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Original Research Article

Investigation of Sulfur Problems in Hydrocarbon Sections

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ABSTRACT

Elimination of sulfur compounds in hydrocarbon fuels is environmentally important, because in the process of combustion of fuels in engines, sulfur compounds in the fuel are converted to sulfur oxides (SO_x), which can lead to acid rain. In addition, (SO_x) resulting from the combustion of sulfur-containing fuels in internal combustion engines, while causing corrosion in the internal parts of the engine, poisoning the catalytic converters installed in the car exhaust and ultimately causing the deactivation of these catalytic converters over time. It is shortened. An important plan of these catalytic converters is to reduce the release of nitrogen oxides into the environment. Sulfur oxides also lead to the rapid deactivation of exhaust filters to prevent particulate matter from escaping into the atmosphere. Therefore, the presence of sulfur compounds in hydrocarbon sections, in addition to creating problems related to the release of sulfur oxides into the atmosphere, leads to an exacerbation of the release of pollutants such as nitrogen oxides and particulate matter into the environment.

Keywords: Sulfur Compounds, Hydrocarbons, Internal Combustion engine, Catalysts, Pollutants.

Introduction

The sulfur content of crude oil varies from 0.03 wt% for light crude oil to 7.89 wt% for super heavy crude oil. Sulfur compounds in crude oil can be divided into two general groups: inorganic sulfur compounds and organic sulfur compounds. Inorganic sulfur compounds include elemental sulfur, SH_2 , pyrite. Organic sulfur compounds in crude oil are saturated or unsaturated and are classified as follows [1-3]. Various process ideas have been explored as alternatives or supplements to the HDS process for desulfurization of hydrocarbon sections, the most important of which are:

- 1.Desulfurization process by reactive adsorption method
- 2.Desulfurization process by selective adsorption method
- 3.Extrusion desulfurization process by extraction method
- 4.Biological desulfurization process
- 5.Oxidation process by desulfurization method [4]

In the following, we will examine these processes. It should be noted that in evaluating the various desulfurization processes, it should be noted that the process in addition to reducing sulfur, does not adversely affect other cutting properties. In other words, desulfurization of hydrocarbon cutting leads to maintaining or improving the qualitative parameters of the cut [5-7].

Desulfurization by reactive adsorption method

Reactive adsorption is one of the proposed alternative processes for hydrogen reduction desorption (HDS) of light hydrocarbon sections. This method uses adsorbents with transition metals that react with sulfur molecules in the presence of hydrogen and in the temperature range (200-400%) and as a result of this reaction, sulfur compounds are converted to hydrocarbons and SH_2 , which SH_2 is immediately adsorbed on the adsorbent. In this method, two types of processes are proposed. One process is based on continuous adsorption reduction and the other is based on a fixed bed system in which the first process has received more attention and development, on the basis of which S-Zorb technology has been proposed. The history of the S-Zorb process dates back to October 2000, when Philips announced that it had developed a new process called S-Zorb, which is suitable for desulfurizing diesel cutting [8-10]. In this process, diesel cutting (with a sulfur content of less than 500 ppm) and a small amount of hydrogen are mixed, the primary role of

which is to prevent the accumulation of coke on the S-Zorb adsorbent. The flow resulting from the vapor mixture then enters a bubble fluid bed reactor and desulfurization is performed by the reaction and adsorption of the products on the adsorbent [11].

To prevent the accumulation of sulfur on the adsorbent and the loss of process performance, the adsorbent is continuously removed from the reactor and is pneumatically transferred to the reducing agent. The adsorbent reduction process is an oxidation process in the presence of air that produces gaseous streams containing SO_2 and CO_2 . This gas stream is sent to the sulfur recovery unit and the reduced adsorbent is contacted with hydrogen gas to regain its original activity. The key point of the S-Zorb process is the formulation of the adsorbent, which has not been fully disclosed, but information is available that indicates that zinc oxide (Zno) is the most important constituent of this adsorbent [12-14]. Because S-Zorb is not essentially a hydro treating technology, it consumes less hydrogen than the conventional HDS process. However, due to the limited adsorption and reduction capacity in this process, this method does not seem suitable for desulfurization of causal cuts with a sulfur content of more than 500 ppm. In other words, this is a complementary process for HDS. Other important problems of this process include the following:

- In this process, it is necessary for the whole feed to be vaporized in order to better contact with the catalyst and liquefaction of the substrate, which is technically difficult or at least in terms of consumption for cuts such as diesel cuts with a final boiling point greater than 380%.
- In the case of diesel cuts, in parts or cases to achieve acceptable desulfurization, the process conditions are similar to those of conventional HDS processes, i.e. the process needs to be performed in the temperature range of 380-420%, with a limited spatial speed at 30 bar. Under these conditions, the reaction process observed for the sulfur compounds of dibenzothiophene derivatives is similar to the process observed in the HDS process, and in practice the S-Zorb process loses its advantage over the HDS process.

Desulfurization process by selective adsorption method

In this category of processes, the research of the Mochida and Song groups is prominent. Both groups used special adsorbents in the fixed bed to adsorb sulfur compounds without converting them to other compounds. The process proposed by Song is known as selective desorption (SARS)

desulfurization, which uses mild adsorption conditions (at 80% temperature). The main purpose of these desulfurization studies is to cut kerosene for use in fuel cells [15].

However, the group has also conducted research on desulfurization of gasoline cutters. In their research, this group has activated various adsorbents such as chloride of intermediate metals on catalytic bases, nickel (Ni) adsorbent (i.e. Ni on SiO₂), metal ions on zeolites (i.e. CeY, Ni-Y), They used NiAL bilayer hydroxides, Ni-SiO₂- AL₂O₃, NiZnAL and even HDS catalysts (CoMO / AL₂O₃). In their review report, interesting differences in adsorption selectivity for different adsorbents are investigated. The most important problem in this desulfurization method is the low adsorption capacity, which manifests itself even in the desulfurization of gasoline cuts with a relatively low sulfur content [16].

The Mochida research group has developed an interesting method for the adsorption of resistant sulfur compounds based on the use of activated carbon adsorbents with high specific surface area and containing large amounts of oxygen compounds.

This type of carbon adsorbent seems to be suitable for adsorption of sulfur compounds resistant to the HDS process, and therefore the use of this process before HDS will probably be the solution. And yet the low adsorption capacity in this process is still relevant and more research is needed in this area. Another important technical issue in the desulfurization method with surface adsorption is the management of how the waste from the sulfur material adsorbed is converted at the end of the process. In addition, in this method, there are ambiguities about the possibility of reducing adsorbents. In summary, desorption processes based on adsorption are still evolving, and various articles and patents are submitted each year for adsorbents with Hadid formulation with better adsorption capacity and more suitable regenerative capacity. But in practice, due to the limitations of the adsorption capacity of sulfur compounds by these adsorbents, the potential of this process in desulfurization of hydrocarbon sections with low sulfur content and as a finishing desulfurization process.

Extrusion desulfurization process by extraction method

Extraction of organic sulfur compounds from hydrocarbon fractions by a range of solvents ranging from common polar solvents to ionic solvents (ILs) has been the subject of extensive research. The most attractive aspect of desulfurization of hydrocarbon sections by extraction method is the mild process conditions (pressure and temperature close to environmental conditions). Solvents most

commonly tested in this study include acetonitrile, lactones such as gamma butyrolactone, and sulfuric solvents such as dimethyl sulfoxide (DMSO) or sulfone. Based on the research, it seems that the selective extraction of aromatic sulfur compounds from hydrocarbon slices is not an easy task. The problem arises from the fact that the polarity of many sulfur-containing aromatic compounds (such as aromatic sulfides) is very similar to that of the corresponding sulfur-free aromatic compounds. Experimental results of extraction of sulfur aromatic compounds show a maximum desulfurization of 50%, which is not desirable, while desulfurization in this method is done at the cost of extracting a significant part of aromatic hydrocarbons in the cut along with sulfur compounds [17-19].

Because of this problem, most researchers in this field have concluded that for effective and selective separation of sulfur compounds from hydrocarbon slices, it is better to first oxidize the sulfur compounds in the hydrocarbon section and change their polarity relative to the corresponding aromatic molecules provided the basis for their selective and effective extraction. This method is the same method of desulfurization by oxidation, which is the main subject of this research and will be described in detail. Extraction of sulfur compounds by a group of different solvents called ionic solvents has been reported by the Wasserscheid group [20].

An ionic liquid is a non-volatile organic salt that, due to its high polarity, has the potential to extract sulfur and nitrogen compounds from hydrocarbon slices. Problems with the use of ionic solvents include the limited capacity to extract sulfur compounds, the solubility of hydrocarbons in these solvents, and the recovery of these expensive solvents. In all respects, ionic solvents are not significantly superior to conventional organic solvents at present. However, research on improving the performance of ionic solvents in the extraction of sulfur and nitrogen compounds from hydrocarbon fractions is ongoing.

Biological desulfurization process (BDS)

Biological desulfurization (BDS) is an old idea that has been around for fifty years. Recently, to solve the technical and economic problems of the HDS process to achieve new standards in the field of permissible sulfur content and use the benefits of biological processes called "green", this process has been refuted. This process in the presence of water and oxygen at temperature and pressure the environment goes on. However, biological desulfurization by anaerobic bacteria in the presence of hydrogen and in the absence of oxygen has also been studied [21-23]. But more

reports have focused on aerobic biological desulfurization. The purpose of the BDS process is to use the specific properties of enzymes to produce low-sulfur fuels. In recent decades, significant research has been conducted on the development of knowledge of enzymes and molecular genetics of the BDS process in order to design and optimize the process and bioreactor. There are generally two primary pathways for BDS of alkylated derivatives of benzothiophene. However, the main focus has been on the so-called 4s pathway for some bacteria that can separate sulfur from dibenzothiophene and the alkylated derivatives of dibenzothiophene. As shown in figure 1, the enzymes in question selectively attack the di-benzothiophen sulfur atom without affecting the fuel carbon. In the 4s reaction pathway, di-benzothiophene is first converted to di-benzothiophene sulfoxide and then oxidized to di-benzothiophene sulfonate. HPBS) becomes. Eventually HPBS is converted to -2-hydroxy biphenyl (HBP) and desulfurization is performed. An important aspect of the 4s pathway compared to other pathways is its high selectivity for sulfur atoms. Figure Shows the steps of desulfurization by biological method [24].

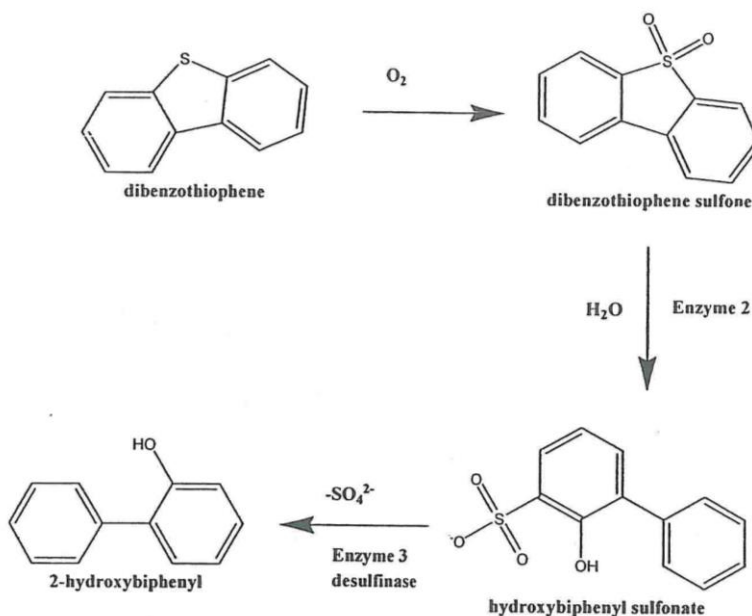


Figure 1: Schematic diagram of the biological oxidation reaction of sulfur compounds with bacteria

Research has shown that for this process to be economical, the BDS process speed must be at least $20\mu \text{ mol} / \text{min} / \text{g}$ dry cell. While in the study conducted by Bio System Energy, a reduction of

67% of the total sulfur from 1850ppm to 615ppm for diesel cutting of HDS product with a speed of $2.8\mu\text{mol} / \text{min} / \text{g}$ dry cell has been reported. The important and disappointing point is that it was not possible to reduce the total amount of sulfur to less than 615ppm with this method. Also, in the study conducted by Maghsoudi et al., It was found that in the optimal conditions of BDS process on diesel cutting, the percentage of desulfurization observed for diesel cuts with initial sulfur values of 1000 ppm and 303ppm are only 48.5 and 23.7%, respectively have been similar results have been reported by different researchers with different bacteria in the 4s pathway [25]. Generally, numerous reports on biological desulfurization have not reported deep desulfurization and have reported a sulfur range of 50-200 ppm in the best conditions. This is quite justified given that the activity of bacteria is concentration dependent and increases at high concentrations. Therefore, the potential of the biological desulfurization method to reach the sulfur range of less than 50 ppm is not significant. Enchira, which announced its focus on the development of biological desulfurization for diesel fuel, recently shut down. In addition, another important aspect to consider in biological systems is the competitive reactions created by other bacteria. For example, in the biological process of H_2S removal, which is a successful process, only the target bacterium survives in the highly toxic H_2S environment and can effectively convert H_2S to elemental sulfur. Therefore, to develop desulfurization biologically, additional studies are needed to prepare the reaction medium for the target bacterial activity. In addition, although bacteria that can convert to benzothiophene and alkyl sulfides have been thoroughly identified and studied, fewer benzothiophene-carrying bacteria have been identified, and in the case of thiophene, only a few have been identified. Very limited species are summarized. In general, in order to develop the biological desulfurization process (BDS), the cooperation of various experts in the field of biotechnology, biochemistry, and refining processes is necessary [23].

Over the past two decades, various research groups have attempted to identify and isolate desulfurizing bacteria from oil slices. To develop the BDS process, the design and construction of pilot units is inevitable. In the current situation, the competition between the BDS process and chemical desulfurization processes seems to be very difficult due to the various improvements that have been made in those processes. In short, although the BDS process guarantees smooth process conditions, it cannot perform the conversion at a reasonable rate that is economically viable. In addition, in this method, there is no possibility of deep desulfurization and reaching new standards.

Deposition desulfurization process

This process is based on the formation and separation of insoluble deposits of sulfur compounds in a charged chemical complex. In this method, first a suitable chemical substance is added to the sulfur hydrocarbon cut, which then causes the formation of an insoluble deposit with sulfur compounds. The next step in this process is the separation of the resulting sediment from the incision by filtration, which will lead to desulfurization of the incision. For example, the separation of 4,6-DMDBT from its solution in hexane and diesel cutting using the precipitating agent 7,5,4,2 tetranitro-9-fluorine (TNF) has been studied. However, the occurrence of serious problems in this desulfurization process such as very low desulfurization efficiency (only 20%), non-selective performance of the precipitant and excessive consumption of the precipitator has caused the development of this process to be stopped on a laboratory scale.

Oxidation (ODS) desulfurization process

In the HDS process, desulfurization is performed by reducing various sulfur compounds to H_2S , while in the ODS desulfurization process, the reaction proceeds in the opposite direction, so that the sulfur compound is oxidized and the properties created change. As a result of this oxidation reaction, separation takes place. In this method, sulfur compounds are usually converted to the corresponding sulfonic compounds. To obtain the final product with low sulfur content, it is necessary to separate the sulfonyl sulfur compounds in the second step. This separation is usually done by solvent extraction or adsorption on an adsorbent. Theoretically, oxidized sulfur compounds, such as sulfones, are much more polarized than sulfonates compared to their corresponding sulfides, so they are easier to separate from the feed. The main advantages of desulfurization by oxidation (ODS) method compared to conventional HDS process are as follows:

1. The operating conditions of the ODS process are very mild compared to the HDS process, so that it is performed in the range of atmospheric pressure and temperature range less than $100\text{ }^\circ\text{C}$, while in this process, the use of hydrogen is not required.
2. The most attractive intrinsic aspect of this process is the greater reactivity of aromatic sulfur compounds, because the nature of this reaction is an electrophilic attack on the sulfur atom in the organic sulfur compound, and this effect increases the electron density on the sulfur atom due to the presence of the ring. Aromatic aromas are enhanced.

In addition, the presence of alkyl groups on aromatic rings in turn leads to a further increase in electron density on the sulfur atom. Therefore, the intrinsic reactivity of molecules such as 4,6-DMDBT in this process is essentially higher than that of DBT, and in fact the order of increasing reactivity for the desulfurization process by oxidation in many oxidation systems is in contrast to the HDS process. In other words, the chemistry of the ODS process in many cases completely complements the HDS process, meaning that sulfur compounds such as 4,6-DMDBT, which are the most resistant compounds in HDS, are easily converted and separated in this process.

Therefore, it is possible to replace the HDS process with ODS or combine these two processes together to produce low-sulfur fuels up to the new stringent standards. Of course, there are different opinions about replacing and combining HDS and ODS processes. Some argue that the production of very low sulfur fuels for refineries that do not have access to low-cost hydrogen sources is more economically viable with the ODS process than HDS. But the use of the ODS process is not limited to direct replacement with the HDS process. The ODS process, if used before the HDS process, provides benefits such as the separation of disturbing compounds in the HDS process, increasing the capacity of the HDS process, and reducing hydrogen consumption. The ODS process, if followed by the HDS process, leads to an increase in the capacity of the HDS units, a shorter residence time in the HDS process, a reduction in hydrogen consumption, and a longer catalyst life in the HDS process. However, due to the existence of HDS units in most modern refineries in the world, the general trend of using the ODS process is to use this process as a complementary process to HDS. In our country, due to the non-availability or limited capacity of HDS units in the main refineries of the country, it is possible to use the ODS process to desulfurize hydrocarbon cuts instead of the HDS process [24].

In practice, however, the process must be evaluated from a technical point of view and the ambiguities in the various parts of the ODS process must be removed. For example, when the liquid-liquid extraction process is used in the second stage of the ODS process to separate oxidized sulfur compounds, a new problem called the loss of part of the hydrocarbon section during the extraction process arises, which needs to be studied precisely. Due to the fact that the desulfurization process by oxidation (ODS) is the subject of this project.

General comparison of alternative or complementary desulfurization processes of HDS process

In this section, we compare the desulfurization processes that replace or supplement the conventional HDS process in terms of operating conditions, process sensitivity to the amount of sulfur present in the feed, and the process potential for bringing the sulfur content of hydrocarbon fuels to new standards. Table 1-3 shows the results of this comparison.

Table 1. Comparison of different alternative or complementary desulfurization processes of HDS process

The potential of the method to achieve	Sensitivity to the amount	Operational conditions	Desulfurization process
New standards	Feed sulfur	Normal - Acute	Reactive absorption
Much		Gentle	Selective adsorption
Medium (depending on feed conditions)	Much	Gentle	Extraction
Low	Much	Quite gentle	Biological (BDS)
Low	Low	Quite gentle	Oxidation (ODS)

As can be seen in this table, the ODS process as a whole provides more advantages than other desulfurization processes. Therefore, this process is investigated as a desulfurization process of light oil cuts in this research.

Study of the effect of solvent to hydrocarbon volume ratio on desulfurization

Studies on kerosene cutting

The volume ratio of solvent to hydrocarbon fraction (S / F) is one of the important parameters of the process of extracting sulfur compounds from hydrocarbon fractions. Desulfurization is expected to increase with increasing this ratio. On the other hand, increasing this ratio reduces the recovery of hydrocarbon section after extraction with different solvents.

Extraction conditions: acetonitrile solvent, $T = 25\text{ }^{\circ}\text{C}$, extraction time 30min, number of extraction steps equal to 1) as shown in figure 1-6, if acetonitrile solvent is used, with increasing S / F from 0.25 to 2 Desulfurization increases from 86.3% to 97.7% while the recovery of kerosene cut after extraction decreases from 98.3% to 86.7%.

Also, with increasing S / F from 2 to 4, the slope of increasing desulfurization is greatly reduced (desulfurization increases only from 97.7% for S / F equal to 2 to 98.5% for S / F equal to 4), but recovery of kerosene after extraction Continuously (from 86.7% for S / F equal to 2 to 75% for S / F equal to 4).

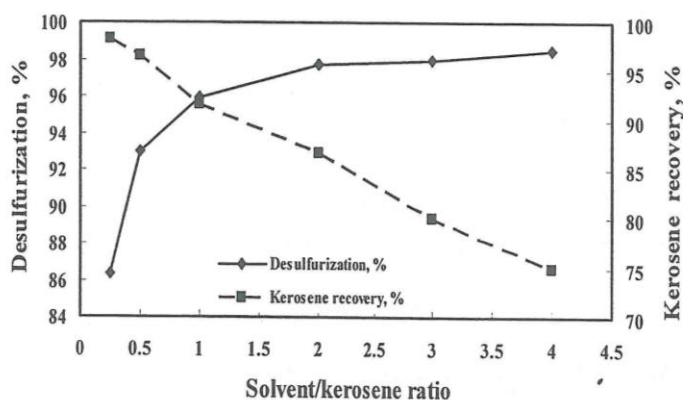


Figure 2: Effect of solvent to hydrocarbon volume ratio on desulfurization and kerosene recovery after extraction

Extraction conditions: solvent methanol, $T = 25\text{ }^{\circ}\text{C}$, extraction time equal to 30min, number of extraction steps equal to 1)

As can be seen, the process of desulfurization and section recovery changes for methanol and ethanol 96% solvents is quite similar to the process observed for acetonitrile. Increasing the S / F from 0.5 to 2 leads to an increase in desulfurization of kerosene from 89.4% to 96.5% for methanol solvent and from 88.8% to 95.1% for ethanol solvent.

On the other hand, increasing the S / F from 0.5 to 2 at the same time reduces the recovery of kerosene after extraction from 91.7% to 83.3% for methanol solvent and from 96.7% to 70.1% for ethanol solvent. Also, increasing the S / F from 2 to 4 does not significantly improve the desulfurization rate (from only 96.5% for methanol solvent and from 95.1% to 97.1% for ethanol solvent) but significantly reduces shear recovery after extraction (from 83.3% to 60% for methanol

solvent and from 70.1% to 27% for ethanol solvent). In general, in the extraction of oxidized sulfur compounds from hydrocarbon sections for all solvents, as a result of increasing the volume ratio of solvent to feed, the process of increasing desulfurization (improving the separation of oxidized sulfur compounds) stops asymptotically, but the recovery of hydrocarbon section after extraction is constantly decreasing [24].

Therefore, increasing the solvent to feed ratio above a certain amount (about 2) has practically no effect on improving desulfurization of kerosene and diesel cuts, and since it significantly reduces the recovery rate of hydrocarbon cuts from extraction, it does not seem appropriate.

Study of the effect of number of extraction steps on desulfurization

Studies conducted on kerosene cutting

The number of extraction steps is one of the most important parameters of extraction processes. In the separation of oxidized sulfur compounds from hydrocarbon sections, it is expected that with increasing the number of extraction steps, the desulfurization rate will increase due to the improved separation of oxidized sulfur compounds. Also, increasing the number of extraction steps from 2 to 5 does not significantly improve the desulfurization rate (desulfurization increases only from 98.7% to 99.1% for methanol solvent and from 97.5% to 99.4% for ethanol solvent) but significantly reduces the open rate. Oil recovery is extracted after extraction (reduction of cut recovery from 83.3% to 56.7% for methanol solvent and from 70% to 36% for ethanol solvent). In general, in the extraction of oxidized sulfur compounds from hydrocarbon sections for all solvents, as a result of increasing the number of extraction steps, the process of increasing desulfurization (improving the separation of oxidized sulfur compounds) stops asymptotically, but the recovery of hydrocarbon sections asymptotically stops, but the recovery of the hydrocarbon section is continuously reduced after extraction. Therefore, increasing the number of extraction steps above 2 for kerosene cutting and above 3 for diesel cutting has practically no significant effect on improving desulfurization of kerosene and diesel cuts, and since it significantly reduces the recovery rate of hydrocarbon cutting, does not seem appropriate. To compare different solvents, it is necessary to consider desulfurization and shear recovery after extraction, which is done using the solvent efficiency factor, E , in section 4-6.

Comparison of the performance of different solvents in the separation of oxidized sulfur compounds from hydrocarbon sections

Solvent efficiency factor, E, is a good criterion for comparing the performance of different solvents in the extraction of oxidized sulfur compounds from hydrocarbon sections. Figures 6-13 and 6-14 show the efficiency factor of the solvent in extracting oxidized sulfur compounds from kerosene cut. As can be seen in the figures, the order of the solvent efficiency factor for acetonitrile, methanol and ethanol is:

Acetonitrile > Methanol < Ethanol

Offer suggestions for future studies

Given the breadth of the present study, each section offers suggestions separately:

In the section of experimental studies of oxidation of sulfur compounds, the following items are presented as suggestions:

1. Determining the main sulfur compounds of hydrocarbon slices and their amount: It seems interesting to study the conversion rate of different sulfur compounds after oxidation and the rate of their separation after solvent extraction. For example, it is very interesting to determine what the total amount of sulfur left after the desulfurization process by oxidation (ODS) is composed of. In this study, at first, such an attempt was made, but due to the many limitations in the qualitative and quantitative analysis of sulfur compounds, it was not possible to do so.

Because, firstly, for this purpose, special analysis devices (gas chromatography device equipped with PFPD detector and new GC-MS devices with high scanning quality) are required, and secondly, for such studies and production of control solutions, sulfur compounds Special such as 4,6-DMDBT, which is very expensive, while not available in Iran and is produced in the world only for desulfurization studies in very small quantities.

2. Mechanistic studies to determine the share of the effect of transfer phenomena and chemical kinetics in the overall speed of the oxidation process: For this purpose, it is necessary to first oxidize individual sulfur compounds such as DBT and BT in solvents such as toluene in the oxidation system under different conditions (temperatures). Different and different mixing speeds) should be studied and then by interpreting the results and using criteria such as HATA modules, the general regime controlling the process speed should be determined. This information is very important in developing suitable reactors for this application.

3. Investigate the possibility of increasing the overall process speed: Examining the application of conditions such as the use of ultrasonic wave energy in the reaction mixture, or adding catalysts along with formic acid to increase the overall process speed is an interesting topic for future studies. Increasing the overall oxidation rate leads to ease of reactor design, reduction of reactor volume and the possibility of continuous process design.

In the section of proposing and building a reactor based on jet techniques, the following items are suggested:

1. Optimization of the number of jets in the reactor mixing chamber: By economic calculations, taking into account the increase in power consumption and improving the performance achieved by increasing the number of jets, the optimal number of jets is obtained. As you know, as the number of jets in the reactor mixing chamber increases, the reactor performance is likely to improve, but at the same time the power consumption will increase. Optimizing the number of jets with economic calculations is an interesting topic for future studies.

2. Determining the effective parameters in increasing the scale of jet reactors: Due to the fact that increasing the scale of this type of reactors as special reactors is not easily possible, for this purpose it is necessary to build at least one other FIJR reactor with different scale and its performance in Oxidation of sulfur compounds to be evaluated. Then try to evaluate the results without reactors by evaluating the results obtained in reactors with different scales. In the studies conducted in the present study, it seems that the Reynolds Jet number is one of the main parameters in this field.

3. Study of jet failure and alloying process: Knowing this information is important in designing reactors based on collision jet techniques. The study of the use of various computational techniques such as computational fluid dynamics (CFD) to model the failure and alliance of jets is one of the interesting topics for future studies.

In the experimental studies section on the separation of oxidized sulfur compounds from hydrocarbon sections, the following are interesting for future studies:

- 1. Comparative study of the performance of ionic solvents with conventional solvents:**
For this purpose, first some ionic solvents that are probably suitable for this application and can be synthesized should be selected and their performance in separating oxidized sulfur compounds from sections. Hydrocarbons to be evaluated. Then the desulfurization rate and the recovery rate of the hydrocarbon section obtained if these solvents and

conventional solvents are used are compared. Of course, if the performance of ionic solvents is better, it is necessary to replace ordinary solvents with ionic solvents, such as how and the possibility of recovery of ionic solvents after the process, as well as economic issues related to these solvents (their high price) carefully evaluated. To be placed.

2. Investigation of solvent recovery processes after extraction: For this purpose, the processes of solvent recovery after extraction and the separation of sulfones and hydrocarbons dissolved in the solvent should be carefully studied. Solvent recovery through distillation is currently proposed, but various aspects of this separation process must be considered. For example, it must be determined how much of the solvent is lost through the sulphon-rich flow and how much fresh solvent is required. It is also necessary to determine what part of the hydrocarbons carried by the solvent during the extraction step. They can be recovered at this stage.

3. How to manage the production of sulfonic waste: For this purpose, all the forthcoming solutions in a refining complex for the management of this waste should be evaluated. For example, the possibility of sending this product to sulfur recovery units after the necessary preliminary processes, as well as the possibility of converting this waste into sulfonates which are valuable materials, or even the possibility of using this waste in sulfur asphalts should be carefully studied and compared. And suggest the best solution. Recently, solutions such as the possibility of using bilayer hydroxide catalysts to separate SO_2 from sulfones and recover the sulfur hydrocarbon fraction have been considered by researchers, which need to be further evaluated.

4. Evaluation of different adsorbents for separation of oxidized sulfur compounds:

Considering the development of different adsorbents with different properties and characteristics, evaluation of the performance of these adsorbents in the process of separation of oxidized sulfur compounds seems interesting. Interpretation of the performance of adsorbents in the field of separation of oxidized sulfur compounds from hydrocarbon sections with pore structure (pore size, percentage of meso and micro porosity) and their specific surface area is one of the interesting research fields in this regard. If a suitable adsorbent with a high adsorption capacity is found for

oxidized sulfur compounds, it will be possible to replace the extraction process with an adsorption process to separate the oxidized sulfur compounds. However, with sufficient studies, the existing ambiguities about the adsorption process such as adsorbent capacity, the possibility of reducing the adsorbent and how to reduce it, the total life of the adsorbent and the number of times the adsorbent can be reduced, which is a good topic for future study [25].

Conclusion

In this study, desulfurization of oil cuts between kerosene distillation with an initial sulfur content of 2335 ppm and diesel with an initial sulfur content of 8000ppm was investigated and the following results were obtained:

1. Oxidized water oxidation system - Formic acid has more advantages compared to other oxidation systems such as simplicity of oxidation system, availability of formic acid as a catalyst, and no need for solvent and solid catalyst in the oxidation medium, so as the main oxidation system was considered in this study.
2. The most important parameters of the Oxidized Water-Formic Acid Oxidation System include the oxidation temperature, the molar ratio of hydrogen peroxide to sulfur (O / S), and the molar ratio of formic acid to sulfur (Acid / S). The effect of these parameters on desulfurization of Hydrocarbon sections of kerosene and diesel were investigated. It was found that the best oxidation conditions in the range of studied parameters, for cutting kerosene (O / S = 5 Acid / S = 30, T = 60C) and for cutting diesel (T = 80C O / S = 5 Acid / S = 30).
3. The reaction system of oxidation of sulfur compounds is a liquid-liquid system. In this system, there may be limitations of interphases transfer phenomena controlling the reaction rate. Therefore, in the development of a reactor system suitable for immediate application, a reactor that provides intense interphase mixing seems appropriate. For this reason, a reactor system based on the technique of collision jets equipped with four jets in the mixing chamber (FIJR) was proposed and built for this purpose. By studying the effect of the most important design and operational parameters on the reactor performance such as current intensity, jet diameter, distance between jets, it was found that reactor performance improves with increasing current intensity and decreasing jet diameter and distance between nozzles. Suitable

conditions in the range of studied parameters were equal to the flow rate of 400 L / h, the diameter of the jet was 2 mm and the distance between the jets was 1 cm. The operation of the FIJR reactor under these conditions for the oxidation of sulfur compounds in kerosene cuts under suitable oxidation conditions resulted in 92% desulfurization of kerosene cuts.

4. The performance of the new FIJR reactor was compared with a conventional STR agitator reactor and it was found that under similar conditions in terms of residence time and reactor input power, the performance of FIJR reactor in oxidation of sulfur compounds is significantly superior to STR reactor.
5. In the case of STR reactor, it was found that increasing the agitator speed beyond the specified limit of 750 rpm has no effect on improving the performance of the reactor and only increases the power consumption.
6. During the oxidation of sulfur compounds, sulfoxides and sulfones are formed, which have a much higher polarity than the primary sulfur compounds. The sulfonates produced, depending on the molecular structure, either remain in the hydrocarbon section, are either extracted by the oxidation-resistant aqueous phase, or remain insoluble and precipitate in both phases.

Therefore, during oxidation, some of the sulfur compounds are separated and some desulfurization is done from the cut. The results of our experiments showed that in case of oxidation of sulfur compounds under similar conditions of suitable oxidation conditions, more than 73% desulfurization of kerosene cut and about 40% desulfurization of diesel section is done only in the oxidation stage. Secondary processes such as liquid-liquid extraction to separate the oxidized sulfur compounds remaining in the hydrocarbon section and to improve the desulfurization of the hydrocarbon section go beyond these values.

7. Liquid extraction process - Liquid is the most important process for separating oxidized sulfur compounds from hydrocarbon slices. The most important parameters of the liquid-liquid extraction process are the type of solvent, the number of extraction steps, and the volume ratio of the solvent to the hydrocarbon section.

To regulate these parameters in the process of extracting sulfur compounds from hydrocarbon cutting, in addition to desulfurization, it is necessary to pay attention to

the recovery of the cut after extraction. In this study, after the initial selection of methanol, 96% ethanol and acetonitrile solvents based on common criteria, the effect of each of these parameters on the rate of desulfurization and shear recovery after extraction was studied for each solvent.

Then, by combining both desulfurization and shear recovery effects in a factor called solvent efficiency factor, E, a comparison was made between the performance of different solvents:

(Acetonitrile > methanol > 96%)

It was also found that increasing the number of extraction steps by more than 2 for kerosene cutting and more than 3 for diesel cutting has little effect on increasing desulfurization but causes a continuous decrease in shear recovery after extraction. The same is true for the volume ratio of solvent to S / F hydrocarbon section, i.e. increasing S / F beyond a certain limit has no effect on improving desulfurization, while continuously reducing the shear recovery rate after extraction.

8. From the extraction of oxidized sulfur compounds from hydrocarbon sections, the highest desulfurization rate observed for both kerosene and diesel sections was more than 99% and the lowest amount of sulfur remaining after the ODS process for kerosene cutting was equal to 13.3ppm and 40ppm for diesel cutting, which is less than the Euro 5 standard (the current standard in our country).
9. By comparing the amount of desulfurization obtained in the simple extraction process with the extraction oxidation process (ODS) and the existence of a large difference in the amount of desulfurization in favor of the ODS process, it was found that the role of oxidation step in desulfurization of hydrocarbon sections by ODS process is very colorful. Because in the oxidation stage, firstly, some of the sulfur compounds are separated, and secondly, the properties of the remaining sulfur compounds in the cut, such as polarity, change in such a way that it is possible to separate them by the extraction process.
10. Adsorption process alone is not suitable for separation of oxidized sulfur compounds from hydrocarbon sections with high sulfur content such as hydrocarbon sections presented in this study because due to limited adsorption capacity of adsorbents in separation of oxidized sulfur compounds, desulfurization can be achieved. There is

not much (more than 90%) in this method. Also, high concentrations of oxidized sulfur compounds in the cut lead to the phenomenon of adsorbent saturation in a short time. On the other hand, by using the adsorption process after extraction, some of these problems are solved and it is possible to achieve hydrocarbon cuts with low sulfur content.

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