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Evaluation of the Potential of Natural Gas Sweetening by Using Imidazolium Ionic Liquid [bmim][NTf_2] based on PC-SAFT Equation of State

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Abstract

In the present study, for the first time, the potential of gas sweetening of Iranian gas composition by using an imidazolium-based ionic liquid solvent called 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][NTf2] has been evaluated. The results are compared with natural gas sweetening using an amine-based solvent. The PC-SAFT equation of state was used as a thermodynamic model in Aspen Plus software version 10. Since the thermophysical properties of the ionic liquid are not available in the software, and these properties for pure and multicomponent systems are in vital demand, all the necessary properties are correlated to PC-SAFT EoS as well as related thermophysical properties. The gas sweetening process is simulated for both ionic liquid and amine-based solvents, and the results are compared. The results show that to meet the sweet gas pipeline specification (4 ppm H2S and 2% CO2), the energy consumption of the ionic liquid-based process is much higher than that of the MDEA-based solvent. This result indicates that ionic-based solvents ([bmim][NTf2]) are not suitable for gas sweetening due to their lack of desirable properties, including low vapor pressure, high thermal stability, high solubility, and tunability.

Keywords: Process Simulation, Ionic Liquid, Natural Gas Sweetening, Aspen Plus.

Introduction

After oil and coal, natural gas is the third most consumed fossil fuel in the world, widely utilized in industrial and residential settings; therefore, it is predicted that natural gas production will peak between 2025 and 2066 [1]. Although natural gas is one of the cleanest fuels among other fossil fuels [2], it still contains acidic gases such as H2S and CO_2 in varying concentrations depending on the natural gas sources and relevant geological features [3]. Hydrogen sulfide is a corrosive compound that can harm the ecosystem even at low concentrations [4]. Moreover, carbon dioxide in the presence of water forms acids and causes corrosion in pipelines and equipment [5]. Therefore, it is essential to remove acid gases from natural gas and reduce the levels of H_2S and CO_2 to acceptable limits before utilizing them for industrial and commercial applications. So far, various methods have been employed to achieve this, including physical and chemical absorption and adsorption, as well as membrane technology [6; 7]. Among these methods, liquid absorption using an amine-based solvent is predominantly utilized on an industrial level [8]. Although amine-based solvents are widely used in gas sweetening units, this method has some disadvantages, such as high energy consumption, corrosion, significant solvent wastage [9; 10], and the formation of foam in the absorption column [11]. In addition, researchers are constantly exploring goals such as lower cost, longer life, greater efficiency, reduced energy consumption, and fewer operational problems in the separation of acid gases from natural gas. Over the past two decades, the use of ionic liquids as new solvents in the absorption and separation of acid gases has gained attention from researchers [12]. Ionic liquids, known as green solvents, are molten salts consisting of an anion and a cation that are liquid at room temperature [13]. Due to their good thermal stability, low viscosity, low volatility, low vapor pressure, and ease of operation [14; 15], ionic liquids

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are considered a promising alternative to amine-based solvents. As a result, significant research has been conducted on their use in recent years. Several experimental studies have been carried out regarding the solubility of acid gases in ionic liquids. Although the main focus of research has been on the solubility of carbon dioxide in ionic liquids [16-21], studies have also been conducted on the solubility of hydrogen sulfide in ionic liquids [22-24]. The results of these laboratory research studies are utilized as a basis for further simulation studies. To remove 90% of CO_2 from post-combustion flue gas with no more than a 35% increase in the cost of electricity, Shifflet et al. examined the IL solvent [bmim][Ac] and found that the IL solvent can reduce energy loss by 16% compared to the MEA solvent. Additionally, the investment rate for the IL solvent process is 11% less than for amine solvents [25]. According to the published literature, most of the conducted research has focused on the use of ionic liquids in the separation of carbon dioxide from flue gases [25-30]; a few studies have been done regarding the sweetening of natural gas by ionic liquids. Furthermore, Barbosa et. al. studied the separation of CO_2 from offshore CO_2-rich natural gas (44% CO_2 and 50% CH_4) using the ionic liquid [bmim][NTf_2]. They reduced the CO2 content in the final natural gas to 3 mol%. Moreover, the results showed that the process of carbon dioxide absorption by the IL solvent resulted in a 19.3% higher profit, 23.6% lower manufacturing cost, and 18% lower investment [26]. For the first time, based on their claim, Kazmi et. al. studied acid gas removal from natural gas using ionic liquids [bmim][PF6] and [bmim][CH_3SO_4] in 2019. They managed to remove 99wt% of acid gases from natural gas using IL and found that these solvents can significantly reduce the heating load and total annualized cost. The heat value required to recover the ionic liquid solvent is 78.6% lower than that of normal amine recovery [11]. However, this recent research indicates that ionic liquids could be a promising substitute for amine solvents. The issue lies in the fact that while the separation of acid gases using IL has been successful up to 99%, the percentage of remaining acidic gases in the purified gas makes it unsuitable for industrial use as sweet gas. Liu et al screened 90 types of ionic liquids and found that 1-butyl 3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][NTf_2] is a potential solvent from the point of view of CO_2 dissolution and CO_2/CH_4 selectivity [27]. Anthony et. al. showed that the solubility of CO_2 in [bmim][NTf_2] increases with an increase in pressure and decreases with an increase in temperature [28]. Moreover, to investigate the effect of an anion in an ionic liquid, Aki et al. studied seven ionic liquids as cations [bmim]. They found that the solubility of CO_2 increases in the ionic liquid whose anion contains fluoroalkyl groups such as [NTf_2] [29]. Also, Jalili et al. studied the solubility of hydrogen sulfide in three ionic liquids: [bmim][PF6], [bmim][BF4], and [bmim][NTf_2]. Moreover, the comparison showed that the solubility of H_2S in [bmim][NTf_2] is higher than that of the others [23].

A review of the extant published literature reveals that a sole comparison of equilibrium solubility is not a reliable method for determining the superiority of a solvent. Rather, consideration must be given to other thermophysical properties and operational conditions of the absorber tower, flash tanks, and regenerator tower, as well as feed gas and sweet gas specifications in a gas refinery [11,25,26].

In the present study, the potential of using the ionic liquid solvent for sweetening natural gas in Iran's oil and gas industry is examined for the first time. The goal is to determine if ionic liquids can effectively absorb acid gases and reduce the levels of hydrogen sulfide and carbon dioxide in sweetened gas to meet pipeline specifications, i.e., 4 ppmv for hydrogen sulfide and 50 ppmv for carbon dioxide. In light of the preceding deliberations, [bmim][NTf_2] was designated as the ionic liquid solvent to conduct a comparative analysis of its performance with that of amine-based solvents in the context of natural gas sweetening processes.

Materials and Methods

Thermodynamic Framework

As explained in the previous section, the aim of the present study is to simulate the gas sweetening process using an ionic liquid. Therefore, choosing a proper thermodynamic model to describe the vapor-liquid equilibria is essential. There are different approaches for modeling vapor-liquid equilibria in process simulators; the first one is using the equation of state (EoS) for the vapor phase and an activity model for the liquid phase ($\gamma-\phi$), the second approach uses EoS for both phases, which is called the ($\phi-\phi$) method and the last approach is using empirical models. In the present study, the second approach is used. The advantages and disadvantages of each method have been discussed in our previous work [30]. In 2001, the PC-SAFT equation of state was established based on the Statistical Associating Fluid Theory and according to the Perturbed Hard Chain Theory by Gross and Sadowski [31]. In the PC-SAFT equation of state, the residual Helmholtz free energy is expressed as the sum of hard chain, dispersion, association, and electrostatic contributions according to the following equation [32]:

$$a^{res} = a^{hc} + a^{disp} + a^{assoc} + a^{elec} \tag{1}$$

where a^{res} is the residual Helmholtz free energy and a^{hc}, a^{disp}, a^{assoc}, a^{elec} are the Helmholtz free energy due to the contributions of hard chain, dispersion, association, and electrostatic, respectively.

In the PC-SAFT equation of state, a molecule is represented as a chain of m_i spherical segments of diameter σ_i, which express the contribution of the hard chain in equation (1). Also, dispersion forces are given by ε_i. Associating molecules have two more parameters: $\varepsilon^{A_iB_i}$ and $K^{A_iB_i}$ which are the association energy and effective association volume, respectively, between sites A and B on molecule i. These two parameters represent the contribution of association in equation (1). In this way, the PC-SAFT model represents an associating molecule by these five parameters: m_i, σ_i, ε_i, $\varepsilon^{A_iB_i}$, and $K^{A_iB_i}$.

The PC-SAFT model has been proven as a suitable model for pure substances and mixtures containing solvents and gases, as well as gas-liquid equilibria (VLE) of polymer systems [33]. In addition to providing accurate answers for vapor-liquid equilibrium systems and high-pressure liquid-liquid systems of polymer solutions, this equation also yields acceptable results for expressing the state of systems containing ionic liquids. Chen et al. showed that PC-SAFT is a suitable equation of state for modeling CO_2 in imidazolium-based ionic liquids over a wide range of temperature and pressure [34]. Rahmati et al. investigated the solubility of H_2S gas in ionic liquids. The results revealed that the error of the PC-SAFT EoS and the SAFT-VR EoS compared to the laboratory data is about 40% [35].

As it is seen in Table 1, the proposed parameters of the PC-SAFT equation of state for the ionic liquid [bmim][NTf_2] are significantly different in the literature [32, 34, 35, 36, 37].

Table 1 PC-SAFT parameters of ionic liquid [bmim][NTf_2] extracted from literature.

Component	M_W(g.mol^{-1})	m_i	$\sigma_i(\mathring{A})$	ε_i/k_B(K)	$\varepsilon^{A_iB_i}/K^{A_iB_i}$(K)	$K^{A_iB_i}$	AAD (%)	Ref.
[bmim][NTf_2]	419.37	8.23	3.81	393.8	-	-	0.2880	[34]
[bmim][NTf_2]	419.37	5.72	4.37	458.9	3450	0.00225	4.29	[34]
[bmim][NTf_2]	419.37	6.05	4.21	375.2	3450	0.00225	0.12	[34]
[bmim][NTf_2]	419.37	7.15	4.058	285	2611	3450	0.016	[35]
[bmim][NTf_2]	-	8.360	3.780	383	-	-	0.15	[32]
[bmim][NTf_2]	-	9.260	3.660	383	1350	0.00225	0.18	[32]
2(1:1)								
[bmim][NTf_2]	-	9.410	3.640	382	1170	0.00225	0.18	[32]
3(2:1)								
[bmim][NTf_2]	-	9.740	3.600	382	1020	0.00225	0.18	[32]
4(2:2)								
[bmim][NTf_2]	419.36	9.3386	3.6072	310.25	4510	0.09837	0.10	[36]
[bmim][NTf_2]	419.37	6.05	4.21	375.2	3450	0.00225	0.12	[37]

The parameters of pure, binary, etc., should be determined to use in any thermodynamic models in a process simulator such as Aspen Plus, To improve accuracy, the PC-SAFT EoS parameters of [bmim][NTf_2] are calculated based on the experimental data of the properties of the pure compound, i.e., density and heat capacity used in this work [38]. The mentioned experimental data reported in the literature are measured from 273.1 to 413.1 K. The results are shown in Table 2.

Table 2 The tuned parameters of PC-SAFT of ionic liquid [bmim][NTf_2].

	M_W(g.mol^{-1})	m_i	$\sigma_i(\mathring{A})$	ε_i/k_B(K)	$\varepsilon^{A_iB_i}/K^{A_iB_i}$(K)	$K^{A_iB_i}$	AAD(%)
[bmim][NTf_2]	419.37	5.9954	4.246	393.407	5180.71	0.02457	0.16

Thermodynamic Properties of [bmim][NTf_2]

Aspen Plus V10 software is used to simulate both sweetening processes using IL and amine solvents. Although Aspen Plus boasts one of the most powerful databases and extensive data on material properties, it lacks comprehensive data on the ionic liquid [bmim][NTf_2]. In addition, it is necessary to determine and introduce the thermophysical information of the IL to the software.

Critical Properties

Critical properties are required for the estimation of some thermo-physical properties for pure and binary systems in the Aspen Plus software. However, since most of the ILs begin to decompose as the temperature gets closer to their typical boiling point, experimentally determining their critical properties is often impossible. Consequently, group contribution methods are commonly employed to estimate these properties. In this study, the method proposed by Valderrama et al. [39-40] is used to estimate the critical properties of ILs. This approach builds upon the concepts introduced by Lydersen [41] and Joback and Reid [42]. The reliability of the method has been validated by comparing the calculated liquid densities of various ILs, demonstrating sufficient accuracy for use in equations of state (EOS) models. Equations 2 to 6 and the parameters listed in Table 3 are applied to estimate the critical properties of [bmim][NTf₂].

$$T_b = 198.2 + \sum n\Delta T_{bM} \tag{2}$$

$$T_c = \frac{T_b}{A_M + B_M \sum n\Delta T_M - (\sum n\Delta T_M)^2} \tag{3}$$

$$P_c = \frac{M}{[C_M + \sum n\Delta P_M]^2} \tag{4}$$

$$V_c = E_M + \sum n\Delta V_M \tag{5}$$

$$\omega = \frac{(T_b - 43)(T_c - 43)}{(T_c - T_b)(0.7T_c - 43)}\log\left(\frac{P_c}{P_b}\right) - \left(\frac{T_c - 43}{T_c - T_b}\right)\log\left(\frac{P_c}{P_b}\right) + \log\left(\frac{P_c}{P_b}\right) - 1 \tag{6}$$

In which T_b is normal boiling temperature, T_c is critical temperature, P_c is critical pressure, V_c is critical volume, ω is acentric factor, n is number of times that a group appears in a molecule, ΔT_{bM} is contributions to the normal boiling temperature, ΔT_M is contribution to the critical temperature, ΔPM is contribution to the critical pressure, ΔV_M is contribution to the critical volume, M is molecular mass, and A_M, B_M, C_M, and E_M are coefficients:

$A_M = 0.5703; B_M = 1.0121; C_M = 0.2573; E_M = 6.7500.$

Table 3 Group Contribution Method Parameters [40]

Group	ΔT_{bM}	ΔT_M	ΔP_M	ΔV_M
Without Ring				
$-CH_3$	23.58	0.0275	0.3031	66.81
$-CH_2-$	22.88	0.0159	0.2165	57.11
>C< [>C-]$^-$	18.18	-0.0206	0.0539	21.78
>N- [>C<]$^+$	11.74	-0.0028	0.0304	26.70
-N=	74.60	0.0172	0.1514	45.54
-F [F-]	-0.03	0.0228	0.2912	31.47
$-SO_2-$	147.24	-0.0563	-0.0606	112.19
With Ring				
=CH-	26.73	0.0114	0.1693	42.55
>N- [>N<]$^+$	86.16	0.0063	0.0538	25.27
-N= [>N=]$^+$	75.55	-0.0011	0.0559	42.15

The result is shown in Table 4. The critical properties of [bmim][NTf_2] which has been estimated based on group contribution method is given in Table 4.

Pure Properties

The experimental data for all temperature-dependent thermo-physical properties of the ionic liquid [bmim][NTf_2] were extracted from the literature. The relevant pressure and temperature range of each property is shown in Table 5. Moreover, these laboratory data were inputted into the software, and using Aspen Plus regression, the data were fitted based on the DIPPR equations proposed by Aspen Plus. The specifics of each property are outlined in Table 6.

Table 4 Estimated critical properties of [bmim][NTf_2]

Critical Parameter	Property Value	Unit
T_b	862.3	K
T_c	1269.93	K
P_c	27.646	bar
V	990.13	mlit/mol
Z_c	0.2592	-
ω	0.3004	-

Table 5 Pressure and Temperature range of employed properties of [bmim][NTf_2].

Property	Temperature (K)	Pressure (kPa)	Experimental data ref.
Density	273.15 ~ 413.15	101.325	[38]
Thermal Conductivity	293 ~ 353	101.325	[43]
Heat Capacity	273.15 ~ 413.15	101.325	[38]
Surface Tension	284.15 ~ 351.56	101.325	[44]
Viscosity	278.15 ~ 373.15	101.325	[45]
Vapor pressure	437.84 ~ 517.45	3.6e-6 ~ 5.15e-4	[46]
Heat capacity of ideal gas	100 ~ 1000	0.2243 ~ 0.7666	[47]

Table 6 Equations of temperature-dependent thermophysical properties of [bmim][NTf_2]

Property	Equation	AAD (%)	Experimental data ref.
Thermal Conductivity	$K = 0.1295 - 7\times10^{-5}T$	0.0683	[43]
Heat Capacity	$C_p = 0.2388$	0.1666	[38]
Surface Tension	$\sigma = 46.769(1-T_r)^{0.2982+11.735T_r-43.9356T_r^2+53.393T_r^3}$	0.0563	[44]
Viscosity	$\mu = \exp(46.769 + \frac{0.2982}{T} + 11.735\ln T - 43.9356T^{53.393})$	0.7287	[45]
Vapor pressure	$P = \exp(22.5619 - \frac{17688.2}{T} + 273.15\ln T)$	2.7359	[46]
Heat capacity of an ideal gas	$C_p^{ig} = 117.959 + 1.17157T - 0.111529T^2$	0.7434	[47]

Binary Properties

The separation of acid gases from natural gas using the ionic liquid solvent [bmim][NTf_2] is performed via liquid physical absorption [48]. This approach relies on the physical dissolution of gases rather than chemical reactions between the solvent and the absorbed species. The key challenge lies in CO_2 and H_2S acid gas solubility in the ionic liquid solvent. Laboratory data from the literature were obtained and used to determine the binary interaction parameter kij between the ionic liquid solvent [bmim][NTf_2] and the major components of natural gas. It was ensured that the regression analysis incorporated data within the vapor pressure range for each element in the system. When necessary, results were unavailable within this range, and extrapolation methods were employed to calculate the required information. The present study examines the binary interaction of [bmim][NTf_2] with methane, ethane, propane, n-butane, i-butane, carbon dioxide, and hydrogen sulfide. The binary interaction parameter k_{ij} of the PC-SAFT equation of state was determined using the flash calculation method to enhance accuracy. For each binary system at constant temperature, a minimum of four data points were selected, and the k_{ij} value for each data point was determined. The kij values obtained for each temperature were fitted as a function of temperature and k_{ij} information required to introduce binary interaction data to Aspen Plus. The kij parameter as a function of temperature is described by Equation 7 for correlated binary interaction data to the PC-SAFT EoS.

$$k_{ij} = A_{ij} + B_{ij} / T_r + C_{ij} \ln T_r + D_{ij} T_r + E_{ij} T_r^2$$
$$T_r = T / T_{ref} \ , T_{ref} = 298.15\,\mathrm{K} \qquad (7)$$

The result is shown in Table 7. The parameters of equation (7) for binary interaction parameters are presented in Table 7.

Table 7 Correlated parameters for binary interaction parameter (kij) for PC-SAFT EoS.

Component j	Temperature (K)	A_{ij}	B_{ij}	C_{ij}	D_{ij}	E_{ij}	Experimental data Ref.
[bmim][NTf_2]-C_1	313 ~371	0.3244	-0.3780	-0.1787	0.0000	0.0000	[49]
[bmim][NTf_2]-C_2	298 ~ 353	-3.6402	3.6470	3.6399	0.0000	0.0400	[50]
[bmim][NTf_2]-C_3	298 ~ 353	-0.2523	0.2823	0.391	0.0000	0.0000	[50]
[bmim][NTf_2]-IC_4	288 ~ 313	0.0459	-0.0175	0.0000	0.0000	0.0000	[51]
[bmim][NTf_2]-NC_4	280 ~ 340	-0.7353	0.7744	0.7892	0.0000	0.0000	[52]
[bmim][NTf_2]-CO_2	283 ~ 323	0.1409	-0.0982	0.0000	0.0000	0.0000	[16]
[bmim][NTf_2]-H_2S	303 ~ 343	0.5565	-0.1608	0.2429	-3763	0.0000	[23]

Simulation of the Sweetening Process

The natural gas composition in this study is simulated based on the natural feed gas of the Iranian gas refinery. The feed enters the system at a pressure of 66.3 bar and a temperature of 24 °C. The simulation replicates the capacity of the industrial-scale sweetening unit currently in operation. The detailed composition of the natural gas feed is provided in Table 8. In order to economically compare two amine-based solvent-sweetening processes with an ionic liquid-based solvent-sweetening process, a natural gas sweetening unit was simulated using the tertiary amine methyl diethanolamine (MDEA) as the conventional solvent.

Table 8 Natural gas feed composition.

Component	Molar Flow rate (kmol/hr)	Mole Fraction (%)
C_1	22675.0	85.55
C_2	1449.2	5.47
C_3	534.6	2.02
IC_4	98.7	0.37
NC_4	151.2	0.57
CO_2	487.6	1.84
H_2S	184.0	0.69
N_2	926.1	3.49
Total	26506.3	1.00

Sweetening Process with Amine Solvent

As it is shown in Fig. 1, as typical process flow diagram of sweetening process by alkanolamine solvent. The sour natural gas enters the absorption tower at a pressure of 66.3 bar and a temperature of 24 °C, with a molar flow rate of 26,506.3 kmol/h. The absorber column, modeled as a RadFrac column, contains 34 trays and operates without a condenser or reboiler. The feed gas is introduced as a vapor phase on the 34th (top) tray. An aqueous amine solvent comprising 55 wt.% water and 45 wt.% MDEA is fed as a liquid on the first tray of the absorber column. Based on industrial plant data, the solvent enters the tower at a flow rate of 11,526.5 kmol/h, a pressure of 65.9 bar, and a temperature of 41.5 °C. A total pressure drop of 0.4 bar is assumed across the column. Inside the absorber column, the rising gas comes into contact with the descending amine solution on the trays.

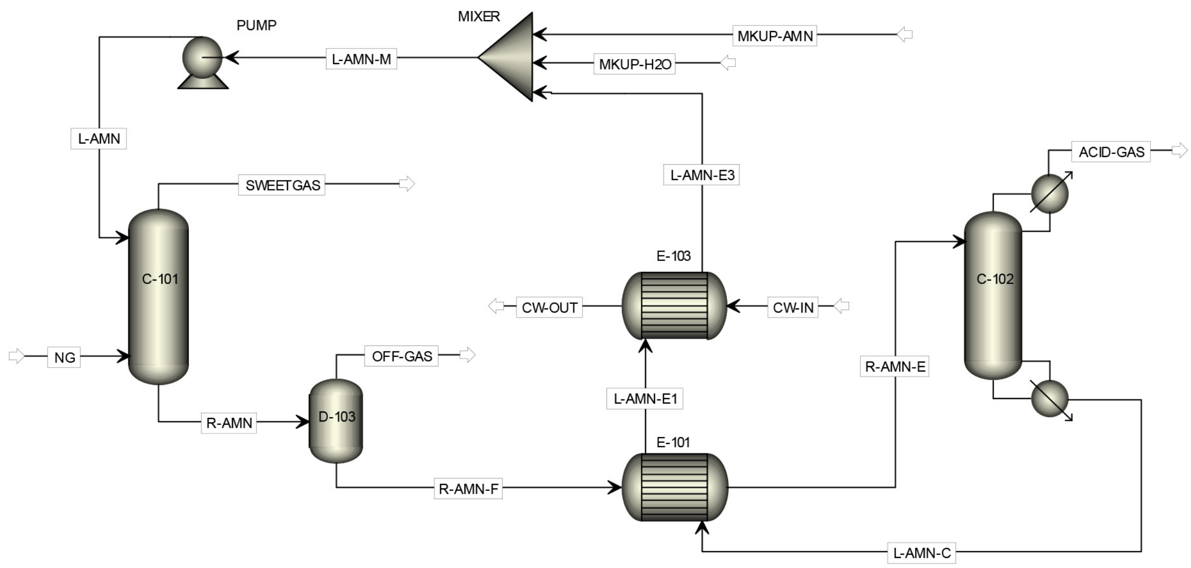


Fig. 1 The Process Flowsheet of acid gas removal from Natural gas process with Amine solvent.

Through chemical reactions and mass transfer, acid gases are absorbed by the solvent. As a result, sweet gas exits from the top of the column, while the amine solution enriched with acid gases and absorbed hydrocarbons exits from the bottom. At the top of the tower, the operating conditions are 53.7 °C and 65.9 bar, whereas the bottom operates at 41 °C and 66.3 bar. The enriched amine solution is then sent to a flash drum operating at 9 bar. The pressure drop leads to the release of absorbed hydrocarbons as vapor (off-gas), which exits from the top of the drum. The remaining liquid amine exits the flash drum at 9 bar and 37 °C. This solution then passes through heat exchanger E-101, where its temperature increases to 96.8 °C before entering the regeneration tower. The regeneration column is also a RadFrac type with 20 trays, with a partial vapor condenser, and a kettle reboiler. It operates at a top pressure of 2.2 bar, with a total pressure drop of 0.25 bar. Inside the regeneration column, steam generated by the reboiler rises and contacts the descending rich amine solution, stripping out the absorbed acid gases. These gases exit from the top of the tower, while the regenerated amine exits from the bottom at 133 °C and 2.6 bar. The regenerated amine is then cooled sequentially through heat exchangers E-101 and E-103 and enters a pump at 40 °C and 2.6 bar. The pump increases the pressure to approximately 66 bar, allowing the amine to be recycled back to the absorption tower for reuse.

Sweetening Process with IL Solvent

The liquid physical absorption method is employed to separate acid gases from natural gas using the ionic liquid solvent [bmim][NTf_2]. As it is shown in Fig. 2, in this process, the solvent liquid and natural gas come into contact in the absorption column, and mass transfer occurs. The sweetened gas exits from the top of the tower, while the ionic liquid, which is rich in acid gases and contains some absorbed hydrocarbons, leaves from the bottom. In the ionic liquid sweetening process, Solvent regeneration is achieved by pressure reduction through two flash drums. Moreover, to assess the impact of thermal load on sweetening efficiency, simulations were conducted with and without heat input in Flash Drum 2. The feed sour natural gas enters the RadFrac-type absorption column at 24 °C and 66 bar, with a molar flow rate of 26,506.3 kmol/h. The gas is introduced as a vapor phase on tray 13, while the ionic liquid enters as a liquid phase on tray 1. After physical absorption, sweet gas exits the top at 24.6 °C and 65.9 bar, and the acid gas-rich solvent exits the bottom at 25.1 °C and 66.3 bar, entering Flash Drum 1. Flash Drum 1 operates at 50 bar, causing a portion of the acid gases and hydrocarbons to vaporize and exit from the top. The remaining liquid solvent is routed to a turbine, which reduces its pressure to create the vacuum needed for Flash Drum 2. The vapor from Flash Drum 1 is compressed from 50 to 66.3 bar and cooled from 64.7 °C to 24 °C before being recycled back to the absorption tower. The liquid exiting Flash Drum 1 (at 50 bar and 25.5 °C) enters Flash Drum 2, which operates at 0.02 bar and 80 °C. This pressure and temperature differential facilitates maximum separation of CO_2, H_2S, and hydrocarbons from the solvent. These gases exit from the top, while the regenerated ionic liquid exits from the bottom. Before being recycled, the recovered solvent is cooled and pumped back to 24 °C and 66 bar, and returned to the absorption tower for reuse.

Results and Discussion

Sensitivity Analysis

In order to find the optimum condition of the sweetening process and to determine how various values of independent variables affect the acid gas content in sweetened gas, sensitivity analysis is carried out. The selected variables and relevant levels have been considered as follows:

- Number of Trays: 19, 17, 15, 13, 11, 9, 7, 5
- IL flow rate (ton/hr): 600, 1000, 2000, 3000, 4000, 5000, 10000, 20000,26600
- FD-1 pressure (bar): 20, 30, 40, 50
- FD-2 pressure (bar): 1, 0.5, 0.1, 0.05, 0.02
- FD-2 temperature (°C): 50, 60, 70, 80

The effect of the mentioned variables on the acid gas existing in sweetened gas is demonstrated in Figs. 3 - 5.

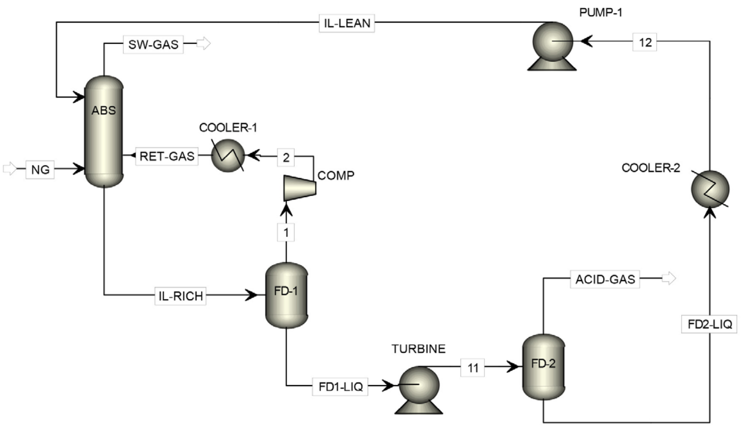
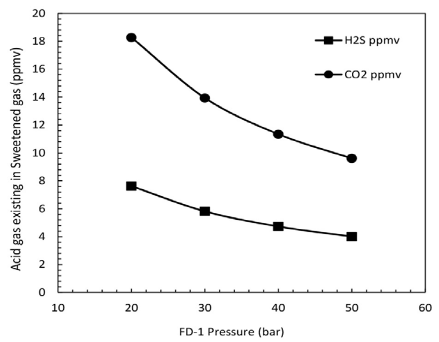
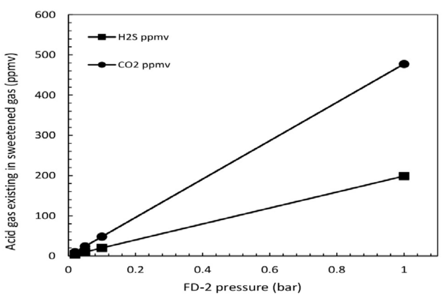


Fig. 2 The process flowsheet of acid gas removal from Natural gas process with [bmim][NTf_2] solvent.



(a)



(b)

Fig. 3 Effect of pressure in flash drums on concentration of acid gases (H_2S and CO_2) in sweet gas. (a): first flash drum ; (b): second flash drum.

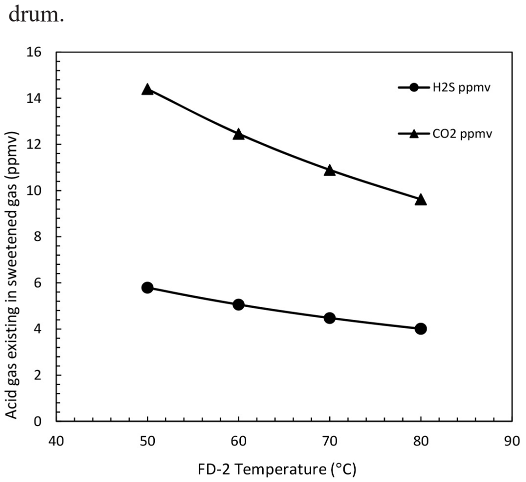
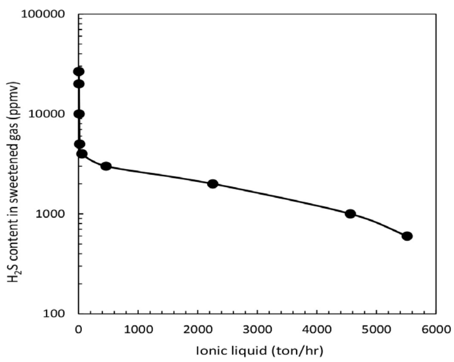
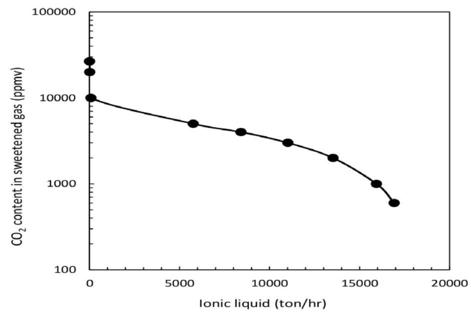


Fig. 4 Effect of the temperature of flash drums FD2 on the concentration of acid gases in sweet gas.



(a)



(b)

Fig. 5 Effect of Ionic-liquid flow rate on concentration of acid gases in sweet gas.(a): effect of ionic liquid flow rate (ton/hr) on H_2S content in sweetened gas (ppmv); (b): effect of ionic liquid flow rate (ton/hr) on CO_2 content in sweetened gas (ppmv).

Comparing the two flash drums, it is evident that the effect of pressure change on sweetening is more significant in flash drum 2 than in flash drum 1. By adjusting the pressure of both flash drums, up to 11.4% of acid gases can be absorbed. To study the influence of thermal changes in the system, various temperatures were assigned to flash drum 2, and the amount of acid gases in the sweetened gas was determined. Additionally, during this phase, flash drum 1 remained adiabatic. To maintain a constant inlet temperature of the absorption tower after the flash drum 2, a cooler with an outlet temperature of 22.6 °C was included in the simulation. This temperature was chosen to match the solvent returning to the tower, which has a temperature of 24°C, aligning with the incoming feed temperature. Increasing the temperature of flash drum 2 from 50 to 80 oC only resulted in a 2 ppmv reduction in hydrogen sulfide and 5 ppmv reduction in carbon dioxide in the sweet gas. An increase in the flow rate of the ionic liquid solvent was implemented, followed by quantification of the residual acid gases in the sweetened gas stream. To achieve the specified sweetening target, defined as a maximum hydrogen sulfide concentration of 4 ppmv, a significantly large volume of the ionic liquid solvent was required. This operational demand indicates that the application of this particular solvent is impractical for industrial-scale gas sweetening under the given conditions.

Hydrocarbon Loss

Selectivity of the solvent toward natural gas components is a critical parameter in the sweetening process. Effective removal of acid gases is essential; however, minimizing the absorption of hydrocarbons—key constituents of natural gas—is equally important. In the present study, the loss of individual hydrocarbon components was quantified. As illustrated in Fig. 6, heavier hydrocarbons exhibited greater solubility in the ionic liquid [bmim][NTf₂] compared to lighter hydrocarbons, a trend consistently observed throughout the sweetening process. Increasing the solvent flow rate significantly altered the extent of hydrocarbon loss, ultimately resulting in the complete removal of propane and butane from the sweet gas, along with the separation of approximately 90% of ethane into the acid gas and solvent phase.

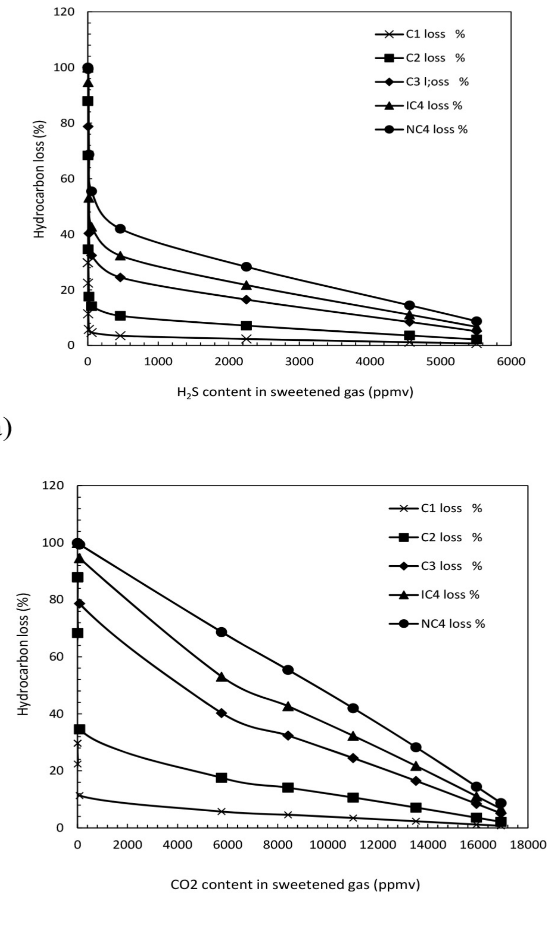


Fig. 6 Effect of co absorption of hydrocarbon and concentration of acid gases (H_2S and CO_2) in sweet gas.(a): effect of co absorption of hydrocarbon loss (%) on H_2S content in sweetened gas (ppmv); (b): effect of co absorption of hydrocarbon loss (%) on CO_2 content in sweetened gas (ppmv).

Energy Consumption

Energy consumption is another critical factor in evaluating solvent-based sweetening processes. The total energy demand accounts for all equipment involved in the process, encompassing both thermal and electrical inputs. For the ionic liquid solvent, the energy required to meet the sweet gas specification of 4 ppmv hydrogen sulfide is substantially high, 1,203,953 kW with heating and 245,746 kW without heating. In contrast, the energy required for sweetening using a conventional amine-based solvent is significantly lower, amounting to only 105,580 kW. Thus, beyond the excessive solvent volume required, the elevated energy demand further underscores the impracticality of using ionic liquids for natural gas sweetening when compared to established amine-based methods.

Conclusions

In the present study, Aspen Plus was employed as a process simulator to evaluate the performance of a natural gas sweetening process using an ionic liquid solvent for Iranian gas composition. For the first time, such an evaluation has been conducted for Iranian gas refineries, it was aim to give a benchmark for ionic liquid solvent against a conventional aqueous MDEA-based solvent in gas sweetening process. Moreover, the PC-SAFT EoS is applied because of its superior accuracy in calculating both primary and secondary (derivatives) of the thermodynamic and thermophysical properties. In the absence of pre-defined parameters for the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([bmim][NTf₂]) in Aspen Plus, all pure and binary parameters are correlated to thermo-physical, and the PC-SAFT EoS, and these parameters are used for simulation of the sweetening process based on [bmim][NTf₂] ionic liquid.

The results reveal that, for the sweetening of feed with a flow of 500 ton/h of Iranian natural gas and to meet the hydrogen sulfide concentration of 4 ppmv in the sweet gas, the required circulation rate of [bmim][NTf₂] solvent is exceedingly high (26,600 ton/h) with thermal load and 89,600 ton/h without it. In contrast, the MDEA-based system only requires approximately 330 ton/h of solvent, resulting in significantly smaller and more feasible equipment design. Additionally, energy consumption for the ionic liquid-based process was calculated at 1,203,953 kW with heating and 245,746 kW without, both of which are substantially higher than the 105,580 kW required for the amine-based system. These findings clearly demonstrate that, under the specified process conditions, the use of [bmim][NTf₂] as a solvent for natural gas sweetening is not viable due to its excessive solvent requirement and noncompetitive energy consumption profile compared to the established amine-based alternative.

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