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Extraction conditions for removal of oxidized sulfur compounds in gas oil

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Abstract−An experimental study was conducted to investigate the extraction of oxidized sulfur compounds from gas oil. Solvents used for this purpose included acetone, acetonitrile, methanol and propanol. The effect of solvent concentration, solvent to gas oil ratio, temperature, time and number of stages was studied. To select the best solvent and conditions for extraction, two criteria were considered: high desulfurization and more hydrocarbon recovery. Results showed that extraction time and temperature have no significant effect. Methanol for low ability of extraction of oxidized sulfur compounds and propanol for low hydrocarbon recovery were excluded from further experiments. After the tests, the optimum conditions for extraction were determined to be 85% acetone, solvent/feed ratio of 1, two stages extraction in ambient temperature and enough time for mixing. In this condition 85% of sulfur compounds of gas oil containing 1,670 ppmw S were separated and 95% of gas oil was recovered.

Key words: Oxidative Desulfurization, Extraction Solvent, Gas Oil, Liquid/Liquid Extraction, Oxidized Sulfur Compounds

INTRODUCTION

Sulfur removal from petroleum is necessary for both industrial and environmental reasons. Sulfur in petroleum products corrodes parts of internal combustion engines and refineries and causes major air pollution and acid rain due to exhaust from diesel engines and emission of sulfur oxides [1,2]. Thus removal of sulfur has become an urgent subject worldwide due to very stringent environmental regulations [3].

The current commercial process for desulfurization is hydrodesulfurization (HDS), which is carried out at high temperatures and elevated pressures. It is difficult to remove polyaromatic sulfur compounds in this process [4]. Moreover, during the deep HDS the energy and hydrogen consumption will be obviously increased. To overcome the limitations of HDS, several new approaches such as oxidation desulfurization (ODS) have been studied in recent years [5].

In ODS process, the sulfur compounds presented in fuel by an oxidizing agent such as hydrogen peroxide, ozone, peracids, hydroperoxides, nitric acid, and nitrogen oxides, etc. are oxidized to give rise to the corresponding sulfoxide and subsequently sulfones [6,7]. These sulfones are polarized compounds such that they can be removed from the fuel by subsequent solvent extraction using water-soluble polar solvents, such as acetonitrile (ACN), which is the most common, [8-11], dimethyl formamide (DMF) [10,12], N-methyl-2-pyrolidone (NMP) [10], alcohols (such as methanol [8,9], ethanol [9,12], propanol [12], 2-ethoxyethanol [11]), furfural [13], dimethyl sulfoxide (DMSO) [14] and γ-butyrolactone [11]. Polarized sulfones also could be removed by adsorption but liquid/liquid extraction is more conventional because availability of solvents and for high amount of solvents, extraction with solvent is more commercial.

Ramirez et al. studied simultaneous oxidation and extraction desulfurization of gas oil and use ACN, DMF, 2-ethoxyethanol and γ-butyrolactone as a solvent for extraction and found out γ-butyrolactone has more ability to sulfur removal [11]. Ali et al. used n-octane as a model fuel which is extracted by polar solvents ACN, DMF and NMP and compared oxidation, extraction, consecutive oxidation and extraction, and simultaneous oxidation and extraction; they found that NMP is the best solvent for the removal of oxidized sulfur species [10]. Caero et al., in a study to obtain the reactivity of different organic sulfur compounds in ODS reaction for a model fuel, used acetonitrile as solvent for extraction. They found the relative ODS activity of different sulfur compounds was affected by diesel/solvent ratio due to the differences in solubility, as the solvent amount was diminished [6]. Molaei et al. for extraction of oxidized sulfur compound in kerosene used methanol, ethanol and propanol, and found propanol has more ability to extract oxidized sulfur compounds. However, in these articles fuel recovery is not investigated. In another article Molaei et al. considered fuel oil recovery and found ACN more effective for this purpose [9,12].

As recoverability of solvent is an important factor in this process, solvents with high boiling point are not suitable because the boiling point of oxidized sulfur compounds is from 270 to 670 °C and high boiling point solvents consume more energy in solvent recovery by distillation and affect the process economy. NMP, DMF, DMSO, γ-butyrolactone and furfural are solvents with high boiling point and also these solvents are more toxic; hence, they are more difficult to handle industrially [9].

This study aims to find the effects of solvent type, solvent to fuel ratio, number of extraction stages, and concentration of solvent, temperature and time on extraction by considering two criteria: desulfurization ability (the ability of solvent for removing sulfur compounds from feedstock) and oil recovery (the ratio of amount of gas oil after treatment to feedstock) for various solvent to select the more suitable condition. Acetonitrile, methanol, propanol and ace-

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tone are chosen as potential solvents for extraction of oxidized sulfur compounds in these experiments because of their high selectivity, low boiling point and low toxicity.

EXPERIMENTAL

1. Materials

Hydrogen peroxide 30 wt%, acetic acid and all polar solvents used for extraction, i.e., methanol, propanol, acetone, and acetonitrile, were purchased from Merck Chemical Co. (Germany). All of the chemicals were used as received without any further treatment. Untreated gas oil obtained from refinery and oxidized by hydrogen peroxide 30 wt% and acetic acid as catalyst [10] was used as feedstock for extraction experiments. Physical specifications of oxidized gas oil are summarized in Table 1 and the physical properties of solvents for the extraction of oxidized sulfur compounds are shown in Table 2.

2. Method & Analysis

Solvent extraction studies for the removal of oxidized sulfur compounds in gas oil were carried out with four different organic solvents: acetonitrile (ACN), methanol (MeOH), propanol and acetone. The studies were conducted in a 350 ml glass reactor equipped with a condenser and mechanical stirrer, and connected to a circulator at constant temperature. Solvent concentration was changed by dilution with distilled water. At first, 50 ml of the hydrocarbon phase obtained from the oxidation stage was charged and an appropriate amount of solvent was added. Then, the mixture was continuously stirred for the known period of time and heated to the specified temperature. The dispersion formed was then allowed to separate into two distinct phases (hydrocarbon and aqueous phases) in a separatory funnel. After complete phase separation, the aqueous phase was removed and the treated gas oil was washed with distilled water. For multi stages extraction, the product of each stage (treated gas oil) was used as feedstock for the next stage and the same procedure was done. Treated gas oil was analyzed for total sulfur content measurement. In Fig. 1 the experimental setup is shown.

By a Sulfur-in-Oil Analyzer (SLFA-2800, Horiba Inc) based on ASTM D4294 method, non-dispersive X-ray fluorescence (NDXRF) was used to determine the total sulfur content in gas.

Table 1. Properties of gas oil feed stock

Specification	Value	Test method
Density (kg/m^3)	821	
Total sulfur (%wt)	0.167	ASTM D-4294
Total aromatic content (%wt)	15.12	IP391/01
Viscosity at 40 °C (m^2/S)	$1.547*10^{-6}$	
Viscosity at 100 °C (m^2/S)	$4.195*10^{-6}$	
Distillation:		ASTM D-86
%Vol	Temp (°C)	
Initial boiling point (I.B.P)	160	
%5	200	
%10	220	
%30	285	
%50	314	
%70	338	
%90	364	
%95	376	
Final boiling point (F.T.P)	378	

RESULTS AND DISCUSSION

1. Influence of Solvent Concentration on Extraction

Solubility of gas oil in a solvent is one of the important factors in selecting the appropriate solvent. Fig. 2 demonstrates the effect of solvent concentration on desulfurization and Fig. 3 shows its effect on gas oil recovery for acetone, acetonitrile, methanol and propanol.

According to the results, as shown in Fig. 2, for all solvents studied, increasing the solvent concentration improves desulfurization with approximately constant slope. Among these solvents acetone follows a different trend as 60% acetone has the lowest ability to

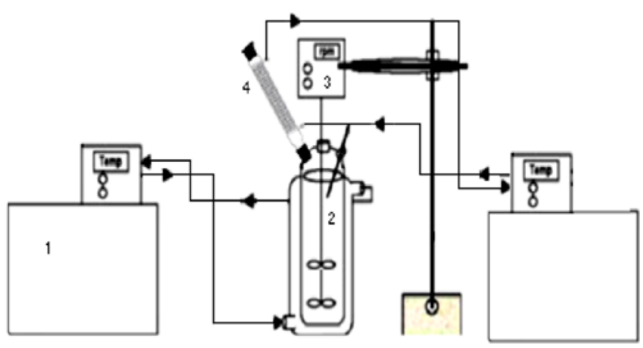

Fig. 1. Experimental set up of the apparatus for extraction of oxidized sulfur.
1. Circulator 2. Reactor 3. Stirrer 4. Condenser

Table 2. Physical properties of potential solvents for the extraction of oxidized sulfur compounds

Solvent	Density (kg/m^3)	Boiling point (°C)	Freezing point (°C)	Viscosity at 20 °C (mPa s)	PEL^a (TWA^b)
Methanol	791	64.7	−98	0.59	200(OSHA^c)
Propanol	790	82	−89	1.94	400(OSHA^c)
Acetonitrile	783	80	−46	0.37	40(OSHA^c)
Acetone	790	56	−95	0.31	1000(OSHA^c)

^{a}Permissible Exposure Limit (PEL): is the maximum amount or airborne concentration of a substance to which a worker may be legally exposed. Most PELs have been defined for substances that are dangerous when inhaled, but some are for substances that are dangerous when absorbed through the skin or eyes
^{b}Time Weighted Average (TWA): This average concentration must not be exceeded during any 8-hour work shift of a 40-hour workweek
^{c}Occupational Safety and Health Administration (OSHA)

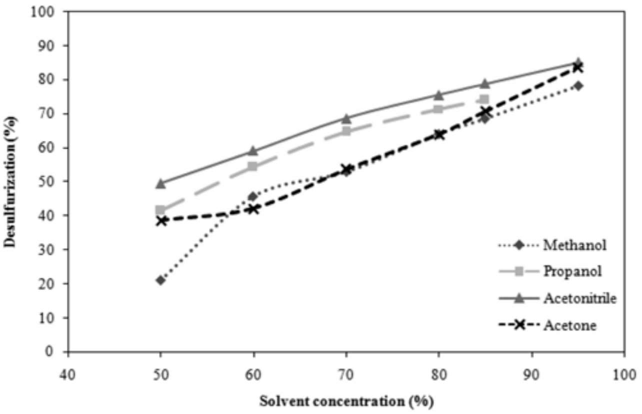

Fig. 2. Effect of solvent concentration on desulfurization. Extraction conditions: T=25 °C, solvent/gas oil ratio=1, mixing time =10 min, and number of stages=1.

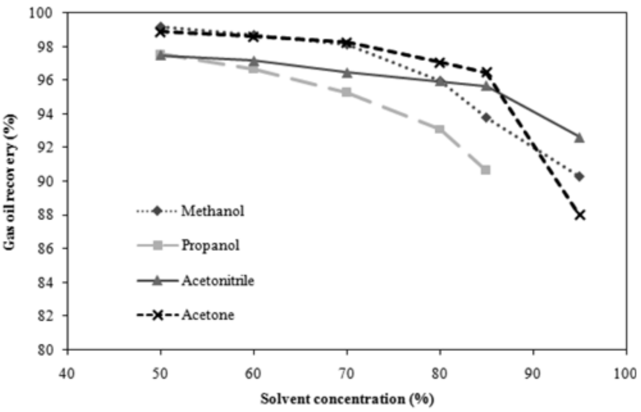

Fig. 3. Effect of solvent concentration on gas oil recovery. Extraction conditions: T=25 °C, solvent/gas oil ratio=1, mixing time =10 min, and number of stages=1.

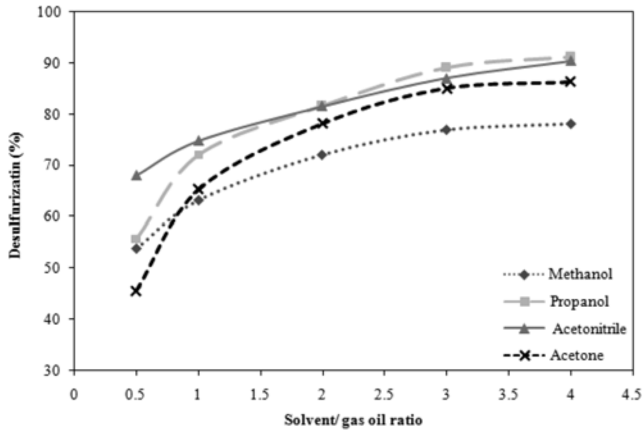

Fig. 4. Effect of solvent/gas oil ratio on desulfurization. Extraction conditions: T=25 °C, solvent concentration=80%, mixing time=10 min, and number of stages=1.

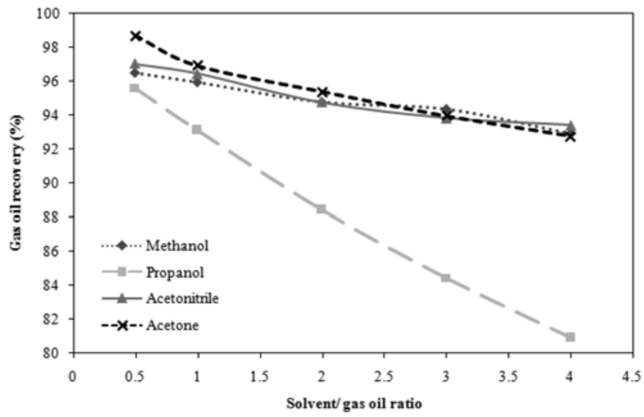

Fig. 5. Effect of solvent/gas oil ratio on gas oil recovery. Extraction conditions: T=25 °C, solvent concentration=80%, mixing time=10 min, and number of stages=1.

extract oxidized sulfur compounds, but at higher concentrations, it can compete with acetonitrile and propanol.

Fig. 3 shows that with increasing solvent concentration, gas oil recovery is reduced. This reduction was more significant especially at high concentrations, for example, changing acetone concentration from 85 to 95% results in almost 10% decrease in gas oil recovery. Since these two different factors affect the process, optimum concentration for each solvent should be experimentally determined.

Results showed that propanol has considerable desulfurization ability, but it has the lowest gas oil recovery and methanol has low desulfurization ability. Comparing these alcohols in extraction of oxidized sulfur from kerosene, Molaei et al. [12] reported that desulfurization ability of 50% propanol is more effective than 50% methanol. This trend is observed for all concentrations of solvents in sulfur extraction from gas oil in this investigation.

As a result, increasing the solvent concentration improves the desulfurization ability and reduces the gas oil recovery, and it is because of increasing the solubility ability of solvent in higher concentration, in other words, water makes the solvent weaker. Acetonitrile and acetone of higher concentrations (80-85%) are more efficient in extraction of oxidized sulfur compounds with acceptable gas oil recovery. It should be noted that all results in this section are for one stage extraction.

2. Influence of Solvent/Gas Oil Ratio on Extraction

The solvent/gas oil ratio is another important parameter in the extraction of oxidized sulfur compounds. Fig. 4 demonstrates the effect of solvent/gas oil ratio on desulfurization and Fig. 5 shows its effect on gas oil recovery for solvents studied.

Investigation of solvent/gas oil ratio in Fig. 4 indicated that in low solvent/gas oil ratios (from 0.5 to 1), desulfurization intensely increases, but on further increasing the solvent/gas oil ratio from 2 to 4, the slope of desulfurization curves decreases and becomes flatter. Also results showed, methanol has the lowest desulfurization ability in comparison with other studied solvents (from 54 to 78% for solvent/gas oil ratio from 0.5 to 4). Acetone is more sensitive to solvent/gas oil ratio as the ratio changes from 0.5 to 4, the desulfurization improves significantly (from 46 to 86%), whereas acetonitrile has the least sensitivity (from 68 to 90%).

Fig. 5 shows that in ratios of over 2, gas oil recovery became less than 95%. Comparing solvents studied showed that increasing solvent/gas oil ratio for propanol results in less gas oil recovery than other solvents. An increase in solvent ratio from 0.5 to 4 results in a decrease in gas oil recovery from 96 to 81% with constant slopes

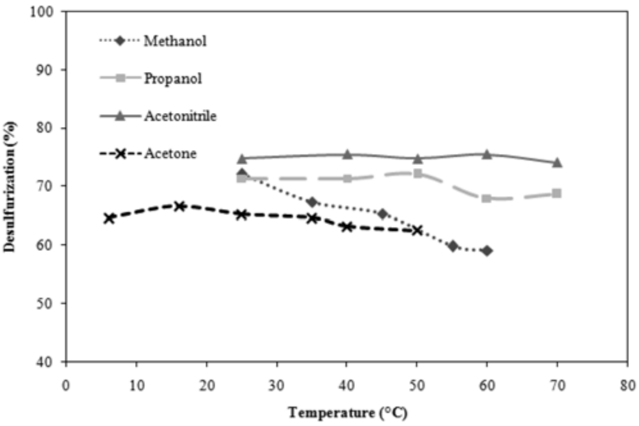

Fig. 6. Effect of temperature on desulfurization. Extraction conditions: solvent/gas oil ratio=1, solvent concentration=80%, mixing time=10 min, and number of stages=1.

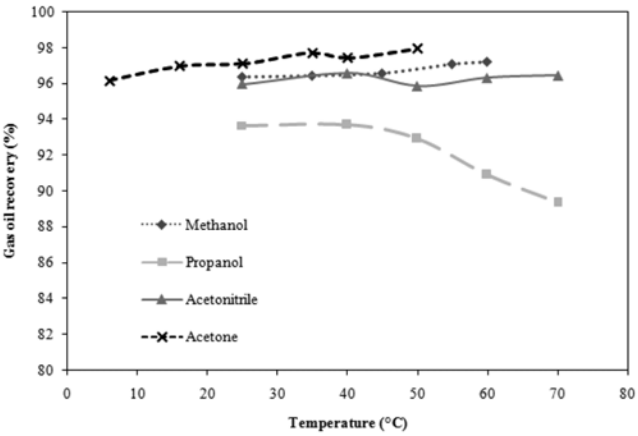

Fig. 7. Effect of temperature on gas oil recovery. Extraction conditions: solvent/gas oil ratio=1, solvent concentration=80%, mixing time=10 min, and number of stages=1.

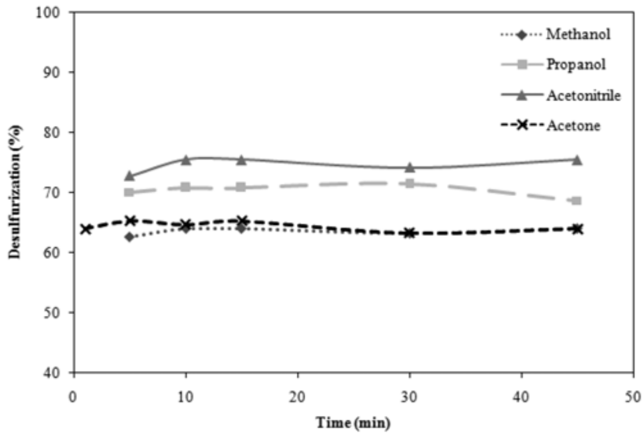

Fig. 8. Effect extraction time on desulfurization. Extraction conditions: solvent/gas oil ratio=1, T=25 °C, solvent concentration =80%, and number of stages=1.

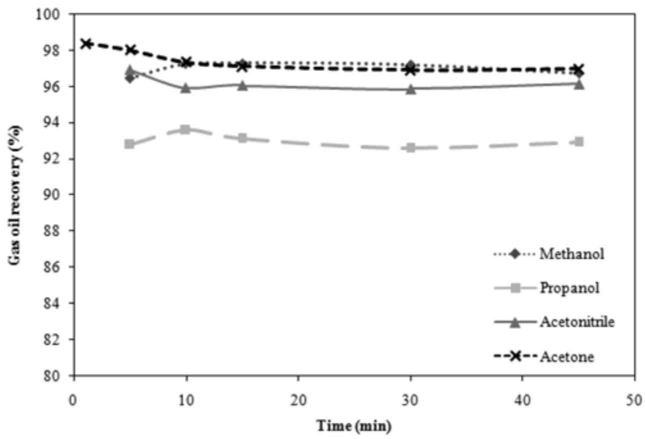

Fig. 9. Effect extraction time on gas oil recovery. Extraction conditions: solvent/gas oil ratio=1, T=25 °C, solvent concentration=80%, and number of stages=1.

for propanol. Therefore, propanol should be used only in low ratios.

In summary, for all solvents studied, higher quantities of solvents result in more desulfurization but less gas oil recovery. Indeed, ratios of over 2 require bigger and then more expensive equipment in addition to giving low hydrocarbon recovery. Therefore, it is not recommended to work with solvent/gas oil ratios of over 2.

3. Influence of Temperature on Extraction

In these experiments, the effect of temperature on extraction of oxidized sulfur compounds is studied. Fig. 6 shows the effect of extraction temperature on desulfurization, and Fig. 7 shows this effect on gas oil recovery for acetone, acetonitrile, methanol and propanol.

As observed from Fig. 6, the effect of temperature on desulfurization is negligible. Fig. 7 indicates that propanol has the lowest gas oil recovery and it decreases from 94 to 89% with increasing temperature from 25 to 70 °C. Although these changes are not significant, the trend in acetone is different from propanol, and changing temperature from 6 to 50 °C results in an increase in gas oil recovery from 96 to 98%. For methanol and acetonitrile, changing the gas oil recovery with temperature is less than 1%, too.

Generally, although it seems that temperature could be a significant factor due to changing the solubility of component, but as experimental results show, temperature has no noticeable effect on extraction of oxidized sulfur compounds in gas oil making room temperature extraction economical.

4. Influence of Mixing Time on Extraction

Another parameter, which is investigated for extraction of oxidized sulfur compounds, is mixing time for the gas oil and solvent. Fig. 8 shows the effect of extraction time on desulfurization, and Fig. 9 shows this effect on gas oil recovery for acetone, acetonitrile, methanol and propanol.

As it can be seen in Fig. 8 and Fig. 9, time is not an efficient factor in desulfurization and gas oil recovery and there is an evident steadiness in mentioned figures.

Consequently, it is clear that mixing for more than 5 or 10 minutes has no significant effect on desulfurization or gas oil recovery and only a good mixing is enough; there is no need to spend much time and energy to mix the gas oil and solvent to get better results.

5. Influence of Extraction Stages Number

The number of extraction stages is an important parameter in the extraction of oxidized sulfur compounds. For this part, based on the results of previous sections, 80-85% acetone and acetonitrile

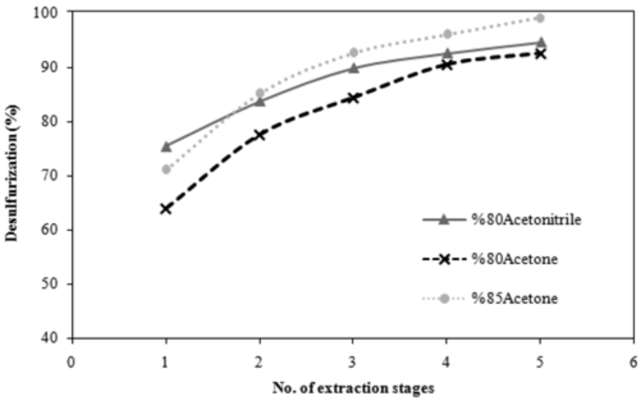

Fig. 10. Effect of stages number on desulfurization. Extraction conditions: solvent/gas oil ratio=1, T=25 °C, mixing time=10 min.

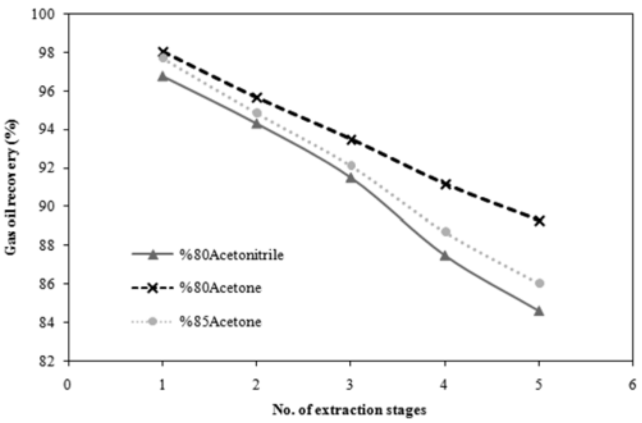

Fig. 11. Effect of stages number on gas oil recovery. Extraction conditions: solvent/gas oil ratio=1, T=25 °C and mixing time =10 min.

with solvent/feed ratio of 1 were chosen as solvents because of good desulfurization ability and acceptable gas oil recovery. Fig. 10 demonstrates the effect of number of extraction stages on desulfurization. and Fig. 11 shows this effect on gas oil recovery.

Fig. 10 shows that increasing the number of extractions improves desulfurization ability and reduces the gas oil recovery. Increasing the number of extractions from 1 to 2 leads to an increase in desulfurization from 71 to 82% for acetonitrile, from 59 to 76% for 80% acetone, and from 67 to 83% for 85% acetone with a decrease in gas oil recovery from 97 to 94% for acetonitrile, 98 to 96% for 80% acetone and 97 to 94% for 85% acetone. So 85% acetone showed the more desulfurization ability in two stages extraction and its desulfurization ability increased more than other studied solvents. After two stages, the slope of desulfurization curve is reduced.

As observed from Fig. 11, increasing the number of extractions decreases gas oil recovery and for all experimented stages the reduction slope is steady. The rate of gas oil recovery for 80% acetone is more than 85% acetone, and for 85% acetone is more than 80% acetonitrile.

Since increase in number of extraction stages from 2 to 5 leads to a small improvement in the desulfurization and significant decrease in the gas oil recovery, which is not economical, two stages extraction is more reasonable.

It should be noted that in one stage extraction, 80% acetonitrile has more ability to extract oxidized sulfur compounds than 85% acetone, but more stages do not yield the same results. More desulfurization is carried out with 85% acetone in more than one stage, and even gas oil recovery here is more than 80% acetonitrile.

CONCLUSIONS

The extraction condition for removal of oxidized sulfur compounds, the products of the oxidation step of gas oil in ODS process, was investigated. It was found that:

Acetonitrile, acetone, methanol and propanol were selected as the potential solvents to extract the oxidized sulfur compounds from gas oil. Among these solvents, methanol has low desulfurization ability and extraction with propanol results in low hydrocarbon recovery. Therefore, acetone and acetonitrile are suitable solvents for extracting oxidized sulfur compounds in gas oil.

Increasing the solvent concentration improves desulfurization with constant slope, but gas oil recovery is reduced. Experimental results show working in 80-85% concentrations for acetone and acetonitrile is more efficient.

For all studied solvents, an increase in the solvent/gas oil ratio results in more desulfurization. However gas oil recovery decreased. Therefore, solvent/gas oil ratios of over 2 are not efficient.

It was shown that the effect of mixing time and temperature is negligible, working at ambient temperature with good mixing for 5 or 10 minutes is sufficient, and there is no need to spend energy to control these parameters.

For all studied solvents, an increase in the number of extraction stages results in more desulfurization, but working in more than two stages is not recommended because of significant decrease in gas oil recovery.

Working in more than one stage showed acetone gives better results in desulfurization and gas oil recovery. Therefore, acetone could be an efficient solvent for extraction of oxidized sulfur compounds in gas oil. Optimum conditions were determined to be 85% acetone, solvent/feed ratio of 1, two stages extraction in ambient temperature and enough time for mixing. In this condition 85% of sulfur compounds of gas oil containing 1,670 ppmw sulfur were separated and 95% of gas oil was recovered.

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