

CHAPTER 2

FUNDAMENTALS AND RELATED WORKS

2.1 HIGH SPEED DIESEL

At this point it would be well to give a definition of diesel fuels. With reference to Fig. 2.1, the more common designation is that portion of the distillation curve from 25 to 65 per cent of the crude-oil barrel, or within the temperature ranges of 375 to 725 °F(150 and 400 °C.). Other properties are evaluated and characteristics determined which influence the fuel performance value in a specific application. In the diesel fuel oil classification many properties are considered significant by the American Society for Testing Materials, such as cetane number, viscosity, carbon residue, sulfur content, flash point, pour point, ash, and copper-strip corrosion.

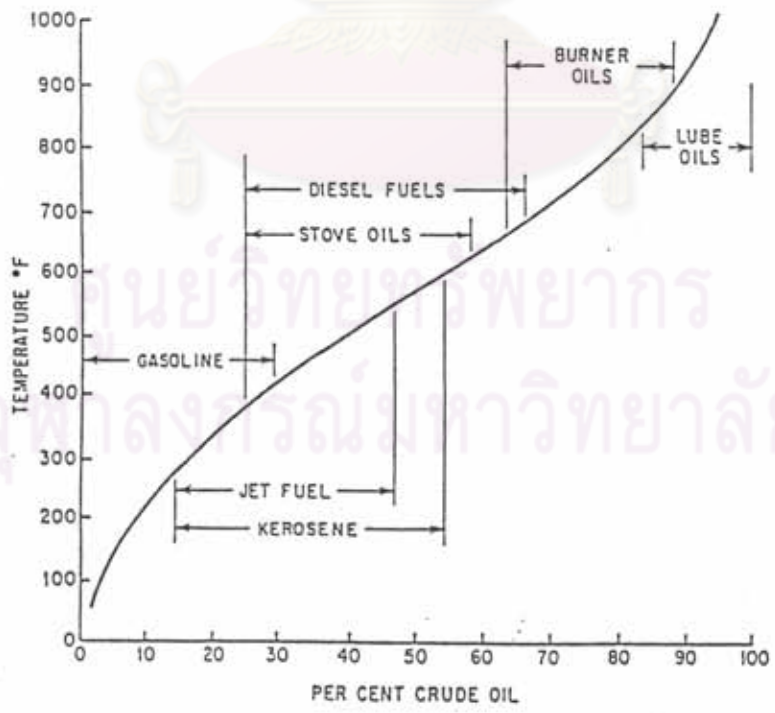


Fig. 2.1 Proportion of diesel fuel and other petroleum products. (Guthrie V.B., 1960)

The properties of commercial fuel oils depend on the refining practices employed and the nature of the crude from which they are produced. Distillate fuel oils, for example, may be produced within the boiling range of 300 and 750 °F. (150 and 400 °C.), having many possible combinations of various properties such as volatility, ignition quality, viscosity, and other characteristics.

Perhaps the first significant property which determines performance value of diesel fuels is that of gravity. Although this is not indicated in the ASTM classification, it is evident that light fuels which are high in API gravity are the more volatile fuels as indicated by the ASTM distillation data but have the lower heat values per gallon, as indicated by the API gravity. In general, the heavier fuels have higher heat values, as indicated by the lower API gravities. The heating values provide the source of energy to the power plant.

The ASTM Classification D 975 of diesel fuel oils is intended as a statement of permissible limits of significant fuel properties used for classifying the wide variety of commercially available diesel fuel oils. These grades and their general applicability for use in diesel engines are broadly indicated as follow:

Grade No. 1-D comprises the class of volatile fuel oils from kerosine to the intermediate distillates. Fuels within this classification are applicable for use in high-speed engines in services involving frequent and relatively wide variation in loads and speeds and also for use where abnormally low fuel temperatures are encountered.

Grade No. 2-D includes the class of distillate gas oils of lower volatility. These fuels are applicable for use in high-speed engines in services involving relatively high loads and uniform speeds, or in engines not requiring fuels having the higher volatility or other properties specified for No. 1-D.

Grade No. 4-D covers the class of more viscous distillates and blends of these distillates with residual fuel oils. These fuels are applicable for use in low- and high-speed engines employed in services involving sustained loads at substantially constant speed.

Table 2.1 Limiting requirements for diesel fuel oils. (Guthrie V.B., 1960)

Grade of diesel fuel oil		Flash point, F		Pour point, F	Water and sediment, % by volume	Carbon residue on 10% residue, %	Asb, % by weight	Distillation temp, F		Viscosity at 100F, kinematic	Sulfur, % by weight	Copper strip corrosion	cetane number
		Min.	Max.					90 percent point	End point				
		Min.	Max.	Max.	Max.	Max.	Max.	Max.	Min.	Max.	Max.	Max.	Min.
No. 1-D	A volatile distillate fuel oil for engines in service requiring frequent speed and load changes	100 or legal	3	Trace	0	0.01	--	625	1.4	--	0.5	No.3	40
No. 2-D	A distillate fuel oil of low volatility for engines in industrial and heavy mobile service	125 or legal	3	0	0	0.02	675	--	1.8	5.8	1	No.3	40
No. 4-D	A fuel oil for low- and medium-speed engines	130 or legal	3	0	--	0.1	--	--	5.8	26.4	2	--	30

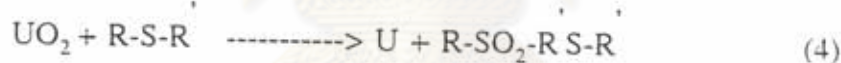
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2.2 METHODS OF OXIDATION

The applicability of a desulfurization scheme depends on the kinetics and the selectivity of the oxidation. The oxidation should be rapid, and the oxidizer should be selective to the sulfur. The most economical oxidizer on an industrial scale, however, is oxygen. Therefore, a method is needed which uses molecular oxygen as the oxidizer. Two schemes have been used to oxidize sulfur compounds with oxygen. They are: (1) Direct application of oxygen or air; this method is suitable for thiols and is usually carried out in basic solution. (2) Indirect oxidation using an oxygen carrier. Oxygen carriers are molecules which can selectively oxidize the sulfur and which can be regenerated or produced using molecular oxygen. Two types of carriers were tried, regenerable and nonregenerable.

Methods with Regenerable Oxygen Carriers. The scheme of oxidation of sulfur compounds with a regenerable oxidizer UO_2 involves two steps

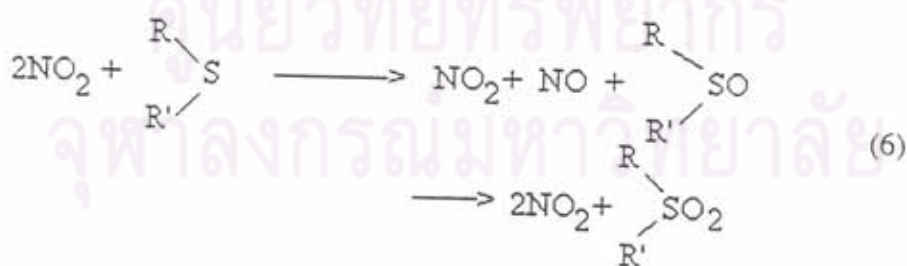
(1) oxidation



(2) regeneration of the oxidizer with molecular oxygen



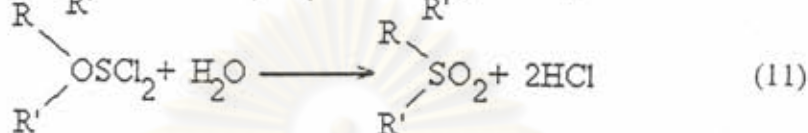
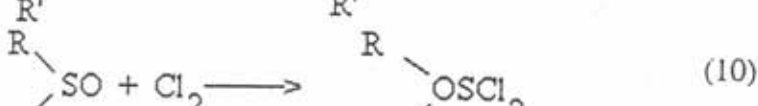
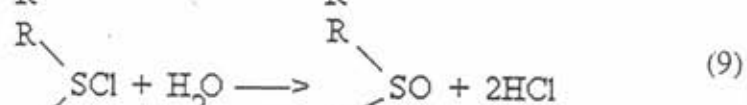
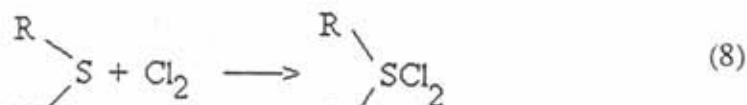
Nitrogen Dioxide as a Regenerable Oxidizer. Oxidation



regeneration

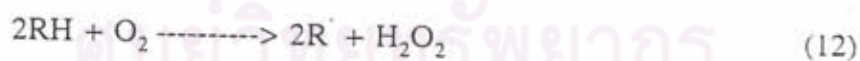


Chlorine as a Regenerable Oxidizer. Chlorine can be applied to desulfurization with oxidation and hydrolysis proceeding as follows



Methods without Regeneration of the Oxidizer. Oxidation of a hydrocarbon by molecular oxygen proceeds via the intermediates of organic hydroperoxides (HP) and peroxy acids (PA). The peroxidic species can selectively oxidize sulfur compounds to the corresponding sulfides and sulfones. Much of the background material on oxidation of hydrocarbons by oxygen has also been discussed previously by numerous authors, and therefore will only briefly be discussed here.

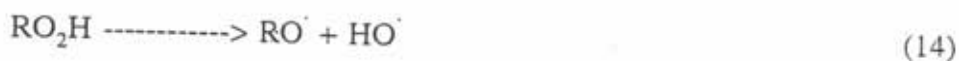
1. Noncatalytic, liquid-phase oxidation of a hydrocarbon (RH) in the presence of excess oxygen proceeds by way of a free-radical mechanism. Initiation can occur with molecular oxygen in accord with the reaction



by an initiator I_2 -



or by the decomposition of intermediates, e.g., the hydrocarbon peroxides, RO_2H



The organic radical HO^\cdot , RO_2^\cdot , RO^\cdot , etc., denoted by A, abstract a hydrogen from a hydrocarbon molecule and produce R^\cdot . In turn, R^\cdot absorbs oxygen very



rapidly, and a peroxy radical RO_2^\cdot is produced as follows



Peroxy radical can abstract a hydrogen from another hydrocarbon molecule and produce a hydroperoxide



or the peroxy radicals can terminate by the reaction



or by similar reactions.

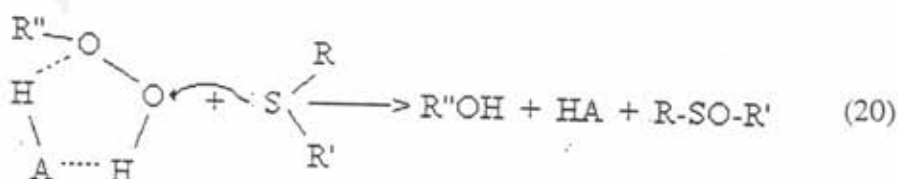
2. Hydrocarbon which contain hydrogen with lower bond energies are oxidized more rapidly than those with higher bond energies. The hydroperoxides that result are more stable and therefore are more selective as oxidizers.

3. Hydroperoxides and peracids can selectively oxidize sulfur compounds to the corresponding sulfoxides and sulfones.

4. The protic nature of the solvent strongly affects the observed from of the rate equation for the oxidation of sulfur compounds. In general, the rate equation has two terms. One accounts for the protic aspect of the solvent, and the other accounts for the degree of association of the hydroperoxide (HP) in accord with the equation

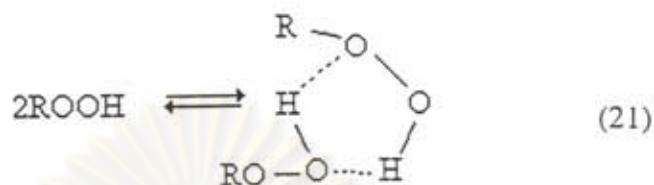
$$d[R-S-R'] / dt = k_2[R-S-R'][HP] + k_3[R-S-R'][HP]^2 \quad (19)$$

All of their observation supported a mechanism of oxidation proposed in the the early work of Overberger and Cummins(1953) wherein it was postulated that the sulfur was oxidized by a nucleophilic attack on a peroxidic complex which contained peroxidic and protic structures



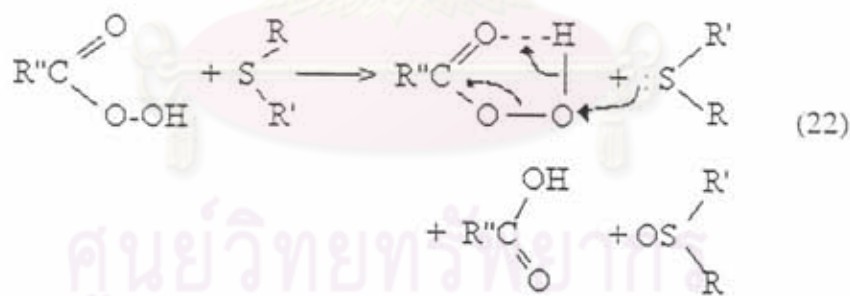
HA denotes the protic molecule, and $R''O_2H$ is the peroxide.

The oxidation of the sulfoxide to the sulfone occurred by the same mechanism. In a protic solvent, the present in excess fulfills the function of HA, and the apparent rate of reaction 19 is first order with respect to the peroxide. In an aprotic solvent, another hydroperoxide molecule will function as HA



Therefore, in an aprotic solvent the apparent rate of reaction 19 depends on the second power of the concentration of hydroperoxide.

5. A special case of interest is that of the peroxy acids which are formed by oxidation of the primary oxidation products, especially aldehydes. Peroxy acids can form intermolecular, cyclic peroxidic complexes. Then in most cases the rate of oxidation of the sulfur compounds depend on the first powers of the concentrations of acids as suggested by the equation,



6. A larger oxidation potential is required to convert sulfoxides to sulfones than to oxidize sulfides to sulfoxides. Thus, if the oxidizer is a hydroperoxide in a protic medium the reaction may stop after sulfoxide is formed.

7. When the n electrons of the sulfur can resonate with the p electrons of the organic radical, a larger oxidation potential will be required to effect the oxidation than for cases where resonance does not exist. Therefore, it is more difficult to oxidize thiophene than aryl and alkyl sulfides.

2.3 LIQUID-LIQUID EXTRACTION

Liquid-liquid extraction is a process for separating component in solution by their distribution between two immiscible liquid phases. Such a process can also be simply referred to as *liquid extraction* or *solvent extraction*; however, the latter term may be confusing because it also applies to the leaching of a soluble substance from a solid.

Since liquid-liquid extraction involves the transfer of mass from one liquid phase into a second immiscible liquid phase, the process can be carried out in many different ways. The simplest example involves the transfer of one component from a binary mixture into a second immiscible liquid phase. One example is liquid-liquid extraction of an impurity from wastewater into an organic solvent. This is analogous to stripping or absorption in which mass is transferred from one phase to another. Transfer of the dissolved component (solute) may be enhanced by the addition of "salting out" agents to the feed mixture, or by adding "complexing" agents to the extraction solvent. Or in some cases a chemical reaction can be used to enhance the transfer, an example being the use of an aqueous caustic solution to remove phenolics from a hydrocarbon stream. A more sophisticated concept of liquid-liquid fractionation can be used in a process to separate two solutes completely. A primary extraction solvent is used to extract one of the solutes from a mixture (similarly to stripping in distillation), and a wash solvent is used to scrub the extract free from the second solute (similarly to rectification in distillation).

2.3.1 USES FOR LIQUID-LIQUID EXTRACTION

Liquid-liquid extraction is used primarily when distillation is impractical or too costly to use. It may be more practical than distillation when the relative volatility for two components falls between 1.0 and 1.2. Likewise, liquid-liquid extraction may be more economical than distillation or steam-stripping a dissolved impurity from wastewater when the relative volatility of the solute to water is less than 4.

In other cases the components to be separated may be heat-sensitive, like antibiotics, or relatively nonvolatile, like mineral salts, and liquid-liquid extraction may provide the most cost-effective separation process. However, the potential use of distillation should generally be evaluated carefully before considering liquid-liquid extraction. An extraction process usually requires (1) liquid-liquid extraction, (2) solvent recovery, and (3) raffinate desolventizing.

2.3.2 DEFINITIONS

The *feed* to a liquid-liquid extraction process is the solution that contains the components to be separated. The major liquid component in the feed can be referred to as the *feed solvent*. Minor components in solution are often referred to as solutes. The *extraction solvent*, or just plain solvent, is the immiscible liquid added to a process for the purpose of extracting a solute or solutes from the feed. The extraction-solvent phase leaving a liquid-liquid contactor is called the *extract*. The *raffinate* is the liquid phase left from the feed after being contacted by the second phase. A wash solvent is a liquid added to a liquid-liquid fractionation process to wash or enrich the purity of a solute in the extract phase.

2.3.3 LIQUID-LIQUID EQUILIBRIA

The separation of components by liquid-liquid extraction depends primarily on the thermodynamic equilibrium distribution of those components between the two liquid phases. Knowledge of these distribution relationships is essential for selecting the ratio of extraction solvent to feed that enters an extraction process and for evaluating the mass-transfer rates of theoretical stage efficiencies achieved in process equipment. Since two liquid phases that are immiscible are used, the thermodynamic equilibrium involved considerable evaluation of nonideal solutions. In the simplest

case a feed solvent F contains a solute that is to be transferred into an extraction solvent S .

The proper design of solvent extraction depends crucially upon an accurate knowledge of the relevant liquid-liquid equilibria. The latter must be either measured or predicted. This chapter is concerned with methods for the correlation of experimentally determined liquid-liquid equilibria and with methods for the prediction of unknown equilibria.

2.3.4 THE PHASE RULE

In an equilibrium system in which the only significant intensive variables are the temperature, pressure, and chemical potential, the phase rule provides a means of determining the number of intensive variables that can be independently varied (within limits) without changing the state of the system. This number of variables is called the number of degrees of freedom (f) and is related to the number of components (c) and number of phases (ϕ) as follows:

$$f = c + 2 - \phi$$

The important assumption in the derivation of this relation are that no chemical reactions take place and that the interfaces between phases are plane.

2.3.5 PHASE DIAGRAMS

The graphical representation of phase equilibria is facilitated by application of the phase rule. Thus, in a binary liquid-liquid system, $f = 2$ and each phase can be represented by a surface in a space diagram where, for example, the three co-ordinates could be the pressure, temperature, and composition. If, in addition, the pressure is fixed, as is usually the case in liquid-liquid extraction, then $f = 1$ and a phase representation of the system can be secured.

2.3.6 DISTRIBUTION COEFFICIENT

The weight fraction of solute in the extract phase y divided by the weight fraction of solute in the raffinate phase x at equilibrium is called *the distribution coefficient, or partition coefficient, K*

$$K = y/x$$

Thermodynamically the distribution coefficient K^* is derived in mole fraction y^* and x^*

$$K^* = y^* / x^*$$

For shortcut calculations the distribution coefficient K' in Bancroft coordinates using the weight ratio of solute to extraction solvent in the extract phase and the weight ratio of solute to feed solvent in the raffinate phase X is preferred

$$K' = Y/X$$

In shortcut calculations the slope of the equilibrium line in Bancroft (weight-ratio) coordinates m is also used

$$m = dY/dX$$

For low concentrations in which the equilibrium line is linear the value of K' is equal to m

The value of K' is one of the main parameters used to establish the minimum ratio of extraction solvent to feed solvent that can be employed in an extraction process.

The relative separation, or selectivity, α between two components, b and c , can be described by the ratio of the two distribution coefficients.

$$\alpha (b/c) = K_b^*/K_c^* = K_b/K_c = K'_b/K'_c$$

This is analogous to relative volatility in distillation.

2.3.7 PHASE DIAGRAMS

Equilateral-triangular diagrams as show in Fig. 1. The isooctane(A)-n-methy pyrrolidone(B)-hexyl sulfide(C) ternary is a Type I system in which only one of the binary pairs is immiscible.



Fig. 2.2 Phase diagram of the system isooctane(A)-NMP(B)-hexyl sulfide(C).
(Zannikos F,1995)

2.3.8 HYDROGEN-BONDING INTERACTIONS

Deviations from Raoult's law in solution behavior have been attributed to many characteristics such as molecular size and shape, but the strongest deviations appear to be due to hydrogen bonding and electron donor-acceptor interactions. Robbins [Chem.eng.Prog.,76(10),58(1980)] presented a table of these interaction, Table 1, that provides a qualitative guide to solvent selection for liquid-liquid extraction, extractive distillation, azeotropic distillation, or even solvent crystallization. The activity coefficient in the liquid phase is common to all these separation processes.

Effect of interaction between groups on solute activity coefficient is:

- + increases activity coefficient
- o mild interaction
- decreases activity coefficient

Table 2.2 Organic-Group Interactions Based on 900 Binary Systems.

(Robbins L.A.,1986)

Slute class		Solvent class											
		1	2	3	4	5	6	7	8	9	10	11	12
H donor groups													
1	Phenol	0	0	-	0	-	-	-	-	-	-	+	+
2	Acid, thiol	0	0	-	0	-	-	0	0	0	0	+	+
3	Alcohol, water	-	-	0	+	+	0	-	-	+	+	+	+
4	Active H on multihalogen paraffin	0	0	+	0	-	-	-	-	-	-	0	+
H acceptor groups													
5	Ketone, amide with no H on N, sulfone, phosphine oxide	-	-	+	-	0	+	+	+	+	+	+	+
6	Tertiary amine	-	-	0	-	+	0	+	+	0	+	0	0
7	Secondary amine	-	0	-	-	+	+	0	0	0	0	0	+
8	Primary amine, ammonia, amide with 2H on N	-	0	-	-	+	+	0	0	+	+	+	+
9	Ether, oxide, Sulfoxide	-	0	+	-	+	0	0	+	0	+	0	+
10	Ester, aldehyde, carbonate, phosphate, nitrate, nitrite, nitrile, intramolecular bonding	-	0	+	-	+	+	0	+	+	0	+	+
11	Aromatic, olefin, halogen aromatic, multihalogen paraffin without active H, monohalogen paraffin	+	+	+	0	+	0	0	+	0	+	0	0
Non-H-bonding groups													
12	Paraffin, carbon disulfide	+	+	+	+	+	0	+	+	+	+	0	0

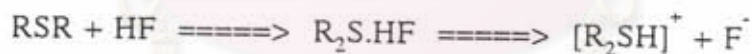
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2.4 LITERATURE SURVEY

A. P. Lien and B. L. Evering (1952) used Hydrogen Fluoride as extraction solvent agent describes the results of treating a wide variety of petroleum stocks with hydrogen fluoride, develops the effects of a number of variables, and interprets the results obtained on refinery stocks in the light of the previously discussed chemistry of hydrogen fluoride extraction.

All runs were carried out in a 1550-mL. Carbon steel reactor equipped with a mechanical stirrer operating at 1725 r.p.m. Unless otherwise stated a contact time of 0.5 to 1.5 hours at room temperature (21° to 26°C) was employed, followed by a setting period of 1.5 to 2.0 hours. After settling, the hydrogen fluoride extract layer was removed from the supernatant hydrocarbon layer by withdrawal through a valve at the bottom of the reaction. The hydrocarbon layer was washed with ammonium hydroxide and water to remove traces of dissolved hydrogen fluoride.

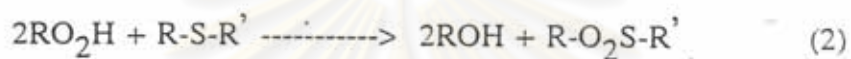
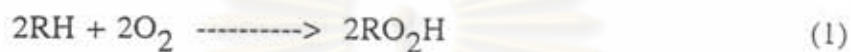
Extraction of organic sulfur compounds with hydrogen fluoride has been postulated to take place through the formation of sulfur-hydrogen fluoride complexes, exemplified as follows:



The complexes are essentially insoluble in the hydrocarbon phase at room temperature, but completely miscible with excess hydrogen fluoride.

With higher boiling feeds, such as catalytic cracking charge stocks, hydrogen fluoride exhibits the important characteristic of extensive aromatic removal, as well as sulfur removal. Hydrogen fluoride extraction of virgin distillates in general produces a raffinate of essentially the same boiling range as the original feed. The data on refractive index and specific dispersion show that in addition to 70% sulfur removal, extensive dearomatization occurred for this particular stock.

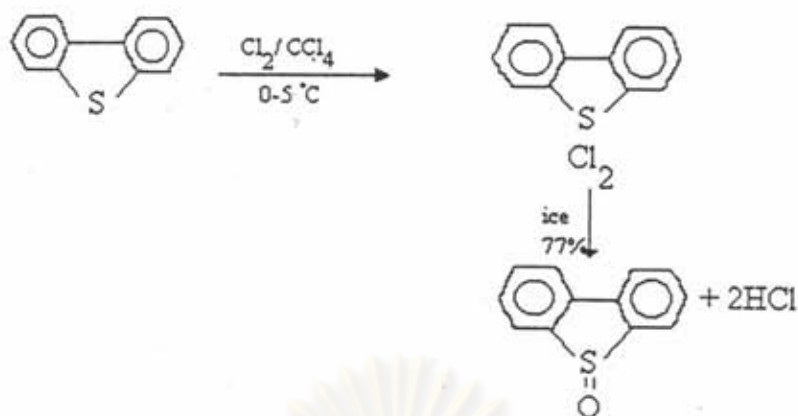
Amir Attar and William H. Corcoran. (1978) review the oxidation reaction of sulfur compounds by two types of oxidant agent; (1) hydroperoxides. (2) peroxy acid. Besides that mechanism of oxidation reaction were present. A fossil fuel can be described as an assembly of organic groups which may compete for a given quantity of reagent in a reactor. When a sulfur-containing fuel is oxidized by molecular oxygen, two types of reaction occur: (1) oxidation of the hydrocarbon part of the fuel to product peroxidic species (PS). (2) selective oxidation of the organic sulfur by the PS to yield sulfoxides and sulfone.



The reactions show that even if the in situ oxidation of the sulfur were absolutely selective, two hydrogens would be oxidized to hydroxy groups for each molecule of sulfone formed.

Nick P. Vasilakos, Russell L. Bone, and William H. Corcoran (1981) studied about the conversion of dibenzothiophene to the corresponding sulfoxide and sulfone by the action of chlorine and water. It then can be considered as a model compound that can be examined in potential desulfurization reactions. Any knowledge so developed can be applied to the desulfurization of fossil fuels, an area of major import in environmental control. Therefore the oxidation of dibenzothiophene by Cl_2 was examined as part of a study of oxidative desulfurization at moderate conditions, namely, at atmospheric pressure and at temperatures less than $100^\circ C$.

Though the Cl_2 - H_2O system is widely used as an oxidizing agent, very few references exist in the literature on the use of this system for the oxidation of dibenzothiophene (DBT). Most of these references are concerned with the first step of the oxidation, i.e., the formation of the sulfoxide.



Because the dibenzothiophene in an aqueous system can be quantitatively oxidized by chlorine to the sulfone, it is expected that the dibenzothiophene structure in fuel oil and coal can be similarly oxidized with a minimum of attack of other atoms by the chlorine. That result suggests that the oxidation of the sulfur then would be accompanied by relatively minor losses of heating value. Even though the sulfur is quantitatively oxidized, desulfurization requires an additional step to split out the sulfone structure.

F. Zannikos, E. Lois, S. Stournas (1995) studied about desulfurization of petroleum fractions by oxidation and solvent extraction.

The known ability of several solvents to extract sulfur compounds selectively from petroleum fractions can be dramatically improved by oxidizing the sulfur from the divalent state (sulfide) to the hexavalent (sulfone). The oxidation process itself leads to the removal of a substantial portion of the existing sulfur and makes the remaining sulfur compounds amenable to efficient removal even by solvents such as methanol which are not effective in selective extraction of the unoxidized sulfur compounds. Thus this combination process is capable of removing up to 90% of the sulfur compounds in petroleum fractions at acceptable yields. The oxidation process has no deleterious effects on the distillation profile and other characteristics of the middle distillate fractions that were examined.