AN INVESTIGATION ON OXIDATIVE DESULFURIZATION OF GAS CONDENSATE

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Abstract

In this research, both oxidation and extraction steps in oxidative desulfurization (ODS) process have been investigated for a gas condensate feedstock in order to derive optimum parameters. The evaluated parameters in the oxidation step were the effect of oxidant to gas condensate ratio, quantity of catalyst and the oxidation reaction time and temperature. In the extraction step, solvent to feedstock ratio for some different solvents have been studied. Results showed that desulfurization of about 83% would be achieved in low pressure and ambient temperature at optimum parameters.

Key words: gas condensate; oxidative desulfurization; sulfone; extraction.

1. Introduction

During two previous decades the environmental regulations for fossil fuels have become more and more severe. The major problem in using fossil fuels is their sulfur content. Thus, methods for reducing this impurity in petroleum products such as gasoline and gas oil have been developed very fast.

In order to effectively control of air pollution due to diesel fuel combustion, the US EPA has released a new regulation requiring the use of low-sulfur diesel fuel. This regulation requires that the sulfur content of diesel fuel used in highway vehicles be limited to 15 ppm [3,5]. Hydrodesulfurization (HDS) is the conventional process for reducing organo-sulfur in gasoline, diesel and other intermediate distillates. This process is highly efficient for removing thiols, sulfides, disulfides, and some thiophene derivatives, but less effective for dibenzo-thiophene derivates with steric hindrance on the sulfur atom (refractory organo-sulfur compounds) such as 4,6- dimethyl dibenzothiophene (4,6-DMDBT), which are present in diesel fuel [8]. Possible ways to increase the efficiency of HDS for producing low sulfur product include use of higher temperatures and pressures, more active catalysts or longer residence times[4]. It is worth to mention that a great deal of CO_2 which is a greenhouse gas would be produced in this process. So, due to these restrictions and also increase in energy price, tendencies toward finding some cheaper methods of desulfurization have been increased. These methods are adsorptive desulfurization, Bio-desulfurization, oxidative desulfurization and so on. Oxidative desulfurization (ODS) process often takes place in the liquid phase and it has a lower operating and investment cost in comparison with the corresponding conventional method of hydrodesulfurization due to lower operating temperature and pressure. Furthermore, it is capable of removing refractory organo-sulfur compounds which have poor reactivity in HDS process [7-8]. Since there is no need of using hydrogen in ODS process, it could be considered as a proper choice while facing shortage or difficulties in providing hydrogen. Oxidative desulfurization can be a complementary and perhaps in some cases an alternative method for hydrodesulfurization process, because it is established for lower operating temperatures and pressures; by inexpensive catalysts, and with lower operating and investment cost.

In recent years, many research studies have been done on ODS. Some researchers have done reviews on results that had been obtained from single and two phase systems,

heterogeneous and homogenous catalysts and different oxidants which used in this process [1-2,6].

ODS process includes two steps named as: oxidation and extraction. During the oxidation step, sulfur compounds in feedstock are oxidized and the corresponding sulfoxides and then sulfones are produced. The reaction rate of converting sulfoxides to sulfones is much faster than sulfoxides producing.

Equation 1 shows the schematic of sulfur compounds oxidation and conversion into sulfones. During the extraction step, oxidized components are separated from feedstock via extracting agents. The oxidized components could be extracted by solvent, adsorption, or some other processes. Since the ODS process is completed in two steps, reaching a maximum desulfurization depends on the efficiency of both steps.

$$\text{R-S-R} \longrightarrow \underset{\underset{O}{\|}}{\text{R-S-R}} \longrightarrow \underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{\text{R-S-R}}} \tag{1}$$

One of the most important parameters in oxidation process is the type of oxidant, which has a great effect on the reaction. There are various types of oxidant which have been studied by different researchers such as t-butyl hydro peroxide (TBHP), ozone, air, nitrogen oxides, nitric acid, hydrogen peroxide and etc. The miscibility of TBHP in hydrocarbons is an advantage in compare to other used immiscible oxidants. At the first time, Lyondell chemical company demonstrated use of TBHP for ODS method. Among other oxidants, hydrogen peroxide is being used widely because of its cheapness, no pollution, weak corrosion and commercially availability. However, H_2O_2 is a rather slow oxidizing reagent in the absence of a catalyst so, it should be used together with a catalyst such as formic acid, acetic acid, V_2O_5/Al_2O_3, V_2O_5/TiO_2, Co-Mo/Al$_2$O$_3$, Mo/Al$_2$O$_3$ and etc. [4,7].

The ODS process has been applied on different fuels such as gasoline and diesel that have significant role in transportations and are more serious from environment viewpoint. But some researchers have been studied on other cuts such as kerosene and the target wasn't reach to fewer than 10 or 15 ppm sulfur content.

In this research work, study was done on desulfurization of natural gas condensate by ODS method. The natural gas condensate is also referred to as simply condensate, or gas condensate, or sometimes natural gasoline. Gas condensate is a liquid mixture of light hydrocarbons with low density, produced mostly from gas reservoir. This liquid has high economic value because large part of hydrocarbons in this liquid are within gasoline boiling range and in some cases a part of diesel boiling range. Derived fuel of this liquid usually has lower impurity and higher quality compared to crude oil thus a lot of attention has been devoted to this important hydrocarbon feedstock. On the other hand, most gas condensates contain more light sulfur compounds (such as H_2S and mercaptans) than crude oil. These compounds causes both environmental and corrosion problems. So it is an obligation to remove these sulfur compounds before any usage and even before transportation.

2. Experimental section

This research covered the effect of important parameters of ODS in condensate feed through a 2-stage process. In the first stage (Oxidation), several parameters such as oxidation time, the effect of catalyst and oxidant quantity have been investigated. And the second stage (extraction) has been carried out in order to obtain the optimum parameters such as solvent type and ratio of solvent to oxidized feed.

2.1 Oxidation stage

Oxidation experiments were carried out in a batch system of a double wall glass reactor (capacity 500 ml) which was equipped with several nozzles for inserting the mixer, thermometer and entering the materials into the reactor. Gas condensate was poured into the reactor mean while the temperature was fixed. After adding the mixture of H_2O_2 and acetic acid to the reactor, mixing operation would be started. This point was taken as the "zero time" of the reaction for the experimental records. Reaction time was studied from 20 to 120 minutes.

2.2 Extraction stage

An applied conventional method for extraction is liquid-liquid extraction. This process is on basis of polar molecules dissolving in polar solvents. In fact, oxidized component is slightly more polar than original sulfur component and because of this characteristic the oxidized component could be extracted by polar solvent. After the oxidation reaction, extraction was done in a double wall extractor with 2 litres capacity. Typical oxidized gas condensate and the extracting solvent was poured into the extractor and its temperature was fixed. The extractor content was agitated for defined time by a mechanical mixer with 1000 rpm speed. A decanter has been used to separate the organic phase from extracting solvent. After the separation of organic phase, its sulfur concentration was measured.

3. Result and discussion

3.1 Oxidation stage

3.1.1 Oxidant to gas condensate ratio

In these experiments the effect of hydrogen peroxide to sulfur content of gas condensate ratio has been studied. The applied temperatures in oxidation reaction and extraction operation were 45 and 25ºC respectively. These temperatures were determined by preliminary experiments and literature review. Acetic acid was chosen as catalyst. To investigate the effect of oxidant quantity on the feed desulfurization, various molar ratios of hydrogen peroxide to sulfur from 1 to 4 were applied.

As it is illustrated in figure 1, at first, sulfur removal increases by increasing the molar ratio of oxidant to sulfur content of feedstock and then the curve flattens, that means in higher ratio there is no significant changing in desulfurization.

Literature review shows that using the reaction temperature above 50ºC causes to rise hydrogen peroxide consuming. Thermal decomposition of H_2O_2 to O_2 in water is significant at temperatures above 50ºC. Thus, one way of oxidant quantity reduction is the control of oxidation reaction temperature at favourite temperatures.
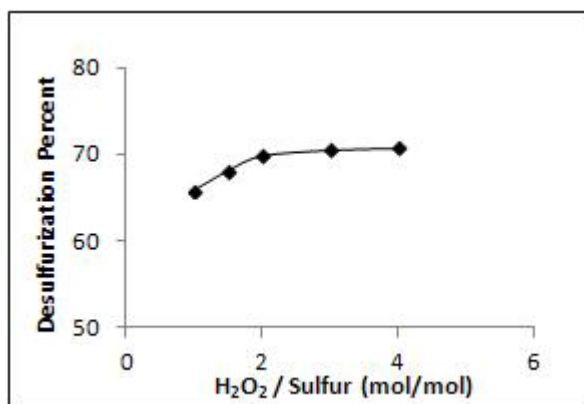

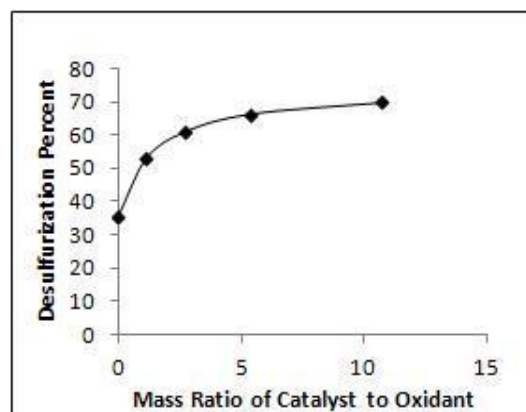Figure 1 The effect of H_2O_2 to sulfur content molar ratio on desulfurization

Figure 2 Mass ratio of catalyst to oxidant effect on desulfurization

3.1.2 Catalyst quantity effect

In this section the effect of acetic acid as a catalyst, on sulfur content reduction was studied. The mass ratios of catalyst to oxidant within the range of 1 to 11 were tested.

In these experiments the optimum molar ratio of oxidant to sulfur content is determined from figure 1 and the rest of conditions remained same as the previous experiments. As illustrated in figure 2, increasing the catalyst to oxidant ratio, causes higher desulfurization and it is clear that in higher ratio, desulfurization slop decreases. Also results show that in absence of the catalyst, desulfurization percent is lower than 40%. It means that H_2O_2 is a good but weak oxidant and the presence of the catalyst is necessary, this result is similar to other previous [9] related researches on other feedstocks.

3.1.3 Oxidation time

To determine the proper time for oxidation reaction, the reaction was carried out in various intervals from 20 to 120 minutes. Figure 3 shows the effect of time on desulfurization of gas condensate.

The results showed that within the first 30 minutes there was a sharp rising in desulfurization, but no significant changes were found after 60 minutes. According to achieved results, it seemed after 1 hour of the reaction, there was no changing in desulfurization percent. Therefore optimum time of desulfurization is about 1 hr.

3.2 Extraction step

Some of the most effective parameters on the efficiency of extraction process are: type of solvent and solvent to feed ratio. So, following experiments were done with the purpose of choosing the proper conditions for extraction step.

3.2.1 The effect of different solvents

In these experiments various solvents such as acetone, propanol, ethylene glycol and ethanol were applied. These solvents are known as polar solvents. They are more attractive because of rather low price and no environmental problem. Extracting time and temperature were 15 minutes and 25 ºC, respectively. Among the investigated solvents, ethylene glycol had a lower extracting efficiency in comparison with other solvents. Furthermore, the results showed that propanol and ethanol had similar extraction abilities that can be due to the same "Hansen solubility parameter". Extraction capabilities of acetone, propanol and methanol are shown in figure 4. It can be seen that acetone and propanol were able to remove more sulfones than methanol. The experiments showed decreasing of 15 % desulfurization when methanol was used in comparison with acetone and propanol.
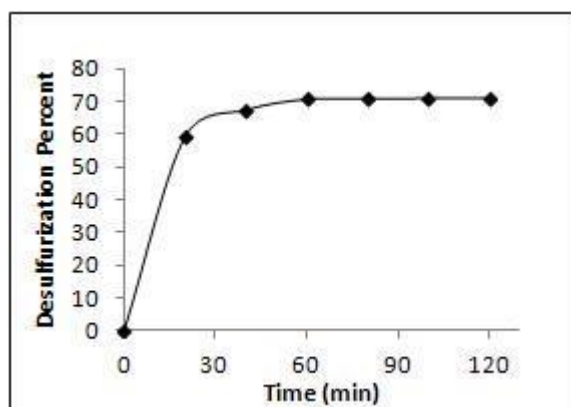

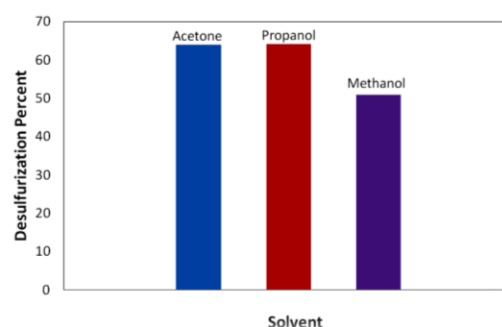Figure 3 The effect of oxidation time on desulfurization

Figure 4 The effects of different solvent type on desulfurization

3.2.2 Solvent to feedstock ratio

In these experiments various ratios of solvent to organic phase were applied from 0.25 to 4. As illustrated in figure 5, by increasing solvent to feed ratio, desulfurization raises with a mild gradient. As this ratio gets closer to 1, the slop becomes smoother. Thus, in the extraction stage, solvent to feed ratio of 1 would also be a proper choice for gas condensate in similar conditions.
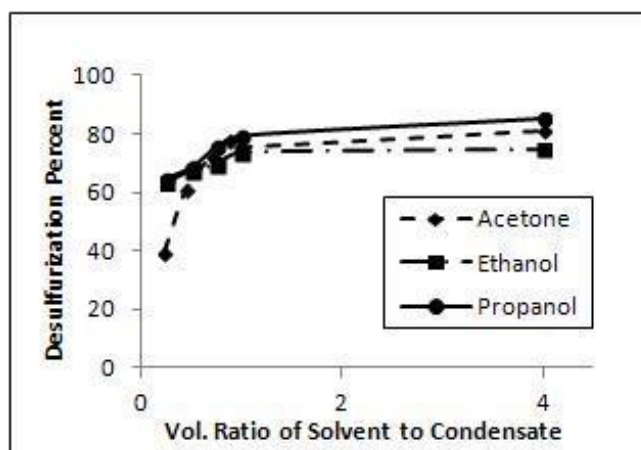

Figure 5 Effect of different volume ratio of the solvent to feed

4. Conclusion

The obtained results from oxidation step showed increasing oxidant (H_2O_2) and catalyst (Acetic acid) cause to more desulfurization and for studied feed, oxidant to sulfur molar ratio of 2-4 was adequate if reaction temperature did not exceed 45ºC. Acetic acid to hydrogen peroxide mass ratio of 5-8 and oxidation time of 60 minutes were suitable in oxidation step. Among studied solvents, propanol and acetone were the best. Optimum volume ratio of solvent to organic phase was determined from 0.8 to 1. At the obtained optimum parameters, the desulfurization efficiency of studied gas condensate by ODS was about 83% that would improve the quality of this feedstock for its applications.

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