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IONIC LIQUIDS FOR THE REMOVAL OF H₂S AND MERCAPTANS FROM NATURAL GAS

Methane is the main component of natural gas but higher alkanes, water, nitrogen, carbon dioxide, H₂S and mercaptans are often present. H₂S and mercaptans have to be removed from natural gas due to their toxicity, corrosion issue and noxious combustion products (SO_x). In this review, we will report the results obtained in the removal of H₂S and mercaptans using ionic liquids, whose properties can be easily tuned with a proper choice of the anion and of the cation.

Introduction

Natural gas is the fossil energy source with the lowest carbon to hydrogen ratio; therefore it has a crucial role in an energy transition aimed to a progressive decarbonization of the energy system.

As a matter of fact, due to its high energy density, natural gas combustion produces less CO₂ emission per unit of energy with respect to oil and coal. This is why natural gas is gaining market share at the expense of both coal and oil, especially in sectors that are difficult to decarbonize, such as heavy-duty transport and heat generation in industry. Also in the power energy generation sector, where the role of renewables is growing faster, the use of natural gas will remain relevant due to its role as a provider of power system flexibility (**World Energy Outlook 2019 IEA**). In such a context it is very important to develop more efficient technologies for the production, purification and treatment of natural gas, in order to favor its utilization.

Natural gas composition can be very variable, even if methane is typically the main component. A representative composition range for natural gas is reported in Tab. 1.

The specifications for the content of impurities in pipeline gas are very low and even lower in gas fed to LNG plant, while the gas coming from wells may contain contaminants in quantity up to 30% vol. or higher.

Compound	Molar fraction
Methane	0.75-0.99
Ethane	0.01-0.15
Propane	0.01-0.10
<i>n</i> -Butane	0.00-0.02
Isobutene	0.00-0.01
<i>n</i> -Pentane	0.00-0.01
Isopentane	0.00-0.01
Hexane	0.00-0.01
Heptane plus higher hydrocarbons	0.00-0.001
<i>Nonhydrocarbons</i>	
Nitrogen	0.00-0.15
Carbon dioxide	0.00-0.30
Hydrogen sulfide	0.00-0.30
Helium	0.00-0.05

Tab. 1 - Natural gas typical composition range [1]

CO₂ and H₂S are very frequently present in natural gas in variable amounts and several industrial processes are available for their separation. The methods for separation of CO₂ and/or H₂S depend on their quantity. For large quantities the preferred method consists of absorption in aqueous alkanolamine solution, whose active component depends on natural gas composition. For the treatment of acid gas, whose main contaminant is CO₂ the first amine to be developed for this use was ethanolamine (MonoEtanol Amine or MEA) [2, 3]. Secondary amines, such as diethanolamine (DEA) proved to be more stable and require less heat for their regeneration than MEA [4]. Mixture of different primary alkanolamine (MEA or 2-amino-2-methyl-1-propanol (AMP)), secondary alkanolamine (DEA) or tertiary alkanolamine (*N*-methyl diethanolamine or MDEA) proved to be more efficient in CO₂ removal than single alkanolamine [5]. When both H₂S and CO₂ are present in similar concentration in the natural gas to be treated, the most proper alkanolamine solution is usually MDEA activated with piperazine (PZ). [6]. There are also natural gas fields in which H₂S concentration largely exceeds that of CO₂, for the treatment of these gasses not only alkanolamine solution but also specific processes, such as cryogenic separation, are currently adopted according to H₂S concentration [7].

The amine plant consists of two units (Fig. 1): an

absorption column, in which CO₂ and H₂S react with amine solution forming in the first case a carbamate in the second one a hydrosulfide; and a regeneration column in which the carbamate and hydrosulfide are decomposed and amine solution is regenerated.

Since absorption reaction is very exothermic, the absorbing column usually works at temperatures lower than 50 °C, often in the presence of cooling equipment.

On the contrary, the regeneration column needs heat to decompose carbamate and hydrosulfide, therefore the regeneration is usually performed at temperatures higher than 120 °C.

These processes are very energy consuming: e.g. the enthalpy of adsorption can be higher than -100 kJ/mole CO₂ for MEA solution [8], since a chemical reaction takes place between the acid component and the amine, therefore the regeneration step requires energy to break down the previous formed chemical bonds. Secondary (DEA) and tertiary alkanolamine (triethanolamine (TEA)) require much lower heat of regeneration than MEA [9].

Furthermore, amines decompose quite quickly under reaction conditions [10] and that often generate also corrosion problem to the plant, mainly in the regeneration unit.

MEA proved to be the most corrosive alkanolamine [11] in regeneration unit, but corrosion is a relevant

issue towards carbon steel also for DEA, MDEA, AMP and PZ [12]. Amines technologies are by far the most applied not only for natural gas sweetening but also for CO₂ and H₂S removal in refineries and petrochemical plants. More recently amines technologies have been proposed for complete capture of CO₂ from flue gas of power plants and of methane steam reforming plants for the production of blue hydrogen, i.e. hydrogen production combined with carbon capture and storage.

However, beside amines other technologies have been applied for acid gas removals. For CO₂ re-

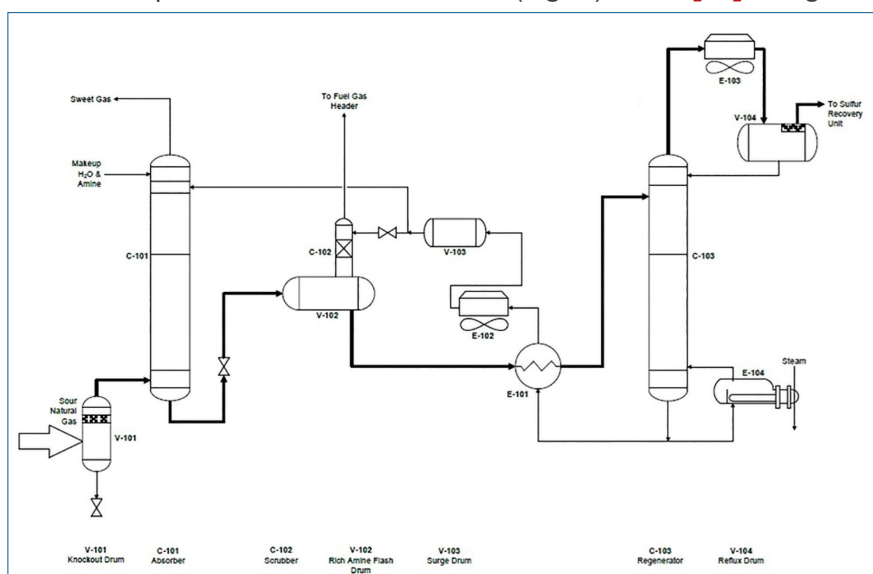


Fig. 1 - Amine treating gas plant



removal at high partial pressure from gases having little or no H_2S alkali salt-based chemical separation systems also find application. Commercially alkali systems include the different hot potassium carbonate processes.

For removal of acid gases at high partial pressures also physical solvents are applied. These technologies depend on the physical solubilities of acid gases for their removal, therefore without reaction. At the proper operating conditions physical solvent can then remove CO_2 , H_2S and mercaptans. Several physical processes are available using proprietary solvents based on alcohols, carbonates, pyrrolidones, and ethers: the most diffused are Purisol [13], Selexol [13] and Rectisol [14].

These industrial solvents have some drawbacks such as degradation due to chemical reactions and elevated costs for refrigeration requirements and materials of construction required for low temperatures (e.g. Rectisol process).

The use of ionic liquids in acid gas treatment and in particular for carbon capture has been proposed more recently. Ionic liquids are water free salts that melts at temperature up to $100\text{ }^\circ\text{C}$ [15]; being melted salts they are liquid in a wide range of temperature, and they possess a unique property in the liquid phase: an almost negligible vapor pressure. Wide range of temperature in the liquid phase and negligible vapor pressure make ionic liquids ideal candidates for absorption and purification of gas mixtures [16].

C. Pomelli and his coworkers at University of Pisa published the pioneering paper on the use of ionic liquids for H_2S absorption [17], starting from this one several groups of research have faced the subject as here summarized.

Ionic liquids as physical solvents for H_2S

Ionic liquids are polar solvents [16] and even though they can dissolve both polar and non-polar molecules they are expected to dissolve preferentially polar molecules in a gas mixture of polar and non-polar molecules, such it is a natural gas.

The first paper on H_2S physical absorption in ionic liquids was written by C. Pomelli *et al.* in 2007 [17]. These authors determined the solubility of H_2S in different ionic liquids at moderate pressure using

NMR: some have the same cation (3-butyl, 1-methyl-imidazolium) with different anion (chloride, tetrafluoroborate, triflate, bis-trifluorosulfonimide) or different anion (substituted pyridinium or imidazolium) with the same cation (bis-trifluorosulfonimide). In all cases the solubility of H_2S is very high, ranging the molar fraction between 0.72 and 0.9 depending on the couple cation-anion chosen.

A.H. Jalili *et al.* [18] two years later determined the solubility of H_2S at higher pressure (up to 1 MPa). The measurement was performed degassing the ionic liquids at low pressure and increasing H_2S in a high pressure equilibrium cell: the absorption was measured in three different ionic liquids based on imidazolium (1-butyl-3-methylimidazolium hexafluorophosphate, ([bmim][PF₆]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]), and 1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide ([bmim][Tf₂N]). In Fig. 2 are reported the performances of these ionic liquids in the absorption of H_2S at different pressures.

The solubility of H_2S proved to follow the same trend shown by C. Pomelli at lower pressure: [bmim][Tf₂N] > [bmim][BF₄] > [bmim][PF₆].

The authors also wrote that the solubility of H_2S in these ionic liquids is much higher than that of CO_2 and therefore these ionic liquids could be used for the selective separation of CO_2 and H_2S in a gas stream containing them both.

These authors supported their assumption determining comparative absorption and diffusion of both CO_2 and H_2S in 1-butyl-3-methylimidazolium tetrafluoroborate at pressure up to 1.1 MPa and temperature between 303.15 to 353.15 K [19]. The solubility of H_2S was about three times higher than

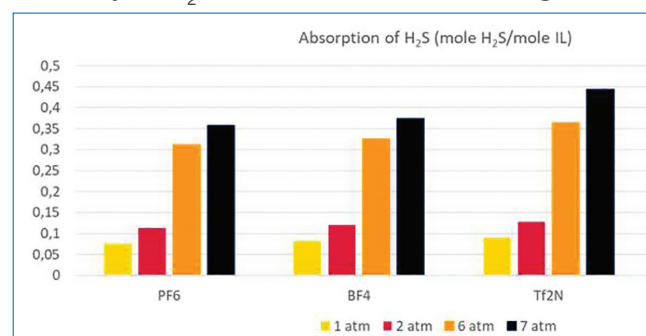


Fig. 2 - Influence of the pressure on H_2S physical absorption on bmim based ionic liquids [18]

that of CO₂ and its diffusion coefficient is of the same order of magnitude as that of CO₂.

Such a high solubility was attributed from the authors not only to the polarity of the molecule, but also to the strong interaction between H₂S and the molecule of the ionic liquids, which was calculated to be in the range of 7-14 kcal/mole, similar to that of the hydrogen bond.

In the same year other authors tried to correlate the solubility of light compounds, such as NH₃, SO₂ and H₂S, in ionic liquids, analyzing the deviation to ideality in liquid phase using the Flory-Huggins model [20]. While for SO₂ and NH₃ the Flory-Huggins model can describe the non-ideality of VLE equilibria, for H₂S the residual contribution to the excess Gibbs energy presents a non-negligible positive contribution that reduces the quality of the predictions by this approach.

Another model to describe the solubility of H₂S in the ionic liquid 1-*n*-butyl-3-methylimidazolium methyl sulfate ([BMIM][MeSO₄]), in mixture of CO₂/H₂S, was Redlich-Kwong tertiary equation of state [21]. The authors demonstrated that VLLE for H₂S/[bmim][MeSO₄] is highly asymmetric with an unusually narrow (mole fraction H₂S between 0.97 and 0.99) LLE gap and they were able to model this extremely narrow and rare LLE gap successfully. The ternary VLE data were extremely useful and sensitive to the binary H₂S/[BMIM][MeSO₄] EOS construction and validated their results. This ionic liquid proved also to be very selective towards H₂S with a selectivity CO₂/H₂S which reached the value 1/13.5.

This selectivity value is quite high and promising for the separation of gas mixture containing both CO₂ and H₂S, while other ionic liquids proved to be much less selective; for example 1-bu-

Ionic liquid	Absorption molar ratio CO ₂ /H ₂ S	Ref.
BMIM Br	3.75	[14]
BMIM PF ₆	3.7	[15]
BMIM [MeSO ₄]	13.5	[13]
BMIM BF ₄	3.0	[11]

Tab. 2 - Physical absorption selectivity with different ionic liquids

tyl-3-methylimidazolium bromide ([BMIM][Br]), demonstrated to have a selectivity CO₂/H₂S of 3.75 [22] similar to 3.7 of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) [23]. Adsorption selectivity with different BMIM-based ionic liquids are listed in Tab. 2.

Relationship between physical absorption of H₂S in ionic liquids depending on the cation and the anion of the ionic liquid, as a function of the pressure and of the temperature, was determined with more than one thousand pieces of data, which were elaborated through Extreme Learning Machine [24]. The model proved to be very accurate with a difference among experimental data and calculated ones, which in the most cases is lower than 5%.

Ionic liquids as chemical solvents for H₂S

Chemical absorption of H₂S has been studied in ionic liquids, whose anion is a carboxylate and the cation is 1-alkyl-3-methylimidazolium [25].

The authors studied three different carboxylic acids: acetate, lactate and propionate with the same cation emim (1-ethyl-3-methylimidazolium). They demonstrated that the chemical absorption of H₂S is dependent on the strength of the carboxylic acid: the higher is pK_a of the acid, hence the lower is the pK_b of the conjugated base, the lower is the chemical absorption of H₂S in the ionic liquid. In fact, the pK_a of lactic acid is 3.86, that of acetic acid is 4.75 and that of propionic acid is 4.87 and the absorption capacity follows the sequence emim (propionate) > emim (acetate) > emim (lactate).

The carboxylate anions aren't strong enough to deprotonate H₂S (PK_{a1}=6.89) but they can react through acid-base interaction and hydrogen bonds formation: the weaker the acid, the higher is the enthalpy of reaction between the ionic liquid and H₂S (see Tab. 3). In fact, ΔH⁰= -25 KJ/mole was measured for

Acid	pK _a	Δ (kJ/mole)
Lactic	3.86	-25
Acetic	4.75	-32
Propionic	4.87	-62.3

Tab. 3 - Influence of acid strength in H₂S chemical absorption (emim)(acid)

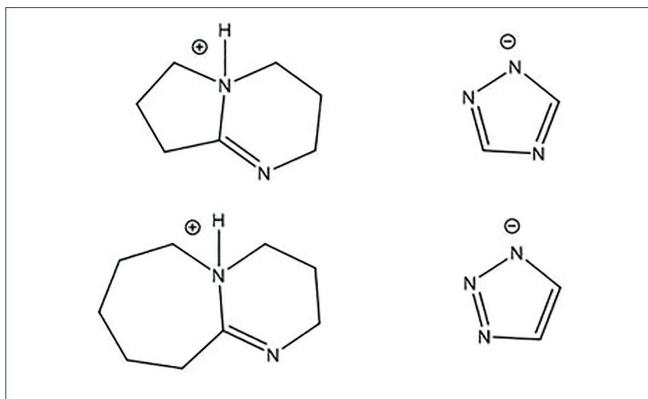


Fig. 3 - Azole based ionic liquids; all combinations cation-anion are described in [18]

emim lactate, $\Delta H^0 = -32$ KJ/mole was measured for emim acetate and $\Delta H^0 = -62.3$ KJ/mole was measured for emim propionate. The authors demonstrated also that the structure of H_2S -ionic liquid complex is AB_2 where A is H_2S and B is the ionic liquid so that in the complex there are two molecules of ionic liquid for each molecule of ionic liquid.

Another interesting ionic liquid for H_2S chemical absorption is that based on ionic liquids based on azole anions [26] and protonated DBU (1,5-diazabicyclo[5.4.0]undec-7-ene) and DBN (1,5-diazabicyclo[4.3.0]non-5-ene) (see Fig. 3). The chemical absorption of H_2S was demonstrated by the authors both by the high molar ratio H_2S /ionic liquid molecule (between 1.05 and 1.2 at ambient pressure depending of the anion chosen) and the high enthalpy of absorption of H_2S in different azole based ionic liquids (between -44.3 and -62.9 kJ/mole).

These ionic liquids demonstrated also to be very selective in H_2S compared to absorption of CO_2 and methane, with a molar ratio H_2S/CO_2 between 4.6 and 7.5 at ambient pressure.

Unfortunately, such selectivity is sharply reduced in the presence of water, which promotes CO_2 absorption through hydrogen carbonate formation. However, the ionic liquid based on azole anion proved to be effective and stable for at least five cycles of absorption and regeneration.

Ionic liquids for mercaptans removal

The first process for the removal of mercaptans from natural gas and light hydrocarbon mixture was described in 2001 [27]. In this patent it was

claimed the use of a strong inorganic base, preferred one is NaOH, dissolved in an ionic liquid. Mercaptans are absorbed in this solution and transformed in sodium alkyl thiolate, which is then oxidized in a further step to disulfide with air. Disulfide is not soluble in the ionic liquid and therefore it is easily separated and the NaOH solution in ionic liquid is then recycled. At present there are no available information of the scaling up of this process.

In a more recent patent [28] the use of basic ionic liquid, made of a quaternary ammonium salt as cation and hydroxide, carbonate or alcoholate as an anion, was claimed to be an efficient scavenger for the removal of mercaptans from natural gas. In the patent no regeneration method is disclaimed therefore the reaction most probably is irreversible.

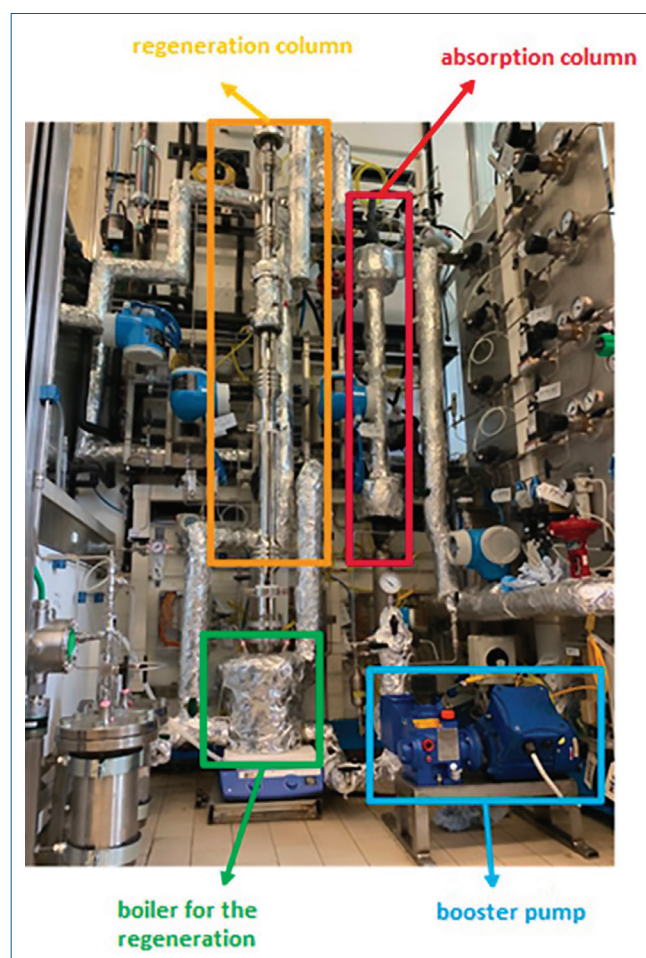


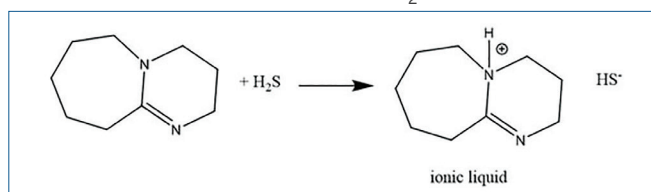
Fig. 4 - Pilot plant in Eni research center for the study of sour gas absorption

Ionic liquids as mixed (chemical and physical solvent) for H₂S and mercaptans

A mixed system, chemical absorption and physical solvent, has been developed to pilot plant scale by Eni research group, in San Donato Milanese research center. A picture of the plant is shown in Fig. 4.

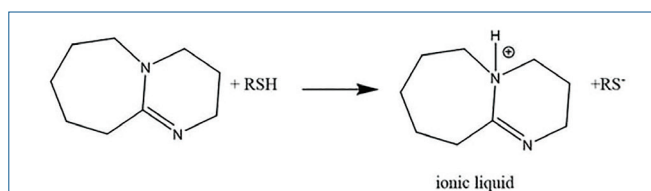
This mixed solution was described in a recent patent [29]: it consists of a strong organic base (preferred one is the DBU), an alcohol and an ionic liquid, preferably 1-methyl-3-butylimidazolium-bis(trifluoromethanesulfonyl)imide.

During the reaction a reversible ionic liquid, thermally reversible, is formed between H₂S and the base [30] (protonated DBU as cation and hydrosulfide as anion) due to chemical interaction, while the preformed ionic liquid absorbs physically H₂S (Scheme 1).



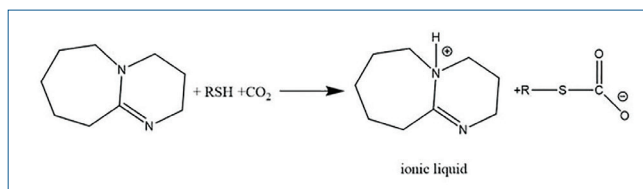
Scheme 1 - Formation of hydrogen sulfide based ionic liquid [22]

This new process is intended to reduce the energy consumption during regeneration because the absorbed H₂S is simply released reducing the pressure. The system can absorb chemically also mercaptans due to two different reaction mechanisms. When CO₂ is not present in the natural gas to be treated, mercaptans are absorbed chemically through acid base interaction with the strong organic base, due to the formation of the ionic liquids in which the cation is protonated DBU and the anion is alkyl thiolate (Scheme 2).



Scheme 2 - Formation of alkyl thiolate based ionic liquid, in absence of CO₂

When CO₂ is present mercaptans, which are much more acidic than the corresponding alcohol (i.e. butanethiol has a pKa of 10.5 vs 15 for butanol) reacts with DBU and CO₂ producing protonated DBU alkyl thiocarbonate (Scheme 3).



Scheme 3 - Formation of alkyl thiolate based ionic liquid, in the presence of CO₂

In both cases the system is reversible, and it can be easily regenerated through thermal treatment.

In a more recent patent [31] it is described a system like the previous one, made of three components: a strong organic base, an alcohol and a physical solvent such as sulfolane, dimethyl sulfoxide or 1-methylpyrrolidin-2-one.

The reactions are the same of the previous patent with the formation of a thermally reversible ionic liquid constituted of the protonated DBU as cation and hydrogen sulfide and/or alkyl thiolate as anion, while the physical absorption takes place in the physical solvent.

The advantage of this new system is that the physical solvent is much cheaper than the ionic liquid claimed in the previous patent [29].

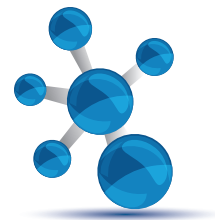
This ionic liquid proved to be very selective toward H₂S and mercaptans. Moreover, compared to alkanolamine and other solvents which are commonly used in natural gas treatment, the energy required for the regeneration step is clearly lower. Based on these properties and results, an acid gas separation process using this class of ionic liquids is under development [32, 33].

Conclusions

Ionic liquids demonstrated to be very efficient physical solvents for reversible H₂S absorption; they are also very selective when the natural gas contains also CO₂ and methane.

In this case the best physical solvent proved to be an ionic liquid, whose anion is methyl sulfonate; with this compound the molar ratio of absorbed H₂S/CO₂ reaches the highest value of 13.5/1 [21].

If the pressure of the gas to be treated is close to ambient pressure and the required concentration in the sweet gas is few ppm, the best choice demonstrated to be a chemical ionic liquid, which can efficiently remove both H₂S and mercaptans from natural gas.



A cheaper solution, which possesses both merits of the chemical ionic liquids (very low concentration of H₂S and mercaptans in the sweet gas) and physical solvent (very low cost of regeneration of the solution after absorption) could be found in mixed physical-chemical systems [32, 33], which are able to exploit the outlet pressure of natural gas from the wells.

Acknowledgment

F. Castaldo, G. Fiori and C. Rizzo, A. Landoni are acknowledged for their helpful discussions and suggestions

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Liquidi ionici per la rimozione di H₂S e mercaptani dal gas naturale

Il metano è il componente principale del gas naturale in cui sono presenti anche altri composti: CO₂, alcani superiori, acqua, N₂, H₂S e mercaptani. H₂S e mercaptani devono essere separati dal gas naturale perché sono tossici, corrosivi e, bruciando, producono SO_x. In questa review sono illustrati i risultati ottenuti nella separazione di H₂S e mercaptani coi liquidi ionici, le cui proprietà possono essere modificate con un'opportuna scelta del catione e dell'anione.