

LUMA H. MAHMOOD¹, MOHAMMAD F. ABID², MOHAMMED I. MOHAMMED³

STUDY ON ULTRASOUND ASSISTED DESULFURIZATION OF LIGHT GAS OIL USING INORGANIC LIQUIDS

The feasibility of removing sulfur from real light gas oil using inorganic liquids (NaOH, Ca(OH)₂ and HCl) at various concentrations assisted with ultrasonication was investigated in a continuous flow setup. Experimental results showed that at the optimum operating time (40 min), 68% of sulfur was removed under mild conditions using 10 wt. % NaOH. Ultrasonication not only facilitated sulfur removal but also improved gas oil properties by decreasing density and viscosity by 1.40 and 4.42%, respectively, while the cetane number (CN) was increased by 7.0%. Solute selectivity (S) depending on sulfur mole fraction (x_s) was correlated using StatPlus 6.7.1.0 software and the following values have been obtained: $S = 53.869e^{-2.552x_s}$, and $S = 29.573 - 41.878x_s$ for mixtures of 10% Ca(OH)₂ + S-compound + oil, and 10% NaOH + S-compound + oil, respectively. The correlation coefficients (R^2) for the above equations were 0.9813 and 0.9611, respectively. An empirical correlation related to sulfur removal as a function of processing time and solvent concentration was found with $R^2 = 0.956$. The results of the present work confirmed the feasibility of employing the hybrid method of ultrasonication with using alkaline liquids for sulfur removal.

1. INTRODUCTION

Desulfurization (DS) of petroleum middle distillates by means of efficient cost-effective processes is one of the main goals of modern oil refineries. Desulfurization methods mainly cover adsorptive desulfurization (ADS), extractive desulfurization (EDS), oxidative desulfurization (ODS), hydrodesulfurization (HDS), biodesulfurization (BDS), and desulfurization with ionic liquids. Though the HDS technique is considered effective in lowering sulfur concentrations in petroleum middle distillates, some sulfur com-

¹Department of Chemical Engineering, University of Technology, Baghdad, Iraq.

²Department of Medical Instrumentation, Al-Hikma University College, Baghdad, Iraq, corresponding author, e-mail address: doctormfa@gmail.com

³Department of Chemical Engineering, Suleyman Dimirel University, Isparta, Turkey.

pounds such as dibenzothiophene and its derivatives are less responsive to this operation. Moreover, deep HDS required highly severe pressure and temperature accompanied by higher costs [1]. In order to realize the desulfurization process, the key is how to select proper adsorbents which cover molecular sieves, activated carbon, ion-exchange resin, and activated carbon fibers [2]. Jochen et al. [3] suggested that EDS with ILs is a good alternative for deep HDS of diesel oil. Duarte et al. [4] reported that despite great advantages provided by the use of ultrasounds, in the last years, few studies related to its direct application in the petroleum industry have been published. Shafeghat et al. [5] used ODS assisted with ultrasonication to remove sulfur from gas oil and gasoline. Ionic liquids have withdrawn interests as extractive materials for DS of middle distillates [6–8], or as an end-step operation for the HDS process [9]. A great variety of chemical treating agents are known which facilitate the desulfurization of various hydrocarbon fractions. Some of the chemical treating agents are alkali metals and their oxides, hydroxides and salts, especially alkali metal salts of weak, non-volatile acids including lithium, sodium, potassium, rubidium and cesium [10].

Published data on the methods of the alkali extraction of mercaptans with regeneration of saturated mercaptides of the alkali solution by oxidation with atmospheric oxygen in the presence of homogeneous [11] or heterogeneous [12] phthalocyanine catalysts have come into the most widespread use. Demirbas [13] carried out an experimental study for desulfurization of lignite and coal using alkaline solution (bicarbonates and hydroxides) from biomass ashes. The author concluded that the alkaline desulfurization is more effective in removing the pyritic sulfur from the coal. Akhmadullina et al. [14] conducted an analysis of the most existing methods employed for the demercaptanization of light hydrocarbon stock (LHCS) utilizing alkali oxides, hydroxides and salts. Demirbas et al. [15] presented strategies for crude oil desulfurization evaluated by reviewing desulfurization literature. Authors indicated that the most important characteristics of crude oil that affect the market price are its sulfur content and gravity. They reported that the sulfur compounds from gasoline are generally removed by treatment with sodium plumbite which is a solution of lead oxide in sodium hydroxide. In the current study, the authors investigated the feasibility of usage efficient and inexpensive inorganic liquids in a continuous process for the DS of gas oil assisted with ultrasonication under ambient conditions. Another objective was to study the equilibrium behavior of the sulfur compound in studied ternary mixtures.

2. MATERIALS AND METHODS

Materials. High purity chemicals of sodium hydroxide (>98%), and calcium hydroxide (>96%) were purchased from Sigma Aldrich, India. Hydrochloric acid (36%) was ordered from Merck, Germany. Light gas oil was obtained from Al-Daura Oil Refinery, Baghdad. Specifications of real gas oil are listed in Table 1.

Table 1

Properties of real light gas oil feed (Al-Daura Oil Refinery, Baghdad)

Parameter	Value	Method of analysis
API gravity at 15.6 °C	40.1	ASTM D1298
Specific gravity at 15.6 °C	0.8246	ASTM D1298
Sulfur content, wt. %	0.214	ASTM D 5623
Cetane number	51.2	ASTM D 7170
Gas oil distilled in crude oil, vol. %	17.1	ASTM D 86
Initial boiling point, °C	195	ASTM 6352
Final boiling point, °C	322	ASTM 6352

Experimental procedure for the selectivity and the partition coefficient. To predict the behavior of the selectivity and partition coefficient for the studied systems, a batch setup was installed. Mixtures of ternary systems components (Inorganics + S-compound + oil) in the immiscible region were mixed in a 50 cm³ glass vessel immersed in a water bath connected to a recirculation Chiller (type Accel 250 LC from Thermo Scientific), to control the vessel temperature (25±1 °C). The mixtures were agitated using a magnetic stirrer for 1 h, and then let to stabilize for a minimum of 2 h. Then, syringes were used to obtain samples from each layer of the mixture. Weight fractions of oil and sulfur compounds were measured by GC.

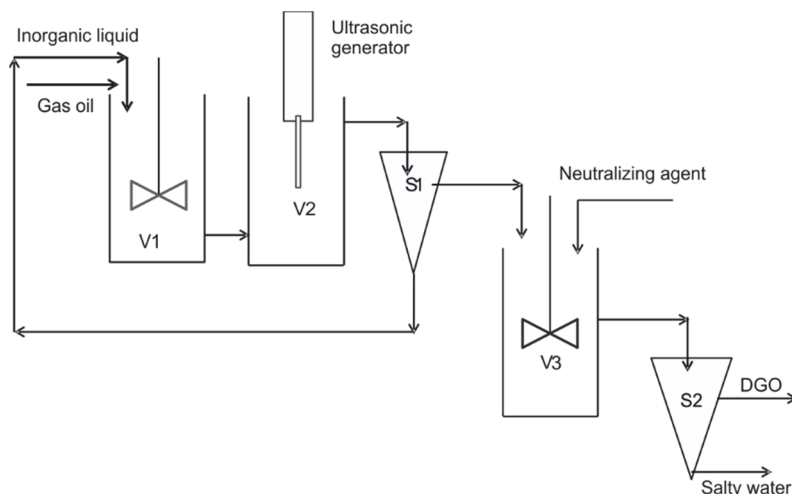


Fig. 1. Experimental setup of the continuous extractive desulfurization process:
 V1 – mixing tank, V2 – ultrasonic generator, V3 – neutralizing tank,
 S1 – liquid–liquid separator, S2 – high speed centrifuge

Experimental setup for continuous operation. Three different concentrations (5, 10, and 15 wt. %) of inorganic materials (NaOH, Ca(OH)₂ and HCl) were prepared in 100 cm³

glass beakers. 50 cm³ of gas oil was taken in the Erlenmeyer flask and added to each prepared ionic aqueous solution in a 250 cm³ glass cylindrical Flask (V1, Fig. 1). The samples were mixed with an electric mixer (IKA RW 20, Cole-Parmer, 300 rpm), the mixture was then transferred to another 250 cm³ glass cylindrical vessel (V2) in which a probe of an ultrasonic generator (model VCX-750, vibra-cell, Sonics) was submerged.

Table 2

Specifications of the ultrasound probe

Characteristics	Value
Power output, W	750
Frequency, kHz	20
Standard probe size	
diameter, mm	13
length, mm	136
Probe material	titanium alloy Ti-6Al-4V
Processing capacity, cm ³	10–350

In Table 2, the characteristics of the ultrasonic probe has been presented. The temperature of the sonication vessel was kept at 40 °C because above this temperature, the extraction of S-compounds would become increasingly poorer [16]. To optimize the sonication time, the mixture was sonicated for various time spans (10, 20, 30, 40, 50, and 60 min) with a 3 min break between sequential ultrasonic periods of 5 min for each span. As the sonication process continued, samples for sulfur determination were drawn periodically by a syringe. The influence of sampling on the mixture volume was neglected because of the small sample amounts (≤ 1.0 cm³ per sample). After completion of the ultrasonic period, the mixture was conveyed to a funnel of liquid–liquid separation (S1) for separating the heavier layer from the oil light layer. Then the oil light layer was transmitted to a 250 cm³ glass beaker (V3) where a neutralizing agent was added (if required). pH meter type (on-line pH meter Model Excel 25PH/mV/ISL) was then utilized to monitor the pH of the solution in V3. The neutralized solution was transferred to a high-speed centrifuge type (Centrisart[®] D-16C, Sartorius Company). Lighter stream (desulfurized gas oil) was analyzed for the concentration of total sulfur utilizing a sulfur analyzer type (XOS, model Sindie OTG). GC has also used for a recheck the analysis results.

The method of analysis. The fractions of the samples in the ternary systems were measured by a gas analyzer type ta3000F from AMETEK[®] Process Instruments, equipped with a column SPB-1 SULFUR 30 m×0.32 mm ID, 4.0 μ m phase and flame ionization detector (FID). The analyzer of sulfur type (XOS, model Sindie OTG) was utilized to measure the total sulfur content of gas oil before and after the DS process. (FTIR) records were carried out in the 400–4000 cm⁻¹ range, using the IR Affinity-1, Shimadzu

analyzer. The cetane number (*CN*) of gas oil was measured using near-infrared diesel oil cetane number testing instrument model FDW-0371, China. The gas oil density was measured using a density meter model DDM 2909 from Rudolph Research Analytical, USA. Initial and final boiling points of gas oil were determined using a distillation tester, model PT-D1401-255 from Genius Laboratories, China.

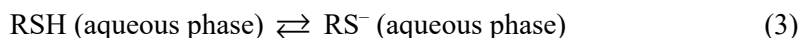
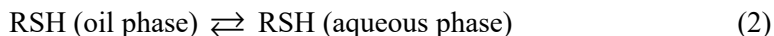
3. THEORY

Ultrasonic irradiation can effectively improve the reaction yield in chemical synthesis mainly due to cavitation when mechanical vibrations are generated into the liquid as ultrasonic waves. When liquids are subjected to high-intensity ultrasonication, acoustic cavitation occurs. This phenomenon is the formation and succeeding violent collapsing of cavitation bubbles, creating shock waves, preparing a great set of conditions for chemical reactions and increasing the chemical reactivity of the system. During this process, short-term localized hotspots could be produced. The violent collapse of each bubble causes a locally high temperature (up to 5000 K), high pressure (up to 100 MPa) and drastic liquid jets. This microenvironment, with extreme local conditions, is suitable for the creation of active intermediates permitting the reaction to progress rapidly. Moreover, ultrasonication may cause increasing the formation of lighter sulfur-molecules due to the breakage of heavier ones [17]. The mechanism of extraction operation is based on the allocation law which states that if a liquid layer consists of two immiscible components, is subjoined a material which is dissolvable in both layers, then the material doled out between the two layers so that the ratio of loading in one solvent to the loading in the other solvent stays stable at stable temperature. It is supposed that the molecular structure of the material is identical in both solvents. The distribution or the partition coefficient (k_d) is [18]

$$k_d = \frac{x_s^1}{x_s^2} \quad (1)$$

where x_s^1 is the S-compound loading in phase 1 (inorganic-rich phase) and x_s^2 is the S-compound loading in phase 2 (hydrocarbon-rich phase). As an approximate approach, the allocation parameter may be estimated equivalent to the ratio of the solubility of S-compound in the two layers. The organic sulfur component is readily dissolved in the polar solvents; moreover the solvents having consanguinity for the sulfur compounds being extra beneficial in their extraction. So, this method was utilized in the present work by applying various solvent systems at similar conditions (e.g., temperature and processing time). Heinrich and Kasztelan [19] reported that mercaptans and sulfides

form the main proportions of the S-compounds that are found in lighter middle distillates of petroleum. It is assumed that S-compound is soluble in the oil phase. The distribution of an S-compound between an oil phase and an aqueous inorganic solution may be represented by:



Equilibrium (2) depends on the solubility of the S-compound in the aqueous phase and in the oil phase. Equilibrium (3) depends on the ionization constant of the S-compound and on the concentration of free hydroxide in water. Cabo [20] presented an equation to correlate the solute distribution ratio k_d , and selectivity S

$$S = \frac{x_s^1}{x_s^2} \times \frac{x_o^2}{x_o^1} \quad (4)$$

where x_o^2 and x_o^1 are mole fractions of gas oil in phase 2 and phase 1, respectively.

4. RESULTS AND DISCUSSION

4.1. SELECTIVITY AND PARTITION COEFFICIENT

It is well known that the solute partition coefficient k_d , and selectivity S , are linked to the amount of solvent required for the separation (k_d) and to the number of required steps to achieve it (selectivity).

Table 3

Experimental data for the system 10% NaOH + S-compound + oil

Ionic liquid-rich phase			Oil-rich phase			k_d	S
x_1^1	x_2^1	x_3^1	x_1^2	x_2^2	x_3^2		
0.893	0.00	0.107	0.00	0.00	1.00		
0.754	0.15	0.096	0.00	0.029	0.971	5.17	52.29
0.677	0.24	0.083	0.00	0.062	0.938	3.87	43.73
0.514	0.412	0.074	0.00	0.157	0.823	2.62	29.13
0.416	0.525	0.059	0.00	0.263	0.737	1.99	24.85
0.34	0.618	0.042	0.00	0.404	0.596	1.529	21.69
0.311	0.646	0.043	0.00	0.471	0.529	1.37	16.85
0.275	0.68	0.045	0.00	0.558	0.442	1.21	11.88

Table 4

Experimental data for the system 10% Ca(OH)₂ + S-compound + oil

Ionic liquid-rich phase			Oil-rich phase			k_d	S
x_1^1	x_2^1	x_3^1	x_1^2	x_2^2	x_3^2		
0.941	0.00	0.059	0.00	0.00	1.00		
0.863	0.078	0.059	0.00	0.044	0.956	1.77	28.68
0.759	0.182	0.059	0.00	0.108	0.892	1.68	25.39
0.663	0.279	0.058	0.00	0.187	0.813	1.49	20.88
0.578	0.367	0.055	0.00	0.272	0.728	1.34	17.73
0.489	0.454	0.057	0.00	0.400	0.600	1.139	11.98
0.47	0.473	0.057	0.00	0.415	0.585	1.134	11.64
0.404	0.541	0.055	0.00	0.544	0.456	0.99	8.21

Thus, they are the key parameters to decide the appropriateness of a solvent as extracting material. The k_d and S values obtained for the liquid–liquid equilibria data of the systems 10% NaOH + S-compound + oil, and 10% Ca(OH)₂ + S-compound + oil are shown in Tables 3 and 4, respectively. These values are plotted versus S-compound molar fraction in the oil-rich phase in Fig. 2. It can be seen that trends of S are qualitatively similar for both liquids. This figure demonstrates that the separation of S-compound from light gas oil with these alkaline liquids is favorable in terms of solubility and selectivity, especially at low mole fractions of S-compound. When higher values of k_d and S are obtained for the studied mixtures the more efficient separation of S-compound from oil is obtained [21].

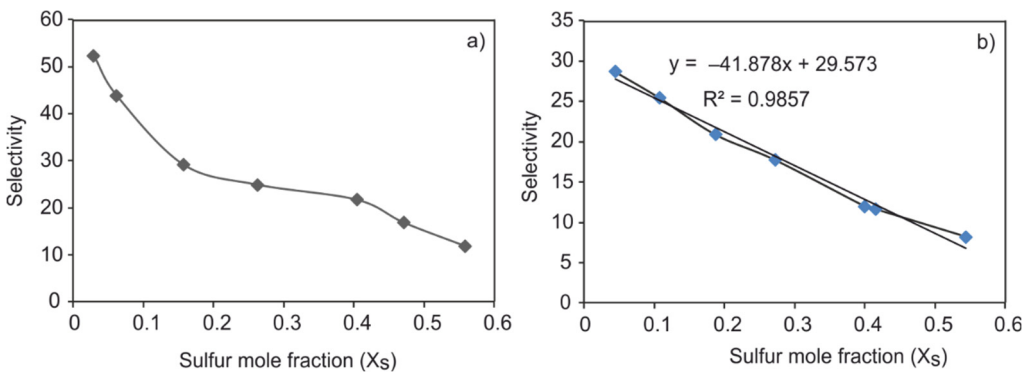


Fig. 2. Variation of selectivity against mole fraction of sulfur for mixtures of: a) 10%NaOH + S-compound + oil, and b) 10% Ca(OH)₂ + S-compound + oil

Based on experimental data, correlation related selectivity vs. sulfur mole fraction in the studied ternary mixture can be represented using StatPlus 6.7.1.0 software by Eqs. (5) and (6).

- for the mixture 10% NaOH + S-compound + oil

$$S = 53.869e^{-2.552x_s}, \quad R^2 = 0.9813 \quad (5)$$

- for the mixture 10% Ca(OH)₂ + S-compound + oil

$$S = 29.573 - 41.878x_s, \quad R^2 = 0.986 \quad (6)$$

4.2. EFFECT OF INORGANIC LIQUID TYPE

Figure 3 illustrates sulfur removal against processing time using various types of inorganic liquids. For 10% NaOH for the processing time increasing from 10 to 50 min, the sulfur removal increases from 35 to 68%. The gradual increase in sulfur removal is attributed to the extraction of mercaptans reacting with caustic solution.

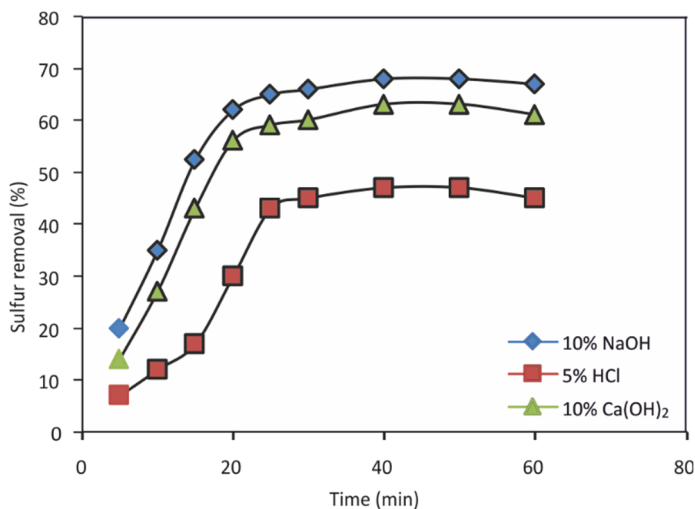
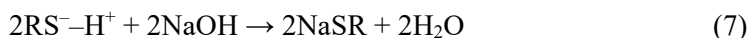
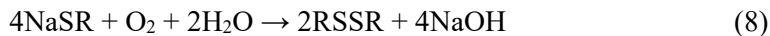


Fig. 3. Sulfur removal against processing time using various types of inorganic liquids

The reaction that takes place in the extractor is:



In the above reaction, RSH is a mercaptan and R is an organic group such as a methyl, ethyl, propyl or others. In industrial field, the second step is referred to as regeneration and it involves heating and oxidizing the caustic solution leaving the extractor [22]. The oxidation results in converting the extracted mercaptans to organic disulfides (RSSR) which are liquids water-insoluble and are then separated and decanted from the aqueous caustic solution. The reaction that takes place in the regeneration step is:



It is worth noting that sulfur removal reached maximum after 40–50 min (Fig. 3). An equilibrium state was established at the final stages of the time span. However, as the processing time increased further from 50 to 60 min, sulfur removal displayed a slightly decreasing trend from 68 to 67%. These results showed that for economic, the optimum operating time for the best sulfur removal can be considered 40 min. For 10% $\text{Ca}(\text{OH})_2$ and 5% HCl used as inorganic liquids, similar dependences have been found, however sulfur removals were lower (Fig. 3) of sulfur removal versus processing time but at lower values of sulfur removals. This confirms that the NaOH aqueous solution offers a higher affinity towards sulfur compounds. The lower sulfur removal was attained using 5% HCl. This is likely due to the high tartness which is not an appropriate medium for the allocation of aromatic sulfur combinations, which demands an alkaline environment rather than an acidic one [23].

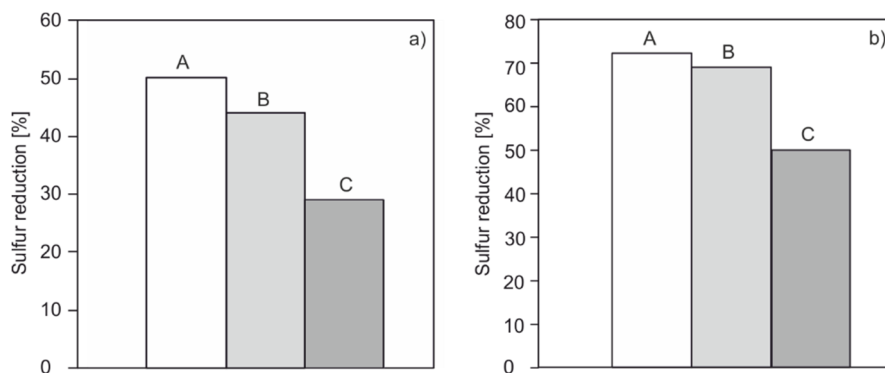


Fig. 4. Sulfur removal in various inorganic liquids after 40 min
(A – 5% HCl, B – 10% $\text{Ca}(\text{OH})_2$, C – 10% NaOH):
a) assisted with ultrasonication, b) without ultrasonication

Figure 4 shows the percentage of sulfur removal achieved by processing the gas oil with different types of inorganic liquids assisted with or without ultrasonication at optimum time, respectively. As shown, the sulfur removal promoted in the order 5% HCl < 10% $\text{Ca}(\text{OH})_2$ < 10% NaOH. This order may be attributed to that NaOH aqueous solution has larger affinity for the S-compounds in the oil distillates. This is possible because of the acidic nature of the sulfur components such as mercaptans, which easily extract from the oil phase inside the alkaline layer of NaOH and turn into sulfides. In the same way, the high DS output using $\text{Ca}(\text{OH})_2$ may also be obtained. A comparison between Figures 4a and 4b shows the noticeable effect of ultrasonication on the DS of gas oil. The increase in sulfur removal due to sonication of inorganics/gas oil mixture was 29.4, 26.3, and 20.7% for 10% NaOH, 10% $\text{Ca}(\text{OH})_2$, and 5% HCl, respectively.

This may be due to the formation of lighter sulfur molecules by the bond breaking of heavier ones facilitating the extraction of S-compound by the inorganic liquids [17].

4.3. EFFECT OF INORGANIC LIQUID CONCENTRATION

Time dependences of sulfur removal in NaOH solutions of various concentrations is shown in Fig. 5. As can be seen, for all concentrations a gradual increase in sulfur removal occurred at the early stages of processing. This may be attributed to the high rate of extraction resulting from the high concentration of sulfur-compound at these stages, creating a high driving force between the two layers. As sulfur concentration decreased, the extraction rate decreased correspondingly until a pseudo-equilibrium state was established at the final stage of the process, i.e., in 25–30 min. Sulfur removal increased upon increasing NaOH concentration.

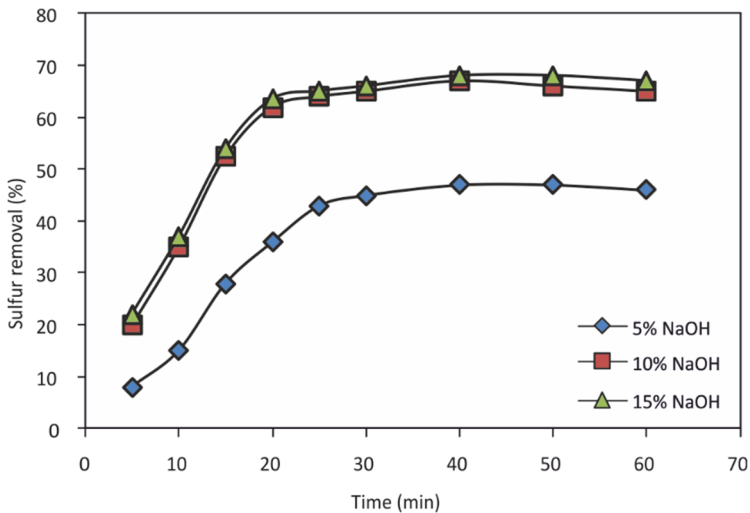


Fig. 5. Time dependences of sulfur removal for various NaOH concentrations

However, there is an optimum concentration of inorganic liquids which may be used to attain the best sulfur removal, after which an increase in NaOH concentration would be only costly [20] (Fig. 5). To determine a predominant operating parameter, all the data related independent variables (i.e., processing time t and NaOH concentration C) with the objective function (i.e., sulfur removal $R\%$) have been treated mathematically using regression analysis technique aided by the Microsoft Excel 2010 (correlation coefficient $R^2 = 0.9566$, multiple $R = 0.9781$, adjusted $R = 0.9149$, standard $e = 11.2922$, and observation (total number of data) = 27). As a result, the following equation has been obtained:

$$R\% = 8.349 + 0.667t + 2.17C \quad (9)$$

However, as is shown in Fig. 5, within 55 min of processing, the average increase in sulfur removal was 21.57% when the concentration of NaOH was increased from 5 to 10 wt. %. Moreover, for 5 and 10 wt. % NaOH within the same processing time, the increase in sulfur removal was 38 and 47%, respectively. These results showed that within the optimum processing time, the time has a predominant effect on the sulfur removal.

4.4. EFFECT OF ULTRASONIC PROCESS ON GAS OIL PROPERTIES

Slamet et al. [24] considered viscosity as the ultimate significant diesel fuel parameter due to its influence on the system of pressurized combustion. Stavarache et al. [25] reported that a method to upgrade the physical properties of diesel fuel (like viscosity) is to employ outer power convey irradiation with various origins (ultrasound, microwaves, infrared waves, ultraviolet, etc.). Some of these power origins are capable to adjust at the chemical framework of the fuel at its micronolecular level with effect on its physical characteristics. Therefore it is of importance to investigate the influence of the sonication process on some properties (e.g., viscosity, *CN*, API) of produced gas oil.

Table 5

Properties of real light gas oil feed before and after 40 min of sonication

Property	Value	
	Before sonication	After sonication
API gravity at 15.6 °C	40.1	42.547
Specific gravity at 15.6 °C	0.8246	0.8130
Viscosity, SSU	32.3	30.87
Cetane number	51.2	55.1
Initial boiling point, °C	165	155.8
Final boiling point, °C	290	280.0

Table 5 lists some properties of gas oil before and after the sonication process. As can be observed, after sonication, both the viscosity and specific gravity decreased, while the *CN* increased. This behavior is due to the collapsing of cavitation bubbles, creating shock waves, increasing the chemical reactivity in the system, formation of lighter sulfur molecules due to breakage of heavier ones. It is known that the value of *CN* is linked to the period desired for fuel to fire after injection to the burning engine. The higher the *CN*, the shorter the firing time is. *CN* increase with the increase of long straight carbon chains which produced by breaking branched carbon chain due to high-intensity ultrasonication [26]. At the optimum operating time, ultrasonication improved

gas oil properties by decreasing the density and viscosity by 1.4% and 4.42% respectively, while the *CN* increased by 7.0%. Published data [27–30] confirmed the trend of the results obtained from the present work.

4.5. FTIR SPECTRUM

The FTIR visions of the real light gas oil are seen in Fig. 6 (lower spectrum) points out the existence of mercaptans by a notable band in the domain of 2360 cm^{-1} because of the S-H. A less bushy moderate band at 1380 cm^{-1} points out the S=O asymmetrical oscillation, which bears a sign of the sulfones chlorides, sulfonates, sulfones or sulfoxides. A broad band at 3420 cm^{-1} demonstrates the existence of the HN or HO which match to the bond related to sulfonamides. The FTIR spectrum of the gas oil cured with NaOH (10%) is shown in Fig. 6 (upper spectrum). The visions indicate that bands in that domain showing mercaptans S-H (at 2370 cm^{-1}) and S=O (at 1380 cm^{-1}) are impotent in strength in (upper spectrum) comparable to the spectrum of the genuine sample.

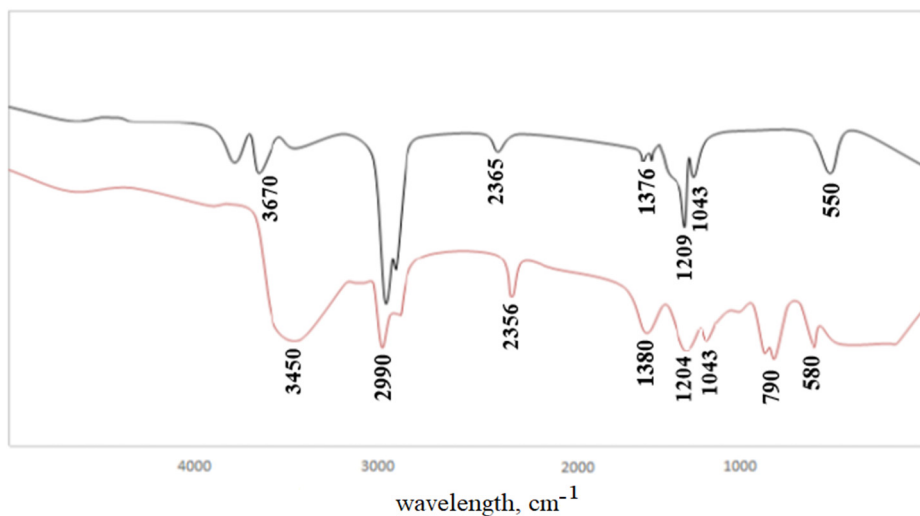


Fig. 6. FTIR spectrum of gas oil before (bottom) and after (top) treatment with 10% NaOH

4.6. ECONOMIC ASPECT

In the present study, the suggested desulfurization process was designed to operate in a continuous production mode under ambient conditions (Fig. 1). The consumption rate of inorganic liquids and sulfur removal from gas oil are considered the main factors affecting the process feasibility. Due to the density difference between gas oil ($\rho_{\text{oil}} = 0.82\text{ g/cm}^3$) and that of inorganic liquids ($\rho_{\text{NaOH}} = 1.11$, $\rho_{\text{Ca(OH)}_2} = 1.124$ and $\rho_{\text{HCl}} = 1.02\text{ g/cm}^3$), separator

(S1) worked with a reasonable efficiency which enabling inorganic liquids to be recycled to the mixing tank (V1). Consumption rates for 10% NaOH, 10 Ca(OH)₂ and 5% HCl per 100 g of desulfurized gas oil (DGO) produced were estimated by 0.97, 2.45 and 2.87 g, respectively, which equivalent to a percentage loss of ~1% of NaOH, ~2.1% of Ca(OH)₂, and ~3% of HCl with desulfurization of gas oil up to 68.0, 60.0 and 47.0% obtained at the optimum operating time of ultrasonication process using inorganic liquids of 10% NaOH, Ca(OH)₂ and 5% HCl, respectively.

5. CONCLUSION

The present work aimed to investigate the feasibility of removing sulfur from light gas oil using different types of efficient and nearly inexpensive inorganic liquids such as NaOH, Ca(OH)₂, and HCl, assisted with ultrasonication at irradiated power of 750 W with 20 kHz, in a continuous operation under mild conditions of temperature and pressure. Study of equilibrium system for the selected ternary mixtures showed that solute selectivity was inversely related to solute mole fraction. It was found that, within 40 min, 10 wt. % NaOH offered a higher sulfur removal of 68% and 48% with and without sonication process respectively. Moreover, it was shown that at optimum operating time ultrasonication not only increased the sulfur removal by 29.4% but it also improved gas oil properties by decreasing density and viscosity by 1.4% and 4.42%, respectively, while Cetane number (CN) was increased by 7.0%.

ACKNOWLEDGEMENT

The present work was completed with the assistance of the Department of Chemical Engineering, the University of Technology for providing space and facilities. Thanks are also due to the Petroleum Research and Development Center, Iraq Ministry of Oil for their cooperation.

REFERENCES

- [1] SONG C., *An overview of new approaches to deep desulfurization for ultraclean gasoline, diesel fuel and jet fuel*, Catal. Today, 2003, 86, 211–263.
- [2] GAWANDE P.R., *Desulphurization techniques for liquid fuel. A review*, Int. J. Eng. Tech., Manage. Appl. Sci., 2014, 2 (7), 121–127.
- [3] JOCHEN E., PETER W., ANDREAS J., *Deep desulfurization of oil refinery streams by extraction with ionic liquids*, Green Chem., 2004, 6, 316–322.
- [4] DUARTE F.A., MELLO P.A., BIZZI C.A., NUNES M.A.G., MOREIRA E.M., ALENCAR M.S., MOTTA H.N., DRESSLER V.L., FLORES E.M.M., *Sulfur removal from hydrotreated petroleum fractions using ultrasound-assisted oxidative desulfurization process*, Fuel, 2010, 90, 2158–2164.
- [5] SHAFEGHAT A., GHAEDIAN M., MEHRABI M., *Desulfurization of gas oil by using ultrasonic waves*, J. Petr. Res., 2015, 24 (80), 85–95.
- [6] MOCHIZUKI Y., SUGAWARA K., *Removal of organic sulfur from hydrocarbon resources using ionic liquids*, Energy Fuels, 2008, 22, 3303–3307.

- [7] LI F.T., LIU Y., SUN Z.M., *Deep extractive desulfurization of gasoline with $xEt_3NHCl_3 FeCl_3$ ionic liquids*, Energy Fuels, 2010, 24, 4285–4289.
- [8] HANSMEIER A.R., MEINDERSMA G.W., DE HAAN A.B., *Desulfurization and denitrogenation of gasoline and diesel fuels by means of ionic liquids*, Green Chem., 2011, 13, 1907–1913.
- [9] NIE Y., LI C.X., MENG H., *N,N -dialkylimidazolium dialkylphosphate ionic liquids: their extractive performance for thiophene series compounds from fuel oils versus the length of alkyl group*, Fuel Proc. Technol., 2008, 89, 978–983.
- [10] STAGNER B.A., KALICHEVSKY V.A., *Chemical Refining of Petroleum*, 2nd Ed., Reinhold Publishing Corporation, New York 1942, 217–237.
- [11] FOMIN V.A., VILDANOV A.F., MAZGAROV A.M., *Implementation demercaptanization process of butane-butylene fraction in the gas fractionation plant in Ryazan Oil Refinery*, Nefteper. Neftekhim., 1987, 12, 14–15.
- [12] AKHMADULLINA A.G., KIZHAEV B.V., NURGALIEVA G.M., *Heterogeneous catalyzation demercaptanization of the light hydrocarbons*, Nefteper. Neftekhim., 1994, 2, 39–41.
- [13] DEMIRBAS A., *Desulfurization of lignite and coal using alkaline solution from biomass ashes*, Energy Expl. Expl., 2002, 20 (5), 371–378.
- [14] AKHMADULLINA A.G., AKHMADULLIN R.M., AGADZHANYAN S.I., *New developments and implementations in the field of hydrocarbon-stock desulfurization*, Chem. Techn. Fuels Oils, 2008, 44 (6), 371–378.
- [15] DEMIRBAS A., ALIDRISI H., BALUBAID M.A., *API gravity, sulfur content, and desulfurization of crude oil*, Petr. Sci. Techn., 2015, 33 (1), 93–101.
- [16] AFSHAR A.S., HASHEM S.R., *Role and effect of temperature on LPG sweetening process*, Int. J. Chem. Mol. Eng., 2011, 5 (7), 628–630.
- [17] MELLO P.A., DUARTE F.A., NUNES M.A.G., ALENCAR M.S., MOREIRA E.M., KORN M., DRESSLER V.L., FLORESS E.M.M., *Ultrasound-assited oxidative process for sulfur removal from petroleum product feedstock*, Ultrason. Sonochem., 2009, 16, 732–736.
- [18] SHAKIRULLAH M., AHMAD I., WAQAS A., ISHAQ M., *Desulfurization study of petroleum products through extraction with aqueous ionic liquids*, J. Chil. Chem. Soc., 2010, 55 (2), 179–183.
- [19] HEINRICH G., KASZTELAN S., *Hydrotreating*, [In:] P. Leprince (Ed.), *Conversion Processes*, Editions TECHNIP, Paris 2001, 533–573.
- [20] CABO B.R., *Desulfurization of fuels with ionic liquids by extraction and oxidative extraction processes*, PhD Thesis, University of Santiago de Compostela, Santiago de Compostela 2013.
- [21] ROBBINS L.A., CUSACK R.W., *Liquid–liquid extraction operations and equipment*, [In:] D.W. Green, J.O. Maloney (Eds.), *Perry's Chemical Engineering Handbook*, 7th Ed., McGraw-Hill, 1997.
- [22] FARSHI A., RABIEI Z., *Kinetic study for oxidation of existing mercaptans in kerosene using impregnated activated carbon with MEROX catalyst in alkaline solution*, Petrol. Coal, 2005, 47 (1), 49–56.
- [23] LEERDAM R.C., *Anaerobic Degradation of Methanethiol in a Process for Liquefied Petroleum Gas (LPG) Biodesulfurization*. PhD Thesis, Wageningen University, the Netherlands, 2007.
- [24] SLAMET S., PURWANTO P., DIDI D.A., HERMA W., *Enhancing biodiesel from Kemiri Sunan Oil Manufacturing using ultrasonics*, 2nd International Conference on Energy, Environmental and Information System (ICENIS 2017), <https://doi.org/10.1051/e3sconf/20183102014>
- [25] STAVARACHE C., VINATORUM M., MAEDY Y., *Ultrasonic versus silent methylation of vegetable oils*, Ultrason. Sonochem., 2006, 13, 401–407.
- [26] THANGAVADIVEL K., MENGHARAJ M., MUDHOO A., NAIDU R., *Degradation of organic pollutants using ultrasound*, [In:] D. Chen, S.K. Sharma, A. Mudhoo (Eds.), *Handbook on Applications of Ultrasound. Sonochemistry for Sustainability*, Taylor and Francis, New York 2012, 447–470.
- [27] HAMIDI H., MOHAMMADIAN E., JUNIN R., RAFATI R., *The effect of ultrasonic waves on oil viscosity*, Petrol. Sci. Techn., 2014, 32 (19), 2387–2395.

- [28] HAMIDA T., BABADAGLI T., *Effects of ultrasonic waves on immiscible and miscible displacement in porous media*, SPE Annual Technical Conference and Exhibition, Dallas, Texas, 9–12 October 2005, <https://doi.org/10.2118/95327-MS>
- [29] BOITSOVA A.T., KONDRASHEVA N.K., KRAPIVSKY E.I., *Investigation of the effect of ultrasonic treatment on the high-viscosity oil from Yarega Field in Komi Republic (Russian Federation)*, J. Fund. Res. En. Appl., 2015, 5 (2), 1–6.
- [30] DOLLAH A., RASHID Z.Z., OTHMAN N.H., HUSSEIN S.N.C.M., YUSUF S.M., JAPPERI N.S., *Effects of ultrasonic waves during waterflooding for enhanced oil recovery*, Int. J. Eng. Tech., 2018, 7 (3), 232–236.