DESULFURIZATION OF HYDROCARBON FUELS BY OXIDATION AND SOLVENT EXTRACTION

Mohamed M. ELGARNI[†], Hamza A KHALFHALLA[‡] and Hadi A. EL AKRAMI[*]

[†, ‡] Petroleum Research Center, P.O. Box 6431 Tripoli-Libya
[*]Department of Chemical Engineering Al-Fateh University P.O. Box 13335 Tripoli Libya

ABSTRACT

The oxidation of model sulfur compounds (di-n-butyl sulfide, dimethyl sulfoxide and dibenzothiophene) and heavy gas oils (HGO) derived from Libyan crude oils were conducted with hydrogen peroxide as oxidant and formic acid as catalyst. The effectiveness of sulfur removal is proportional to reaction temperature in the range of 40 to 60 °C, and maximum 30 ml of formic acid. On the other hand, increasing the amount of hydrogen peroxide leads to reduction in both conversion as well as initial reaction rate. In addition to the oxidative sulfur removal, extraction of unoxidized and oxidized gas oils was also investigated using methanol, dimethylformamide (DMF) and N-methyl pyrrolidone (NMP) as solvents. The removal of sulfur compounds by solvent extraction became more effective for the oxidized samples than for the unoxidized samples. Through oxidation and extraction the sulfur content in heavy gas oils are reduced from 0.1550 to 0.0457 wt % for HGO(A) and from 0.1066 to 0.0148 wt % for HGO(B) by XRF sulfur-in-oil analyzer.

Key Words: Oxidative Desulfurization, Extraction, H_2O_2, HCOOH

1. INTRODUCTION

The removal of sulfur from petroleum products is necessary for both industrial and environmental reasons. Sulfur in petroleum products poisons catalytic converters, corrodes parts of internal combustion engines and refinery facilities because of the formation of oxy-acids of sulfur. Air pollution due to exhausts from diesel is a major concern to the public as well. New fuel regulations call for <50 ppm sulfur in Europe by 2005 and 15 ppm in the US by 2006 (Fairbridge and Ring, 2001). The conventional method for reducing sulfur is catalytic hydrodesulfuraization (HDS). In the HDS method hydrogen and the organic sulfur compounds react together at high temperature and high partial pressure of hydrogen. The effectiveness of HDS process depends on the type of sulfur compounds. The complete removal of sulfur present in petroleum as sulfides, disulfides and mercaptans are relatively easy and an inexpensive process. However, benzothiophenes (BTs) and dibenzothiphenes (DBTs) are difficult to remove by this process. Particularly, the strictly hindered ones, 4-methyldibezothiophene and 4,6-dimethyldibezothiophene are the most resistant compounds in the current HDS processes and they retard the rate of HDS (Otsuki et al., 2000). In order to remove DBTs compounds by HDS, it would require more hydrogen capacity and maintenance of high temperature and pressure for longer

contact time. This would increase operating costs and enhance the likelihood that complete saturation of olefins and aromatics will occur resulting in losses of hydrocarbons. Thus, it is likely that HDS processing has reached a stage where increasing temperature and pressure are just not enough to remove the residual sulfur without affecting the yield of diesel fuel from hydrotreatment processes (Yelda et al., 2002). An oxidative desulfurization (ODS) process has the significant advantage over HDS, namely the sulfur compounds that are the most difficult to reduce by HDS are the most reactive by ODS. In effect, the ODS process has the reverse order of reactivity as compared to the HDS process. This effect arises because the reactivity of sulfur compounds for oxidation is augmented with an increase of electron density on the sulfur atom (Otsuki et al., 2000). Many types of oxidants have been used and various consequences of ODS methods have been reported (Wang et al., 2003 and references there in). (Aida and Yamamoto, 1994) reported that peroxyacids such as performic acid, pertrifluoroacetic acid, and a mixture of formic acid or trifluoroacetic acid and H_2O_2 were some of the most positive oxidants for selective oxidation of sulfur compound in fuel oil.

2. EXPERIMENTAL SECTION

2.1. MATERIALS

Three types of model sulfur compounds are selected to evaluate the reactivity of sulfur in an oxidation reaction. Dibutylsulfide, Dimethylsulfoxide and Dibenzothiophene were purchased from Sigma/Aldrich and used without treatment. Hydrogen peroxide (30 wt. % H_2O_2) was used as oxidant. Methanol, N-methyl pyrrolidone (NMP), Di-methyl formamaide (DMF), Dodecane, Decahydronaphthalene (cis and trans-mixture) were used as solvents and supplied by Surechem products Ltd. Formic acid (99 wt.% HCOOH) was used as a catalyst and supplied by British Drug Hose (BDH). Two heavy gas oils were used in the present study (HGO(A) and HGO(B)) which are derived from Libyan crude oils and their properties are shown in Table 1.

Table 1. Properties of heavy gas oils

Property	HGO(A)	HGO(B)	Test Method
Specific gravity at 60/60 ^{0}F	0.8576	0.8810	ASTM D1298
Viscosity (cSt) (50 ^{0}C)	7.06	7.12	ASTM D445
Flash point closed cup, ^{0}C	115	127	ASTM D 93
Sulfur content (wt %)	0.1550	0.1066	ASTM D4294
Pour point (^{0}C)	27	9	ASTM D97
Cetane index	53.4	54.6	ASTM D976

2.2. REACTOR

A 500 ml four necked flask fitted with a mechanical stirrer, a thermocouple and a thermometer was used to carry out the oxidation reaction. The reaction flask was placed in a heating mantel equipped with a temperature controller (within ±2 ^{0}C).

2.3. PROCEDURE OF OXIDATION EXPERIMENTS

A 1.25 ml of hydrogen peroxide is added to 30 ml of solution containing model sulfur compound and solvent in the reactor. The flask is placed into the heating mantel and stirred at 750 rpm. When the required reaction temperature has been reached (approximately 10 minutes) 30 ml of formic acid catalyst was added to the flask to initiate the reaction. This procedure was carried at different temperatures (20, 40, 60 and 80 ^{0}C). Samples from the reactor are taken at 2.5, 5, 7.5, 15, 25 and 35 minutes. The collected samples were left to settle for few minutes after which two layers were formed; the top layer (solvent) and the bottom layer (oxidant-catalyst). The top layer is analyzed by XRF in order to determine the content of sulfur. The same procedure was used for the heavy gas oils using equal volumes of the formic acid and heavy gas oil (30 ml) and half volume of hydrogen peroxide (15 ml) at different reaction temperatures, 40, 60, 80 and 100 ^{0}C. Samples are taken for analysis at different time intervals (5, 15, 25, 35, 70, 90, 180, 270 and 360 minutes). After each run, the mixture is allowed to cool down to the room temperature whereupon two layers are formed. The top layer (oil) was separated, washed successfully with water, 5% aqueous sodium bicarbonate and was finally dried over anhydrous magnesium sulfate, then analyzed by XRF to measure sulfur content.

2.4. PROCEDURE OF EXTRACTION EXPERIMENTS

The extraction of sulfur compounds from the oxidized oil layer and the original HGO were conducted with NMP, DMF and methanol at different solvent/oil ratios. Prior to the extraction, the oxidation of HGO was performed at 60 ^{0}C for 90 minutes. The extraction was done at 25 ^{0}C for HGO(B) and 40 ^{0}C for HGO(A) for two hours. For HGO(A), it was necessary to carry out extraction at 40 ^{o}C in order to dissolve wax formed at ambient condition. The phases are then allowed to separate and their volumes are measured, the hydrocarbon phases were washed with distilled water and then analyzed for their sulfur content.

3. RESULTS AND DISCUSSION

3.1. OXIDATION OF MODEL SULFUR COMOUNDS

Figure 1 shows the effect of reaction time on the conversion of di-n-butylsulfide in the presence of formic acide/H_2O_2 at different reaction temperatures. It is clear from this Figure that the initial reaction rate of oxidation is high and conversion values above 75 % have been obtained within 5 minutes. This Figure also shows that as the reaction temperature increase up to 60 ^{o}C, the initial reaction rate as well as the final conversion increase. But the initial reaction rate and conversion values at 60 and 80 ^{o}C are similar. Figure 2 shows the oxidation of di-methylsulphoxide with H_2O_2 as a function of reaction time over various temperatures. As shown in this Figure the initial rate of oxidation is less than that for di -n-butyl sulfide and the reaction rate strongly increases after 5 minutes, but the reaction does not stop as in the case of di - n-butyl sulfide. Both the initial reaction rate and the final conversion values increase upon increasing the reaction temperature, however above 60 ^{o} C leveling off occurs

in the apparent rate of reaction. This is probably due to mass transfer limitation as the kinetic curves fully overlap. The steps between 2.5 and 5 minutes require further investigation. This unusual behavior can be due to (i) product solubility problem, (ii) partial poisoning by the product (product-substrate interaction).
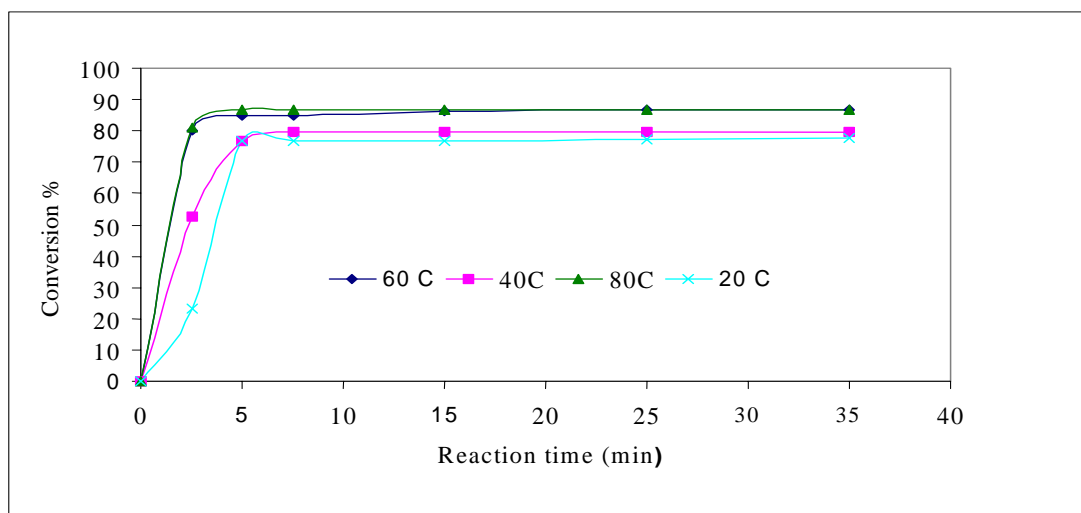

Figure 1. Oxidation of di -n-butyl sulfide in formic acid/ H_2O_2 system at different temperatures
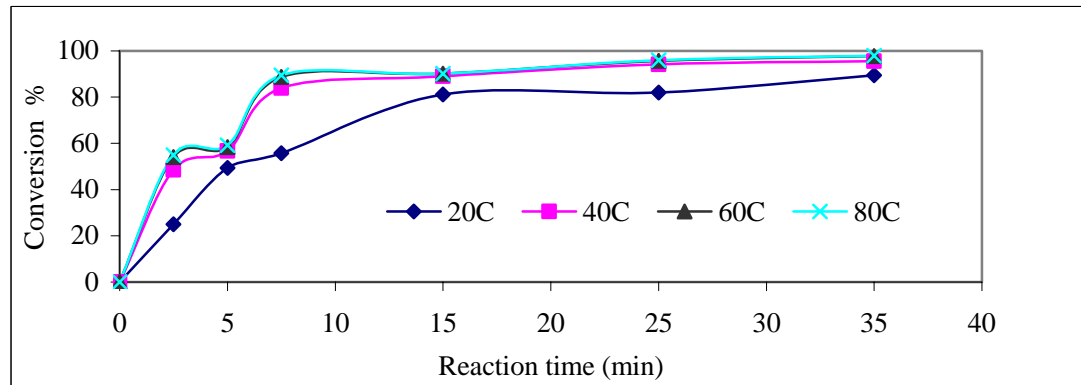

Figure 2. Oxidation of di-methylsulfoxide at different temperatures

Figure 3 shows the results of oxidation of dibenzothiophene with H_2O_2 as a function of reaction time and reaction temperatures. It can be seen that as the reaction temperature increases, the initial reaction rate increase at reaction time below 5 minutes whilst, 98 wt% conversion of DBT has been achieved after 5 minutes for all reaction temperatures. On the other hand when the reaction temperature exceeds 40 ^{o}C and reaction time above 4 minutes, the reaction proceeds with constant conversion, or in other words the operating conditions have no significant influence on the oxidation of DBT.
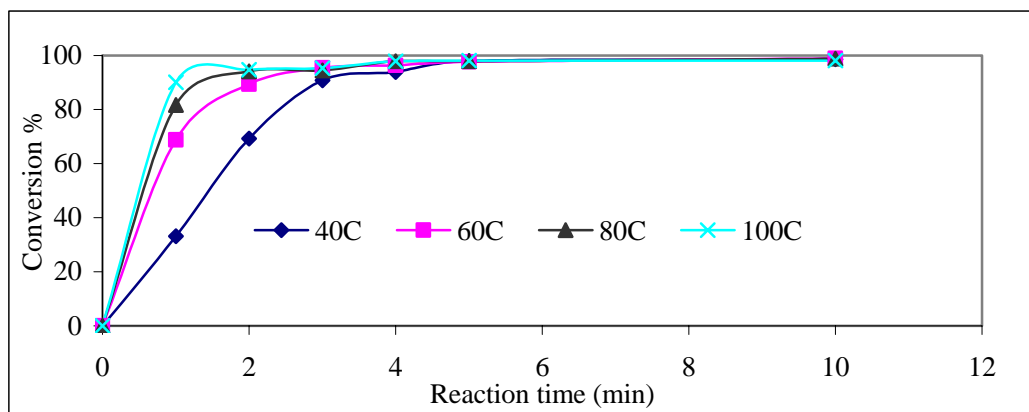
Figure 3. Oxidation of DBT at different reaction temperatures

It is obvious from the comparison of Figure 1 and Figure 3 that the initial rate of oxidation of DBT is faster than in case of the corresponding n-dibutylsulfide. This can be attributed to the fact that DBT has higher electron density than the sulfide and, hence, higher reactivity (Otsuki et al., 2000). The oxidation of DBT with hydrogen peroxide and formic acid has been reported by (Attar and Corcoran, 1978). They postulated that the divalent sulfur of DBT can be oxidized by the electrophilic addition reaction of oxygen atoms to the hexavalent sulfur of DBT sulfone. Hence, the reactivity of oxidation becomes higher for a sulfur atom with a higher electron density.

3.2. OXIDATION OF HEAVY GAS OILS (HGO)

Figure 4 shows the oxidation of HGO(A) with H_2O_2 as a function of reaction time over various temperatures. The results indicated that at 40° C there is a partial poisoning after 5 minutes of reaction but at 60, 80, and 100 ^{o} C the reaction stops after 25 minutes due to the poisoning effect of the reaction products. Figure 5 shows the oxidation of HGO(B) with H_2O_2 as a function of reaction time over various temperatures. As seen from this Figure the results indicated that the oxidation activities increased with the increasing temperature up to 60^0C. Above the reaction temperature of 60 ^{o} C the kinetic curves fully overlap. This could be caused by several reasons such as: (1) Mass transfer limitation (2) Decomposition of H_2O_2 at high temperature (3) High molecular weight sulfones produced owing to reaction temperature above 60 ^{o}C.

3.3. EFFECT OF CATALYST AMOUNT ON THE OXIDATION REACTION

It can be seen from Figure 6 increasing the amount of the catalyst increase both the initial rate and the final conversion. Higher amount of formic acid, gives higher conversion. These results from the fact that probably the products formed are well soluble in formic acid. In this case the probability for the interaction between the product and the initial sulfur compound is decreasing. Addition of more formic acid above 30 cm^3 had no further improvement in the rate of reaction and final conversion.
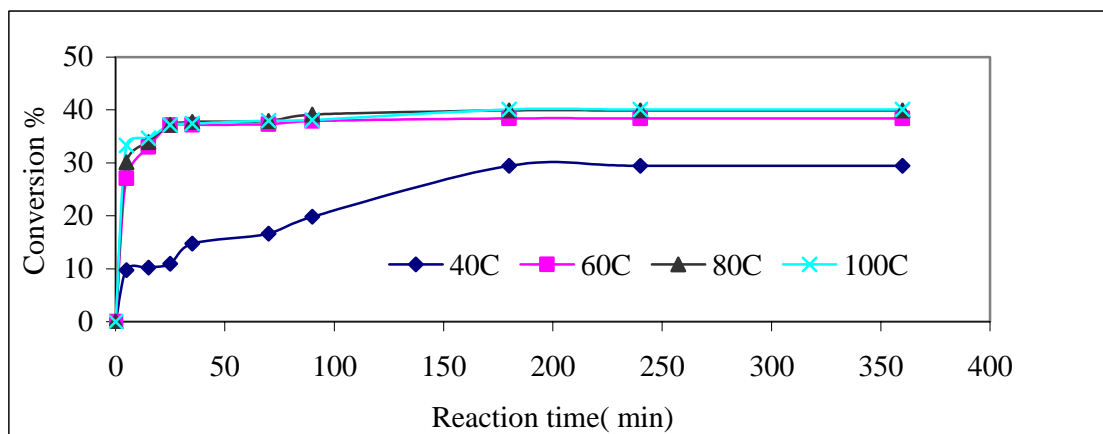
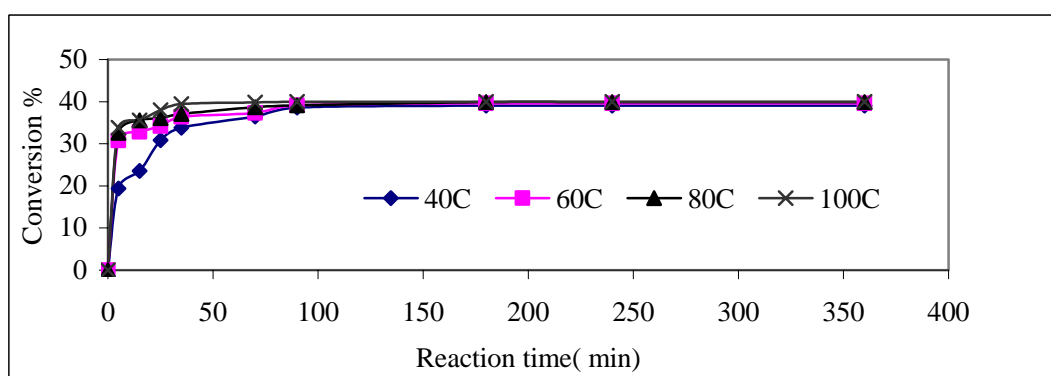Figure 4. Oxidation of HGO(A) at different reaction temperatures

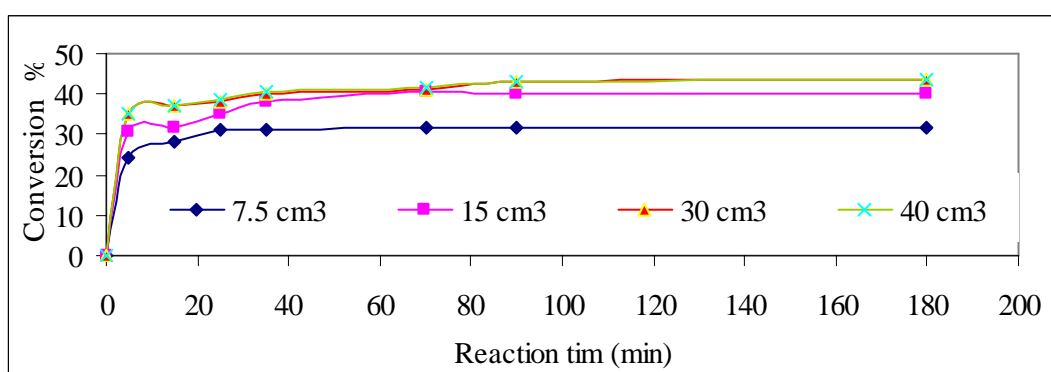Figure 5. Oxidation of HGO(B) at different reaction temperatures

Figure 6. Effect of catalyst amount on the oxidation reaction at 60 ^{0}C

3.4. EFFECT OF OXIDANT AMOUNT ON THE OXIDATION REACTION

As shown in Figure 7, there is a strong negative effect of the oxidant both on the initial rate and the final conversion. The negative effect of H_2O_2 can be attributed to the presence of large amount of water. The higher is the amount of water the lower is the probability for the interaction between the sulfur compound dissolved in the oil phase and H_2O_2 present in the water phase.
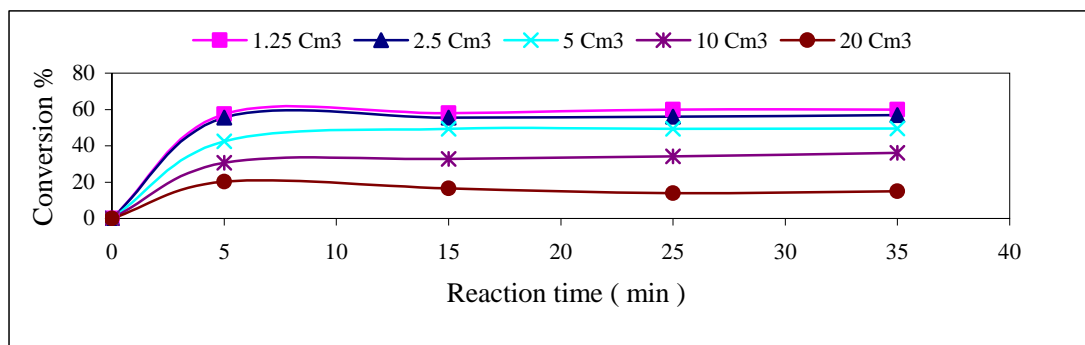
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Figure 7. Effect of oxidant amount on the oxidation reaction at 60 ^{0}C

3.5. EXTRACTION

HGO(A) was extracted by using methanol and NMP before and after oxidation. The results are reported in Tables 3 and 4 respectively. As shown in Table 3 the extraction with methanol is more effective after oxidative sulfur removal. However, efficiency of sulfur removal is almost constant above the solvent/HGO ratio of 3. Whereas, the efficiency of sulfur removal using NMP is high as seen in Table 4, HGO(B) was extracted by using methanol, NMP and DMF before and after oxidation. Tables 5-7 show the results. The efficiency of sulfur removal using DMF is higher than both methanol and NMP. It can be observed that methanol is not an effctive solvent in the case of extraction of unoxidized HGO, whereas the NMP and DMF can achive substantial desulfurization albeit relatively low yields (Tables 6 and 7). When the HGO was first oxidized and then treated with various solvents, a further subtantial reduction of sulfur content could be obtained. In this particular case it was found that DMF is as effective as the very polar NMP and methanol in removing sulfur compounds selectively with different solven/HGO(B) ratios. Furthermore DMF give better yields than NMP except at the solvent (DMF)/HGO(B) ratio of 5 for the oxidized HGO(B). Plots of solvent effctiveness (S.E = percent conversion/oil loss) vs solvent/HGO ratio for extraction of unoxidized HGO(B) is shown in Figure 8 and for oxidized HGO(B) are shown in Figures 9 and 10. Figures 8 and 9 give S.E factors for the case when conversion was calculated on the basis of original sulfur content (0.1066 wt %) whereas in Figure 10 conversion is based on oxidized sample sulfur content (0.0609 wt %). Figures 8 and 9 clearly show that methanol is the most effective of these solvents for the case when conversion is based on the original sulfur content. However, when the S.E factor is calculated from conversion based on sulfur concentration after HGO(B) is oxidized, DMF with solvent/ HGO(B) ratio of 1 has been found as the most effective.

Table 3. Extraction of HGO(A) by methanol

Methanol/HGO(A) volume ratio	Unoxidized		Oxidized[*]	
	S%	Yield%	S%	Yield%
0.5	0.155	99..5	0.093	99
1	0.146	98	0.084	98.5
3	0.117	96	0.057	97
5	0.115	95	0.056	95

Table 4. Extraction of HGO(A) by NMP

NMP/HGO(A) volume ratio	Unoxidized		Oxidized	
	S%	Yield%	S%	Yield%
1	0.1253	93	0.0817	81
3	0.1032	89	0.0543	78
4	0.0981	85	0.0461	75
5	0.0976	83	0.0457	74

*oxidation at 60 ^{0}C, 90 min.(S %= 0.097), amount of H_2O_2:15 cm^3 amount of formic acid: 30 cm^3

Table 5. Extraction of HGO(B) by methanol

Methanol/HGO(B) volume ratio	Unoxidized		Oxidized[**]	
	S%	Yield%	S%	Yield%
0.5	0.1066	99	0.0607	98
1	0.0982	98	0.0584	97.5
3	0.0903	96	0.0514	97
5	0.0790	95	0.0475	96.5

Table 6. Extraction of HGO(B) by NMP

NMP/HGO(B) volume ratio	Unoxidized		Oxidized	
	S%	Yield%	S%	Yield%
1	0.0733	80	0.0307	78
3	0.0652	79	0.0243	77
4	0.0623	74.5	0.0164	74
5	0.0614	74	0.0155	70

Table 7. Extraction of HGO(B) by DMF

DMF/HGO(B) volume ratio	Unoxidized		Oxidized	
	S%	Yield%	S%	Yield%
0.5	0.0901	97.5	0.0356	95
1	0.0599	82.5	0.0225	90
3	0.0448	80	0.0172	86
5	0.0397	78	0.0148	70

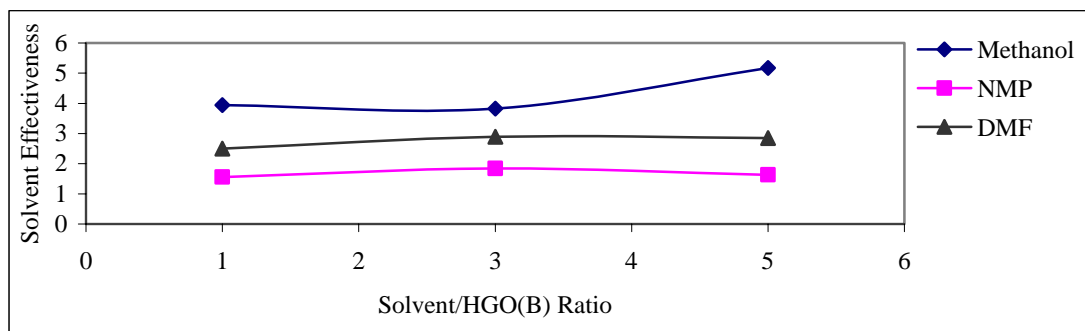**oxidation at 60 ^{0}C, 90 min.(S %= 0.0609), amount of H_2O_2:15 cm^3, amount of formic acid: 30 cm^3

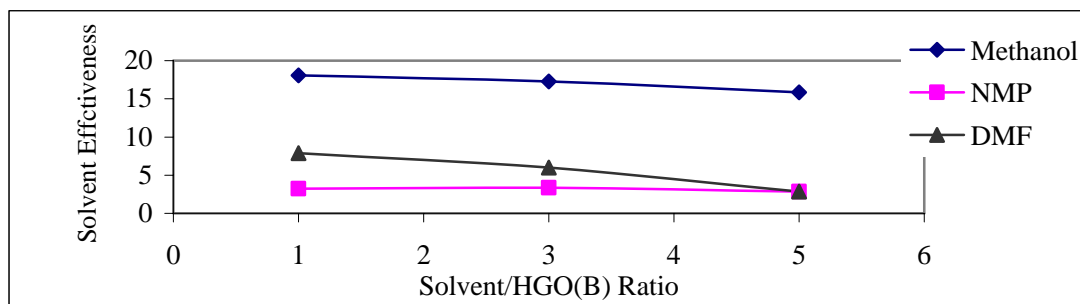Figure 8.Solvent effectiveness in sulfur removal from unoxidized HGO(B) based on original sulfur content

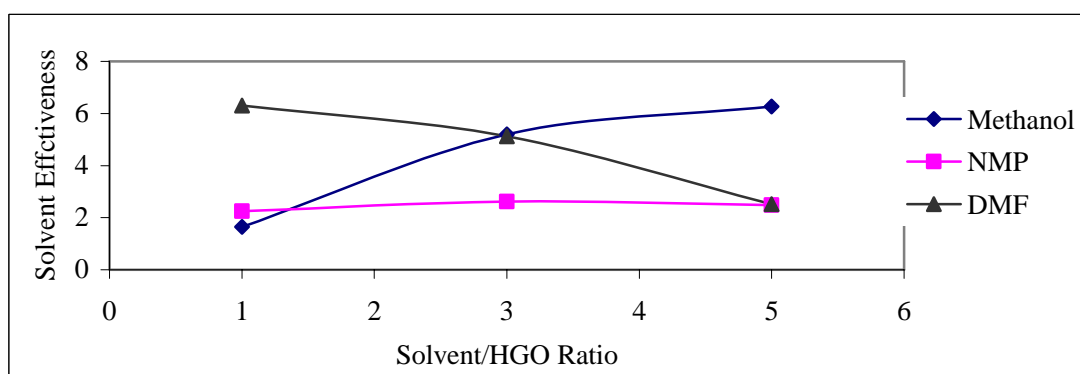Figure 9.Solvent effectiveness in sulfur removal from oxidized HGO(B) based on original sulfur content

Figure 10.Solvent effectiveness in sulfur removal from oxidized HGO(B)) based on oxidized sulfur content

3.6. EFFECTS OF ODS ON HGO(B) PROPERTIES

The physical properties of the original HGO(B) and desulfurized HGO(B) are listed in Table 8. As shown in this Table the oxidation and extraction processes lead to the removal of a substantial portion of the sulfur and nitrogen that are originally present without any negative effects on the other properties of fuel. In fact, improtant properties as cetane number has improved by at least 3 points. Furthermore, undesirable aromatics and poly nuclear aromatic (PNA) compounds had been reduced.

Table 8. Effects of oxidation and extraction on HGO(B) properties

Physical property	Original	*Oxidized	Extraction	
			Methanol 1:5	NMP 1:3
API	29.1	30	31.1	32.5
Cetane number	53.7	56.8	56.9	59.7
Cetane index	54.6	55.2	56.9	59.4
Total aromatic wt%	16.2	14.4	12.5	6.3
PNA wt%	4.6	3.8	3	1.8
N_2 PPM	176	39	19	-----
S PPM	1066	609	475	244

* Oxidation at 60 ^{0}C, 90 min.(S %= 0.0609), amount of H_2O_2:15 cm^3, amount of formic acid: 30 cm^3

4. CONCLUSION

The oxidation of sulfur compounds followed by their extraction is an effective method for reducing these species. The effectiveness of sulfur removal is proportional to reaction temperature in the range of 40 to 60 ºC, and maximum 30 ml of formic acid. On the other hand, increasing the amount of hydrogen peroxide leads to reduction in both conversion as well as initial reaction rate. Through oxidation, the sulfur content in HGO(B) and HGO(A) are reduced from 0.1066 to 0.0609 wt % and from 0.1550 to 0.0970 wt% respectively. DMF was found as the most efficient solvent able to reduce the total sulfur content from 0.0609 to 0.0148 wt% for HGO(B). However, combining sulfur removal efficiency and oil yield, methanol was found to be the most attractive with solvent effectiveness factor of 15.83 compared to 2.87 for DMF. It is important to mention that when sulfur conversion is based on the concentration of sulfur in oxidized HGO rather than the original sulfur, DMF with solvent/HGO ratio of (1:1) is more effective than other solvents. Final solvent selection should be based on economic and environmental considerations. It is confirmed that the oxidation and extraction processes lead to the removal of a substantial portion of the sulfur and nitrogen that are originally present without any negative effects on other fuel properties.

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