Deep eutectic solvents for CO$_2$ capture from natural gas by energy and exergy analyses

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ABSTRACT

Nowadays, environmental issues and the energy crisis are among the most important challenges to researchers. The necessity of increasing the energy efficiency of industrial processes is vital. If this efficiency increase is additionally done by using sustainable components, environmental issues are also alleviated. Deep eutectic solvents (DESs) are a new generation of green solvents with unique properties. This has led to the exponential growth of research in the field, oriented towards green chemistry and green processing. This study investigates the feasibility of utilizing DESs in the petroleum industries by considering the case study of capturing CO$_2$ from natural gas, resulting in a purified gas with greater heating value. The idea is to utilize the DES as an absorbent, in place of the conventional Selexol. The pressure swing absorption process was simulated for two different DES, namely Reline and Glyceline. The purity of the methane stream was 89.1% when using Selexol, and 90.1% and 79.6% for Reline and Glyceline, respectively. The carbon dioxide stream showed even greater purity differences when DESs were used (98.3%, 98.4% and 94.9% CO$_2$ when using Reline, Glyceline, and Selexol, respectively). Furthermore, energy and exergy analyses were carried out on the proposed plants. While the overall duties were less for the plants using DESs (-51.27, -11.13, and 15.17 and kW for Reline, Glyceline, and Selexol, respectively), the exergy destructions were not (146.78, 165.64, 96.54 kW for Reline, Glyceline, and Selexol, respectively). The results indicated the feasibility of using DESs as potential physical solvents in such industries.

1. Introduction

The growing world population and the improved quality of life have led to increasing demands for energy, the main source being the fossil fuels. Among the different types of fossil fuels, natural gas has the least harmful impacts on the environment. However, nowadays, due to technological improvements, extraction from reservoirs containing sub-quality natural gases is becoming more economically feasible. Sub-quality natural gas usually contains relatively high amounts of impurities, such as carbon dioxide, which have to be removed because they are corrosive and they decrease the heating value of natural gas [1,2].

To separate carbon dioxide from a gas stream by absorption, there are generally two methods available; physical and chemical absorption. Physical absorption by solvents such as Selexol, methanol, propylene carbonate, and dimethyl carbonate is preferred over chemical absorption when the partial pressure of carbon dioxide in the gas stream is high [2].

However, it is important to emphasize that the physically-absorbing solvents mentioned above have various environmental issues.

Therefore, in carbon dioxide capture processes, it is most desirable to replace conventional solvents with green solvents that are friendlier to the environment [1–3]. There are very few studies in the literature devoted to this. Martinez [3] studied the separation of carbon dioxide from methane by using the ionic liquid of 1-hexyl-3-methylimidazolium tetracyanoborate as a physical solvent. She investigated the pressure swing absorption process and compared the performance of the investigated ionic liquid with that of conventional Selexol. She found that in some cases, the process using the 1-hexyl-3-methylimidazolium tetracyanoborate ionic liquid requires smaller amounts of solvent in comparison to the Selexol process, and consequently, the process is less energy intensive. Following this study, Zubeir et al. [4] investigated the use of another ionic liquid, 1-hexyl-3-methylimidazolium tricyanomethanide, as the physical solvent for sweetening a synthetic natural gas consisting of carbon dioxide and methane. They simulated pressure swing absorption (PSA), temperature swing absorption (TSA), and a combination of both, and found that the combination of PSA and TSA leads to a more feasible separation.

However, it is reported in the literature that ionic liquids have a number of disadvantages and limitations [5–7]. Therefore, a new

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generation of sustainable solvents, called the deep eutectic solvents (DESs), have recently been introduced by Abbott [8], as possible alternatives to ionic liquids. DESs are mixtures of two or more components, consisting of hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD). Because of the formation of hydrogen bonds between these components, the melting point of the resulting DES is lower than the melting points of the individual HBA and HBD [9,10]. The vast majority of DESs have highly desirable properties, particularly very low vapour pressures. They are also mostly biodegradable and sustainable, allowing them to be classified as green solvents [11–14]. Furthermore, a most desirable characteristic of a DES is that it can be designed (tuned) to have the desired physical and thermodynamic properties. This can be done by an engineered selection of the HBA and HBD (among the very wide list of possible components), and their corresponding molar ratio [15,16]. Because of these special properties of DESs, researchers have seriously started to investigate the potential of applying DESs in a wide range of applications [9–21]. Among the favourable properties of DESs, is the rather high capacity to physically dissolve gases. This makes them candidate solvents for gas capture and gas separation in various industries [5]. If they can prove themselves as industrially-efficient absorbents for carbon dioxide in separation plants, they have the potential to replace conventional solvents.

In this study, the goal was to investigate, natural gas purification from its carbon dioxide impurities using a DES as the absorbent. This is the first study in literature to suggest the use of deep eutectic solvents for CO_2 capture from natural gas. Therefore, we follow an industrial perspective, by considering not only the feasibility of utilizing DESs as absorbents and evaluating the resulting product purities, but also by carrying out the energy and exergy analyses of the processes. Reline and Glyceline were considered as the physically-absorbing DESs for selective carbon dioxide capture in the pressure swing absorption process.

2. Process simulation

2.1. Process description

The gas stream is treated by pressure swing absorption. Pressure swing adsorption (PSA) is a process used to separate gas impurities from a gas mixture according to differences in the solubilities of the species in the absorbent material (solvent). The resulting streams are the purified gas mixture, and the absorbent stream which is then regenerated by reducing the pressure, in order to desorb the dissolved gases [3,4]. In this study, we have considered the PSA process using either Reline (1 choline chloride + 2 urea) or Glyceline (1 choline chloride + 2 glycerol) as the physical solvent. For the purpose of comparison, the same process is also considered with Selexol as a conventional solvent. The resulting CO_2 stream is compressed to 100 bar, to be transported to a carbon storage site or to be re-injected for enhanced oil recovery. The PSA process is assessed at different absorption pressures, ranging from 20 to 35 bars.

Fig. 1 shows the process flow diagram (PFD) of pressure swing absorption for gas absorption [2–4]. The most important part of the process is an absorber, consisting of 12 trays (stages). The feed to the plant is 50 kmol/h (1501.25 kg/h) of an equimolar mixture of CO_2 and CH_4, which is fed to the bottom of the absorber [2–4]. A high-pressure isothermal flash tank (HP-FLASH) is incorporated to recover the CH_4, co-absorbed in the solvent. The top stream (gas phase) leaving HP-FLASH (FL1-TOP) is recompressed (RE−COM) and cooled down (RE-HX1) before being recycled to the bottom of the absorber and mixed with the feed. The solvent is fed to an atmospheric-pressure adiabatic flash tank (LP-FLASH) to extract the remaining dissolved CO_2 in the solvent, and also, to produce a solvent with high purity. The stream of solvent can be fed to a desorption unit to recover and recycle the solvent. In this study, because our focus was on the process of absorption using different solvents, and furthermore, the simulation of the desorption process requires extra commercial information which is

unavailable, we did not consider the desorption unit of the solvent and have assumed fresh solvent to be available for absorption [2–4]. This solvent, after being pumped (SOL-PUMP) to reach the absorber pressure, and after passing through a heat exchanger (SOL-HX) for temperature reduction, is fed to the top of the absorber. The CO_2-rich gas from the process is compressed to 100 bars through several stages of compression (CO_2 − COM 1–4).

This plant was actually simulated based on the commercial Selexol plant. Operating conditions were taken from the Selexol plant, and considered as the "base case" design [2–4]. Then, by changing the type of solvent and/or the most important operating conditions of the plant, such as the solvent flow rate, the temperature of the high pressure flash tank, or the absorber pressure, the effect of each of these variations was determined on the composition and flow rate of the produced CO_2 and CH_4 streams, as well as the total duty and exergy destruction of the plant. Table 1 presents the values of the base-case operating conditions of the plant, while Table 2 gives the specifications of the synthetic gas feed and the solvent to the plant at the base-case conditions.

2.2. Solvent characterization

2.2.1. Deep eutectic solvents

In this study, two of the better-known and more-commonly investigated DESs, namely Reline and Glyceline, were chosen as solvents of the PSA process. The reason for selecting these DESs is based purely on the availability of the physical properties, necessary for simulation, including for example, the experimental densities. The solubilities of carbon dioxide in each of these solvents were calculated by the φ-φ approach, with the aid of the Peng Robinson Equation of State (PR EoS). As common in literature, the modelling of each DES was carried out by considering it as a pseudo-component, by implementing the physiochemical properties of the DES. The necessary binary interaction coefficients between the components were optimized based on available literature data and the capability of the PR EoS in calculating the gas solubilities in the DESs was investigated. These results are given in the Supplementary Data (Figs. S1–S3). Our investigation of the literature indicated that the mechanism of absorption of CO_2 and CH_4 in Reline is governed by gas occupation in the free volumes of the solvent [22]. Densities, critical properties, and ideal gas heat capacities obtained from the literature, were used to define the appropriate pseudo-components of Reline and Glyceline. It is important to highlight that the choices of Reline and Glyceline were not based on high absorption capacity for CO_2, but rather, on the limitation of the availability of physical property data, therefore, they are not necessarily the best-performing DESs for this process. Tables S1–S3 of the Supplementary section present the critical properties, the densities within the temperature and pressure range of 298.15–323.15 K and 0.1–50 MPa, respectively, and the ideal gas heat capacities within the entire liquidus temperature range for Reline and Glyceline.

2.2.2. Selexol

The commercial solvent of Selexol is actually a mixture of the dimethyl ethers of polyethylene glycol ($CH_3O(CH_2CH_2O)_nCH_3$), with $n = 3$–9, having an average molecular weight of 272.8 g/mol [2,4,23]. Table S4 of the Supplementary material presents the approximate composition and characterization of Selexol. However, because of the unavailability of the properties of the pure component making up the commercial Selexol mixture, similar to the study by Zubeir et al. [2,4], we have selected the dimethyl ether of pentaethylene glycol (DE-PentaG), with n = 5 and a molecular weight of 266.3 g/mol, as the component to represent Selexol.

2.3. Energy and exergy analyses

The basic mass and energy balances in each of the steady state equipment of the plant are given by Eqs. (1) and (2), respectively.
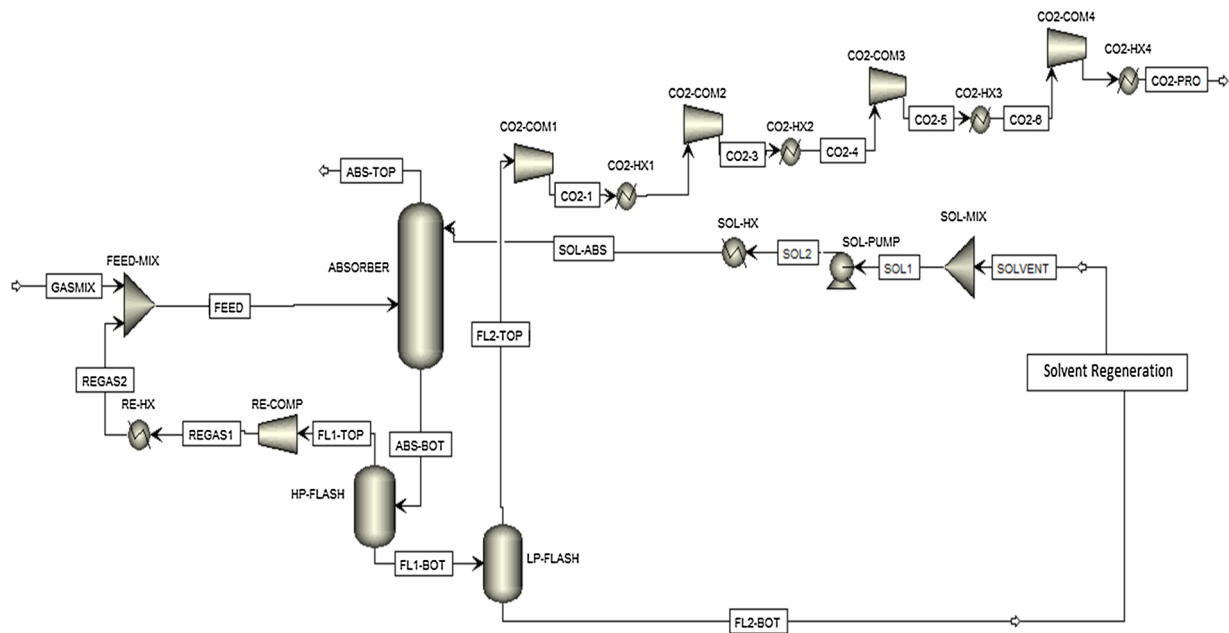
Fig. 1. Process flow diagram (PFD) of the PSA process for carbon dioxide absorption.

Table 1
Base-case operating conditions of the absorption plant.

#	Equipment	Characteristic	
1	Absorber	Number of Trays	12
		Feed Tray	12
		Solvent Tray	1
		Pressure (bar)	28.0
		Pressure Drop (bar)	0.0
2	HP-Flash	Temperature (K)	306.2
		Pressure (bar)	9.3
		Liquid Entrainment	0
3	LP-Flash	Pressure (bar)	1.0
		Duty	0
		Liquid Entrainment	0
4	RE-COMP	Isentropic compressor	η = 0.80
		Discharge pressure (bar)	35.0
5	CO₂-COM1	Isentropic compressor	η = 0.80
		Discharge pressure (bar)	3.2
6	CO₂-COM2	Isentropic compressor	η = 0.80
		Discharge pressure (bar)	10.0
7	CO₂-COM3	Isentropic compressor	η = 0.80
		Discharge pressure (bar)	31.4
8	CO₂-COM4	Isentropic compressor	η = 0.80
		Discharge pressure (bar)	100.0
9	SOL-PUMP	Pump	η = 0.85
		Discharge pressure (bar)	35.0
10	RE-HX	Heater temperature (K)	301.50
		Pressure drop	0.0
11	CO₂-HX1	Heater temperature (K)	298.15
		Pressure drop	0.0
12	CO₂- HX 2	Heater temperature (K)	298.15
		Pressure drop	0.0
13	CO₂- HX 3	Heater temperature (K)	298.15
		Pressure drop	0.0
14	CO₂- HX4	Heater temperature (K)	298.15
		Pressure drop	0.0
15	SOL- HX	Heater temperature (K)	293.15
		Pressure drop	0.0

$$\sum \dot{m}_{in} = \sum \dot{m}_{out} \tag{1}$$

$$\dot{Q} + \dot{W} + \sum \dot{m}_{in}h_{in} - \sum \dot{m}_{out}h_{out} = 0 \tag{2}$$

where $\dot{Q}$ and $\dot{W}$ are the heat transferred and the work produced/consumed, respectively, by the equipment, and $\dot{m}$ and h are the flow rates

Table 2
Gas feed and solvent stream properties and characterization.

#	Stream	Temperature (K)	Pressure (bar)	Total Flow (kg/h)	Composition (Mole-Frac)	
1	GASMIX	301.15	35.0	1500	CH₄	0.5
					CO₂	0.5
					Solvent	0.0
2	SOLVENT	298.15	1.0	17500	CH₄	0.0
					CO₂	0.0
					Solvent	1.0

and specific enthalpies of the input or output streams, respectively [24].

Energy analysis is based on the first law of thermodynamics, while exergy analysis follows a thermodynamic analysis procedure and is based on the second law of thermodynamics [24]. Energy analysis is carried out by estimation of the duty, which is defined as the overall energy transfer of an equipment, consisting of both heat and work. The overall duty would refer to the summation of the duties of all of the equipment in the plant. On the other hand, exergy analysis is quite useful for studying the efficiency of the energy. Exergy is an index of how close the actual performance approaches the ideal. Actually, an exergy analysis can distinguish the causes and locations of thermodynamic losses of a plant more clearly than the corresponding energy analysis [24].

Exergy is defined as the maximum theoretically useful work that can be obtained from a system when it is in equilibrium with the surrounding environment. In general, because a real system does not have ideal behaviour, there is always some exergy destruction. The exergy destruction is estimated by implementing the exergy balance on the steady state system using Eq. (3),

$$\dot{E}_Q + \dot{W} + \sum \dot{E}_{in} - \sum \dot{E}_{out} = \dot{I}_d \tag{3}$$

where $\dot{I}_d$ is the exergy destruction rate, and $\dot{E}_{in}$ and $\dot{E}_{out}$ are the exergies of the input and output streams of the system, respectively, which are dependent on the flow rate as given by,

$$\dot{E} = \dot{m}e \tag{4}$$

The specific flow exergy, e, is defined by Eq. (5),

$$e = h - h_0 - T_0(s - s_0) \qquad (5)$$

where h and s are the specific enthalpy and entropy of the stream, respectively. The subscript zero corresponds to an arbitrary reference state [24].

$\dot{E}_Q$ is the exergy transfer due to the heat transfer, $\dot{Q}$, and is defined by Eq. (6).

$$\dot{E}_Q = \sum \left(1 - \frac{T_0}{T}\right)\dot{Q} \qquad (6)$$

where T_0 is the reference state temperature that corresponds to the state at which the system is in equilibrium with the environment, and T is the boundary temperature at which heat transfer occurs [24].

3. Results and discussions

As previously explained, the general aim of this study was to compare the capability of Reline and Glyceline, as compared to Selexol, to be used as a physical solvent in the PSA process of carbon dioxide absorption, by considering the product, as well as the energy and exergy analyses. The results were initially compared for a base-case design, and then sensitivity analyses were carried out on a number of operating parameters that had considerable impact on the operation and efficiency of the plant.

3.1. Base-case

With the base-case operating parameters presented in Tables 1 and 2, and with the reference state for exergy calculations considered at the temperature and pressure of 303.15 K and 1 bar, respectively, the results were calculated. Table 3 presents the estimated values of the resulting carbon dioxide-rich and methane-rich stream flow rates and compositions for all of the three investigated solvents at the base-case conditions.

As indicated by the table, the purities of both the produced carbon dioxide and methane streams are more or less the same for all of the investigated solvents, however, the proposed DESs show somewhat higher purification of the carbon dioxide-rich stream. For the methane-rich stream, Reline gives the best purities, while Glyceline results in the lowest purities.

Furthermore, the effects of utilizing the different solvents were investigated on the duty and the exergy destruction of each equipment individually, as well as the overall plant, at the base-case conditions. Table 4 presents the calculated energy and exergy information, separately for each equipment.

The total duty and the total exergy destruction are the sum of the duties and exergy destructions of all of the individual equipment of the plant. By comparing the values for the different solvents, it is shown that Reline is the preferred solvent in terms of total duty, while Selexol is the prior solvent in terms of total exergy loss. The final selection of a solvent depends on the main purpose of design, but at the same time, by considering all of the limitations and factors that are specific for any design.

Figs. 2 and 3 present graphical comparisons of the absolute values of calculated duties and exergy destructions, respectively, at the base-case operational conditions for each specific equipment in the plant with the different solvents. The values of duties and exergy destructions of the equipment differ for the various solvent. The reason is the differing physical properties of the solvents, resulting in differing viscosities, compositions, and flow rates, which can affect many conditions of the plant in a complex manner, ultimately resulting in different values of duties and exergy destructions.

From these figures, it is concluded that heat exchangers have the greatest amounts of transferred duties. It is also observed that the absorber and flash tanks are responsible for the greatest amounts of exergy destruction in the plant, followed by the heat exchangers. Therefore, the absorber and flash tanks (Figs. 2 and 3) have great priority for optimization by researchers, from the perspective of both energy and exergy conservation and management of the plant.

It is important to mention that the discussions corresponding to Tables 3 and 4, and to Figs. 2 and 3, correspond only to the base-case. Therefore, if the operational conditions of the plant are altered, it is possible that the above conclusions and trends will not be valid. In order to have a more comprehensive investigation, the most significant operating conditions of the plant, i.e., the solvent flow rate, HP-FLASH temperature, and absorber pressure, were varied and the effects of these changes on the resulting masses and energies are presented in the sections that follow. For each particular operating condition of the plant, the change was carried out individually on that parameter alone, while all of the other operating parameters were kept constant at the base-case values, in order to observe the effect of that one particular operating condition individually.

3.2. Effect of solvent flow rate

One of the most important parameters in the PSA process is the flow rate of the solvent relative to the feed. This factor contributes significantly to the capital investment, as well as the operating costs. For this purpose, the flow rate of the solvent was varied within a wide range for the three solvents, from 15 to 20 ton/h. The effects of these changes on the molar compositions of the produced carbon dioxide-rich and methane-rich streams is presented in Fig. 4a.

As can be seen from Fig. 4a, the deep eutectic solvents are in general, capable to produce CO_2 streams of higher purity than Selexol. This is due to the fact that both of the investigated DESs have higher CO_2/CH_4 distribution coefficients than Selexol. Additionally, it is observed that the purity of the carbon dioxide stream does not change much by changing the solvent flow rate. This holds for all three solvents. This is because within the range of solvent flow rates specified, the overall concentration of the solvent in the absorption column is quite high, and in fact, approaching the limit where the distribution ratio of the resulting absorbent phase is not significantly affected by changes in the solvent flow rate. With respect to the produced methane stream, however, the increase of solvent flow rate results in the increase of the composition of the produced methane, and the rates of increase are steeper for Reline and Glyceline than for Selexol. At lower solvent flow rates, Selexol, and at higher solvent flow rates, Reline, show the best performance in the aspect of methane purity.

Apart from studying the concentrations of the products, it is also important to investigate the systems from an energetic point of view, including the overall duty and the exergy destruction of the plant. Fig. 4b and c present the total duty and the total exergy destruction of the plant for all three investigated solvents, by changing the solvent flow rate.

Based on these two figures, by increasing the solvent flow rate, the total duty of the plant decreases for Reline and Glyceline, while it is almost constant for Selexol. The total exergy destruction of the plant increases by increasing the solvent flow rate for all of the solvents. However, the rate of increase is steeper for Reline and Glyceline than it is for Selexol. The main reason for the increasing or decreasing

Table 3
Comparison of the concentrations and flow rates of the produced carbon dioxide-rich and methane-rich streams of the PSA plant at the base-case conditions (The feed gas is 1500 kg/h of an equimolar mixture of CO_2 and CH_4 at 301.15 K and 35 bar. The solvent is a pure stream of 17500 kg/h at 298.15 K and 1 bar).

#		Selexol	Reline	Glyceline
1	Purity of produced CO_2 (mole %)	94.9	98.3	98.4
2	Purity of produced CH_4 (mole %)	89.1	90.1	79.6
3	Flow rate of CO_2-rich stream (kg/h)	418.7	865.0	723.0
4	Flow rate of CH_4-rich stream (kg/h)	392.8	395.7	396.7

Table 4

Comparison of the calculated values of duty and exergy destruction for each equipment in the plant for all of the three investigated solvents at the base-case operating conditions (The feed gas is 1500 kg/h of an equimolar mixture of CO_2 and CH_4 at 301.15 K and 35 bar. The solvent is a pure stream of 17500 kg/h at 298.15 K and 1 bar).
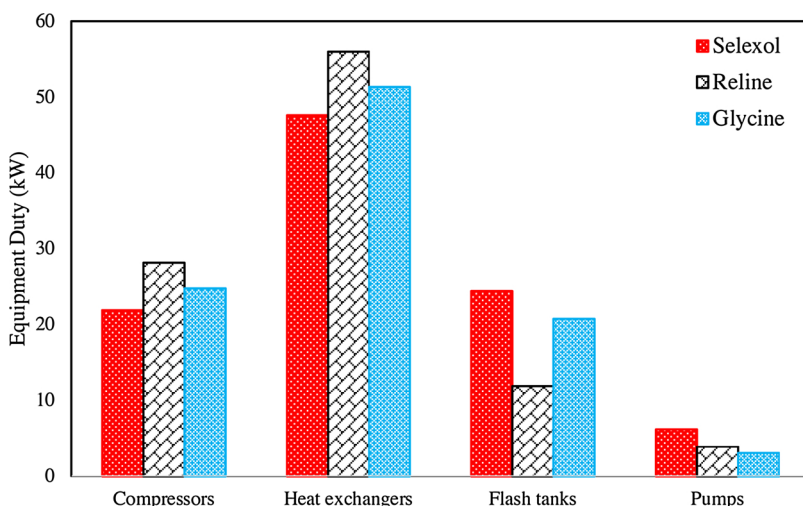
#	Equipment	Selexol		Reline		Glyceline	
		Duty (kW)	Exergy destruction (kW)	Duty (kW)	Exergy destruction (kW)	Duty (kW)	Exergy destruction (kW)
	Compressors						
1	CO2-COM1	11.53	1.76	22.43	3.41	19.12	2.88
2	CO2-COM2	10.94	1.70	22.04	3.35	18.22	2.78
3	CO2-COM3	10.59	1.63	20.98	3.17	17.60	2.66
4	CO2-COM4	9.40	1.42	18.52	2.75	15.53	2.30
5	RE-COMP	25.24	3.65	35.65	5.07	32.60	12.23
	Heat exchangers						
6	CO2-H1	−12.26	1.88	−23.34	3.73	−20.13	3.33
7	CO2-H2	−11.73	1.69	−23.73	3.74	−19.57	3.10
8	CO2-H3	−13.42	1.94	−26.88	4.21	−22.51	3.57
9	CO2-H4	−32.74	3.62	−68.71	8.67	−57.37	7.27
10	RE-HX	−32.00	5.37	−45.91	8.31	−42.02	7.60
11	SOL-HX	−44.68	0.40	−49.42	1.29	−51.61	1.28
	Flash tanks						
12	HP-FLASH	75.23	19.48	50.54	19.36	86.25	20.02
13	LP-FLASH	0.00	15.00	0.00	23.90	0.00	38.54
	Pump						
14	SOL-PUMP	19.07	0.42	16.55	0.85	12.75	8.24
	Mixers						
15	SOL-MIX	0.00	2.0×10^{-7}	0.00	4.0×10^{-6}	0.00	9.0×10^{-6}
16	FEED-MIX	0.00	0.28	0.00	0.15	0.00	0.13
	Absorber						
17	ABSORBER	0.00	36.30	0.00	54.80	0.00	49.70
18	**Total**	**15.17**	**96.54**	**−51.27**	**146.78**	**−11.13**	**165.64**

behaviour of the total duty and exergy destruction lies in the competing effects of the heat exchangers with the flash tanks and the compressors. By increasing the solvent flow rate, the heat exchangers transfer greater amounts of energy out, while the flash tanks and compressors consume more energy. For Reline and Glyceline, the amount of liberated duty in the heat exchangers is greater than the consumed duties in the flash tanks and compressors. This leads to more-negative values of the total duty. However, for Selexol, by increasing the solvent flow rate, the amount of liberated and consumed duties do not change much, and consequently, changes are hardly observed for the total duty.

Also, in order to investigate the flow rates of the produced carbon dioxide-rich and methane-rich streams of the plant, Fig. S4 is presented in the Supplementary Data section.

3.3. Effect of temperature of the high-pressure flash tank

One other important operating condition of the PSA plant is the temperature of the high-pressure flash tank (HP-FLASH). This is based on Figs. 2 and 3, which indicate that flash tanks have significant roles in the energies and exergies of the plant. Additionally, based on Table 4, HP-FLASH has greater effects than LP-FLASH because the former operates at constant temperature conditions, and controlling the temperature of this equipment at a fixed value requires large amounts of energy, while LP-FLASH works at adiabatic conditions. Therefore, the temperature in HP-FLASH is of great importance and has a major role in the energy and exergy of this equipment, and consequently, the PSA plant.

Fig. 5a indicates the effects of the HP-FLASH tank temperature on the purities of the produced carbon dioxide-rich and methane-rich streams by the three solvents.

It is shown that by increasing the temperature of HP-FLASH, the composition of the produced carbon dioxide stream does not change much. All of the three solvents show a similar trend for carbon dioxide. However, Reline and Glyceline produce carbon dioxide streams with
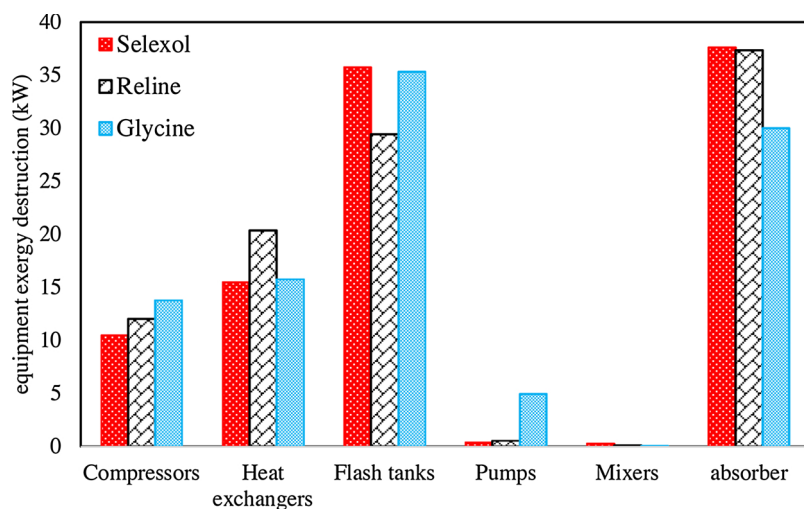

Fig. 2. Comparison of the absolute values of calculated duties for the different equipment types in the plant for all of the investigated solvents at the base-case operating conditions. (The feed gas is 1500 kg/h of an equimolar mixture of CO_2 and CH_4 at 301.15 K and 35 bar. The solvent is a pure stream of 17500 kg/h at 298.15 K and 1 bar).

Fig. 3. Comparison of the absolute values of calculated exergy destructions for the different equipment types in the plant for all of the investigated solvents at the base-case operating conditions. (The feed gas is 1500 kg/h of an equimolar mixture of CO_2 and CH_4 at 301.15 K and 35 bar. The solvent is a pure stream of 17500 kg/h at 298.15 K and 1 bar).

higher purities than does Selexol. Regarding methane, in contrast to carbon dioxide, decreasing purities are observed with increasing temperatures of HP-FLASH. Selexol and Glyceline have almost the same trending slopes, while Reline shows both a steeper decreasing trend, and higher purities for the produced methane.

Fig. 5b and c show the effect of changing the HP-FLASH temperature on the total duty and the exergy destruction of the PSA plant, respectively. Based on these figures, by increasing the temperature of HP-FLASH, the values of total duty of the plant increase to higher values. This was to be expected, because as explained earlier, HP-FLASH has a significant contribution to the total duty and exergy destruction of the plant. This is because the flash process occurs at constant temperature. Since the flash process is exothermic, it would require the addition of energy to keep the process at constant temperature. If higher flash temperatures are chosen, greater amounts of energy are required. This would result in increasing values of the total duty of the plant as the HP-FLASH temperature is increased. The slope of this increase depends on the thermophysical properties of the solvent. The slope of total duty versus temperature is higher for Glyceline and Reline than for Selexol (Fig. 5b). Regarding exergy loss, by increasing the temperature of HP-FLASH, the values of total exergy destruction of the plant slightly increase to higher values for Glyceline, while being almost constant for Reline and Selexol. However, Glyceline has the highest amount of exergy destruction as compared to Reline and Selexol (Fig. 5c).

Furthermore, Fig. S5 of the Supplementary Data, shows the variations of the flow rates of the produced carbon dioxide and methane streams with changing HP-FLASH tank temperatures for the three investigated solvents.

3.4. Effect of absorber pressure

The absorber is the heart of the PSA plant since it is where the main process of carbon dioxide separation from methane occurs, based on the differing solubilities of these gases in the solvent. The absorber pressure is one of the most effective parameters on the operation of the absorber, as it dramatically affects the solubility. Thus, it is a parameter that can consequently affect both the purity and the flow rate of the produced carbon dioxide and methane streams.

Fig. 6a shows the changes in the purities of the produced carbon dioxide-rich and methane-rich streams by changing the absorber pressure for all three investigated solvents. Based on this figure, Reline produces the highest-purity methane as compared to Glyceline or Selexol, while all three solvents show an increase in methane purity with increasing pressures. However, changing the absorber pressure does not significantly change the composition of the produced carbon dioxide for any of the three solvents. Both Reline and Glyceline produce more pure

carbon dioxide than does Selexol.

To investigate the effect of the absorber pressure on the energy and exergy of the plant, Fig. 6b and c are presented, respectively. As shown, by increasing the pressure of the absorber, the total duty of the plant decreases for all of the investigated solvents. This is because as the absorber pressure is increased, the feed gas pressure to the absorber must be increased, therefore, the pressure of the recycled gas stream from HP-FLASH to the absorber should be increased, which leads to a higher duty of the RE−COMP compressor and the RE-HX heat exchanger. While RE-COMP increases the duty and exergy, RE-HX decreases them. The competition between these two equipment indicates the amount of changes in the duty of the plant. As can be deduced from both Figs. 14 and 15, the RE-HX heat exchanger is dominant in this competition because the total duty of the plant decreases with increasing absorber pressures. The effects of the other equipment, in the case of changing the absorber pressure, are insignificant compared to the RE−COMP compressor and RE-HX heat exchanger. The slopes of depression of total duty with respect to absorber pressure are almost the same for the three investigated solvents. However, similar to the base-case, over the investigated pressure range, Selexol shows the highest duty and Reline has the lowest. Also, in the case of total exergy destruction, the value increases by increasing the absorber pressure for all of the investigate solvents. This is expected, because both the RE−COMP compressor and the RE-HX heat exchanger have greater exergy transfers and also greater exergy destructions upon the increase of absorber pressure. Glyceline shows the highest value of total exergy destruction and a steeper increasing slope as compared to Reline and Selexol at higher absorber pressures. This difference, and the greater exergy destructive behavior of Glyceline with respect to Reline and Selexol, was also observed in Fig. 5c.

In Fig. S6 of the Supplementary Data, the effects of changing the absorber pressure on the flow rates of the produced streams are shown.

From all of the above sensitivity analyses, depending on the desired goal of the operation, being purity, yield, cost, or environmental aspects, it is recommended to carry out engineering optimization calculations to determine the best operation conditions, particularly the type of solvent and its flow rate, for the specific goal in mind.

As an example, we have carried out calculations as a case study, where the main goal is the purity of the carbon dioxide stream. This was done for each of the three solvents with the goal of the plant set to produce a CO_2-rich stream with a purity of 95%. The results are compared in Table 5 for each of the three absorbents. While the two DESs, as compared to Selexol, result in larger flow rates of the produced CO_2-rich stream with a purity of 95%, they produce methane streams with lower purities and smaller flow rates.
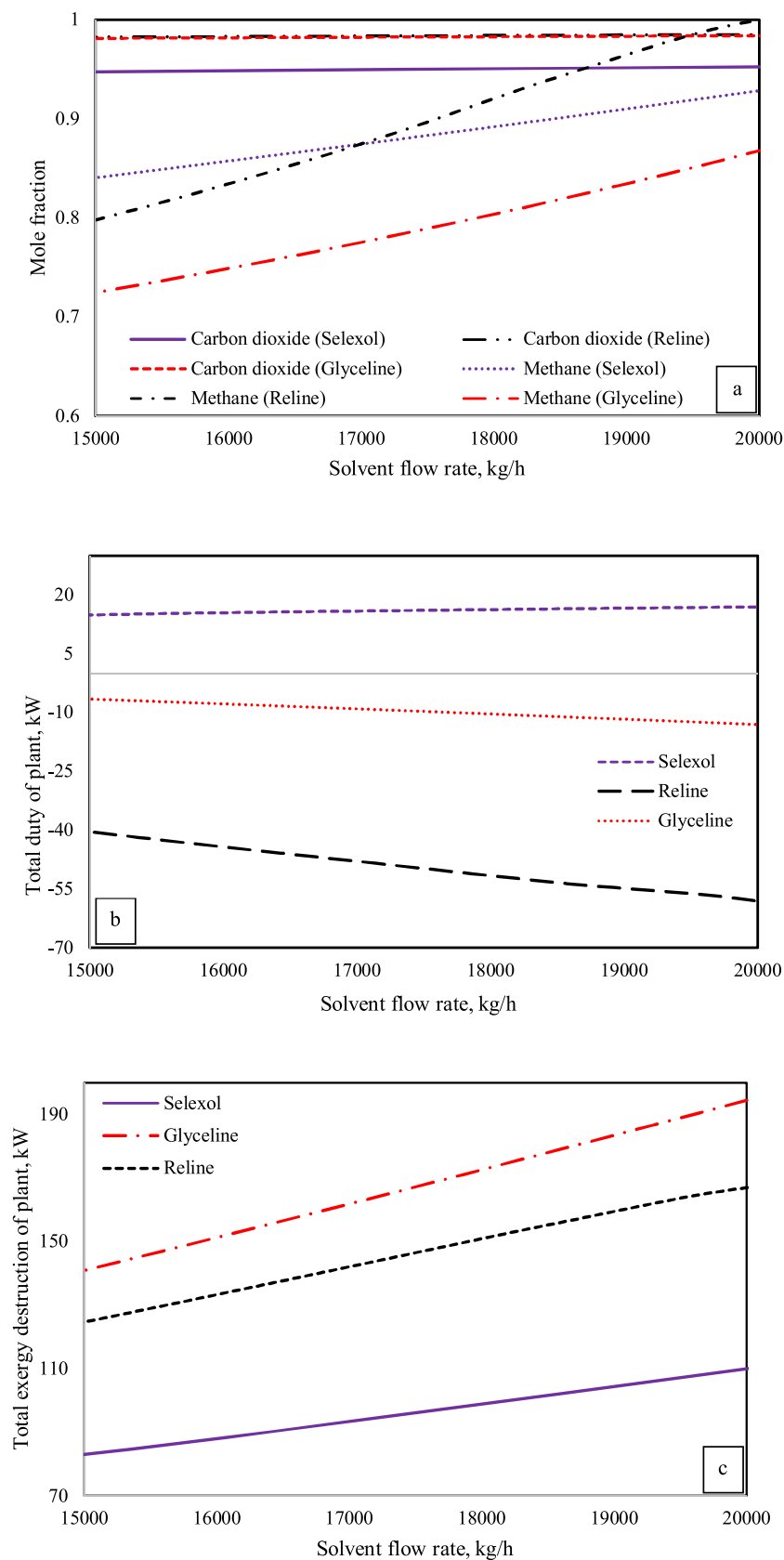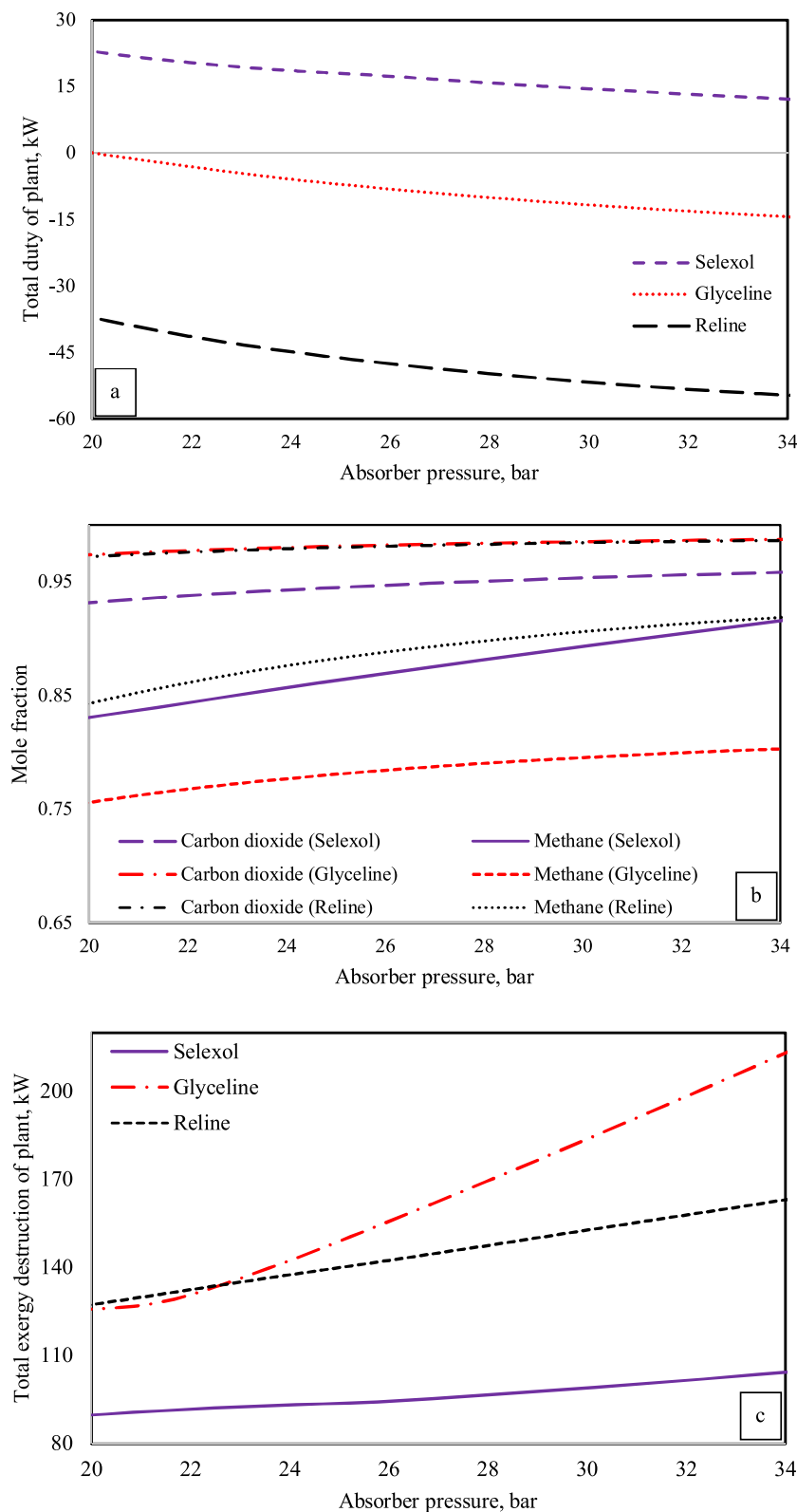
Fig. 4. Comparison of the effect of solvent flow rate on the composition of the final purified carbon dioxide and methane streams (a), total duty of the plant (b), and total exergy destruction of the plant (c), by considering different solvents. (The feed gas is 1500 kg/h of an equimolar mixture of CO_2 and CH_4 at 301.15 K and 35 bar. The solvent is a pure stream at 298.15 K and 1 bar).
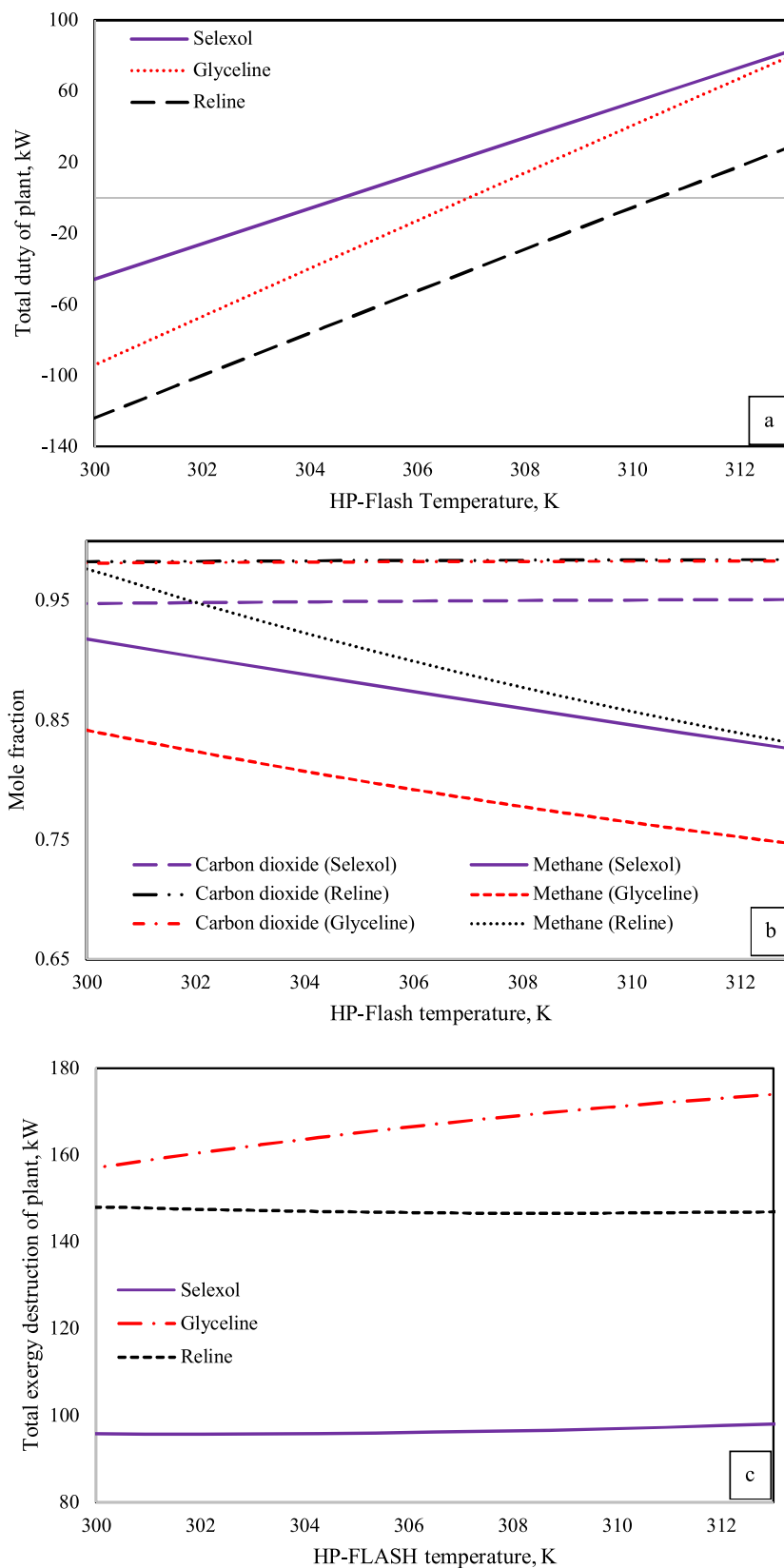
Fig. 5. Comparison of the effect of the high-pressure flash tank (HP-FLASH) temperature on the composition of the final purified carbon dioxide and methane streams (a), total duty of the plant (b), and total exergy destruction of the plant (c), by considering the different solvents (The feed gas is 1500 kg/h of an equimolar mixture of CO_2 and CH_4 at 301.15 K and 35 bar. The solvent is a pure stream of 17500 kg/h at 298.15 K and 1 bar).

Fig. 6. Comparison of the effect of absorber pressure on the composition of the final purified carbon dioxide and methane streams (a), total duty of the plant (b), and total exergy destruction of the plant (c), by considering the different solvents (The feed gas is 1500 kg/h of an equimolar mixture of CO_2 and CH_4 at 301.15 K and 35 bar. The solvent is a pure stream of 17500 kg/h at 298.15 K and 1 bar.

3.5. Comparison with a similar process using an ionic liquid

It is also interesting to compare the results of the proposed absorbent with other green solvents. Since no other work is available on deep

eutectic solvents, we investigated a similar process using an ionic liquid. For this purpose, the work of Martinez [3] was considered, which used the 1-heyxl-3-methylimiazolium tetracyanoborate ionic liquid as the solvent. We considered the same base case conditions as the study of

Table 5
Comparison of the plants when the goal of the plant is the production of a CO_2-rich stream with a purity of 95% using each of the three solvents. The operating conditions, except the absorber pressure, correspond to the base-case conditions.

#		Selexol	Reline	Glyceline
1	Absorber pressure (bar)	28.0	14.8	14.8
2	Flow rate of CO_2-rich stream (kg/h)	413.0	676.3	574.1
3	Purity of produced CH_4 (mole %)	88.1	77.6	71.3
4	Flow rate of CH_4-rich stream (kg/h)	392.8	389.1	391.3
5	Total duty (kW)	15.91	−20.14	13.82
6	Total exergy destruction (kW)	96.53	115.09	116.55

Martinez [3] with one exception: the solvent flow rate. She used a solvent flow rate of 21696 kg/h, while we considered 17500 kg/h. At these conditions, both studies succeeded to produce the same purity of CO_2 in the carbon dioxide-rich stream (~ 0.98) for their introduced solvents. However, we produced a less-pure methane stream (~ 0.90 for Reline and ~ 0.80 for Gyceline) with respect to Martinez's study (~ 0.95). Regarding the total duty of the plant, the ionic liquid required −67.12 kW, while the corresponding values were −51.27 and −11.13 kW for Reline and Glyceline, respectively. In general, the calculated results for DESs and the ionic liquid are not significantly different to render one type of solvent as absolutely superior to the other. While the amount of solvent flow rate in our study is almost 20% less than Martinez's study, the purity of the methane stream is greater when the ionic liquid is used.

4. Conclusions

In this study, a feasibility study was carried out for the utilization of deep eutectic solvents in the petroleum industries. For this purpose, we carried out simulations on the case study of CO_2 removal from natural gas by using a DES as a physical solvent in place of the commercially-used Selexol. The pressure swing absorption process was simulated with three different solvents; two DESs, namely Reline and Glyceline, and the commercial Selexol. At the typical operating conditions of conventional plants, the resulting methane stream had purities of 89.1%, 90.1%, and 79.6% when using Selexol, Reline, and Glyceline, respectively. The purities of the carbon dioxide-rich stream were even more improved when using DESs (98.3%, 98.4% and 94.9% CO_2 for Reline, Glyceline, and Selexol, respectively). The plants were further investigated concerning their energy and exergy destructions. The overall duty of the entire plant was less when using deep eutectic solvents (−51.27, −11.13 kW for Reline and Glyceline, respectively, and 15.17 kW for Selexol). The exergy destructions of the plant were also estimated to be 146.78, 165.64, and 96.54 kW for Reline, Glyceline, and Selexol, respectively. These results indicate that DESs do indeed have the potential to be used in CO_2 capture processes, since the resulting products from the DES processes show competing purities and acceptable energy and exergy losses. It is also noteworthy that in this comparison, a set of currently-established operating conditions was used which were optimized to the current processes using conventional solvents. It is obvious that each plant has its own set of optimized conditions, therefore, it is anticipated that DES plants will function even superior than the case study above, when the operating conditions are custom-fit to the specific DES, rather than using the operating conditions optimized to conventional solvents, as given above. With such room for improvement, employing this novel generation of green solvents may prove to be even more valuable, considering its environmental benefits, as well as the reduced energy requirements.

In addition to a base-case scenario of fixed operating conditions, a number of different operating conditions of the units were varied individually and the effects of the changes in each were investigated on the other variables of the plant, particularly, the purities and flow rates of the CO_2-rich and methane-rich product streams, as well as the total duty and exergy destruction of the plant. The temperature of the high-pressure flash tank and the absorber pressure were considered in the analyses as influential operating parameters, in addition to the flow rate of the solvent. It was found that the optimum operating conditions fully depend on what the desired goal of the plant is. If it is desired to produce carbon dioxide with the highest purity and the greatest flow rate, then Reline and Glyceline are better. If the desired goal of the plant is to produce high-purity methane, which is often the reason for natural gas purification in the first place, then Reline is suggested as the marginally better solvent. In case of energy and exergy analyses, the results indicate that, in general, the process with Reline has the lowest required total duty among the plants, while Selexol shows the lowest amount of exergy destruction. The extent of energy duties and exergy losses can be altered by changing the operating conditions of the plant. Thus, in general, by considering the main goal of the plant, the best conditions can be optimized accordingly.

This study confirms the feasibility of the untilization of DESs in the removal of CO_2 from natural gas. It is emphasized here that this was only an initial feasibility study, and the two DESs selected were by no means the most appropriate ones for CO_2 absorption. The selection was merely based on the availability of the required physical data of the DESs, which is still at a very early stage in this novel field of green chemistry. In the next stages, research must be targeted towards finding task-specific DESs which have higher capacities for CO_2 absorption. This is a task that has much, since in fact, designability is the great characteristic of DESs, and so, there is much room for progress in this field. Other pollutants of natural gas, such as H_2S, may also have the feasibility to be treated with DESs. We anticipate that deep eutectic solvents have the potential to, not only be used for gas sweetening, but also many other engineering tasks in the petroleum industries.

Acknowledgement

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jece.2019.103411.

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