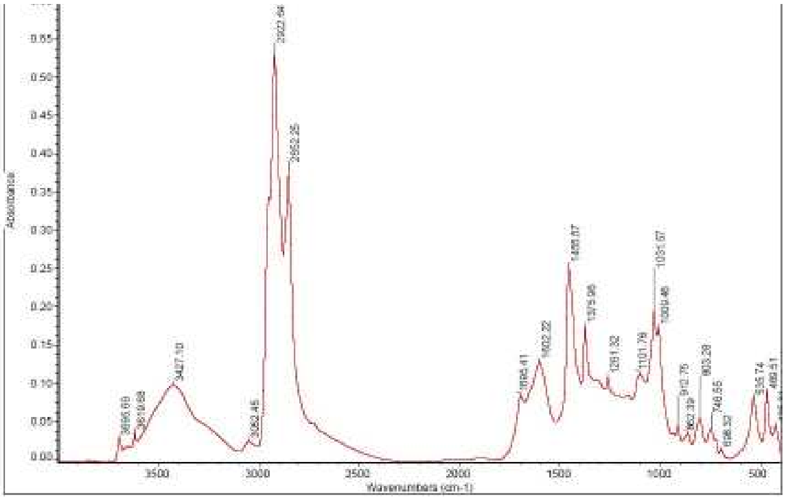
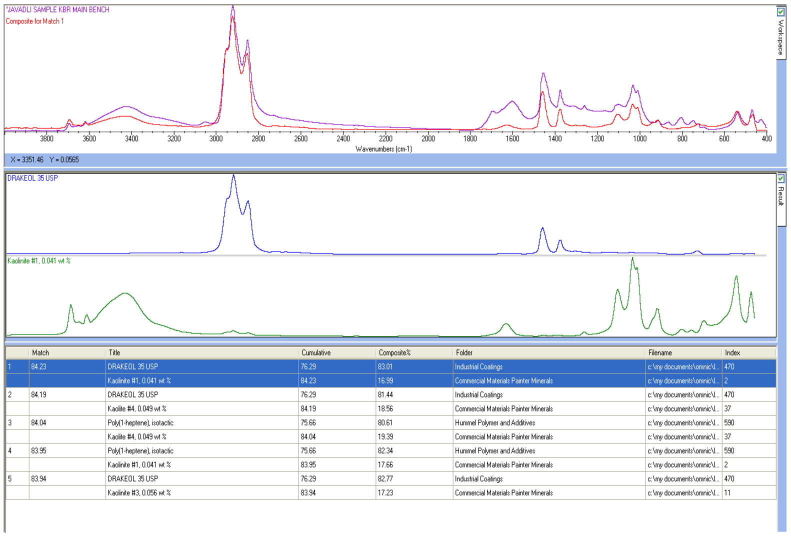


Figure 12. IR spectra of sediments precipitated while autoxidation of bitumen in the presence of heptane at 145 °C



	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	84.23	DRAKEOL 35 USP	76.29	83.01	Industrial Coatings	c:\my documents\omnic\l...	470
		Kaolinite #1, 0.041 wt %	84.23	16.99	Commercial Materials Painter Minerals	c:\my documents\omnic\l...	2
2	84.19	DRAKEOL 35 USP	76.29	81.44	Industrial Coatings	c:\my documents\omnic\l...	470
		Kaolite #4, 0.049 wt %	84.19	18.56	Commercial Materials Painter Minerals	c:\my documents\omnic\l...	37
3	84.04	Poly(1-heptene), isotactic	75.66	80.61	Hummel Polymer and Additives	c:\my documents\omnic\l...	590
		Kaolite #4, 0.049 wt %	84.04	19.39	Commercial Materials Painter Minerals	c:\my documents\omnic\l...	37
4	83.95	Poly(1-heptene), isotactic	75.66	82.34	Hummel Polymer and Additives	c:\my documents\omnic\l...	590
		Kaolinite #1, 0.041 wt %	83.95	17.66	Commercial Materials Painter Minerals	c:\my documents\omnic\l...	2
5	83.94	DRAKEOL 35 USP	76.29	82.77	Industrial Coatings	c:\my documents\omnic\l...	470
		Kaolinite #3, 0.056 wt %	83.94	17.23	Commercial Materials Painter Minerals	c:\my documents\omnic\l...	11

Figure 13. Analysis of IR spectra with Thermo Nicolet SPECTA software to identify composition of sediments from autoxidation of bitumen with heptane at 145 °C

The unoxidised S-species are very weak IR absorbers and it is difficult to identify sulphur species in bitumen based on the Figures 12 and 13 above. During autoxidation approximately 4.4 wt % of bitumen precipitated as sediments. Sediments are mixture of at least two components; a mineral fraction and an organic fraction. The best match for the mineral fraction is clay (Kaolinite), which consists mainly of a hydrated silica-alumina mixture. The organic fraction resembled the mineral oil (Drakeol), although the asphalthene fraction likely contains aromatic material too. The IR absorption at 1602 cm^{-1} is typical of a conjugated C=C system and aromatics [93].

5. DISCUSSION

5.1. Autoxidation of bitumen

Initially autoxidation experiments were conducted in the absence of diluent. Reactions were at 145 and 175 ^{o}C at atmospheric pressure. Firstly, the effect of temperature on the autoxidation process was identified in terms of sulphur removal degree and viscosity of bitumen after the oxidation. As we see from Figure 10 above, there is severe increase in the viscosity value of the bitumen: 1-2 times increase after autoxidation at 145 ^{o}C and 7-8 times increase after autoxidation at 175 ^{o}C. It happens due to free radical condensation, in other words, broken bonds come together and make larger molecules which causes an increase in viscosity value.

During autoxidation of bitumen in the absence of diluent, we removed 10-12 wt% of sulphur as H_2S and SO_2 from the bitumen. Some part of the organosulfur compounds gets oxidized but stay as a sulfoxide or sulfone compounds in the system. Those sulphur compounds can be efficiently extracted by water at low temperature, 60 ^{o}C: 37 wt% of sulphur can be extracted from the bitumen autoxidised at 145 ^{o}C and 13 wt% of sulphur can be extracted from the bitumen autoxidised at 175 ^{o}C. Sulfur compounds (e.g. benzothiophene) and their oxides have a significant difference in their partition coefficient in the same binary system. So water is likely to extract some part of oxidised sulphur compounds [25]. Thus, autoxidation in the absence of diluent at temperatures below 150 ^{o}C is more efficient in comparison to temperatures between 150-180 ^{o}C in terms of sulphur removal.

The reported change in autoxidation kinetics at 150 ^{o}C [85], is also accompanied by a change in selectivity. Instead of having more sulfoxides and sulfones that are produced at 175 ^{o}C, the nature of the species were changed, causing them to be less extractable. The exact nature of this change has not been determined, but based on the increase in viscosity; the decrease in extraction may be because larger molecules were made.

However, the experiments demonstrated that diluent is necessary for the system in order to avoid bitumen hardening.

5.2. Autoxidation of bitumen and water

Autoxidation in the presence of water, in other words, using water as a diluent in the system was not helpful to avoid bitumen hardening as a result of free radical addition. On the other hand, we even determined higher viscosity than autoxidised bitumen in the absence of diluent. In the presence of water as diluent there was a 5-6 times increase in viscosity after autoxidation at 145 °C compared to only 1-2 times without water. Likewise, there was a 10-12 times increase in viscosity after autoxidation at 170 °C in the presence of water, compared to a 7-8 times increase without water.

Previous research shows that presence of water in a porous medium affects oxidative desulfurization with air [88]. Moreover, water affects the selectivity of the process during autoxidation of light fractions [89]. It was also reported that in the presence of water the low temperature oxidation (LTO) of heavy oil resulted in improved product quality and reduced viscosity compared to oxidation without water [90].

However, in the batch reactor system, the outcome of the bitumen oxidation experiments did not correspond with the reports in literature. This might be due to high pressure in the reactor. (We had to keep the pressure high enough in the reactor to make sure that water is in liquid phase at 145 and 170 °C.) The difference with respect to the work of Wichert [89], as well as Lee and Noureldin [90], might also be due to higher oxygen availability. (Oxygen availability was increased by both pressure and continuous air flow). Studies on heavy hydrocarbon oxidation [91] indicated that oxygen availability affects the reaction pathway. The same is likely true of heavy oil oxidation.

During autoxidation of bitumen in the presence of water, we removed 16 wt% of sulphur as H_2S and SO_2 from the bitumen at 145 °C. However, it was doubled at 170 °C, in other words, 32 wt% of sulphur can be removed as H_2S and SO_2 from the bitumen. Additional sulfoxide and sulfone compounds can be extracted and removed by water at low temperature, 60 °C: 30 wt% of sulphur can be extracted from the bitumen autoxidised at 145 °C and 5 wt% of sulphur can be extracted from the bitumen autoxidised at 170 °C, Figure 11. In summary, autoxidation in the presence of water at the temperatures below 150 °C is more efficient in comparison to temperatures above 150 °C, as shown by reaction at 170 °C, in terms of sulphur removal.

During autoxidation of bitumen, the H_2S and SO_2 are mainly coming from aliphatic sulfides because it is easier to break sulphur bonds from them in comparison to aromatic sulphur compounds. It is likely that the aromatic sulphur compounds are mainly converted to sulfoxide or sulfone species, rather than being desulfurized directly.

Water is not a good solvent or moderator for the autoxidation system to avoid bitumen hardening. However, water extraction during autoxidation can prevent some free radical addition reactions. The level of desulfurization at 170 °C versus 145 °C of the bitumen and water mixture is 0.8. The same ratio for neat bitumen is only 0.5. At least some of the oxidized sulphur compounds that could not be removed from the bitumen during neat autoxidation at 175

°C, could be removed in the presence of water. Although this change could also be caused by water being involved in the reaction chemistry, it is unlikely that it contributes much [92].

5.3. Autoxidation of bitumen and heptane

Dilution of bitumen is employed in the oil sands industry during solvent deasphalting to precipitate the asphalthene fraction. Dilution of bitumen is also employed to make the bitumen transportable in pipelines. The selection of heptane as solvent is therefore in line with industrial practise to employ naphtha, although our intent was different. The presence of an organic solvent such as heptane in the system was used to prevent bitumen hardening.

During the autoxidation process almost all of the bitumen is dissolved in the heptane. Impurities within bitumen, such as clay minerals, precipitated during autoxidation, but not necessarily due to autoxidation. The 0.8:1 volume ratio of heptane to bitumen resulted in a severe viscosity decrease and the viscosity was not meaningfully different after autoxidation at 145 ^{o}C, Figure 10. In fact, we do not need that much decrease in bitumen viscosity, although is indicates that free radical addition, aggregation and bitumen hardening was effectively reduced. So for commercial applications in oil and gas industry, a lower volume ratio of organic solvent to bitumen should be applied to make the process more cost effective.

During autoxidation approximately 14 wt % of sulphur can be removed from the bitumen as H_2S and SO_2. However, before extraction of sulfoxide or sulfone compounds from oxidised bitumen, the organic solvent should be separated and recycled, which is a disadvantage of this method. However, the presence of the organic solvent has an advantage in terms of separation of some impurities from bitumen, such as clay and minerals.

During autoxidation approximately 4.4 wt % of bitumen precipitated as sediments. Sediments were analysed with IR and Thermo Nicolet SPECTA software was used to detect composition. Sediments are mixture of at least two components; a mineral fraction and an organic fraction (see Figures 12 and 13). The best match for the mineral fraction is clay (Kaolinite), which consists mainly of a hydrated silica-alumina mixture. The organic fraction resembled the mineral oil (Drakeol), although the asphalthene fraction likely contains aromatic material too. The IR absorption at 1602 cm^{-1} is typical of a conjugated C=C system and aromatics [93].

5.4. Autoxidation of model oil

It was difficult to identify the selectivity of the bitumen autoxidation since bitumen contains many different types of compounds. So, the model organosulfur compound, dibenzothiophene (DBT), was diluted with heptane to prepare model oil and it was autoxidised at 145 and 170 °C. The results from Antek sulphur analyser shows that air is an efficient oxidant to remove sulphur from aromatic sulphur compounds. 46 wt% of the sulphur was removed from model oil containing dibenzothiophene at 145 °C, whereas sulphur removal was 38 wt% at 170 °C. This result again demonstrates that temperatures below 150 °C are more efficient for oxidative desulfurization of aromatic sulphur compounds in comparison to higher temperatures (Appendix C).

GC-MS and GC-FID was used to identify the compounds in the product and quantify the selectivity of the autoxidation process. Dibenzothiophene sulfone formation is more than dibenzothiophene sulfoxide formation at 145 °C. However, at 170 °C sulfoxide and sulfone formation are almost at the same level (Appendix C). It was also identified that at 170 °C more sulphur are oxidised compared to 145 °C, yet, the nature of the oxidized sulphur compounds are such that less sulphur is extractable after oxidation at 170 °C.

GC-MS-FID analyses show that temperatures below 150 °C (145 °C) are more efficient in comparison to temperatures between 150-180 °C (170 °C) in terms of selectivity of the process. At 170 °C the organic solvent or hydrocarbon is oxidised to a greater extent than at 145 °C. It is also confirmed by elemental analysis of precipitated sediments and autoxidised model oil solutions at 145 and 170 °C, Appendix C. Elemental analysis of autoxidised model oils show that the organic solvent is affected less at 145 °C in comparison to 170 °C.

Quantification by GC-FID is biased, because the analysis did not take response factors into account for the oxidized products and DBT.

5.5. Industrial implications of this work

The organic sulphur compounds can be divided into two groups; the first group can be removed by procedures like HDS and the second group which are more resistant to HDS. The more refractory sulphur containing compounds must also be removed to meet the current government regulations associated with sulphur levels in transportation fuels. The most commonly applied and traditional method, HDS, is able to remove those refractory sulphur compounds, however, the process is expensive due to its high temperature and pressure requirements.

It is fact that fuel consumption and exploitation of petroleum resources increase over time all over the world. The remaining part of the petroleum resources is mainly more viscous and heavier, with higher sulphur content. Therefore, desulfurization of heavy petroleum products having higher sulphur content with HDS will make the final fuel more expensive. Alternative desulfurization methods under mild reaction conditions have some benefits such as that the final fuel price will be lower, less undesirable products or pollutants will be produced, less energy will be consumed during desulfurization process, etc. Sulphur removal by cheap oxidative desulfurization methods or biodesulfurization may potentially be applied after HDS in the near future and replace HDS in some applications in the far future.

Vapor Extraction Process (VAPEX) is one of the new methods in bitumen extraction operations. It is similar to SAGD; however, in VAPEX a hydrocarbon solvent is injected into the reservoir instead of steam. The synergy with the present work, which indicated that there is benefit in employing an organic diluent for ODS is clear.

Toe to Heel Air Injection (THAI) is a new method in bitumen extraction operation as well. In this method oil is ignited in the reservoir and any air that bypasses the combustion zone autoxidises the heavy oil. The insights generated in the present work are therefore relevant to THAI.

Our small scale laboratory experiments show that air has potential to be employed as an oxidant to pre-refine bitumen in the absence of catalysts at low temperatures. Advantages of the results of this research are twofold: Firstly, this method can be applied in situ, or in a porous medium. In addition to extraction from the formation, air plays a role in partial upgrading of bitumen right in the formation. Secondly, this method can be applied in current refineries as a pre-refining technology and it does not require much capital cost or extensive changes in the design of the plants. At present it is best to be considered as a pre-hydrodesulfurization or post-hydrodesulfurization method.

It is a fact that HDS is cost effective method while desulfurization of aliphatic sulphur compounds and does not require severe reaction conditions. However, in the case of complex aromatic sulphur compounds, HDS is not an ideal method. So, low temperature autoxidation can be applied before or after HDS to remove sulphur from aromatic compounds in a cost effective way.

6. CONCLUSION

Literature research shows that oxidative desulfurization (ODS) with cheap oxidants (e.g. air) and biodesulfurization have some advantages over traditional HDS. Advantages include moderate reaction conditions, less capital cost, little change in the calorific value of fuel and less greenhouse gas emissions. As a result, the final refined product or fuel price will be lower, less undesirable products or pollutants will be produced and less energy will be consumed during desulfurization process. Thus, in the near future ODS and biodesulfurization have good potential to be utilized in large scale industrial application such as pre-HDS methods.

The effect of temperature on bitumen autoxidation is not similar to straight-run diesel fuel autoxidation. In the case of bitumen, a higher temperature does not mean higher desulfurization degree. In the presence or absence of water, temperatures below 150 ^{o}C (145 ^{o}C) are more efficient in bitumen upgrading in comparison to temperatures between 150-180 ^{o}C (170 ^{o}C). Temperature does not show this effect only on desulfurization degree, but also on bitumen viscosity. At temperatures above 150 ^{o}C (170 ^{o}C) bitumen gets much harder or heavier in comparison to temperatures below 150 ^{o}C (145 ^{o}C) as a result of free radical addition.

Bitumen viscosity is one of the main obstacles that should be overcome to make it flow in the reservoir or make it transportable in pipelines. Water is not as good a moderator for bitumen during oxidative desulfurization as it is for ODS of straight run diesel fuels. It does not improve the selectivity of the process, whereas bitumen is desulfurized less and becomes more viscous during autoxidation in the presence of water. On the other hand, organic solvents, or light fractions of fuel (naphtha) were found to be very good moderators during autoxidation of bitumen. Bitumen loses a higher amount of sulphur as H_2S and SO_2 during autoxidation in the presence of organic solvents. Moreover, bitumen is dissolved, or becomes much less viscous in the presence of organic solvents.

Water can be used for extraction of oxidised sulphur compounds. At low temperatures (60 ^{o}C), oxidised sulphur compounds can be extracted from bitumen after autoxidation. Water demonstrated more efficiency in terms of extraction capability from the bitumen autoxidised at 145 ^{o}C than the bitumen autoxidised at 170 ^{o}C. Because during autoxidation at 170 ^{o}C, larger and more complex compounds are formed in the bitumen by free radical addition reactions.

Selectivity of oxidative desulfurization is important as well, because oxidation of hydrocarbons during desulfurization is undesirable. Hydrocarbons are oxidised in both temperature ranges, below and above 150 °C. However, the extent of hydrocarbon oxidation is lower at 145 °C in comparison to at 170 °C.

Air is capable to desulfurize bitumen in the absence of catalysts and can be employed as an oxidant.

Autoxidation has potential to be employed in upstream (extraction), mid-stream (pre-refining) and downstream (refining) operations in the heavy oil industry. In upstream operations air can be used during extraction of bitumen, which would do partial bitumen upgrading right in the formation. In downstream operation, autoxidation can be applied as a pre- or post-treatment method in addition to traditional HDS. On the other hand, autoxidation as a pre-refining method would not require much capital costs to implement, or result in high operation costs.

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8. APPENDIX

8.1. Appendix A

Details of Viscosity Measurements

8.1.1. Viscosity measurements of original raw bitumen

Table A1. Viscosity of original bitumen at 45 °C

t, s	Ω, 1/min	M, Nm	T, °C	Shear Rate, 1/s	Shear Stress, Pa
36	0.12	0.0021	45	0.27	14
66	0.16	0.0031	45	0.40	20
96	0.21	0.0040	45	0.49	26
126	0.26	0.0049	45	0.60	32
156	0.33	0.0061	45	0.76	40
189	0.33	0.0061	45	0.76	40
219	0.26	0.0051	45	0.60	33
249	0.21	0.0041	45	0.49	27
279	0.16	0.0032	45	0.38	21
308	0.12	0.0022	45	0.27	15

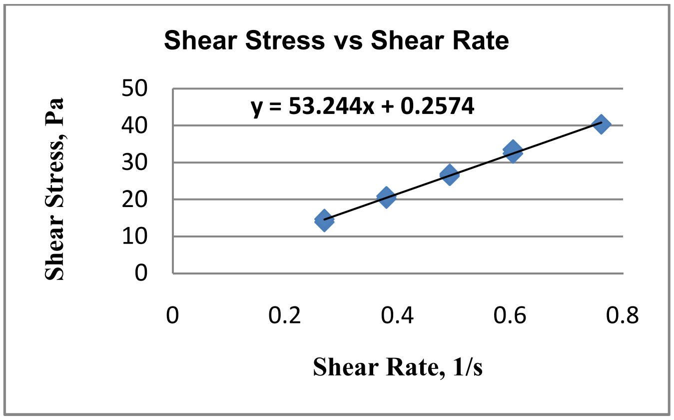

Figure A1. Original bitumen - shear stress vs. shear rate at 45 °C

k = μ = 53 Pa·s

Table A2. Viscosity of original bitumen at 60 °C

t, s	Ω, 1/min	M, Nm	T, °C	Shear Rate, 1/s	Shear Stress, Pa
36	0.12	0.00048	60	0.27	3.2
66	0.16	0.00065	60	0.38	4.3
96	0.21	0.00083	60	0.49	5.5
126	0.26	0.0010	60	0.60	6.7
157	0.33	0.0012	60	0.76	8.1
189	0.33	0.0012	60	0.76	8.1
219	0.26	0.00099	60	0.60	6.5
249	0.21	0.00080	60	0.49	5.3
279	0.16	0.00059	60	0.37	3.9
309	0.12	0.00043	60	0.27	2.8

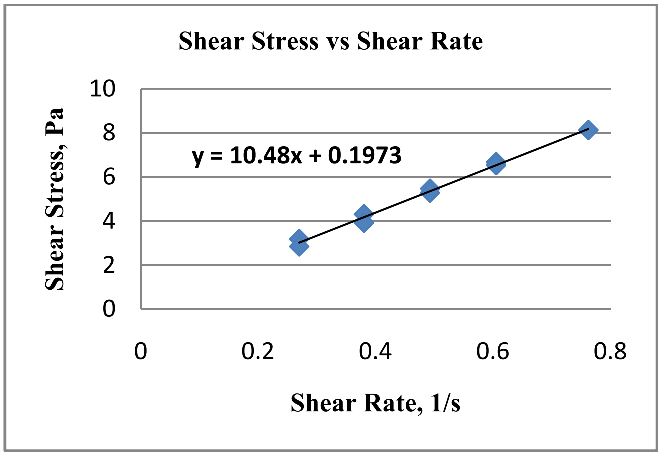

Figure A2. Original bitumen - shear stress vs. shear rate at 60 ^{o}C

k = μ = 11 Pa·s

8.1.2. Viscosity measurements of autoxidised bitumen in the absence of diluent

Table A3. Viscosity of autoxidised (145 ^{o}C) bitumen in the absence of diluent at 45 ^{o}C

t, s	Ω, 1/min	M, Nm	T, °C	Shear Rate, 1/s	Shear Stress, Pa
36	0.36	0.0094	45	0.85	62
66	0.48	0.011	45	1.14	72
96	0.61	0.014	45	1.43	95
126	0.73	0.020	45	1.72	132
156	0.85	0.022	45	1.99	146
189	0.85	0.021	45	1.99	136
219	0.73	0.015	45	1.72	99
249	0.61	0.014	45	1.43	90
278	0.48	0.012	45	1.14	77
309	0.36	0.010	45	0.85	65
576	0.21	0.0046	45	0.49	30
606	0.25	0.0058	45	0.58	38
637	0.28	0.0067	45	0.67	44
666	0.32	0.0080	45	0.76	53
696	0.36	0.0088	45	0.85	58
728	0.36	0.0089	45	0.85	58
758	0.32	0.0085	45	0.76	56
788	0.28	0.0081	45	0.67	53
818	0.25	0.0072	45	0.58	47
849	0.21	0.0061	45	0.49	40

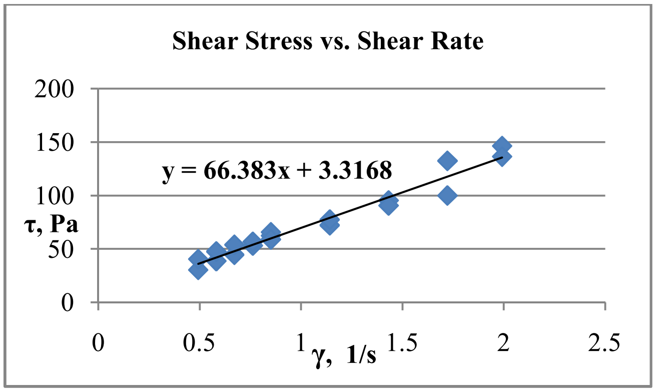

Figure A3. Autoxidised bitumen in the absence of diluent (145 ^{o}C) - shear stress vs. shear rate at 45 ^{o}C

k = μ = 66 Pa·s

Table A4. Viscosity of autoxidised (145 ^{o}C) bitumen in the absence of diluent at 60 ^{o}C

t, s	Ω, 1/min	M, Nm	T, °C	Shear Rate, 1/s	Shear Stress, Pa
36	0.21	0.0012	60	0.49	8.26
66	0.24	0.0014	60	0.58	9.44
96	0.28	0.00175	60	0.67	11.56
126	0.32	0.0019	60	0.76	12.62
157	0.36	0.0021	60	0.85	14.20
189	0.36	0.0021	60	0.85	14.14
219	0.32	0.0019	60	0.76	12.62
249	0.28	0.0017	60	0.67	11.36
279	0.24	0.0015	60	0.58	9.97
309	0.21	0.0012	60	0.49	8.06

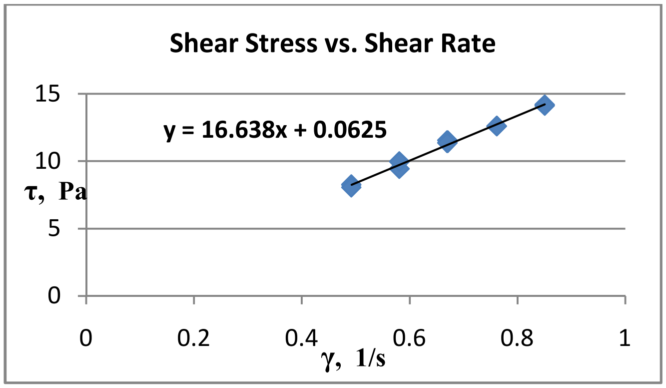

Figure A4. Autoxidised bitumen in the absence of diluent (145 ^{o}C) - shear stress vs. shear rate at 60 ^{o}C

k = μ = 17 Pa·s

Table A5. Viscosity of autoxidised (175 ^{o}C) bitumen in the absence of diluent at 45 ^{o}C

t ,s	Ω , 1/min	M, Nm	T in °C	Shear Rate, 1/s	Shear Stress, Pa
36	0.066	0.012	45	0.15	75
66	0.085	0.016	45	0.20	105
96	0.12	0.021	45	0.26	136
126	0.15	0.024	45	0.35	160
156	0.17	0.027	45	0.40	179
188	0.17	0.027	45	0.40	175
218	0.15	0.026	45	0.35	169
248	0.12	0.022	45	0.26	142
278	0.086	0.017	45	0.20	110
309	0.067	0.012	45	0.15	81

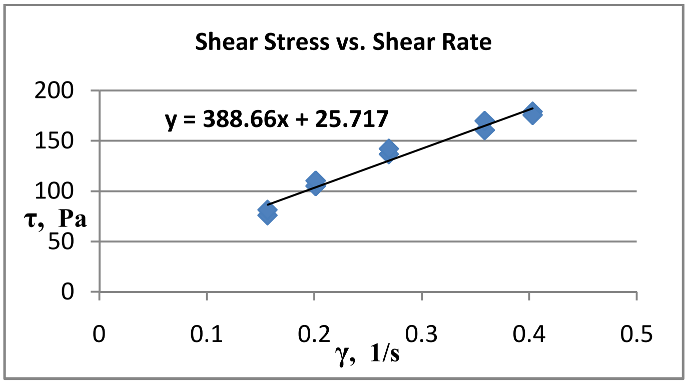

Figure A5. Autoxidised bitumen in the absence of diluent (175 ^{o}C) - shear stress vs. shear rate at 45 ^{o}C

k = μ = 389 Pa·s

Table A6. Viscosity of autoxidised (175 ^{o}C) bitumen in the absence of diluent at 60 ^{o}C

t, s	Ω, 1/min	M, Nm	T, °C	Shear Rate, 1/s	Shear Stress, Pa
498	0.12	0.0059	60	0.26	39
528	0.16	0.0075	60	0.37	49
558	0.21	0.0089	60	0.49	59
588	0.26	0.010	60	0.60	67
619	0.33	0.012	60	0.76	79
651	0.33	0.012	60	0.76	79
681	0.26	0.010	60	0.60	66
711	0.21	0.0083	60	0.49	54
741	0.16	0.0065	60	0.37	43
771	0.12	0.0049	60	0.26	32

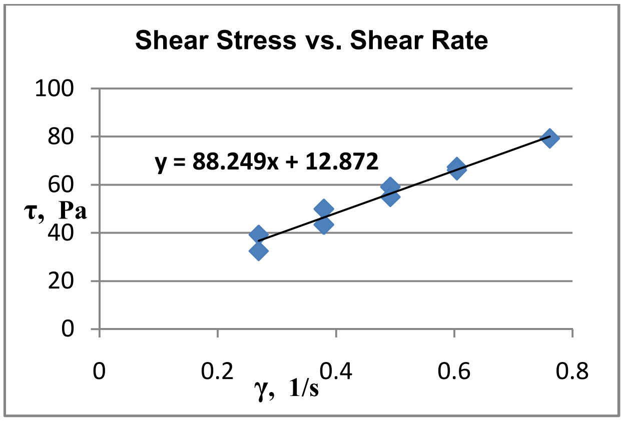

Figure A6. Autoxidised bitumen in the absence of diluent (175 ^{o}C)- shear stress vs. shear rate at 60 C

k = μ = 88 Pa·s

8.1.3. Viscosity measurements of autoxidised bitumen in the presence of water

Viscosity of autoxidised bitumen samples (in the presence of diluent) was measured at 45 and 60 ^{0}C by Brookfield Viscometer (*Brookfield Cone/Plate Viscometer, Model HBDV-III UCP, Cone Spindle: CPE-41, Sample Volume: 2 mL, Shear rate (sec^{-1}): 2.0 N*) which provides dynamic viscosity directly. The original feed mixture before autoxidation and phase separation contained water: bitumen in a 1:1ratio.

Table A7. Viscosity of autoxidised bitumen in the presence of water

	Viscosity, Pa·s	
Temperature	**45 ^{o}C**	**60 ^{o}C**
Autoxidised Bitumen in the presence of water, 145 ^{o}C	296	63
Autoxidised bitumen in the presence of water, 170 ^{o}C	477	123

8.1.4. Viscosity measurements of autoxidised bitumen in the presence of organic solvent

Table A8. Viscosity of autoxidised bitumen in the presence of heptane

	Viscosity, Pa·s	
Temperature	**45 ^{o}C**	**60 ^{o}C**
Bitumen and Heptane mixture “before” autoxidation	0.00161	0.00131
Autoxidised Bitumen in the presence of heptane, 145C	0.00114	0.00106

8.2. Appendix B
Details of Desulfurization Degree Analyses

8.2.1. Sulphur Content of bitumen autoxidised at 145 C in the absence of diluent

Table B1. Bitumen autoxidised in the absence of diluent at 145 °C

Bitumen autoxidised at 145 °C in the absence of diluent	**Average Sulphur Concentrations, ng/μL**
Sample 1	837
Sample 2	815
Sample 3	813
Sample 4	837
Sample 5	797
Sample 6	784
Sample 7	832
Sample 8	820
Sample 9	830
Average	**818.3**
Standard Deviation	**18.4**

Example, Sample 8:

$$Sulphur\ Content, g/g = \frac{820\frac{ng}{\mu L} \times 20mL \times 1000\frac{\mu L}{mL}}{0.36g \times \frac{1\times10^9 ng}{1g} \times \frac{0.98g}{1g}} = 0.04648$$

Solution Volume: 20mL
Bitumen weight in solution: 0.36g
Purity or error % in sample preparation measurements (volume, weight: 98%)

Sulphur content of bitumen autoxidised at 145 °C in the absence of diluent
≈ 4.65 wt%

Total sulphur removal after autoxidation at 145 °C in the absence of diluent
≈ 10 wt %

This value represents the sulphur removal on account of autoxidation as gaseous products, e.g. SO_2

8.2.2. Sulphur content of bitumen autoxidised at 145 C in the absence of diluent and extracted with water at 60 C

Table B2. Bitumen autoxidised in the absence of diluent at 145 ^{o}C and extracted with water

Bitumen after autoxidation at 145 ^{o}C in the absence of diluent and extraction with water at 60 ^{o}C	**Average Sulphur Concentrations, ng/µL**
Sample 1	310
Sample 2	305
Sample 3	297
Sample 4	309
Sample 5	311
Sample 6	308
Average	**306.6**
Standard Deviation	**5.2**

Example, Sample 2:

$$Sulphur\ Content, \frac{g}{g} = \frac{305\frac{ng}{\mu L} \times 20mL \times 1000\frac{\mu L}{mL}}{0.23g \times \frac{1\times10^{9}ng}{1g} \times \frac{0.98g}{1g}} = 0.027063$$

Solution Volume: 20mL
Bitumen weight in solution: 0.23g
Purity or error % in sample preparation measurements (volume, weight: 98%)

Sulphur content of bitumen after autoxidation at 145 ^{o}C in the absence of diluent and extraction with Water at 60 ^{o}C ≈ 2.70 wt%

Sulphur removal after extraction at 60 ^{o}C with water from bitumen autoxidised at 145 ^{o}C in the absence of diluent ≈ 37wt%

$$\text{Total Sulphur Removal} = \text{After Autoxidation} + \text{After Extraction}$$

$$\text{S, wt\%} \approx 10\text{wt\%} + 37\text{wt\%} \approx 47\text{wt \%}$$

8.2.3. Sulphur content of bitumen autoxidised at 175 C in the absence of diluent

Table B3. Bitumen autoxidised in the absence of diluent at 175 °C

Autoxidised bitumen at 175 °C in the absence of diluent	**Average sulphur concentrations, ng/µL**
Sample 1	595
Sample 2	587
Sample 3	610
Sample 4	602
Sample 5	592
Sample 6	590
Sample 7	583
Sample 8	606
Average	**595.6**
Standard Deviation	**9.5**

Example, Sample 5:

$$Sulphur\ Content, g/g = \frac{592\frac{ng}{\mu L} \times 20mL \times 1000\frac{\mu L}{mL}}{0.27g \times \frac{1\times10^{9}ng}{1g} \times \frac{0.98g}{1g}} = 0.04474$$

Solution Volume: 20mL
Bitumen weight in solution: 0.27g
Purity or error % in sample preparation measurements (volume, weight: 98%)

Sulphur content of bitumen autoxidised at 175 °C in the absence of diluent $\approx$ 4.47 wt%

Total sulphur removal after autoxidation at 175 °C in the absence of diluent $\approx$ 12 wt %

This value represents the sulphur removal on account of autoxidation as gaseous products, e.g. SO_2

8.2.4. Sulphur content of bitumen autoxidised at 175 C in the absence of diluent and extracted with water at 60 C

Table B4. Bitumen autoxidised in the absence of diluent at 175 °C and extracted with water

Bitumen after autoxidation at 175 °C in the absence of diluent and extraction with water at 60 °C	Average Sulphur Concentrations, ng/µL
Sample 1	540
Sample 2	535
Sample 3	527
Sample 4	534
Sample 5	536
Sample 6	539
Sample 7	526
Sample 8	530
Average	**533.4**
Standard Deviation	**5.2**

Example, Sample 3:

$$Sulphur\ Content, \frac{g}{g} = \frac{527\frac{ng}{\mu L} \times 20mL \times 1000\frac{\mu L}{mL}}{0.28g \times \frac{1\times10^{9}ng}{1g} \times \frac{0.98g}{1g}} = 0.038411$$

Solution Volume: 20mL
Bitumen weight in solution: 0.28g
Purity or error % in sample preparation measurements (volume, weight: 98%)

Sulphur content after autoxidation at 175 °C in the absence of diluent and extraction with water at 60 °C ≈ 3.84%

Sulphur removal after extraction with water at 60 °C from bitumen autoxidised at 175 °C in the absence of diluent ≈ 13 wt%

$$\text{Total Sulphur Removal } = \text{After Autoxidation} + \text{After Extraction}$$

$$\text{S, wt\%} \approx 12\text{wt\%} + 13\text{wt\%} \approx 25 \text{ wt \%}$$

8.2.5. Sulphur content of bitumen autoxidised at 145 C in the presence of water

Table B5. Bitumen autoxidised in the presence of water at 145 ^{o}C

Bitumen Autoxidised at 145 ^{o}C in the Presence of Water	**Average Sulphur Concentrations, ng/µL**
Sample 1	364
Sample 2	367
Sample 3	365
Sample 4	366
Sample 5	364
Sample 6	365
Sample 7	372
Average	**366.1**
Standard Deviation	**2.8**

Example, Sample 4:

$$Sulphur\ Content, \frac{g}{g} = \frac{366\frac{ng}{\mu L} \times 20mL \times 1000\frac{\mu L}{mL}}{0.174g \times \frac{1\times10^{9}ng}{1g} \times \frac{0.98g}{1g}} = 0.042927$$

Solution Volume: 20mL
Bitumen weight in solution: 0.174g
Purity or error % in sample preparation measurements (volume, weight: 98%)

Sulphur content of bitumen autoxidised at 145 ^{o}C in the presence of water
≈ 4.3 wt%

Total sulphur removal after autoxidation at 145 ^{o}C in the presence of water
≈ 16 wt %

8.2.6. Sulphur content of bitumen autoxidised at 145 C in the presence of water and extracted with water at 60 C

Table B6. Bitumen autoxidised in the presence of water at 145 °C and extracted with water

Bitumen after autoxidation at 145 °C in the presence of water and extraction with water at 60 °C	Average sulphur concentrations, ng/µL
Sample 1	141
Sample 2	138
Sample 3	133
Sample 4	139
Sample 5	142
Sample 6	138
Sample 7	144
Average	**139.3**
Standard Deviation	**3.5**

Example, Sample 4:

$$Sulphur\ Content, \frac{g}{g} = \frac{139\frac{ng}{\mu L} \times 20mL \times 1000\frac{\mu L}{mL}}{0.1028g \times \frac{1\times10^{9}ng}{1g} \times \frac{0.98g}{1g}} = 0.027595$$

Solution Volume: 20mL
Bitumen weight in solution: 0.103g
Purity or error % in sample preparation measurements (volume, weight: 98%)

Sulphur content of bitumen after autoxidation at 145 °C in the presence of water and extraction with water at 60 °C ≈ 2.76%

Sulphur removal after extraction at 60 °C from bitumen autoxidised at 145 °C in the presence of water ≈ 30wt%

$$\text{Total Sulphur Removal} = \text{After Autoxidation} + \text{After Extraction}$$

$$\text{S, wt\%} \approx 16\text{wt\%} + 30\text{wt\%} \approx 46\ \text{wt}\ \%$$

8.2.7. Sulphur content of bitumen autoxidised at 170 C in the presence of water

Table B7. Bitumen autoxidised in the presence of water at 170 ^{o}C

Bitumen Autoxidised at 170 ^{o}C in the Presence of Water	**Average Sulphur Concentrations, ng/µL**
Sample 1	423
Sample 2	423
Sample 3	422
Sample 4	410
Sample 5	419
Sample 6	422
Sample 7	408
Average	**418.1**
Standard Deviation	**6.4**

Example, Sample 5:

$$Sulphur\ Content, g/g = \frac{419\frac{ng}{\mu L} \times 20mL \times 1000\frac{\mu L}{mL}}{0.2485g \times \frac{1\times10^{9}ng}{1g} \times \frac{0.98g}{1g}} = 0.03444$$

Solution Volume: 20mL
Bitumen weight in solution: 0.2485g
Purity or error % in sample preparation measurements (volume, weight: 98%)

Sulphur Content of Bitumen Autoxidised at 170 ^{o}C in the Presence of Water
≈ 3.4 wt%

Total Sulphur Removal after Autoxidation at 170^{o}C in the Presence of Water
≈ 32 wt %

8.2.8. Sulphur content of bitumen autoxidised at 170 C in the presence of water and extracted with water at 60 C

Table B8. Bitumen autoxidised in the presence of water at 170 ^{o}C and extracted with water

Bitumen after autoxidation at 170 ^{o}C in the presence of water and extraction with water at 60 ^{o}C	**Average sulphur concentrations, ng/µL**
Sample 1	490
Sample 2	463
Sample 3	479
Sample 4	493
Sample 5	485
Sample 6	501
Sample 7	499
Sample 8	505
Average	**489.4**
Standard Deviation	**13.7**

Example, Sample 3:

$$Sulphur\ Content, \frac{g}{g} = \frac{479\frac{ng}{\mu L} \times 20mL \times 1000\frac{\mu L}{mL}}{0.305g \times \frac{1\times10^{9}ng}{1g} \times \frac{0.98g}{1g}} = 0.032051$$

Solution Volume: 20mL
Bitumen weight in solution: 0.305g
Purity or error % in sample preparation measurements (volume, weight: 98%)

Sulphur content of bitumen after autoxidation at 170 ^{o}C in the presence of water and extraction with water at 60 ^{o}C ≈ 3.2%

Sulphur removal after extraction at 60 ^{o}C from bitumen autoxidised at 170 ^{o}C in the presence of water ≈ 5 wt%

$$\text{Total Sulphur Removal} = \text{After Autoxidation} + \text{After Extraction}$$

$$\text{S, wt\%} \approx 32\text{wt\%} + 5\text{wt\%} \approx 37\ \text{wt}\ \%$$

8.2.9. Sulphur content of model oil after autoxidation at 145 C

Table B9. Sulphur content of Heptane and DBT mixture after autoxidation at 145 ^{o}C

Autoxidised Heptane and DBT mixture (145 ^{o}C)	**Sulphur Concentrations, ng/µL**
Sample Injection 1	389.4
Sample Injection 2	386.6
Sample Injection 3	390
Sample Injection 4	392.9
Sample Injection 5	400.3
Sample Injection 6	404.9
Sample Injection 7	401.4
Sample Injection 8	411.2
Sample Injection 9	409.7
Sample Injection 10	400.7
Average	**398.71**
Standard Deviation	**8.6**

$$Sulphur\ removal, wt\% = 1 - \frac{398.71\frac{ng}{\mu L}}{736.267\ ng/\mu L} = 0.4585$$

Total sulphur removal after autoxidation of model oil at 145^{o}C ≈ 46 wt %

Table B10. Sulphur content of Heptane and DBT mixture after autoxidation at 170 ^{o}C

Autoxidised Heptane and DBT mixture (170 ^{o}C)	**Sulphur Concentrations, ng/µL**
Sample Injection 1	453
Sample Injection 2	442.8
Sample Injection 3	448
Sample Injection 4	456.3
Sample Injection 5	454.8
Sample Injection 6	455.4
Sample Injection 7	451.2
Sample Injection 8	460.1
Sample Injection 9	445.1
Sample Injection 10	463
Average	**452.97**
Standard Deviation	**6.4**

$$Sulphur\ removal, wt\% = 1 - \frac{452.97\frac{ng}{\mu L}}{736.267\ ng/\mu L} = 0.3847$$

Total sulphur removal after autoxidation of model oil at 175^{o}C ≈ 38 wt %

8.2.10. Sulphur content of bitumen autoxidised at 145 C in the presence of organic solvent, heptane

Table B11. Sulphur content of bitumen autoxidised at 145 °C in the presence of heptane

Autoxidised bitumen in the presence of heptane (145 °C)	**Sulphur concentrations, ng/µL**
Sample Injection 1	1344
Sample Injection 2	1319
Sample Injection 3	1311
Sample Injection 4	1303
Sample Injection 5	1295
Sample Injection 6	1366
Sample Injection 7	1322
Sample Injection 8	1287
Sample Injection 9	1320
Sample Injection 10	1306
Average	**1317**
Standard Deviation	**23.3**

$$Initial\ Sulphur\ Concentration = 1530\ \mathrm{ng/\mu L}$$

$$Sulphur\ removal\ degree, wt\ = 1 - \frac{1317\frac{ng}{\mu L}}{1530\frac{ng}{\mu L}} = 0.139$$

Total sulphur removal after autoxidation of bitumen at 145°C in the presence of heptane ≈ 14 wt %

8.3. Appendix C
Details of GC-MS & FID Analyses

8.3.1. Analysis of original model oil

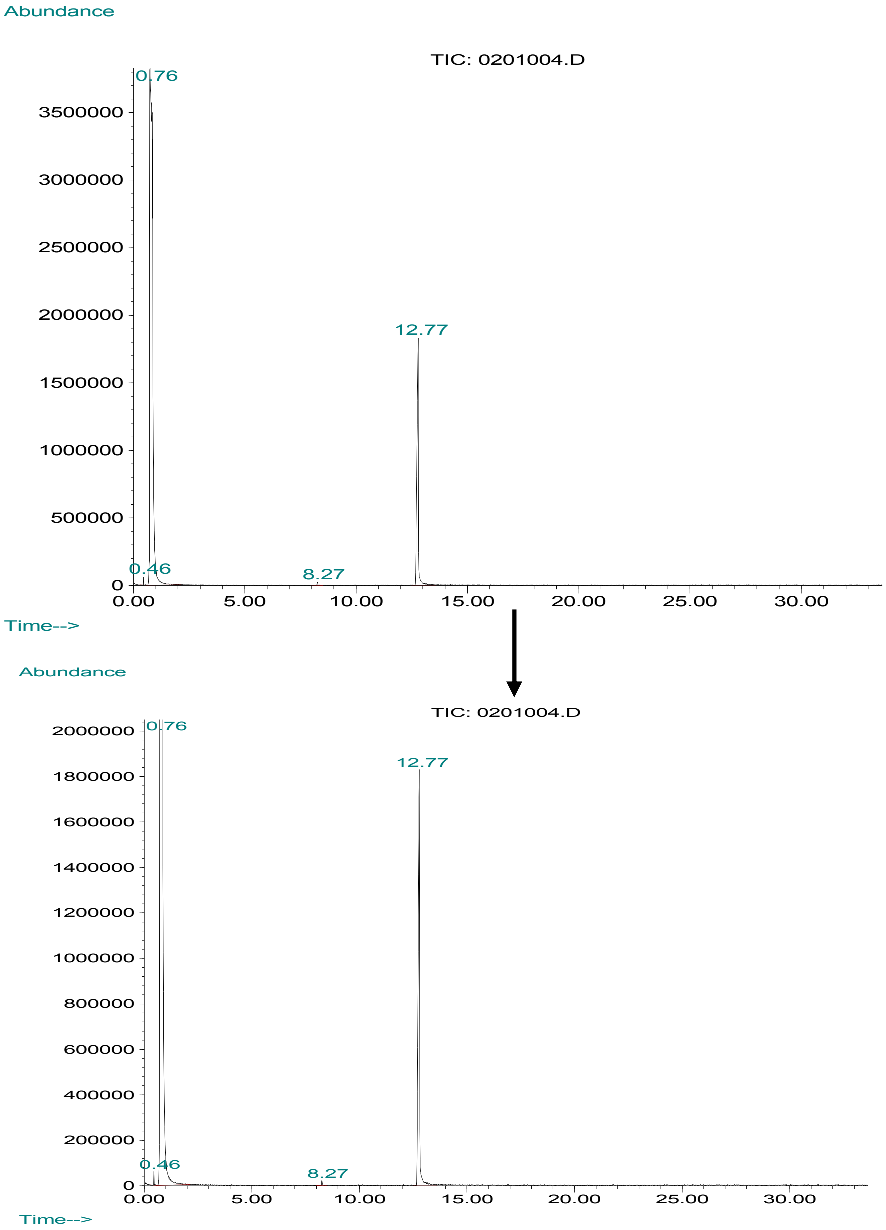

Figure C1. GC-MS curve of original mixture of heptane and DBT before autoxidation, Total Ion Count (TIC) Signal

Table C1. Area percent report, Original Model Oil Signal TIC

Peak #	R.T., min	First Scan	Max Scan	Last Scan	PK, TY	Peak Height	Peak Area	Peak % Max	% of Total
1	0.458	23	40	54	BV3	47183	522936	0.14%	0.114%
2	0.766	54	68	192	PB 2	3716502	371443262	100.00%	80.741%
3	8.274	728	752	771	BB3	21119	635850	0.17%	0.138%
4	12.774	1136	1162	1235	BB	1695292	87440537	23.54 %	19.007%

Sum of corrected areas: 460042585

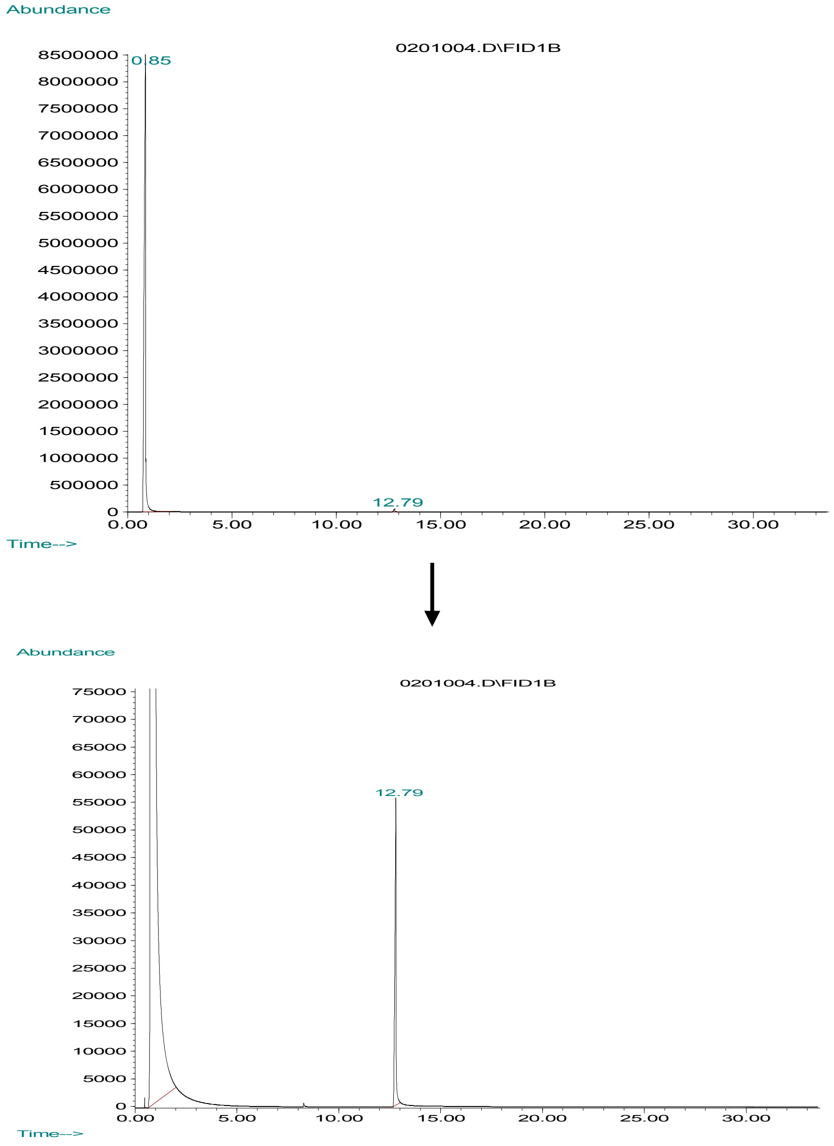

Figure C2. GC-FID curve of original mixture of heptane and DBT before autoxidation, Signal 0201004.D\FID1B

Table C2. Area percent report, Original model oil, Signal 0201004.D\FID1B

Peak #	R.T. min	Start min	End min	PK TY	Peak Height	Peak Area	Peak % max	% of Total
1	0.851	0.630	2.017	BB	8502266	428065386	100.00%	99.464%
2	12.795	12.649	13.016	BB	53017	2308660	0.54%	0.536%

Sum of corrected areas: 430374046

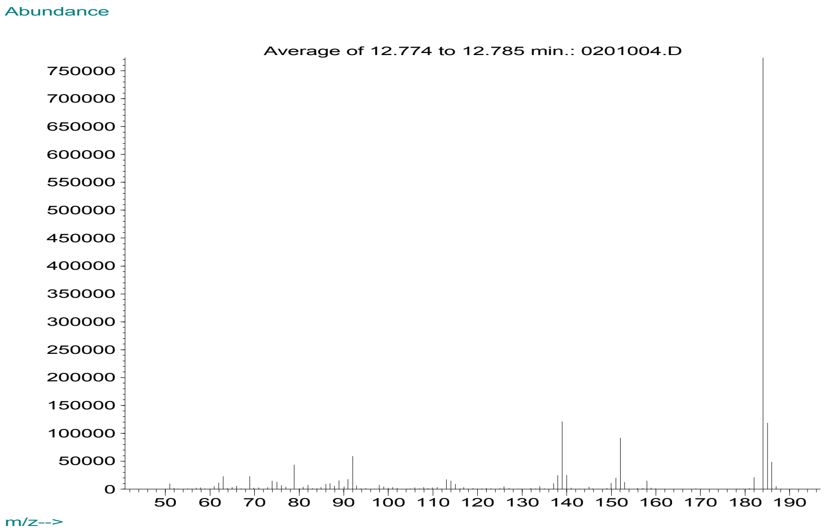

Figure C3. The mass spectrum for the peak at 12.77 in the original mixture, this corresponds to electron impact mass spectrum of dibenzothiophene.

Table C3. Identification of the compounds in the curves of original mixture of heptane and dibenzothiophene through database

Peak #	RT	Area, %	Compound
1	0.46	0.11	Methane, dichloro-
2	0.77	80.74	Heptane
3	8.27	0.14	1,1′-Biphenyl Naphthalene, 2-ethenyl-
4	12.77	19.01	Dibenzothiophene

In the preparation of model oil 98% pure dibenzothiophene was diluted with 99% pure heptane. As we see from the Table C3 above, 99.75% of solution is consisted of heptane and dibenzothiophene. It can be assumed that identification of dichloromethane and 1, 1-biphenyl were related to impurities within the heptane (dichloromethane is miscible with organic solvents), dibenzothiophene or inside the equipment.

8.3.2. Analysis of model oil after autoxidation at 145 C

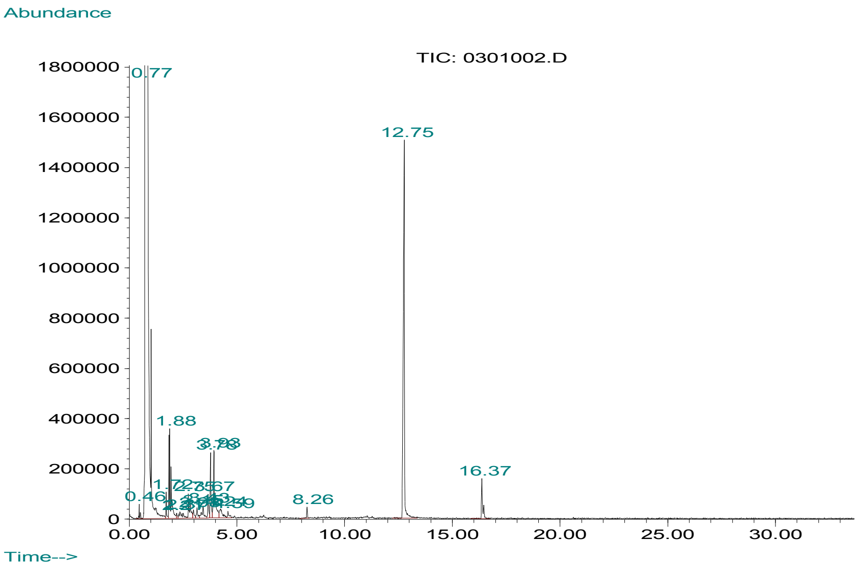

Figure C4. GC-MS curve of mixture of heptane and DBT after autoxidation at 145 ^oC, TIC Signal

Table C4. Area percent report, Model Oil after autoxidation at 145 ^oC, Signal TIC

Peak #	R.T., min	First Scan	Max Scan	Last Scan	PK TY	Peak Height	Peak Area	Peak % Max	% of Total
1	0.459	26	40	52	BV3	46907	1148201	0.31%	0.229%
2	0.766	52	68	152	VV4	3746362	373446419	100.00%	74.584%
3	1.721	152	155	164	VV	78925	1797142	0.48%	0.359%
4	1.886	164	170	197	VV3	351870	15566471	4.17%	3.109%
5	2.204	197	199	204	VV3	19590	641072	0.17%	0.128%
6	2.368	204	214	242	VV8	25145	2707647	0.73%	0.541 %
7	2.753	242	249	266	VV2	85578	4845802	1.30%	0.968%
8	2.983	266	270	278	VV4	32729	1428458	0.38%	0.285%
9	3.148	278	285	295	VV4	40722	1775277	0.48%	0.355%
10	3.433	295	311	327	VV2	43791	2899827	0.78%	0.579%
11	3.664	327	332	339	VV	81906	2887126	0.77%	0.577%
12	3.773	339	342	350	VV	230023	6750660	1.81%	1.348%
13	3.938	350	357	378	VV	275334	13653633	3.66%	2.727%
14	4.234	378	384	410	VV9	34729	3417631	0.92%	0.683%
15	4.586	410	416	433	VV5	24095	1225664	0.33%	0.245%
16	8.252	719	750	758	BV	42983	1107046	0.30%	0.221%
17	12.752	1111	1160	1215	BB	1400469	58975916	15.79%	11.779%
18	16.374	1442	1490	1522	BB2	154725	6432885	1.72%	1.285%

Sum of corrected areas: 500706876

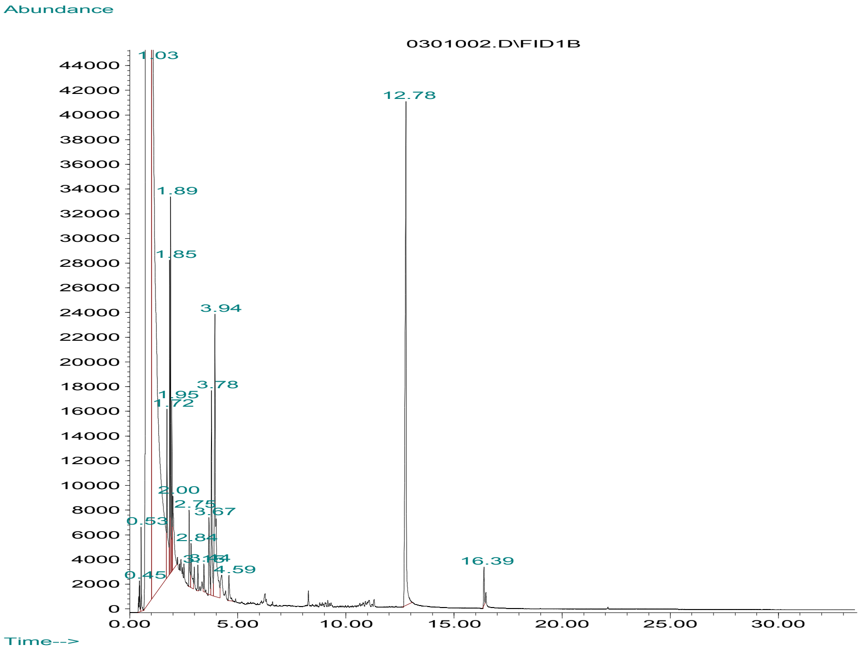

Figure C5. GC-FID curve of mixture of heptane and DBT after autoxidation at 145 °C, Signal 0301002.D\FID1B

Table C5. Area percent report, Model Oil after autoxidation at 145 °C, Signal 0301002.D\FID1B

Peak #	R.T. min	Start min	End min	PK TY	Peak Height	Peak Area	Peak % max	% of Total
1	0.451	0.374	0.506	BV	2299	62281	0.02%	0.015%
2	0.530	0.506	0.642	VV	6730	82291	0.02%	0.020%
3	0.849	0.642	1.015	PV	8342743	407630051	100.00%	96.822%
4	1.026	1.015	1.697	VV	121292	8203534	2.01%	1.949%
5	1.724	1.697	1.827	VV	13614	350623	0.09%	0.083%
6	1.852	1.827	1.871	VV	24794	316571	0.08%	0.075%
7	1.893	1.871	1.927	VV	30419	437017	0.11%	0.104%
8	1.951	1.927	1.978	VV	13604	207730	0.05%	0.049%
9	2.000	1.978	2.187	VV	5982	276841	0.07%	0.066%
10	2.753	2.696	2.816	BV	6121	118040	0.03%	0.028%
11	2.842	2.816	2.959	VV	3554	107742	0.03%	0.026%
12	3.153	3.091	3.202	PV	2077	44888	0.01%	0.011%
13	3.435	3.403	3.495	VV	2221	44901	0.01%	0.011%
14	3.666	3.564	3.748	BV	6216	166241	0.04%	0.039%
15	3.783	3.748	3.867	VV	16591	412201	0.10%	0.098%
16	3.943	3.867	4.176	VV	22645	914828	0.22%	0.217%
17	4.590	4.544	4.766	PB	2045	66674	0.02%	0.016%
18	12.777	12.604	13.055	BB	40627	1490559	0.37%	0.354%
19	16.386	16.317	16.436	BV	3088	75664	0.02%	0.018%

Sum of corrected areas: 421008676

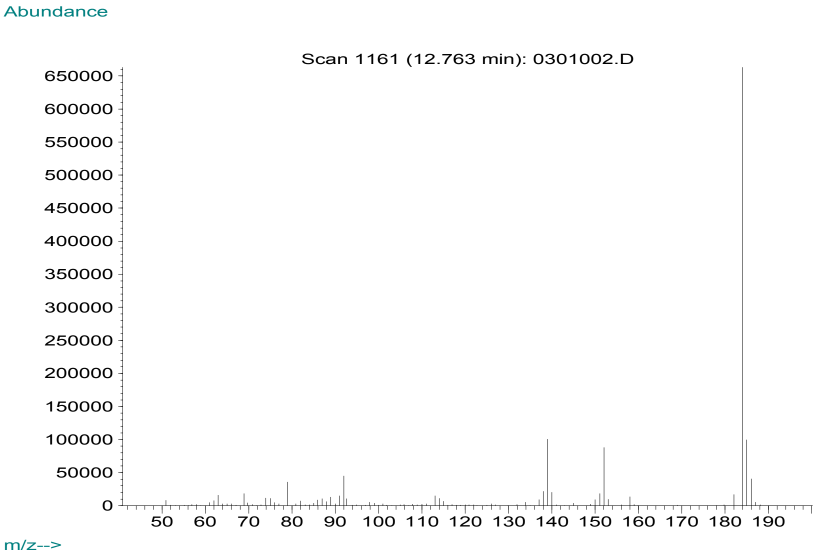

Figure C6. The mass spectrum for the peak at 12.75 in the mixture (145 °C)

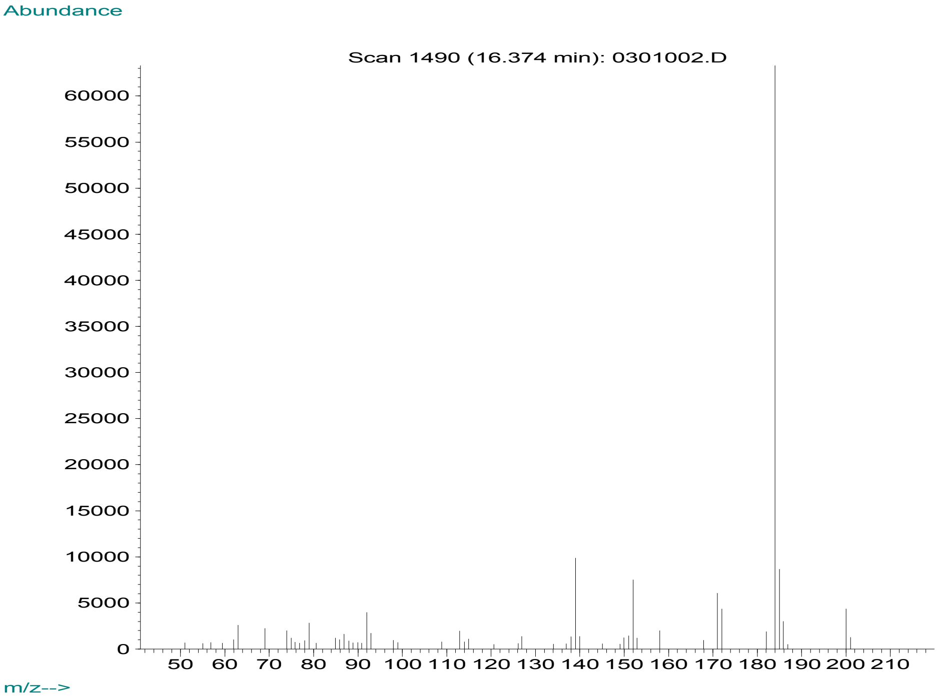

Figure C7. The mass spectrum for the peak at 16.37 in the mixture (145 °C), the change in molecular ion of 16 m/z indicates that this is likely the sulfoxide of dibenzothiophene

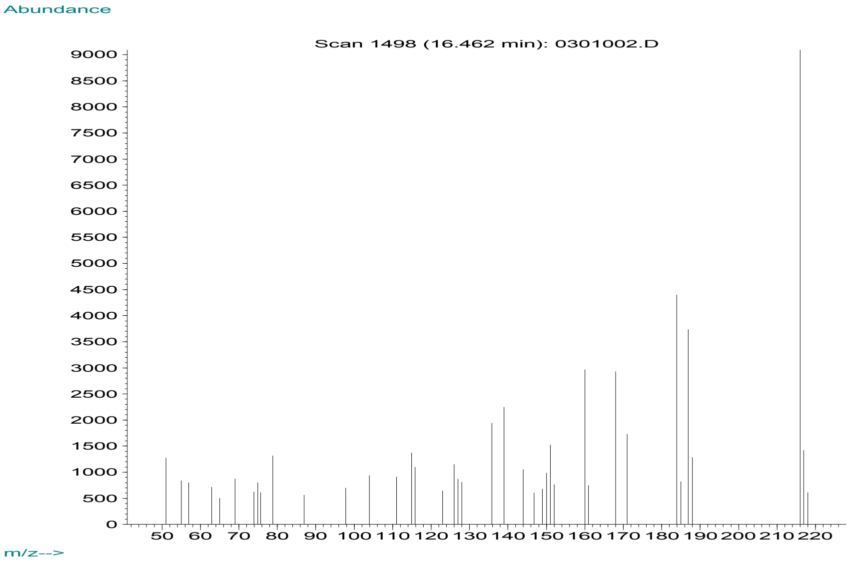

Figure C8. The mass spectrum for the peak at 16.46 in the mixture (145°C), The change in molecular ion of 32 m/z indicates that this is likely the sulfone of dibenzothiophene.

Table C6. Identification of the compounds of mixture of heptane and dibenzothiophene after autoxidation conducted at 145 °C. Identification is based on the best match in the MS database, which in some instances make no sense from a chemistry point of view.

Peak #	RT	Area, %	Compound
1	0.46	0.23	Methane, dichloro-
2	0.77	74.58	Heptane
3	1.72	0.36	Cyclohexane, methoxy- 4-Heptanone
4	1.89	3.11	2-Hexanone, 5-methyl- 2-Heptanone
5	2.20	0.13	Ethanal-n-methyl-n-formylhydrazone 1-Allyloxy 3-t-butoxypropan-2-ol 2-[3,3-Dideuteroallenyl]ethylsucci
6	2.37	0.54	2-Heptadecanol 1-Eicosanol Nonadecanol
7	2.75	0.97	2,4-Heptanedione 3-Methyldioxopiperazine Hexane, 2-methyl-
8	2.98	0.29	2-Hexen-1-ol, 2-ethyl- 3-Hexanone, 2,5-dimethyl- Octane, 2,4,6-trimethyl-
9	3.15	0.35	Decane, 2,5,6-trimethyl- Heneicosane, 11-(1-ethylpropyl)- Hexane, 3-ethyl-
10	3.43	0.58	Heptane, 2,5-dimethyl- Diaziridine, 1,2-dipropyl- Isothiazole, 4-methyl-
11	3.66	0.58	2-Butene, 1-propoxy-, (E)- 1,1-Cyclobutanedicarboxlyic acid Eicosane
			Permethylated and reduced product

12	3.77	1.35	3-Butenyl ethyl ether Guanosine
13	3.94	2.73	Cyclohexanol, 4-methyl- Heptane, 3,5-dimethyl- Hexane, 4-ethyl-2-methyl-
14	4.23	0.68	Tetracosane, 2,6,10,15,19,23-hexam Pentadecane, 2,6,10,14-tetramethyl Pentadecane, 2,6,10,14-tetramethyl
15	4.59	0.24	1,6-Hexanediol Tetrahydrogeranyl 2-methyl butyrat
16	8.25	0.22	1,1´-Biphenyl
17	12.75	11.78	Dibenzothiophene
18	16.37	1.28	Dibenzothiophene sulfoxide

8.3.3. Analysis of model oil after autoxidation at 170 C

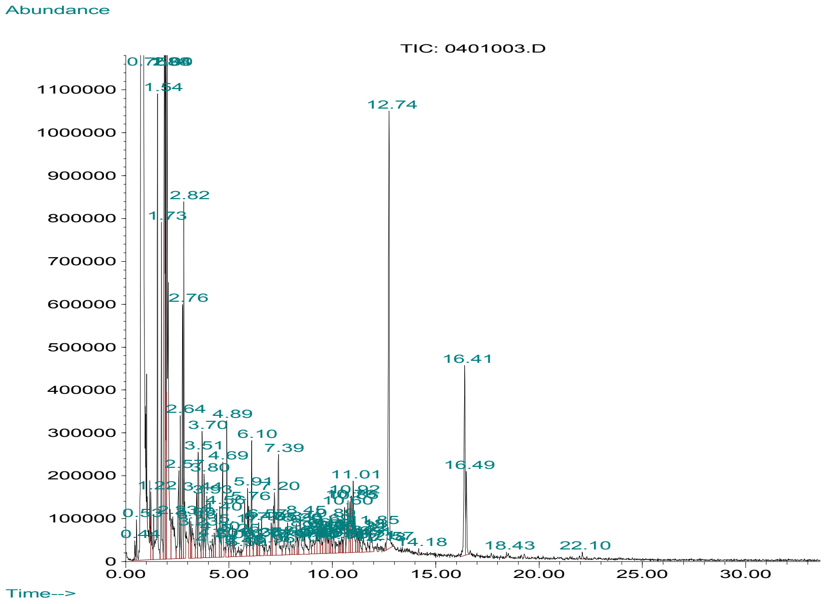

Figure C9. GC-MS curve of mixture of heptane and DBT after autoxidation at 170 ^{o}C, TIC Signal

Table C7. Area percent report, Model Oil after autoxidation at 170 ^{o}C, Signal TIC

Peak #	R.T., min	First Scan	Max Scan	Last Scan	PK TY	Peak Height	Peak Area	Peak % Max	% of Total
1	0.445	28	39	43	BV	36224	895700	0.26	0.105
2	0.533	43	47	54	VV 3	83771	1900040	0.54	0.223
3	0.752	54	67	109	VV 3	3817975	349013563	100.00	40.93
4	1.224	109	110	119	VV 2	130931	4204314	1.20	0.493
5	1.542	119	139	149	VV 2	1069835	22345551	6.40	2.622
6	1.729	149	156	163	VV	719339	14744823	4.22	1.730
7	1.883	163	170	172	VV	1345235	39386193	11.29	4.622
8	1.938	172	175	178	VV 2	1529027	35226640	10.09	4.133
9	2.003	178	181	198	VV 2	1192875	53811432	15.42	6.314
10	2.223	198	201	220	VV 7	91436	10160538	2.91	1.193
11	2.563	220	232	236	VV	194055	8405309	2.41	0.986
12	2.640	236	239	244	VV	310605	5806669	1.66	0.681

13	2.761	244	250	252	VV 2	598400	13705459	3.93	1.608
14	2.816	252	255	263	VV 2	788775	17696111	5.07	2.076
15	3.090	275	275	284	VV 5	90896	3696609	1.06	0.434
16	3.167	284	287	290	VV 2	81772	2119033	0.61	0.249
17	3.233	290	293	306	VV 7	70013	4792000	1.37	0.562
18	3.430	306	311	315	VV 2	144478	4609688	1.32	0.541
19	3.518	315	319	330	VV 2	243222	8651608	2.48	1.015
20	3.705	330	336	340	VV 2	287886	7050956	2.02	0.827
21	3.793	340	344	350	VV 3	192614	6057895	1.74	0.711
22	3.924	350	356	368	VV	136563	5820238	1.67	0.683
23	4.100	368	372	377	VV 6	28756	1358362	0.39	0.159
24	4.199	377	381	386	VV 4	42765	1584702	0.45	0.186
25	4.297	386	390	393	VV 3	54077	2024791	0.58	0.238
26	4.396	393	399	411	VV10	100917	6835572	1.96	0.802
27	4.561	411	414	420	VV	118843	3711586	1.06	0.436
28	4.693	420	426	433	VV 3	217805	6869684	1.97	0.806
29	4.890	440	444	452	VV	303918	7033425	2.02	0.825
30	5.055	452	459	463	VV 3	37792	1620427	0.46	0.190
31	5.176	463	470	474	VV	73592	2203428	0.63	0.259
32	5.252	474	477	484	VV 4	51498	1589664	0.46	0.187
33	5.461	484	496	502	VV 5	23378	1329298	0.38	0.156
34	5.582	502	507	510	VV 4	17746	560699	0.16	0.066
35	5.757	510	523	532	VV 2	118423	4895002	1.40	0.574
36	5.911	532	537	545	VV 2	147993	6403634	1.83	0.751
37	6.098	545	554	560	VV	270240	7656069	2.19	0.898
38	6.262	560	569	575	VV 7	39850	2656578	0.76	0.312
39	6.361	575	578	581	VV 3	40090	1395691	0.40	0.164
40	6.438	581	585	589	VV 5	75052	2629366	0.75	0.309
41	6.570	589	597	607	VV 5	76020	4099532	1.17	0.481
42	6.767	612	615	623	VV 7	35133	1413314	0.40	0.166
43	6.965	623	633	637	VV 9	21014	1335619	0.38	0.157
44	7.053	637	641	644	VV 2	74967	2161064	0.62	0.254
45	7.206	644	655	661	VV 3	144672	7887224	2.26	0.925
46	7.393	661	672	688	VV	232300	8307044	2.38	0.975
47	7.689	688	699	704	VV 6	38474	2299885	0.66	0.270
48	7.843	704	713	721	VV 2	71643	2944888	0.84	0.346
49	7.975	721	725	731	VV 6	31908	1436864	0.41	0.169
50	8.106	731	737	741	VV 7	24321	1265733	0.36	0.149
51	8.260	741	751	755	VV 4	71870	3051645	0.87	0.358
52	8.326	755	757	761	VV 5	40829	1301158	0.37	0.153
53	8.458	761	769	784	VV 5	84397	4862976	1.39	0.571
54	8.666	784	788	807	VV 3	53315	3037824	0.87	0.356
55	8.919	807	811	817	VV 9	32792	1471890	0.42	0.173
56	9.083	817	826	831	VV 10	32460	1998849	0.57	0.235
57	9.226	831	839	842	VV 5	50196	2222863	0.64	0.261
58	9.281	842	844	855	VV 10	35200	2711058	0.78	0.318
59	9.445	855	859	867	VV 4	53929	2618538	0.75	0.307
60	9.621	867	875	878	VV 7	48296	2496494	0.72	0.293
61	9.698	878	882	885	VV 5	65843	2258560	0.65	0.265
62	9.764	885	888	895	VV 3	54877	2390000	0.68	0.280
63	9.884	895	899	902	VV 4	79110	2372673	0.68	0.278
64	9.939	902	904	911	VV 4	50772	1879859	0.54	0.221
65	10.00	911	915	922	VV 7	38085	1921736	0.55	0.225
66	10.17	922	925	936	VV 7	26369	1811188	0.52	0.213
67	10.32	936	939	942	VV 5	28005	837795	0.24	0.098

68	10.37	942	944	948	VV 5	272729	828809	0.24	0.097
69	10.45	948	951	954	VV 4	36375	1132210	0.32	0.133
70	10.51	954	956	958	VV 3	30361	579433	0.17	0.068
71	10.59	958	964	969	VV 2	105597	3671711	1.05	0.431
72	10.75	969	978	983	VV 3	119759	5561600	1.59	0.653
73	10.85	983	987	990	VV	114953	3264033	0.94	0.383
74	10.92	990	994	998	VV 4	130585	5232623	1.50	0.614
75	11.01	998	1002	1012	VV 3	161989	5833067	1.67	0.684
76	11.18	1012	1017	1020	VV 5	51265	1870906	0.54	0.220
77	11.24	1020	1023	1027	VV 4	42692	1539803	0.44	0.181
78	11.32	1027	1030	1041	VV 8	42793	1889378	0.54	0.222
79	11.50	1041	1047	1061	VV 10	31458	2269784	0.65	0.266
80	11.70	1061	1065	1074	VV 6	23033	1201361	0.34	0.141
81	11.84	1074	1078	1093	VV 8	55490	2789228	0.80	0.327
82	12.17	1106	1108	1115	VV 4	19234	607754	0.17	0.071
83	12.56	1137	1143	1146	PV 4	17754	483671	0.14	0.057
84	12.73	1146	1159	1176	VV	1015515	34915688	10.00	4.097
85	14.17	1287	1290	1300	PV 8	14185	388942	0.11	0.046
86	16.40	1473	1493	1497	PV	432077	16879249	4.84	1.981
87	16.92	1497	1501	1513	VV 2	193545	5735830	1.64	0.673
88	18.43	1669	1678	1682	PV 7	9404	203071	0.06	0.024
89	22.10	2006	2012	2022	VV 3	16650	495273	0.14	0.058

Sum of corrected areas: 852237740

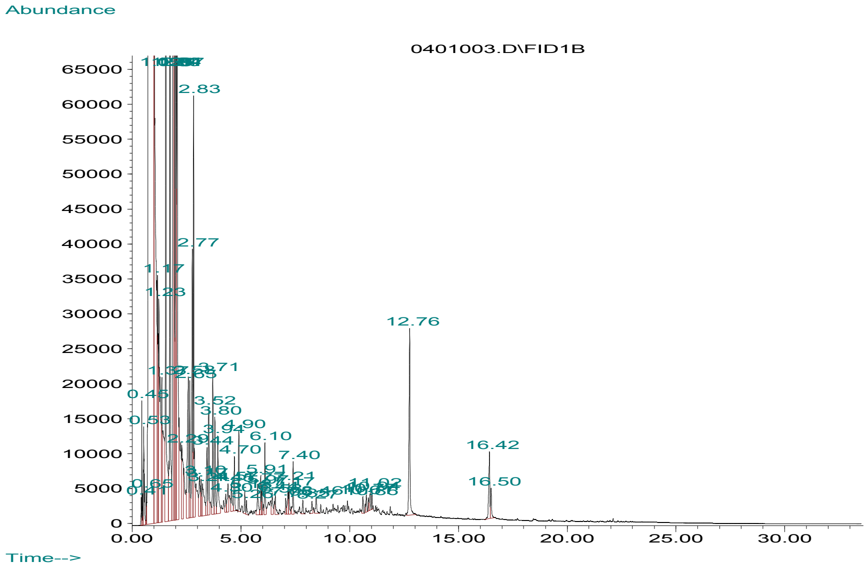

Figure C10. GC-FID curve of mixture of heptane and DBT after autoxidation at 170 °C, Signal 0401003.D\FID1B

Table C8. Area percent report, Model Oil after autoxidation at 170 °C, Signal 0401003.D\FID1B

Peak #	R.T. min	Start min	End min	PK TY	Peak Height	Peak Area	Peak % max	% of Total
1	0.414	0.369	0.436	BV	3832	51114	0.01	0.013
2	0.449	0.436	0.505	VV	14922	167078	0.05	0.042
3	0.535	0.505	0.619	VV	13277	327512	0.09	0.082
4	0.649	0.619	0.664	VV	4905	58064	0.02	0.015

5	0.841	0.664	1.005	VV	7846561	362906479	100.00	90.946
6	1.021	1.005	1.154	VV	89544	4367534	1.20	1.095
7	1.171	1.154	1.215	VV	35212	1004766	0.28	0.252
8	1.228	1.215	1.341	VV	31337	1459703	0.40	0.366
9	1.365	1.341	1.404	VV	20508	574288	0.16	0.144
10	1.547	1.498	1.670	VV	100030	2343969	0.65	0.587
11	1.740	1.670	1.825	VV	93127	2018550	0.56	0.506
12	1.891	1.825	1.909	VV	135798	3464365	0.95	0.868
13	1.944	1.909	1.972	VV	168954	4195498	1.16	1.051
14	2.012	1.972	2.036	VV	97753	2509203	0.69	0.629
15	2.070	2.036	2.146	VV	97191	2990981	0.82	0.750
16	2.288	2.265	2.358	VV	10550	478506	0.13	0.120
17	2.581	2.484	2.619	VV	19596	818020	0.23	0.205
18	2.652	2.619	2.696	VV	19489	389502	0.11	0.098
19	2.767	2.696	2.793	VV	38495	865459	0.24	0.217
20	2.827	2.793	2.899	VV	61106	1271063	0.35	0.319
21	3.096	3.047	3.145	VV	5709	237462	0.07	0.06
22	3.170	3.145	3.202	VV	5272	137431	0.04	0.034
23	3.239	3.202	3.380	VV	4582	309181	0.09	0.077
24	3.443	3.380	3.479	VV	9597	303349	0.08	0.076
25	3.524	3.479	3.575	VV	15345	464778	0.13	0.116
26	3.709	3.655	3.760	VV	20044	444209	0.12	0.111
27	3.803	3.760	3.875	VV	13745	391542	0.11	0.098
28	3.938	3.875	4.068	VV	11077	390887	0.11	0.098
29	4.303	4.260	4.339	VV	2607	76024	0.02	0.019
30	4.406	4.339	4.441	VV	4045	141267	0.04	0.035
31	4.568	4.538	4.644	VV	4081	123889	0.03	0.031
32	4.703	4.644	4.833	VB	7775	230439	0.06	0.058
33	4.903	4.833	4.984	BV	11509	216228	0.06	0.054
34	5.180	5.099	5.229	PV	3279	79649	0.02	0.02
35	5.261	5.229	5.342	VV	1986	48908	0.01	0.012
36	5.769	5.692	5.854	VV	4402	152697	0.04	0.038
37	5.914	5.854	5.942	VV	5641	131553	0.04	0.033
38	5.967	5.942	6.008	VV	4099	93144	0.03	0.023
39	6.104	6.058	6.166	VV	10309	245473	0.07	0.062
40	6.441	6.393	6.493	VV	3119	109792	0.03	0.028
41	6.582	6.558	6.737	VV	2742	87522	0.02	0.022
42	7.060	7.013	7.095	VV	2313	59972	0.02	0.015
43	7.165	7.095	7.188	VV	3687	117511	0.03	0.029
44	7.211	7.188	7.278	VV	4460	106704	0.03	0.027
45	7.403	7.329	7.449	VV	7556	178488	0.05	0.045
46	7.848	7.756	7.939	VV	2028	60924	0.02	0.015
47	8.268	8.164	8.309	PV	1750	56908	0.02	0.014
48	8.461	8.377	8.613	VB	2326	89888	0.02	0.023
49	10.607	10.545	10.670	VV	2400	65029	0.02	0.016
50	10.768	10.731	10.820	VV	2473	69271	0.02	0.017
51	10.865	10.820	10.891	VV	1913	44735	0.01	0.011
52	10.944	10.891	10.983	VV	2480	86469	0.02	0.022
53	11.022	10.983	11.056	VV	2881	54036	0.01	0.014
54	12.758	12.614	13.044	VB	26954	907609	0.25	0.227
55	16.424	16.184	16.462	BV	9474	327645	0.09	0.082
56	16.501	16.462	16.646	VB	4317	132098	0.04	0.033

Sum of corrected areas: 399034368

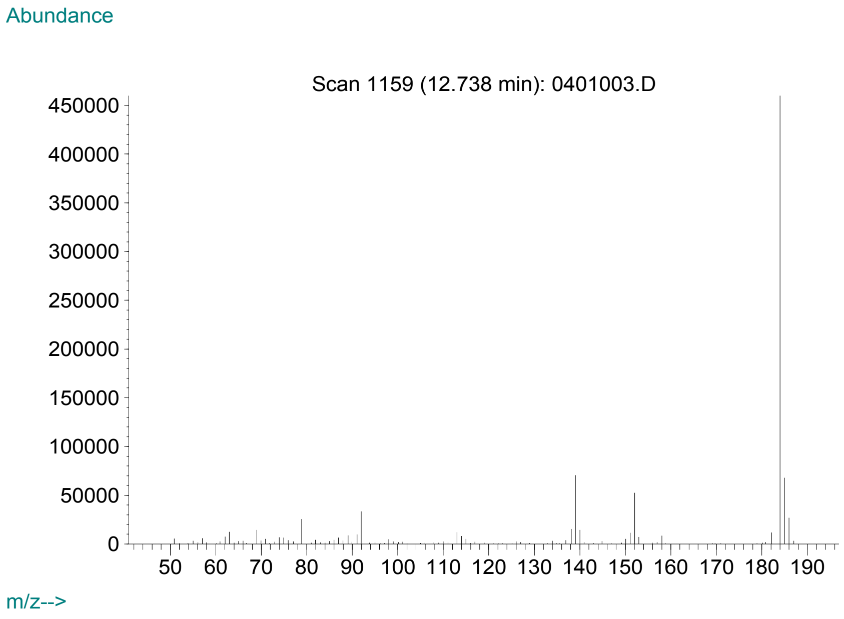

Figure C11. The mass spectrum for the peak at 12.74 in the mixture (170C), which is DBT

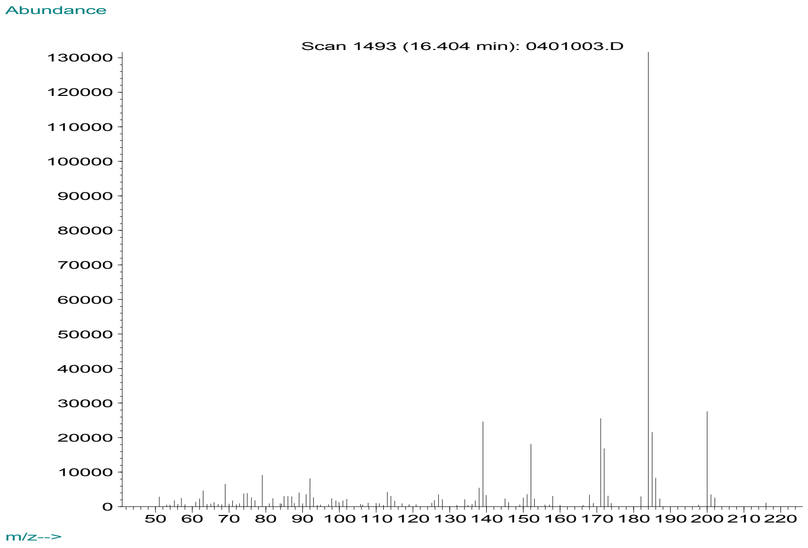

Figure C12. The mass spectrum for the peak at 16.41 in the mixture (170C), which is sulfoxide of DBT

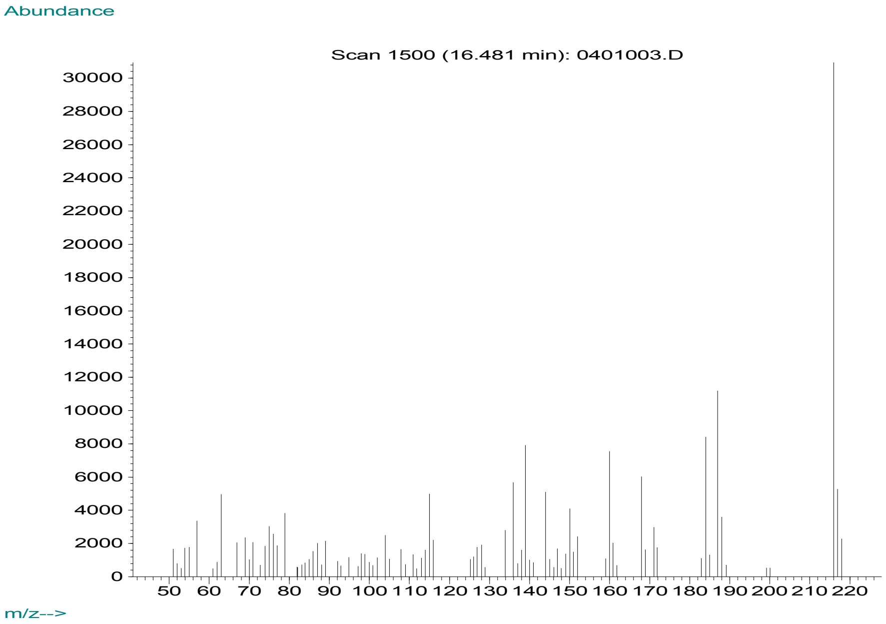

Figure C13. The mass spectrum for the peak at 16.49 in the mixture (170C), which is the sulfone of DBT

Table C9. Identification of the compounds in the curves of mixture of heptane and dibenzothiophene after autoxidation at 170 ^{o}C through database, Identification is based on the best match in the MS database, which in some instances make no sense from a chemistry point of view

Peak #	RT	Area, %	Compound
1	0.445	0.105	Decanal 2-Butanamine 2-Buten-1-ol
2	0.533	0.223	Pentane, 2-methyl- Pentanoic acid, 3-methyl-
3	0.752	40.93	Heptane
4	1.224	0.493	Furan, tetrahydro-2,4-dimethyl-, t Heptane Silane, ethenyltrimethyl-
5	1.542	2.622	Propanoic acid, 1-methylpropyl est Butane, 1-(1-methylpropoxy)-
6	1.729	1.730	4-Heptanone
7	1.883	4.622	3-Heptanone
8	1.938	4.133	2-Heptanone
9	2.003	6.314	3-Heptanol 3-Hexanol, 5-methyl-
10	2.223	1.193	2-Hexenal 3-Hexanol, 3-methyl- 1-Pentene, 2,3-dimethyl-
11	2.563	0.986	2(3H)-Furanone, dihydro-5-methyl- Furan, tetrahydro-2,5-dimethyl-, t
12	2.640	0.681	Cycloheptane Cyclohexanone Succinimide, N-methoxy-
13	2.761	1.608	2-Heptanone, 4-methyl- 1-Pentene, 3-ethyl- Silane, ethenyltrimethyl-
14	2.816	2.076	1-Nonanol

			Cyclobutane, isopropyl-
15	3.090	0.434	Oxirane, 2-methyl-3-propyl-, cis- Butanoic acid, 3-methyl-, butyl es Propanoic acid, 2-methyl-, 2-methy
16	3.167	0.249	Nonane 2H-Pyran-2-one, 6-ethyltetrahydro- [1'-13C]-Octyne
17	3.233	0.562	1-Hexene, 3,5,5-trimethyl- Ethanol, 2-[(2-ethylhexyl)oxy]- .alpha.-D-Galactopyranoside, methy
18	3.430	0.541	Glycocyanidine Phenol-d5 Heptane, 2-iodo-
19	3.518	1.015	Cyclobutanone, 3-ethyl- Cyclopentane, 1,2-dimethyl-, cis- Cyclopentane, 1,2-dimethyl-
20	3.705	0.827	2-Heptanol, acetate 6,8-Dioxabicyclo(3.2.1)octan-2.bet 1,6-Anhydro-2,3-Dideoxy-beta-d-thr
21	3.793	0.711	n-decane-2,3-d2 Silane, ethenylethyldimethyl- Silane, ethenyltrimethyl-
22	3.924	0.683	Heptane, 3-ethyl-2-methyl- Nonane, 2,2,4,4,6,8,8-heptamethyl- Nonane, 2,5-dimethyl-
23	4.100	0.159	3-Octanol, 2-methyl- n,n-dimethylhomoserine lactone 1-Decanol, 2-ethyl-
24	4.199	0.186	Oxirane, [(dodecyloxy)methyl]- Dodecane, 6-Cyclohexyl- Undecane 5-cyclohexyl-
25	4.297	0.238	Permethylated and reduced product 1r-4-Acetamido-2,3c-Epoxy-Cyclohex 1-Hexanamine, 2-ethyl-
26	4.396	0.802	Butyl 2-Methylbutanoate Octane, 2,4,6-trimethyl- Hexadecane
27	4.561	0.436	Decane, 2,6,8-trimethyl- 1-Hexanol, 2,2-dimethyl- 2-Decene, 5-methyl-, (z)-
28	4.693	0.806	Heptane, 2,3,6-trimethyl- 2-Decene, 5-methyl-, (z)- Decane, 2,5-dimethyl-
29	4.890	0.825	Octane, 3-methyl- 2-Decene, 5-methyl-, (z)- Decane, 2,6,6-trimethyl-
30	5.055	0.190	Hexane, 4-ethyl-2-methyl- Hexanoic acid, 2-methylpropyl este 1-Butanamine, N-butyl-N-nitroso-
31	5.176	0.259	2(3H)-Furanone, dihydro-5-propyl- 2(3H)-Furanone, 5-hexyldihydro-
32	5.252	0.187	1-hepten-3-ol-6,6-d2 Xanthosine .alpha.-D-Galactopyranoside, methy
33	5.461	0.156	Cyclohexane, 1,2-dimethyl-, cis- Cyclohexane, 1,4-dimethyl-, trans- 1-(2-Methylpropenyl)aziridine
34	5.582	0.066	Permethylated and reduced product

			Silane, trichloroeicosyl-
35	5.757	0.574	Butanoic acid, 1-methyloctyl ester Butanoic acid, 1-methylhexyl ester Butanoic acid, 2-methylpropyl este
36	5.911	0.751	Butanoic acid, 1-methyloctyl ester Cyclohexane, methoxy- Propanoic acid, 2-methyl-, 2-methy
37	6.098	0.898	Butanoic acid, 1-methylhexyl ester Butanoic acid, 1-methyloctyl ester Decane, 2-methyl-
38	6.262	0.312	2-Hexanone, 6-methoxy- Undecane, 2,6-dimethyl- Propanoic acid, 2-methyl-, propyl
39	6.361	0.164	Permethylated and reduced product Ethanol, 2-(2-butoxyethoxy)- Guanosine
40	6.438	0.309	Tetradecane, 5-methyl- 2-Azido-2-methylbutane Undecane, 6-ethyl-
41	6.570	0.481	Oxirane, pentyl- Nonane, 3-methyl- Decane, 2,6,7-trimethyl-
42	6.767	0.166	1-(2-Methylpropenyl)aziridine 9-Octadecene, (E)- Cyclopentane, 1,2-dimethyl-3-(1-me
43	6.965	0.157	Octadecane, 6-methyl- 1-Heptadecanamine
44	7.053	0.254	2-Butene, 1,4-diethoxy- Decane, 3-ethyl-3-methyl- 4-Octanone, 2,3-epoxy-2-methyl-
45	7.206	0.925	dl-.alpha.-hydroxyglutaric acid Hexane, 1-(hexyloxy)-2-methyl- Pentyl 3-methylbutanoate
46	7.393	0.975	Oxirane, (2-methylbutyl)- Heptane, 2,2,3,3,5,6,6-heptamethyl Hexane, 1-(hexyloxy)-2-methyl-
47	7.689	0.270	Hexatriacontane Heneicosane
48	7.843	0.346	Octane, 2,4,6-trimethyl- Hexatriacontane Docosane, 11-decyl-
49	7.975	0.169	Tritetracontane Hexadecane, 2,6,10,14-tetramethyl- Tetracosane
50	8.106	0.149	Tetradecane, 1-chloro- Heneicosane Tritetracontane
51	8.260	0.358	1,1'-Biphenyl
52	8.326	0.153	Heptane Pentanoic acid, 2-methyl-, 1-methy
53	8.458	0.571	Tetracontane, 3,5,24-trimethyl- Heptyl Hexanoate Hexane, 1-(hexyloxy)-3-methyl-
54	8.666	0.356	Alanine Diketopiperazine Derivativ 2H-1,2,3-Thiadiazine, 6-methyl-2-p 2-Piperidinone
55	8.919	0.173	1-Heptadecanamine Tricosane

			Triacontane
56	9.083	0.235	Thiazole, 5-methyl- Cyclohexanol, 2-methyl-, cis- Cyclohexanol, 2-methyl-
57	9.226	0.261	2,5-Hexanedione cis-methyl-hydroxyoctanic acid la Furan, 2,5-dihydro-2,5-dimethoxy-
58	9.281	0.318	Oxirane, [(dodecyloxy)methyl]- 1-Eicosanol Cyclohexanol, 2-methyl-
59	9.445	0.307	2(3H)-Furanone, dihydro-4,4-dimeth 1-Hexanol, 2,2-dimethyl- 1,3,2-Oxazaborinane, 2-butyl-
60	9.621	0.293	Heptacosane Nonadecane, 9-methyl- Heptadecane, 2,6,10,15-tetramethyl
61	9.698	0.265	Menthone-D1 1-Thiacyclohept-2-ene Hexane, 1-(hexyloxy)-3-methyl-
62	9.764	0.280	n-difluorophosphinodimethylhydroxy 4,5-Decanediol, 6-ethyl- 4-Heptanol, 2,6-dimethyl-4-propyl-
63	9.884	0.278	4-Decanone 2H-Azepin-2-one, hexahydro- Quinuclidine-3,3-D2
64	9.939	0.221	Octadecane, 2,2,4,15,17,17-hexamet Heptadecane, 2,6,10,15-tetramethyl N,n-dimethylhomoserine lactone
65	10.060	0.225	1-Heptadecanamine Tetradecane, 1-chloro-
66	10.170	0.213	Permethylated and reduced product 1,3,4-Trimethyl-2,6-anhydro-fructo Nonane, 2-methyl-
67	10.324	0.098	Tetradecane, 2,5-dimethyl- Nonane, 2,2,4,4,6,8,8-heptamethyl- 2,2,3,3,6,8,8-heptamethylnonane
68	10.378	0.097	Hexatriacontane Octacosane Triacontane
69	10.455	0.133	1-Heptadecanamine 1-Octanol, 2-butyl-
70	10.510	0.068	Permethylated and reduced product Dodecane, 2,6,11-trimethyl- Decane, 2-methyl-
71	10.598	0.431	2-Pentene, 4,4-dimethyl-, (E)- Hexanal, 3,5,5-trimethyl- 1-Piperazinamine, 4-methyl-, dihyd
72	10.752	0.653	Butane, 2-methoxy-2,3,3-trimethyl- 1,6:3,4-Dianhydro-2-deoxy-.beta.-D 7-Oxabicyclo[4.1.0]heptane
73	10.850	0.383	2-Propenoic acid, 2-methyl-, octyl Butane, 1-propoxy- 1-Propanamine, 2-methyl-N-(2-methy
74	10.927	0.614	7-Oxabicyclo[4.1.0]heptane 3-Chloro-1-cyclohexyloxy-3-methyl- 7-Oxabicyclo[4.1.0]heptane
75	11.015	0.684	3-Hexanol, 2,5-dimethyl- Cyclopentane, ethyl- 2-Butenoic acid, methyl ester, (E)

76	11.180	0.220	1,3,4-trimethyl-2,6-anhydro-fructo Tetracontane, 3,5,24-trimethyl- Permethylated and reduced product
77	11.246	0.181	1,3,4-trimethyl-2,6-anhydro-fructo 2,4-Imidazolidinedione, 3-butyl- 3-methyl-5-pyrazolone-1,4,4-D3
78	11.322	0.222	Nonane, 2-methyl- Decane Decane, 1,1'-oxybis-
79	11.509	0.266	Permethylated and reduced product 2-hydroxypropyl 2-ethylhexanoate Tetracontane, 3,5,24-trimethyl-
80	11.707	0.141	Heneicosane Tricosane Docosane
81	11.849	0.327	Undecane, 2,6-dimethyl- Propionaldehyde, ethylhydrazone 3-deuterocyclohexa-2-en-1-ol
82	12.179	0.071	Pentanoic acid, 3,5-dioxo-, methyl Hexose, 2,3-dideoxy-5,6-O-(1-methy 1-Dodecanol
83	12.563	0.057	Decane, 1-fluoro- 1,2-Ethanediamine, N-(2-aminoethyl Decane, 2,6,6-trimethyl-
84	12.738	4.097	Dibenzothiophene
85	14.176	0.046	Phenanthridine Acridine
86	16.404	1.981	Dibenzothiophene sulfoxide
87	16.492	0.673	3-Ethyl-1,2,3,4-tetrahydrodibenzot 1-Ethyl-1,2,3,4-tetrahydrodibenzot Dodecahydro-1,3,4,6-ethanediyliden Dibenzothiophene Sulfone
88	18.435	0.024	2',6'-dihydroxy-3',4'-dimethoxyace Androstan-3-ol, (3.alpha.,5.beta) 3-Pyridinecarboxylic acid, 1,6-dih
89	22.101	0.058	5-Thiazolecarboxylic acid, 2,4-dim Ethanone, 1-cyclopentyl- Pyrrolidine, 1-acetyl-