

Original Article



Investigating the Problems of Sulfur in Hydrocarbon Cuts

Roozbeh Behzadi *

Department of Chemical Engineering, Islamic Azad University, Science and Research Branch, Tehran, Iran



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ABSTRACT

The removal of sulfur compounds in hydrocarbon fuels is important from an environmental point of view, because in the combustion process of fuels in engines, sulfur compounds in the fuel are converted into sulfur oxides (SO_x), which will cause the problem of 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, causes poisoning of the catalytic converters installed in the exhaust of cars, and finally causes the deactivation of these catalytic converters in a short period. An important plan of these catalytic converters is to reduce the emission of nitrogen oxides into the environment. Likewise, sulfur oxides lead to the rapid deactivation of the filters installed in the exhaust to prevent the release of suspended particles into the atmosphere. Therefore, the presence of sulfur compounds in hydrocarbon fractions, in addition to cause problems related to the release of sulfur oxides into the atmosphere, leads to the aggravation of the problem of the release of pollutants such as nitrogen oxides and suspended particles into the environment.

Introduction

Sulfur compounds in crude oil The amount of sulfur in crude oil ranges from 0.03 wt% for light crude oil to 7.89 wt% for extra heavy crude oil. Sulfur compounds in crude oil can be divided into two general groups of inorganic sulfur compounds and organic sulfur compounds. Inorganic sulfur compounds include elemental sulfur, SH₂, and pyrite [1-3].

Organic sulfur compounds in crude oil are saturated or unsaturated and are classified as follows:

Development of New Desulfurization Processes

Various process ideas have been investigated as alternative or complementary processes to the HDS process for desulfurization of

*Corresponding Author: Behzadi. Roozbeh . roozbehbehzadi02@gmail.com

hydrocarbon cuts, the most important of which are as follow:

- (1) Desulfurization process by reactive absorption method;
- (2) Desulfurization process by selective surface absorption method;
- (3) Desulfurization process by extraction method;
- (4) Biological desulfurization process; and
- (5) Desulfurization process by oxidation method.

We will examine these processes in the following. It should be noted that in the evaluation of different desulfurization processes, attention should be paid to the fact that the process in question does not adversely affect other cutting properties in addition to sulfur reduction. In other words, desulfurization of hydrocarbon cutting leads to maintain or improve cutting quality parameters [4-6].

Desulfurization by Reactive Absorption Method

Reactive absorption is one of the proposed alternative processes for hydrogen reductive desulfurization (HDS) of light hydrocarbon cuts. In this method, adsorbents with transition metals are used, which react with sulfur molecules in the presence of hydrogen and in the temperature range (200-400 °C), and as a result of this reaction, sulfur compounds are converted into hydrocarbons and SH_2 , which is SH_2 .

It is immediately absorbed on the adsorbent. There are two types of processes in this method. One process is based on the continuous regeneration of the adsorbent and the other process is based on the fixed bed system [7-9]. The history of the S-Zorb process dates back to October 2000, when the Philips oil company announced that it had achieved a new process, called S-Zorb, suitable for desulfurization of diesel cuttings.

In this cutting process, diesel (with less than 500 ppm sulfur content) and a small amount of hydrogen are mixed, whose primary role is to prevent the accumulation of coke on the S-Zorb absorber. Then, the flow resulting from steam mixing enters a bubbling fluid bed reactor and desulfurization is carried out due to the

reaction and absorption of products on the adsorbent.

In order to prevent the accumulation of sulfur on the adsorbent and the loss of process performance, the adsorbent is continuously removed from the reactor and pneumatically transferred to the regenerator. The adsorbent regeneration process is an oxidation process in the presence of air that produces gas streams containing SO_2 and CO_2 .

This gas flow is sent to the sulfur recovery unit and the regenerated adsorbent is contacted with hydrogen gas to restore its original activity. The most important point of the S-Zorb process is the adsorbent formulation of this process, which has not been fully announced, but there is information that shows that zinc oxide (Zno) is the most important component of this adsorbent.

Due to the fact that S-Zorb is not considered as a hydro treating technology, hydrogen consumption is less than the conventional HDS process. However, due to the limited capacity of absorption and regeneration in this process, this method does not seem suitable for desulfurization of causal cutting with a sulfur content of more than 500 ppm. In other words, this is a complementary process for HDS [10].

Other Important Problems of This Process Include the Following

(1) In this process, it is necessary for the entire feed to be vaporized in order to better contact the catalyst and fluidize the bed, which is technically difficult for cuts such as diesel cuts with a final boiling point greater than 380 °C, or at least in terms of consumption. Energy is a problem.

(2) In the case of diesel cuts, in parts or cases to achieve acceptable desulfurization, the process conditions are similar to the conventional HDS process conditions, that is, it is necessary to carry out the process in the temperature range of 380-420 °C with a limited space velocity at a pressure of 30 bar.

In this situation, the reactivity trend observed for sulfur compounds of dibenzothiophene derivatives is similar to the trend observed in the HDS process, and practically the S-Zorb

process loses its advantage over the HDS process.

Desulfurization Process by Selective Surface Absorption Method

In this category of processes, the research of Mochida and Song groups is prominent. Both groups have used special adsorbents in the fixed bed to absorb sulfur compounds without converting them into other compounds.

The process presented by Song is known as selective surface adsorption desulfurization (SARS), which uses mild adsorption conditions (at 80 °C). The main goal of these studies is desulfurization of kerosene cut for use in fuel cells. However, this group has also conducted research in the field of desulfurization of gasoline cutting.

In their research, this group used various adsorbents such as chloride of intermediate metals on catalytic bases, activated nickel (Ni) adsorbent (i.e. Ni on SiO₂), metal ions on zeolites (i.e. CeY, Ni-Y), NiAL double layer hydroxides, NiAL double layer hydroxides, NiZnAL, and even HDS catalysts have been used.

In their review report, interesting differences in selectivity of absorption for different adsorbents have been investigated. The most important problem in this desulfurization method is the low absorption capacity, which shows itself even in the desulfurization of cut gasoline with a relatively low amount of sulfur.

Mochida's research group has presented an interesting method for the absorption of resistant sulfur compounds, which is based on the use of activated carbon adsorbent with a high specific surface and containing large amounts of oxygen compounds.

These types of carbon adsorbents seem to be suitable for the absorption of sulfur compounds resistant to the HDS process, and therefore it is likely that using this process before HDS will be a solution, however, the low absorption capacity in this process is still relevant and more research is needed in this context.

Another important technical issue is desulfurization by surface absorption. Management is the way to convert the waste

from sulfur materials absorbed at the end of the process [11].

In addition, in this method, there are ambiguities in the field of the possibility of reviving the absorbents.

In brief, desulfurization processes based on surface absorption are still being developed, and every year various articles and patents are presented about iron-formulated adsorbents with better absorption capacity and more appropriate regeneration capability. However practically, due to the limitations in the absorption capacity of sulfur compounds by these adsorbents, the potential of this process in desulfurization of hydrocarbon cuts with low sulfur content and as a complete desulfurization process.

Desulfurization Process by Extraction Method

The extraction of organic sulfur compounds from hydrocarbon fractions by a range of different solvents from common polar solvents to ionic solvents (IL) has been the subject of extensive research.

The most attractive aspect of desulfurization of hydrocarbon fractions is the extraction method of mild process conditions (pressure and temperature close to ambient conditions). Solvents that have been mostly tested in this research include acetonitrile, lactones such as gamma butyrolactone, and sulfur-containing solvents such as dimethyl sulfoxide (DMSO) or sulfonate.

By examining the research done, it seems that the selective extraction of aromatic sulfur compounds from hydrocarbon fractions 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 the corresponding sulfur-free aromatic compounds.

The experimental results of the extraction of sulfur-containing aromatic compounds show a maximum desulfurization of 50 percent, which is not desirable. Furthermore, desulfurization in this method is done at the cost of extracting a significant part of the aromatic hydrocarbons present in the cut along with sulfur compounds. Due to the existence of this problem, most of the active researchers in this field have come to

the conclusion that for effective and selective separation of sulfur compounds from hydrocarbon fraction, it is better to first oxidize the sulfur compounds present in hydrocarbon fraction and change their polarity with respect to molecules corresponding aromaticity provided the basis for their selective and effective extraction [12].

The extraction of sulfur compounds by a group of different solvents known as ionic solvents has been reported by the Wasserscheid group. An ionic liquid is a non-volatile liquid organic salt that, due to its high polarity, has the potential to extract sulfur and nitrogen compounds from hydrocarbons.

The problems of using ionic solvents include the limitation of extraction capacity of sulfur compounds, the solubility of hydrocarbons in these solvents, and the recovery of these expensive solvents. Given all aspects, in the current situation, ionic solvents do not have a significant advantage over conventional organic solvents. Of course, research on improving the performance of ionic solvents in extracting sulfur and nitrogen compounds from hydrocarbon fractions is still ongoing.

Biological Desulfurization Process (BDS)

Biological desulfurization (BDS) is an old idea that has been proposed for fifty years. Recently,

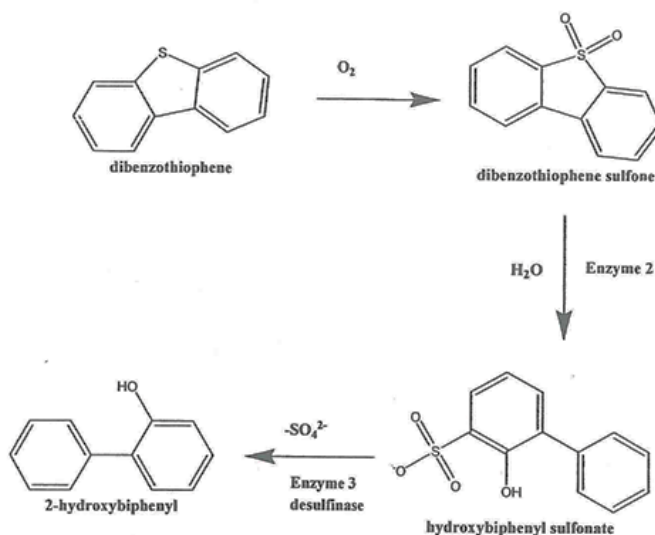
to solve the technical and economic problems of the HDS process, reach new standards in the field of the amount of sulfur allowed, and use the advantages of the so-called "Green" biological processes, it has been referred to this process.

This process takes place in the presence of water and oxygen at ambient temperature and pressure. Of course, biological desulfurization by anaerobic bacteria in the presence of hydrogen and in the absence of oxygen has also been studied.

However, the available reports have mostly dealt with aerobic biological desulfurization. The purpose of the BDS process is to use the specific properties of enzymes to produce fuels with low sulfur content.

In the past decades, significant research has been done in the field of developing the knowledge of enzymes and molecular genetics of the BDS process to design and optimize the process and bioreactor.

Generally, there are two primary routes for BDS of alkyl derivatives of dibenzothiophene. Besides, the main attention has been focused on the so-called 4s pathway for some bacteria that have the ability to separate sulfur from dibenzothiophene and alkyl derivatives of dibenzothiophene [13].



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

As seen in Figure 1, the desired enzymes selectively attack the sulfur atom of dibenzothiophene without affecting the fuel carbon. In the 4s reaction pathway, dibenzothiophene is initially converted into dibenzothiophene sulfoxide, and then oxidized to dibenzothiophene sulfone, and this product is further transformed into 2-hydroxyphenylbenzene sulfonate (HPBS) due to enzymatic activity and opening of the thiophene ring, HPBS becomes 2-hydroxybiphenyl (HBP) and this way desulfurization is done. The important aspect of the 4s pathway compared with other pathways is the high selectivity towards the sulfur atom [14].

According to the conducted research, it has been determined that for this process to be economical, the speed of the BDS process should 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 total sulfur from 1850 ppm to 615 ppm was reported for HDS diesel cutting at a rate of 2.8 $\mu\text{mol}/\text{min}/\text{g}$ dry cell. The important and disappointing point is that it was not possible to reduce the total amount of sulfur to less than 615 ppm with this method. Furthermore, in the study conducted by Maghsoudi *et al.*, it has been determined that in the optimal conditions of the BDS process on diesel cutting, the percentage of desulfurization observed for diesel cuttings with initial amounts of sulfur of 1000 ppm and 303 ppm was only 48.5 and 23.7 percent, respectively.

Similar results have been reported by different researchers with different bacteria in the 4s pathway.

Generally, the numerous reports available in the field of biological desulfurization have not reported deep desulfurization and in the best conditions, they have reported reaching the sulfur range of 50-200 ppm. This problem is completely justified considering that the activity of bacteria depends on the concentration and increases in high concentrations.

Therefore, the potential of the biological desulfurization method to reach the sulfur range of less than 50 ppm is not significant. Enchira Company, which announced its field of activity as the development of biological desulfurization for diesel fuel, has recently

stopped its activity in this field. In addition, another important aspect that should be considered in biological systems is the competitive reactions created by the other bacteria. For example, in the biological process of removing H_2S , which is a successful process, only the target bacteria survive in the highly toxic environment of H_2S and can effectively convert H_2S into elemental sulfur [15].

Therefore, for the development of biological desulfurization, it is necessary to conduct additional studies to prepare the reaction environment for the activity of the target bacteria.

In addition, despite the fact that bacteria that can convert dibenzothiophene and alkyl sulfides have been fully identified and investigated, fewer benzothiophene-bearing bacteria have been identified, and in the case of theophany, the identified bacteria are only limited to a few species.

In general, to develop the process of biological desulfurization (BDS), the cooperation of various experts in the fields of biotechnology, biochemistry, and refining processes is necessary. During the last two decades, different research groups tried to identify and isolate bacteria capable of desulfurization from oil cuttings.

To develop the BDS process, it is inevitable to design and build pilot units. In the current situation, the competition of the BDS process with chemical desulfurization processes seems very difficult due to the various advances achieved in those processes. In brief, despite the fact that the BDS process guarantees mild process conditions, it cannot perform the conversion at a suitable speed that is economically significant. In addition, in this method, there is no possibility of deep desulfurization and reaching new standards.

Desulfurization Process by Sedimentation Method

This process is based on the formation and separation of the insoluble precipitate of sulfur compounds in a charged chemical complex. In this method, a suitable chemical substance is initially added to the sulfur containing

hydrocarbon, which then causes the formation of an insoluble deposit with sulfur compounds.

The next step in this process is to separate the sediment from the cut by filtration, which will lead to desulfurization of the cut.

As an 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-fluorene (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 precipitating agent, and high consumption of the precipitating agent have caused the development of this process to stop on a laboratory scale [16].

Oxidation Desulfurization Process (ODS)

In the HDS process, desulfurization is done by reducing various sulfur compounds to H_2S , while in the oxidation desulfurization (ODS) process, the reaction proceeds in the opposite direction so that the sulfur compound is oxidized and by changing the properties caused by this separation oxidation reaction is done. In this method, sulfur compounds are usually converted into corresponding sulfonic compounds.

To obtain the final product with low sulfur content, it is necessary to separate the sulfonic 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 polar than the corresponding sulfides. Therefore, they are easier to separate from feed. The main advantages of oxidation desulfurization (ODS) compared with the 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 carried out in the atmospheric pressure range and the temperature range is less than $100\text{ }^\circ\text{C}$, while there is no need to use hydrogen in this process.

(2) The most attractive inherent 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 present in the organic sulfur compound and this effect is caused by the increase of electron density on the sulfur atom due to the presence of aromatic rings is strengthened. In addition, the presence of alkyl groups on the aromatic rings also leads to a greater increase in the electron density on the sulfur atom. Therefore, the inherent reactivity of molecules such as 4,6-DMDBT in this process is basically higher than DBT, and in fact, the order of increasing reactivity for the oxidation desulfurization process in many oxidation systems is contrary to the HDS process.

In other words, the chemistry of the ODS process is in many cases completely complementary to the HDS process, which means 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 to combine these two processes together to produce fuels with low sulfur content according to the strict new standards. Of course, there are different opinions about the replacement and combination of HDS and ODS processes. Some believe that producing very low sulfur fuels for refineries that do not have access to cheap sources of hydrogen with the ODS process is more economically attractive than HDS.

However, the application of ODS process is not limited to direct replacement with HDS process. The ODS process, if used before the HDS process, provides advantages such as the separation of interfering compounds in the HDS process, increasing the capacity of the HDS process and reducing hydrogen consumption [17].

If the ODS process is placed after the HDS process, it leads to an increase in the capacity of the HDS units, a reduction in the residence time in the HDS process, a reduction in hydrogen consumption and a longer lifetime of the catalyst in the HDS process.

Of course, 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-existence or

limited capacity of HDS units in the main refineries of the country, it is possible to use the ODS process for desulfurization of hydrocarbon cuts instead of the HDS process.

However, in practice, this process should be evaluated from technical aspects and the ambiguities in different parts of the ODS process should be resolved.

For example, when the liquid-liquid extraction process is used in the second stage of the ODS process to separate the oxidized sulfur compounds, a new problem called the loss of a part of the hydrocarbon fraction during the extraction process is raised, and it is necessary to precisely study this effect. Given that the

desulfurization process by oxidation method (ODS) is the subject of this project.

A General Comparison of Alternative or Complementary Desulfurization Processes to the HDS Process

In this section, we compare desulfurization processes that replace or supplement the common HDS process in terms of factors such as operating conditions, sensitivity of the process to the amount of sulfur in the feed, and the potential of the process to bring the amount of sulfur in hydrocarbon fuels to new standards (Table 1).

Table 1 The results of this comparison and comparison of different desulfurization processes alternative or complementary to the HDS process

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

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

Studying the Effect of Solvent Volume Ratio on Hydrocarbon Cutting on Desulfurization

Studies Conducted on Kerosene Cutting

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 the increase of this ratio. On the other hand, increasing this ratio decreases the recovery of hydrocarbon fraction after extraction with different solvents (Figure 1).

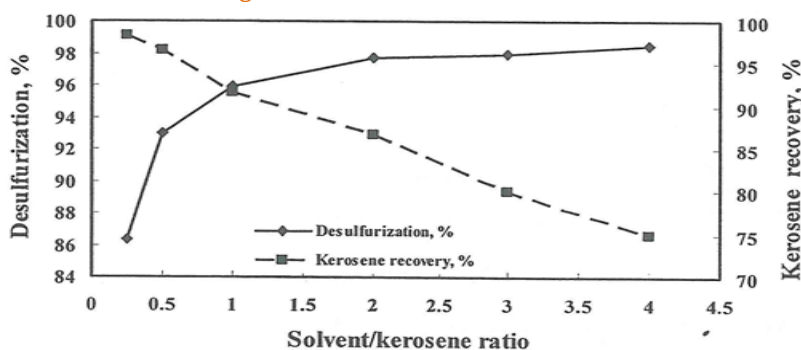


Figure 2 Effect of volume ratio of solvent to hydrocarbon cut on desulfurization rate and kerosene recovery after extraction

As can be seen in Figure 2, in case of using acetonitrile solvent with increasing S/F from 0.25 to 2, desulfurization is increased from 86.3% to 97.7%. However, the recovery of kerosene after extraction decreases from 98.3% to 86.7%. Also, with the increase of S/F from 2

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

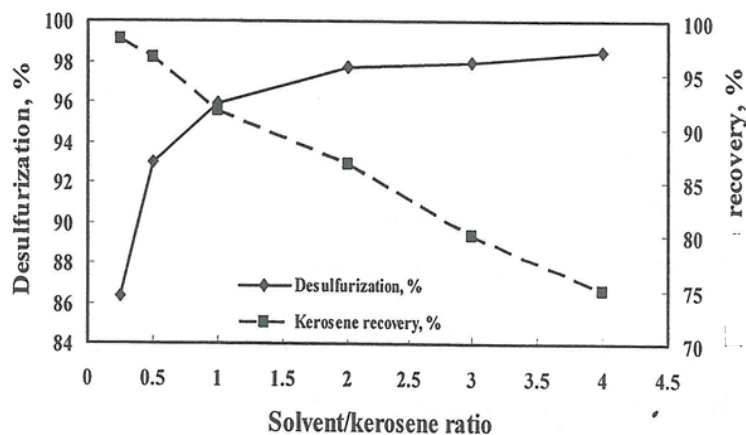


Figure 3 Effect of volume ratio of solvent to hydrocarbon cutting on desulfurization rate and recovery of kerosene after extraction Extraction conditions :) Methanol solvent, T=25 °C, extraction time equal to 30 min, number of extraction steps equal to 1)

Based on Figure 3), the process of changes in desulfurization and cutting recovery for methanol and 96% ethanol solvents is completely similar to the process observed for acetonitrile solvent. Increasing 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 S/F from 0.5 to 2 simultaneously 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. Likewise, increasing S/F from 2 to 4 does not significantly improve the desulfurization rate (only from 96.5% for methanol solvent and from 95.1% to 97.1% for ethanol solvent), but it causes a significant decrease in cutting recovery after extraction.

Studies Conducted on Diesel Cutting

Figures 4 to 6 illustrate the process of changes in desulfurization and recovery of hydrocarbon fraction of diesel as a function of the volume ratio of solvent to hydrocarbon fraction S/F for

acetonitrile, methanol, and ethanol solvents. As can be seen, in the case of diesel cutting, the general trend observed is similar to that of kerosene cutting [18].

In general, in the extraction of oxidized sulfur compounds from hydrocarbon fractions 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 fraction after extraction is decreases continuously [19].

Therefore, increasing the ratio of solvent to feed above a certain value (about 2) practically does not have an effect on improving the desulfurization of kerosene and diesel cuts, and since it causes a significant decrease in the amount of recovery of hydrocarbons cut from extraction, it does not seem appropriate.

To compare different solvents, it is necessary to consider desulfurization and cutting recovery after extraction, which is done using the solvent efficiency factor E in section 4-6.

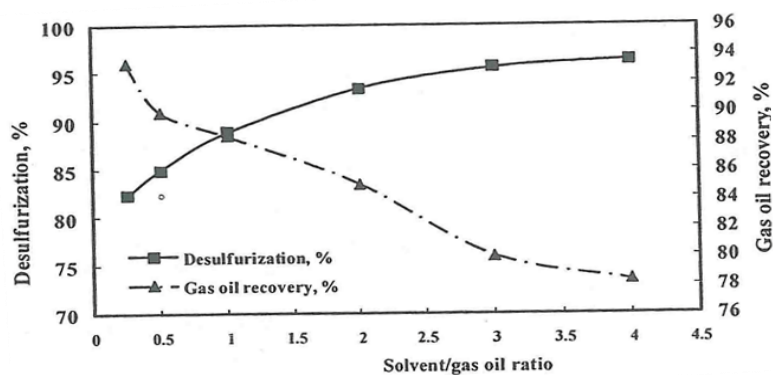
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Figure 4 The effect of volume ratio of solvent to hydrocarbon cutting on the amount of desulfurization and recovery of diesel after extraction. **Extraction conditions:** (Acetonitrile solvent, T=25 °C, extraction time equal to 30 min, number of extraction steps equal to 1)

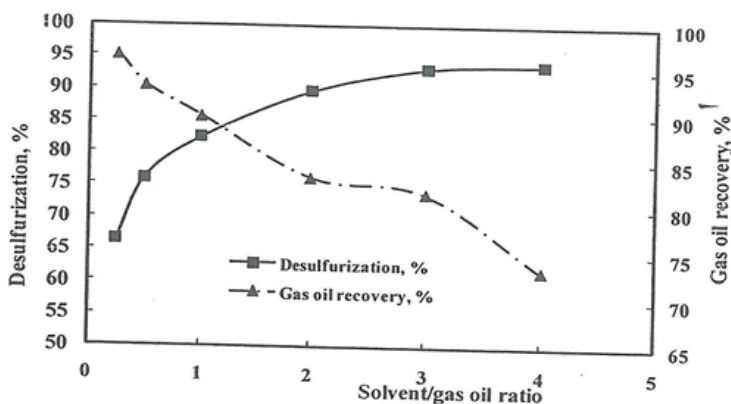
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Figure 5 The effect of volume ratio of solvent to hydrocarbon cut on the amount of desulfurization and recovery of diesel after extraction. **Extraction conditions:** (Methanol solvent, T=25 °C, extraction time equal to 30 min, number of extraction steps equal to 1)

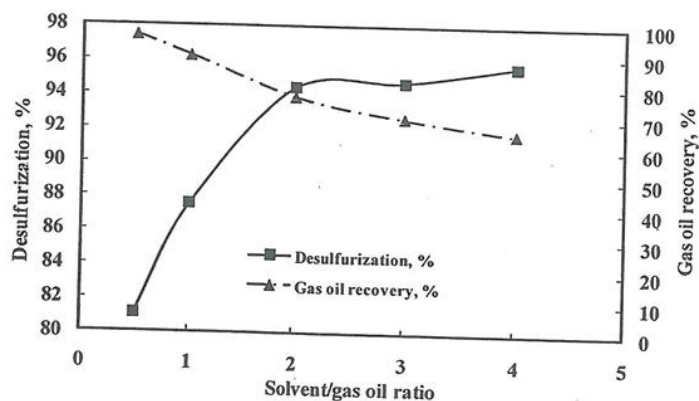
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Figure 6 The effect of volume ratio of solvent to hydrocarbon cut on the amount of desulfurization and recovery of diesel after extraction. **Extraction conditions:** (96% ethanol solvent, T=25 °C, extraction time equal to 30 min, number of extraction steps equal to 1)

Studying the Effect of the 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 fractions, it is expected that with the increase in the number of extraction steps, the desulfurization rate will increase due to the improvement of the separation of oxidized sulfur compounds.

Figures 7 to 9 demonstrate the effect of increasing the number of extraction steps on the amount of desulfurization and kerosene cut recovery for acetonitrile, methanol, and ethanol solvents. As can be seen in Figure 7, if acetonitrile solvent with S/F equal to 0.5 is used in each step of extraction, increasing the number of extraction steps from 1 to 2 leads to an increase in the desulfurization rate from 96.7% to 97.3%.

Increasing the number of extraction steps from 2 to 5 leads to a decrease in the slope of the desulfurization process (increasing desulfurization from 97.3% to 98.7%), while the recovery of kerosene continuously decreases (from 92% to 85%).

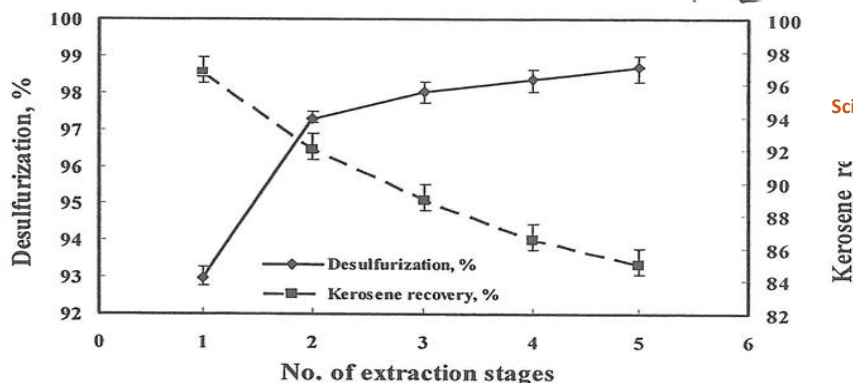


Figure 7 The effect of number of extraction steps on the amount of desulfurization and recovery of kerosene cut after extraction. **Extraction conditions:** (Acetonitrile solvent, volume ratio of solvent to cut equal to 0.5, T=25 °C, extraction time equal to 30 min)

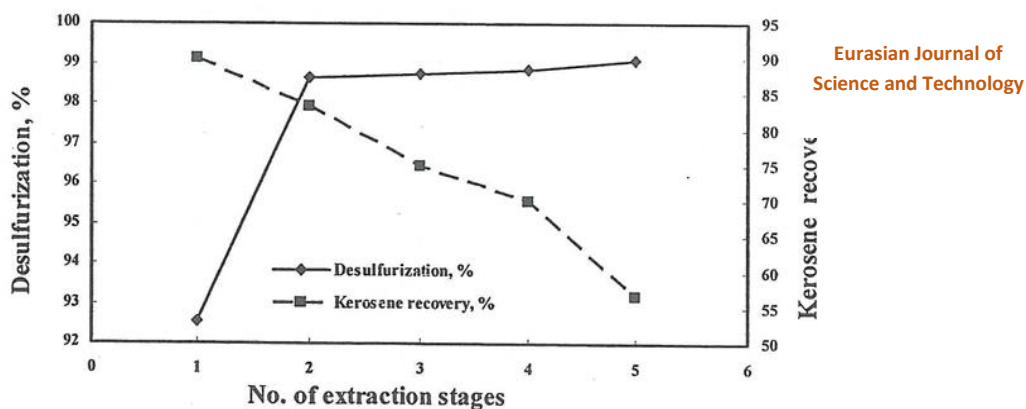


Figure 8 The effect of the number of extraction steps on the amount of desulfurization and recovery of kerosene cut after extraction. **Extraction conditions:** (Methanol solvent, volume ratio of solvent to cut equal to 1, T = 25 °C, extraction time equal to 30 min)

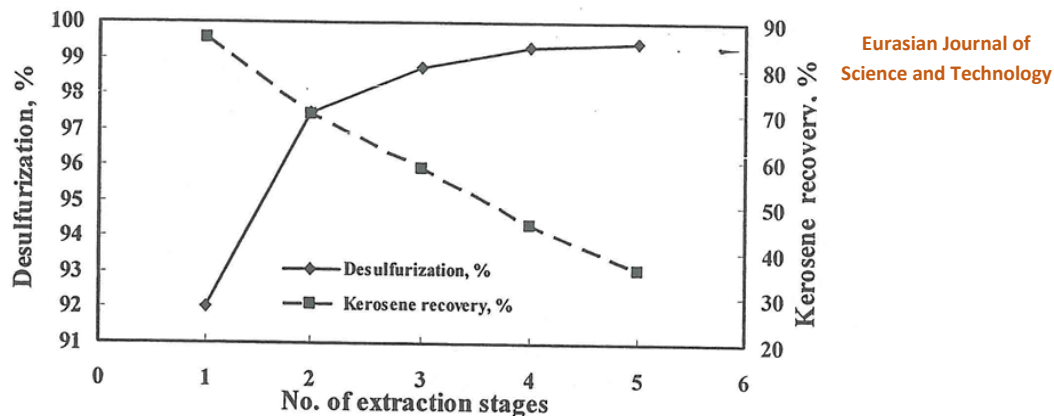


Figure 9 The effect of the number of extraction steps on the amount of desulfurization and recovery of kerosene cut after extraction. **Extraction conditions:** (96% ethanol solvent, volume ratio of solvent to cut equal to 1, T=25 °C, extraction time equal to 30 min)

As can be seen from Figures 8 and 9, the process of changes in desulfurization and cutting recovery for methanol and 96% ethanol solvents is completely similar to the process observed for acetonitrile solvent. Increasing the number of extraction steps 1 to 2 in S/F conditions equal to 1 each step leads to an increase in desulfurization of kerosene from 92.5% to 98.7% for methanol solvent and from 92% to 97.5% for ethanol solvent. On the other hand, it simultaneously reduces the recovery of kerosene after extraction from 90% to 83.3% for methanol solvent and from 86.7% to 70% for ethanol solvent. Likewise, increasing the number of extraction steps from 2 to 5 does not significantly improve the amount of desulfurization (desulfurization only increases

from 98.7% to 99.1% for methanol solvent and from 97.5% to 99.4% for ethanol solvent), but it significantly reduces the amount of open oil recovery after extraction (cut recovery reduction from 83.3% to 56.7% for methanol solvent and from 70% to 36% for ethanol solvent) [20].

Studies Conducted on Diesel Cutting

Figures 10 to 12 indicate the process of changes in desulfurization and recovery of hydrocarbon cut of diesel as a function of number of extraction steps for acetonitrile, methanol, and ethanol solvents. As can be seen, in the case of diesel cutting, the general trend observed is similar to that of kerosene cutting.

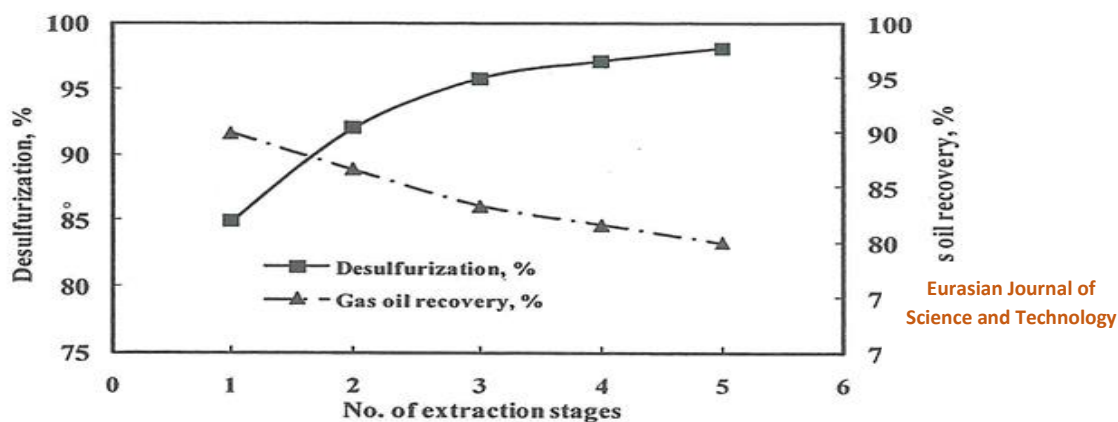


Figure 10 The effect of number of extraction steps on the amount of desulfurization and recovery of diesel after extraction. **Extraction conditions:** (Acetonitrile solvent, volume ratio of solvent to cut equal to 0.5, T=25 °C, extraction time equal to 30 min)

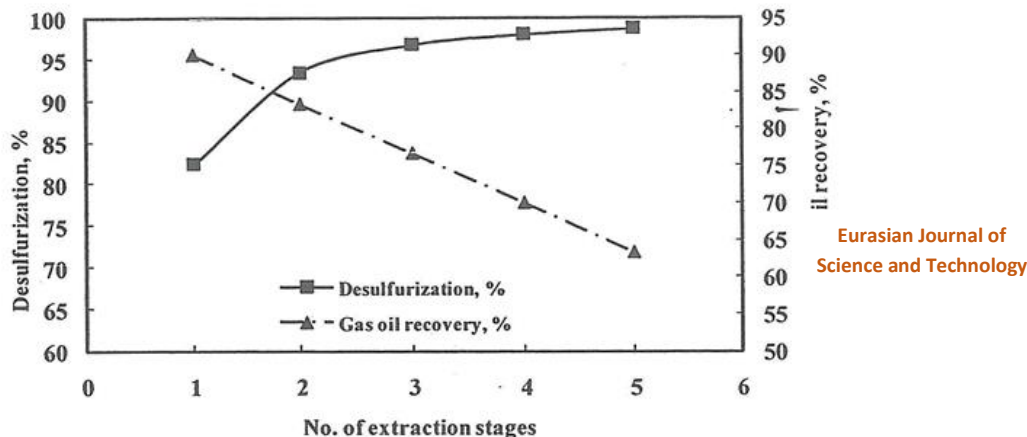


Figure 11 The effect of number of extraction steps on the amount of desulfurization and recovery of diesel cut after extraction. **Extraction conditions:** (Methanol solvent, volume ratio of solvent to cut equal to 1, T=25 °C, extraction time equal to 30 min)

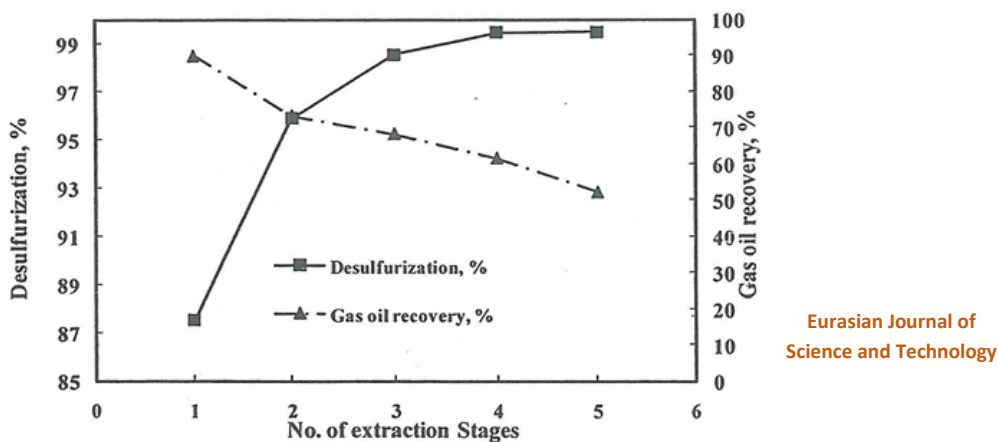


Figure 12 The effect of number of extraction steps on the amount of desulfurization and recovery of diesel cut after extraction. **Extraction conditions:** (96% ethanol solvent, volume ratio of solvent to cut equal to 1, T = 25 °C, extraction time equal to 30 min)

In general, in the extraction of oxidized sulfur compounds from hydrocarbon fractions 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 fraction stops asymptotically, but the recovery of hydrocarbon fraction after extraction decreases continuously [21].

Therefore, increasing the number of extraction stages above 2 for kerosene cutting and above 3

for diesel cutting practically does not have a significant effect on improving the desulfurization of kerosene and diesel cuttings, and since it causes a significant decrease in the amount of recovery of hydrocarbon cuttings, it is appropriate.

Comparison of the Performance of Different Solvents in the Separation of Oxidized Sulfur Compounds from Hydrocarbon Fractions

Solvent efficiency factor, E, is a suitable measure to compare the performance of different solvents in the extraction of oxidized sulfur compounds from hydrocarbon fractions.

Discussion

According to the scope of the current studies, suggestions are presented separately in each section:

In the section of experimental studies on the oxidation of sulfur compounds, the following are offered as suggestions:

Determining the Main Sulfur Compounds of Hydrocarbon Fractions and Their Amount

Investigating the conversion rate of different sulfur compounds after oxidation and their separation rate after solvent extraction seems to be interesting. As an example, it is very interesting to determine the total amount of remaining sulfur after applying the oxidation desulfurization process (ODS).

In this study, an attempt was made to do such a task, but due to the existence of many limitations in the qualitative and quantitative analysis of sulfur compounds, it was not possible to do it. Because, firstly, for this purpose, special analytical devices (gas chromatography device equipped with PFPD detector and new GC-MS devices with high scan quality) are needed, and secondly, to conduct small studies of this kind and produce control solutions for specific sulfur compounds. Such as 4,6-DMDBT, which is very expensive.

In addition, it is not available in Iran and is produced in a very small amount in the world only for desulfurization studies [22-24].

Conducting Mechanistic Studies to Determine the Contribution of Chemical Kinetics and Transfer Phenomena in the Overall Speed of the Oxidation Process

In this regard, it is necessary to initially oxidize individual sulfur compounds such as

DBT and BT in solvents such as toluene in the present oxidation system under different conditions such as (temperatures different and different mixing speeds) should be studied and further determined by interpreting the results and using criteria such as Hatta modulus and the general regime controlling the speed of the process.

This information is very important in developing suitable reactors for this application.

Investigating the Possibility of Increasing the Overall Speed of The Process

Investigating the application of conditions such as the use of ultrasonic wave energy in the reaction mixture or adding accompanying catalysts along with formic acid to increase the overall speed of the process is an interesting topic for future studies. Increasing the overall speed of oxidation leads to ease in designing the reactor, reducing the volume of the reactor and the possibility of designing the process in a continuous manner.

In The Proposal and Construction Section of the Reactor Based On the Jet Technique, the Following Items Are Suggested

Optimizing the Number of Jets in the Mixing Chamber of the Reactor

The optimal number of jets is obtained by economic calculations, taking into account the increase in power consumption and the improvement of performance obtained due to the increase in the number of jets.

Knowingly, by increasing the number of jets in the mixing chamber of the reactor, the performance of the reactor will probably 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 [25].

Determining the Effective Parameters in Increasing the Scale of the Jet Reactor

Given that increasing the scale of these types of reactors as special reactors is simply not

possible, for this purpose it is necessary to build at least another FIJR reactor with a different scale and its performance in oxidation. Sulfur compounds should be evaluated.

Then, the main dimensionless numbers should be determined by evaluating the obtained results in reactors with different scales. In the investigations carried out in the present study, it seems that the Reynolds number of the jet is one of the main parameters in this field [26].

Investigating the Process of Failure and Coalescence of Jets

Knowing this information is important in the design of reactors based on the technique of impinging jets. Investigating the use of different computational techniques such as Computational Fluid Dynamics (CFD) for modeling the failure and coalescence of jets is one of the interesting topics for future studies.

In The Section of Experimental Studies on The Separation of Oxidized Sulfur Compounds From Hydrocarbon Fractions, The Following Are Interesting For Future Studies:

Comparative Study of Ionic Solvents Performance with Normal Solvents

For this purpose, first, some ionic solvents should be selected which are probably suitable for this application and it is possible to synthesize them, and their performance in separating oxidized sulfur compounds from cuts hydrocarbon to be evaluated.

Then, the amount of desulfurization and the amount of hydrocarbon cut recovery obtained when using these solvents and common solvents are compared. Of course, if the performance of ionic solvents is better, to replace normal solvents with ionic solvents, such things as the way and the possibility of recovering ionic solvents after the process, as well as the economic issues related to these solvents (their high price) should be carefully evaluated.

Investigating Solvent Recovery Processes after Extraction

For this purpose, solvent recovery processes after extraction and the method of separating sulfones and hydrocarbons dissolved in the solvent should be carefully studied.

Currently, solvent recovery through distillation is proposed, but different aspects of this separation process should be evaluated. For example, it should be determined that how much of the solvent is lost with the flow rich in sulfone, and accordingly, how much fresh solvent is needed.

In addition, it is necessary to determine what part of the hydrocarbons carried by the solvent in the extraction stage can be recovered in this stage [27].

How to Manage Production Sulfonylurea Waste

In this regard, all possible solutions in a refining complex to manage 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, compared, and should suggest the best solution. Recently, in this field, solutions such as the possibility of using double-layer hydroxide catalysts to separate SO₂ from sulfones and recover the hydrocarbon part of sulfone have been noticed by researchers, and it is necessary to further evaluate these methods [28].

Evaluation of Different Adsorbents for the Separation of Oxidized Sulfur Compounds

Concerning the development of different adsorbents with different properties and characteristics, it seems interesting to evaluate the performance of these adsorbents in the process of separation of oxidized sulfur compounds.

Interpreting the performance of adsorbents in the field of separating oxidized sulfur compounds from hydrocarbon fractions with

pore structure (pore size as well as the percentage of meso and micro porosities) and their specific surface is one of the interesting research fields in this case [23].

If a suitable adsorbent with a high absorption capacity for oxidized sulfur compounds is found, it will be possible to replace the extraction process with a surface absorption process to separate oxidized sulfur compounds [24-26].

However, it is necessary to clear the existing ambiguities about the absorption process such as the capacity of the absorbent, the possibility of regeneration of the absorbent and its regeneration method, the overall lifespan of the absorbent, and the number of times that the absorbent can be regenerated, which is a good topic for future research [29].

Conclusion

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

(1) Hydrogen peroxide-formic acid oxidation system compared with other oxidation systems has more advantages such as the simplicity of the oxidation system, availability of formic acid as a catalyst, and no need for solvent and solid catalyst in the oxidation environment. Therefore, as a main oxidation system was considered in this study.

(2) The most important parameters of hydrogen peroxide-formic acid oxidation system include the oxidation temperature, molar ratio of hydrogen peroxide to sulfur (O/S), molar ratio of formic acid to sulfur (Acid/S), and the effect of these parameters on the desulfurization of cuttings Kerosene and diesel hydrocarbons were investigated. It was found that the best oxidation conditions in the range of studied parameters for kerosene cutting (O/S=5 Acid/S=30, T=60C) and for diesel cutting (T=80C O/S=5 Acid/S=30).

(3) The reactive system of oxidation of sulfur compounds is a liquid-liquid system. In this system, it is possible that the limitations of

interphase transfer phenomena control the reaction rate. Therefore, in the development of a suitable reactor system, it seems appropriate to use a reactor that provides the strong interphase mixing. Therefore, a reactor system based on impinging jets technique 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 reactor performance, such as flow intensity, jet diameter, and distance between jets, it was found that reactor performance improves by increasing flow intensity and decreasing jet diameter and distance between nozzles. The suitable conditions were obtained in the range of studied parameters equal to flow intensity of 400 L/h, jet diameter equal to 2 mm, and distance between jets equal to 1 cm. The operation of the FIJR reactor under these conditions for the oxidation of sulfur compounds in kerosene cut led to 92% desulfurization of kerosene cut in the suitable oxidation conditions.

(4) The performance of new FIJR reactor was compared with the conventional STR stirred reactor and it was found that under the same conditions in terms of residence time and reactor input power, the performance of the FIJR reactor in the oxidation of sulfur compounds is significantly superior to the STR reactor.

(5) In the case of the STR reactor, it was found that increasing the stirrer 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, whose polarity is significantly higher than the primary sulfur compounds. Depending on molecular structure, the produced sulfones either remain in the hydrocarbon fraction or are extracted by the aqueous phase that is prone to oxidation, or remain insoluble and precipitate in both phases. Therefore, in the oxidation course, part of the sulfur compounds is separated and the desulfurization of the cutting is done to some extent. The results of our experiments showed that in the case of oxidation of sulfur compounds under conditions similar to suitable

oxidation conditions, more than 73 percent desulfurization from kerosene cutting and about 40 percent desulfurization from diesel cutting is done only in the oxidation stage. The secondary processes such as liquid-liquid extraction to separate the oxidized sulfur compounds remaining in the hydrocarbon cut and improve the desulfurization of the hydrocarbon cut are beyond these values.

(7)The liquid-liquid extraction process is the most important process for separating oxidized sulfur compounds from hydrocarbon fractions. 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 fraction. To adjust these parameters in the process of extracting sulfur compounds from hydrocarbon cutting, it is necessary to pay attention to cut recovery after extraction in addition to desulfurization. In this study, after the initial selection of methanol, 96% ethanol, and acetonitrile solvents based on the common criteria, the effect of each of these parameters on the amount of desulfurization and cutting recovery after extraction was studied for each solvent. Then, by combining both the effects of desulfurization and cutting recovery in one factor called the solvent efficiency factor, E, a comparison was made between the performance of different solvents (Acetonitrile > Methanol > 96%)

(8)It was also found that increasing the number of extraction steps more than 2 for kerosene cutting and more than 3 for diesel cutting does not have much effect on increasing desulfurization, but it causes a continuous decrease in cutting recovery after extraction. Regarding the volumetric ratio of solvent to hydrocarbon fraction S/F, the situation is similar, that is, increasing S/F beyond a certain limit has no effect on improving desulfurization, while it causes a continuous decrease in the amount of fraction recovery after extraction.

(9)From the extraction of oxidized sulfur compounds from hydrocarbon fractions, the highest desulfurization rate observed for both kerosene and diesel fractions was more than 99 percent, and the lowest amount of residual sulfur after applying the ODS process for kerosene fractions was equal to 13.3 ppm and

for cutting diesel, it was equal to 40ppm, which is lower than the Euro5 standard (the current standard of our country).

(10)By comparing the amount of desulfurization obtained in the simple extraction process with the oxidation extraction process (ODS) and the existence of a significant difference in the amount of desulfurization in favor of the ODS process, it was determined that the role of the oxidation step in the desulfurization of hydrocarbon cuts with the ODS process is very colorful because in the oxidation stage, firstly, part of the sulfur compounds are separated, 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.

(11)The surface absorption process alone is not suitable for separating oxidized sulfur compounds from hydrocarbon cuts with high sulfur content, such as the hydrocarbon cuts discussed in this study, because due to the limitation of the adsorption capacity of adsorbents in separating oxidized sulfur compounds, it is possible to achieve high desulfurization (beyond 90 percent) that does not exist in this method. Also, the high concentration of oxidized sulfur compounds in the cutting leads to the phenomenon of saturation of the adsorbents in a short time. On the other hand, using the surface absorption process after extraction, some of these problems are solved and it is possible to reach hydrocarbon cuts with low sulfur content.

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