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# SULFUR REDUCTION OF HEAVY FUEL OIL BY OXIDATIVE DESULFURIZATION (ODS) METHOD

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**Abstract**

Heavy fuel oil usually contain of high amount of sulfur. Development a process for desulfurization of fuel oil is difficult as it is contained of heavy hydrocarbons and different impurities. In this research the decreasing of fuel oil sulfur amount was carried out by using of oxidative desulfurization method(ODS). Oxidative desulfurization process consist of two stage: 1.Reaction Stage : catalyst, fuel oil and chemicals (peroxide,..) mixing and production of sulfones, 2. Extraction stage :sulfones compounds and treated fuel oil separation section by using extractor solvent. Pressure in reaction was atmospheric and constant and a stirrer was utilized to help further mixing with speed of 750 RPM. The experimental tests showed following results: sulfur removal procedure has been carried out efficiently with ODS method, sulfur amount from high level of 2.75 %w was decreased to amount of 1.14% w and chemical mixing of $H_2O_2$/acetic acid has better effect in comparision with chemical mixing of $H_2O_2$/ formic acid for desulfurization of heavy fuel. Oxidation reaction was optimised by changing the molar ratio of oxidant and catalyst to sulfur amount in the range of 5-10. In this research the effect of parameters like acid and oxidant amounts and increasing the temperature were investigated in desulfurization reaction. Based on experimental tests , which was carried out on fuel oil of Tehran refinery, it has indicated that the oxidation amount of sulfur compounds has been increased with the rise in the temperature till 60°C.

***Keywords**: Oxidative Desulfurization; Fuel Oil; Sulfur; Removing; Peroxide; catalyst.*

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## 1. Introduction

New environmental concerns regulation required low sulfur in hydrocarbon based distillated fuels. It is impossible to clean the air, or in particular to reduce air pollution from the transportation sector without removing sulfur out of fuels. Sulfur itself is a main pollutant in fuels. No significant air pollution reduction strategy can work without reducing sulfur to near –zero levels. Regarding sulfur effect in pollution of air the desulfurization of petroleum –derived fuels becomes an important part of refining processes. Sulfur content in fuel during combustion will convert to $SO_X$ and this compound is source of acid rain and air pollution. Therefore nowadays very stringent regulation for low sulfur fuels are being imposed in oil refineries throughout the world to reduce the sulfur content of their products to a very low limit of 10-50 ppm. At present, the conventional industrial desulfurization process for middle distillate fuel in refineries is hydrodesulphurization (HDS) process.

HDS is a process for desulfurization that is carried out at high temperature as 400°C and pressure 70barg on existing of solid catalyst. The investment and operating cost of HDS process is high.

Among the above HDS process, oxidative desulfurization (ODS) has much attention as an alternative process for desulfurization because of its two primary advantages about the HDS process. The greatest advantage of ODS is its capability to carry out in the liquid phase under low temperature (30-70oC) and low pressure (atm.) condition.

Review of literature research showed that sulfur reduction for fuel oil is not investigated by ODS method and this research is first research in application of ODS method for sulfur reduction on fuel oil. However, there are many research in application of ODS for diesel fuel (gasoil) and other light fuels. ODS reaction has two step as following, first step :oxidation and second step: extraction .In first step oxidation process was performed with hydrogen peroxide as an oxidant (H2O2 ) in the presence of formic acid or acetic acid as a catalyst. In next step of process liquid-liquid extraction was carried out by using solvent of acetonitrile.

## 2. The necessity of desulfurization of petroleum fuels

The desulfurization of petroleum fuels shall be carried out regarding following reasons:

### 2.1 Corrosion

Corrosion will occurred in petroleum industry due to existing $H_2S$/sulfur products/ mercaptans/disulfides. In petroleum industries corrosiveness cases are at least in three general fields which consist on: 1. Production 2. Transportation 3. Purging operation [2].

### 2.2 Destruction and pollution of environment

The hydrocarbon products that were derived from petroleum due to existing sulfur converting to sulfur oxides in effect of ignition and combustion reaction. Sulfur oxides that spread in maximum amount in atmosphere are sulfur dioxide ($SO_2$) that usually small amount of sulfur trioxide ($SO_3$) exist beside the sulfur dioxide too and its amount would not be more than 1-2 percent. The two kinds of oxides show by $So_{x.}$ These gases besides creation of respiratory disorders, for the reason of solubility in water, produce the acid solution that could form the acid-rains. Among the environment outcomes of acid-rains could mention the large environmental damages, erosion of buildings and structures, waste of agronomy products and jungles and also hazard the hesitancy in lakes [3].

### 2.3 Deactivation of catalysts

Deactivation of the catalysts because of existing toxic gases as $H_2S/SO_2/NO_2/NO$ could be damaged. In effect of deactivation of catalyst, activity and selectivity of the catalyst changes during the time. The toxic gas will be preventing that feed can diffused to catalyst pores.

## 3. The major sulfur compounds in fuel oil

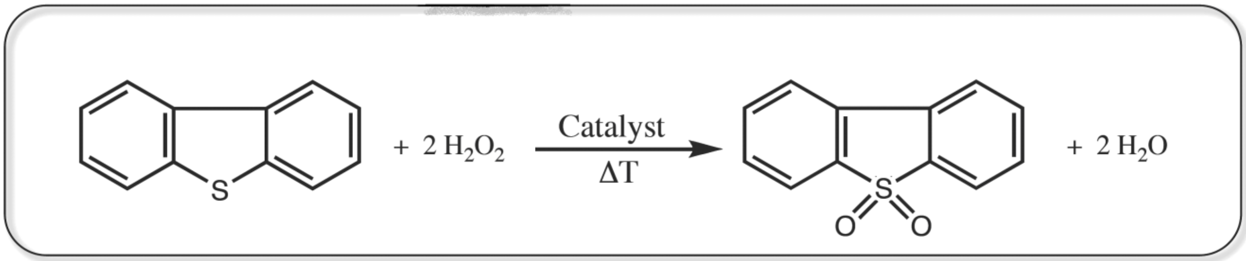
The major sulfur compounds in fuel oil are as following lists:
Pure sulfur: Pure sulfur exists in heavy blends of the oil.
Hydrogen Sulfides ($H_2S$): Hydrogen Sulfides exist in oil products naturally.
Sulfides (R-S-R): These sulfur compounds could enter to a saturation bond or a ring with 4 or 5 carbons.
Disulfides (R-S-S-R): These compounds are usually transitory thermally and converted to olefins or $H_2S$ in confined temperature between 150-175°C.
Thiols or mercaptans (RSH): Mercapatns are usually existing in petroleum and petroleum cuts gasoline, kerosene, gasoil and condensate. Large amount of thioles are due to destruction of the other sulfur compounds in distillation or cracking operations. They are exists in lower boiling point of hydrocarbon cuts.
Thiophenes: Thiophenes and their derivatives usually exist in blends with higher than 250°C [2].

## 4. Sulfur reduction of fuel by oxidative desulfurization (ODS) method

### 4.1 HDS and ODS processes

Hydrodesulphurization (HDS) is a current industrial method to remove aliphatic and acyclic sulfur –containing compounds from diesel oil. The process usually use using Co/Mo and Ni/Mo type catalyst and allows removing sulfur compound by their conversion to H2S however it is important to point out that this process requires high temperature (up to 400°C), high hydrogen pressure (up to 100 atm), use of metal catalyst and large reactors with long reaction time resulting in higher operation costs. Studies on HDS process indicated that this process is efficient for marcaptans, thioethers, sulfides, disulfides and thiophene removal, but it has shown limitations regarding the treatment of alkylated aromatic sulfur compounds. Oxidative desulfurization has been studied from the beginning of the 1960. During the year of 1990 some significant industrial processes for desulfurization from petroleum blends were used oxidation with peroxides and liquid-liquid extraction. Oxidative desulfurization has been considered a promising method for deep desulfurization technology because it can be carry out under mild conditions, such as relatively low temperature ,pressure and cost of operation when it is compared with HDS.The use of oxidative process would conceivable the converting of thiophene, benzothiophene, dibenzothiophene and other alkyl derivatives to sulfones and sulfoxides. The reaction of oxidative desulfurization has showed in below:

Oxidative desulfurization of Benzothiophene



In ODS process is sulfur compounds oxidized by use of proper oxidant and converted to corresponding sulfoxides and sulfones and oxidized compounds were extracted with a non-miscible solvent.

Oxidation of thiophene derivatives by use of peroxides is conceivable perfectly and this is an incipient principle for desulfurization of fuel oil and other petroleum blends.

Peroxides are more expensive in comparison with the air, however oxidation of sulfur compounds in fuels by use of air, oxygen or ozone showed low conversion only up to 45% Of course some inexpensive oxidants like nitrogen oxides and nitric acids were studied too but the tests did not have proper results.

The main reasons for the use of hydrogen peroxide as oxidant agent are [1]

1- low cost,
2- non-polluting,
3- non- strongly corrosive
4- Commercial availability.
5- Environmentally friendly [4].

### 4.2 The benefits of ODS process are as following lists:

- Easy deletion of sulfur species that were resistant against the hydrodesulphurization.
- Availability of air in refineries.
- Reduction the sulfur in fuels to new level of ultra low sulfur.
- Good proportion with small and middle refineries.
- Have potential for ultimate desulfurization.
- Fuel oil desulfurization to low amount [5]

### 4.3. The disadvantage of ODS process

- ODS process is not commercial till now and HDS process is industrial process that many technologist were developed it.
- So much chemical is used in ODS process and chemical have environmental effect and its effect was not solved till now.

## 4.4. Engineering scheme

The ODS process including following steps:
1-Reaction (could be done in mixing vessel)
2-Separation (could be done is separator)
3-Extraction (could be done in mixing and separation vessel)

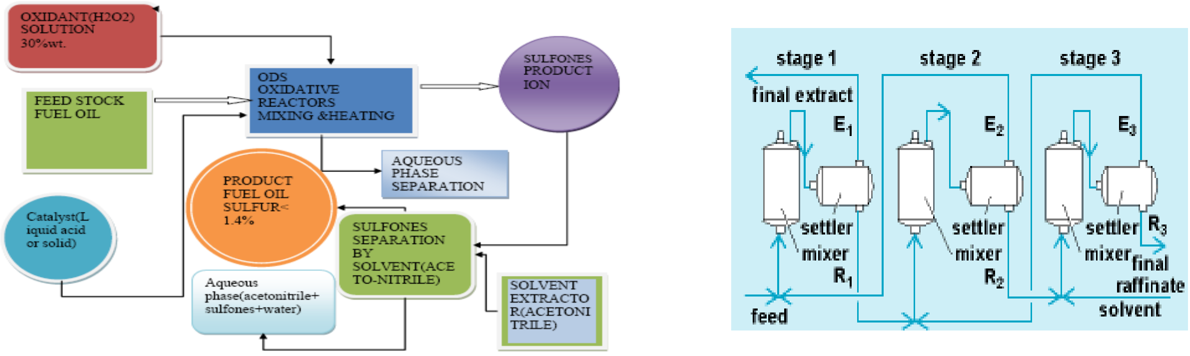


Figure 1 ODS process steps

As described earlier the application of process from engineering point of view could be commercialized by using mixing and settler system including following equipment:
1-Mixing tank (or static mixer)
2- Separation tank
3-Fuel oil extraction procedure including mixing and separation stages.
The laboratory and engineering process scheme of ODS process was shown in figure 1

## 5. Experimental tests

### 5.1 Experimental setup

The laboratory reactor system that have been chosen for this investigation was a glass batch reactor that compeletly mixing accomplish between the reaction materials consist on fuel oil, catalyst and oxidant. For control of temperature in reaction a heater was used. Also, for complete mixing of the reactor materials a stirrer was set with mixer till oxidative reaction between fuel oil and oxidant accomplish to the best form. For regulation and control of reaction temperature, a thermometer was used in the reactor system. At last the experimental set-up including following assesories:
-a glass batch reactor with volume 500mL
-a mixer with strirr for mixing two phase of oil and chemical
-a thermometre for measument of temperature
-a heater for heating the glass reactor till maximu temp 80°C

### 5.2 Test run procedure for oxidative desulfurization of fuel oil

### *5.2.1 First step: reaction*

A typical procedure was as follows. In first step oxidation reaction of sulfur compound in existence of oxidant and catalyst will be carry out. A 100mL of fuel oil was infused in glass reactor, first reactor is equipped with mixer and stirr then fuel oil is heated till adjusted temperature and after a dedicated chemicals including solution of 30wt.% $H_2O_2$ as oxidant with acid formic or acid acetic as catalyst are mixed with fuel oil. The mixtures was stirrered at a rate 750 RPM in reactor at temperature range 30-60°C for 90 minutes. The glass reactor is equipped with thermometer for measurment of temperature. After the completion of the reaction,aqueous phase and oil phase were separated and then a sample of oil as 25mL will infused in decanter till next step of extraction to be done. At figure 2 – Test run for ODS of fuel oil with chemical on heating & mixing condition was shown.

Figure 2 Test run for ODS of fuel oil with chemical on heating & mixing condition

### *5.2.2 Second step: extraction*

The second stage of this process is separation of oxidized compounds via liquid-liquid extraction with selective solvent. Obviously for separating the oxidized sulfuric compounds from fuel oil, the selection of solvent is too important. The solvent should have high polarity and also was not solvable in fuel oil.

In this stage to specification above, acetonitrile was chosen among the various solvents. These solvents were not soluble in water like: DMSO, DMF and acetonitrile. [6]. the two first solvents have high ability in extraction of sulfones but their boiling point is high (573K) which is close to sulfones boiling point. So separation and reuse of those would be difficult. However, acetonitrile is suitable for extraction due to its low boiling point and would be separated from sulfones via distillation conveniently.

At first oxidized fuel oil infused in decanter and then, the equivalent of fuel oil amount, acetonitrile was added to decanter. Therefore began to shake the decanter till the acetonitrile separated the sulfur compound of the fuel oil. After shaking, (Ten minutes) wait for a while till the mixture became two phase. Next open the screw of the decanter slowly and then fuel oil that is heavier than the solvent separated at the bottom of the decanter. Therefore evacuate the fuel oil and then 10mL of it would send to the fuel oil's analysis center for measuring the sulfur amount. The amount of sulfur is measured by X-Ray fluorescence test (XRF) ASTM-D 4294.

### 5.3 Measuring the sulfur in fuel oil via XRF (ASTM D4294)

This apparatus usually measures the sulfur amount between ranges 100ppm-3 %wt. The XRF apparatus type 1100 measures only one sample and XRF apparatus type 1800 measures more than one sample (8 samples) simultaneously. Calibration and standardization of the apparatus was done via 4 standard samples of petroleum and oil cuts. In this method the existing total sulfur in fuel oil that in room temperature would become liquid or liquid able with the thermal medium or would dissolve in hydrocarbon solvents, would be measured. These materials could be as diesel fuel, jet fuel, kerosene or the other petroleum compounds that are produced from distillation like naphtha, residual oil, fuel oil and gasoline.

Samples like gasoline (with high vapor pressure or light hydrocarbons) could not measure accurately with this method, because they waste during the analysis. Testing method of ASTM D 2622 and 4294 has high working capacity, less stages for preparation of the sample, more ability and accuracy in measuring sulfur in heavy fuel. The outfits of this method are more expensive than the other methods [7].

## 6. Experimental test of sulfur reduction of fuel oil by ODS with using solution mixture of hydrogen peroxide and formic acid

In this survey, the effect of formic acid /acid acetic amount in existence of peroxide hydrogen for sulfur reduction in fuel oil was investigated. According criteria of reaction the mole ratio of catalyst /sulfur and mole ratio of oxidant /sulfur shall be controlled and the amount of it shall be between 5-10.According this idea the laboratory tests were designed and tested. First amount of sulfur in fuel oil was measured, the result show that sulfur amount in fuel oil is 2.7 wt%, the sulfur mole was calculated for 100mL fuel oil as 0.07593 gr-mole and according criteria of 5-10 for mole of acid and oxidant the mole range was calculated as 0.3796-0.7593grmole .According following criteria the laboratory tests were designed and carry out in Table 1.

Table 1 Effect of acid formic catalyst on sulfur reduction of fuel oil by ODS method with hydrogen peroxide

| no. | Stirrer (RPM) | Temperature (°C) | Pressure (bar) | Fuel oil (gr) | Formic acid (gr) | $H_2O_2$ (gr) | sulfur in fuel oil %wt. |
|---|---|---|---|---|---|---|---|
| 1 | 750 | 60 | 0 | 100 | 8 | 15 | 2.15 |
| 2 | 750 | 60 | 0 | 100 | 15 | 30 | 1.9 |
| 3 | 750 | 60 | 0 | 100 | 30 | 30 | 1.7 |
| 4 | 750 | 60 | 0 | 100 | 50 | 40 | 1.5 |
| 5 | | | | Fuel oil feed | | | 2.7 |

The result shows that with increasing concentration of oxidant and catalyst(acid formic) the sulfur amount was decreased to low amount of 1.1 wt% .also it was concluded that acid formic is very effective catalyst ,but it was existed problems with increasing concentration of acid formic that it was produced sticky polymer material. So regarding producing sticky material it was decided that step of high concentrated acid adding was changed as following: first it was added low amount and then add reminded amount slowly to the reaction at last the result showed that sulfur amount decrease to 1.14 wt%. However, small amount of sticky material problem was existed again. So it was decided that catalyst type was changed to acid acetic, Again the same laboratory tests as acid formic was designed. The tests were tested and the result showed that minimum amount of sulfur in fuel oil was decreased to amount of 1.47 wt%. The results of tests have been shown in table3.

The date shows that sulfur level is decreased from 2.7 wt% to 2.15, 1.9, 1.7, 1.5 wt% respectively. During these test runs formic acid concentration will increase and sulfur level is decreased. However, producing of sticky substances in reaction with acid formic was a problem that was existed.

## 7. Optimizing the oxidative desulfurization of fuel oil by changing catalyst adding step

The all tests data for this step have been shown in Table 2. Due to obtained sticky substances in above; the procedure changed and has decided to add the amount of acid in two parts for amount of 30g. At first 15gr. Of formic acid was added to feed and the rest was added 15 minutes later.

Table2 Effect of catalyst adding step of acid formic on sulfur reduction of fuel oil ODS method with $H_2O_2$

| No. | Stirrer (RPM) | Temperature (°C) | Pressure (atm) | Fuel oil (gr) | Acetic acid (gr) | $H_2O_2$ (gr) | Sulfur %wt. | Reaction condition |
|---|---|---|---|---|---|---|---|---|
| 1 | 750 | 60 | atm | 100 | 30 | 30 | 1.35 | 1 |
| 2 | 750 | 60 | atm | 100 | 30 | 30 | 1.14 | 2 |

*1 - Adding 15 gr acid in first step and then adding 15 gr of reminded gradually step wise during one hour*
*2 - Change type of stir to large dimension and efficient one*

After oxidation, extraction and sulfur measurement in reminded fuel oil by XRF method, the results became better but still sticky substances were existed. In this case for optimizing the oxidation process, the type of the stirrer was changed to large stir and the reaction was carried out again. For this reaction sulfur amount is reached to 1.14 wt%., and this sulfur amount was lowest value of the executed tests and it was best result of ODS reaction for heavy fuel oil.

As again a sticky substance was existed in reaction. For this reason the acid type was changed in next experiments and acetic acid was used.

## 8. Effect of solution mixture of hydrogen peroxide and acetic acid on sulfur reduction in ODS reaction of fuel oil

Due to obtaining sticky substances in reactions with formic acid, the type of acid catalyst was changed and the effect of acetic acid on ODS process was investigated. The obtained results have been shown in Table 3.

Table 3 Effect of catalyst change to acid acetic on sulfur reduction of fuel oil by ODS method with hydrogen peroxide

| No. | Stirrer (RPM) | Temperature (°C) | Pressure (atm) | Fuel oil (gr) | Acetic acid (gr) | $H_2O_2$ (gr) | Sulfur in fuel oil %wt. |
|---|---|---|---|---|---|---|---|
| 1 | 750 | 60 | atm | 100 | 8 | 15 | 1.83 |
| 2 | 750 | 60 | atm | 100 | 30 | 30 | 1.57 |
| 3 | 750 | 60 | atm | 100 | 50 | 40 | 1.47 |

It is indicated that increasing the acid amount has positive effect on reduction process of sulfur weight percent in fuel oil and also the results are close to formic acid’s result . Moreover there was not any sticky substances in fuel oil.But at last it was evaluated that formic acid is more stroger than acetic acid.

## 9. Effect of temperature on ODS reaction in fuel oil

In another tests, the effect of temperature on the reaction-process of sulfur reduction by ODS method was studied. As it showed in Table 4, could deducted that rising the temperature would increase the oxidative rate of the sulfur compounds in fuel oil and reduction process of sulfur weight percent plunged early till 50-60°C and then increasing the temperature would have inverse effect on reduction process of sulfur weight percent.

Table 4 Effect of temperature on sulfur reduction of fuel oil by ODS method with hydrogen peroxide and formic acid

| No. | Stirrer (RPM) | Temperature (°C) | Pressure (atm) | Fuel oil (gr) | Formic acid (gr) | $H_2O_2$ (gr) | Sulfur in fuel oil %wt. |
|---|---|---|---|---|---|---|---|
| 1 | 750 | 30 | atm | 100 | 30 | 30 | 1.83 |
| 2 | 750 | 50 | atm | 100 | 30 | 30 | 1.75 |
| 3 | 750 | 60 | atm | 100 | 30 | 30 | 1.7 |
| 4 | 750 | 70 | atm | 100 | 30 | 30 | 1.80 |

## 10. Conclusion

In this research sulfur reduction of heavy fuel oil with sulfur content of 2.75 wt% by using oxidative desulfurization method (ODS) was investigated. Chemicals solution mixture including of hydrogen peroxide as an oxidant and formic acid or acetic acid as a catalyst were used In ODS process. The sulfur reduction reaction was carryout at different chemical composition with temperature 60°C and atmospheric pressure. All tests were carried out for 1.5hr time and after test a sample of fuel oil was washed by acetonitrile for separation of sulfones and reminded fuel was sent for sulfur analyzing by X-Ray method. The reaction result showed that the ODS method can be reduced sulfur level from high amount of 2.75%wt. To lower amount of 1.14%wt. The different tests showed that increasing acid formic concentration has positive effect on fuel oil sulfur reduction but producing sticky material problems was existed in reaction. So the catalyst of acid acetic was purposed for mixture solution with hydrogen peroxide as oxidant. The optimized ratio of chemical mixture solution to fuel oil for better sulfur level reduction is about 30% volume for two types (acid formic and acid acetic) of catalyst. The major parameters for reaction was ratio of oxidant and catalyst to sulfur content, the tests showed that this ratio are in the range of 5-10.The optimized temperature for reaction was 60°C ,increasing temperature from 60°C had negative effect on reaction.

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