

Composition, process and apparatus to remove sulfur from refined crude oil fraction**DESCRIPTION**Field of the invention

- 5 The present invention relates to a composition, a process and an apparatus to remove sulfur from refined crude oil fraction, in particular from heavy fuel oils, more in particular from fuel oils used in marine transportation.

Background of the invention

- 10 Crude oil is a complex mixture of hydrocarbon compounds, generally viscous, dark greenish-brown fluids due to the variety of compounds present in them. The physical properties including viscosity, volatility and density, vary considerably depending upon the source. The proportion of elements in crude oil generally varies in the following ranges: carbon (83-87%), hydrogen (10-14%), sulfur (0.02-8%), nitrogen (0.1-2%), oxygen (0.05-1.5%) with small quantities of metallic constituents such as
- 15 vanadium and nickel which are less than 1000 ppm. Sulfur, oxygen, nitrogen and metals make up most impurities found in crude oil. The sulfur content of crude oil is an important characteristic which effects the oil price.

- Crude oil can be separated into different boiling point fractions, common refined fractions of crude oil include gasoline, kerosene, diesel oil, heavy oil, and lubricating oil. The refined fractions derived from
- 20 crude oil have physical and chemical characteristics that differ according to the type of crude oil and the subsequent refining processes. Generally, as the fraction becomes heavier a) the concentration of sulfur containing species increases; b) more of the sulfur is contained in thiophenic structures; c) there is an increase in fouling species, such as metals and coke precursors; d) the density, molecular mass, boiling point temperature, and viscosity increase; e) increasing asphaltene content
- 25 and precipitation tendency are observed.

- The refined crude oil fractions are commonly used as energy resource and as fuel in the transportation sector, the last one representing around 20% of the global energy consumption and is the biggest consumer of oil in the world. Sulfur contained in the refined crude oil fraction is converted by combustion to SO_x, which is a major source of acid rain, thus the presence of sulfur species is
- 30 clearly a major issue in air pollution, airborne particulate emission and public health.

Specifications that govern fuels, in particular transportation fuels, have over the years become increasingly stringent with respect to sulfur content. For environmental protection purpose, many countries have mandated reduction of sulfur level in diesel and gasoline fuel down to 10 ppm. Moreover, the International Maritime Organization (IMO) announced the implementation of a global

sulfur limit of 0.5% m/m (mass/mass) in ship fuel by 2020. Therefore, to continue using refined fractions of crude oil it is urgent to set up efficient and affordable desulfurization procedures.

Many fuel desulfurization methods are known, such as catalytic hydrodesulfurization (HDS), extractive desulfurization, either with traditional solvents and ionic liquids, oxidative desulfurization, biodesulfurization and desulfurization through alkylation, chlorinolysis, and by using supercritical water. None of the methods reported above are able to eliminate completely S-compounds from fuels.

Commercially, catalytic methods such as hydrodesulfurization (HDS) and some chemical processes for sulfur compounds reductions are the most commonly applied techniques. In the HDS technology the fuel is heated and mixed with H₂ gas before being fed into a fixed bed reactor that contains pelleted catalyst known as the "hydrotreater". The operational temperature of the hydrotreater is commonly in the range of 300-380 °C and the pressure is above 30 bar, thus this method requires high energy and consumes large amount of hydrogen.

Alternative methods to classical HDS processes include extraction, oxidation, precipitation, adsorption, distillation and alkylation. Extractive desulfurization (EDS) depends upon the different partitioning of sulfur compounds between the organic phase and the extractant phase. EDS does have some advantages in that it is simple and can be carried out at moderate conditions in term of pressure and temperature, without using a catalyst or hydrogen gas. The selectivity of an extractive solvent is an important factor in EDS design as it controls efficiency, reusability and recyclability. In petroleum and hydrocarbon industry, various solvents such as ethers, amines in alcohols and other volatile organic compounds have been used. Conventional solvents have limitations in terms of environmental issue and recycle ability, as a difficulty with the technique is regenerating the extractive solvent.

Ionic liquids (IL), also called liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts or ionic glasses are a new class of outstanding good solvents miscible with water or organic solvents, they can be liquid at temperatures of -96°C and some are liquid at over 400°C. Ionic liquids' low volatility makes them desirable substitutes for volatile organic compounds (VOCs). ILs consist of organic cations, such as ammonium, choline, imidazolium, phosphonium, pyrazolium, pyridinium, pyrrolidinium, quinolinium and sulfonium, and a wide range of anions such as halides, tetrafluoroborate, hexafluorophosphate, bistriflimide, triflate and tosylate.

Recently, researchers have used ILs for extractive desulfurisation (EDS) in place of molecular solvents. For example, the use of imidazolium-based ion liquid 1-butyl-3-methylimidazolium hexafluoro phosphate [BMIM]PF₆ or 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM]BF₄ as extractive agents for the removal of S-compounds from model fuels as well as real fuels such as

diesel and gasoline has been described in Dharaskar, S. A. et al in 3rd International Conference on Chemical, Agricultural and Medical Sciences (CAMS-2015) Dec 10-11 Singapore (<http://dx.doi.org/10.15242/IICBE.C1215007>). The diesel/IL mass ratio as well as the gasoline/IL mass ratio reported therein is 5:1; the S-removal % is comprised between 41.5% and 61.1%.

5 The use of 1-ethyl-3-methylimidazolium diethylphosphate [EMIM]DEP in the desulfurization of diesel oil has been described by Seeberg, A. J. et al., in Green Chem (2010) 12: 602-608; the authors have found that the efficiency of the extraction increases if the S-species are previously oxidized to the corresponding sulfoxides and sulfones. The diesel/IL mass ratio reported therein is 1:1.

Heavy Fuel Oil (HFO) is characterized by a high content of sulfur compounds and by the refractory
10 nature of the sulfur compounds present in the oil. Moreover, HFO has high viscosity and high boiling point. Since heavy fuel oils generate high calorific value and are relatively inexpensive, a large amount of heavy fuel oil is consumed all over the world for facilities in various industries including stationary combustion for the production of steam for industrial uses or for generating electricity. Heavy fuel oil is also used in marine transportation.

15 As reviewed by Javadli, R et al. in Appl Petrochem Res (2012), 1:3-19, few of the known technologies are viable and/or efficient for the desulfurization of heavy oil, mainly due to the properties of heavy oil itself. Javadli et al. reports that although ionic liquids have a high distribution coefficient for sulfur compounds such as dibenzothiophene in model mixtures, the distribution coefficient in real straight run distillate is rather low, and even worse in heavy fuel oils; therefore,
20 ionic liquid are not ideal solvents for extractive desulfurization of real straight run distillates, in heavy oil the situation becomes worse. Moreover, as ionic liquids are high boiling solvent, the recovery of extracted sulfur compounds is more challenging than with organic solvents. For example, direct removal of sulfur compounds from ionic liquids by distillation is not applicable to heavy oil as the boiling point of heavier organosulfur compounds present in the heavy oil, such as alkylated
25 dibenzothiophenes, are high (>340°C) and it would require vacuum distillation. Re-extraction of sulfur compounds with low-boiling-point solvent would require an additional separation step. Addition of water to ionic liquids to reduce the distribution coefficient of sulfur compounds in ionic liquids requires the final removal of the water, a step which requires energy consumption.

According to Javadli et al. there are no reports on the extractive desulfurization of heavy oil by ionic
30 liquids. Javadli et al. teaches that the approach with the best chance of leading to a breakthrough in desulfurization of heavy oil is autoxidation followed by thermal decomposition of the oxidized heavy oil; there is also scope for synergistically employing autoxidation in combination with biodesulfurization and hydrodesulfurization.

The effective desulfurisation of the refined crude oil fractions need to 1) reduce the amount of pollutants in air, 2) employ the minimum energy during the desulfurisation process), 3) have a minimal effect on the price of the fuel.

5 In view of the above, there is still the need to find improved methods for desulfurization of refined crude oil fractions, in particular for desulfurization of heavy fuel oil, more in particular from fuel oils used in marine transportation.

Summary

10 The Applicant has faced the problem of improving the desulfurization of refined crude oil fractions and has found a composition comprising specific ionic liquids which is useful for extractive desulfurization of such oil fractions; surprisingly this composition is useful also for the extractive desulfurization of oils having an high sulfur content such as heavy fuel oil, in particular marine fuel oil.

15 As will be discussed deeply in the experimental part, the Applicant has found that the ionic liquids composition according to the invention is able to effectively remove sulfur from marine fuel oil by extraction. In particular, the Applicant has found that desulfurization of marine fuel oil by extraction with the ionic liquids composition according to the invention in combination with specific process conditions is able to remove more than 90% of the sulfur from marine fuel oil without the addition of any oxidizing agent. For example, without the addition of a peroxide, such as hydrogen peroxide,
20 sodium peroxide or an organic peroxide. Without being linked to any theory, the Applicant speculates that the specific ionic liquid composition of the invention at the specific process conditions exercises itself an oxidizing action.

Moreover, the ionic liquid composition of the invention is capable of being reused multiple times, until a maximum of 5 times.

25 It is thus an object of the present invention to provide a ionic liquid composition designed to improve desulfurization of refined crude oil fractions with respect to the prior art.

It is also object of the present invention to provide a process and an apparatus for desulfurization which allow to improve desulfurization of refined crude oil fractions with respect to the prior art.

It is in particular object to improve desulfurization of heavy fuel oil for marine transportation.

30 In particular, it is object of the present invention to increase the amount of sulfur removed by extraction with the ionic liquid composition.

Another object of the present invention is to shorten the extraction time.

It is also object of the present invention to reduce costs related to desulfurization of refined crude oil fractions.

These and other objects are achieved through a ionic liquid composition, a process and an apparatus designed to lower the concentration of both heavy metals and sulfur within crude oil fractions, in particular heavy fuel oil, in particular marine fuel products. The working principle is based on emulsification with ionic liquids containing specific task acids. Once a selected quantity of fuel and ionic liquids are blended and satisfactory emulsified, it is passed through a catalytic reactor. The catalytic reactor/process is arranged inline between a mixing tank and a settling tank. The catalytic process binds heavy metals including all sulfur to the ionic liquids. Due to difference in gravity, the emulsion is left to settle in a separate tank. When settled, the processed oil is transferred to a service tank or separate clean storage tank for use when needed. The settled ionic liquids containing heavy metals and sulfur is transferred to a separate flashing unit. The flashing separates the ionic liquids from the heavy metals and sulfur, which is left as a sludge residue within the flashing unit. The ionic liquids are capable of being reused multiple times. The sludge residue is transferred to holding tanks or to separate drying and bagging unit for further handling.

In a first aspect, the present invention relates to a ionic liquid composition comprising or consisting of two or more compounds having

- an imidazolium cation substituted by one or more straight or branched C₁-C₆ alkyl group and
- an anion selected from the group consisting of R₅COO⁻, Cl⁻, Br⁻, [BF₄]⁻, [PF₆]⁻, [SbF₆]⁻, [R₆SO₄]⁻, [OTs]⁻, [OMs]⁻, wherein R₅ is C₁-C₆ alkyl, C₃-C₈ cycloalkyl, benzyl, C₂-C₆ alkenyl, and R₆ is C₁-C₆ alkyl.

In an aspect according to the first aspect, the imidazolium cation is substituted in position 1 and 3 by a straight or branched C₁-C₆ alkyl group, more preferably is substituted in position 1 by butyl and in position 3 by methyl.

In an aspect according to the first aspect, the anion is selected from Cl⁻, [BF₄]⁻ and [PF₆]⁻.

In an aspect according to the first aspect, a suitable ionic liquid is 1-butyl-3-methyl imidazolium hexafluoro phosphate.

In an aspect according to the first aspect, another suitable ionic liquid is 1-butyl-3-methyl imidazolium tetrafluoroborate.

In an aspect according to the first aspect, a further suitable ionic liquid is 1-butyl-3-methyl imidazolium chloride.

In an aspect according to the first aspect, the composition comprises or consists of:

- 1-butyl-3-methyl imidazolium hexafluoro phosphate,
- 1-butyl-3-methyl imidazolium tetrafluoroborate, and
- 1-butyl-3-methyl imidazolium chloride.

In an aspect according to the first aspect, the composition comprises or consists of:

- from 30 to 50 % by volume, such as from 35 to 44 % by volume or from 40 to 45% by volume of 1-butyl-3-methyl imidazolium hexafluoro phosphate,
 - from 20 to 30% by volume, such as from 22 to 27 % by volume or from 26 to 29% by volume of 1-butyl-3-methyl imidazolium tetrafluoroborate,
 - 5 - from 25 to 35% by volume, such as from 26 to 29 % by volume or from 28 to 32% by volume of 1-butyl-3-methyl imidazolium chloride
- with respect to the total volume of the composition.

In an aspect according to the previous aspects, the volume ratio between 1-butyl-3-methyl imidazolium hexafluoro phosphate, 1-butyl-3-methyl imidazolium tetrafluoroborate and 1-butyl-3-methyl imidazolium chloride is comprised between 1:0.63:0.74 and 1:0.61:0.66.

The composition does not require an oxidizing agent.

The composition does not require a metal salt, e.g. a salt of a Group IB, IIB, VIB, or VIIIB metal, such as a salt of copper, nickel, zinc, cobalt, molybdenum, silver or palladium.

The composition may additionally comprise water (e.g. demineralized water) and/or an organic solvent (e.g. methanol). The organic solvent may be polar. Suitable organic solvents include methanol, ethanol, propanol, butanol, acetone, butan-2-one, tetrahydrofuran, methyl acetate, ethyl acetate, and/or acetonitrile).

The two or more compounds may constitute at least 0.5%, at least 1% at least 3%, at least 5%, at least 10%, at least 20%, at least 30%, at least 50%, at least 70%, at least 80%, at least 90% at least 95%, at least 97%, at least 98% or at least 99% of the composition and/or the two or more compounds may constitute 99% or less, 98% or less, 95% or less, 90% or less, 70% or less, 50% or less, 25% or less, 10% or less, 5% or less, 3% or less or 2% or less of the composition. Percentages may be by mass or volume.

In a second aspect, the present invention relates to the use of the ionic liquid composition, according to one or more of the previous aspects, as extractive agents for the removal of S-compounds from a refined crude oil fraction.

In an aspect according to the second aspect, suitable refined crude oil fractions are selected from gasoline, kerosene, diesel oil, heavy oil, and lubricating oil, optionally is heavy oil.

In an aspect according to the second aspect, the refined crude oil fraction is heavy fuel oil for maritime transportation.

In an aspect according to the second aspect, the S-removal % is higher than 70%, optionally is higher than 75%, 80% or 85%, optionally is higher than 90%.

In a third aspect, the present invention relates to an emulsion comprising:

- a mixture comprising the ionic liquid composition according to one or more of the previous aspects of the invention and demineralized water, and
- a refined crude oil fraction.

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The invention also resides in the mixture, i.e. a composition comprising or consisting of water; and

two or more compounds having:

- an imidazolium cation substituted by one or more straight or branched C₁-C₆ alkyl group;
- 10 - an anion selected from the group consisting of R₅COO⁻, Cl⁻, Br⁻, [BF₄]⁻, [PF₆]⁻, [SbF₆]⁻, [R₆SO₄]⁻, [OTs]⁻, [OMs]⁻, wherein R₅ is C₁-C₆ alkyl, C₃-C₈ cycloalkyl, benzyl, C₂-C₆ alkenyl, and R₆ is C₁-C₆ alkyl.

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The two or more compounds may constitute from 1% to 3% by mass of the composition and the water may constitute from 97% to 99% by mass of composition, with respect to the total mass of the composition.

In a fourth aspect, the present invention relates to a process for desulfurization of a crude oil fraction through the ionic liquid composition of one or more of the previous aspects.

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In an aspect according to the fourth aspect, the process comprises:

- mixing a ionic liquid composition according to any of the previous aspects with a batch of refined crude oil fraction in a mixing tank to manufacture an emulsion comprising at least the refined crude oil fraction and the ionic liquid composition;
- feeding the emulsion through a catalytic reactor to bind at least S-compounds, and optionally 25 other metals, of the refined crude oil fraction to the ionic liquid composition;
- feeding the emulsion into a settling tank and storing the emulsion in said settling tank for a settling time in order to leave the S-compounds bond to the ionic liquid composition to separate by gravity from a desulfurized refined crude oil fraction and to settle down in the settling tank.

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In an aspect according to the fourth aspect, the desulfurized refined crude oil fraction is then transferred to a storage or service tank.

In an aspect according to the fourth aspect, the settled ionic liquid composition containing S-compounds is then transferred to a flashing unit.

In an aspect according to the fourth aspect, before mixing the ionic liquid composition with the batch of refined crude oil fraction, the ionic liquid composition is mixed with demineralized water and then the mixture of ionic liquid composition and demineralized water is fed to the mixing tank containing or configured to contain the batch of refined crude oil fraction.

5 In an aspect according to the fourth aspect, in the flashing unit, S-compounds are separated from the ionic liquid composition and form a residual sludge in said flashing unit.

In an aspect according to the previous aspect, the ionic liquid composition free of S-compounds is fed to a separate re-use tank to be reused in the process and/or the residual sludge is transferred to holding tank and, optionally, dried and packed for further handling.

10 In an aspect according to the fourth aspect, the emulsion in the mixing tank is maintained at a mixing temperature between 60°C and 100°C, optionally of 80°C.

In an aspect according to the fourth aspect, the emulsion in the settling tank is maintained at a settling temperature between 40°C and 60°C, optionally of 50°C.

15 In an aspect according to the fourth aspect, the settling time is between 60 min and 180 min, optionally of 120 min.

In an aspect according to the third or the fourth aspect, the emulsion comprises:

- from 5% to 20% by mass of a mixture comprising the ionic liquid composition according to the first object of the invention and demineralized water, and
- from 80% to 95% by mass of a refined crude oil fraction,

20 with respect to the total mass of the emulsion.

More preferably, according to the third object of the invention, the emulsion comprises:

- from 5% to 15% by mass of a mixture comprising the ionic liquid composition according to the first object of the invention and demineralized water, and
- from 85% to 95% by mass of a refined crude oil fraction,

25 with respect to the total mass of the emulsion,

In an aspect according to the third or the fourth aspect, the above mixture comprises from 1% to 3% by mass of the ionic liquid composition and from 97% to 99% by mass of demineralized water, with respect to the total mass of the mixture.

30 In an aspect according to the third or the fourth aspect, the water is demineralized through a reverse osmosis system.

In an aspect according to the third or the fourth aspect, a mass ratio between the oil fraction and the ionic liquid composition is 550:1, more preferably is 450:1.

In an aspect according to the third or the fourth aspect, suitable refined crude oil fractions are selected from gasoline, kerosene, diesel oil, heavy oil, and lubricating oil, preferably is heavy oil.

In an aspect according to the third or the fourth aspect, the refined crude oil fraction is heavy fuel oil for maritime transportation.

In a fifth aspect, the present invention relates to an apparatus for desulfurization of a refined crude oil fraction configured to perform the process of the fourth aspect.

5 In an aspect according to the fifth aspect, the apparatus comprises:

a mixing tank having a first inlet in fluid communication with a tank of refined crude oil fraction;

a fresh ionic liquid composition tank and/or a re-use ionic liquid composition tank in fluid communication with a second inlet of the mixing tank;

at least one settling tank having an inlet in fluid communication with an outlet of the mixing tank;

10 wherein said at least one settling tank has a first upper outlet for delivering desulfurized refined crude oil fraction and a second lower outlet for delivering settled ionic liquid composition containing S-compounds;

a catalytic reactor located between the outlet of the mixing tank and the inlet of said at least one settling tank.

15 In an aspect according to the previous aspect, the apparatus comprises a flashing unit configured to separate the S-compounds from the ionic liquid composition; wherein the flashing unit has an inlet connected to the second lower outlet of said at least one settling tank for receiving the settled ionic liquid composition containing S-compounds, a first upper outlet in fluid communication with an inlet of the re-use tank for delivering the ionic liquid composition free of S-compounds to said re-use tank, a
20 second lower outlet for delivering residual sludge S-compounds.

In an aspect according to the fifth aspect, the catalytic reactor comprises mixing devices configured to further mix emulsion flowing through the catalytic reactor and to increase the rate of chemical reactions in the emulsion.

25 Definitions

HFOs are classified according to different parameters by different organizations so there are different numerical specifications for heavy fuel oil grades.

ASTM D396 classifies heavy fuel oils as oils number 4 to 6 on the base of their viscosity. In general, the boiling point and carbon chain length of the fuel increases with fuel oil number; the higher the
30 molecular weight of the oil's component, the higher the level of polyaromatic compounds, polycycloparaffins and hetero-atoms (N, O, S and metals) increase, and the lower the level of paraffins; viscosity also increases with number and the heaviest oil has to be heated to get it to flow. Price usually decreases as the fuel number increases.

In the UK, the British Standard BS 2869 assigns Class G or H to heavy fuel oil on the base of their viscosity and sulfur content.

In the European Union the Engler degree is generally used to classify fuels: heavy fuel oils are oils having a viscosity greater than 12° Engler at 50°C.

5 In Russia, Mazut is the term denoting residual fuel oil, "furnace mazut" is the heaviest residual fraction of the crude, almost exactly corresponding to US Number 6 fuel oil and further graded by viscosity and sulfur content.

In the maritime field, another type of classification is used for fuel oils; according to that classification, marine fuel oil is a synonym of heavy fuel oil and denotes a pure or nearly pure residual oil, roughly
10 equivalent to US Number 6 fuel oil.

As used herein, with the expressions "heavy fuel oil", "heavy oil", "heavy fuel", "residual fuel oil", "residual oil", "residual fuel", "marine fuel oil", "marine oil" and "marine fuel" we mean the products that consist primarily of the residuum of the refining process after virtually all of the higher quality hydrocarbons have been removed from crude oil feedstock. With the above expressions as used
15 herein, both pure heavy oil and mixtures containing mainly heavy oil are meant. Among the heavy fuel oils that can be utilized more effectively because of the invention are oils classified as number 4 to 6 according with ASTM D396 as well as those having a viscosity value higher than 12° Engler at 50°C.

20 Description of drawings

Figure 1 schematically shows an apparatus for desulfurization of a refined crude oil fraction according to the present invention; and

Figure 2 is a flowchart of a process for desulfurization of a refined crude oil fraction according to the present invention.

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Detailed description

Figure 1 schematically shows an apparatus 1 for desulfurization of a refined crude oil fraction according to the present invention.

Suitable refined crude oil fractions may be selected from gasoline, kerosene, diesel oil, heavy oil,
30 and lubricating oil. In an embodiment, the refined crude oil fraction is heavy fuel oil for maritime transportation.

The apparatus 1 comprises a mixing tank 2 having a first inlet 2a in fluid communication with a tank 3 of refined crude oil fraction and a second inlet 2b in fluid communication with a fresh ionic liquid composition tank 4 and/or a re-use ionic liquid composition tank 4'. The mixing tank 2 comprises

mixing elements, not shown in drawings, configured to blend the liquid content of the mixing tank 2. The mixing tank 2, including flanges and connections, may be assembled of welded mild steel plates, rockwool insulation and galvanized cover plates. The mixing elements of the mixing tank 2 of the disclosed embodiment comprise two macerating pumps, one duty and one stand-by, to ensure satisfactory emulsification. The macerating pumps operates in on/off mode for each batch. Continuously level control, including temperature monitoring, may be displayed locally as well as on a remote control system. The mixing tank 2 is equipped with heating devices 5, such as internal steam heating coils and/or electrical heating elements with temperature control.

According to the process of the invention, batches of refined crude oil fraction from the tank 3 are processed. For each batch, a predetermine quantity of refined crude oil fraction is transferred to the mixing tank 2. An amount of a mixture comprising a ionic liquid composition (which will be detailed in the present description) and demineralized water calculated as a function of the actual sulfur content within the batch of refined crude oil fraction is transferred from the fresh ionic liquid composition tank 4 and/or from the re-use ionic liquid composition tank 15 into the mixing tank 2. In the mixing tank, the refined crude oil fraction with the mixture comprising the ionic liquid composition and the demineralized water is emulsified to obtain an emulsion comprising: the mixture comprising the ionic liquid composition and demineralized water, and the refined crude oil fraction. The refined crude oil fraction inlet supply should be maintained at approx. 60°C - 80°C (a pre-heater may be installed if necessary). The refined crude oil fraction with the mixture comprising the ionic liquid composition and the demineralized water is heated to and maintained at a mixing temperature T_{mix} of 80°C through the heating devices 5 for a better emulsification.

The apparatus 1 comprises two settling tanks 6, each having an inlet 6a in fluid communication with an outlet 2c of the mixing tank 2. Each of the settling tanks 6 has a first upper outlet 6b connected to a storage or service tank 7 for refined crude desulfurized oil fraction resulting from the process of the invention and a second lower outlet 6c. The settling tanks 6, including flanges and connections, may be assembled of welded mild steel plates, rockwool insulation and galvanized cover plates. Each settling tank 6 is equipped with internal cone baffle plates 8 to reduce the overall settling time. Each settling tank 6 is provided with level and temperature controls which may be displayed locally as well as on the remote control system. The emulsion is stored in said settling tanks 6 for a settling time "t" in order to leave the sulfur compounds (S-compounds) bond to the ionic liquid composition to separate by gravity from a desulfurized refined crude oil fraction and to settle down in each settling tank 6. The emulsion in the settling tanks 6 is maintained at a settling temperature T_{settl} of 50°C for the cited settling time "t" which may be of 120 minutes.

A catalytic reactor 9 is located between the outlet 2c of the mixing tank and the inlets 6a of the settling tanks 6. The catalytic reactor 9 comprises duct or ducts, mechanical elements, e.g. blades, movable or fixed, or other mixing devices configured to further mix the emulsion flowing through the catalytic reactor 9 and to increase the rate of chemical reactions in said emulsion. The catalytic reactor 9 allows to improve binding of at least S-compounds, and optionally other metals, of the refined crude oil fraction to the ionic liquid composition. The catalytic process is arranged inline between the mixing tank 2 and settling tanks 6.

After the settling time "t", the liquid in each settling tank 6 is divided in two parts: an upper part 10 of desulfurized refined crude oil fraction and a lower part 11 of the sulfur compounds (S-compounds) bond to the ionic liquid composition. A continuously double acting level control system allows monitoring the oil/liquid composition level interface.

The desulfurized refined crude oil fraction 10 is then transferred to the storage or service tank 7 through the first upper outlets 6b for use when needed. The settled ionic liquid composition containing S-compounds 11 is then transferred to a flashing unit 12 part of the apparatus 1. The flashing unit 12 is configured to separate the S-compounds from the ionic liquid composition. The flashing unit 12 leaves the heavy metals and sulfur as a sludge residue in the bottom part. The flashing unit 12 has an inlet 12a connected to the second lower outlet 6c of each settling tank 6 for receiving the settled ionic liquid composition containing S-compounds 11. The flashing unit 12 has a first upper outlet 12b in fluid communication with an inlet 4'a of the re-use tank 4', for delivering the ionic liquid composition free of S-compounds to said re-use tank 4', and a second lower outlet 12c for delivering residual sludge S-compounds to a holding tank 13. The residual sludge S-compounds may be transferred to a separate drying and bagging unit, not shown, for further handling. The ionic liquid composition free of S-compounds fed to the separate re-use tank 4' may be reused in the process.

The fresh ionic liquid composition tank 4 has an outlet 4a connected to the second inlet 2b of the mixing tank 2 through a duct. The re-use ionic liquid composition tank 4' has an outlet 4'b connected to said duct between said outlet 4a and said second inlet 2b. The fresh ionic liquid composition tank 4 has a first inlet 4b connected to a source of demineralized water 14 and a second inlet 4c connected to an outlet 15a of a concentrate ionic liquid composition tank 15. The fresh ionic liquid composition tank 4 is also acting as a mixing tank between concentrated ionic liquids supplied from the concentrate ionic liquid composition tank 15 and demineralized water supplied optionally through a reverse osmosis desalination system.

According to the process of the invention, before mixing the ionic liquid composition with the batch of refined crude oil fraction, the concentrate ionic liquid composition from the concentrate ionic liquid

composition tank 15 is mixed with demineralized water in the fresh ionic liquid composition tank 4 and then the mixture of ionic liquid composition and demineralized water is fed to the mixing tank 2 containing or configured to contain the batch of refined crude oil fraction.

The apparatus 1 is designed for continuous safe monitored batch operations. Operating pressures within mixing tank 2 and settling tanks 6 are kept at atmospheric pressure and fuel oil temperature is maintained below its flash point. High temperatures are only present within the tank steam heating coils 5, as well as, within the flashing tank 12. Partial vacuum may also be applied within the flashing tank 12.

The ionic liquid composition consists of two or more compounds having:

- an imidazolium cation substituted by one or more straight or branched C₁-C₆ alkyl group and
- an anion selected from the group consisting of R₅COO⁻, Cl⁻, Br⁻, [BF₄]⁻, [PF₆]⁻, [SbF₆]⁻, [R₆SO₄]⁻, [OTs]⁻, [OMs]⁻, wherein R₅ is C₁-C₆ alkyl, C₃-C₈ cycloalkyl, benzyl, C₂-C₆ alkenyl, and R₆ is C₁-C₆ alkyl.

In an embodiment, the composition comprises or consists of:

- 1-butyl-3-methyl imidazolium hexafluoro phosphate,
- 1-butyl-3-methyl imidazolium tetrafluoroborate, and
- 1-butyl-3-methyl imidazolium chloride.

In an embodiment, the composition comprises or consists of:

- from 35 to 44 % by volume of 1-butyl-3-methyl imidazolium hexafluoro phosphate,
- from 22 to 27 % by volume of 1-butyl-3-methyl imidazolium tetrafluoroborate,
- from 26 to 29 % by volume of 1-butyl-3-methyl imidazolium chloride

with respect to the total volume of the composition.

In an embodiment, a volume ratio between 1-butyl-3-methyl imidazolium hexafluoro phosphate, 1-butyl-3-methyl imidazolium tetrafluoroborate and 1-butyl-3-methyl imidazolium chloride is comprised between 1:0.63:0.74 and 1:0.61:0.66.

In an embodiment, the emulsion comprises:

- from 5% to 20% by mass of a mixture comprising the ionic liquid composition according to the first object of the invention and demineralized water, and
 - from 80% to 95% by mass of a refined crude oil fraction
- with respect to the total mass of the emulsion.

In an embodiment, the emulsion comprises:

- from 5% to 15% by mass of a mixture comprising the ionic liquid composition according to the first object of the invention and demineralized water, and
- from 85% to 95% by mass of a refined crude oil fraction

with respect to the total mass of the emulsion,

In an embodiment, the above mixture comprises from 1% to 3% by mass of the ionic liquid composition and from 97% to 99% by mass of demineralized water, with respect to the total mass of the mixture.

- 5 In an embodiment, a mass ratio between the oil fraction and the ionic liquid composition is 550:1, more preferably is 450:1.

The Applicant has found that the S-removal % obtained through the invention may be higher than 70%, optionally higher than 75%, 80% or 85%, optionally higher than 90%.

10 Examples

Example 1: preparation of the ionic liquid (IL1) composition.

A ionic liquid composition according to the present invention was prepared with the following ingredients (all percentage by volume):

- 44% by volume of 1-butyl-3-methyl imidazolium hexafluoro phosphate,
15 27% by volume of 1-butyl-3-methyl imidazolium tetrafluoroborate,
29% by volume of 1-butyl-3-methyl imidazolium chloride.

- To prepare 10 liters of a ionic liquid composition according to the present invention 4.4 liters of 1-butyl-3-methyl imidazolium hexafluoro phosphate, 2.7 liters of 1-butyl-3-methyl imidazolium
20 tetrafluoroborate and 2.9 liters of 1-butyl-3-methyl imidazolium chloride were mixed for 2 hours at 25°C.

Example 2: preparation of the emulsion of heavy oil and IL.

- The ionic liquid composition prepared in example 1 was first mixed with demineralized water, then
25 the resultant mixture was added to the heavy oil in a mixing tank.

Specifically:

- 9,8 liters of demineralized water and define amount of the ionic liquid composition prepared in example 1 (2% by mass with respect to the total mass of the mixture) were mixed.;
90 liters of marine fuel oil (IFO) and define amount of the mixture prepared above (10% by mass
30 with respect to the total mass of the emulsion) were mixed in the mixing tank to give the title emulsion.

Example 3: determination of sulfur content.

The S-content was determined by X-Ray Fluorescence Spectrometer (XRF) by SGS Italia SPA, Genova, Italia according to the International Standard ISO 8754, second edition 2003.

Initial sulfur content of the oil (Inlet oil) used to prepare the emulsion of example 2 and sulfur content of the oil recovered after subjecting the emulsion of example 2 to the process according to the invention (Outlet oil) were determined.

Sulfur content and the S-removal % of each sample are reported in Table 1.

Table 1

Sample	S-content (% m/m)	S-content (ppm)	S-removal (%)
Inlet oil	2.23	22300	-
Outlet oil	0.030	300	98,66

As can be seen from the results reported above, the IL1 composition prepared in example 1 when emulsified with a marine fuel oil is able to effectively remove sulfur from such oil.

As reported by Javadli, R et al. cited above, few of the known technologies are viable and/or efficient for the desulfurization of heavy oil, mainly due to the properties of heavy oil itself, and there are no reports on the extractive desulfurization of heavy oil by ionic liquids.

Surprisingly, the Applicant has found that IL1 is able to deeply remove sulfur (by more than 98%) from oils having high sulfur content, such as the marine fuel oil used in example 2, whose initial sulfur content is higher than 2% m/m (higher than 20000 ppm), moreover this accomplishment is reached without the addition of any oxidizing agent.

Furthermore, it is worth noting that IL1 is able to reduce the sulfur content to a very low level, i.e. 0.030 % m/m, which complies with the sulfur limit announced by the International Maritime Organization, to be implemented in ship fuel by 2020, i.e. 0.5% m/m.

Another advantage carried out by IL1 consists in the fact that it can be used in very low quantity with respect to the oil (the oil/IL1 mass ratio in the emulsion of example 2 is 450:1) and is capable of being reused multiple times, until a maximum of 5 times; moreover, the process of extractive desulfurization by IL1 does not require high energy. Thus overall, the costs related to desulfurization of oils having high sulfur content, such as marine fuel oil, are greatly reduced.

Summarizing, the IL composition according to the present invention, and the process and the apparatus thereof, represent an improvement in the field of desulfurization of refined crude oil

fractions, in particular for desulfurization of heavy fuel oil and marine fuel oil as they reduce the amount of pollutants in air, employ the minimum energy during the desulfurisation process, and have a minimal effect on the price of the fuel.