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Study on Desulfurization of Light Gas Oil Using Ionic Liquids Assisted with Ultrasonication

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Abstract: The present work aimed to investigate the feasibility of sulfur extraction from real light gas oil using different types of inorganic ionic liquids (ILs) assisted by ultrasonic waves in a continuous flow setup. Experimental results showed that within 30 min, 66% of sulfur was removed under mild conditions using 10 wt%NaOH assisted by ultrasonic waves. We found that ultrasonic waves not only facilitated the sulfur removal but also it improves gas oil properties by decreasing density and viscosity while cetane number (CN) showed a different trend. The authors presented a correlation of solute selectivity as a function of sulfur mole fraction.

Keywords: Ionic liquids, desulfurization, ultrasonic waves, petroleum middle distillates.

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INTRODUCTION

Desulfurization (DS) of petroleum middle distillates using an efficient cost-effective process 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 by ionic liquids. Though the HDS technique is considered useful in lowering sulfur concentrations in petroleum middle distillates, some sulfur compounds 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). The key is how to select proper adsorbents which cover molecular sieves, activated carbon, ion-exchange resin, and activated carbon fibers (2) to realize the desulfurization process. Jochen *et al*. (3) suggested that EDS with ILs is a good alternate for deep HDS of diesel oil. Duarte *et al*. (4) reported that despite the significant advantages provided by the use of ultrasound, in the last years, few studies related to its direct application are available in the petroleum industry. Shafeghat *et al.* (5) used ODS assisted by ultrasonic waves to remove sulfur from gas oil and gasoline.

The ILs have withdrawn remarkable interest as extractive materials for DS of middle distillates (6-8), or as an end-step operation for the HDS process (9). Many consider ILs as green chemical solvents with unique physical and chemical properties, like insignificant vapor pressure, high thermochemical stability, and readily be recycled. Moreover, they have high relevance with sulfur-compounds (S-compounds), in particular with aromatic S-components, and have good miscibility with middle distillates, which nominates ILs as good extracting agents for desulfurization of fuels (10-11). Many organic ILs are expensive, for example, imidazolium-based ILs (12). Fluoride based ILs can absorb humidity and produce toxic hydrogen fluoride known as a defective product (13-14). In the current study, we investigated the feasibility of usage effective-cost ILs in a continuous process for extractive desulfurization (EDS) of gas oil under ambient conditions. Another objective was to study the equilibrium behavior of sulfur compounds in studied ternary mixtures.

MATERIALS AND METHODS

Materials

The authors purchased high purity chemicals of sodium chloride (99.0 wt% min), sodium hydroxide (> 98%), and calcium hydroxide (> 96%) from Sigma Aldrich, India. We ordered hydrochloric acid (36%) from Merck, Germany. We also obtained light gas oil from Al-Daura Oil Refinery, Baghdad. Table 1 lists the specifications of real gas oil.

Table 1. Properties of real light gas oil feed (Al-Daura Oil Refinery, Baghdad).

Property	Method of analysis	Value
API@15.6 ^{0}C	ASTM D1298	40.1
Sp.gr @ 15.6 ^{0}C	ASTM D1298	0.8246
Sulfur content (ppm)	ASTM D 5623	2140
Cetane number	ASTM D 7170	51.2
Distilled (vol.%) in crude oil	ASTM D 86	17.1
I.B.P (°C)	ASTM 6352	195
E.B.P (°C)	ASTM 6352	322

Experimental procedure for selectivity and partition coefficient

The authors installed a batch setup to predict the behavior of selectivity and the partition coefficient for the studied systems. Mixtures of ternary systems components (IL + S-compound + oil) in the immiscible region were mixed in a 50 mL glass vessel immersed in a water bath and connected to a recirculation Chiller type Accel 250 LC from Thermo Scientific, to control the vessel temperature at (25±1 °C). The mixtures were agitated using a magnetic stirrer for 1 h, and then let stabilize for a minimum of 2 h. We considered that these periods being enough to attain a proper equilibrium between constituents producing a pure yellow aqueous solution. Then, we used syringes to obtain samples from each layer of the mixture. GC was used to measure the weight fractions of oil and sulfur compounds, and we tabulated the results.

Experimental setup for continuous operation

Of each ionic material (sodium hydroxide, calcium hydroxide, and hydrochloric acid), three different concentrations (5, 10, and 15 wt%) were prepared separately in 100- mL glass beakers. 50 mL of gas oil was taken in an Erlenmeyer flask and added to each prepared ionic aqueous solution in a 250 mL-cylindrical glass Flask (V1), respectively. The mixing was applied at 300 rpm by an electric mixer type (IKA RW 20, Cole-Parmer). We selected this mixing speed as the optimum value after a series of mixing experiments. We then transferred the mixture to another 250- mL glass cylindrical vessel (V2), which contained an ultrasonic generator (Model VCX-750, vibra-cell, Sonics) whose probe immersed in the mixture. Table 2 lists the characteristics of the ultrasonic probe. We kept the temperature of the sonication vessel at 40 °C because, above this temperature, extraction of S-compounds becomes increasingly more inadequate (15). The authors sonicated the mixture for 30 min with a 4 min of a break between sequential ultrasonic periods of 5 min. As the sonication process continued, samples for sulfur determination were drawn periodically by a syringe. We neglected the influence of sampling on mixture volume because of the small sample amounts (≤ 1.0 mL per sample). After ultrasonic periods of 30 min, we conveyed the mixture to a funnel of liquid-liquid separation (S1) to let separate the denser layer from the oil light layer. Then the oil light layer was transmitted to a 250-mL glass beaker (V3) where a neutralizing agent was added (if required). We then utilized a pH meter type (On-line pH meter Model Excel 25PH/mV/ISL) to monitor the pH of the solution in V3. We transferred the neutralized solution to a high-speed centrifuge type (Centrisart® D-16C, Sartorius Company). The authors analyzed the lighter stream (desulfurized gas oil) for the concentration of total sulfur utilizing a sulfur analyzer type (XOS, Model: Sindie OTG). We rechecked the analysis result with GC. Figure 1 shows a plot of the experimental setup in **Figure 1**.

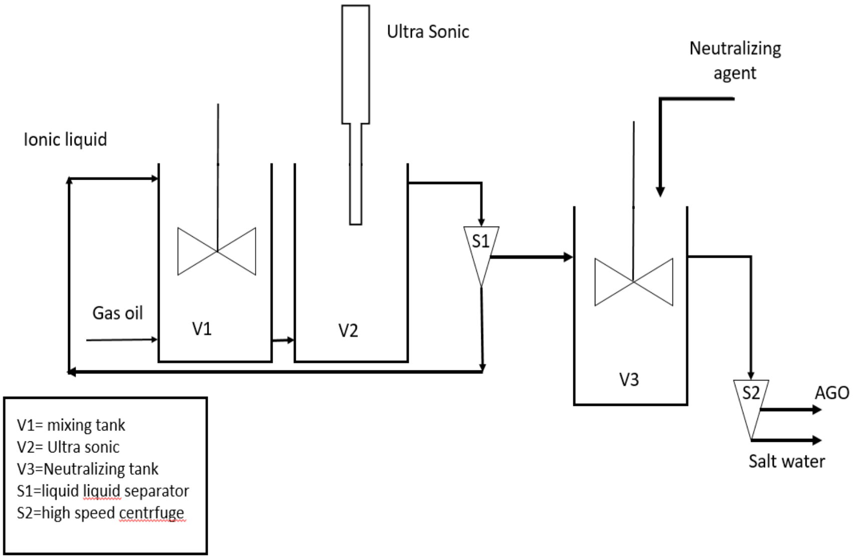


Figure 1: Experimental setup of the continuous extractive desulfurization process.

Table 2: Specifications of the ultrasound probe.

Characteristics	Values
Power Output	750 Watts
Frequency	20 kHz
Standard Probe Size	Diameter: 13 mm ; Length:136 mm
Probe Material	Titanium Alloy Ti-6Al- 4V
Processing Capacity	10 mL – 350 mL

Method of analysis

The fractions of the samples in the ternary systems were measured by GC type ta3000 (AMETEK® Process Instruments), equipped with a column SPB-1 SULFUR 30 m x 0.32 mm ID 4.0 μm phase and flame ionization detector (FID). We utilized the analyzer of sulfur type (XOS, Model: Sindie OTG) to measure the total sulfur content of gas oil before and after the EDS process. (FTIR) records were carried out in the 400–4000 cm^{-1} range, using the IR Affinity-1, Shimadzu analyzer. Cetane number (CN) of gas oil was measured using near infrared diesel oil cetane number testing instrument model FDW-0371, China. Gas oil density was measured using **density meter model DDM 2909** from Rudolph Research Analytical, USA. Initial and end boiling points of gas oil were determined using distillation tester, model: PT-D1401-255 from Genius Laboratories, China.

THEORETICAL ASPECTS

It is scientifically apparent that ultrasonic irradiation can effectively improve the reaction yield in chemical synthesis. The result is cavitation when mechanical vibrations generate into the liquid as ultrasonic waves. When one subjects liquids to high-intensity ultrasonic waves, it creates acoustic cavitation. 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 in the system. During this process, short-term, localized hotspots can form. The violent collapse of each bubble causes locally high temperatures (up to 5000 K), high pressure (up to 1000 atm), and drastic liquid jets. This micro-environment, with extreme local conditions, is suitable for the creation of active intermediates permitting the reaction to progress rapidly. Moreover, ultrasonic waves may assist in increasing the formation of lighter sulfur-molecules due to the breakage of heavier ones (16).

The basis of the mechanism of extraction is on the allocation law, which states that if a liquid layer consists of two immiscible components, it subjoins 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 a stable temperature. It is supposed that the molecular structure of the material is identical in both solvents. The distribution or partition coefficient (k_d) is presented by Eq. 1 (17).

$$k_d = \frac{x_s^1}{x_s^2} \qquad \text{(Eq. 1)}$$

where x_s^1 the S-compound loading in phase 1 (i.e., IL-rich phase) and x_s^2 is the loading of S-compound in phase 2 (i.e., hydrocarbon-rich phase). As a comparative approach, the allocation parameter may be estimated equivalent to the ratio of the solubility of S-compound in the two layers. One dissolves organic sulfur components readily in the polar solvents; moreover the solvents having consanguinity for the sulfur compounds being extra beneficial in their extraction. So, we have utilized this method in the present work by applying various solvent systems at identical conditions (*e.g.,* temperature and processing time). Heinrich and Kasztelan (18) reported that mercaptans and sulfides form the main proportions of S-compounds that are present in the lighter middle distillates of petroleum. One assumes that the S-compound is soluble in the oil phase. Eqns may represent the distribution of an S-compound between an oil phase and an aqueous inorganic ionic solution. (2 – 3) following:

$$RSH_{\text{(oil phase)}} \rightleftharpoons RSH_{\text{(aqueous phase)}}$$

$$RSH_{\text{(aqueous phase)}} \rightleftharpoons RSH^{-}_{\text{(aqueous phase)}}$$

(Eq. 2)(Eq. 3).

Equilibrium 1 depends on the solubility of the S-compound in the aqueous phase and in the oil phase. Equilibrium 2 depends on the ionization constant of the S-compound and on the concentration of free hydroxide of water. Cabo (19) presented Eq. 4 to correlate to the solute distribution ratio, k_d, and selectivity, S,

$$S = \frac{x_s^1}{x_s^2} \cdot \frac{x_0^2}{x_0^1} \qquad \text{(Eq. 4)}$$

Where x_0^2 and x_0^1 are mole fractions of gas oil in phase 2 and phase 1 respectively.

RESULTS AND DISCUSSION

Selectivity and partition coefficient

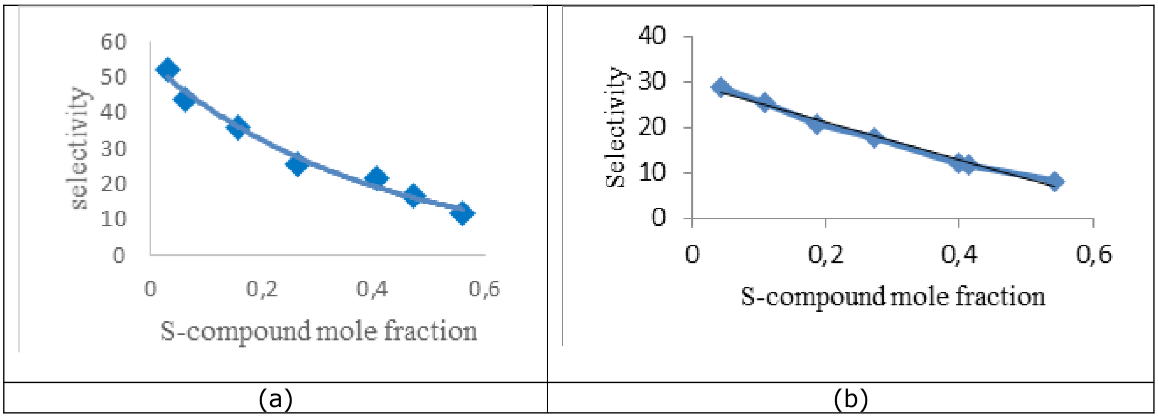
It is a well-known fact that the solute partition coefficient, k_d, and selectivity, S, are linked to the amount of solvent required for the separation (k_d) and to the number of required steps to achieve it (selectivity). Thus, they are key parameters to decide the appropriateness of a solvent as an extracting material. The k_d and S values obtained for the Liquid-liquid Equilibria data of studied systems *i.e.*, [10% NaOH + S-compound+ Oil], and [10% $Ca(OH)_2$+ S-compound + Oil] respectively are shown in Tables 3 and 4. We drew these values versus the sulfur compound's molar fraction in the oil-rich phase in **Figure 2**(a-b). The trends of S are qualitatively similar for both ILs. This figure demonstrates that the separation of S-compound from light gas oil with these ILs is favorable in terms of solubility and selectivity, especially at low mole fractions of S-compound. When we obtain higher values of k_d and S for the studied mixtures, we obtain a more efficient separation of S-compound from the oil (20).

Table 3: Experimental data of (10% NaOH + S-compound + Oil) system.

Ionic liquid-rich phase			Oil-rich phase				
x_1^1	x_2^1	x_3^1	x_1^2	x_2^2	x_3^2	k_d	S
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 of (10% $Ca(OH)_2$ + S-compound + Oil) system.

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



(a) (b)

Figure 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 the experimental data, related correlation selectivity *vs.* sulfur mole fraction in studied ternary mixtures can represent using StatPlus 6.5.1.0 software by Eqs (5-6).

for the mixture (10% NaOH +(S-compound)+ oil):

$S = 53.969\ e^{-2.552x_s}$, $R^2 = 0.9813$ (Eq. 5)

for the mixture (10%$Ca(OH)_2$+(S-compound)+ oil):

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

Effect of IL type

Figure 3 illustrates the variation of sulfur removal against processing time using various types of ILs. It is apparent that for using 10% NaOH as the processing time continues to increase from 5, 10, 15, and 20 min, the sulfur removal (%) rises steadily from 20, 35, 52, and 62%. However, as the processing time increased further from 20, 25 to 30 min, sulfur removal showed slower increases from 52, 62, and 65. Therefore, the operating system may establish an equilibrium state at the final stages of the process. For 10% $Ca(OH)_2$ and 1N HCl, the same behaviors were shown in **Figure 3** of sulfur removal versus processing time but at lower values of sulfur removals. So the aqueous solution of NaOH offers a higher affinity towards sulfur compounds. We attained the lower sulfur removal with 1N HCl. It 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 environment (21).

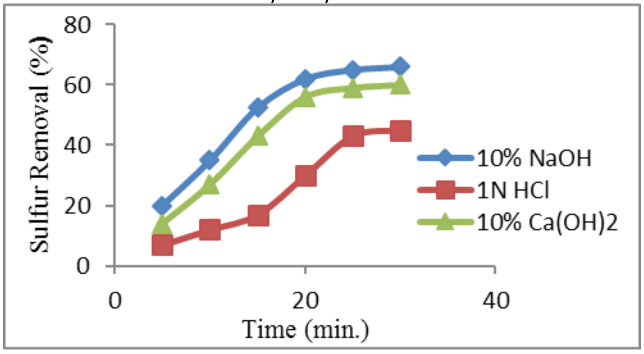
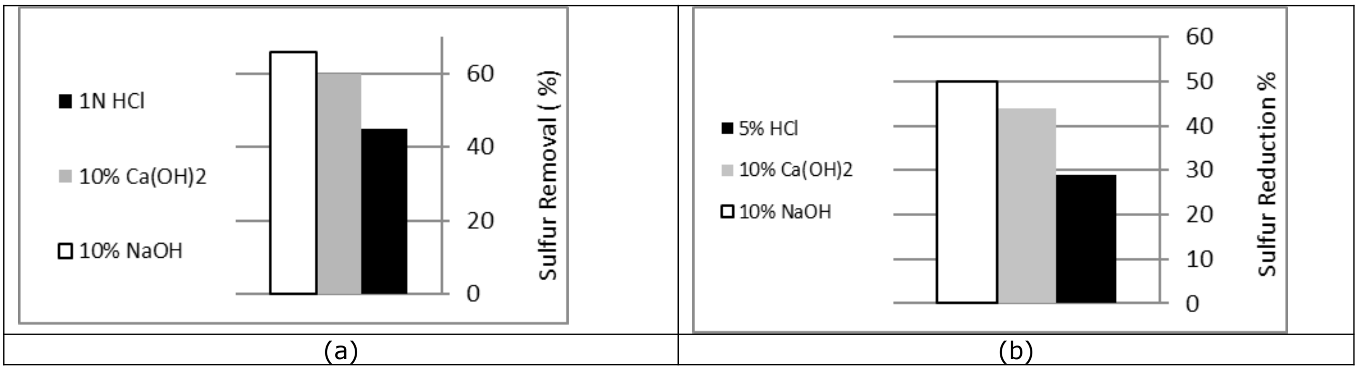


Figure 3: Variation of sulfur removal against processing time using various types of IL.

Figure 4 (a-b) shows the higher percentage of sulfur removal achieved by processing gas oil with different types of ionic liquid assisted with or without ultrasonic waves, respectively. As shown, sulfur removal (%) promoted in the arrangement of using 1N HCl < 10% $Ca(OH)_2$ < 10% NaOH. We may attribute this trend to that NaOH aqueous solution has larger consanguinity for the S-compounds in the oil distillates. It is possibly because of the acidic feature of the specific sulfur components such as mercaptans, which easily disseminates from the oil phase inside the alkaline stratum of NaOH and turns into sulfides. In the same way, the high EDS output gained with $Ca(OH)_2$ may also be elucidated fundamentally, as mentioned above. Although the alkalinity feature of $Ca(OH)_2$ is minimal than that of NaOH, yet, DS effectiveness of $Ca(OH)_2$ is analogous with that of NaOH, which proposes that calcium endures some grade of chemical charisma to mercaptans and sulfides. A comparison between **Figure 4**a and **4**b depicts the noticeable effect of ultrasonic waves on EDS of gas oil. The increase in sulfur removal due to the sonication of the IL/gas oil mixture was 24.2% for 10% NaOH, 10% Ca(OH)$_2$, and 1N HCl, respectively. It may be due to the ultrasonic waves which assist in increasing the formation of lighter sulfur-molecules due to bond breaking of heavier molecules facilitating the extraction of S-compound by ILs (16).



(a) (b)

Figure 4: Variation of sulfur removal (%) against type of ionic liquid (a) assisted with ultrasonic waves; (b) without ultrasonic waves.

Effect of IL concentration

Figure 5 shows a variation of sulfur removal against processing time using a different concentration of NaOH solution. As can be seen in the figure, for all concentrations a steep increase in sulfur removal occurred at the early stages of processing. One may attribute to the high rate of extraction, which is positively affected by the high concentration of sulfur compound existed at these stages, creating a higher driving force of sulfur concentration between the two layers. After then, as sulfur concentration decreased continuously, the extraction rate decreased correspondingly until a pseudo-equilibrium state was established at the final stage of the process *i.e.* at 25-30 min. **Figure 5** indicates that sulfur removal was positively affected by the concentration of NaOH. However, **Figure 5** depicts that there is an optimum concentration of IL which may be used to attain the best sulfur removal, after which any increase in NaOH concentration would be only costly (19).

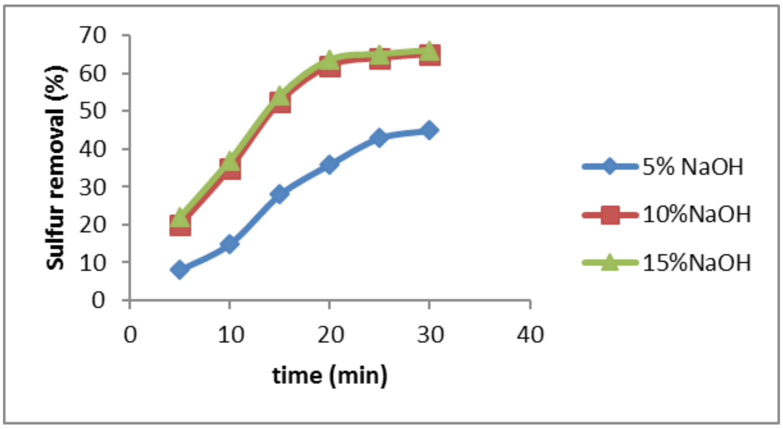


Figure 5: Influence of the concentration of aqueous %NaOH sulfur removal at various processing times.

Effect of ultrasonic process on gas oil properties

Slamet *et al.* (22) considered viscosity as the last significant diesel fuel characteristic due to its influence on the system of pressurized combustion. Stavarache *et al.* (23) reported that a method to upgrade the physical properties of diesel fuel (like viscosity) is to employ external power convey irradiation with various origins (ultrasound, microwaves, infrared waves, ultraviolet, *etc*.). Some of these power origins are capable of adjusting at the micro-molecular grade the chemical framework of the fuel, with instant 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 lists the measured properties of gas oil before and after the sonication process. As can be observed, both viscosity and the specific gravity of gas oil decreased while CN shows a different trend. This behavior is due to the collapsing of cavitation bubbles, creating shock waves, increasing the chemical reactivity in the system. Moreover, ultrasonic waves assist in increasing the formation of lighter sulfur-containing molecules due to the breakage of heavier ones. We know that the value of CN links to the period desired for fuel to fire after injection to the burning engine. The more the CN, the speedier is the firing time. This CN rises with long straight carbon chains produced by breaking the branched carbon chain due to high-intensity ultrasonic waves (24).

Table 5. Measured properties of real light gas oil feed before and after sonication process.

Property	Values	
	Before	After
API@15.6 ^{0}C	40.1	42
Sp.gr @ 15.6 ^{0}C	0.8246	0.8155
Viscosity, SSU	32.3	31
Cetane number	51.2	54.8
I.B.P (°C)	165	157
E.B.P (°C)	290	281

Effect of mixing speed

To investigate the influence of mixing speed on stabilization time and S-compound extraction, we performed a series of experiments, Figure 7 shows these trends. As can be seen in Figure 7, that a percentage extraction of S-compound of 37, 65. 4 and 66 % is attained by a stirring speed of 200, 300, and 350 rpm respectively with a stabilization time of 2 hours. The positive impact of stirring speed on percentage extraction of the S-compound may attribute to the reduction in the mass transfer limitations because of the turbulence action. However, from the power savings point of view, a stirring speed of 300 rpm is selected for operation.

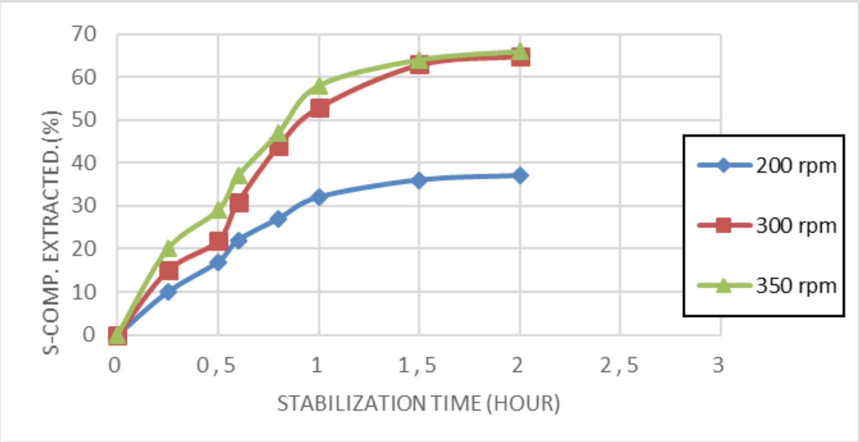


Figure 7: Effect of mixing speed on stabilization time and S-compound extraction.

FTIR spectra

Figure 7 shows the FTIR spectra of the real light gas oil, and **Figure 7** (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 thick moderate band at 1380 cm^{-1} points out the S=O asymmetrical oscillation, which bears a sign of the sulfonyl chlorides, sulfonates, sulfones or sulfoxides. A broad band at 3420 cm^{-1} demonstrates the existence of the HN or HO, which matches to the bond related to sulfonamides. The FTIR spectrum of the gas oil cured with NaOH (10%) is in **Figure 7** (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 actual sample.

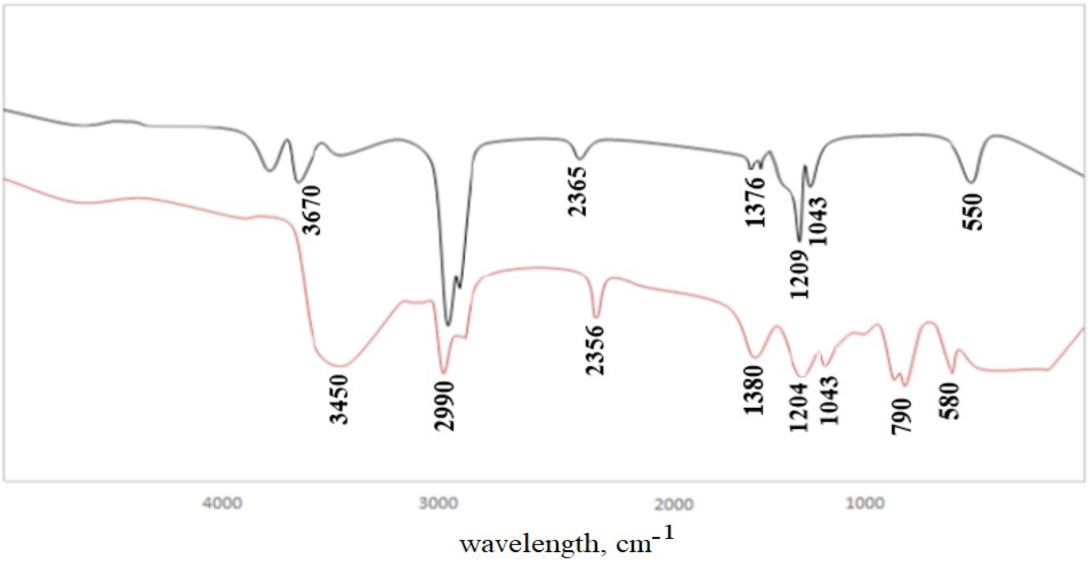


Figure 7: FTIR spectrum of gaseous oil before treatment with 10% NaOH (bottom) and after EDS with 10% NaOH (top).

EDS mechanism

Figure. 8 displays the probable pathway of sulfur extracted by NaOH**.** Since the DS of divalent sulfur of 4,6-DMDBT compounds follows the nucleophilic extraction mechanism, the extraction step began with the nucleophilic attack of electron density rich in the sulfur atom (4,6-DMDBT) to the electrophilic character of $^{-}$OH in NaOH. The (CH3)3C–O_ was then re-joined with the hydroxyl and the 4,6-DMDBT sulfoxide formed.

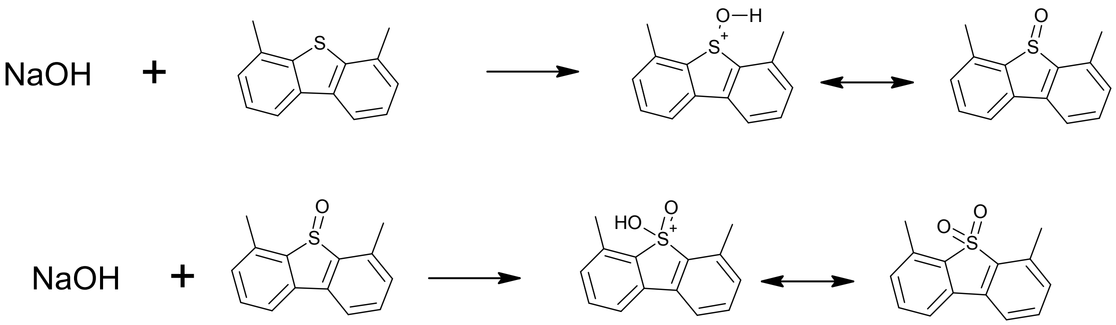


Figure 8: EDS mechanism of S-compound by NaOH.

Economic Aspects

In the present study, we designed the suggested extractive desulfurization process to operate in a continuous production mode under ambient conditions (see Fig. 1). The consumption rate of ionic liquids and sulfur removal from gas oil are considered the main factors affecting the process feasibility. Due to the density difference between gas oil ($\rho oil = 0.82\ g/cm^3$) and that of ionic liquids ($\rho_{NaOH} = 1.11\ g/cm^3$ and $\rho_{HCl} = 1.02\ g/cm^3$), separator (S1) worked with a reasonable efficiency which enabling ionic liquids to recycle to the mixing tank (V1). Consumption rates for 10% NaOH and 1N HCl per 100 g of desulfurized gas oil (DGO) produced were estimated by 0.97 and 2.87 g respectively which equivalent to a percentage loss of (~ 1%) for NaOH and (~ 3%) for HCl with desulfurization of gas oil up to 66.0 and 60.0% obtained by an ultrasonication process using ILs of 10% NaOH and 1 N HCl, respectively.

CONCLUSION

The present work aimed to investigate the feasibility of sulfur extraction from light gas oil using different types of cost-effective inorganic ionic liquids (ILs) such as NaOH, $Ca(OH)_2$, and HCl, assisted by ultrasonic waves at irradiated power of 750W with 20 kHz, in continuous operation under mild conditions of temperature and pressure. The study of the equilibrium system for the selected ternary mixtures showed that solute selectivity was inversely related to solute mole fraction. We have found that, within 30 min, 10 wt% NaOH offered a higher sulfur removal of 66% and 50% with and without sonication process, respectively. Moreover, we showed that ultrasonic waves not only increased the sulfur removal by 24.2% but it also improved gas oil properties by decreasing density and viscosity by 1.30 and 4.02% respectively while cetane number (CN) was increased by 6.3%.

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