

## DESULPHURIZATION STUDY OF PETROLEUM PRODUCTS THROUGH EXTRACTION WITH AQUEOUS IONIC LIQUIDS

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(Received: April 20, 2009 - Accepted: May 14, 2010)

### ABSTRACT

Desulphurization of jet fuel, diesel oil, heavy residue and commercial furnace oil is carried out through extraction with aqueous solutions of sodium chloride, barium chloride, sodium hydroxide, mercury chloride, arsenic trioxide, potassium iodide, lead acetate, calcium hydroxide, zinc chloride, aluminum chloride, hydrochloric acid and sulphuric acid. Among the solutions used,  $\text{HgCl}_2$  and  $\text{Ca(OH)}_2$  were found to be the most efficient for the removal of sulphur compounds from the fractions under study at 40 °C temperature and 30 min of shaking time. The total sulphur depletion of 60 % and 58 % has been achieved in case of jet fuel oil, 71 % and 62 % in case of diesel oil, 68 % and 67 % in case of heavy residue and 67 % and 69 % in case of commercial furnace oil with 10%  $\text{HgCl}_2$  and 5%  $\text{Ca(OH)}_2$  aqueous solutions, respectively.

**Key Words:** Desulphurization, Ionic Liquids, Petroleum, Environment.

### INTRODUCTION

The presence of sulphur compounds in petroleum is always objectionable due to their process and environmental problems. Sulphur occurs in many forms in petroleum like free sulphur,  $\text{H}_2\text{S}$ , mercaptans, sulphides, disulphide and thiophenes<sup>1</sup>. These compounds are undesirable in the petroleum because of their potential corrosion problems in refining process<sup>2-4</sup>. Further more, these compounds are responsible for environmental problems<sup>5-8</sup>. Keeping in view the hazardous effects of the sulphur in petroleum, much attention is being paid to desulphurization in the recent years to protect the environment<sup>9,10</sup>. Primitive techniques such as doctor sweetening was developed in 1860's, while the others developed later on were based on the oxidation of thioles to sulphides and disulphides<sup>11,12</sup>. These processes were used to eliminate the corrosion and bad odour but not the sulphur compounds. Later on desulphurization in the presence of hydrogen was practiced. In conventional hydrodesulphurization (HDS), severe operating conditions of high temperature and pressure are unavoidable. Moreover, high consumptions of hydrogen and expensive cobalt molybdenum catalysts are other disadvantages of the method<sup>13</sup>. Research is underway to improve the profitability of the process<sup>14-15</sup>. Even with the conventional processes, it is difficult to reduce the sulfur content to less than 15 ppm. Therefore, new economical and more effective methods are sought through out the world<sup>16-18</sup>.

Among the new methods, desulphurization through ionic solutions is gaining importance due to no hydrogen consumption, and much less severe conditions are required. The process is limited to desulphurization of lighter petroleum products<sup>19-21</sup>. In case of high boiling fractions, only small degree of desulphurization is achieved due to increase in viscosity which alters the interfacial properties and solubility of these fractions<sup>22</sup>. The process awaits further development for meaning full desulphurization of heavy petroleum fractions.

In the present work, we report on the application of some ionic solutions for desulphurization of various petroleum fractions. The comparative study of the various aqueous ionic solutions on the extraction of the sulphur compounds has also been carried out.

### EXPERIMENTAL

#### Sample collection and fractionation

Crude oil sample of Jhal Magsi oil field (Balochistan, Pakistan) was obtained through Oil and Gas Development Corporation Limited (OGDCL), Islamabad, Pakistan. The sample was kept in a metal can. The crude oil was distilled using distillation apparatus (Stanhope Seta limited model 11860-0) adopting IP-24/84 method to obtain distillate fractions like kerosene, diesel, heavy residue and commercial furnace oil. The fractions obtained were characterized by determining various physico-chemical parameters by employing standard ASTM and IP procedures. The analysis of Jhal Magsi crude oil distillate fractions are provided in Table 1.

**Table 1.** Physico-chemical characteristics of Jhal Magsi crude oil and its distillate fractions.

Characteristics	Kerosene	Diesel	Heavy residue	Furnace oil
Specific gravity	0.7902	0.8360	0.8635	0.9480
API gravity	45.810	37.750	32.760	17.750
Kinematic visco				
(cSt) at 100°F	2.217	3.814	4.437	5.107
Aniline point (°C)	60.0	66.0	74.0	82.0
Flash point (°C)	46.3	52.1	138.0	171.0
Ash contents (wt %)	0.065	0.05	0.205	0.33
Conradson carbon residue				
(wt %)	0.18	0.21	2.15	3.21
Total sulphur (wt %)	1.184	1.564	1.217	3.309

#### Desulphurization of fractions

10 % aqueous solutions of sodium chloride, sodium hydroxide, barium chloride, mercury chloride, potassium iodide, lead acetate, zinc chloride and aluminum chloride, 5 % aqueous solutions of arsenic trioxide and calcium hydroxide, and 1 N aqueous solutions of hydrochloric acid and sulphuric acid were prepared.

20 ml of the petroleum fraction was taken in the Erlenmeyer flask. 20 ml of the aqueous solution was added. Flask was fixed in the sonicator and the temperature was kept at 40 °C. The mixture was shaken for 30 min with a 2 min of rest between successive sonication of 5 min. After a total of 30 min sonication, the mixture was transferred to a separating funnel and was kept for 10 min to allow complete separation of lower solvent layer from the upper oily layer. The two layers were then separated and the oily layer was analyzed for the level of total sulphur.

#### Sulphur determination and fractions characterization

Total sulphur in the petroleum fractions was determined by carbon sulphur analyzer (Leco SC-144DR equipped with computer software). Total sulphur was also determined by bomb washing method (ASTM designation D 129-83 and IP designation 61/84). Infra red spectra of the fractions were taken by FTIR Spectrophotometer (Model No. FTIR-8201 ICP, Shimadzu, Japan).

## RESULTS AND DISCUSSION

### Desulphurization through liquid-liquid extraction

Liquid-liquid extraction is extensively used in the purification of organic compounds, and the same is very helpful in removing the unwanted sulphur compounds from the petroleum hydrocarbons.

The process of extraction is concerned with the distribution law or partition law which states that if to a system of two liquid layers, made of two immiscible or slightly miscible components, is added quantity of a third substance which is soluble in both layers, then the substance distributes itself between the two layers so that the ratio of concentration in one solvent to the concentration in the other solvent remains constant at constant temperature. It is assumed that the molecular state of the substance is same as in both solvents. If  $C_A$  is the concentration in the layer A and  $C_B$  is the concentration in the layer B, then at constant temperature:

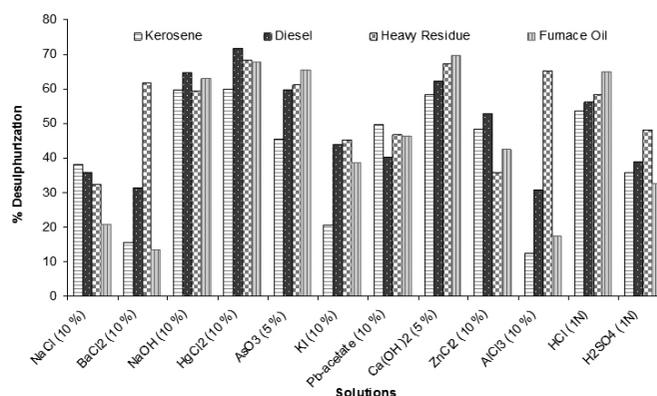
$$C_A / C_B = \text{Constant} = k$$

The constant  $k$  is termed as the distribution or partition coefficient. As very rough approximation the distribution coefficient may be measured equal to the ratio of the solubilities in the two solvents. Organic sulphur compounds are mostly soluble in the polar solvents; besides the solvents having affinity for the sulphur compounds can be more helpful in their extraction. Thus, this technique was applied in the present study by using different solvent systems at same temperature and at the same contact time.

Desulphurization of kerosene oil, diesel oil, heavy residue and commercial furnace oil was conducted by liquid-liquid extraction at same temperature (40 °C) and same shaking time (30 min). Sulphur depletion for these fractions expressed as % desulphurization is provided in the Table 2 and Figure 1 as their comparative study.

**Table 2.** % Desulphurization of distillate fraction after extraction with various ionic solutions.

Solution	% Desulphurization			
	Kersone	Diesel	Heavy Residue	Furnace oil
NaCl (10 %)	37.95	35.80	32.13	20.85
BaCl <sub>2</sub> (10 %)	15.66	31.30	61.54	13.23
NaOH (10 %)	59.62	64.81	59.33	62.95
HgCl <sub>2</sub> (10 %)	60.11	71.75	68.33	67.68
AsO <sub>3</sub> (5 %)	45.47	59.83	61.19	65.61
KI (10 %)	20.49	43.78	45.19	38.75
Pb-acetate (10 %)	49.77	40.28	46.64	46.50
Ca(OH) <sub>2</sub> (5 %)	58.36	62.13	67.22	69.77
ZnCl <sub>2</sub> (10 %)	48.25	52.89	35.86	42.44
AlCl <sub>3</sub> (10 %)	12.37	30.70	65.18	17.57
HCl (1N)	53.65	56.22	58.40	65.11
H <sub>2</sub> SO <sub>4</sub> (1N)	35.91	38.78	48.11	32.39



**Fig.1.** % Desulphurization of kerosene, diesel, heavy residue and furnace oil through liquid-liquid extraction with aqueous ionic solutions.

Table-2 displays the extraction of kerosene oil, diesel oil, heavy residue and commercial furnace oil with aqueous ionic solutions including NaCl (10 %), BaCl<sub>2</sub> (10 %), NaOH (10 %), HgCl<sub>2</sub> (10 %), AsO<sub>3</sub> (5 %), KI (10 %), Pb-acetate (10 %), Ca(OH)<sub>2</sub> (5 %), ZnCl<sub>2</sub> (10 %), AlCl<sub>3</sub> (10 %), HCl (1N), H<sub>2</sub>SO<sub>4</sub> (1N), respectively. The comparative study of desulphurization capabilities of these solutions is overviewed.

### Desulphurization of Kerosene oil

In case of kerosene oil, the highest desulphurization yields achieved are 60.11 %, 53.65 %, 58.36 and 59.61 % with HgCl<sub>2</sub> (10 %), HCl (1N), Ca (OH)<sub>2</sub> (5 %) and NaOH (10 %), respectively. In case of extraction with aqueous solutions of NaCl (10 %), BaCl<sub>2</sub> (10 %), AsO<sub>3</sub> (5 %), KI (10 %), Pb-acetate (10 %), ZnCl<sub>2</sub> (10 %), AlCl<sub>3</sub> (10 %) and H<sub>2</sub>SO<sub>4</sub> (1N), desulphurization performance is exhibited by attaining the yields of 37.95 %, 15.66 %, 15.29 %, 20.49 %, 49.7 %, 48.25 %, 12.37 % and 35.91 %, respectively.

In case of kerosene oil, the sulphur compounds mostly prevailing include mercaptans, sulphides, disulphides and thiophenes<sup>23</sup>. NaOH is extensively used in a variety of sweetening processes like caustic treatment, Merox process, chelate sweetening, inhibitor sweetening etc. which shows that NaOH has greater affinity for the sulphur compounds in the petroleum fractions. This is probably due to the acidic character of the certain sulphur compounds like mercaptans, which readily distributes from the oil phase in to the alkaline layer of NaOH and converts to sulphides<sup>24</sup>. Similarly, the high desulphurization yield obtained with Ca(OH)<sub>2</sub> can also be explained on the same basis, as mentioned above. Although the basic character of Ca(OH)<sub>2</sub> is less than that of NaOH, however, desulphurization activity of Ca(OH)<sub>2</sub> is comparable with that of NaOH, which suggests that calcium bears some degree of chemical affinity towards mercaptans and sulphides.

High desulphurization yield of HgCl<sub>2</sub> can be explained on the basis of utilization of chlorides salts of the metals for the desulphurization purposes, e.g. the use of CuCl<sub>2</sub> as slurry or fixed bed has been reported for the sweetening of gasoline and kerosene, which converts sulphur compounds (mercaptans) into sulphides and then disulphides<sup>25</sup>. In the present study, among different chloride solutions employed for desulphurization, HgCl<sub>2</sub> has shown the highest desulphurization yield. The high desulphurization activity of HgCl<sub>2</sub> may be attributed to its greater reactivity towards sulphur compounds among the other metal chloride solutions used in this study, suggesting that sulphur compounds particularly mercaptans initially shift to polar phase of HgCl<sub>2</sub> solutions, which may followed by formation of mercury thionates as gummy precipitate<sup>26,27</sup>. On the other hand, low desulphurization activity of other chlorides solutions show that after phase transfer the cations like sodium, barium, copper, zinc and aluminum fail to form metal thionates, and some of the mercaptans might transfer back to organic phase. The same reason may also be attributed to the poor desulphurization activity of KI. Lead acetate on the other hand contains highly reactive cation (Pb<sup>++</sup>) for sulphur moieties, and has been reported as desulphurization reagent<sup>28,29</sup>, hence the desulphurization capability is comparatively better than NaCl, BaCl<sub>2</sub>, AlCl<sub>3</sub> and KI.

Arsenic is also found to be highly reactive towards sulphur compounds and is reported to be used in various desulphurization processes<sup>30</sup>. In the present study, it also showed promising results. HCl is although an acidic chloride solution, but its higher desulphurization yield suggests that, due to high polarity of HCl, the polar sulphur compounds like mercaptans and sulphides may readily shifted to the acid solution, by simple extraction process. Similarly, sulfuric acid which although is extensively used for the removal of sulphur in a variety of

processes like Howe-Baker process and sulfining process<sup>9</sup>, where it is used for sweetening process in which the sulphur bearing molecules are oxidized to less harmful sulphides, but not for the removal of the sulphur bearing molecules. It might be suggested that due to high concentration, sulphuric acid failed to extract and consequently oxidized the sulphur compounds due to which it gave low desulphurization yield.

#### Desulphurization of Diesel oil

In case of diesel oil, the highest desulphurization yields of 64.95, 71.74, 59.83, 62.21 and 65.21 % are achieved with aqueous solutions of HgCl<sub>2</sub> (10 %), HCl (1N), Ca(OH)<sub>2</sub> (5 %), NaOH (10 %) and AsO<sub>3</sub> (5 %), respectively. On the other hand, relatively poor desulphurization yields of 35.80, 31.30, 43.77, 40.28, 52.89, 30.69 and 38.78 % are attained with the solutions of NaCl (10 %), BaCl<sub>2</sub> (10 %), KI (10 %), Pb-acetate (10 %), ZnCl<sub>2</sub> (10 %), AlCl<sub>3</sub> (10 %) and H<sub>2</sub>SO<sub>4</sub> (1N), respectively (Table.2).

**Table 3.** Sulphur contents of distillate fraction after extraction with various ionic solutions.

Solution	% Desulphurization			
	Kersone*	Diesel**	Heavy Residue***	Furnace oil****
NaCl (10 %)	0.96	0.99	0.75	2.55
BaCl <sub>2</sub> (10 %)	1.31	1.06	0.43	2.80
NaOH (10 %)	0.63	0.55	0.45	1.20
HgCl <sub>2</sub> (10 %)	0.62	0.44	0.35	1.04
AsO <sub>3</sub> (5 %)	0.84	0.62	0.43	1.11
KI (10 %)	1.23	0.87	0.61	1.98
Pb-acetate (10 %)	0.78	0.93	0.61	1.73
Ca(OH) <sub>2</sub> (5 %)	0.65	0.59	0.36	0.98
ZnCl <sub>2</sub> (10 %)	0.80	0.73	0.71	1.86
AlCl <sub>3</sub> (10 %)	1.36	1.07	0.39	2.66
HCl (1N)	0.72	0.68	0.46	1.13
H <sub>2</sub> SO <sub>4</sub> (1N)	0.76	0.95	0.58	2.18

\* sulphur contents of original kerosene 1.19 % wt , \*\* original diesel 1.54 % wt ,

\*\*\* virgin heavy residue 1.11 % wt and \*\*\*\* virgin furnace oil 2.23 % wt

Sulphur compounds contained in diesel oil include high molecular weight sulphides, disulphides, thiophenes, benzothiophenes and dibenzothiophenes. The results of desulphurization closely resembles to that obtained in case of kerosene oil. As mentioned earlier, NaOH has been very active in sweetening processes suggesting its high desulphurization potential that is probably attributed to its high alkaline nature. In this aqueous alkaline layer, the highly acidic sulphur compounds readily distribute from the oily phase, which can easily be extracted. The same approach can also be used to explain the high desulphurization yield attained with Ca(OH)<sub>2</sub>. HgCl<sub>2</sub> has also shown promising sulphur depletion. The reason is high affinity of metal chlorides towards sulphur compounds in term of reactivity, which has been proved in the earlier work<sup>26-27</sup>. HgCl<sub>2</sub> extraction is associated with the formation of gummy precipitate, which is probably considered to be solid mercuric sulphides produced during the reaction between mercuric chloride and mercaptans in the diesel oil. On the other hand, the poor desulphurization yields with NaCl, BaCl<sub>2</sub>, ZnCl<sub>2</sub> and AlCl<sub>3</sub> show that these solutions are unable to extract sulphides or thiophenes from organic phase and their cations lack strong interaction with sulphur moieties like Hg. Low desulphurization yields of KI and lead acetate, may also be explained on the same basis.

Promising results of sulphur depletion exhibited by arsenic oxide in case of diesel oil may be explained on the basis of reactive nature of arsenic. Similarly, the efficient performance of HCl in desulphurization may be explained in the same way as in case of kerosene oil. Sulphuric acid has been although used for the removal of sulphur in a variety of conventional processes. In the present study, sulphuric acid did not show promising results. The reason may be due to high concentration of the acidic solution which is unsuitable for dissolution of the sulphur bearing molecules, which are also itself acidic in nature.

#### Desulphurization of Heavy residue

The sulphur compounds present in the heavy residue are mostly high molecular weight sulphides and aromatic hetero cyclic sulphur compounds particularly thiophene, benzothiophene and dibenzothiophene. The percentage of aromatic sulphur heterocycles is higher than the aliphatic sulphides and mercaptans. The extraction of these compounds is relatively difficult than mercaptans. From the Table.2 it is clear that in case of heavy residue, maximum desulphurization activity is achieved with HgCl<sub>2</sub> (10 %), HCl (1N), Ca(OH)<sub>2</sub> (5 %), NaOH (10 %), BaCl<sub>2</sub> (10 %) and AsO<sub>3</sub> (5 %), which have attained 59.33, 68.35, 61, 67.22, 61.53 and 58.11 % desulphurization, respectively. While the rest of the solutions have exhibited poor desulphurization activity. In case of extraction with NaCl (10 %), KI (10 %), Pb-acetate (10 %), ZnCl<sub>2</sub> (10 %), AlCl<sub>3</sub> (10 %) and H<sub>2</sub>SO<sub>4</sub> (1N), desulphurization yields obtained were 32.13, 45.18, 46.64, 35.85, 45.18 and 48.40 %, respectively.

The data in the Table.2 shows that the desulphurization yields with NaOH and Ca(OH)<sub>2</sub> are very high, which can be explained on the basis of their highly alkaline nature which provides efficient medium for the dissolution of acidic sulphur compounds. Caustic treatment has been practiced for desulphurization of crude oil and lighter petroleum fractions earlier but not for heavy residue. The present observation evident that the same practice is also effective in the removal of aromatic sulphur compounds. High desulphurization yield with HgCl<sub>2</sub> can be explained on the basis that chlorides salts of certain metals are highly reactive towards sulphur. The extraction with HgCl<sub>2</sub> is associated with the formation of white gummy precipitate, which may probably be due to the formation of the solid mercury sulphides or mercury salts of sulphur heterocycles. The same explanation can also be given for BaCl<sub>2</sub>. The other chloride salts like NaCl, ZnCl<sub>2</sub> and AlCl<sub>3</sub> and KI on the other hands do not exhibit the same phenomenon which may probably be due to low reactivity of their cations towards sulphur compounds, due to which all these solutions showed low desulphurization yields.

The HCl solution is also found effective for desulphurization of heavy residue, which may be explained on the fact that the chloride salts of the heavier sulphur compounds are formed during the extraction process, which distribute in the polar acidic layer of the acid solution and hence easily extracted. The high desulphurization efficiency of arsenic oxide solution can be attributed to high reactivity of arsenic towards sulphur compounds, which is already reported<sup>26</sup>.

Lead is highly reactive metal towards sulphur bearing hydrocarbons particularly thioles, as its use for desulphurization of lighter hydrocarbons in different forms has been reported earlier<sup>28,29</sup>, but in case of heavy residue, the percentage of aromatic sulphur compounds is higher than thioles and sulphides. Therefore, the overall desulphurization yield is poor for lead acetate. Sulphuric acid also exhibits poor desulphurization yield which may be attributed to high concentration (acidity), which is not a suitable medium for the distribution of aromatic sulphur compounds, which requires an alkaline medium rather than an acidic medium.

#### Desulphurization of Commercial furnace oil

Like heavy residue, commercial furnace oil also contains high molecular weight sulphur compounds out of which the aromatic sulphur heterocycles e.g. thiophene, benzothiophenes and dibenzothiophenes are of main concern. Desulphurization of commercial furnace oil was also viewed. The data in the Table-2 shows that in case of furnace oil, the desulphurization yields obtained with NaOH (10 %), HgCl<sub>2</sub> (10 %), ArO<sub>3</sub> (5 %), Ca(OH)<sub>2</sub> (10 %) and HCl (1N) are quite appreciable, attaining 62.94, 67.68, 65.61, 69.76 and 65.11 % desulphurization, respectively. On other hand the poor desulphurization yield is attained with other solutions. The percent desulphurization attained with aqueous solutions of NaCl (10%), KI (10 %), Pb-acetate (10 %), ZnCl<sub>2</sub> (10 %), AlCl<sub>3</sub> (10 %) and H<sub>2</sub>SO<sub>4</sub> (1N) was 20.85 %, 13.23 %, 38.74 %, 46.49 %, 42.4 %, 17.57 % and 32.38 %, respectively.

High desulphurization yields by NaOH and Ca(OH)<sub>2</sub> can be explained as due to their capability of solubilizing the acidic sulphur compounds by providing an efficient alkaline medium. Due to high polarity of sulphur heterocycles, their distribution is more pronounced in these ionic solutions, which can be seen from their high desulphurization yield as compared to kerosene and diesel oil. Similarly, high desulphurization yield of HgCl<sub>2</sub> is attributed to its high reactivity towards sulphur compounds, which is already mentioned. Although, the formation of gummy precipitate was not observed in this case, however, the distribution of sulphur compounds was greater in this medium. Similarly, high desulphurization yield of arsenic oxide may be attributed to its very reactive nature towards sulphur compounds, forcing the aromatic sulphur compounds to aqueous solution which was easily removed by the separation of oily and aqueous media. Pronounced desulphurization shown

by HCl was also due to its high polarity on the basis of which the polar sulphur compounds were shifted to the HCl solution.

The poor desulphurization efficiency exhibited by aqueous solutions of NaCl, KI, ZnCl<sub>2</sub>, AlCl<sub>3</sub> and Pb-acetate may be explained on the basis their low reactivity, due to which the sulphur bearing heterocycles were unable to shift from its oily phase. Salts of lead are although very reactive towards thioles, forming lead thiolates, which is extensively practiced in precipitative desulphurization of lower distillates fractions, but in case of commercial furnace oil, the concentration of thioles is negligible as compared to substituted thiophenes, and the reactivity of the same metal is very low with these compounds, which in turn has resulted in poor desulphurization yield. Similarly, the low desulphurization yield obtained with the sulphuric acid can be explained on the fact that high acidity bearing sulphur compounds were unable to shift in the highly concentrated acidic solution of sulphuric acid.

#### FTIR Analysis

##### Kerosene oil

The FTIR spectrum of the original kerosene oil is provided in Fig. 2 (a) indicates the presence of marcaptans by a prominent band in the range of 2356 cm<sup>-1</sup> due to S-H<sup>31</sup>. A less intense medium band at 1376 cm<sup>-1</sup> represents the S=O asymmetric vibration, which gives an indication of the sulphones chlorides, sulphonates, sulphones or sulphoxides<sup>31</sup>. A wide band at 3417 cm<sup>-1</sup> show the presence of the NH or OH which may corresponds to the bond associated with sulphonamides<sup>31</sup>. The FTIR spectra of the kerosene oil treated with HgCl<sub>2</sub> (10 %) and Ca(OH)<sub>2</sub> (5%) are indicated in the Fig. 2 (b) and 2 (c). The spectra show that bands in this range indicating marcaptans S-H (at 2365 cm<sup>-1</sup>) and S=O (at 1376 cm<sup>-1</sup>) are weaker in intensity in (b) as compared to spectra of the original sample. While in case of spectrum (c), the band at 2356 cm<sup>-1</sup> is missing, showing substituted thiole desulphurization has occurred.

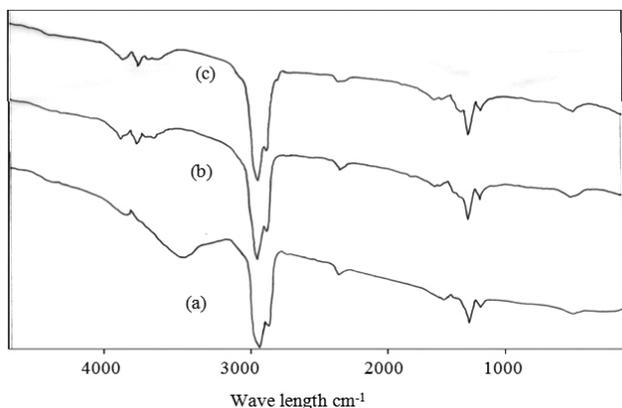


Fig.2. FTIR spectra of original and desulphurized kerosene oil (a) Virgin Kerosene (b) treated with HgCl<sub>2</sub> (c) treated with Ca(OH)<sub>2</sub>.

##### Diesel oil

The FTIR spectrum of the original diesel oil is provided in Fig-3 (a) shows a medium broad band in the range of 2356 cm<sup>-1</sup> which is given due to S-H stretching vibration, indicating the presence of marcaptans. An intense peak in the range of 1380 cm<sup>-1</sup> corresponding for S=O bond, showing the presence of the sulphones<sup>31</sup>. The evidence of the presence of sulphides is given by a weak band centered at 1204 cm<sup>-1</sup> produced by sulphidic C=S bond. An intense band in the range of 1043 cm<sup>-1</sup> indicates the presence of the sulphoxides emerging due to the S-O bonds. The spectra of the diesel oil treated with HgCl<sub>2</sub> (10 %) and Ca(OH)<sub>2</sub> (5 %) indicated in the Fig. 3(b) and 3(c), show a less intense band indicating marcaptans S-H (at 2365 cm<sup>-1</sup>) while the bands corresponding for sulphoxides S=O (at 1376 cm<sup>-1</sup>) are weaker in intensity in respective spectra, as compared with the spectrum of the original sample. While the bands representing sulphides and sulphones are totally missing.

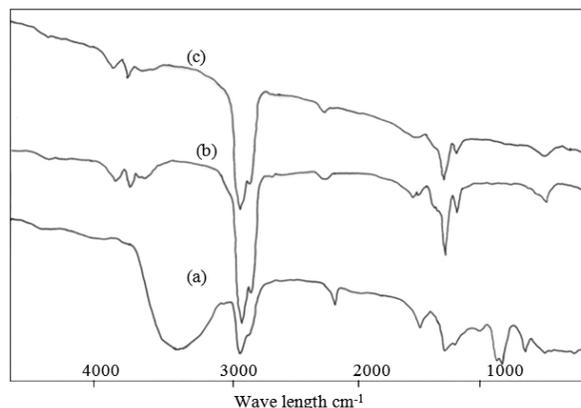


Fig.3. FTIR spectra of original and desulphurized diesel oil (a) Virgin diesel (b) treated with HgCl<sub>2</sub> (c) treated with Ca(OH)<sub>2</sub>.

##### Heavy Residue

The FTIR spectrum of the original heavy residue is provided in Fig 4 (a) shows the presence of the marcaptans giving a broad and intense band at 2343 cm<sup>-1</sup>, sulphoxides by a strong absorption band at 1374 cm<sup>-1</sup> and sulphides by a weak band slightly near 1300 cm<sup>-1</sup>. The spectra of the heavy residue treated with HgCl<sub>2</sub> (10 %) and Ca(OH)<sub>2</sub> (5 %) indicated in the Fig 4(b) and 4 (c), respectively, which show the absorption band arising due to marcaptans is reduced in intensity in the spectrum (b) and completely missing in the spectrum (c), only the intensity of the band given for S=O of sulphones is same. On the other hand, the band corresponding to sulphides is missing in both of the spectra.

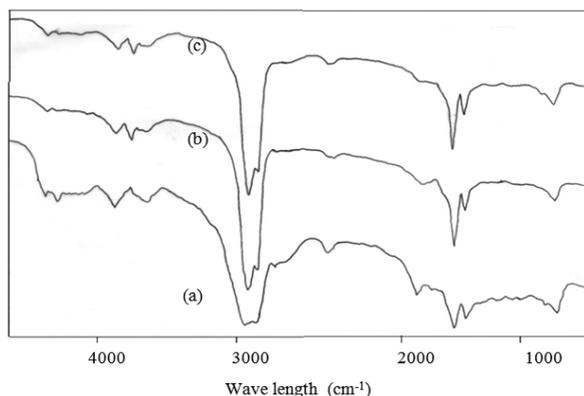
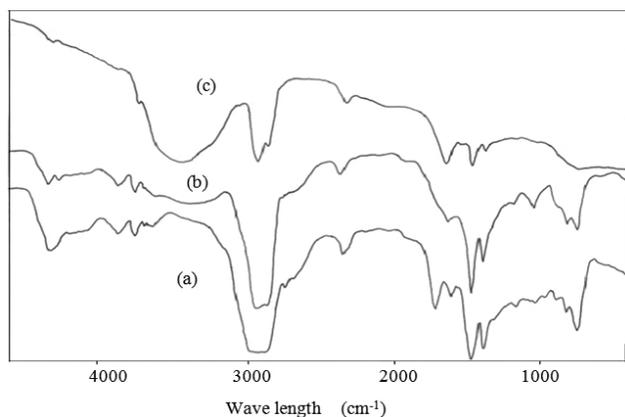


Fig.4. FTIR spectra of the original and desulphurized heavy residue (a) Virgin heavy residue (b) treated with HgCl<sub>2</sub> (c) treated with Ca(OH)<sub>2</sub>.

##### Commercial furnace oil

The spectrum of the original commercial furnace oil is given in the Fig.5 (a) showing a wide and a high intensity band at near 2355 cm<sup>-1</sup>, which characterizes the presence of marcaptans. Similarly, at position 1374 cm<sup>-1</sup>, a strong band is present which corresponds to S=O of sulphones. The presence of sulphides is also indicated by a strong absorption band at 1164 cm<sup>-1</sup>. A band lying at position 1031 cm<sup>-1</sup> corresponds to sulphoxides S=O bond. The FTIR spectra of the commercial furnace oil treated with HgCl<sub>2</sub> (10%) and Ca(OH)<sub>2</sub> (5%) represented by Fig. 5 (b), and 5 (c), respectively indicating the characteristic bands showing marcaptans configuration have relatively lower intensity, indicating the decrease in their concentration, while the characteristic absorption band for sulphones remains same in intensity and bands correspond to sulphides and sulphoxides are missing in the spectra of the treated samples.



**Fig.5.** FTIR spectra of original and desulphurized commercial furnace oil. (a) Virgin furnace oil (b) treated with  $\text{HgCl}_2$  (c) treated with  $\text{Ca(OH)}_2$ .

The above discussion clearly depicts that the liquid-liquid extraction has removed much of the sulphur in the form of sulphides, mercaptans and sulphones.

### CONCLUSION

Desulphurization of petroleum fractions by extraction with ionic solutions is an economic, simple and an efficient process. The sulfur contents of the kerosene, diesel oil, heavy residue and commercial furnace oil can be lowered upto 60, 71, 68 and 70 % respectively. The process has advantage of easy handling and use of less expensive reagents over the conventional hydrodesulphurization, oxidative desulphurization and adsorptive desulphurization etc, which make use of expensive chemicals, equipments, difficult to process and are more time consuming. The process, however, has room for improvement to achieve better results.

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