



Application on Extractive desulfurization using substituted pyrimidine ionic salt and its some transition metals complex salts

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ABSTRACT

The pyridine base ionic liquid was produced. Using various Lewis acids made from transition metal chloride, a succession of complicated salts was created from it. The substances were identified using spectroscopic and physical techniques, including magnetic susceptibility, conductivity, elemental analysis, mass spectroscopy, infrared spectroscopy, and nuclear magnetic resonance ($^1\text{H-NMR}$). Tests were conducted on [em-Py]I and its complex salts during the extractive desulfurization procedure (EDS). They are treated using a model fuel with a 2000 ppm sulfur content that was made by dissolving dibenzothiophene (DBT) in n-hexane. The GC-FID method was used to evaluate the ratio of sulfur removal. It was investigated whether it was possible to reuse the extractant more than once without regeneration and what the ideal (EDS) process conditions were. All compounds have good ability to desulfurization especially the complex salts, the ability of desulfurization increase by increasing the metal content in compounds such as Lewis acids or others.

Keywords: Extractive desulfurization, Complex salts, Lewis acids, Pyrimidine-based-ionic liquids.

تطبيقات في عمليات إزالة الكبريت الاستخلاصية باستخدام الملح الايوني المعوض للبيريدين و املاحه المعقدة لبعض من العناصر الانتقالية

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ملخص البحث:

تم إنتاج سائل بيريدين الأيوني الأساسي. و باستخدام أحماض لويس المختلفة المصنوعة من كلوريد فلز انتقالي ، تم إنشاء سلسلة من الأملاح المعقدة منه. تم تحديد المواد باستخدام تقنيات التحليل الطيفي والفيزيائية ، بما في ذلك الصفات المغناطيسية ، والتوصيل ، والتحليل العنصري ، والتحليل الطيفي الشامل ، والتحليل الطيفي بالأشعة تحت الحمراء ، والرنين النووي المغناطيسي $^1\text{H-NMR}$. تم إجراء الاختبارات على المركبات المحضرة من الملح العضوي واملاحه المعقدة لعملية إزالة الكبريت الاستخلاصية، حيث يتم معالجتها باستخدام وقود نموذجي يحتوي على ٢٠٠٠ جزء في المليون من الكبريت الذي تم تصنيعه عن طريق إذابة ثنائي بنزوثيوفين (DBT) في الهكسان ثم استخدام طريقة GC-FID لتقييم نسبة إزالة الكبريت. تم التحقيق فيما إذا كان من الممكن إعادة استخدام المستخلص أكثر من مرة دون تجديد وما هي ظروف العملية المثالية . تتمتع المركبات بقدرة جيدة على إزالة الكبريت وخاصة الاملاح المعقدة وتزداد قدرة نزع الكبريت عن طريق زيادة المحتوى المعدني في مركبات مثل احماض لويس أو غيرها.

الكلمات المفتاحية : عمليات إزالة الكبريت ، الاستخلاص، السوائل الايونية ، حوامض لويس.

INTRODUCTION

Sulfur dioxide emissions from engine combustion damage vehicles' pollution control systems and raise pollution levels. It is advisable to drastically lower the sulfur level in the fuel to maximize the effectiveness of pollution control equipment[1-3].

The Hydrodesulfurization (HDS) techniques are pretty compelling. Nonetheless, they are only occasionally used, particularly for aromatic sulfur compounds. Furthermore, the HDS procedure might be expensive when dealing with aromatic sulfur compounds. It necessitates specific pressure and temperature conditions, which affect other fuel components like olefin compounds and lower the octane rating. In addition, extreme conditions might impact the process's catalysts [4, 5].

Consequently, the kind and amount of sulfur compounds in the fuel determine the most suitable desulfurization strategy. Other techniques, such as oxidation desulfurization (ODS), adsorption desulfurization (ADS), and others, are practicable (6-8). Extraction desulfurization (EDS), particularly for aromatic sulfur compounds like thiophene, benzothiophene, and its derivatives, is an essential alternative technique. As the (EDS) procedure doesn't require any specialized equipment and is performed in a laboratory environment with the necessary temperature and pressure, the fuel's chemical structure and physical properties are not altered, and the octane number value is not decreased [6-8].

Acetonitrile, pyrrolidine, DMF, and DMSO are the most significant solvents utilized in the (EDS) procedure. Due to the proximity of polarity with some other aromatic

compounds, it is observed that the selectivity to extract the sulfur compounds is not feasible. Since the extraction procedure only uses an efficiency of up to 50%, a significant amount of solvent is required. Ionic liquids (ILs) are among the materials that can help increase the selectivity of sulfur compounds. Hence it is preferable to employ them [8, 9].

Ionic liquids are regarded as the most promising materials and solvents due to their unique viscosity, thermal stability, and solubility characteristics. The anion or the cation can be changed to regulate and alter the properties of ionic fluids. The usage of (ILs) in the (EDS) process depends critically on (ILs') solubility in the fuel. The solubility of ionic liquids with a nitrogen base in fuel, on the other hand, results in a rise in nitrogen gas emissions (NO_x), which increases pollution and raises the expense of reusing ionic liquids. For these reasons, it is necessary to select ionic liquids for (EDS) combustion byproducts that do not dissolve in the fuel [10, 11].

In order to determine which pyridine-based ionic liquids are insoluble in diesel fuel, the treated fuel was examined using the (EDS) procedure (HPLC). The outcomes demonstrated that there was no ionic liquids package. Under the same conditions, it was discovered that the effectiveness of extraction improves as the aromatic character of the sulfur compounds (thiophene (T), benzothiophene (BT), and dibenzothiophene (DBT)) increases. Ionic liquids without a transition metal typically perform poorly in the (EDS) procedure. The outcomes proved that, in identical conditions (EDS process), ionic liquids containing metals are more effective than ionic liquids alone and more effective than metal halides. Several transitional metals chloride-containing ionic liquids are employed, including non-hydrous FeCl₃ and CuCl with 3-butyl-1-methylimidazolium chloride

[BMIM]Cl (EDS). Because of the increasing acidity with metallic components, the amount of sulfur eliminated rises [12, 13].

The (EDS) technique was used in this study to evaluate certain ionic liquids based on pyridine with several transition metal halides using a model of diesel oil containing (DBT) as an aromatic sulfur component. Moreover, the ideal conditions for extractive desulfurization were established.

METHODOLOGY

Every chemical compound employed is extremely pure and comes from reliable, global businesses without any modifications. The methods that had been approved were used to prepare and characterize the chemical compounds [11, 13-15].

Synthesis of [em-Py]I: 4-Ethyl-1-Methyl-pyridinium (1)

To create the exothermic ionic liquid [em-Py]I, 4-ethyl pyridine was combined with methyl iodide in a 1: 1 molar ratio, and the reaction was continuously stirred for an hour before cooling. To increase the yield of the product, more methyl iodide is added. Following completion, a brownish-yellow precipitate was produced, and any unreacted methyl iodide was eliminated by washing the product repeatedly with hexan.

Synthesis of 4-ethyl-1-methyl-pyridinium iodide complex salts [em-Py]Fe₂ICl₆ (2), [em-Py]₂M₂I₂Cl₄ (M= Co, Ni, and Cu) (3-5):

Some may transition metal complex salts of the [em-Py]I was produced by reacting the [em-Py]I with metal chloride (CoCl₂, NiCl₂, and CuCl₂) in a ratio of 2:2 and with ferric chloride in a ratio of 1:2. (FeCl₃). The metal chloride is added gradually, the ionic liquid is

dissolved in the necessary amount of ethanol (10 ml), and the reaction is carried out by continuously stirring the mixture for two hours. After the reaction is complete, the solution is divided in half by evaporation, set aside for 24 hours, and the complex salt leads to the formation. The solution is then filtered, and the precipitate is then washed with diethyl ether.

Characterization of the compounds that were generated

A variety of physical and spectroscopic techniques were used to thoroughly characterize each of the produced compounds. The ¹H: NMR experiment was conducted with the solvent DMSO:d⁶ (Bruker Avance DPX 400 MHz). Thermo Electron Corporation's Flash EA 1112 Series measured the elements. With a Trio-1000 mass spectrometer, the GC-Mass is determined; the JASCO Canvas FT: IR 4200 analyzes the infrared spectrum (KBr and CsI desk). At the same time, the SensAA GCB scientific equipment system measured atomic absorption (Avanta 2.01 software). The electronic spectrum was measured with a Shimadzu 1800 UV-Vis spectrometer, magnetic susceptibility with a Sherwood MK1, and melting point with an electrothermal melting point of 9100.

The HANNA EC-214 conductivity meter was used to record the conductivity. The (STRUMENTAZIONE 4200 CARLO ERBA) FID-detector was used for gas chromatography, and the set temperature was: 280 °C for the take-in injector, 275 °C for the detector, and 125 °C for three minutes before ramping up to 185 °C for ten minutes for the oven. Information about gas flow rate: 1 kg/cm² for hydrogen gas, 1 kg/cm² for make-up gas (air), 1.5 kg/cm² for air, and 2 kg/cm² for helium gas. Column attributes SE-30,

length 28 M, diameter 0.50 mm, and 1.2 m film thickness. The physical information and quantitative analyses of the produced compounds are shown in Table (1).

Table (1): physical information and quantitative analyses of the produced compounds

No.	Compounds	CHN cal./(found)			M%	Cl%	Color	m.p °C	μ_{eff} (BM)	Transitions	UV band cm^{-1}
		C%	H%	N%							
1	[em-Py]I	38.57	4.86	5.62	---	---	Brown yellow	45	---	n \rightarrow π^* $\pi\rightarrow\pi^*$	28248
	C ₈ H ₁₂ IN	(38.23)	(4.62)	(5.44)							34602
2	[em-Py]Fe ₂ Cl ₆	17.20	2.32	2.12	20.02	36.55	Black red	75	5.60	⁵ E \rightarrow ⁵ T ₂	11950
	C ₈ H ₁₂ Cl ₆ Fe ₂ IN	(16.76)	(2.11)	(2.44)	(19.48)	(37.09)					12505
3	[em-Py] ₂ Co ₂ I ₂ Cl ₄	13.45	1.92	2.05	17.25	30.85	Dark olive	125	4.32	⁴ A ₂ (F) \rightarrow ⁴ T ₂ (F) ⁴ A ₂ (F) \rightarrow ⁴ T ₁ (F) ⁴ A ₂ (F) \rightarrow ⁴ T ₁ (P)	14750
	C ₈ H ₁₂ Cl ₆ Co ₂ I ₂ N	(13.60)	(1.71)	(1.98)	(16.68)	(30.10)					16500
4	[em-Py] ₂ Ni ₂ I ₂ Cl ₄	13.75	1.82	2.20	17.15	30.05	Dark Olive	82	3.75	³ T ₁ (F) \rightarrow ³ T ₂ (F) ³ T ₁ (F) \rightarrow ³ A ₂ (F) ³ T ₁ (F) \rightarrow ³ T ₁ (P)	12500
	C ₈ H ₁₂ Cl ₆ Ni ₂ I ₂ N	(13.61)	(1.71)	(1.98)	(16.62)	(30.12)					14200
5	[em-Py] ₂ Cu ₂ I ₂ Cl ₄	12.90	1.80	2.30	16.85	30.20	Dark Brown	138	2.40	² T ₂ \rightarrow ² E	14300
	C ₈ H ₁₂ Cl ₆ Cu ₂ I ₂ N	(13.42)	(1.69)	(1.96)	(17.76)	(29.72)					14300

DISCUSSION AND ANALYSIS

Ionic liquid characteristics and its complex salts fine and the mixing ratio of metal chloride have been determined. The dibenzothiophene (DBT) content of the model fuel oil was (2000 ppm), and it was made by dissolving (DBT) in n-hexane by weight %. All of the produced compounds were employed in the (EDS) procedure, which involved mixing salts with model fuel in a 100 ml quick-fit conical flask for a particular amount of time (SK-L180) at 25°C. Pro linear array laboratory shaker (350 r/min) utilized for shaking to do

systematic tests with various times and concentrations and to optimize the optimal conditions. GC-FID equipment was used to measure the concentration of (DBT) before and after the treatment; hexadecane C_{16} was utilized as the standard.

Analysis of (EDS) optimization conditions

The model oil was subjected to a number of reaction circumstances (concentration, duration, and temperature) in order to optimize the ideal conditions for the (EDS) process. To select the best compound, 10 ml of 2000 ppm (DBT) was tested with 0.05 g of extractant mixed in 5 ml DMSO with 30 minutes of shaking. All experiments were conducted at 25°C. The results of the (EDS) under the given conditions are shown in Figure (1).

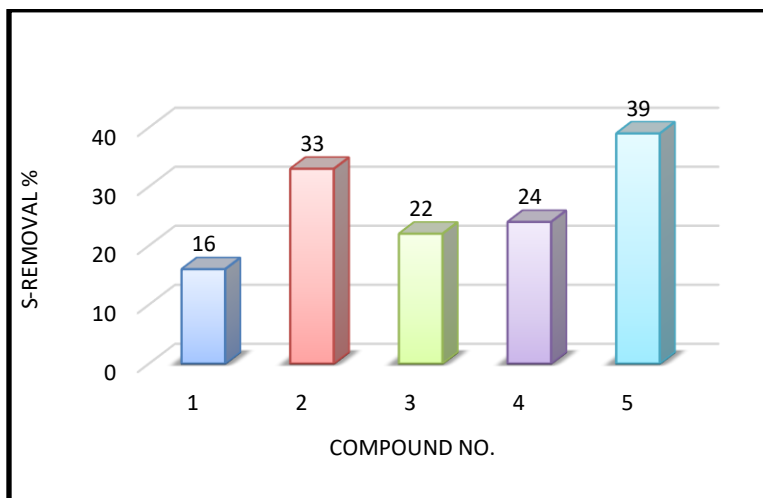


Fig. 1. Desulfurization process of prepared compounds (1-5)

According to the results in Figure (1), the [em-Py]I (1)(IL) gave 16% of sulfur removal because the proposed removal mechanism depends on the interference of aromatic electrons in the sulfur compounds with their counterparts in a ring Pyridine (-interactions),

which depends on electron density. Ionic liquids of pyridine are one of the crucial extracting factors used in desulfurization processes [16, 17]. As all the compounds under study share the same cation, the extractant factor efficiency depends on the type of cation and the type of anion. The anion is hence responsible for the variation in desulfurization performance. It is evident from a comparison of the outcomes that the complex salts are more effective than the ionic liquid alone. In addition to the ionic liquid, Lewis acids (metal chlorides) also function as extraction agents. All desulfurization optimization condition have shown in Figures 2-4.

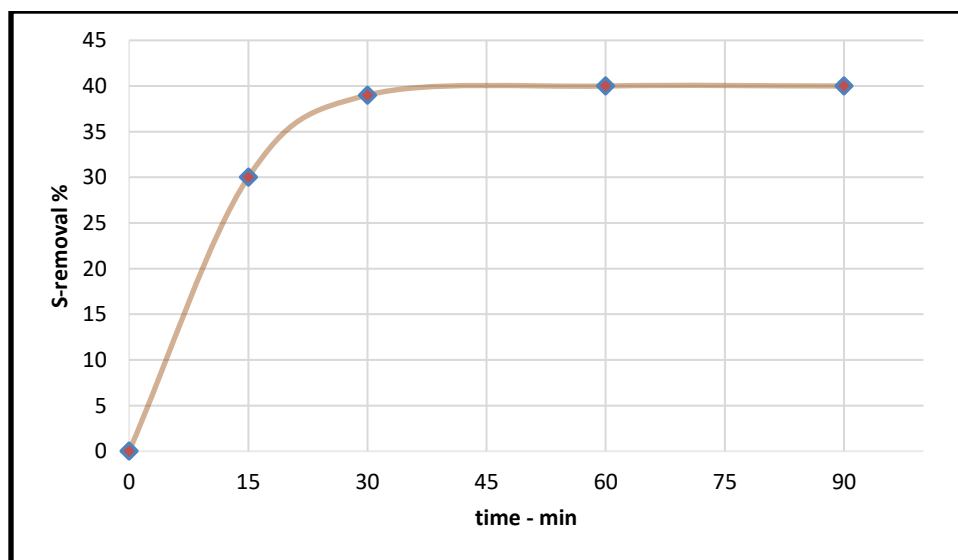


Fig. 2. Time effect on the extraction process

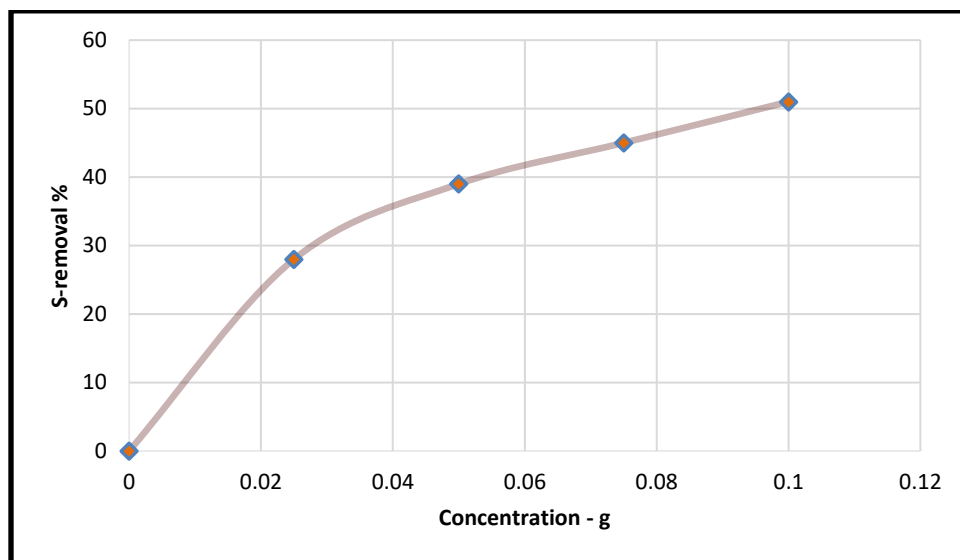


Fig. 3. Concentration effect on the extraction process

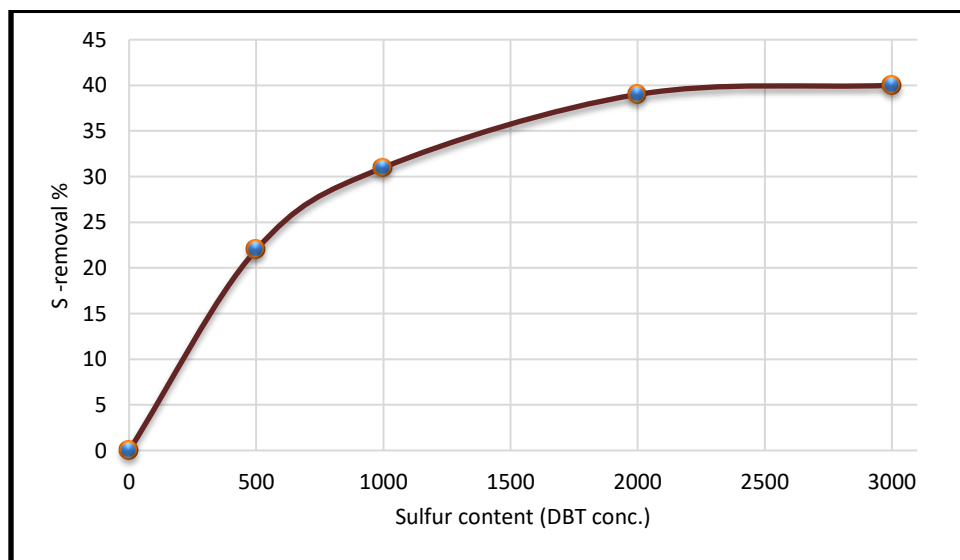


Fig. 4. DBT concentration effect on the extraction process

The hypothesized mechanism is the interaction of the metal (M= Fe(II), Ni(II), Co(II), and Cu(II)) and the halide linked to the metal with the sulfur and aromatic electrons

in sulfur compounds [17, 18]. Ionic liquids play a significant role in desulfurization processes, and Lewis acids generally perform less well than complex salts in this regard [19, 20]. According to the statistics, the copper complex salts $[em-Py]_2Cu_2I_2Cl_4$ have been selected for research in the best condition (S-removal 39%) [6, 7, 15]. We see that lengthening the period improves the extraction process' effectiveness, but this benefit is just temporary. The effectiveness of the sulfur removal process is improved by the rise in complex salt concentration, but there are very few differences, and it is not economically viable. Moreover, raising the sulfur level marginally improves the efficiency of the extraction process. The capacity of complex salts or ionic liquids to be reused repeatedly without regeneration may be adversely affected by the use of high sulfur content solutions. It is feasible to propose that (duration = 30 minutes, the complex salt concentration of 0.05 g, and sulfur content (DBT) is 1000 ppm) are the ideal conditions for the extraction procedure.

CONCLUSION

Particularly those containing Lewis acids, the newly created ionic liquids made from pyridine-base compensators demonstrated potential efficacy in the (EDS) procedure (transition metal chlorides). The findings demonstrated that the extraction process became more effective when the concentration of the extracted material, the extraction period, and the sulfur concentration in the oil model all increased. The study also demonstrated the feasibility of reuse, but with lower (EDS) efficiency, of the ionic liquid and its complex salts, at the experimental conditions utilized in the extraction sulfur removal methods.

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