[Research Note]

Desulfurization of Heavy Oil by Using Combination of Oxidation and Mild Thermolysis

Reyhaneh FARAMARZI^{†1), †2)}, Jafar Towfighi DARIAN^{†2)}, Maryam GHAEDIAN^{†1)*},
Amin SHAFEGHAT^{†1)}, and Mohammadali SAFAVI^{†1)}

^{†1)} Petroleum Refining Technology Development Div., Research Institute of Petroleum Industry,
P.O. Box 14665-137, Tehran 1485733111, IRAN

^{†2)} Dept. of Chemical Engineering, Tarbiat Modares University, P.O. Box 14115-114, Tehran 1411713116, IRAN

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Heavy fuel oils usually have high sulfur content and most of the sulfur compounds have bulky thiophenic structures which resist desulfurization. Oxidation of these sulfur compounds to sulfones weakens the C–S bonds and sulfur can be removed as SO₂ by thermolysis. This study investigated oxidative desulfurization of heavy vacuum gas oil (2.81 wt% S). Oxidation was achieved with hydrogen peroxide and formic acid. Then, the oxidized feed underwent thermolysis at 355–410 °C for 0.5–3 h to identify the maximum desulfurization with minimum feed conversion to light products. The effects of parameters such as time and temperature were studied. Temperature had significant effects in comparison to other parameters. Desulfurization of 65 % with 6 wt% conversion of feedstock to light products was achieved under the optimum conditions.

Keywords

Oxidative desulfurization, Heavy oil, Mild thermolysis, Sulfur dioxide

1. Introduction

Heavy fuel oils are the oil fractions produced from petroleum refining processes with at least 50 vol% in the boiling range above 250 °C. Heavy fuel oils usually contain significant amounts of sulfur compounds, so combustion as fuel leads to emissions of SO_x, especially SO₂, which are important contributors to air pollution¹⁾. Consequently, commercial shipping, which is the biggest user of heavy oil fractions, has been forced to reduce the sulfur content of fuel oil from 3.5 to 0.5 wt% according to the regulations of the International Maritime Organization (IMO)²⁾. However, desulfurization of heavy fuel oil is harder than for light fractions, because of the following properties^{3),4)}:

- (a) Complex and aromatic sulfur compounds including bulky thiophenic structure compounds are very common components.
- (b) High contents of organic metal components, which deactivate the catalysts used in desulfurization processes.
- (c) High molecular weight components and presence of asphaltene, which lead to coke formation.

Desulfurization methods include hydrosulfurization (HDS), extractive desulfurization, adsorptive de-

sulfurization, biodesulfurization, supercritical water desulfurization and oxidative desulfurization (ODS)⁵⁾. The conventional method for desulfurization is catalytic hydrosulfurization performed under specific conditions (high temperature and pressure) with the consumption of hydrogen, but involves significant costs, especially for heavy oils. Additionally, aromatic sulfur compounds are difficult to remove with the HDS method^{6)–8)}. ODS is considered by researchers to be one of the most useful desulfurization methods, and consists of two steps. First, a chemical reaction occurs between the oxidant and sulfur compounds to form the corresponding sulfones, which have different properties to the unoxidized sulfur compounds⁹⁾. Second, sulfur is removed from the oxidized feedstock, which can be achieved by extraction, adsorption, thermal dissociation, etc.^{5),10)}.

Most of the above-mentioned methods remove the entire organic content of oxidized sulfur compounds rather than only the sulfur atoms. If the sulfur content is low and contained in low molecular weight compounds, such elimination causes substantial feedstock losses. However, the sulfur content in the heavy oil fraction is usually more than 1 wt% and the sulfur compounds have higher molecular weights in comparison with light fractions. Therefore, the loss of feedstock will be significantly higher during the extraction of the oxidized sulfur compounds. Sulfur removal from

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* To whom correspondence should be addressed.

* E-mail: ghaedianm@ripi.ir

VGO using extraction and adsorption of oxidized sulfur compounds found that sulfur content could be reduced from 1.48 to 0.01 wt% using dimethyl formamide as solvent, but 60 % of the valuable hydrocarbons were also lost during extraction, so that adsorption is not suitable for removing sulfones from heavy oils¹⁰. Use of paraffinic hydrocarbon solvent to separate sulfones from a medium vacuum residue in the presence of catalyst¹¹ reduced the sulfur content from 2.6 to 1.7 wt% with 37 wt% hydrocarbon losses. Use of acetonitrile as solvent reduced the oxidized sulfur compound from 2.75 to 1.47 %, but the feedstock loss after extraction was not reported¹². These findings show that extraction after oxidation of sulfur compounds can achieve deep reductions in sulfur content, but only after several consecutive extraction steps which sharply reduce product recovery. Serial extractions with dimethyl formamide reduced the oxidized sulfur compound content of VGO from 2.17 to 0.01 wt% after 10 cycles, with 12 % feedstock loss¹³. Therefore, a process to minimize the loss of feedstock during desulfurization of heavy fuels is very desirable.

Review of the literature concerning heavy oil desulfurization indicates that oxidation followed by thermal treatment is effective for desulfurization of heavy oils. Oxidizing sulfur compounds can donate oxygen atoms to sulfur and reduce the strength of the bond between sulfur and carbon atoms, resulting in easier desulfurization, so sulfur atoms can be selectively eliminated as SO₂ by thermal treatment methods.

Cracking of other hydrocarbon bonds is an important problem that should be minimized during liberation of SO₂. Generally, the energy required for C–C bond cleavage is 347–356 kJ/mol and 400–424 kJ/mol for C–H bond cleavage^{14,15}, whereas the bond dissociation energy for C–S bonds is lower, for example, 320 kJ/mol for dimethylsulfide³. Additionally, oxidizing a sulfur-containing compound will weaken the C–S bonds in sulfones by around 40 kJ/mol compared to the initial sulfur compounds^{16,17}. Therefore, removal of sulfur as gaseous SO₂ should be possible with insignificant hydrocarbon bond cracking.

Various studies have investigated the order of cleavage of different bonds in hydrocarbons. Pyrolysis of atmospheric residue¹⁸ showed that only volatilization of light alkanes without thermal cracking occurred in the range of 100–350 °C. However, thermal cracking was occurred in the range of 350–500 °C, beginning with the scission of alkyl groups located in external sites of asphaltene structures. Thermal dissociation was found for the C–S bond in the range of 350–430 °C, and for stronger bonds like C–C in the range of 430–500 °C.

A few studies have investigated the use of thermal dissociation in the second step of ODS. The sulfur content of Kuwait atmospheric residue was decreased

Table 1 Properties of the Vacuum Gas Oil

Property	Value	ASTM test method
S content	[wt%] 2.81	D5453
Density at 15.56 °C	[g/cm ³] 0.9498	D4052
Initial boiling point	[°C] 387	
95 vol% recovery	[°C] 515	D1160

to 1.9 wt% from 4.05 wt%¹⁹, achieved by selective oxidation followed by thermal treatment in the range 350–400 °C for one and a half hours with 30 % feedstock conversion. Sulfur content of atmospheric residue derived from Kuwait crude oil was reduced from 4 to 3 wt% without using additives and to 2.8 wt% using soda lime as additive by oxidation, following thermal treatment at 370 °C²⁰, but feedstock conversion was not reported. Sulfur content of Kuwait atmospheric residue was reduced from 4 to 2.8 wt% by thermal treatment in the second step of ODS at 370 °C for 1 h using silica–alumina as additive²¹. Moreover, a two-stage method comprising oxidative desulfurization and hydro treatment caused a significantly greater sulfur reduction to 1.6 wt%, in comparison to two successive steps of oxidative desulfurization or hydro treatment.

The present study investigated the oxidative desulfurization of vacuum gas oil by intensive oxidation followed by thermal treatment of the oxidized feedstock to achieve the maximum possible desulfurization together with minimum feedstock conversion to lighter products by minimum dissociation of C–C bonds. The effects of the operating conditions including reaction temperature and time of desulfurization, and feedstock conversion to light products were also studied.

2. Experimental

2.1. Materials

Hydrogen peroxide (30 wt%) was used as the oxidant and formic acid as the catalyst for the oxidation reaction. The properties of the vacuum gas oil that was used as feedstock are presented in **Table 1**.

2.2. Equipment and Procedure

Oxidation was carried out at atmospheric pressure and 55 °C using oxidant and catalyst with molar ratios of 4 : 1 for the oxidant/sulfur and 2 : 1 for the oxidant/catalyst as severe conditions to ensure complete oxidation. Feedstock 200 g was poured into a glass reactor stirred at 1300 rpm, which was heated to reaction temperature by circulating hot heating fluid, and then hydrogen peroxide as oxidant and formic acid as catalyst were mixed with the feedstock. The required reaction time was 2 h, then the reaction mixture was decanted for water washing and separation of the aqueous and organic phases.

Thermal treatment of the oxidized feedstock was performed in the thermal treatment reactor to rupture the

Fig. 1 Schematic Diagram for Thermal Treatment Experiment (TIC: Temperature Indicator Controller, PI: Pressure Indicator, TI: Temperature Indicator)

C-S bond. **Figure 1** shows the schematic diagram of the experimental apparatus used for thermal treatment of the feedstock.

Oxidized feed 120 g was poured into a stainless-steel autoclave. Nitrogen with low flow rate was used to purge the reactor prior to the start of each run, to maintain the reactor pressure, prevent sudden increases in temperature and to discharge the reaction products. Electrical heater and magnetic stirrer were used to provide the required heating. To control the temperature, three thermometers were used due to the thickness of the autoclave wall, one for measuring the temperature of the feed and two embedded on the external wall. Furthermore, one thermometer was specified to determine the temperature of the liquid product. The experiments were conducted at 355-375 °C for 0.5-3 h and continued up to 410 °C at shorter times. The reactor was operated under 2 bar (1 bar = 10^5 Pa) pressure to maintain the vacuum gas oil in the liquid phase and prevent vaporization. The distillates were accumulated in a vessel and the gas was passed to a gas scrubber.

3. Results and Discussions

The effects of time and temperature parameters on desulfurization were investigated in the ranges of 355-375 °C for 0.5-3 h and continued up to 410 °C. Changes in feedstock conversion caused by the operation conditions, effect of oxidation on amount of desulfurization and yield of feed conversion were also studied.

Sulfur contents of the feedstock and products were measured and the weight percent desulfurization of feedstock was determined by following equation:

$$\text{Desulfurization wt\%} = \frac{\text{Feedstock S content (wt\%)} - \text{Liquid Products S content (wt\%)}}{\text{Feedstock S content (wt\%)}} \times 100$$

The various products are defined as follows.

Gaseous product: non-condensable gaseous effluent from the autoclave during the thermolysis process.

Fig. 2 Effect of Temperature on Desulfurization at Different Times

Light liquid product: condensable vapors emitted from the autoclave during the thermolysis process.

Light products: total outlet flow from the autoclave under the reaction conditions including condensable and non-condensable vapor products, or the total of gaseous and light liquid products.

3.1. Effect of Temperature and Time on Desulfurization

Figure 2 shows the effect of temperature on feed sulfur removal at different times. In general, higher temperature at constant time would lead to more desulfurization, but the desulfurization rate was changed by prolonging the operation time.

Desulfurization will occur if sufficient energy for dissociation of the SO₂ group reaches the sulfonated component. As **Fig. 2** illustrates, higher temperature had a sharp positive effect on desulfurization at lower operating time. This can be expected as higher temperature increases energy absorption by the feedstock, so providing enough energy to break the stronger C-S bonds and eliminating more sulfur content as SO₂ groups. The effect of higher temperature on sulfur removal was decreased dramatically over longer times, especially for higher temperatures (above 365 °C). Therefore, heating of the sample for longer times can provide adequate energy to remove the SO₂ group at lower temperature.

Figure 2 also shows the effect of time on sulfur removal. Longer operation times at any temperature led to more desulfurization with different slopes. More time was required at lower temperature to reach the required energy for breaking C-S bonds, whereas increasing reaction time to 3 h at higher temperature did not achieve so much improvement in desulfurization, so the same energy amount can be used to remove sulfur as SO₂ in less time. In other words, the effect of time decreased at higher temperature. Therefore, desulfurization was approximately the same for all considered times at 375 °C.

Generally, the experiments indicated that both temperature and time had increasing effects on desulfuriza-

tion with different slopes.

3.2. Effect of Temperature and Time on Feed Conversion

Higher temperature provides enough energy for cracking and breaking the C-C bonds of hydrocarbon compounds, in addition to removal of SO₂ groups. **Figure 3** indicates the yield of feedstock conversion to light products, include gaseous and light liquids, at various temperatures and times. **Figure 3** shows that the feedstock conversion at higher temperature, despite desulfurization, increased noticeably with longer time in the range of 1.5 to 3 h. Therefore, the rate of feed conversion to light products increased and was faster by increasing these parameters at all temperatures and times, because hydrocarbon cracking also occurred. The bond dissociation energy for scission of small branches was attained at lower times and for larger branches at longer times. Therefore, the feedstock was cracked to light liquids rather than to gaseous products. **Figures 4** and **5** indicate the amounts of gaseous and light liquid products with longer times at different temperatures, respectively. Feedstock conversion to light liquid products showed a sharp increase rather than a gradual change in the quantity of gaseous product with increasing time.

Therefore, increasing the temperature caused cracking of more hydrocarbon bonds and unoxidized C-S bonds in addition to elimination of SO₂ groups. Based on these results, experiments were performed to define the optimum operation conditions to maximize desulfurization, and to control feedstock conversion to light product to less than 10 wt%. To reach these tar-

gets simultaneously, experiments were carried out at higher temperatures and lower times (**Table 2**).

Table 2 shows that reaction at 395 °C for 0.5 h caused 65.3 % desulfurization with 6.3 % feed conversion to light products, which was close to the results of reaction at 390 °C for 1.5 h. The present study suggests that increasing the operating temperature by about 5 °C has equal effects to longer reaction time of just one hour. However, increasing the temperature to 410 °C for time of 0.5 h achieved the same desulfurization as at 390 °C but higher feed conversion occurred. Therefore, the optimum conditions with the process goal of maximum desulfurization with minimum feed conversion were determined as 395 °C for 0.5 h.

These desulfurization and feed conversion yields are both improved compared to previous results for different heavy fuel oils with the use of additive, whereas the present results were achieved without additive. In

Fig. 3 Effect of Cracking Time on Feedstock Conversion

Fig. 4 Effect of Cracking Time on Gaseous Product Yield

Fig. 5 Effect of Cracking Time on Light Liquid Product Yield

Table 2 Feed Conversion and Desulfurization at Higher Temperature

Temperature [°C]	Time [h]	Feed conversion to light products [wt%]	Desulfurization [wt%]
390	0.5	5	64.8
390	1.5	8.8	58.2
395	0.5	6.3	65.3
410	0.5	11	65.9

Fig. 6 Effect of Oxidation on Desulfurization and Feedstock Conversion

addition, the HDS method has disadvantages with significant hydrogen consumption and other severe problems such as catalyst deactivation in the desulfurization of heavy oils.

3.3. Effect of Mild Thermolysis on Oxidized and Unoxidized Feedstock

To investigate the oxidation effect on desulfurization, experiments were performed on original (unoxidized) feedstock and oxidized feedstock at 390 °C for 1.5 h. The results were completely different for both desulfurization and cracking (Fig. 6). Figure 6 shows that desulfurization was not possible without oxidizing the feedstock, *i.e.* the sulfur content of unoxidized feed was not changed by heat treatment and just 1.7 wt% of feed was converted to gaseous product due to scission of small alkyl groups linked to aromatic compounds, whereas significant sulfur content reduction was obtained by oxidizing the feedstock and desulfurization was raised to 64.8 %. The feedstock conversion was increased to 8.8 wt% due to cracking of oxidized compounds. The great difference indicates that desulfurization was more related to rupturing C–S bonds in oxidized sulfur compounds.

4. Conclusion

Oxidative desulfurization of vacuum gas oil as a typical heavy hydrocarbon cut with high sulfur content was investigated, using oxidation followed by thermal dissociation. Desulfurization and hydrocarbon conversion of the oxidized feedstock was investigated at different temperatures and times. Higher temperature at constant times as well as longer time at fixed temperatures resulted in more desulfurization, but temperature had significantly more effect than time.

The bond dissociation energy for scission of small

branches was attained in short times. This energy would be enough to break longer branches at longer times, so the amount of light liquid product increased and led to greater feedstock conversion.

Thermal treatment could not reduce the sulfur content without prior oxidation of the feedstock. The amount of desulfurization was dramatically increased after oxidizing the feedstock.

The optimal conditions were 395 °C for 0.5 h with 65.3 % desulfurization and 6.3 % feedstock conversion.

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