Efficient separation scheme for binary mixture of CO_2 and H_2S using aromatic components

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Abstract

Separating a mixture of CO_2 and H_2S into two products through distillation is both difficult and complicated because of similar relative volatility between the two gasses, especially when a CO_2 concentration exceeds 80%. Therefore, the separation process can involve many separating stages. However, adding a solvent (agent) to the distillation column during the separation process makes this procedure easier.

In this work, different solvents (ethylbenzene, o-Xylene, m-Xylene, and toluene) and operating conditions (temperature, pressure, and reflux ratio) for separating CO_2 from H_2S have been simulated through distillation using Aspen HYSYS software. Further, four different aromatic compounds (solvents) for different concentrations (from 0 to 40 mol %) have been evaluated to increase the CO_2/H_2S relative volatility, reducing the quantity of the solvent required and energy consumption.

M-Xylene was found to be the best solvent for separating CO_2 from H_2S because of the significant effect on relative volatility, the low quantity required for high CO_2 recovery, and the low energy for generating the solvent.

1. <u>Introduction</u>

With fossil-fuel consumption accounting for more than 80% of energy use, CO_2 concentration in the atmosphere is bound to increase [1] [2, 3]. This increase in CO_2 concentration is considered the main cause of climate change and the increase in global temperatures [4-6]. However, once CO_2 is captured and transported, it can be injected underground for storage [7] and/or enhanced oil recovery processes (EOR) [8, 9]. Moreover, in EOR, it is preferred that CO_2 containing less than 100 PPM H_2S [10] is injected, as it might be a safety hazard [11] and corrosive [12]. On the other hand, high-purity hydrogen sulfide can be converted to hydrogen fuel and sulfur through photoelectrochemical processes and other methods [13].

Several experimental and theoretical researchers have focused on the reactive absorption of H_2S and CO_2 from gas mixtures containing small or trace amounts of H2S or both gasses. These researchers have mostly been driven by the need for natural gas sweetening [14]. Adsorption has also been studied both experimentally and theoretically as a method for removing trace amounts of H2S from biogas or other gas mixtures containing CO2 [15], ion exchange resins [16], or centrifugation [17]. In addition, separating CO2/H2S using ionic liquids at room temperature has been reported. For example, separating CO2/H2S using ([bmim][MeSO4]) based on a modified RK (Redlich-Kwong) EOS [18].

Few studies have reported on separating binary mixtures of CO_2 and H_2S. [19] investigated separating the binary mixture of H_2S and CO_2 using pressure swing adsorption (SPA) in molecular sieves 4A, 5A, and 13X.

Separating a mixture of CO_2/H_2S into two products through distillation is difficult and complicated because of the converging relative volatility of the two gases [20]. The relative volatilities of CO_2 and H_2S are close, especially when the CO_2 concentration goes beyond 80% [20] [10]; as a result, the separation process can be complicated and several separating stages

will be required [10]. However, adding a solvent (agent) to the distillation column during separation can better facilitate this procedure.

Nomenclatures			
CO2	Carbon dioxide	O-Xylene	Ortho Xylene
H2S	Hydrogen Sulfide	M-Xylene	Meta Xylene
EOR	Enhance Oil Recovery		
$C3^+$	Propane and Heavier Hydrocarbon		
RV	Relative Volatility		
PR	Peng Robinson		
SRK	Soave Redlich Kwong		
EOS	Equation of State		
EB	Ethylbenzene		

Furthermore, many solvents have been used in distilling CO_2/H_2S to improve the separation process and reduce costs and energy consumption [10]; however, solvent selection requires many considerations such as relative volatility, the low freezing point, and H_2S/ agent separation [10, 20].

Yao et al. [12] added hydrocarbons ($C3^+$) as solvents (agents) to the distillation column (above the feeding point) to increase the relative volatility of CO_2/H_2S. However, there are many disadvantages to using such agents (alkanes) as solvents. These disadvantages include [21] poor selectivity between CO_2 and H_2S compared to other solvents, such as aromatic solvents that require a higher reflux rate and a higher solvent circulation rate. Accordingly, the refrigeration duty will be higher; and [21] the low molecular weight of alkanes also leads to a significant loss in the solvents.

Aromatic compounds are very effective solvents in CO_2/H_2S separation because of their high molecular weight and low freezing points. Separation occurs best when the solvent molecular weight is between 90 and 125 and the freezing point is below -45 °C; this avoids solvent solidification [12]. In addition, because of these solvents' high selectivity, the circulation rate and overhead reflux ratio of the distillation column can be reduced. Accordingly, the regeneration requirement and reflux rates will be reduced [12].

In this work, different solvents and operating conditions for separating a CO_2-H_2S binary mixture have been simulated by distillation using Aspen HYSYS software. Furthermore, three aromatic compounds have been evaluated for increasing the relative volatility of CO_2/H_2S, reducing the quantity of the solvent required and the energy consumption.

1.1. Process description

Separating liquid mixtures through distillation depends on differences in the components' volatility. The separation becomes easier as the relative volatilities increase. The gas feed stream (1) at 1000 kgmole/hr enters the middle of the first distillation column (T-100) at -15°C and 10 bar with CO_2 contents from 10-90 mol%. The first distillation column has 30-40 theoretical stages and operates at 7 bar. In case of O-Xylene, the firs column (T-101) operates at 20 bar to prevent freezing of the agent (O-Xylene), this is because of the freezing point of O-xylene (-25 °C) is higher than the other solvents. Aspen HYSYS simulation was used in the steady state mode and the Peng-Robinson equation of state was applied for the dynamic studies. The solvent at 8°C and 8 bar was fed to stage 2 near the top of the column, as this is the location where the relative volatility of CO_2 to H_2S has to be increased [10]. The amount of solvent added was based on the CO_2 concentration in the feed [10]. Although it is possible to add the solvent to the top of the column, including into the condenser, this is not usually preferable

because the agent cannot then be separated efficiently from the overhead product. Thus, adding the solvent at a point below the column top is desirable for additive separation from the desired overhead product [10]. The overhead product of the first distillation column is CO_2, which has less than 100 ppm H2S. The bottom product enters the heat exchanger to increase the stream temperature and then enters the second distillation column (T-101), which is a solvent recovery column. . The solvent recovery column has 10 theoretical stages and operates at 5 bar. The reflux ratio and H_2S mole fraction in the bottom stream were selected to set the column specs. The reflux ratio and H_2S mole fraction were set at 0.6 and 10^{-5} respectively. The top product of the second column is a pure H_2S and the bottom product is the aromatic solvent. Afterward, the solvent is recycled to the first distillation column.
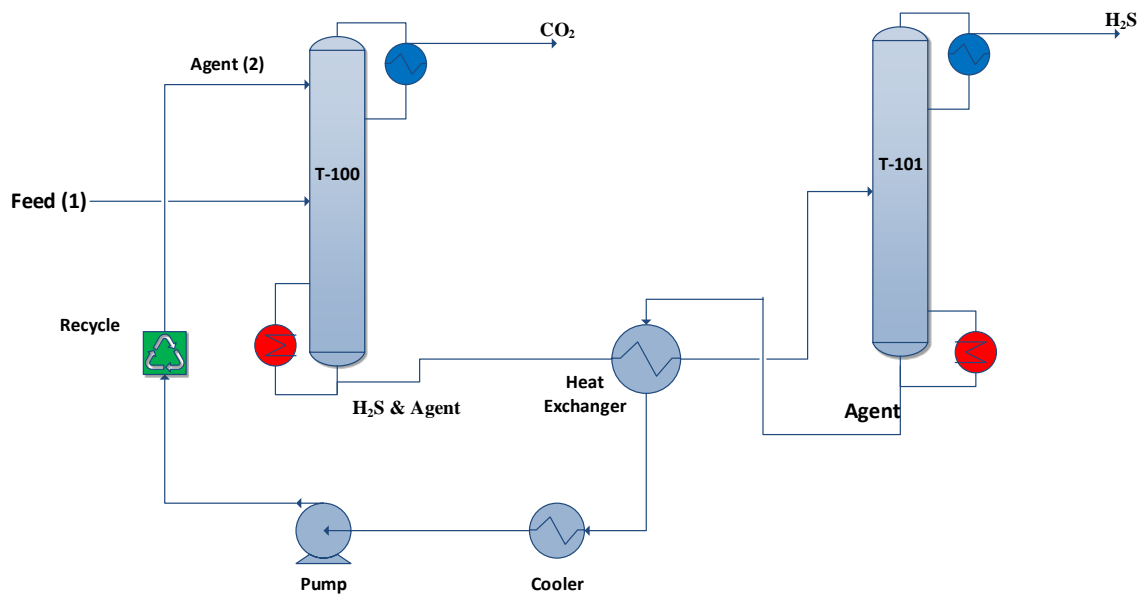

Fig. 1. Process flow diagram of CO_2/H_2S separation

Table1

The operating parameters were applied in simulation process

	T-100			
	M-Xylene	O-Xylene	E.B	Toluene
Feed (CO2& H2S) (Kgmole/hr)	1000	1000	1000	1000
CO_2/H_2S Composition	90/10	90/10	90/10	90/10
Feed Temp. (°C)	-10	-10	-10	-10
Feed Pressure (bar)	10	21	10	10
Feed stage point	15	20	20	20
Agent (Kgmole/hr)	310	410	430	400
Agent Temp. (°C)	8	8	8	8
Agent Pressure (bar)	10	21	10	10
Agent stage point	2 (Below the condenser)	=	=	=
Theoretical stages	30	40	40	40
Column Pressure (bar)	8	20	8	8
Column Overhead Temp. (°C)	-45	-20	-52	-52
Column Bottom Temp. (°C)	60	160	50	66
Overhead H2S (ppm)	70	70	70	70
Bottom CO2 (ppm)	0	0	0	0
Reflux Ratio	1	1	1	1

2. Numerical implementation

In this study, the distillation processes (Fig. 1) have been simulated using Aspen HYSYS 7.2, which is a set of comprehensive process-modeling tools used by the world's leading oil and gas producers, refineries, and engineering companies for process simulation and process

optimization in design and operation. The Peng-Robinson (PR) equation of estate has been selected for all simulation calculations.

2.1. Selection of equation of state

The thermodynamic model has a huge impact on such kind of simulation process. HYSYS provides enhanced equations of state (PR and SRK) for the strict treatment of hydrocarbon systems and sour gases separation. For oil, gas, and petrochemical applications, the Peng–Robinson EOS (PR) and Soave Redlich Kwong (SRK) are usually recommended [18, 22]. The PR and Soave Redlich Kwong equations of state have been enhanced to yield accurate phase equilibrium calculations for systems ranging from low-temperature cryogenic systems to high-temperature, high-pressure reservoir systems [22]. In addition, Vitu, S. et al. [23] used PR EOS to predict the phase equilibria of CO_2 and Hydrocarbon system and found accurate results in many cases. Moreover, Jaubert et al. [24] have chosen PR EOS to predict the phase equilibria of syntheses petroleum fluids (Alkanes, aromatics, CO_2, H_2S, N_2 and more) and they reported that the model was a successful due to the high accuracy results for nonpolar compounds using PR EOS. In 2008, Privat et al. [25] have added H_2S group for their model to calculate the temperature dependent binary interaction parameters (*Kij*) and they obtained an accurate behavior prediction of the system containing H_2S. The PR equation of state in HYSYS simulation applies a functionality to some specific component-component interaction parameters. Key component receiving special treatment include He, H_2, N_2, CO_2, H_2S, MEG, TEG, CH_3OH and more. For other EOS model, K_{ij} will be generated automatically by HYSYS for improved VLE property predictions. Last and not least, PR EOS has been relied on in this simulation process due to the compatibility of this model to describe and predict the CO2, H2S and aromatic compounds thermodynamic properties.

2.2. Algorithm and basic equation used for simulation

2.2.1. CO_2 separation column

A distillation column was selected for simulating the CO_2 separation column.

Column specs: Tow specs should be defined for the distillation column until the degree of freedom becomes zero. The reflux ratio and H_2S mole fraction in the top product were selected as column specs.

Solving methods: Inside-out: With the "inside-out" based algorithms, simple equilibrium and enthalpy models are used in the inner loop to solve the overall component and heat balances as well as any specifications. The outer loop updates the simple thermodynamic models with rigorous model calculations. The inside-out algorithm has become one of the most popular methods because of its robustness and its ability to solve a wide variety of columns [22].

2.2.2. Heater and Cooler

The heater and cooler operations are one-sided heat exchangers. The inlet stream is heated (or cooled) to the desired outlet conditions while the energy stream provides (or absorbs) the enthalpy difference between the two streams. These operations are useful to discover the energy required to cool or heat a process stream with a utility and without focusing the conditions of the utility itself [22].

2.2.3. Pump

The pump operation is used to increase the pressure of an inlet liquid stream. Depending on the supplied information, the pump calculates either an unknown pressure, temperature, or pump efficiency [22].

2.2.4. Recycle

The capability of any Flowsheet simulator to solve recycles reliably and efficiency is critical. In this respect, HYSYS has inherent advantages over other simulators, having the unique ability to back-calculate through many operations in a non-sequential manner, which allows many problems with recycling loops to be solved explicitly

The recycle installs a theoretical block in the process stream. The feed into the block, also known as the calculated recycle stream, and the product is the assumed recycle stream [22].

3. Process Performance

The aim of this optimization work is to study the effect of various types of solvents on different concentrations of CO_2 and H_2S. Therefore, the optimization section will apply various solvents with various quantities that can be achieved by entering them into simulation tools and changing the CO_2-H_2S stream compositions as can be shown in table2. The following optimizations steps are assumed:

1. Using 10-90 mol% CO_2 concentrations in inlet stream.
2. Investigating 0, 10, 20 and 40 mol% of Ethylbenzene.
3. Investigating 0, 10, 20 and 40 mol% of O-Xylene.
4. Investigating 0, 10, 20 and 40 mol% of M-Xylene.
5. Investigating 0, 10, 20 and 40 mol% of Toluene.

Table 2. Process Optimization Results

10/90 mol% CO2/H2S (1000 kgmole/hr)	Ethylbenzene	M-Xylene	O-Xylene	Toluene
Solvent Quantity (kgmole/hr)	120	80	130	140
Solvent Regeneration column Duty (MW)	1.2	1	2.7	1.4
No. of Trays (T-100)	20	20	20	20
Reflux Ratio(T-100)	1.5	1.5	1.5	1.5
(T-100) Top Temp($^\circ$C)	-52	-45	-20	-52
(T-100) Pressure (bar)	8	9	20	8
50/50 mol% CO2/H2S (1000 kgmole/hr)				
Solvent Quantity (kgmole/hr)	260	230	250	290
Solvent Regeneration column Duty (MW)	2.6	2	2.8	2.2
No. of Trays (T-100)	30	30	30	30
Reflux Ratio(T-100)	1.5	1.5	1.5	1.5
(T-100) Top Temp($^\circ$C)	-52	-45	-20	-52
(T-100) Pressure (bar)	8	9	20	8
90/10 mol% CO2/H2S (1000 kgmole/hr)				
Solvent Quantity (kgmole/hr)	430	310	410	400
Solvent Regeneration column Duty (MW)	2.9	2.5	3.3	2.5
No. of Trays (T-100)	30	30	30	30
Reflux Ratio(T-100)	1.5	1.5	1.5	1.5
(T-100) Top Temp($^\circ$C)	-52	-45	-20	-52
(T-100) Pressure (bar)	8	9	20	8

4. Result and discussion

4.1. Solvents Quantity

As can be seen in Figure 2, the solvent's amount has to be increased with increasing CO_2 concentration in the feed stream and this is consistent with the previous literature [12, 20]. The amount of solvent added will be dependent upon factors such as the feed's composition, operating pressure, throughput of the column, recovery of overhead, and bottoms product desired [10]. Based on the results shown in Figure 2, the amount of solvent required for m-Xylene was about 22.5% lower than that required for toluene at 90 mol% CO_2. This is because of the difference in the solvent's properties such as freezing point and molecular weight [12].
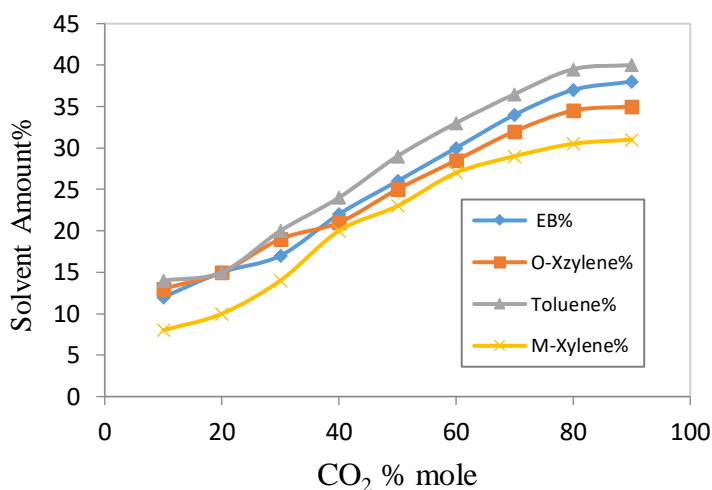
Fig.2. Effect of various CO_2 concentrations in mole% on solvent amount (%)

4.2. Relative Volatility

The relative volatility is a measure comparing the vapor pressures of the components in a liquid mixture of chemicals. This measure is widely used in designing large industrial distillation processes. In effect, the relative volatility indicates the ease or difficulty of using distillation to

separate more volatile components from those that are less volatile. The relative volatility of two components can be expressed as the ratio of their K values:

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{(y_i/x_i)}{(y_j/x_j)} \tag{9}$$

Where:

α = Relative Volatility

K = Equilibrium Constant

y = Vapour phase component fraction

x = Liquid phase component fraction

Figures 3-6 show the relative volatility of carbon dioxide to hydrogen sulfide at different concentrations of Ethylbenzene, m-Xylene, o-Xylene, and toluene respectively. As can be noticed in Figure 3, the relative volatility of CO_2 to H_2S was 1.2 at high concentration of CO_2 and with no agent present; however, the relative volatility increases by approximately 50% when a 40% concentration of ethylbenzene is added. Figure 3 shows that by adding 40% of m-Xylene, the relative volatility increases by approximately 60% in comparison to when no solvent is present. In Figure 5, the relative volatility increases by 63% when a 40% concentration of o-Xylene is added. Figure 6 shows that the relative volatility of CO2 to H2S increases by about 55% when 40% toluene is added. Increases in the relative volatility of CO2 to H2S using aromatic compounds are as a result of properties such as molecular weight, freezing point, and volatility. In addition, it was noticed that easier separation can occur at the high relative volatility of CO_2 to H_2S [12].
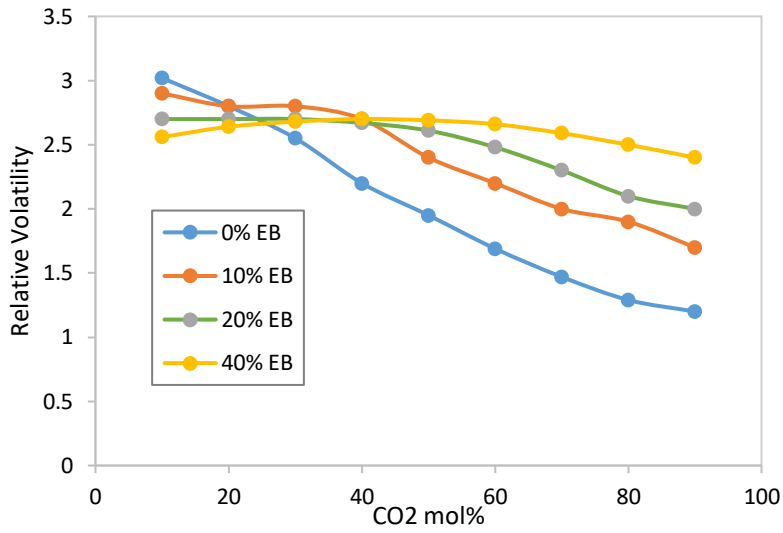
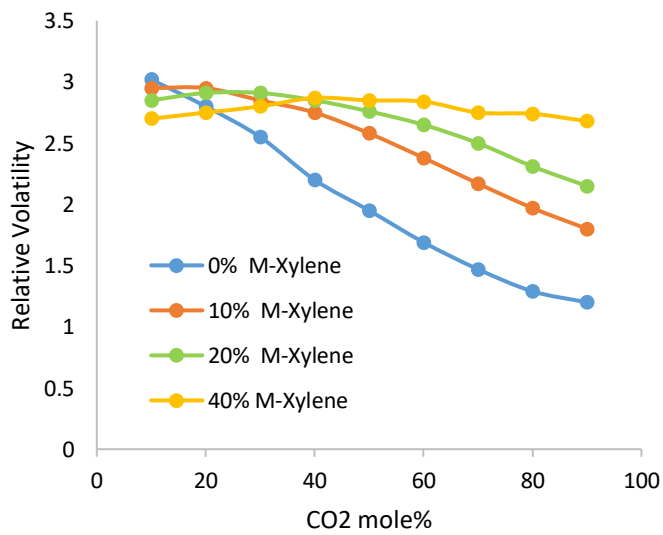Fig.3. Relative volatility of CO_2 to H_2S for various EB concentrations.

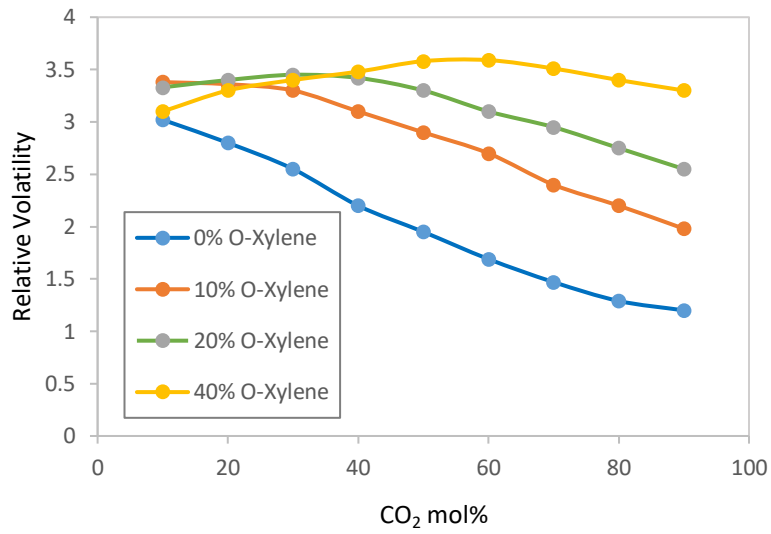Fig.4. Relative volatility of CO_2 to H_2S for various M-Xylene concentrations.

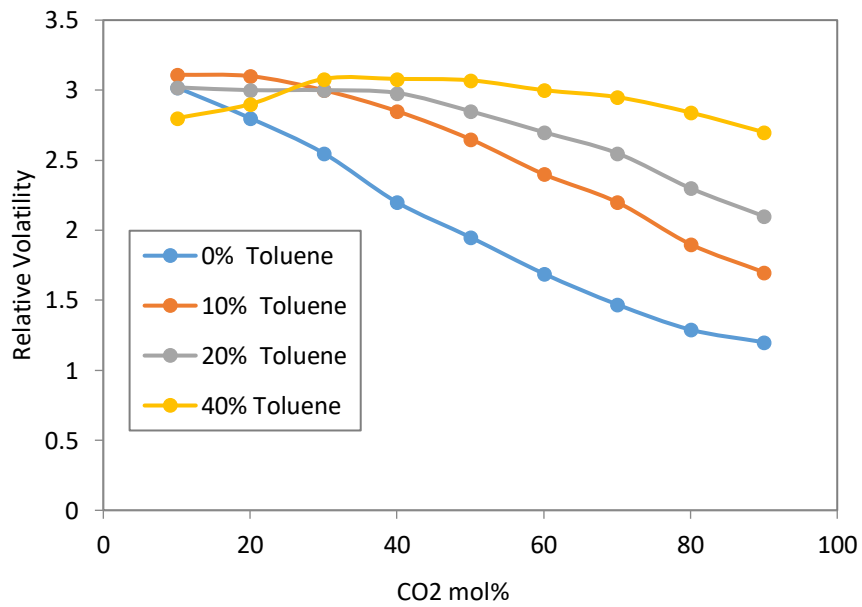Fig.5. Relative volatility of CO_2 to H_2S for various O-Xylene concentrations.

Fig.6. Relative volatility of CO_2 to H_2S for various Toluene concentrations.

4.3. Energy Consumption

Figure 7 shows that the total duty required to separate H2S from a binary mixture that contains 90 mol% of CO2 decreases from o-Xylene to m-Xylene solvent. The amount of total duty required by m-Xylene is 29.77% lower than that of o-Xylene. This is because the freezing point of m-Xylene (-48°C), which is much lower than the freezing point of o-Xylene (-24°C), makes the separation process easier [10].
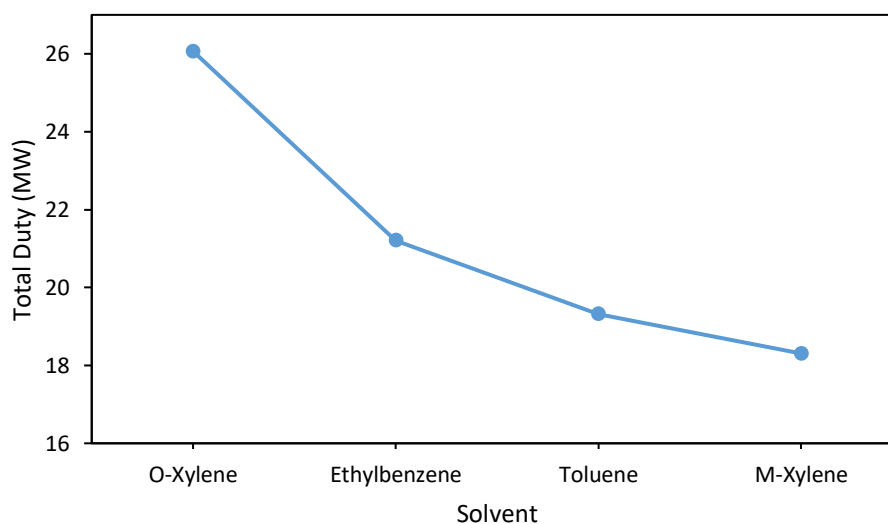

Fig.7 Amount of duty required for separation H2S from 90 mol% of CO2

4.4. Effect of Solvents on Phase Diagram

Figure 8 displays the practical difficulty of obtaining a substantially complete separation of carbon dioxide from hydrogen sulfide in a binary mixture. It can be seen that the bubble and dew points plot for the pure binary at 10 bar tends to pinch together. This separation becomes difficult at 80% carbon dioxide or higher [10, 12]. Thus, the overhead product from a column

would normally be limited to about 80% carbon dioxide, unless many of theoretical stages are added to the column [10]. To solve this issue (i.e. the separation), a solvent is added into these gas mixture to increase the relative volatility. As can be seen in Figure 9, when 20% solvent is added, it widens the phase diagram of CO2-H2S, which eases the separation process.
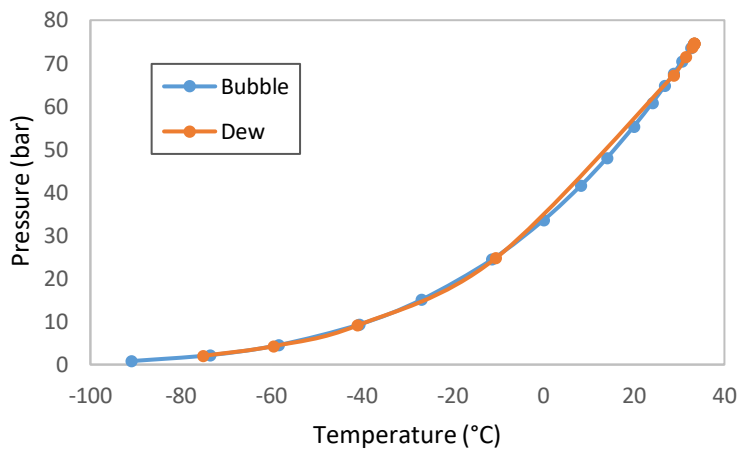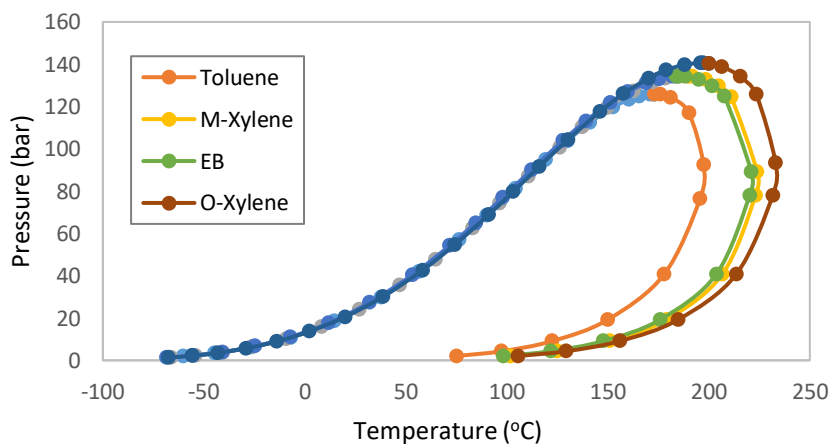

Fig.8. Phase diagram of 90% CO_2 and 10% H_2S

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Fig. 9. Phase diagram of 90% CO_2 and 10% H_2S in 20% solvent

4.5. CO2 and H2S Purities and Recoveries

As can been seen in Figure 9 and Table 3, the purities and recoveries of H2S and CO2 using aromatic compounds are quite high (greater than 99.9%) in comparison to the results, which have been done in other separation processes such as PSA (18). This is because the selectivity of aromatic compounds for H2S is high. The highest purity and recovery for CO2 using PSA were 92% and 93% respectively while for H_2S were 71% and 91% respectively. In addition, the low H2S purity and recovery obtained with SPA could be due in part to another factor affecting the PSA system performance. One such factor could be the purge-to-feed ratio, which is the ratio of desorption purge flow rate to the feed flow rate during adsorption [19]. Furthermore, the properties of aromatics compounds, such as freezing points, high selectivity, and the molecular weights, also have an effect to obtain a high purity and recovery for CO_2 and H_2S.

Table 3. Purities, Recoveries of CO2, and H_2S for various CO_2 concentrations

10% CO_2	ETHYLBENZENE	M-XYLENE	O-XYLENE	TOLUENE
H_2S PPM (CO2 PURITY)	80 (>99.9%)	80 (>99.9%)	80 (>99.9%)	80 (>99.9%)
CO_2 RECOVERY (%)	99.99	99.99	99.99	99
H_2S RECOVERY	99.99	99.99	99.99	98
H2S PURITY (CO2 PPM)	0	0	0	0
50% CO_2				
H_2S PPM (CO_2 PURITY)	80 (>99.9%)	80 (>99.9%)	80(>99.9%)	80(>99.9%)
CO_2RECOVERY (%)	99.99	99.99	99.99	99
H_2S RECOVERY	99.99	99.99	99.99	98
H_2S PURITY (CO_2 PPM)	0	0	0	0
90% CO_2				
H_2S PPM (CO_2 PURITY)	70 (>99.9%)	70 (>99.9%)	70(>99.9%)	70(>99.9%)
CO_2RECOVERY (%)	99.99	99.99	99.99	99
H_2S RECOVERY (%)	99.99	99.99	99.99	98
H_2S PURITY (CO_2 PPM)	0	0	0	0

1. Conclusion

Although separating H2S/CO2 from gaseous mixtures has been presented before, demonstrations for CO2/H2S as a binary mixture reported in the literature are limited. In this study, new solvents have been used to separate the carbon dioxide from hydrogen sulfide in a distillation column by simulation using Aspen HYSYS to improve the separation process. It is difficult to separate CO2 from H2S using standard distillation columns with no solvent, especially at high concentrations of CO2, because of their low relative volatility. Aromatic compounds have been used as solvents to increase the relative volatility between CO2 and H2S. In this study, m-Xylene has shown to be highly efficient as a solvent for separating CO2 from H2S because of the significant effect on relative volatility and low quantity required for high CO2 recovery also low energy is required to regenerate the solvent. When selecting solvents, the effect of the agent on relative volatility, the low freezing point of the solvent to avoid solid formation in the column, and the ease of separation of the solvent from H2S to recover the solvent and recirculate it to the first distillation column are some factors for consideration. It is important to achieve a high purity of CO2 for EOR purposes and hydrogen sulfide converted processes.

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