



ISSN: 2588-5596

JGT

JOURNAL OF GAS TECHNOLOGY

Volume 7 • Issue 2 • Winter 2022 • www.jgt.irangi.org



Journal of Gas Technology, JGT

Volume 7, Issue 2, Winter 2022

Publisher

Iranian Gas Institute

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Email: ijgt.igi@gmail.com

EISSN: 2588-5596

Open Access Journal

Journal of Gas Technology is a peer reviewed, open access journal.

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Simulation and Sensitivity Analysis of Flare Gas Recovery for Application in Hydrocarbon Reservoirs as Injection Gas

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ARTICLE INFO

ORIGINAL RESEARCH ARTICLE

Article History:

Received: 9 October 2022

Revised: 20 December 2022

Accepted: 31 December 2022

Keywords:

Flare gas

Gas injection

Gas condensate reservoir

Simulation

ABSTRACT

Flare gas recovery is one of the essential processes in reducing the greenhouse gas emissions caused in the oil and gas industry. On the other hand, due to the reduction of pressure and production rate of hydrocarbon reservoirs especially in Iran, it is necessary to provide solutions for reservoirs pressure maintenance. Therefore, in this paper the potential application of the separated carbon dioxide from the flare gas in Parsian refinery was investigated for injection into a gas condensate reservoir. For this purpose, the flare gas recovery process was simulated using Aspen HYSYS software and operational enhancements were applied. Next, the injection of the separated carbon dioxide into a gas condensate reservoir was simulated in Petrel software, and the best scenario was determined. The obtained results indicated that maximum CO₂ recovery is achieved using Diisopropanolamine as solvent with the flow rate 1930 USGPM. The reservoir simulation results revealed that CO₂ injection prevents severe pressure drop and causes the reservoir pressure to decline with a lower slope. Thus, the reservoir production rate increases and becomes more stable. The most stable production rate was attained for injection rate of 305 million cubic meters per day.

DOR: [20.1001.1/JGT.2023.1986515.1022](https://doi.org/10.1001.1/JGT.2023.1986515.1022)

How to cite this article

M.M. Sabaghian, M. Hajipour, Simulation and Sensitivity Analysis of Flare Gas Recovery for Application in Hydrocarbon Reservoirs as Injection Gas. Journal of Gas Technology. 2022; 7(2): 04 -15. (http://jgt.irangi.org/article_703835.html)

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Available online 31 December 2022

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1. Introduction

As global energy consumption increases, it is essential to prevent the loss of energy resources. Fossil fuels are the most used energy resources and therefore, they should be used in the best possible way. Unfortunately, a significant amount of these resources is wasted daily due to improper utilization and traditional methods. For instance, at least 120 million cubic meters of gas is burned in the flares annually in South Pars refineries. Always a part of the gas produced from oil reservoirs as associated gas is burned in flares, and there is no serious intention for flare gas recovery. In fact, gas flaring provides safety for refineries and well head facilities, and flare gas recovery requires technology development and economic justification.

Although recovery and reduction of flare gas directly led to environmental protection, gas flaring will continue until gas recovery operations have economic justification, suitable capital recovery time, and appropriate technology. A large amount of hydrocarbon and other toxic gases enter the atmosphere from flares, which causes serious air pollution. According to the Canadian Health Association and other published papers in the literature, about 250 known toxins including benzene, mercury, nitrogen oxides, carbon dioxide, methane, acidic gases, and aromatic hydrocarbons are discharged into the air during flaring operations. The effects of flare gas pollution are not only reported in the operational sites including production wells or refineries but also air pollution is observed in places far beyond refineries. Pollutants that are released in the air, cause acid rain which contaminate freshwater and directly affect agricultural crops. In recent decades, optimization of the flare gas amount has been an important topic and extensive research has been done in this field.

Khanipour et al. (2016) carried out a study on nitrogen gas separation from flare gas and return of the recovered gas to the methanol synthesis reactor. Their simulation results showed that

the returned gas to the reactor was capable of increasing methanol production. Also, in this study, the simulation and investigation of key factors in membrane gas separation indicated that 98.5% of nitrogen and 92.8% of recovered methane can be separated. Moreover, the emission of 300 tons carbon dioxide to the environment can be prevented daily.

In 2015, a study was conducted to reduce the volume of flare gas. In this study, three approaches for flare gas recovery including gas injection into the feed stream of South Pars gas refineries, gas injection into South Pars reservoir and gas injection into Aghajari oil field through the fifth national gas transmission pipeline were proposed. The appropriate solution from operational point of view was gas compression and injection to the fifth national pipeline. To implement this method, the required outlet pressure of the flare gas recovery unit was about 40 bar, which was much lower than the required pressures of other two solutions (i.e., 80 and 200 bar). Moreover, 10 MMSCMD flare gas recovery can be obtained and gas transmission capacity across the fifth national gas transmission pipeline is increased more than 12%. It should be mentioned that this amount of recovered gas is equivalent to 40% of the gas production capacity of one of the South Pars Refinery (Hashemi Fard and Shafiee, 2020).

Different methods for flare gas recovery in gas refineries and liquefied natural gas companies were examined from exergy point of view. The concept of exergy is derived from the second law of thermodynamics, and the analysis based on this concept usually yields more accurate results than methods based on the first law of thermodynamics. The results of this study indicated that simultaneous generation of electricity and heat using flare gas helps saving gas consumption (about 5793 kg/h) and reducing exergy losses. If there is no demand for generated electricity, the flare gases can be returned to steam generation unit which results in reduction of gas consumption about 5605 kg/h (Kazeruni et al., 2013).

Adeli et.al. investigated an economic approach to the application of flare gas in Nigerian oilfields. Their study was conducted in two parts to identify the existing approaches and the influencing factors. As most of the associated gas loss in the world occurs in Nigeria, the recovery of flare gas is essential in this country. In this study environmental problems of gas flaring were explored and various solutions were proposed (Adewale and Ogunrinde, 2010). Vickers et al studied the recovery of flare for injection into hydrocarbon reservoirs. The most significant part of this research was the design of a new system for more gas storage. Moreover, a mathematical model has been proposed based on experimental data (Vickers et al., 2012).

Saadawi (2013) introduced a plan to reduce the volume of flare gas to zero within 10 years in UAE. This is done by selecting different types of compressors suitable for the field under study. In this study a comprehensive comparison was performed on the design of different compressor systems and flare gas recovery units. Wallace et al. (2015) studied the Bacon Formation which is the world's largest shale reservoir. In their studies, they concluded that flare gases can be used as drilling rigs fuel supply in drilling and hydraulic fracturing operations. Changing the fuel type from diesel to natural gas can significantly save drilling costs. The aim of all this research is to optimize the recovery of hydrocarbon compounds in flare gas which are industrially and economically valuable.

In 2017, a study was conducted on enhanced gas recovery operations in gas reservoirs and a comprehensive EGR program was proposed. The results of their simulation using black oil and compositional models indicated that CO₂ injection is the most effective operation for increasing the gas recovery in gas reservoirs (logna, 2017)

Hassan et al. (2017) conducted studies on improving gas recovery in shale and tight gas reservoirs in Saudi Arabia. In this research, different methods such as hydraulic fracturing, application of magnetic nanoparticles, thermal and microbial recovery methods were

investigated. Finally, it was concluded that the mixture of CO₂ and CH₄ as injection gas has the most impact on gas recovery for this type of reservoirs.

Kalar and Wu (2014) conducted studies on carbon dioxide injection to improve gas recovery and proposed various patterns for direction and depth of injection to improve recovery. Bauer et. al. (2012) indicated that separation of high purity carbon dioxide from recovered flare gases is technically and economically feasible in Tunisia. Many researches have been performed on the recovery of flare gas and various applications have been proposed for its optimal use (Salu et al., 2014; Amer et al., 2018; Ding et al., 2019; Wang and Rezaee, 2020; Hamza et al., 2021; Cao et al., 2022; Dai et al., 2022; Guo et al., 2023).

In gas condensate reservoirs, reverse condensation occurs when the reservoir pressure decreases below the dew point pressure. In fact, as the reservoir pressure drops below the dew point, the gas in the reservoir begins to liquefy and appears as liquid droplets in the reservoir rock. The volume of these liquids increases with further decrease in reservoir pressure. The presence of gas condensates inside the reservoir causes problems, the most important of which is the reduction of gas relative permeability. Gas injection is the best solution to maintain the reservoir pressure above the dew point and improve the production of gas condensate reservoirs.

The objective of this study is assessment of the feasibility of flare gas recovery in Parsian refinery for application as injection gas into a gas condensate reservoir. Therefore, the separation of carbon dioxide from the flare gas was first simulated using ASPEN HYSYS software and the best absorbent was selected for maximum separation efficiency. Then, sensitivity analysis was performed on the operational parameters and their effects on gas recovery were investigated and discussed. Moreover, the simulation and feasibility study of the separated carbon dioxide injection into a gas condensate reservoir were carried out in PETREL software.

The composition of the flare gas in Parsian refinery is reported in Table 2. The temperature and pressure of the gas stream are 32.93 °C and 70 bar, respectively.

Table 2. Composition of flare gas

Component	Mol%
H ₂ O	0.00
CO ₂	1.08
H ₂ S	0.00
N ₂	3.82
Methane	89.12
Ethane	3.72
Propane	1.17
i-Butane	0.26
n-Butane	0.35
i-Pentane	0.16
n-Pentane	0.11
n-Hexane	0.22

The absorption tower has two outlet streams including sweet gas and solvent flow which contains CO₂, H₂O, and amine. Sweet gas from the top of the absorption tower can be used for different purposes such as urban or refinery fuel, feed stream to methanol synthesis unit and GTL process. To separate carbon dioxide from the liquid solvent, the outlet stream from the bottom of absorption tower is sent to amine regenerator. The regenerated amine is added to fresh solvent and used in absorption tower.

2.1. Selection of Amine Type

First, according to the operating conditions, the best type of amine solution should be selected so that maximum efficiency in carbon dioxide separation can be achieved. To this end, the separation process was simulated using various types of amine solutions and CO₂ recovery was calculated. The obtained results are compared in Table 3. It was found that, Diisopropanolamine (DIPA) has the best performance among other amine types.

Table 3. CO₂ recovery using different amine solutions

Amine type	CO ₂ recovery (%)
(MEA)	93.26
(DEA)	96.86
(TEA)	96.81
(MDEA)	96.79
(DIPA)	97.08

2.2. Operation Improvement

Since the main objective of this study was to separate carbon dioxide from flare gas for injection into a gas reservoir, some improvements were proposed and performed in separation operation to increase carbon dioxide recovery. Operational improvements were implemented by adding a cooler and a two-phase separator at the outlet of the regenerator.

The separated carbon dioxide in the regenerator contains water vapor. Therefore, it is not suitable for injection into gas reservoirs. To increase the purity of carbon dioxide, the outlet stream from the regenerator was sent to a cooler to convert the water vapor into liquid. After that, a two-phase separator was used to separate liquid water. Thus, carbon dioxide was separated with purity of 97% by choosing the best solvent and performing operational improvements.

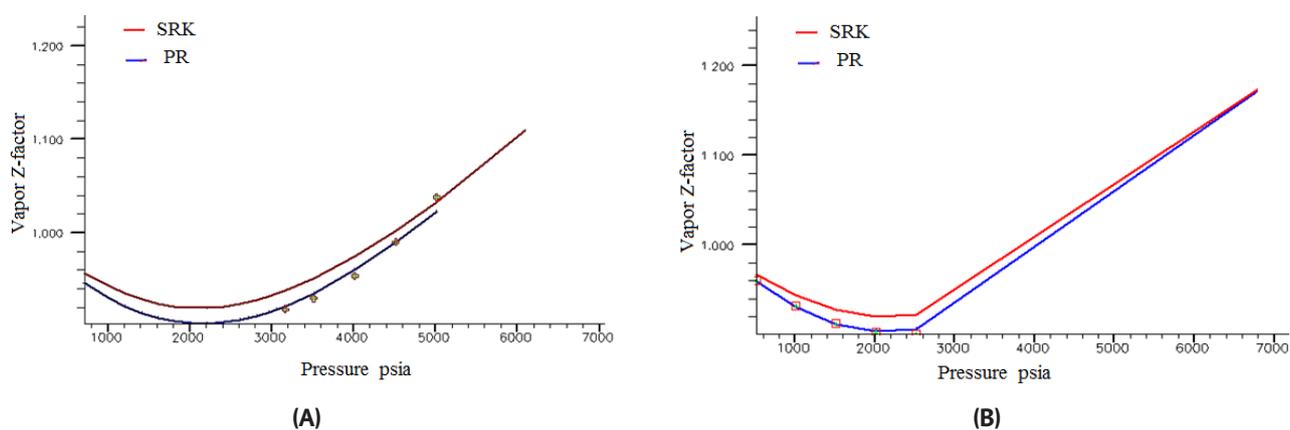
3. Reservoir Simulation

The studied reservoir was a gas condensate reservoir with the pressure of 3286 psia and temperature of 180 °F at the datum depth of 1670 m. Compositional model was applied to simulate the gas injection operation in Petrel software. The reservoir grids were determined so that the number of blocks in x, y and z directions were 74, 49 and 17, respectively.

Table 4 shows the reservoir fluid properties used for fluid characterization and developing PVT model. In order to develop the fluid model, experimental data of CCE, CVD, and separator tests were used. As shown in (Figure 2), Peng Robinson equation of state (PR EOS) fits the experimental data better than SRK EOS.

Table 4. Reservoir fluid data using in PVT model

Reservoir temperature (F)	180	
Reservoir pressure (psia)	3286	
Datum depth (m)	1670	
Average porosity (%)	13	
Horizontal permeability (md)	27	
Vertical permeability (md)	5.5	
Gas Liquid Ratio (SCF/STB)	80000	
Dew Point Pressure (psia)	3163 @ 180 °F	
Gas formation volume factor	0.00525	
Separator Liquid	Oil Density (g/cc)	0.7564 @ 60 °F
Flashed to	Shrinkage Factor	0.8397
Ambient	Gas Liquid Ratio (SCF/STB)	296
Conditions	Gas specific gravity	1.055

**Figure 2. EOS tuning results (A) CCE test (B) CVD test**

4. Results and Discussions

In this study, the simulation of carbon dioxide separation from flare gas in Parsian refinery was carried out after implementation of operational improvements. Then, feasibility of the separated gas injection into a gas condensate reservoir was investigated. To determine the optimum operating conditions, sensitivity analysis was carried out on important parameters affecting both carbon dioxide separation and injection processes.

4.1. Regenerator outlet temperature

Since a cooler was added at the top of the regenerator tower, the outlet temperature should be adjusted to achieve the maximum carbon dioxide recovery. The impact of regenerator outlet temperature on carbon dioxide recovery is shown in (Figure 3). It can be seen that, the lower the temperature, the higher the purity of carbon dioxide. The maximum purity of CO_2 (i.e., 97.81%) was obtained at the temperature of $-28\text{ }^\circ\text{C}$. This can be justified by the fact that as the temperature reduces, more water vapor becomes liquid and therefore, carbon dioxide with higher purity is obtained from regenerator.

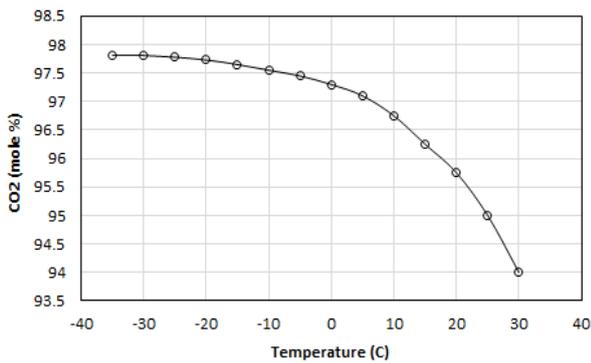


Figure 3. Impact of regenerator outlet temperature on carbon dioxide recovery

4.2. Amine solution concentration

One of the most important and effective parameters in absorption process is the solvent concentration. Therefore, variations in amine solution concentration in absorption tower and its effect on carbon dioxide recovery were evaluated. To investigate the impact of solvent concentration on CO₂ separation efficiency, sensitivity analysis was performed on the concentration of the selected type of amine solution, namely diisopropanolamine (DIPA).

(Figure 4) indicates the variations of carbon dioxide recovery against amine concentration. It can be seen that the maximum carbon dioxide recovery is achieved using 25% amine solution. In previous published studies available in the literature, it has been reported that the best concentration of amine solution in absorption process is between 20% and 40%. In fact, at concentrations less than 20%, the absorption rate is significantly low and at concentrations more than 40%, corrosion and foaming occur in the absorber.

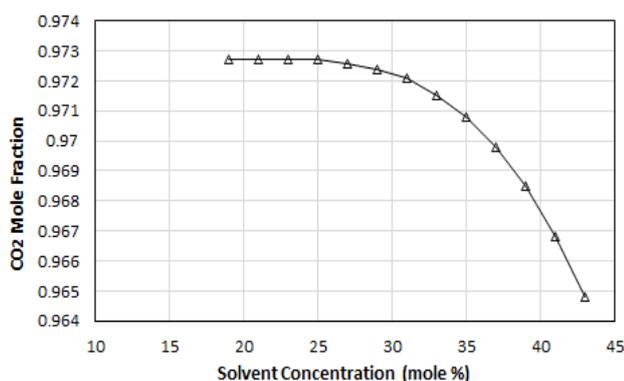


Figure 4. Effect of amine concentration on carbon dioxide recovery

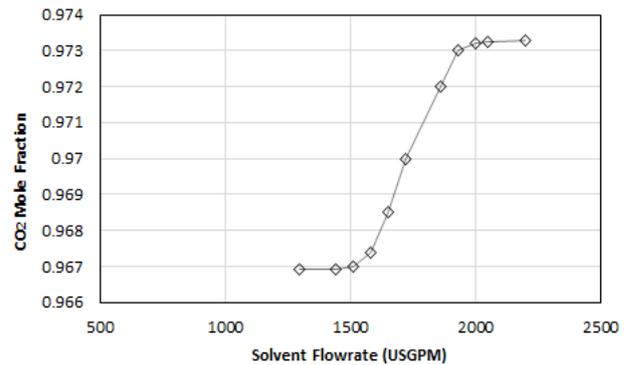


Figure 5. Effect of amine flow rate on carbon dioxide recovery

4.3. Solvent Flow Rate

In addition to the appropriate concentration for the solvent, the solvent flow rate has also a significant effect on the separation efficiency. The optimum solvent flow rate is determined according to economic considerations so that minimum solvent loss and maximum CO₂ absorption are achieved. The impact of solvent flow rate on carbon dioxide separation efficiency was explored while amine type and concentration were constant at values obtained from previous analysis. As shown in (Figure 5), the optimum solvent flow rate is 1930 USGPM.

4.4. Gas injection simulation results

In this section, the simulation results of the separated carbon dioxide injection into a gas condensate reservoir are presented. First, history matching was performed on the reservoir model from 2007 to 2017, and then the model was applied for the prediction of gas production from 2017 to 2026. It should be mentioned that the reservoir production rate was 15 million cubic meters per day. Moreover, the minimum bottom hole pressure was assigned 140 bar.

(Figure 6) shows reservoir production history from 2007 to 2017 as well as production rate prediction from 2017 to 2027. As can be seen in this figure, the model matches well the production history. It is observed that after about 5 years of production, i.e., in 2023, a significant drop in production rate occurs and the reducing trend continues until 2027.

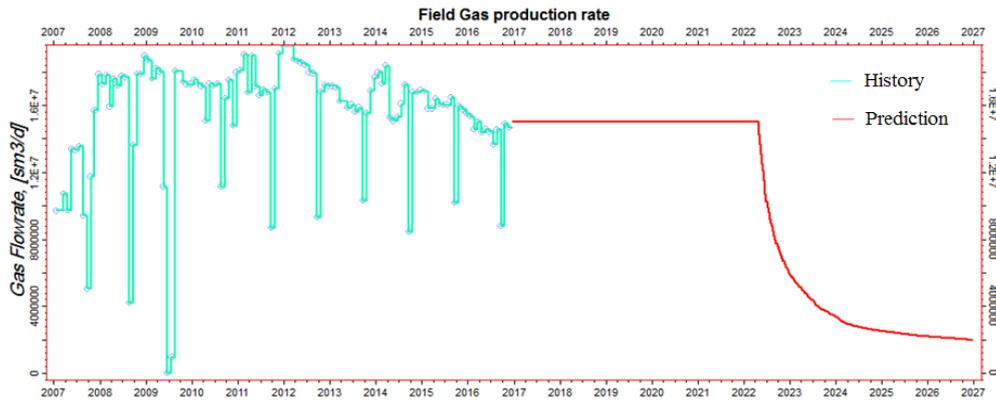


Figure 6. History match and prediction of gas production rate

The reservoir pressure variations from 2007 to 2017 and the model prediction from the end of 2017 to 2027 is illustrated in (Figure 7). It can be seen that if the reservoir pressure

drop continues due to natural depletion, the reservoir pressure declines to a minimum and gas production decreases greatly until 2023.



Figure 7. Reservoir pressure variations

(Figure 8) compares the reservoir production rate for two scenarios, i.e., natural depletion and CO₂ injection with the rate of 305,000 m³/day.

It can be seen that the production rate reaches a constant value after CO₂ injection into the reservoir.

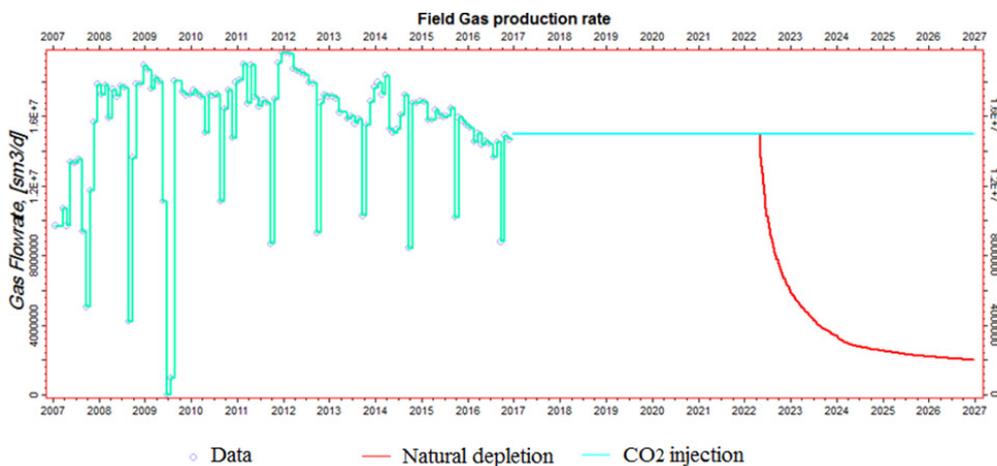


Figure 8. Production rate for natural depletion and gas injection scenarios

(Figure 9) indicates a comparison of the reservoir pressure for natural depletion and gas injection scenarios. It is shown that CO₂ injection prevents severe pressure drop, and

pressure decline occurs with a lower slope. Thus, the reservoir production rate increases and becomes more stable.

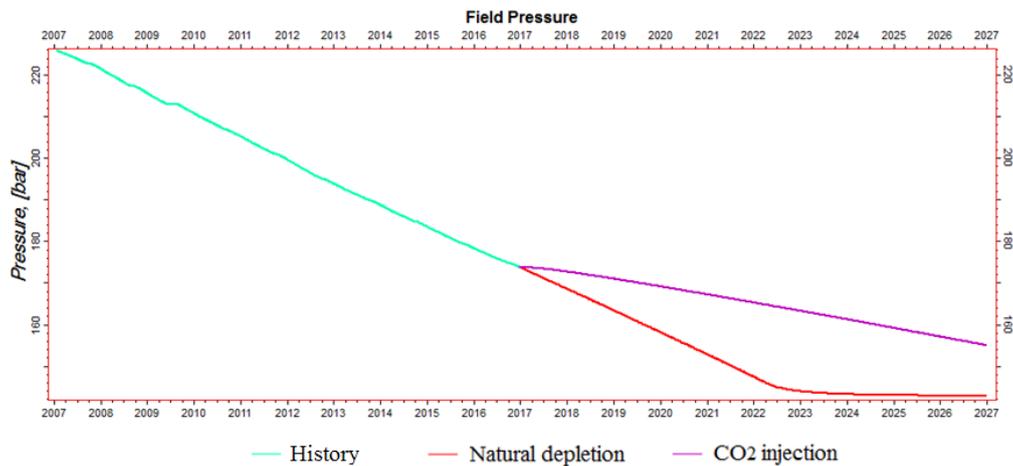


Figure 9. Reservoir pressure for CO₂ injection and natural depletion scenarios

The reservoir pressure drop in different scenarios of daily production from 15 to 25 million cubic meters is shown in (Figure 10). The maximum pressure drop in the reservoir occurs for production rate of 25 million cubic meters

per day. In fact, the reservoir pressure is reached to the minimum value in 2022. Therefore, carbon dioxide injection is required to maintain the reservoir pressure.

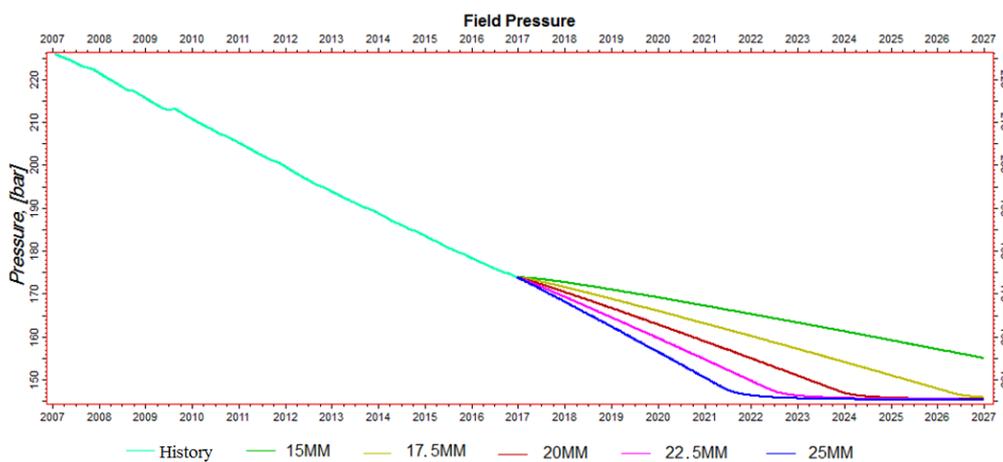


Figure 10. Reservoir pressure for different production rates in natural depletion scenario before gas injection

(Figure 11) illustrates daily gas production rates in different scenarios. As can be seen, stable production and longer production time are obtained at lower production rates.

When the production rate is 25 million cubic meters per day, despite the higher cumulative production, the duration of stable production is lower compared to other scenarios.

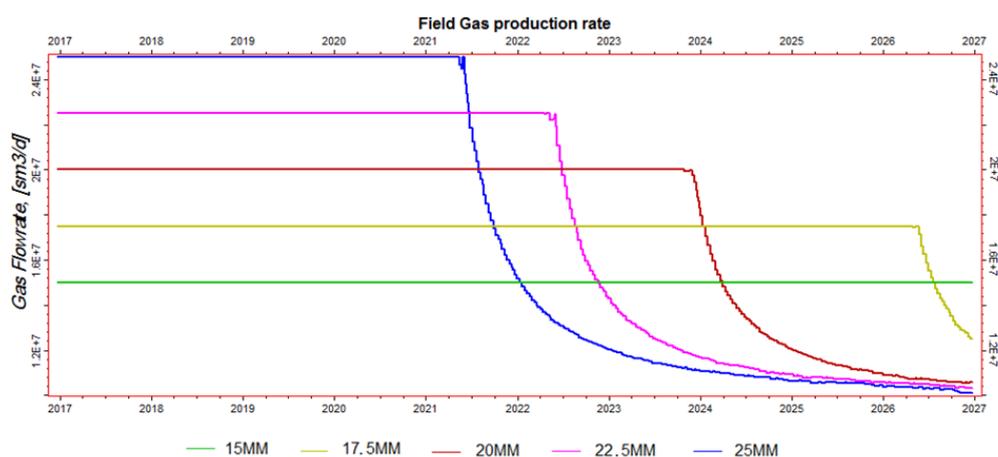


Figure 11. Gas production rates for different production scenarios before gas injection

Sensitivity analysis on carbon dioxide injection rate is presented in (Figure 12). In this analysis, the model results were compared for gas injection flow rates from 200 to 595 million

cubic meters per day. It can be seen that the most stable production rate is achieved for injection rate of 305 million cubic meters per day.

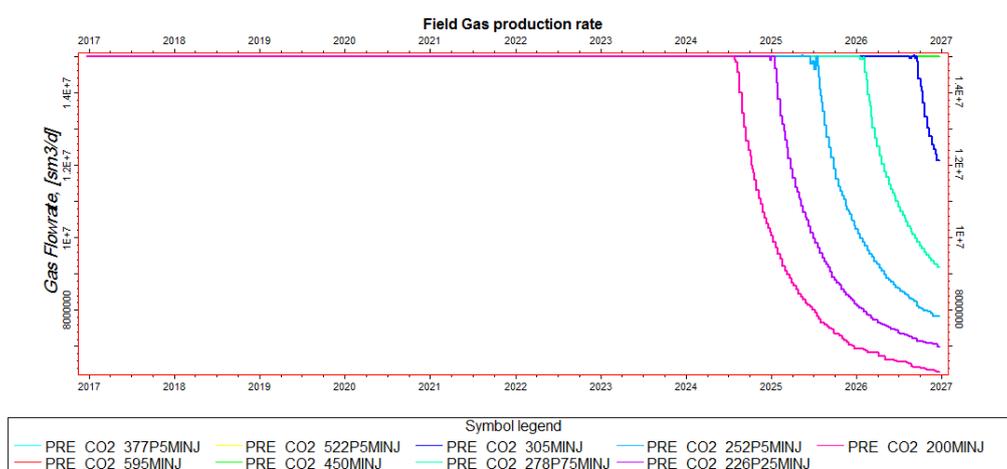


Figure 12. Production rate for various gas injection flow rate

Based on the composition of flare gas in Parsian refinery, the injection of recovered carbon dioxide leads to 2.52% increase in the reservoir recovery factor. It should be noted that the amount of CO₂ that can be recovered from flare gas in South Pars field is much higher than the amount obtained in Parsian refinery and can result in further increase in reservoir recovery factor.

5. Conclusions

In this paper, the separation of carbon

dioxide from flare gas in Parsian refinery was simulated and the feasibility of the recovered gas injection into a gas condensate reservoir was studied. The carbon dioxide separation process was simulated using ASPEN HYSYS software and sensitivity analysis was carried out on important operating parameters. The gas injection operation was simulated in Petrel software and the variations of reservoir pressure and production rate were investigated at different conditions. Based on the performed analysis, the main findings are as follows:

- In the process of carbon dioxide separation from the flare gas, diisopropanolamine (DIPA) was selected as the solvent with maximum efficiency.
- Sensitivity analysis on the operating parameters in the gas separation process showed that the optimum separator temperature is $-28\text{ }^{\circ}\text{C}$, optimum solvent concentration and flow rate are 25% and 1930 USGPM, respectively.
- Based on the simulation results, in the optimum scenario, the production rate is 25 million cubic meters per day with 305,000 cubic meters per day carbon dioxide injection.
- After separation of carbon dioxide from the flare gas, the remaining sweet gas can be used in GTL process to produce high value-added liquid hydrocarbons such as naphtha, kerosene, diesel fuel, gasoline, LPG, and chemicals with higher added value.

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Comparison of Vapor Recompression and Bottom Flashing Methods in Energy Optimization of Natural Gas Sweetening Process

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ARTICLE INFO

ORIGINAL RESEARCH ARTICLE

Article History:

Received: 28 August 2022

Revised: 26 October 2022

Accepted: 31 December 2022

Keywords:

Sour gas sweetening

Heat integration

Vapor recompression

Bottom flashing

ABSTRACT

The sweetening of sour gas by amine solvent has attracted a lot of attention due to the high ability of amines to remove acidic compounds from natural gas. In this process, an adsorption column and a distillation column are used to recover the amine. The operating costs of the conventional sour gas sweetening process are very high due to the high energy consumption in the solvent recovery column. Therefore, process energy optimization is very essential. In this research, first, the conventional gas sweetening process was subjected to heat integration (HI) so instead of using utility in supplying process energy, the energy of process flows has been used. Then, the amine recovery column is thermally integrated into this process by Vapor Recompression (VRC) and Bottom Flashing (BF) methods. The results showed that the HI, VRC, and BF processes reduced energy consumption compared to the conventional process about 25%, 88%, and 90%, respectively. Although the compressor consumption of the VRC and BF processes is almost the same, the reduction in hot and cold utility consumption in BF is 33% higher than in VRC. So, the BF process performs better than the VRC process. Moreover, BF process could reduce total annual cost (TAC) of the base process in the maximum value of 96%. That is why BF process is selected as the best choice of heat integration in this case study.

DOR: [20.1001.1/jgt.2023.560634.1009](https://doi.org/10.1001/jgt.2023.560634.1009)

How to cite this article

S. Ahmadi, N. Eyvazi-Abhari, M. Esperi, H. Asvadi, F. Ezati Kamkar, S. Rahbari, Comparison of Vapor Recompression and Bottom Flashing Methods in Energy Optimization of Natural Gas Sweetening Process. Journal of Gas Technology. 2022; 7(2): 16 -23. (http://jgt.irangi.org/article_704725.html)

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Available online 31 December 2022

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1. Introduction

More than 40 percent of the world's natural gas reserves are sour, which contains significant amounts of sulfur and carbon dioxide. The percentage of natural gas reserves rises to 60 percent for the Middle East. Due to the contaminations of the environment caused by sour gas consumption, it is necessary to remove acidic compounds before use (Chen et al., 2021). The process of removing carbon dioxide and hydrogen sulfide compounds from sour gas is called gas sweetening (Abd et al., 2020). Until now various processes have been proposed for sweetening of natural gas, among which can be mentioned to adsorption processes by chemical solvents, physical solvents, and physical-chemical solvents. Using amines is the most common method of sour gas sweetening. Amines have a high ability to absorb acidic compounds of sour gas. Among amines, monoethanolamine (MEA) is a common solvent for the adsorption of carbon dioxide and hydrogen sulfide. MEA is the cheapest alkanoamine, so it has the highest theoretical capacity to absorb carbon dioxide (Aghel et al., 2020). In the sweetening operation of sour gas by amine, the gas flow and the liquid amine solution are contacted in an adsorption column. Normally, the gas to be sweetened enters the adsorption column from below, and the sweetened gas exits from the top of the adsorption column. The solvent also enters from the top of the adsorption column and exits from the bottom of the adsorption column. To reduce the viscosity of the circulating fluid, the circulating amine is diluted with water. The liquid amine solution containing the acidic compounds of the sour gas is transferred to a solvent recovery unit where the acidic compounds are removed from the amine (Long and Lee, 2017). The acid-free amine solution is removed from the bottom of the column, cooled, and returned to the adsorption column. Sweetening gas by using amine solvent is a process with high energy consumption, therefore, energy optimization in the amine plant becomes a concern for most

operating companies (Song et al., 2017). In recent years, various methods have been proposed to reduce the energy consumption (Mix et al., 1981), such as HiDiC method, feed splitting method, external heat pump method, and so on (Díez et al., 2009). VRC and BF are the two methods that have been used in this study to reduce the energy consumption of distillation columns. In the VRC method, the output vapor from the top of the column is compressed by passing through the compressor, and pressure and temperature increase. Then the vapor releases heat, by exchanging heat in a heat exchanger, and heats the liquid flowing out from the bottom of the column (Cong et al., 2018). In the BF method, the flow pressure and temperature are reduced by passing the downflow of the column through the throttle valve. The cooling flow passes through the heat exchanger and heats up so receives heat from the outlet flow above the column (Díez et al., 2009; Jogwar and Daoutidis, 2009). Dai et al, to reduce the operating cost of the process of removing acidic compounds from natural gas, added two flash columns between the two columns of adsorption and distillation in the conventional process and successfully reduce energy consumption by 2.2×10^9 kJ/h (Dai et al., 2019). To reduce the energy consumption of the process of removing acidic gas compounds, Long and Lee used the heat pump arrangement and heat integration of several distillation columns and reduced the reboiler heat duty and operating cost by 62.5% and 45.9%, respectively (Long and Lee, 2017). Amri and Zahid presented an improved layout of the sweetening unit. In the proposed method, the energy consumption of the process was reduced by 22% due to the reduction of the amine circulation flow. The results showed that the proposed method has an 18% lower annual cost compared to the initial case (Al-Amri and Zahid, 2020).

This study aims to reduce the overall energy consumption of the natural gas sweetening process. First, the heat integration between the heater and the cooler used in this process is

done to reduce the total energy consumption of the process (HI). Then the methods of heat integration of VRC and BF to reduce the total energy consumption of the solvent recovery column in the integrated thermal process of gas sweetening are investigated. In both VRC and BF methods, the need for hot and cold utility can be reduced by creating heat exchange between the adsorption and desorption sections. Therefore, in this paper, using these two methods, an attempt has been made to reduce the overall energy consumption of the solvent reduction distillation column. Of course, compressors must be used in both processes, and the output pressure of the compressor as the main variable in process energy optimization must be accurately calculated. All processes

are accurately simulated and the total energy consumption and TAC for each process are calculated and compared.

2. Case Study

In this study, natural gas sweetening is performed by using monoethanolamine solvent. In the adsorption column, carbon dioxide and hydrogen sulfide are released from the gas, and sweet gas is released from the top of the adsorption column. In the second column, the solvent recovery operation is developed and the bottom product of the column with the specifications of the input solvent is returned to the first column. The feed conditions of the sour gas and the solvent are given in (Table 1).

Table 1. Information about the Sour Gas and the Solvent Feed

Process Characteristic	Sour Gas	Solvent (MEA)	
Temperature (°C)	30	30	
Pressure (kPa)	3000	5000	
Molar flow (kmole/h)	3888	4377	
Mole fraction	Methane	0	
	Ethane	0	
	Propane	0	
	i-butane	0	
	n-butane	0	
	i-pentane	0	
	n-pentane	0	
	Carbon dioxide	0.03	0
	Hydrogen sulfide	0.02	0
	Nitrogen	0.01	0
	Water	0.01	0.8878
	Monoethanolamine	0	0.1122

3. Process Simulation

Aspen Hysys V.11 was used to simulate the processes. The Acid Gas-Chemical Solvents equation is used as the thermodynamic package. Also, instead of using shortcut methods, the Modified HYSIM Inside-Out solution method has

been used rigorously to solve the columns.

3.1. Conventional Process

(Figure 1), shows the simulation of the conventional natural gas sweetening process by using amine solvent, in Aspen Hysys software.

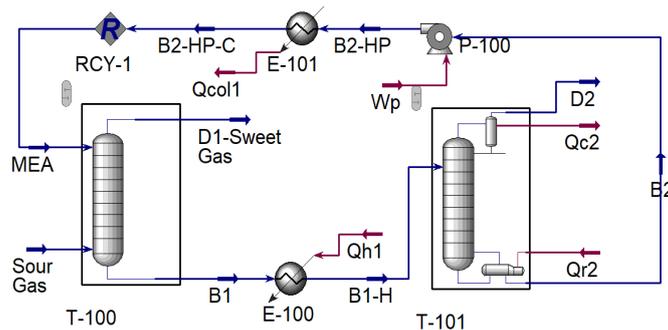


Figure 1. Conventional natural gas sweetening process in Aspen Hysys

In this process, both absorption and distillation columns have 20 trays. The bottom flow of the adsorption column, which contains solvent, hydrogen sulfide, and carbon dioxide, after heating enters the fifth tray of the second column to recover the solvent. The pressures at the top and bottom of the adsorption column are 4800 kPa and 4900 kPa, respectively. The pressures at the top and bottom of the distillation column are 101.3 kPa and 130 kPa, respectively. The top product of the first column is sweet gas. The bottom product of the second column, which is

the solvent, is returned to the absorption column.

3.2. Heat Integration of the Process

By heat integration between inlet flow to the second column and bottom flow of the second column in a heat exchanger, the consumption of hot utility is eliminated and the amount of cold utility is reduced. The temperature of the second column downflow reached 83.86°C. To reduce the temperature of the flow to 30°C, a cooler is needed, which is also shown in (Figure 2).

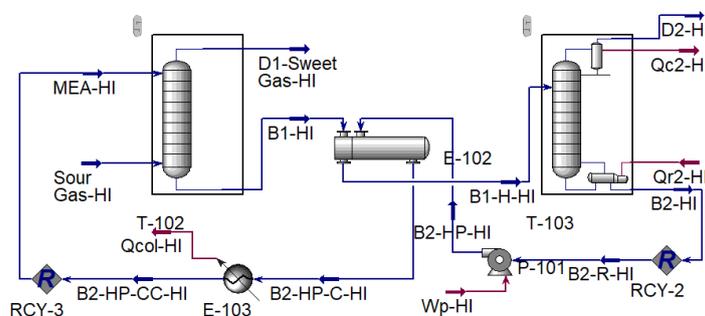


Figure 2. Heat integration simulation of the conventional natural gas sweetening process in Aspen Hysys

3.3. Vapor Recompression Method

(Figure 3), shows the simulated heat integration of VRC process in Aspen Hysys.

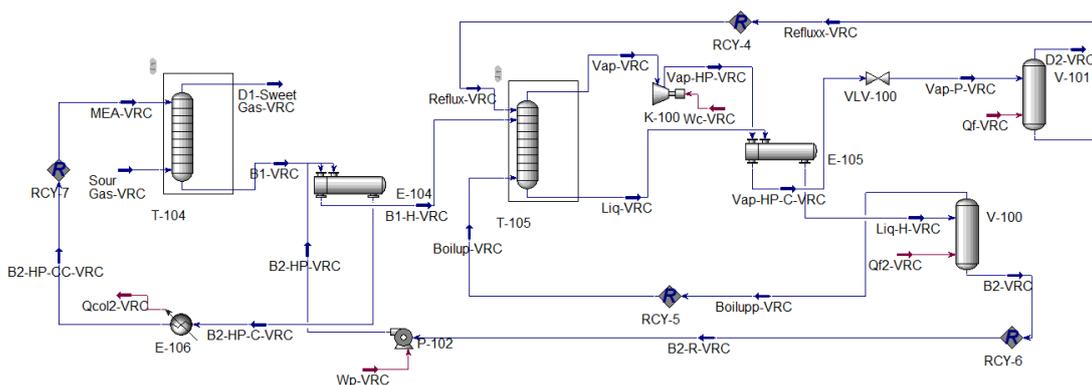


Figure 3. Simulation of the VRC heat integration process in Aspen Hysys

As shown in (Figure 3), the vapor at the top of the column is compressed by passing through the compressor to a pressure of 165 kPa. The minimum allowable temperature difference of the heat exchanger is 5 °C ($\Delta T_{appmin} = 5$). First, the cooled fluid output from the exchanger passes through the throttle valve. Then, reaches the product pressure above the column and enters the two-phase separator. The vapor flow is the top product and the liquid flow is as the second column's reflux. The heated fluid output

from the heat exchanger also enters another two-phase separator, thus the liquid flow is the bottom product and the vapor flow is as the second column's boilup. The bottom product returns to the absorption column after increasing the pressure and decreasing the temperature to 30°C in the cooler.

3.4. Bottom Flashing Method

(Figure 4), shows the BF method heat integration process simulation in Aspen Hysys.

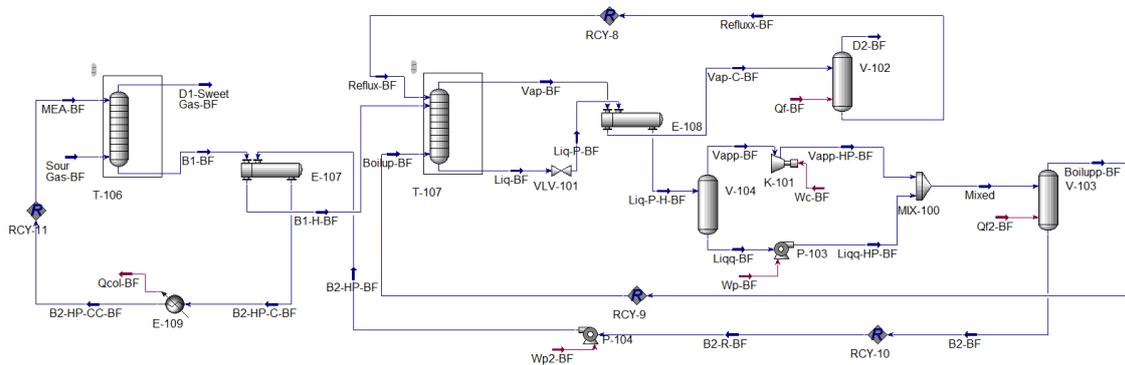


Figure 4. Simulation of BF heat integration process in Aspen Hysys

As shown in (Figure 4), the pressure of the outlet fluid from the bottom of the second column decreases to 77 kPa by passing through the throttle valve and receiving heat from the top vapor flow of the column in the heat exchanger. Pressure of the heated fluid increases and enters a separator and creates the bottom product and boilup. The cooled liquid leaving the exchanger

enters a separator and creates top product and reflux.

4. Results and Discussion

In this article, 4 different processes for sweetening natural gas are examined. (Table 2), shows the energy consumption of each process.

Table 2. Energy Consumption in Different Processes

Process	Hot Utility(MW)	Cold Utility(MW)	Compressor Consumption (MW)
Conventional Process	65288.747	65293.053	---
Heat Integration Process	49070	49065.651	---
VRC Process	2691	5311.696	2354
BF Process	1429	3936	2545

The energy of a process is calculated by using eq. (1).

$$Q = Q_c + Q_r \quad (1)$$

Where Q , Q_c , and Q_r indicate the process energy consumption, cold utility and hot utility, respectively.

But in VRC and BF methods, due to the compressor, the energy consumed is obtained from eq. (2).

$$Q' = Q_c + Q_r + 3W_{comp} \quad (2)$$

Where Q' , Q_c , Q_r and W_{comp} represent the

process energy consumption, cold utility, hot utility and compressor consumption, respectively. Since compressor efficiency has been considered 33%, factor 3 is used to convert compressor electricity energy consumption to heat energy in this equation (Babaie and Esfahany, 2020).

(Figure 5), shows a comparison of energy consumption in the investigated processes.

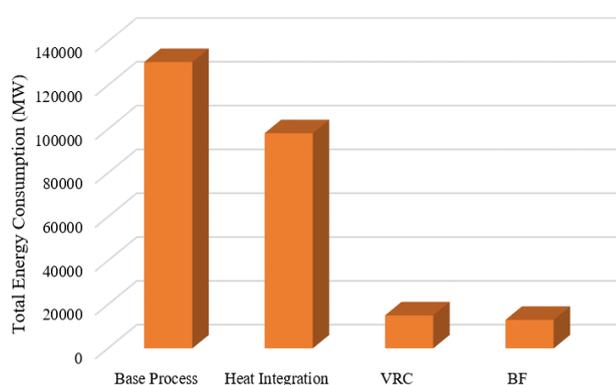


Figure 5. Comparison of energy consumption between different processes

According to (Figure 5), the BF method has the lowest amount of energy consumption and is therefore selected as the best process, the most important reason for this choice is to significantly reduce the need for hot and cold utilities.

Since in the studied heat integration processes, VRC and BF, as the best process in energy saving, the number of equipments are increased compared to the base process, TAC has been studied for all four processes and the results are compared. As it's clear from eq. (3), TAC is the summation of operating costs and annualized capital investments. In this equation,

payback factor has been considered as five years to annualize the capital cost. Therefore, both operating and capital costs (C_{Op} and C_{Cap}) affect the amount of TAC. In eq. (4) & (5), it's determined which factors affect C_{Op} and C_{Cap} .

$$TAC = f(C_{Op}, C_{Cap}) = C_{Op} + \frac{C_{Cap}}{\text{Payback Factor}} \quad (3)$$

$$C_{Op} = f(C_{Utility}, T_{cond}, Q_{cond}, T_{reb}, Q_{reb}, C_{elect}) \quad (4)$$

$$C_{Cap} = f(P, H_{Col}, D_{Col}, A_{HX}, C_{pump}, C_{Compressor}) \quad (5)$$

Economic calculations are carried out based on the equations and costs for capital investment proposed by Sieder et al. (Sieder et al., 2009). The considered cost index to correlate capital cost has been reported from chemical engineering plant cost index for 2022 (CE=622.5). Operating costs of columns were calculated by selecting the suitable utility types for reboilers and condensers according to their temperatures (Babaie and Esfahany, 2020). Furthermore, operating costs of compressor and pump were determined based on the cost of electricity (Li and Kiss, 2021).

The results of TAC calculations for the all considered processes indicate that, although BF process utilizes the most equipments of them, but it could reduce TAC of the base process in the maximum value. In (Table 3), number of each equipment is summarized for each process and in (Figure 6), the comparison of TAC reduction percentage compared to the base process is proposed for the three considered heat integration processes.

Table 3. Number of Different Equipments in the Processes

Process	Heat Exchanger	Distillation Column	Separator	Pump	Compressor
Base Process	4	2	0	1	0
HI	4	2	0	1	0
VRC	5	2	2	1	1
BF	5	2	3	2	1

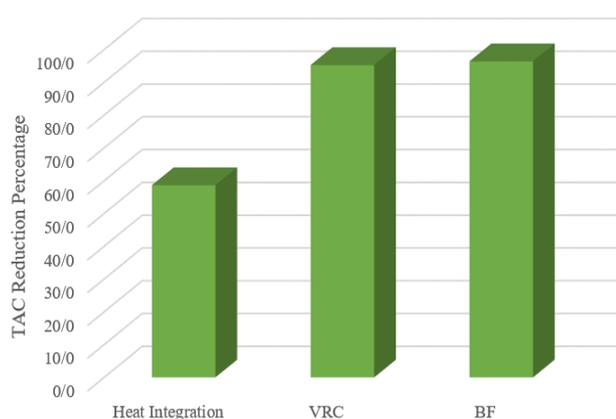


Figure 6. Comparison of TAC reduction percentage compared to the base process

5. Conclusion

In this study, the sweetening process of sour gas by using amine solvent is investigated. In this process, an absorption column is used to separate carbon dioxide and sulfur, and a distillation column is used to recover amine. The energy consumption of the sweetening process is high, so it is necessary to use energy optimization methods. VRC and BF have been used. Also, by using heat integration in VRC and BF methods, new processes with less energy consumptions were proposed. The results show that the three processes HI, VRC and BF have reduced total energy consumption about 25%, 88%, and 90%, respectively, compared to the conventional process. Significant reduction in energy consumption in all three methods drastically reduces the amount of vapor consumed and cold water consumed, which significantly reduces operating costs and thus a significant reduction in TAC, as it concluded after TAC calculations for the four processes. Results indicated that HI, VRC, and BF processes could decrease TAC of the base process about 56.8%, 95.3%, and 96.4% respectively. Therefore, the BF method is selected as the best heat integration method in this study. The compressor consumption in VRC and BF process is the same. The consumption of hot utility and cold utility

is reduced 47% and 26% in BF compared to VRC, which indicates better performance of the BF process than VRC.

Nomenclature

<i>BF</i>	Bottom flashing
<i>HI</i>	Heat integration
<i>HIDiC</i>	Internally heat-integrated distillation Column
<i>MEA</i>	Monoethanolamine
<i>TAC</i>	Total annual cost
<i>VRC</i>	Vapor recompression

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A Comprehensive Review on Advantages and Issues of Nanotechnology in the Oxidative Desulfurization Method for the Production of Ultra-Clean Fuels

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ARTICLE INFO

REVIEW ARTICLE

Article History:

Received: 11 October 2022

Revised: 22 December 2022

Accepted: 09 January 2023

Keywords:

Nanocatalyst

Oxidative desulfurization

Fuel oil

ABSTRACT

Today, producing clean fuel oil is one of the major challenges in the world. One of the factors that causes environmental pollution is the sulfur compounds in crude oil. In today's world, there are strict rules for reducing the amount of sulfur in fuel. There are several ways to remove sulfur compounds from fuels, such as hydrodesulfurization (HDS), extractive distillation, biodesulfurization, adsorption desulfurization, and oxidative desulfurization (ODS). Some refractory sulfur compounds that are not removed from the fuel oil by the HDS can be easily removed by oxidation method. Nowadays, the ODS method is known as a complement to the HDS method. In the oxidation method, sulfur compounds are converted to the corresponding sulfonates by catalysts and oxidants and then separated from the feed by polar solutions or adsorbents. Various researches have been done on the Catalysts and oxidants of the ODS method. In this study, a comprehensive review has been carried out on the application of nanotechnology in the oxidative desulfurization method. Based on previous researches and available articles, nanocatalysts used in the oxidation process can be classified into five groups; polyoxometalates, transition metal oxide, carbon materials, ionic liquids and metal-organic frameworks (MOF). Also, different nanocatalysts and oxidants and optimal conditions to achieve the highest conversion percentage for the removal of sulfur compounds were investigated.

DOR: [20.1001.1/jgt.2023.1974394.1021](https://doi.org/10.1001.1/jgt.2023.1974394.1021)

How to cite this article

Z. Mobasheri, S.H. Zohdi, A Comprehensive Review on Advantages and Issues of Nanotechnology in the Oxidative Desulfurization Method for the Production of Ultra-Clean Fuels. Journal of Gas Technology. 2022; 7(2): 24 -34. (http://jgt.irangi.org/article_704726.html)

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Available online 09 February 2023

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1. Introduction

The presence of sulfur in petroleum feeds has adverse environmental effects. Sulfur compounds in crude oil include thiophenes (T), benzothiophenes (BT), and dibenzothiophenes (DBT) and mercaptans which produces sulfur oxide (SO_x), these are the main causes of environmental pollution (Figure 1) (Hossain, 2019). In recent years, desulfurization of crude oil has received much attention and refineries are required by world law to reduce sulfur to less than 10ppm (Kalantari, 2016). Also, the amount of sulfur allowed for fuel cells should be less than 0.1ppm (Stanislaus, 2010). Many different methods, such as hydrodesulfurization (HDS), biodesulfurization (BDS), adsorption desulfurization (ADS) and oxidative desulfurization (ODS), have been used to desulfurize fuel oil (Hossain, 2019). The hydrodesulfurization reaction takes place in the presence of metallic catalysts (Ni, Mo and Co) and hydrogen gas at high temperatures (up to 400 °C) and pressures (up to 100 atm) (Ahmed, 2020; Meman, 2014). Hydrodesulfurization (HDS) is very efficient in removing T, BT, DBT, but some sulfur compounds in heavy oil cuts require higher operating conditions (High temperature and pressure) and that means more operating costs (Campos-Martin, 2010; Rezvani, 2020). It is very difficult and expensive to achieve ultra-clean fuel using hydrodesulfurization method for environmental reasons (Meman, 2014).

Oxidative desulfurization (ODS) method has attracted a lot of attention compared to HDS method due to the mild reaction conditions (low temperature and pressure) and no need to use hydrogen (Dai, 2008). Oxidation desulfurization has two main steps. At first, sulfur compounds are oxidized to other compounds such as sulfone. This conversion occurs in the presence of oxidants. In the second stage, oxidized compounds will be removed from the reaction mixture by the extraction methods (Hossain, 2019). In recent years, different catalysts have

been used for oxidative desulfurization. One of the cases that has been widely used in the production of catalysts is the use of nanotechnology. This paper reviewed the works about the applications of nanotechnology in the oxidative desulfurization method.

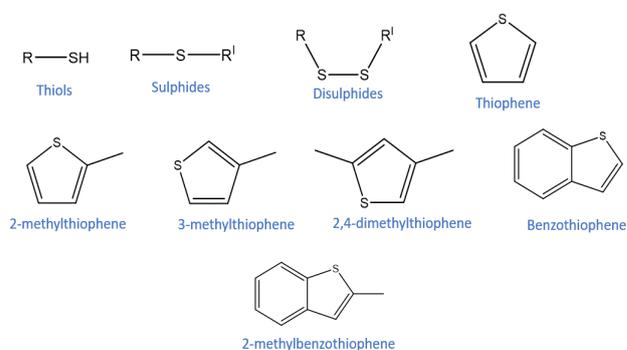


Figure 1. Sulfur compounds in crude oil (Hossain, 2019)

2. Nanotechnology in Catalytic Oxidation Desulfurization Process

2.1. Polyoxymetalate Catalytic Oxidation System

Polyoxymetalates are one of the subdivisions of transitional metal ions and polyoxoanions. They are robust catalysts due to the presence of multifunctional active sites in their structure. like protons, oxygen atoms, and metals. Polyoxymetalates have been considered in the desulfurization process as efficient catalysts in the presence H₂O₂ oxidant (Wang, 2015).

Rezvani et al. applied polyoxometalate@ceramic@polyaniline nanocatalyst for oxidative desulfurization of simulated fuels and gasoline containing sulfur refractory compounds (such as Th, BT, and DBT) in a mixture of hydrogen peroxide/acetic acid as an oxidizing agent and acetonitrile was used as an extraction solvent. The sulfur content was finally reduced to 97% at optimal condition; reaction temperature of 35 °C and reaction time 1 h (Rezvani, 2019).

Nogueira et al. examined silica nano-sized sphere catalysts [PW₁₁Zn (H₂O) O₃₉]⁵⁻, for oxidative desulfurization of olefins. The nanocomposite proved to be a very powerful

and versatile heterogeneous catalyst for the oxidation of various olefins and also for the oxidative desulfurization of a model oil, in the presence of H_2O_2 as the oxidant and MeCN as the solvent. After 1 h, in temperature of 50 °C and three consecutive ODS cycles desulfurization of DBT reached 100%. Also, desulfurization of 4, 6-DMDBT after three consecutive ODS cycles, 2h and temperature of 50 °C reached 100% efficiency (Xiong, 2015).

Ahmed et al. studied oxidative desulfurization (ODS) of light naphtha feedstock in a batch reactor using new homemade nano-catalyst, zinc oxide supported on zeolite nanoparticles, and used air as oxidant. The experimental results showed that at 54.4 °C for 163.6 minutes and an initial concentration of 335.3 ppm and in the presence of nanocatalysts (ZnO/zeolite nanoparticles) the conversion was more than 99% (Ahmed, 2020).

Liu et al. studied the removal of sulfur compounds from crude oil using the oxidative desulfurization method, with magnetically recoverable catalysts $Cs_{2.5}H_{0.5}PW_{12}O_{40}/nano-Fe_3O_4/SiO_2$ and $H_3PW_{12}O_{40}/nano-Fe_3O_4/SiO_2$. The results of catalyst characterization showed that the produced catalyst had a magnetic property, which makes it easily extracted under a magnetic field. Under the experiment conditions (temperature 60 °C and 180min), the sulfur removal rates by using $H_3PW_{12}O_{40}/nano-Fe_3O_4/SiO_2$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}/nano-Fe_3O_4/SiO_2$ reached 99.4% and 91.4% respectively in the model oil. This catalyst had a good catalytic effect for model oil and was also recyclable, but its effect on real oil was not yet acceptable (Liu, 2017).

Mohammadi Meman et al. investigated the deep oxidative desulfurization of sour petroleum fractions with H_2O_2 as oxidant and MnOx/FMWNT heterogeneous nano-catalyst. The sulfur removal efficiency reached 99.85% at temperature of 25 °C and time 30 min and atmospheric pressure (Meman, 2014).

Chen et al. used the HPW-NH₂-HHSS catalyst

as an effective catalyst for Oxidative-adsorptive desulfurization of fuels. They investigated the effect of reaction parameters such as reaction temperature, reaction time, initial DBT concentration, catalyst dose and O/S molar ratio on sulfur removal of the OADS reaction efficiency. Under optimal conditions; temperature of 60 °C, sulfur concentration 300 mg/l, O/S molar ratio 2.5 and time of 30 minutes, DBT removal reached 99.36%. At the end, they considered the polarity and size of the catalyst pores to be the main factors influencing the reaction efficiency (Chen, 2020).

Ghahramaninezhad et al. used a polyoxometalate (Mo_{132}) nanoballs supported over the Zeolitic imidazolate framework-8) and tert-butyl hydroperoxide (TBHP) as oxidant to desulfurize the model fuel. The reaction was performed in a batch reactor system. Under the optimal conditions, temperature of 80 °C, time of 8 h, catalyst dosage 150 mg, O/S molar ratio 1 and initial sulfur concentration 500 ppm reached 95% conversion (Ghahramaninezhad, 2019). Saha et al. Used nano silver supported on titanium dioxide (Ag/TiO_2) as catalyst and Tertiary-butyl hydroperoxide as oxidant to remove thiophene from the model oil. They examined the effect of various parameters such as catalyst weight, O/S molar ratio, silver charge on the catalyst and reaction temperature. Finally, the conversion rate of 63 was the highest reported in 90 minutes and 10 wt% Ag/TiO_2 catalyst (Saha, 2019).

Jarullah et al. used the new nano-catalyst CuO+NiO supported on HY zeolite and air as an oxidizer to oxidative desulfurize the light gas oil. Under optimal conditions; the temperature of 413 K and the time of 90min using the (20%CuO+10%NiO) catalyst reached a conversion rate of 92.15 to remove sulfur (Jarullah, 2020).

Xiao et al. Used a flower-like $WO_3 \cdot H_2O$ catalyst and H_2O_2 as an oxidant to remove dibenzothiophene in the sample oil. Under

optimal conditions, the temperature of 70 °C, Sulfur compounds was reduced from 4000 to 220 µg/g in 60 minutes (Xiao, 2016).

He et al. used PtCu/BNNS as a catalyst and O₂ as an oxidizer to oxidative desulfurization of fuel oil. They examined the effect of the

reaction parameters and in the optimal reaction conditions; the temperature of 110 °C and the time of 7h, the amount of sulfur reached 7.9ppm, and the conversion was 92.1% (He, 2020). (Table 1) compares some of the Polyoxymetalate nanocatalysts in ODS process.

Table 1. Polyoxymetalate Nanocatalysts in ODS Process

Catalyst	Source of sulfur	Oxidizing agent	Reaction condition	Sulfur removal efficiency%	Ref.
Polyoxometalate@ Ceramic@ Polyaniline	Real gasoline	Hydrogen peroxide/acetic acid	T = 35 °C, t = 60 min	97	(Rezvani, 2020)
[PW ₁₁ Zn (H ₂ O) O ₃₉] ⁵⁻	DBT	H ₂ O ₂	T = 50 °C, t = 60 min	100	(Xiong, 2015)
ZnO /Zeolite nanoparticle	light naphtha feedstock	air	T = 54.4 °C, t = 163.6 min	99	(Ahmed, 2020)
Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ / NanoFe ₃ O ₄ /SiO ₂	Model oil	H ₂ O ₂	T = 60 °C, t = 180 min	99.4	(Liu, 2017)
MnOx/FMWNT	sour petroleum	H ₂ O ₂	T = 25 °C, t = 30 min	99.85	(Meman, 2014)
HPW-NH ₂ -HHSS	DBT	H ₂ O ₂	T = 60 °C, t = 30 min	99.36	(Chen, 2020)
ZIF-8@{Mo ₁₃₂ }	DBT	TBHP	T = 80 °C, t = 8 h	95	(Ghahramanin-ezhad, 2019)
Ag/TiO ₂	Th	Tertiary-butyl hydroperoxide	T = Not specified, t = 90 min	63	(Saha, 2019)
CuO+NiO supported on HY zeolite	light gas oil	air	T = 140 °C, t = 90 min	92.15	(Jarullah, 2020)
WO ₃ ·H ₂ O	DBT	H ₂ O ₂	T = 70 °C, t = 60 min		(Xiao, 2016)
PtCu/BNNS	real diesel fuel	O ₂	T = 110 °C, t = 7 h	92.1	(He, 2020)

2.2. Carbon Nano Materials

Recently, the use of carbon nanotubes in desulfurization has been considered due to its special structural properties. Wang et al. examined the performance of carbon nanotubes supported Cs_{2.5}H_{0.5}PW₁₂O₄₀ as an effective catalyst for the oxidative desulfurization of diesel. According to laboratory studies, it was concluded that the catalyst has a high efficiency for oxidizing DBT. The efficiency obtained is equal to 100% under optimal conditions; temperature of 60 °C, catalyst dosage 1.0 wt. % and 30min (Wang, 2010). Zhang et al. Studied the effect of carbon nanotubes as a new catalyst and molecular oxygen as oxidant in the oxidation desulfurization of model oil.

Experimental results showed that when CNT-SZ was used as catalysts, the sulfur removal efficiency reached 100% at 150 °C within 40min (Zhang, 2020).

There are also studies showing that carbon nanotubes have been used as a support. Wang et al. used tungsten trioxide catalyst immobilized on CNT to remove dibenzothiophene by oxidative desulfurization method. H₂O₂ was used as an oxidant. CNT was dispersed and the catalyst was charged on it in the presence of ionic liquid [C₁₆ mim] Cl. They also examined the effect of different forms of WO₃ catalysts based on the same CNT. Finally, it was concluded that the use of tungsten trioxide catalyst in the form

of tetrahedral was most effective and in the optimal reaction conditions, the conversion percentage of DBT reached 90.73 % (Wang, 2019).

Gao et al. synthesized and compared two types of carbon nanotube-based polyoxometalate catalysts (POM@CNTs, CNTs@

PDDA@Mo₁₆V₂) for oxidative desulfurization of model fuels. Finally, they concluded that the CNTs@PDDA@Mo₁₆V₂ catalyst was more efficient in the presence of H₂O₂ oxidant and the conversion rate of dibenzothiophene reached 99.4% at 70 °C (GAO, 2018). (Table 2)shows the applications of carbon materials in ODS process.

Table 2. Carbon Materials in ODS Process

Catalyst	Source of sulfur	Oxidizing agent	Reaction condition	Sulfur removal efficiency%	Ref.
Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ / MWNT	DBT	H ₂ O ₂	T = 60 °C, t = 30 min	100	(Wang, 2010)
CNT-SZ	DBT	H ₂ O ₂	T = 150 °C, t = 40 min	100	(Zhang, 2020)
WO ₃ /CNT	DBT	H ₂ O ₂	T = 60 °C, t = 60 min	90.73	(Wang, 2019)
CNTs@PDDA@Mo ₁₆ V ₂	DBT	H ₂ O ₂	T = 70 °C, t = min	99.4	(Gao, 2018)

2.3. Ionic Liquids

Today, the use of ionic liquids as catalysts in the desulfurization process has been studied and considered. Ionic liquids, also known as green solvents, have unique physical and chemical properties such as electrical conductivity and high partial vapor pressure, fluidity over a wide temperature range, and good solubility. However, some weaknesses, such as high prices, difficult separation of these compounds, and the retention of some ionic liquid in the fuel, have limited the use of ionic liquids. Of course, there are solutions to these problems. One of these solutions is the stabilization of ionic liquids on the basis of solid catalysts such as silica and gamma alumina. Also, Saberi et al. used the magnetic separation method using iron oxide nanoparticles to solve the separation problem (Azimzadeh, 2017; Cruz, 2019; Poursaberi, 2013).

Poursaberi et al. investigated the efficiency of iron oxide magnetic nanoparticles as catalysts for oxidative desulfurization of model and real oil. Ionic liquid was used to synthesize the catalyst and modify the surface of iron oxide nanoparticles. The conversion of sulfur aromatic compounds using this catalyst (Fe₃O₄/APTES/IL) in 15 minutes and 25 °C reached 51.3% and after

5 repetitions reached 90.3%. Also, using this catalyst, oxidized compounds were removed magnetically (Poursaberi, 2013).

Cruz et al. synthesized two types of titanium catalysts for the oxidative desulfurization of model oil and the removal of dibenzothiophene. One catalyst was synthesized using ionic liquid (Titanium hybrid mesoporous silica nanoparticles (ILBF4-x%TiCp₂-MSN)) and the other without ionic liquid (TiCp₂-MSN). The results showed that the catalyst synthesized with ionic liquid has a better efficiency for removing sulfur compounds and under optimal conditions: Temperature 60 °C and time 6h and in the presence of H₂O₂ as an oxidizer the conversion rate of DBT reached 99.1% (Cruz, 2019).

Wang et al. Used ionic liquid to synthesize photocatalytic nano-titanium oxide (nano-TiO₂) catalysts. The results showed that this catalyst had a good ability to remove sulfur compounds in gasoline using the ODS method and using UV radiation for 10 hours reduced amount of sulfur in gasoline to 8 ppm (Wang, 2012). Li et al. also used this catalyst without UV irradiation to remove DBT and 4,6-dimethyldibenzothiophene, and reached a conversion rate of 100% (Li, 2016).

Xun et al. synthesized a Phosphomolybdate-based ionic liquid $[(C_8H_{17})_3NCH_3]_3PMo_{12}O_{40}$ catalyst based on magnetic mesoporous silica ($\gamma-Fe_2O_3@SiO_2@mSiO_2$) to produce a magnetic catalyst for oxidative desulfurization of DBT in model oil. Using this magnetic catalyst in the

presence of air as an oxidant, debenzothiophene was completely removed in 5 hours at a temperature of 120 °C and reached a conversion rate of 100% (Xun, 2019). (Table 3) indicates the applications of Ionic liquids nanocatalysts in ODS process.

Table 3. Ionic Liquids Nanocatalysts in ODS Process

Catalyst	Source of sulfur	Oxidizing agent	Reaction condition	Sulfur removal efficiency%	Ref.
$Fe_3O_4/APTES/IL$	DBT		T = 25 °C, t = min	90.3	(Poursaberi, 2013)
$ILBF_4-x\%TiCp_2-MSN$	DBT	H_2O_2	T = 60 °C, t = 6h	99.1	(Cruz, 2019)
nano-TiO ₂	Gasoline	O ₂	T = 25 °C, t = 10h	94.3	(Wang, 2019)
nano-TiO ₂	DBT	H_2O_2	T = 70 °C, t = 50s	100	(Li, 2016)
$[(C_8H_{17})_3NCH_3]_3PMo_{12}O_{40}/\gamma-MMS$	DBT	air	T = 120 °C, t = 5h	100	(Xun, 2019)

2.4. Transition Metal Oxide

The choice of heterogeneous catalyst for oxidative desulfurization has been considered due to its easy separation and good catalytic properties. One of the types of heterogeneous catalysts used in the oxidative desulfurization process is transition metal oxides (MTO₂). Catalysts such as molybdenum, vanadium, tungsten, zinc, cobalt, etc. These catalysts are based on materials such as alumina, silica, titanium oxide, etc. for stabilization and usability. One of the best cases in which the supports can be used is to use them in the nanostructure mode, because in this structure the support has the best performance and the catalyst is spread on it better (Haghighi, 2020).

Yao et al. used molybdenum oxide nanoparticles based on graphene-analogous boron nitride to remove DBT from oil by oxidative desulfurization. Due to the effect of particle size control and the interaction of catalyst particles with the support on improving aerobic oxidative desulfurization, the catalyst and the support are used as nanostructures. Using this catalyst and molecular oxygen as an oxidant under optimal conditions, DBT was

completely removed within 3 hours and the conversion reached 100% (Yao, 2018).

Chen et al. also used molybdenum oxide nanocatalysts for oxidative desulfurization of model oil. To stabilize the nanocatalysts, they fixed them on a mesoporous titanium phosphonates support. High specific surface area and high and uniform dispersion of molybdenum oxide on the support as well as more active sites and the coupling property between the support and the active component are the reasons for using the support in the nanostructured state. Using this catalyst at a temperature of 40 °C and a time of 30 minutes, the removal of sulfur compounds reaches 100% (Chen, 2021).

Zou et al. used vanadium pentoxide nanoparticles (V_2O_5 NP_s) for aerobic oxidation desulfurization. Using oxygen in the air as an oxidant and under optimal conditions: the temperature of 120 °C and the time of 4 hours conversion reached 99.7% (Zou, 2021).

Li et al. used pure nano-TiO₂ as catalyst for the oxidative desulfurization of simulated fuels

directly without UV irradiation and with H_2O_2 as an oxidant. The results showed that the nanocatalyst had very good properties and high catalytic activity, because the conversion rate was near to 100% after 50 seconds under optimal operating conditions; the molar ratios of H_2O_2 to sulfide as well as DBT to 4,6DMDBT were 10:1 and 15:1, respectively (Li, 2016).

Bazyari et al. studied ultra-deep desulfurization of model fuel oil with titania-silica nanocomposite catalysts. The effects of various parameters such as metal loading, reaction temperature and calcination temperature were investigated. The experimental results showed that loading the metal at 50% at high acidity caused the conversion rate of 98% in 20 minutes (Bazyari, 2016).

Lu et al. applied CeO_2/TiO_2 nanotubes for photocatalytic oxidative desulfurization of model oil. It was found that nearly 90% of the sulfur compounds in the model oil were photocatalytically oxidized and removed by the catalyst CeO_2/TiO_2 nanotube arrays in 5 hours (Lu, 2016).

Rezvani et al. also used a titanium oxide supported catalyst ((TBA) $4PW_{11}Fe@TiO_2@PVA$) for oxidative desulfurization of the fuel. Using this catalyst and $H_2O_2/HOAc$ as oxidant and

benzothiophene (BT) 96%, dibenzothiophene (DBT) 99%, 4-MDBT 97% and 4,6-DMDBT 98% were removed. Under optimal reaction conditions: at 60 °C and 2 hours, 97% of the sulfur compounds were removed (Rezvani, 2019).

Zhao et al. used copper phthalocyanine molecular sieve catalyst supported on HZSM-5 zeolite ($Cu_2(PcTN) 2/W-HZSM-5$) to desulfurize fuel oil. They examined the effect of reaction temperature, reaction time, and catalyst load. Under optimal reaction conditions: temperature 60 °C, time of 3 hours and catalyst loading of 0.1 g, conversion percentages reached 93.82%, 91.23%, 87.32% for TH, BT and DBT, respectively (Zhao, 2015).

Yang et al. used molybdenum supported on 4A molecular sieve catalyst ($MoO_3/4A$) to oxidative desulfurization of BT and DBT from n-octane. They used cyclohexanone peroxide (CYHPO) as an oxidant and examined the effect of the reaction parameters; molybdenum loading, reaction temperature, reaction time, the molar ratio of CYHPO/DBT and the weight of catalyst $MoO_3/4A$ and achieved 99% conversion rate under optimal conditions (Yang, 2016). (Table 4) summarized the conditions and removal efficiency of Transition metal oxide nanocatalysts in ODS process.

Table 4. Transition Metal Oxide Nanocatalysts in ODS Process

Catalyst	Source of sulfur	Oxidizing agent	Reaction condition	Sulfur removal efficiency%	Ref.
MoOxNPs/g-BN	DBT	O_2	T = Not specified, t = 3 h	100	(Yao, 2018)
5%Mo/TiO ₂ -350	DBT	TBHP	T = 40 °C, t = 30 min	100	(Chen, 2021)
V ₂ O ₅ NPs	Fuel oil	O_2	T = 120 °C, t = 4 h	99.7	(Zou, 2021)
TiO ₂ -SiO ₂	DBT	TBHP	T = 80 °C, t = 20 min	98	(Bazyari, 2016)
CeO ₂ /TiO ₂	Model oil	H_2O_2	T = Not specified, t = 5 h	90	(Lu, 2016)
(TBA) $4PW_{11}Fe@TiO_2@PVA$	Model oil	$H_2O_2/HOAc$	T = 60 °C, t = 2 h	97	(Rezvani, 2019)
$Cu_2(PcTN) 2/W-HZSM-5$	DBT	H_2O_2	T = 60 °C, t = 3 h	87.32	(Zhao, 2015)
$MoO_3/4A$	DBT	CYHPO	T = 100 °C, t = 30 min	99	(Yang, 2016)

2.5. Metal Organic Frameworks

Metal organic frameworks (MOFs) are a type of crystalline material that have been considered for their unique properties such as large internal surface area and high porosity. This material consists of the bonding of small metal ions, including metal, to several organic ligands, such as sulfoxalate, and carboxylate, via a coordination bond. One of the most important properties of MOFs is that the size and shape of the pores can be precisely controlled by selecting its components such as metals and organic binders and how they are connected to each other. Using this property, nanostructured catalysts can be produced from these materials (Soleimani, 2017).

Li et al. used POM@MOF-199@MCM-41 catalysts and molecular oxygen (O₂) as oxidants for oxidative desulfurization of the model fuel. POM and MOF-199 were used in the nanostructured state, which improved the catalyst synthesis. By examining different

reaction parameters: temperature, time and amount of catalyst, it was concluded that at a temperature of 85 °C and time of 180 minutes and the amount of catalyst 2 g / l, benzothiophene was removed up to 98.5% (Li, 2016).

GhahramaniNejad et al. used ZIF-8@{Mo₁₃₂} nano catalyst to remove DBT from model oil by oxidative desulfurization method. Using TBHP as an oxidant under optimal conditions: temperature of 80 °C and time 12 hours conversion of DBT reached 92% (Ghahramaninezhad, 2019).

Xu et al. synthesized a POM Co-MOF catalyst in Nano sheet structure using the top-down method. By comparing the performance of the nano sheets catalyst and the bulk state, it was found that the nanostructured state has a better performance for oxidative desulfurization. Using this nanostructured sheet catalyst, DBT in the model oil was completely removed in 60 minutes. (Table 5) shows the applications of Metal organic framework nanocatalysts in ODS process.

Table 5. Metal organic framework nanocatalysts in ODS process

Catalyst	Source of sulfur	Oxidizing agent	Reaction condition	Sulfur removal efficiency%	Ref.
POM@MOF-199@MCM-41	DBT	O ₂	T = 85 °C, t = 180 min	98.5	(Li, 2016)
ZIF-8@{Mo ₁₃₂ }	DBT	TBHP	T = 80 °C, t = 12 h	92	(Ghahramaninezhad, 2019)
[Co ₂ (H ₂ O) ₄ (BTX) ₃][PMo ₁₂ O ₄₀]	DBT	H ₂ O ₂	T = Not specified, t = 60 min	100	(Xu, 2018)

3. Conclusion

Hydrogen desulfurization is used as a well-known method in oil refineries. However, this method alone is not effective due to high operating conditions as well as high cost and inability to remove some sulfur compounds. One of the effective methods along with HDS method is oxidation desulfurization method (ODS). The oxidation method has received much attention due to its moderate operating

conditions as well as its selectivity in the removal of sulfur compounds. Various studies have been conducted on the factors affecting this method. One of the investigated factors is the effect of different nanostructured catalysts on this method. According to studies, titanium nanocatalysts have a significant effect on the removal of sulfur and have achieved a high conversion rate in a relatively short period of

time. Also, carbon nanotubes have achieved a 100% conversion rate in the removal of sulfur compounds due to their suitable structure and high surface area.

Acknowledgement

The authors would like to acknowledge the financial and instrumental supports from the University of Sistan and Baluchestan, Iran.

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Energy Optimization of the Sweetening Unit of Gachsaran Natural Gas Refinery by the Use of Vapor Recompression

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ARTICLE INFO

ORIGINAL RESEARCH ARTICLE

Article History:

Received: 25 August 2022

Revised: 28 October 2022

Accepted: 19 December 2022

Keywords:

Sour gas sweetening

Natural gas

Vapor Recompression Column

Energy optimization

ABSTRACT

Globally, Iran ranks 6th in natural gas production. Producing over 1 billion cubic feet of dry natural gas, the Gachsaran gas refinery is a major revenue source for the country. Tens of thousands of barrels are sent to the Bandar-e-Emam petrochemical plant every day, and the Gachsaran oil and gas refinery always aims to partially supply the feed for this petrochemical complex by sweetening sour natural gas feed containing some H_2S and CO_2 . Due to the high energy consumption of the sweetening unit, energy optimization of this process is significant. Vapor Recompression Column was used for optimizing sweetening process energy in the Gachsaran gas unit, and the distillation column's top vapor was compressed to transfer its thermal energy to the bottom. The results show that Vapor Recompression Column consumed about 75% less energy than the conventional process mostly due to warm and cold utility savings. The output pressure of the compressor added in this process was calculated accurately. If the compressor output pressure increases excessively, this method becomes inefficient and uneconomical.

DOR: [20.1001.1/JGT.2023.560313.1006](https://doi.org/10.1001.1/JGT.2023.560313.1006)

How to cite this article

M. Shahbahrami, T. Khansari, S. Pirayande, M. Gholizadeh, S. Najafi Barzegari, Energy Optimization of the Sweetening Unit of Gachsaran Natural Gas Refinery by the Use of Vapor Recompression. Journal of Gas Technology. 2022; 7(2): 35 -40. (https://jgt.irangi.org/article_706498.html)

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Available online 31 December 2022

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1. Introduction

Nowadays, natural gas has become an important resource around the world and is increasingly being used as an energy carrier. In the last 10 years, natural gas accounted for 22% of the world's energy consumption. After the United States, Saudi Arabia, Canada, the United Arab Emirates and Russia, Iran ranks 6th in the production of natural gas in thousands of barrels per day (Dale, 2022). Natural gases often have impurities such as hydrogen sulfide, carbon dioxide, water vapor, heavy hydrocarbons, and mercaptan. Natural gas with over 4 ppm of hydrogen sulfide gas is considered sour. H_2S and CO_2 are removed to prevent corrosion and increase the thermal value of gas. There are different way of separating acidic gases from gas mixtures, such as chemical absorption, physical absorption, and membrane processes. Regardless, chemical absorption with amino-based solvents is one of the best currently available technologies for simultaneously absorbing H_2S and CO_2 (Darani et al., 2021; Karthigaiselvan and Panda, 2021; Moghadasi et al., 2021). Nejat et al. studied the effect of mixing a chemical amino solvent with a physical solvent on gas sweetening energy requirements and observed 30 to 42% savings using methyl diethanolamine (MDEA) with a physical solvent such as sulfinol compared to the chemical amino system (Nejat et al., 2018). In a gas sweetening project, M.A. Al-Lagtah et al. proposed an energy-saving design by evaluating the divided ring and removing and returning some enriched amino to the absorber, reducing operational costs by 50% (Al-Lagtah et al., 2015). Al-Amri & Zahid proposed two sweetening AGR units instead of AGR-AGE and reduced energy consumption over the base method by 22% (Al-Amri and Zahid, 2020). Making improvements to natural gas sweetening energy efficiency very important.

Despite the numerous studies on natural gas sweetening, its excessive energy consumption is a major problem. Gachsaran refinery's

sweetening unit uses an absorption and a distillation column. The distillation column responsible for amin recovery consumes a great deal of energy, making process energy optimization a necessity. The thermal integration of gas sweetening has been studied extensively. Using the heat exchanger network (HEN), Othman et al. studied natural gas sweetening with the MDEA solvent and optimized energy by 62.6% (Othman et al., 2021). Using lean vapor compression (LVC), Al Hatmi et al. used the MDEA and MDEA-PZ solvents for natural gas sweetening in Oman oil field and reduced reboiler energy by 40-50% (Hatmi et al., 2018).

This study used the vapor recompression column (VRC) method for thermal integration of the solvent recovery column in the Gachsaran refinery. The vapor recompression method involves the steam that is released from the top of the tower entering the compressor, which causes a rise in the steam's pressure, temperature, and dew point. It is therefore conceivable to heat the bottom flow of the tower using a heat exchanger in this manner (Feng et al., 2017; Feng et al., 2020; Rix et al., 2023; Shrikhande et al., 2020). Since the VRC method allows for reducing or eliminating hot and cold utility, it could significantly reduce the energy consumption of the Gachsaran refinery sweetening unit. However, the VRC method uses a compressor that significantly affects energy consumption and total annual cost (TAC). To justify the process, the compressor's output pressure should be calculated accurately.

2. Case Study

Sour gas sweetening at Gachsaran unit was studied, and (Table 1) shows information about sour gas and amin.

Process Simulation: Aspen HYSYS V.10 was used for process simulation, and Modified HYSIM inside-out was used for accurately solving columns. The thermodynamic acid gas-chemical solvents package was used in gas sweetening.

In this process, first the sour gas and amine respectively enter the absorption column from

the bottom and the top to remove carbon dioxide and hydrogen sulfide from the top product. Then, the amine is transferred to the amine recovery unit and re-enters the process.

Table 1. Properties of Sour Gas and Amine in Gachsaran Natural Gas Refinery

a) Chemical composition of Sour Gas (%Mole fractions)										
H ₂ O	H ₂ S	CO ₂	Methane	Ethane	Propane	i-butane	n-butane	i-pantane:	n-pantane	n-hexane
0.0022	0.0082	0.0202	0.6913	0.1331	0.0872	0.0121	0.0282	0.0063	0.0064	0.0048

b) Chemical composition of Amine (%Mole fractions)	
H ₂ O	DEAmine
0.9305	0.0695

c) Sour Gas operating conditions		
Temperature (°C)	Pressure (kPa)	Molar Flow (kmol/h)
43.3	35500	6477.7

d) Amine operating conditions		
Temperature (°C)	Pressure (kPa)	Molar Flow (kmol/h)
60	6152	6477.7

2.1. Conventional Simulation

(Figure 1) shows the conventional simulation of the Gachsaran gas sweetening unit.

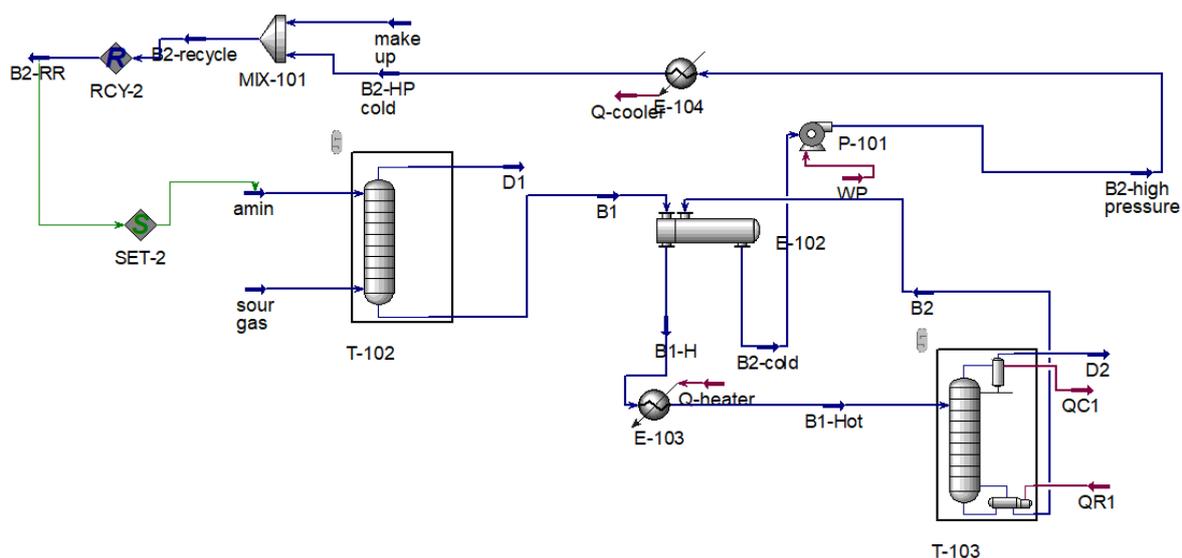


Figure 1. Simulation of conventional gas sweetening in Aspen Hysys

(Figure 1) shows the top amine flow and bottom sour gas flow in the absorption column. There are 30 trays, and the absorption tower's top and bottom pressure are respectively 3500 and 5100 kPa.

The combined carbon dioxide-hydrogen sulfide content in the absorption column's top product will be zero, and the bottom product will be transferred to the distillation column's recovery unit after reaching 100 °C. The

distillation column has 25 trays and 13 feed trays with 107.6 kPa of top pressure and 138 kPa of bottom pressure.

2.2. VRC Simulation

The vapor out of the top of the distillation column enters the compressor to increase

its pressure and temperature. Then, a heat exchanger provides the necessary heat for evaporating the distillation column's bottom liquid output.

(Figure 2) shows the natural gas sweetening simulation in the Gachsaran unit using the VRC method.

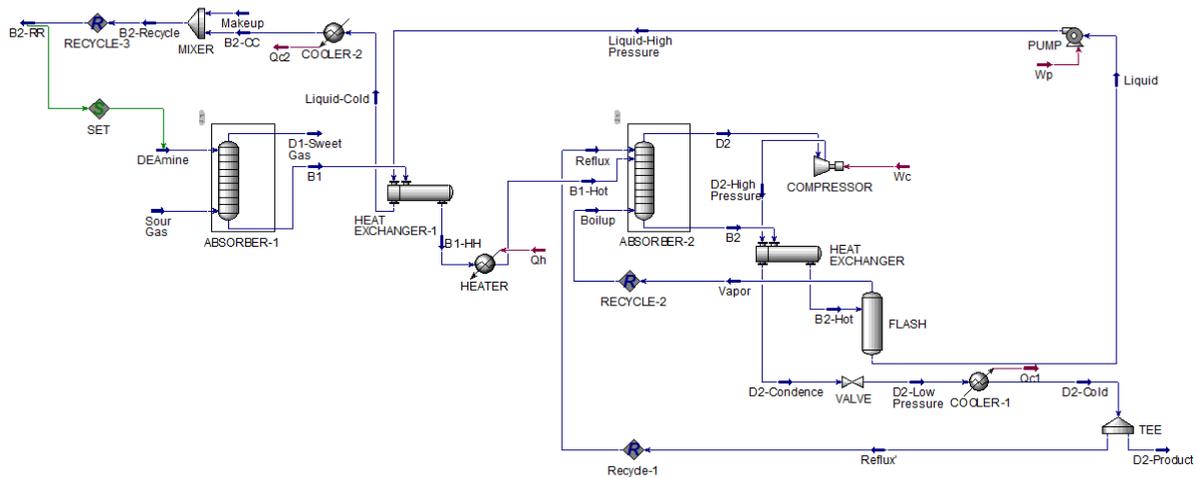


Figure 2. VRC sweetening simulation in Aspen Hysys

(Figure 2) shows that the feed first enters tray 13 of the distillation column. The column's top output vapor enters the compressor and is compressed up to 315 kPa, and the pressure increase raises flow temperature to 248.5 °C. This flow and the liquid from the bottom of the column enter a heat exchanger. After reaching the intended temperature and pressure, the heat exchanger's output flows are divided into two; one returns to the distillation column as the return flow, and the other is transferred to the heat exchanger to preheat the absorption column's bottom product for minimizing the cooler and heater's thermal load, which will significantly affect energy consumption.

3. Results and discussion

This study used VRC for natural gas sweetening in Gachsaran unit. Distillation tower energy consumption is obtained using Eq. 1.

$$Q = Q_R + Q_C \quad (1)$$

Where Q , Q_C , and Q_R respectively represent distillation column energy consumption, cold utility, and hot utility.

Since the VRC method also uses a compressor, the distillation column's energy consumption is calculated using Eq. 2.

$$\bar{Q} = Q_R + Q_C + 3W_C \quad (2)$$

Where \bar{Q} , Q_C , Q_R , and W_C respectively represent column energy consumption, cold utility, hot utility, compressor work consumption. The VRC method is utilized to increase the hot utility from 71234.535 MW to 1.259 MW and the cold utility from 71228.23 MW to 7898.8285 MW in comparison to the conventional method, Which this work has been done to lower the heat load of the condenser and reboiler of the column. Eliminating the condenser and reboiler of the distillation column have been able to save 99% of the energy that is used in the hot

utility and 88.91% of the energy that is used in the cold utility.

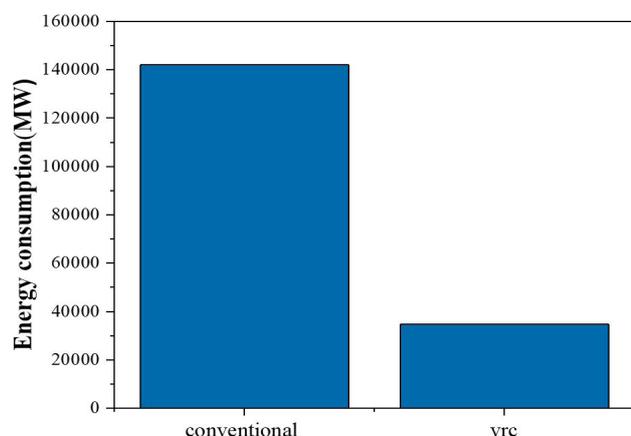


Figure 3. Compares the energy consumption of the conventional and VRC gas sweetening processes

Despite using a compressor, the VRC method significantly reduces energy consumption.

4. Conclusion

Globally, Iran ranks 6th in natural gas production. Producing over 1 billion cubic feet of dry natural gas, the Gachsaran gas refinery is a major revenue source for the country.

The natural gas sweetening unit of Gachsaran refinery has a distillation and an absorption column. Using the diethanolamine solvent, the absorption column completely eliminates H₂S and CO₂ from natural gas, and the distillation column fully recovers the used solvent. However, Gachsaran gas refinery's sweetening unit, especially its distillation column, consumes a great deal of energy. To reduce energy consumption, the distillation column's hot and cold utility requirement should be reduced. The conventional unit of the Gachsaran gas refinery has been simulated. In this simulation, the hot and cold utilities were estimated to be approximately 71234.535 MW and 71228.23 MW, respectively; therefore, the VRC method was used for reducing the distillation column's energy consumption. The hot utility and cold

utility have decreased by about 99% and 88.91% respectively by the VRC method. Despite using a compressor, VRC reduced energy consumption by 75% compared to the conventional method mostly due to the significant reduction in hot and cold utility. The output pressure of the compressor added in this process was calculated accurately. If the compressor output pressure increases excessively, this method becomes inefficient and uneconomical.

Nomenclature

<i>HEN</i>	Heat exchanger network
<i>LVC</i>	Lean vapor compression
<i>MDEA</i>	Methyl diethanolamine
<i>TAC</i>	Total annual cost
<i>VRC</i>	Vapor recompression column

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JOURNAL OF GAS TECHNOLOGY

Volume 7 / Issue 2 / Winter 2022 / Pages 41-62

Journal Homepage: <http://jgt.irangi.org>

Assessment of Unconventional Natural Gas Resources

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ARTICLE INFO

REVIEW ARTICLE

Article History:

Received: 14 September 2022

Revised: 5 October 2022

Accepted: 19 December 2022

Keywords:Unconventional gas
Shale gas, Tight gas
Coalbed methane
Gas hydrate

ABSTRACT

In the 21st century, the petrochemical industry has experienced a significant increase in oil and gas consumption due to the growing global population and energy demand. Among nonrenewable resources, natural gas stands out as the cleanest option, making it an essential resource for the energy industry in comparison to other hydrocarbons. Unconventional gas, including shale gas, tight gas, coalbed methane, and gas hydrate, has emerged as a substantial hydrocarbon resource. This study aims to explore the environmental impacts, geological features, obstacles, and technical challenges associated with the exploitation of unconventional gas reservoirs, encompassing aspects such as energy demand, consumption and production, water pollution, greenhouse gas emissions, and reservoir geology properties. The paper also reviews the various approaches to developing unconventional gas in different countries, with a particular focus on the United States. The findings indicate that the feasible development of unconventional gas is indeed possible in different countries. However, the future outlook for this resource will heavily rely on several factors, including addressing environmental concerns, investment in renewable energy, and the state of global gas markets.

DOR: [20.1001.1/JGT.2023.2000565.1026](https://doi.org/10.1001.1/JGT.2023.2000565.1026)**How to cite this article**S. Sahraei, Assessment of Unconventional Natural Gas Resources. Journal of Gas Technology. 2022; 7(2): 41 -62.
(https://jgt.irangi.org/article_707479.html)

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Available online 31 December 2022

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1. Introduction

The world has been concerned about global energy demand since World War II, when sharply rising oil prices led to global recessions and high inflation in the last quarter of the 20th century (Brown et al., 2013). In recent years, due to environmental pollution, climate change and rapid developments in technology, the energy industry tends to consume and fossil invest in low-carbon fuels (natural gas resources) and renewable energies. Although there has been significant development and investment in renewable energy in the last decade. But the fossil fuels play a fundamental role in the future. However, the world has seen rapid growth in energy demand and unconventional oil and gas are considered as indispensable bridge fuel that will allow society to continue to use new resources of fossil fuels instead of conventional oil and gas (Islam et al., 2020). There is large volume of unconventional gas resources in different countries and these have been known for a long time. Unconventional gas resources are contained large accumulations of gas with low production rates (20 Mcf/d to 500 Mcf/d), trapped in low permeability formations with diffuse boundaries and no well-defined hydrocarbon-water contacts (Conti et al., 2016; Sahraei et al., 2022).

The category of unconventional gas comprises of various types of gas, including shale gas, tight gas, coalbed methane (CBM), and hydrates. Shale gas is usually in shale, mudstone, siltstone, and fine-grained sandstone. Tight gas often has been stored in tight sandstone or sometimes limestone. Coalbed methane is typically adsorbed onto the surface of coal seams, while gas hydrates are commonly found in deep water and Arctic regions. Shale, is the main sources of gas all over the world, tight gas is just sandstone gas which cannot easily flow toward existing wells, Coal Bed Methane is a form of natural gas found in coal deposits

with low permeability and gas hydrate is a solid clathrate that contains a significant amount of methane under seafloors. Their common characteristic is the very low permeability and the permeability mostly has been improved by artificial (hydraulic fracturing (HF)) or natural fractures (Jin et al., 2022; Su et al., 2020).

In the last decade, the production of unconventional gas reservoirs has enabled a new era of economic advantages (economically competitive over the past several years), moderate greenhouse gas emissions (fewer CO₂ emissions per generated energy unit than coal and oil) and altering geopolitics and energy policy at international levels (Hultman et al., 2011). Moreover, new technologies such as horizontal drilling technology, multistage HF, has led to production from shale gas, tight gas and coalbed methane reservoirs, but hydrate gas has not yet been produced commercially (Hancock et al., 2019; Wang et al., 2021). In the future, the extraction of gas hydrates in seafloors potentially lead to a significant increase in natural gas reserves. Economically recoverable gas hydrate deposits may contain an energy content comparable to that of the estimated total conventional gas resource (Wallmann et al., 2020). Unconventional gas resources already have been developed economically in some places. Economically unrecoverable resources may become recoverable, as soon as their production technology becomes less expensive or the characteristics of the market are such that companies guarantee the return of their investment. In order to economically exploit gas from such reservoirs, the development of HF in the heterogeneous porous media under such complicated conditions should be expanded (Tian et al., 2022).

Due to environmental concerns and the high production costs associated with unconventional natural gas (UNG), there are relatively low expectations for UNG production in Europe. In fact, France, Bulgaria, the Czech

Republic have been temporarily banned from unconventional gas development. These rules are related to environmental risks and energy market restriction. There is uncertainty about the export potential of European gas when the Middle East conventional resources are more quickly accessible (Janda et al., 2018; Holz et al., 2015).

Technological advancements and increasing gas prices are expected to rapid in the growth of unconventional gas production in the United States (US), and this trend is expected to expand worldwide. Sustainable development of shale gas resources is already underway in several regions of North America, such as Texas, Oklahoma, Louisiana, Pennsylvania, among others (Soeder, 2018; Mei et al., 2022). As gas demand increases and crude oil price rises, the substantial question for researchers is whether UNG can be developed with appropriate approach with minimal impact on groundwater and climate. After a background of unconventional gas resources, this review focuses on the technical and environmental assessment of unconventional gas development. We studied and briefly summarize various aspect of UNG development. The result indicates the increase in natural gas consumption can be compensated by UNG resources, but this market development will depend on the supply and demand, which will be influenced by environmental policies and renewable energy investment.

2. Definitional issues

2.1. Natural gas reservoirs

Natural gas is the cleanest burning fossil fuel and emits significantly less carbon dioxide, particle pollution, sulfur, and nitrogen oxide than other hydrocarbons. Natural gas resources are generally classified as conventional and unconventional reservoirs. The difference between conventional and unconventional natural gas is not only based on gas composition but also on the deposit geology characteristics,

well drilling and well completion. In terms of geology structure, the main distinguishing feature of unconventional oil and gas rocks is their pore sizes and reservoir traps (Fangzheng, 2019; Nia et al., 2016). Conventional resources occur in a discrete reservoir with discrete traps by the cap rocks, in contrast, unconventional resources are distributed continuously in basin slopes or centers with no obvious trap boundary (Chengzao et al., 2021). The "continuous type hydrocarbon accumulation" theory proposed by Schmoker et al. in 1995 was a milestone of petroleum geology (Zou et al., 2018). Unconventional gas includes shale gas, tight gas, coalbed methane, and gas hydrates (Figure 1) (Capuano, 2018).

2.2. Coalbed methane

Coalbed methane is a type of unconventional natural gas that is typically found in coal mines. CBM resources are naturally fractured and contain a significant amount of methane as well as other hydrocarbons. Methane is primarily trapped within the micropores of the coal matrix and secondarily in fractures and cleats. Unlike conventional gas deposits where free gas is accumulated in the pores of the formation, CBM can contain significant amounts of methane that is adsorbed in nanoscale pores (Miao et al., 2018; Jia et al., 2021). CBM is typically stored in the pores, cleats, and fractures of the coal as follows:

- ✓ Micropores containing a large volume of methane in a dissolved state
- ✓ Macropores having free and dissolved gas in water.
- ✓ Cleats and open fractures having a fraction of water and gas volumes

Most of the coalbeds contain significant amounts of water. The pressure from this water keeps the methane in place. In order to produce methane from CBM, the water trapped in cleats and fractures of reservoir rock should

be removed which can lower the pressure, and the methane easily flows up to the well. The process of dewatering of the formation from the coal surface may continue for several months before economic gas production can be achieved (Mohamed et al., 2020; Satter et al., 2015). In the case of US-based operations, each well is estimated to produce between 1.7 to 14.3 million liters of flowback and produced water. The majority of this water, ranging from 92% to 96%, consists of naturally occurring brines. The remaining 4% to 8% of the produced water is made up of the injected hydraulic fracturing fluids that are returned to the surface (Willems et al., 2022). In North America, flowback-produced waters can be introduced into surface water environments through authorized discharges permitted under the National Pollutant

Discharge Elimination System (NPDES), as well as through accidental spills and leaks. On the other hand, in Australia, where coal bed methane production remains prevalent in the natural gas industry, approximately 80% of flowback-produced water from coal bed methane is effectively and beneficially reused within the agricultural sector or through reinjection into underground water reservoirs (Willems et al., 2023).

CBM resources is found in shallow depth of less than 1000 meters, while tight/shale gas is exploited at a depth of about 3500 meters. Both tight gas and shale gas are produced faster, while CBM is produced at lower speed. However, the reduction rate for shale/tight gas is faster, between 70-90% during first year exploitation (Dadwal, 2012).

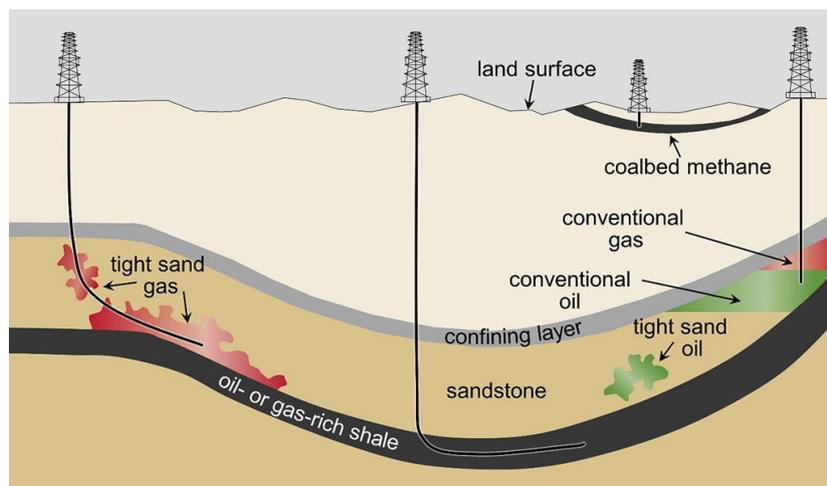


Figure 1 schematic of onshore oil and gas resources (Capuano, 2018).

2.3. Shale and tight gas

Shale gas or tight gas refers to UNG trapped in fine grained low-permeability sedimentary rocks (usually below 0.1 mD), impermeable (tight) sandstone, siltstones, limestones or dolomite. Shale gas can be generated from the thermogenic or biogenic process. Biogenic natural gases are produced through the anaerobic biodegradation of organic matter, while thermogenic natural gases form as a result of the thermal decomposition of organic matter under high pressure and depth (Vinson

et al., 2017; Milkov et al., 2020). Tight gas is a gas accumulated in relatively very low porosity and impermeable rock pores of limestone or sandstone, rather than shale formations. Shale gas is a type of natural gas that is trapped in fine-grained sedimentary rock formations. Its production typically requires HF technology. In contrast, tight gas sandstones act only as reservoirs. Coalbeds and shales, on the other hand, can serve both as a source rock and as a gas reservoir (McGlade et al., 2013; Rutter et al., 2022).

Effective porosity, permeability, pore size diameter, and the capillary pressure are some of the parameters controlling the fluid properties of a reservoir. (Table 1) shows reservoirs properties of unconventional and conventional gas resources. According to (table 1), the geological properties of conventional gas are more suitable, with porosity of 15%-30%, permeability of 10-1000 mD, pore size diameter higher than 2000 nm, and recovery efficiency of 50%-80%. In contrast, properties of unconventional reservoirs are poorer, especially in case of shale gas reservoirs. Typical coal porosity ranges from 0.5% to 5%, with 1-2% being the most common for current coals with commercial production. Shale and tight porosity are estimated to be under 10%. The hydrate gas sedimentary rock porosity is generally of < 30%, permeability of <100 mD and total organic carbon (TOC) of 0.5-2 wt. %. (Aminian et al., 2014). Permeability mainly controlled by pore-throat size. Pore-throat sizes are generally greater than 2000 nm in conventional reservoir rocks, range from about 20 to 700 nm in tight-gas, and range from 5 to 600 nm in shales, about 100 nm in hydrates and below 1000 nm in coalbed methane (Nelson et al., 2018). The porosity is directly associated

with the TOC of the unconventional resources. The TOC content of reservoirs can range from as low as 0.5% in organic shale to as high as 90% in coal. Shales with TOC contents below 6% are the most common, accounting for roughly 74% of total resources (Mahmood et al., 2018; Wang et al., 2018).

The primary difference between unconventional and conventional gas resources lies in the forces that drive their accumulation. Conventional gas resources accumulate due to buoyancy, typically in structural or stratigraphic traps. There are abundant micro-nano pores in unconventional gas resources which caused strong capillary displacement forces in reservoirs. Therefore, buoyancy forces cannot dominate gas capillary pressure and thus cannot be the principal driving force for gas exploitation. In addition to the factors associated with the fluid properties, the rock parameters are also important. These are controlled by depositional environment of reservoir basin (Jiang et al., 2015; Song et al., 2015). (Table 2) indicate the most important field or basin in China and US. As mentioned before, unconventional gas has different lithology and reservoir condition compare to conventional reservoirs.

Table 1. Properties of unconventional gas reservoirs (Zou et al., 2018; Aminian et al., 2014; Wang et al., 2018; Yin et al., 2017)

	Gas storage	Porosity (%)	Permeability (mD)	Pore diameter (nm)	Geological rock	TOC (Wt. %)	Development technique	Ref.
Conventional	Free gas	15-30	10-1000	> 2000	Sandstone, limestone, dolomite	--	Vertical drilling, EOR	50-80
Coalbed	Mainly adsorbed gas	0.5-5	< 0.1	< 1000	Coal formation	Up to 90%	Horizontal drilling, HF	20-30
Methane	Mainly free gas	< 10	< 0.1	20-700	Sandstones Limestones	< 20	Horizontal drilling, HF	20-50
Tight gas	Free and absorbed gas	< 10	< 0.1	5-600	Sandstone, limestone	0.5-25	Horizontal drilling, HF	20-40
Shale gas	Crystalline compounds	< 30	< 100	~ 100	Sandstone, Siltstone	0.5-2	Horizontal drilling, In Situ thermal treatment	50-80

Table 2. Top unconventional gas resources (Jin et al., 2022; Satter et al., 2015; Wang et al., 2018; Jiang et al., 2018; Kamali et al., 2012; Liang et al., 2014; Hu et al., 2017; Yoon et al., 2018; Kamari et al., 2018; Karthikeyan et al., 2018))

Country	Field or Basin	Reservoir type	Lithology	Recoverable gas content ($\times 10^8$ m ³)	Formation properties			
					Area (km ²)	Depth (ft)	Average Porosity (%)	Average Permeability (nD)
U.S.	Barnett	Shale gas	Siliceous Mudstone	14100	7500	5000-8000	6	150
U.S.	Haynesville	Shale gas	Argillaceous Calcareous	71075	23300	10000-14500	6	658
U.S.	Horn River	Shale gas	Brittle Shale	13300	12950	6600-13000	3	230
U.S.	Eagle Ford	Shale gas	Bituminous Shales	2550	3500	4500-14000	11	1100
U.S.	Marcellus	Shale gas	Argillaceous Mudstone	74000	180000	5000-9000	10	600
U.S.	Bakken	Shale gas	Sandstone Siltstone Carbonite	27000	518000	5000-12000	5	20
U.S.	San Juan	Shale gas	Coal	3679	4144	2000-3000	8	200
U.S.	Uinta	Coalbed methane	Sandstone	4740	37500	1000-7000	8.7	95
China	Ordos	Shale and Tight gas	Sandstone Dolomite	30000	9167	6560-16400	6.7	604
China	Sichuan	Shale and Tight gas	Shale Dolomite	20000-30000	230000	6560-17000	5.7	351
China	Songliao	Shale and Tight gas	Sandstone	1046	285	7200-11500	5	224
China	Turpan-Hami	Shale and Tight gas	Sandstone	Not found	35000	9800-12000	9.1	106
China	Junggar	Shale and Tight gas	Dolomite Siltstone	8800-12100	130000	13800-15700	6.5	125

2.4. Gas hydrate

Gas hydrate is a compound including of a lattice of host molecules (water) that enclose various sized gas molecules such as methane, nitrogen, and carbon dioxide without chemical bonding. Methane is typically the most abundant guest molecule found in gas hydrate resources. Gas hydrates have a volumetric conversion factor that can vary between approximately 160 to 180, meaning that they can hold significantly more gas than an equivalent reservoir volume of free methane (Gabitto et al., 2010). Gas hydrate formation is controlled by factors such as temperature, pressure and reservoir rocks. Under low-temperature and high-pressure conditions, gas hydrate is not stable and these

conditions are not available in most basins. These conditions predominantly occur in continental slope sediment roughly between 4000 to 6000 ft under surface (depending on local conditions) (Hancock et al., 2019). Gas hydrate can be either thermogenic or biogenic gas. Biogenic hydrates predominate in depths >1000 meters, while thermogenic hydrates have been located in the 400-to-800-meter depth range with only a few sites such as in the Gulf of Mexico, Cascadia, and in the Caspian Sea (Zhang et al., 2019; Koh et al., 2007).

The gas clathrate forms differently shaped lattice to accumulate gas molecules. Clathrate hydrates typically exhibit one of three distinct

structures: the body-centered cubic lattice structure I (sl), the diamond lattice structure II (sII), and the hexagonal lattice structure (sH). In each structure, water molecules arrange in unique patterns to create cavities of varying diameters, which are held together by hydrogen bonds and Van der Waals forces between the gas and water molecules. Most gas hydrates adopt the sl structure and have been identified in various locations, including the Gulf of Mexico, Ulleung Basin, and the South China Sea. In contrast, thermogenic hydrate sediments that form sII and sH structures can exist under milder conditions and have been found in several deposits, such as those in the Gulf of Mexico and Caspian Sea (Chong et al., 2016; Bavoh et al., 2020).

3. Unconventional Gas around the World

According to recent assessments, the total proven unconventional oil and gas reservoirs (excluding hydrates) around the world are estimated to be 5833.5×10^8 t, with unconventional oil resources accounting for 4209.4×10^8 t. The assessment also estimates that the global recoverable unconventional gas resources are approximately $227 \times 10^{12} \text{m}^3$, with tight gas and shale gas accounting for $161 \times 10^{12} \text{m}^3$ and coalbed methane accounting for $49 \times 10^{12} \text{m}^3$ see (Figure 2). (Figure 2) shows the

distribution of technically recoverable global gas resources around the world, with shale and tight gas primarily concentrated in North America, Central Asia, and the Asia-Pacific region, and coalbed methane mainly produced in Canada, the US, Australia, and China. Gas hydrate, on the other hand, is found in continental margins and polar regions and is estimated to be 300 times more abundant than the gas in the remaining recoverable conventional reserves in the United States (Tong et al., 2018; Jianchao et al., 2018).

The global unconventional oil and gas resources are distributed mainly in 363 basins in 60 countries. Recoverable unconventional gas reservoirs mainly concentrate in 106 basins in 37 countries, the top countries include the US, Iran, Canada, China, Russia, Australia, Saudi Arabia, Brazil, Argentina and Libya, with 76.8% of the global resources. While some countries are actively pursuing the production and exploitation of their unconventional gas reserves, others are still in the process of exploring and developing these resources. Some countries have yet to make a decision about developing their unconventional resources, either because their unconventional gas reserves are relatively small or because their conventional gas reservoirs are much larger (Tong et al., 2018; Cooper et al., 2016).

Unconventional gas, a global phenomenon

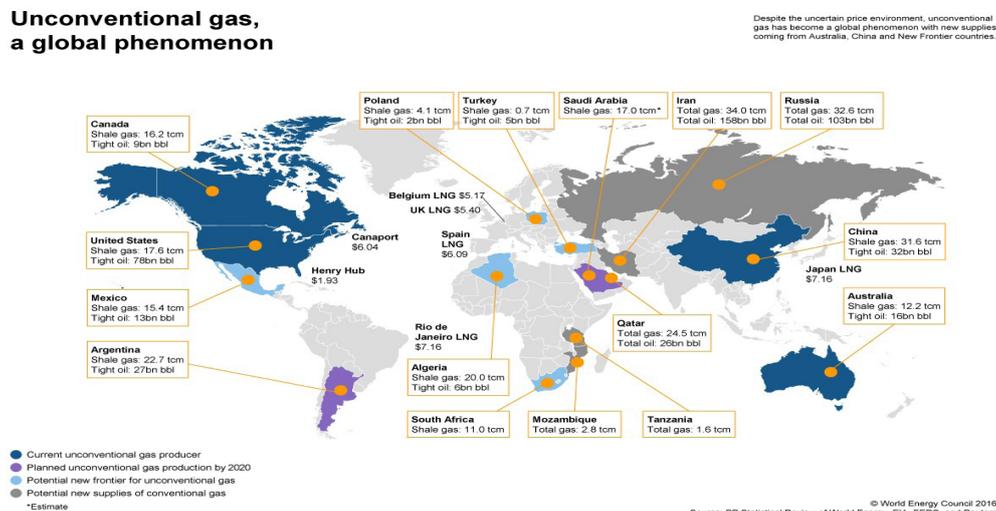


Figure 2. technically recoverable global conventional and unconventional gas resources (source: BP statistical review of world energy, EIA, FERC and Reuters)

According to estimates, the US has approximately $39 \times 10^{12} \text{m}^3$ of recoverable gas resources, accounting for 17.4% of the global total. The majority of these resources are shale gas. China has an estimated $31 \times 10^{12} \text{m}^3$ of recoverable gas resources, accounting for 13.9% of the global total. These resources are largely comprised of shale gas, coalbed methane, and tight gas. Russia has an estimated $29 \times 10^{12} \text{m}^3$ of recoverable gas resources, accounting for 12.6% of the global total, with shale gas and coalbed methane being the primary sources. Canada has an estimated $16 \times 10^{12} \text{m}^3$ of recoverable gas resources, accounting for 7% of the global total, with coalbed methane and shale gas being the primary sources (Hongjun et al., 2016). In the European Union, countries such as Poland and France have estimated technically recoverable shale resources of 4.19 billion and 3.87 billion, respectively. Other countries with predicted technically recoverable shale gas resources include Romania ($1.44 \times 10^9 \text{m}^3$), Denmark ($900 \times 10^6 \text{m}^3$), the United Kingdom and the Netherlands ($730 \times 10^6 \text{m}^3$ each), as well as Germany and Bulgaria ($481 \times 10^6 \text{m}^3$ each) (Reins, 2014).

4. World Production and Consumption

Over the past decade, advanced HF, directional drilling and related technologies significantly enable the production of oil and natural gas, particularly from unconventional oil and gas resources. Aguilera et al assessed the supply curves of CvNG and UNG (excluding gas hydrates) for the global gas markets. Based on their estimates, there is currently sufficient natural gas reserves to meet global energy demands for almost 400 years at current consumption rates. If production were to increase at a rate of 2% per year, these reserves would last for around 110 years (Aguilera et al., 2014).

Global unconventional gas production in 2015 reached $8227 \times 10^8 \text{m}^3$, accounting for 23%

of total gas production. Tight gas was the first unconventional deposits that has been developed economically. The Cauthage field in the US produced daily gas of $340 \times 10^4 \text{m}^3$ in 1955 and became the US's largest tight gas reserves in 1976. The US tight gas production was more than $600 \times 10^8 \text{m}^3$ in 1998 and $1200 \times 10^8 \text{m}^3$ in 2015 (Chengzao, 2017). According to a study by Jia et al., the unconventional gas industry has experienced rapid growth. Based on predictions, coalbed methane production is expected to remain at $136 \times 10^9 \text{m}^3$ in 2035, while unconventional natural gas production is projected to increase to $115 \times 10^9 \text{m}^3$. In addition, an estimated $9 \times 10^9 \text{m}^3$ of dissolved gas is expected to contribute to a total domestic natural gas production of $260 \times 10^9 \text{m}^3$ (Jia et al., 2021). In 2019, shale oil production in the United States represented a significant portion, accounting for 63.3% of the total oil production within the country. Looking at global reserves, in 2020, China had proved unconventional oil and gas reserves of 350 million tons, while the world's total proved unconventional reserves amounted to 5.45 billion tons of oil equivalent. These reserves contributed to more than 50% of the newly added global reserves during that period (Jia et al., 2023). Between 2009 and 2019, the United States saw a significant increase in the annual production of shale gas and tight oil (including shale oil). Specifically, shale gas production increased from 1.4×10^{11} to $7.2 \times 10^{11} \text{m}^3$, while tight oil production increased from 3.2×10^7 to 3.9×10^8 tons. Outside of North America, China has become a major player in the exploitation of unconventional petroleum resources. In 2020, China's annual production of shale gas exceeded $2 \times 10^{10} \text{m}^3$, while tight gas and tight oil production reached over $4.5 \times 10^{10} \text{m}^3$ and 3×10^6 tons, respectively (Zou et al., 2022).

(Table 3) shows natural gas consumption and projection of world in future. The results indicate that the US and Russia were the largest gas consumers in 2016 by using 75 Bcf/D and 38 Bcf/D respectively. In the future, global gas

consumption by 33% between 2016 and 2040. It will reach 502 Bcf/D. All of the growth in energy consumption comes from developing economies and population growth. China, India and other emerging Asia are expected to consume half of the natural gas demand by 2040. Among the different countries, China will have the largest growth in global gas

consumption. Chengzao et al. have developed a predictive model for estimating the potential of tight gas resources in China. According to their model, the geological resources of tight gas in China are estimated to range from 17.4×10^{12} to 25.1×10^{12} m³, with an estimated extractable resource of 8.8×10^{12} to 12.1×10^{12} m³ (Chengzao et al., 2012).

Table 3. World gas consumption and projection in future, 1990-2040 (Global BP, 2017).

Year	1990	1995	2000	2005	2010	2016	2020	2025	2030	2035	2040
Billion Cubic feet per day											
North America	62	72	77	76	82	93	102	109	114	120	126
US	53	61	64	60	66	75	81	85	89	93	97
S. & Cent. America	6	7	9	12	15	17	18	20	23	26	29
Brazil	0	0	1	2	3	4	4	6	7	8	8
Europe	33	38	45	51	53	47	49	51	51	51	50
EU	32	36	43	48	48	41	43	44	44	44	42
CIS	61	51	50	54	55	53	55	56	55	55	53
Russia	39	35	35	38	40	38	41	41	40	40	38
Middle East	9	14	18	27	38	49	54	62	68	74	80
Africa	4	5	6	8	10	13	15	19	22	27	33
Asia Pacific	15	20	28	39	55	70	84	97	109	120	131
China	2	2	2	5	11	20	31	39	46	53	60
India	1	2	3	3	6	5	6	8	10	11	14
Other Asia	5	8	12	18	21	25	28	31	33	35	38
World	189	206	233	268	308	342	377	413	444	474	502
OECD	102	118	133	140	152	160	170	179	185	192	195
Non-OECD	87	88	101	128	157	182	207	234	259	282	307

(Figure 3) shows the global consumption of primary energy resources in terms of Million's toe and their ratio in percentage. As the results indicate different countries would have to invest more in renewable energy and natural gas by the year 2040. Renewable energy will account for 40% of energy consumption, while Natural gas grows much faster than oil or coal and the share of natural gas consumption will be 26%. Coal consumption will decrease in the next 10 years. However, China remains the world's largest coal market, accounting for 40% of global demand in 2040. The share of coal energy declining from about a third today to less than a quarter in 2040. In contrast, renewable energy, together

with nuclear and hydro, account for more than 80% of China's energy demand by 2040 (Global BP, 2017).

The first economically CBM well was drilled in the Appalachian basin in the early 1980s. For over a decade, CBM has been extracted from various coal basins in North America, including the San Juan and Powder River basins. Currently, CBM accounts for approximately 10% of total US gas production, with the majority of production coming from the Black Warrior basin, San Juan in Colorado, and the Powder River basin. In 2016, CBM production in the US amounted to roughly 4% of the country's total natural gas consumption (Joshi et al., 2022).

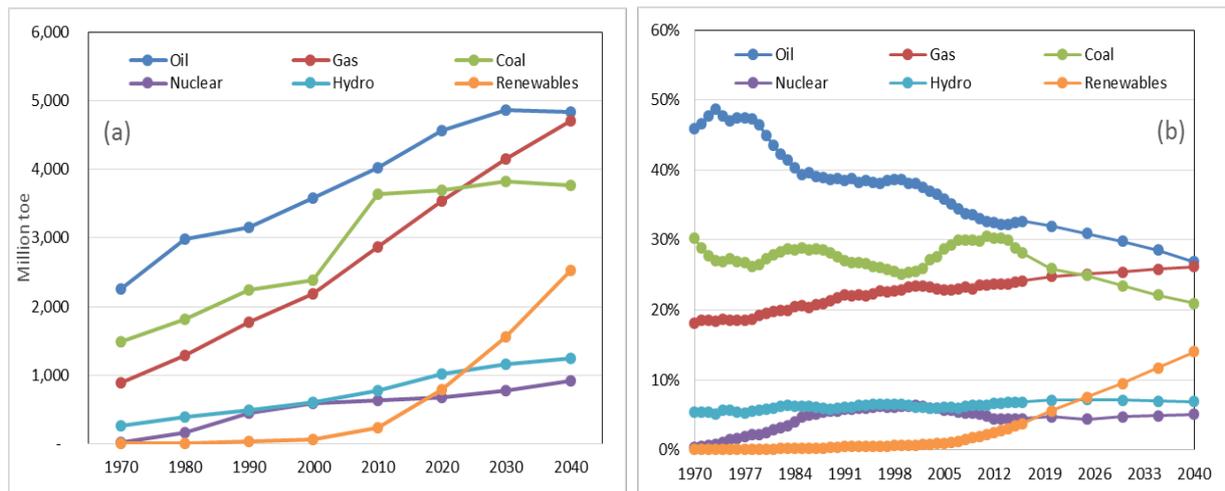


Figure 3. Estimate of global natural gas consumption, (a) Mtoe, (b) percent (Global BP, 2017).

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According to projections, US energy production is expected to increase by approximately 31% from 2017 through 2050, due to increases in the production of renewables, natural gas, and crude oil. However, it should be noted that crude oil production is expected to increase only during the first 15 years of the projection period. Natural gas production accounts for nearly 39% of U.S. energy production. Unconventional resources play a substantial share of total U.S. natural gas production because of the shale gas resources. However, by using more in transportation, electricity generation and petrochemical industry, the total growth in gas demand may be much faster than expected by EIA. It is expected that the global unconventional oil and gas yield reached more than 20% of the total production by 2030. While shale gas exploration is being

conducted in many countries around the world, commercial production from shale reservoirs is currently limited to only four countries: the United States, Canada, China, and Argentina. Shale gas production in the US began in 2007 and has been ongoing since then (Solarin et al., 2020). (Figure 4(a)) shows several U.S. shales deposits have been developed in gas production. Over the past 10 years, Barnett is the most productive gas field in Texas due to annual production and is growing at an annual rate of more than 10%. Exploitation of the Marcellus formation in the United States led to an increase in gas production starting in 2004. In 2011, further increases in gas production were observed due to exploitation of the Cretaceous Eagle Ford Formation and the Jurassic Haynesville Shale (Solarin et al., 2020; Kirat, 2021). According to a report by the Energy Information Administration (Capuano, 2018), the United States has been the leading global producer of natural gas since 2009, when its production surpassed that of Russia. The report states that the US currently produces approximately 20% of the world's total supply, with around 40% of this production coming from shale gas fields. Notably, the US is the only country in the world that has engaged in shale gas production (Figure 4(b)). The report also projects that shale gas exploitation will grow by over 113% by 2043, and is expected to make up 79% of US natural gas production.

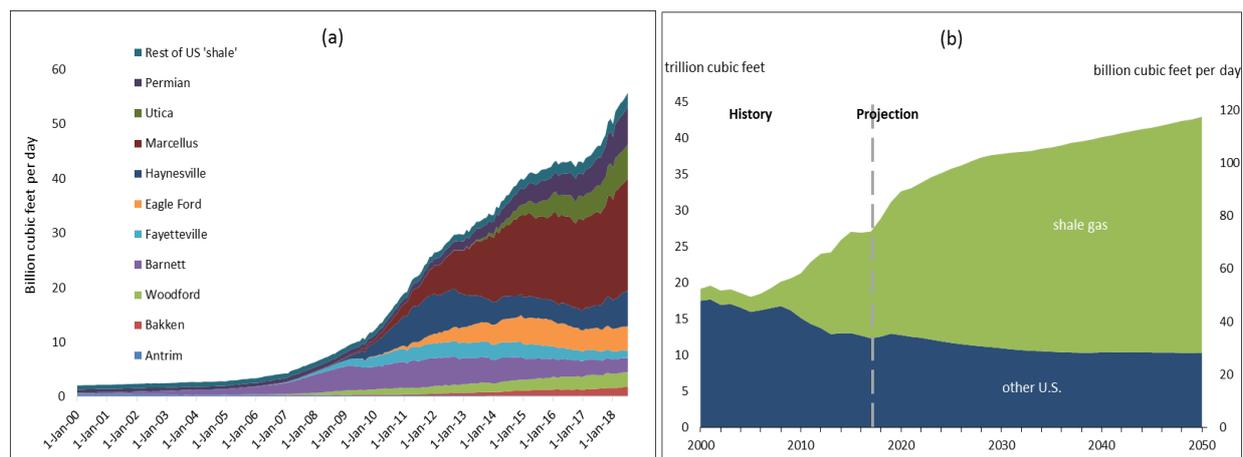


Figure 4. (a) U.S. dry natural gas production history and projection between 2000-2050 years (b) production of shale gas (Capuano, 2018).

The U.S. program has two plans, focusing on both the North Slope of Alaska and the Gulf of Mexico. Japan, India and the South Korean have expanded their gas hydrate program focusing on Nankai area, Ulleung Basin by using the drillship since 2010 respectively. The goal is to explore an appropriate site for a future production test. There are also gas hydrate development programs in Brazil, Colombia, Iran, Mexico, South Africa, and Uruguay. As U.S. achieves economical exploitation over the next years, it seems that other nations will begin programs to evaluate the gas hydrate resource potential (Yu et al., 2021; Chong et al., 2017).

5. Challenges Ahead

5.1. Potential risks to ecosystem health

UNG development includes several steps such as (1) well pad and infrastructure construction; (2) pipelines related to drilling and other facilities; (3) HF; (4) flow back of fracturing fluid which contains gas and fluid formation; (5) subsequent connection of production unit to the distribution system (Adgate et al., 2014). Each part of this process has potential of adverse effects, including significant sources of contamination for surface and ground water, producing more greenhouse gases, particulate air pollution, increased frequency of earthquakes, and harmful association with

humans or livestock farming health (Deziel et al., 2022). In general, comprehensive environmental impact assessment and associated assumptions of unconventional gas production requires four steps. (1) Water resources, (2) air quality and climate change, (3) public health, (4) socioeconomic and community effects. Therefore, it could be argued that unconventional gas production poses public debate on the balance between the economic benefits of extraction of oil and gas and the associated environmental and health risks (Orak et al., 2021; Vengosh et al., 2017). However, unconventional gas development is controversial because of various sustainability problems related to its development and distribution.

Natural gas is predominantly composed of methane, which is a potential greenhouse gas. Methane has been estimated to have a climate impact that is 84-87 times greater than carbon dioxide over a 20-year period, making it a significant contributor to global warming. Consequently, methane emissions to the atmosphere from the development of unconventional gas (shale gas up to date) can have a large influence on the greenhouse footprints of UNG and related climate changes. The available data for estimating fugitive methane emissions from unconventional gas were poorly documented. Several recent studies

by evaluating trends in downstream emissions (storing gas and delivering it to market) and upstream emissions (drilling and HF activity) for different shale regions (the Eagle Ford in Texas, the Bakken in North Dakota and Marcellus shale), estimated that the life cycle fugitive methane emissions of shale gas (considering from well to final consumer) were ~1.5 times higher than that of conventional natural gas (CvNG) (Deziel et al., 2022; Howarth et al., 2011; Schneising et al., 2014; Fernando et al., 2021). In the various researches, there is no obvious relationship between the methane in conventional and unconventional fields. The results demonstrate that the rate of emission depends on the well pad condition and natural gas production rate. Omara et al. have addressed methane emissions fluxes at the large scale in Pennsylvania and West Virginia in the Marcellus region. The total annual CH₄ emissions from 88,500 CvNG well pads were much greater than 3390 UNG well pads. The results show that CvNG well pads emissions 16% of total CvNG gas production. In contrast, UNG well pads emitted 0.64% of total production. The greater prevalence of avoidable process and operating conditions (e.g., unresolved equipment maintenance issues) have led to more methane emission in the CvNG well pads (Omara et al., 2016). McKenzie et al. evaluated the risks to human life's living near natural gas wells. They calculated cancer risks for residents living near wells compared to residents who live in remote areas during well completions. The results show that health effects resulting from gas emissions during development of unconventional gas resources are higher in residents close to the well pads (McKenzie et al., 2012). Benzene is the major factor of life-threatening cancer. Because of greater scale operations and above-ground infrastructure for economical producing rate, environmental impacts of unconventional gas exploitation are greater than for conventional gas deposits (Apergis et al., 2021). However, the emissions from this process could substantially increase the greenhouse gases in comparison

to other renewable energy resources and many of the above-mentioned concerns have been further substantiated. Buchanan et al. evaluated the effects of water resources consumption in the development of Marcellus Shale which may have adverse effects on freshwater biological ecosystems. The results indicate that surface water discharge, can have significant environmental consequences and must be properly managed. Water resources withdrawals can significantly change natural flow regimes especially small drainage streams and the health of fish community (Buchanan et al., 2017).

As already mentioned, it is necessary to consider the influence of exploitation of unconventional resources on environment. Extraction unconventional gas reservoirs requires considerable amounts of water, that reduces the water levels, and it may affect human health. Another environmental constrains is the management of the fracturing flow-back. The flow-back should be restored and disposed. different disposal options are available: injection into used wells; treatment on site, then water can be reused for extraction of unconventional gas; or disposal an offsite treatment plant. each of these may cause significant damage to environmental or human health (Delgado et al., 2016). The high frequency of toxic chemicals used for HF including halides can persist in the environment and contaminated water (Vengosh et al., 2017).

Fracturing fluid primarily composed water as base fluid and sand (90 and 9% volume, respectively) and chemical additives (0.5-2% volume) used to hydraulic stimulate of unconventional gas resources. Some of the chemicals in (Table 4) are known to be toxic and carcinogenic. The amount of water and chemicals, including friction reducers, scale inhibitors, biocides, surfactants, corrosion inhibitors, clay stabilizers, iron control agents, gelling agents, cross-linkers, breakers, and pH

adjustors, injected into a wellbore can vary depending on reservoir conditions, such as permeability, pressure, in-situ stress distribution, depth, and type of rock formation, as well as the number of stages in the well. Typically, between 3 and 50 million liters of water are injected along with varying amounts of chemicals at different application rates (McLaughlin et al., 2016; Yap, 2016; Khan et al., 2021). Each of these chemicals have distinct application. For instance, proppant form a thin layer between fracture faces to sustain the crack. The breakers ($1-400 \text{ mg L}^{-1}$) reduces the viscosity of fluids and allows removal of residual polymers from fractures. $100-300 \text{ mg L}^{-1}$ of Buffer agent are used to control pH of fluid and effectiveness of other chemical additives. The role of Crosslinker is to enhance fluid viscosity and elasticity as temperature changes. The higher viscosity increases the fracture width so that improves transport of proppant and reduces friction pressure. The most cross linkers used in fracturing fluid is quaternary Ammonium Chloride. The other chemicals and their application rates are shown in (Table 4) (Stringfellow et al., 2014; Barati et al., 2014). Flow back water contain injected hydraulic fracturing fluids and the fluids and chemicals within the formation. So, the waste water has different effects on environment around the well. Vengosh et al. studied the effect of shale gas development and HF on water resources in the US.

Studies suggest that the exploitation of shale gas can have a range of negative impacts, including: (1) pollution of shallow aquifers, which can potentially lead to the salinization of groundwater due to the underground leakage of fugitive gas; (2) contamination of surface water resources or shallow groundwater resulting from spills or improper disposal of hydraulic fracturing fluids; (3) the introduction of toxic chemicals into the soil, river basins, or lakes exposed to wastewater or fluids used in hydraulic fracturing operations; and (4) the excessive extraction of water resources for

large-volume hydraulic fracturing fluids, which could exacerbate water shortages, particularly in water-scarce regions (Vengosh et al., 2014).

The UNG exploitation includes the equipment, labor, water, chemicals, and many other materials during production operation. Adgate et al (Adgate et al., 2014) evaluate the population health effects of UNG development in the US. The most important possible worker's health effects are damage caused by chemical stressors (e.g., H_2S and silica). Research has identified stressors that can negatively impact local workers involved in shale gas extraction. These stressors include exposure to hazardous chemicals, such as volatile organic compounds, diesel exhaust, and hydraulic fracturing wastes, which can migrate offsite through spills, leaks, or accidents. Patterson et al. investigated spill data from 2005 to 2014 at 31481 artificial fractured unconventional oil and gas wells in four states: Colorado, New Mexico, North Dakota, and Pennsylvania. During the first three years of well-life, 75 to 94% of spills occurred when wells were drilled and produce oil and gas in large volumes. In all four states, 50% of spills were due to storage and transmission of streams through the pipeline (Patterson et al., 2017). The HF can react with the formation and change the quality of flow-back water. For instance, Jackson et al. evaluated the flow-back fluids from gas wells in Fayetteville, Marcellus, and Barnett formations. The flow back fluids contain dissolved salts. In case of Marcellus, common salts are, Na 5363 mg/L ; Ca 77 mg/L ; SO_4 149 mg/L . The flow-back fluids usually require on-site storage followed by recycling, reinjection, or disposal into a saline aquifer (Jackson et al., 2013). The results of environmental effects of unconventional gas that have been above-mentioned are related to shale, tight gas and coal bed methane. The environmental impact of gas hydrates exploitation is still unknown. Therefore, further research is required to evaluate the effects of dissociation of hydrate sediments which may have impacts on sea-floor stability.

Table 4. Most ingredient used in HF fluid in gas production well (Cooper et al., 2016; Khan et al., 2021; Barati et al., 2014; Yap et al., 2016).

	Additive	Application rates	Purpose
Clay Stabilizer	Choline Chloride Tetramethyl ammonium Chloride	500-2000 mg L ⁻¹	Prevents clays from swelling
Proppant	Sand	~ 9% volume fraction	Form a thin layer between fracture faces to prop the fractures open
Crosslinker	Ammonium chloride Boric Acid Borate Salts Potassium hydroxide	0.5-250 mg L ⁻¹	Maintains fluid viscosity, more elasticity and better proppant transport as temperature increases
Gelling Agent	Derivative of Guar Ethylene Glycol	10-1000 mg L ⁻¹	Better proppant suspension and fluid stabilizer
Scale inhibitors	Phosphonic acid salts Sodium polycarboxylate Sodium acrylate,	75-400 mg L ⁻¹	Protect piping and prevent from plugging
Corrosion inhibitor	Formic acid Acetaldehyde	10-7000 mg L ⁻¹	Form protective layer and preventing corrosion
Iron Control	Citric Acid Acetic Acid ammonium chloride Sodium Erythorbate	50-200 mg L ⁻¹	Prevents precipitation of metal oxides (control iron precipitation)
Biocide	Glutaraldehyde Quaternary Ammonium Chloride	10-800 mg L ⁻¹	Control bacteria in the water that degrade fracturing chemicals and produces corrosive by-products
Friction reducer	Polyacrylamide	30-1200 mg L ⁻¹	Reduce fluid surface tension and facilitate removal of fracturing fluid from the formation.
Breaker	Methanol Ethanol Sodium Chloride Isopropanol	1-400 mg L ⁻¹	The breaker reduces the viscosity of fluids and allows removal of residual polymers from fractures
Buffer agent	Potassium Hydroxide Potassium Carbonate Acetic Acid Sodium hydroxide Sodium Carbonate Acetaldehyde Acetone	100-300 mg L ⁻¹	Adjusts the pH of fluid to maintain the effectiveness of other chemical additives.
Surfactant	Sodium lauryl sulfate Isopropyl Alcohol 2-Butoxyethanol	500-1800 mg L ⁻¹	Fluid stabilizer (control viscosity and surface tension)

5.2. Challenges of Production development

The extraction and production of unconventional gas reservoirs are still not fully understood, and for some reservoir types, we are still in the early stages of development. As a

result, methods for evaluating hydraulic fracture properties are also in their early stages and are not yet fully developed. In recent times, there has been a growing utilization of nanomaterials

and technologies in the hydraulic fracturing of unconventional oil and gas reservoirs, resulting in notable advancements. Nanomaterials can be customized in terms of their surface properties and activity to enhance the efficiency of fracturing fluid systems. This makes them particularly well-suited for application in challenging formation conditions, such as high temperatures and pressures (Mao et al., 2022; Marsden et al., 2022). Unconventional gas exploitation will face challenges in the following aspects: using significant amount of water in HF, deep water drilling hazard (in particular in gas hydrate accumulation). The depth of most shale gas basin in North America are usually more than one kilometer (e.g., the eastern extent of the Colorado ~300 m depth). Many coalbed gas formations are predominantly in shallow depths (less than 600 m) and horizontal fracturing is used in such cases. The empirical studies propose that horizontal fracturing predominates in shallower than 450 m depth, while vertical fracture being used in depth more than 600 m depth (Jackson et al., 2013; Tan et al., 2019).

Porosity, Permeability and pore size distribution are key parameters for developing an unconventional accumulation. Porosity of unconventional deposits is less than 10%, pore size of less than 1 μm and permeability values of less than $1 \times 10^{-3} \mu\text{m}^2$ which mean that the gas cannot flow easily within the rock under natural forces in the reservoir (Caineng et al., 2013).

Over the past decade, there has been significant growth in the use of horizontal drilling, hydraulic fracturing, and micro-seismic monitoring to exploit previously inaccessible or unprofitable hydrocarbon resources in shale gas reservoirs. HF is typically performed using a fracturing fluid made up of water, sand, and chemical additives. This extraction method involves injecting millions of gallons of water, sand, and chemicals under high pressure into the wellbore through horizontal or vertical drilling, which induces the unconventional

gas reservoir and allows for the extraction of natural gas (Vengosh et al., 2017). The pumped fluid reaches the pressure of 8000 psi and may fracture a shale formation depth of 3000 feet in the lateral direction. The HF decomposes shale matrix and connects natural fractures to improve the reservoir permeability. The production of shale gas by HF compared to the conventional gas, consume large volume of water and chemicals with two orders of magnitude (Deziel et al., 2022). The amount of water required for HF is significant, ranging from 3000-21000 m^3 , which constitutes 86% of the direct water needed to extract shale and 56% of the total consumption in the shale gas lifecycle. As production scales up, water consumption in a watershed is expected to increase. However, it can be difficult to accurately attribute changes in water levels solely to shale gas production, as other activities such as power plants and agricultural land use should also be taken into account when assessing water usage in a watershed (Cooper et al., 2016).

In 2013, Scanlon et al. compared the amount of water used in hydraulic fracturing for oil and gas production in the Eagle Ford shale and Bakken formations. They found that the average water use per well was similar for both oil and gas fields in the Eagle Ford, ranging from 4.7 to 4.9 million gallons per well. In contrast, the average water consumption in the Bakken formation was approximately half that of the Eagle Ford, at 2.0 million gallons per well. The Pennsylvania Department of Conservation and Natural Resources estimates that completion of a horizontal well in the Marcellus shale formation can require up to 3.0 million gallons of water (Scanlon et al., 2014; Conard et al., 2020; Kotsakis et al., 2012). In multiphase reservoirs containing gas and water, a threshold capillary pressure must be overcome to displace the wetting phase from the pores. Once this threshold pressure is exceeded, fluid flow is primarily controlled by capillary pressure and the pressure gradient. In

cases where capillary pressure prevents viscous gas flow, molecular diffusion becomes more prominent. In shale deposits, the interaction of reservoir gases with the dispersed organic accumulation is one of the primary mechanisms that controls gas transport, according to studies by Bizhani et al. (2022) and Amann-Hildenbrand et al. (2012)).

6. Economic implications

The development of unconventional gas reservoirs can provide several potential opportunities and benefits. The need to drill large numbers of horizontal wells and perform hydraulic fracturing operations can support local businesses, making unconventional gas production more akin to a manufacturing process than traditional oil or gas production. Additionally, the replacement of coal with gas in the power sector can offer environmental benefits, such as reduced conventional pollution and greenhouse gas emissions. A study by Cronshaw et al. found that the US was able to reduce its greenhouse gas emissions by nearly 5% between 2010 and 2012 due to the increased use of natural gas in the power sector (Cronshaw et al., 2016). Unconventional gas development has many qualities that make it an efficient. The HF and directional drilling have the ability to drill multiple wells from a single well, which can be led to a considerable decline in surface footprint of the exploitation process. Unconventional gas resources reduce greenhouse gas emissions because natural gas has lower carbon and the combustion of natural gas emits 50% to 80% less CO₂ per unit of energy than that of coal (about 56% for gas and 79% for oil) (Schneising et al., 2014).

Bocora et al. conducted an assessment of the economic benefits of unconventional gas development in the US, where companies have discovered several large deposits of shale gas. The use of technologies such as horizontal drilling and hydraulic fracturing has

enabled economically large-scale production. The development of unconventional gas reserves in the US could result in \$3.2 trillion in investments and create 1.4 million new job opportunities (Bocora, 2012). Furthermore, the US has increased its natural gas production and is now looking to become a net exporter of natural gas to other markets such as the European Union or Japan, where the market price is higher. It can be seen that; unconventional gas exploitation is much lower in other countries due to economic and technologic backwardness (Shirazi et al., 2022; Le et al., 2017). Le et al. evaluated opportunities and challenges of Unconventional gas development in Vietnam. The gas consumption in Vietnam is projected to reach 17 billion cubic meters in 2025, and the estimates of Vietnam's gas demand will grow 188% between 2015 to 2040 years. The conventional gas resources may not be sufficient. So, unconventional gas could potentially provide the shortfall. The potential of unconventional gas in Vietnam remains at an initial stage of evaluation. In the recent years, CBM resources have been exploited and confined to the Red River Basin (Le et al., 2017).

7. Conclusions

The paper discusses the assessment of unconventional gas resources, as the future fossil fuel of the world. Low permeability is the Achilles heel for unconventional resources and horizontal wells with the option of the fluid fracturing process would facilitate the reservoir development. According to the research, the main challenges for the development of unconventional gas reservoirs are high production cost of unconventional gas, environmental restrictions, low production efficiency, undeveloped techniques for deep seafloors gas reservoirs and inadequate understanding of gas hydrate resources.

List of Acronyms

<i>Bcf/D</i>	Billion cubic feet per day
<i>bcm</i>	Billion cubic meters
<i>CBM</i>	Coalbed methane
<i>CvNG</i>	Conventional natural gas
<i>EOR</i>	Enhanced oil recovery
<i>gal</i>	Gallon
<i>HF</i>	Hydraulic fracturing
<i>HFF</i>	Hydraulic fracturing fluid
<i>Mtoe</i>	Million tonnes of oil equivalent
<i>nD</i>	Nano Darcy
<i>NP-</i>	National Pollutant Discharge Elimination
<i>DES</i>	System
<i>TOC</i>	Total organic carbon
<i>UGR</i>	Unconventional gas resources
<i>UNG</i>	Unconventional natural gas
<i>Wt. %</i>	weight percent
<i>Mcf</i>	1000 cubic feet

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JOURNAL OF GAS TECHNOLOGY

Volume 7 / Issue 2 / Winter 2022 / Pages 63-70

Journal Homepage: <http://jgt.irangi.org>

Using the Feed Splitting Technique in Optimizing the Energy for the Natural Gas Sweetening Unit of the Ilam Gas Refinery

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ARTICLE INFO

ORIGINAL RESEARCH ARTICLE

Article History:

Received: 25 August 2022

Revised: 28 October 2022

Accepted: 19 December 2022

Keywords:

Natural Gas Sweetening

Diethanolamine

Ilam Gas Refinery

Feed Splitting

ABSTRACT

The sweetening unit of the Ilam Gas Refinery plays a major role in providing olefin feed, and at the present time, the provinces of Ilam, Kermanshah, Hamedan, Kurdistan, and Lorestan in Iran are the consumers of the gas produced by this refinery. The gas sweetening unit of the Ilam Gas Refinery has an absorption and distillation column. H₂S and CO₂ are removed by diethanolamine in the absorption column, and the entrainer is recovered in the distillation column. The concern is the high energy consumption of this process, particularly the distillation column. In this study, a novel method for heat integration of the distillation column of the gas sweetening unit of the Ilam Gas Refinery was used, so that the feed entering the distillation column was splitted into two sections prior to feeding. Afterwards, the bottom section was preheated by the bottom product of column. Preheating the bottom section of feed decreased the reboiler and condenser duties. The results demonstrate that the proposed method decreases the energy consumption by 17%.

DOR: [20.1001.1/JGT.2023.582725.1017](https://doi.org/10.1001/JGT.2023.582725.1017)

How to cite this article

Z. Asgari, M. Yazdani, E. Nozari, H. Saeidi, Using the Feed Splitting Technique in Optimizing the Energy for the Natural Gas Sweetening Unit of the Ilam Gas Refinery. Journal of Gas Technology. 2022; 7(2): 63 -70. (https://jgt.irangi.org/article_707271.html)

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Available online 31 December 2022

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1. Introduction

Given the eco-friendly policies and H₂S toxicity, the process of gas sweetening is essential to remove H₂S and CO₂ from the refinery gas (Zhu et al., 2021a). Different techniques have been used to remove acidic components from natural gas, such as absorption through physical solvents, chemical solvents, mixed solvents, adsorption, cryogenic separation and low temperature separation (Han and Ho, 2019; Jiang et al., 2019; Kheirini et al., 2018; Langè et al., 2015; Rezakazemi et al., 2018). Among these, absorption through Alkanolamine solvents is widely used in numerous applications. Amines, also known as reducing solvents, are extensively employed in sweetening of natural gas. Such solvents have some advantages, such as low vapor pressure and energy consumptions as well as high capacity and consistency. The conventional natural gas sweetening solvents usually involve Monoethanolamine (MEA), diethanolamine (DEA), and methyl diethanolamine (MDEA) (Abd and Naji, 2020; Jamekhorshid et al., 2021). A variety of studies have been conducted on natural gas sweetening.

Song et al. used MEA solvent and heat pump to improve the energy savings of natural gas sweetening process. In their paper, the extra condensate heat was saved via vapor recompression and the excess pressure was saved simultaneously by the expander. The total energy needed for the absorption process could be decreased to 7.2 megawatts, and the waste heat and pressure could be recovered by 38.1 MW. In comparison with the normal process, 33.4 MW of excess heat could be recovered (Song et al., 2017). Additionally, the energy consumed by the proposed method might be decreased to 1.78 MJ to remove 1 kg of CO₂. Park et al. analysed the low temperature process known as LT based on the distillation process to enhance the energy efficiency in the sweetening process and CO₂ removal in

large scale. Every one of the simulations were conducted by Aspen Hysys, which evaluated the sensitivity of key coefficients under different operating circumstances. The results showed that the best design and operating conditions were achieved at a pressure of 4254 kpa and lateral flow ratio of 0.55 at 40 trays. The findings of operating cost for the LT process estimated 15.22 thousand dollars per hour. A new separator and a turbo expander were also proposed as modifications to the process. This new design increased the vapor fraction and recovered a greater power in the turbo expander. The operating pressure of the distillation column could be enhanced through such changes in operating conditions, reducing the existing carbon dioxide in the remaining gas and the flow of carbon dioxide entering the amine process. Compared to the initial state, the new configuration lowered the energy cost of the process by around 5% (Park et al., 2021). Hosseini et al. proposed an optimization approach for increasing CO₂ absorption as well as reducing energy consumption. Two objective functions of CO₂ absorption and energy recovery were defined and developed by the variables affecting the process. This optimization was carried out using a genetic algorithm and Aspen Hysys. The results demonstrated that the energy consumption for absorbing 94% of CO₂ using MDEA/PZ mixed solvents was much lower than the energy consumption for absorbing 90% of CO₂ from MEA solvent (Hosseini-Ardali et al., 2020). Zhu et al. suggested the pre-allocation method of sour gases accompanied by multi-feeding operation to optimize the distribution of temperature and concentration. The results of this method indicated that energy consumption and exergy loss were decreased by 6.5% and 16.5%, and the total economic profit was increased by 66.56% compared to the conventional natural gas sweetening (Zhu et al., 2021b).

Ilam Gas Refinery was built to supply the gas consumed in Ilam province and the western

provinces of Iran, and also to provide the petrochemical feedstock for Ilam Petrochemical Co. and boost the gas pressure in western Iran. This refinery was initially launched at the autumn season of 2007 to purify the gas at the Tang-e-bijar gas field. This refinery was designed and constructed in two phases. The feed of the Ilam Gas Refinery was mainly supplied by the sour gases of the Tang-e-bijar gas field, entering the first phase of Ilam Gas Refinery through a pipeline at the capacity of 6.8 million m³ per day, and reaches 10.2 million m³ per day by adding a capacity of 3.4 million m³ in the final phase.

This paper aims to optimize the energy of the natural gas sweetening unit of the Ilam Gas

Refinery. Hence, a new method was used for heat integration of the distillation column of the sweetening unit. In this technique, first the feed to the distillation column was splitted into two sections. Afterwards, the bottom sections of feed were preheated by the bottom products of the column. This decreased the reboiler and condenser duties. Feed splitting fraction and preheating rate of the bottom section of feed were the main variables of this technique that shall be calculated precisely.

2. Case Study

In this research, the gas sweetening of the Ilam Gas Refinery was studied. The conditions of feed and solvent used are presented in (Table 1).

Table 1. Feed/Solvent Conditions

Process Characteristic		Sour Gas	Solvent
Temperature [°C]		33.6	50
Pressure [kPa]		7600	7590
Molar flow rate [kgmol/h]		6144	8438
Mole fraction	Methane	0.8324	
	Ethane	0.0551	
	Propane	0.0230	
	i-Butane	0.0044	
	n-Butane	0.0062	
	i-Pentane	0.0021	
	n-Pentane	0.0021	
	n-Hexane	0.0013	
	n-Heptane	0.0006	
	n-Octane	0.0010	
	N ₂	0.0013	
	CO ₂	0.0374	
	H ₂ S	0.0325	
	H ₂ O	0	
MDEAmine	0		
DiM-Sulphide	0.0001	0.8976	
E-Mercaptane	0.0003	0.1024	
M-Mercaptane	0.0001		
COS	0		

The gases produced from the oil reserves or in the gas industries contain various amounts of impurities. The presence of impurities in the industrial gases causes damage to the equipment and decreases the quality of industrial gases. The leakage of impurities into the environment will also cause contamination. In such cases, the impurities of gas flow are needed to be eliminated. Acidic gases, including carbon dioxide, hydrogen sulfide, and sulfur dioxide, are one of the most important impurities of gas flow. Absorbing acid gases is a critical process in many chemical industries, such as gas sweetening.

3. Process Simulation

Aspen Hysys V.10 was used to simulate the processes. The fugacity of the liquid and vapor phases was calculated by Acid gas-chemical solvent fluid package. Modified HYSIM Inside-Out was also the solving method for distillation columns.

3.1. Conventional gas sweetening process of the Ilam Gas Refinery

(Figure 1) represents the simulation of the conventional gas sweetening process of the Ilam Gas Refinery in Aspen Hysys. The feed stream entered the flash column for initial separation and then the sour gas and diethanolamine entered the bottom and top sections of the absorption column as the amine solvents, respectively. The absorption column had 20 trays and its high and low pressures were equal to 7580 kPa and 7600 kPa, respectively. The distillate product (sweet gas) and the bottom product were removed from the absorption column at a molar flow of 5784 kmol/h and 8798 kmol/h, respectively. After preheating, the downstream of the absorption column entered the 20-tray distillation column to purify the amines. The distillation column trays are considered ideal. The high and low pressures of the distillation column were 69 kPa and 110 kPa, respectively. The purified amine discharged from the distillation column returned to the first column.

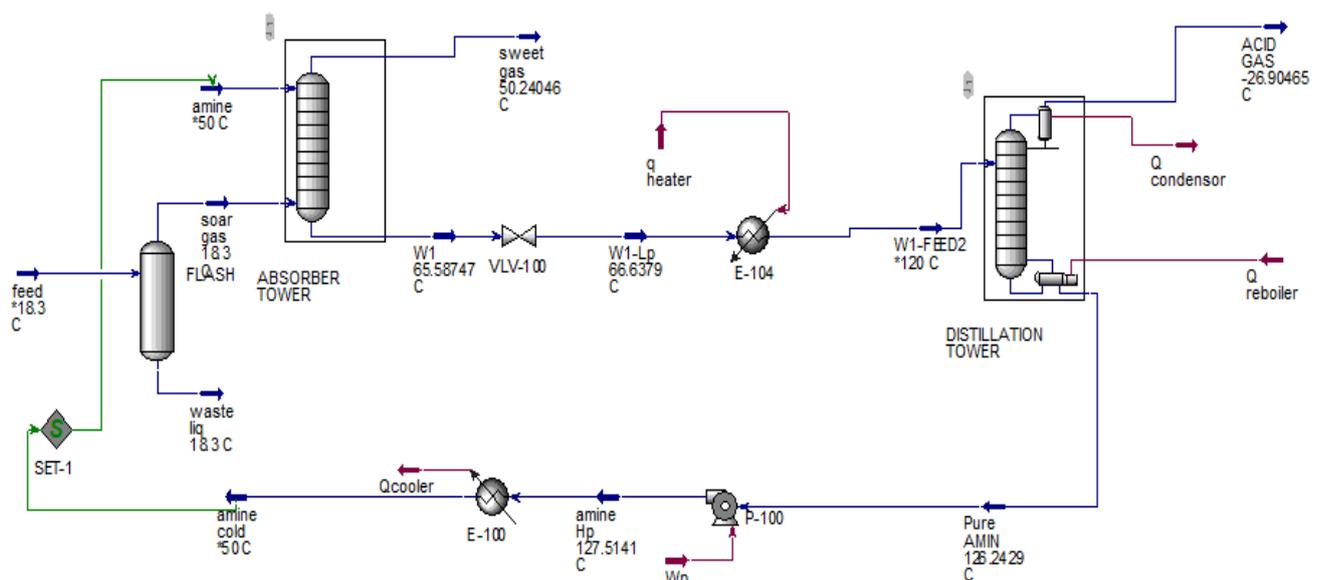


Figure 1. Simulation of the Conventional Gas Sweetening Process of the Ilam Gas Refinery in Aspen Hysys

4. Results and discussion

This study investigated the sweetening of gas at the Ilam Gas Refinery using diethanolamine. The process was simulated by 2 methods with and without heat integration and (Figure 3) shows the energy consumption in each method. The quantity of energy consumed for the distillation column is calculated by the following equation (1):

$$Q_D = Q_C + Q_H \quad (1)$$

Where Q_D , Q_C , and Q_H represent the energy consumption of the distillation column, cold utility, and hot utility consumed for distillation column. The amount of total hot and cold utility is equal to:

$$Q_{hot\ utility} = Q_h + Q_{heater} \quad (2)$$

$$Q_{cold\ utility} = Q_C + Q_{cooler} \quad (3)$$

(Figure 3) shows a comparison between energy consumption in both processes:

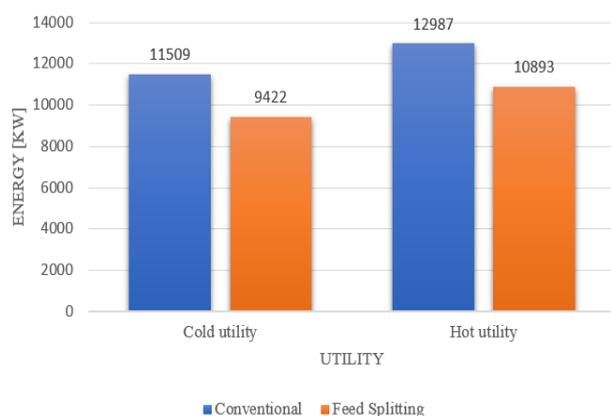


Figure 3. Comparison of Energy Consumption in Two Processes

The results show that the suggested method consumes lower energy than the traditional method, and therefore, the developed method is considered appropriate. The cooler has a thermal load of 2868 KW in the conventional process and 2611 KW in the feed splitting process. Moreover, in both processes, the pump power consumption is 655 KW.

5. Conclusions

The feed of the Ilam Gas Refinery was mainly supplied by the sour gases of the Tang-e-bijar gas field and injected into gas transmission pipelines after sweetening. The problem is the high energy consumption of the solvent recovery column at the natural gas sweetening unit of the Ilam Gas Refinery. Hence, the energy optimization is a necessity. In this paper, feed splitting was used for heat integration of this process. Compared to other heat integration methods such as vapor recompression and heat pump, feed splitting has the advantage of not requiring additional equipment, like compressors. In the proposed technique, the feed entering the distillation column was splitted into two sections. The bottom section of the feed was preheated by the bottom product to reduce the reboiler and condenser duties. Accordingly, the proposed method reduced the energy consumption by 17%.

Nomenclature

<i>DEA</i>	Diethanolamine
<i>LT</i>	Low temperature
<i>MDEA</i>	Mmethyl diethanolamine
<i>MEA</i>	Monoethanolamine
<i>PZ</i>	Piperazine

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شبیه‌سازی و آنالیز حساسیت بازیابی گاز مشعل جهت کاربرد در مخازن هیدروکربنی به‌عنوان گاز تزریقی

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چکیده

بازیابی گاز مشعل یکی از فرآیندهای ضروری در کاهش انتشار گازهای گلخانه‌ای در صنایع نفت و گاز است. از طرفی با توجه به کاهش فشار و میزان تولید مخازن هیدروکربنی به‌ویژه در ایران، ارائه راهکارهایی برای نگهداری فشار مخازن ضروری است، بنابراین در این مطالعه پتانسیل استفاده از دی‌اکسید کربن جدا شده از گاز فلر در پالایشگاه پارسین برای تزریق به یک مخزن گاز میعانی بررسی شد. برای این منظور، فرآیند بازیابی گاز مشعل با استفاده از نرم‌افزار Aspen HYSYS شبیه‌سازی و بهبودهای عملیاتی اعمال شد. سپس تزریق گاز دی‌اکسید کربن جدا شده به یک مخزن گاز میعانی در نرم‌افزار Petrel شبیه‌سازی شده و بهترین سناریو تعیین شد. نتایج به دست آمده نشان داد که بیشترین بازیابی CO_2 با استفاده از دی‌اکسید کربن پالایشگاه پارسین به‌عنوان حلال با دبی ۱۹۳۰ USGPM حاصل می‌شود. نتایج شبیه‌سازی مخزن نشان داد که تزریق CO_2 از افت فشار شدید جلوگیری کرده و موجب می‌شود که فشار مخزن با شیب کمتری کاهش یابد، بنابراین، نرخ تولید مخزن افزایش یافته و پایدارتر خواهد بود. پایدارترین نرخ تولید از مخزن برای نرخ تزریق ۳۰۵ میلیون مترمکعب در روز به‌دست آمد.

واژگان کلیدی: گاز فلر، تزریق گاز، مخزن گاز میعانی، شبیه‌سازی

مقایسه دو روش تراکم بخار و تبخیر ناگهانی محصول پایین در بهینه‌سازی انرژی فرآیند شیرین‌سازی گاز طبیعی

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چکیده

شیرین‌سازی گاز ترش به کمک حلال آمین به دلیل توانایی بالای آمین‌ها در حذف ترکیبات اسیدی از گاز طبیعی، همواره مورد توجه بوده است. در این فرآیند از یک برج جذب و یک برج تقطیر به منظور بازیابی آمین استفاده می‌شود. به دلیل مصرف انرژی بالا در برج بازیابی حلال، هزینه‌های عملیاتی فرآیند متداول شیرین‌سازی گاز ترش بسیار بالا است. از این رو بهینه‌سازی انرژی فرآیند یک امر ضروری محسوب می‌شود. در این پژوهش ابتدا فرآیند مرسوم شیرین‌سازی گاز مورد انتگراسیون حرارتی (HI) قرار گرفته است به نحوی که به جای استفاده از یوتیلیتی در تأمین انرژی فرآیند، از انرژی جریان‌های فرآیندی استفاده شده است. سپس برج بازیابی آمین در این فرآیند با استفاده از روش‌های تراکم بخار (VRC) و تبخیر ناگهانی محصول پایین (BF) یکپارچه حرارتی شده است. نتایج نشان می‌دهد که سه فرآیند HI، VRC و BF نسبت به فرآیند مرسوم به ترتیب حدوداً ۲۵ درصد، ۸۸ درصد و ۹۰ درصد کاهش مصرف انرژی داشته است. با وجود اینکه کار مصرفی کمپرسور در دو فرآیند VRC و BF تقریباً یکسان است، اما کاهش مصرف یوتیلیتی سرد و گرم در فرآیند BF نسبت به VRC ۳۳ درصد بیشتر بوده است. بنابراین، فرآیند BF عملکرد بهتری را نسبت به فرآیند VRC دارد. علاوه بر آن، فرآیند BF هزینه کلی سالیانه فرآیند مرسوم را در بیشترین مقدار به میزان ۶۹ درصد کاهش می‌دهد. به همین علت فرآیند BF به عنوان بهترین انتخاب انتگراسیون حرارتی برای این مطالعه موردی انتخاب شده است.

واژگان کلیدی: شیرین‌سازی گاز ترش، انتگراسیون حرارتی، تراکم بخار، تبخیر ناگهانی محصول پایین

مروری جامع بر مزایا و مسائل نانوتکنولوژی در روش گوگردزدایی اکسایشی برای تولید سوخت‌های فوق تمیز

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چکیده

امروزه تولید سوخت پاک یکی از چالش‌های بزرگ در جهان است. یکی از عواملی که باعث آلودگی محیط‌زیست می‌شود، ترکیبات گوگردی موجود در نفت خام است. در دنیای امروز قوانین سخت‌گیرانه‌ای برای کاهش میزان گوگرد در سوخت وجود دارد. روش‌های مختلفی برای حذف ترکیبات گوگرد از سوخت‌ها وجود دارد، مانند گوگردزدایی هیدروژنی (HDS)، تقطیر استخراجی، گوگردزدایی زیستی، گوگردزدایی جذبی و گوگردزدایی اکسایشی (ODS). برخی از ترکیبات گوگردی که توسط روش گوگردزدایی هیدروژنی از سوخت حذف نمی‌شوند را می‌توان به راحتی با روش اکسیداسیون حذف کرد. امروزه روش گوگردزدایی اکسایشی به عنوان مکمل روش گوگردزدایی هیدروژنی شناخته می‌شود. در روش گوگردزدایی اکسایشی، ترکیبات گوگردی توسط کاتالیزورها و اکسیدکننده‌ها به سولفونات‌های مربوطه تبدیل می‌شوند و سپس توسط محلول‌ها یا جاذب‌های قطبی از خوراک جدا می‌شوند. تحقیقات مختلفی بر روی کاتالیزورها و اکسیدکننده‌های روش گوگردزدایی اکسایشی انجام شده است. در این مطالعه مروری جامع بر روی کاربرد نانوتکنولوژی در روش گوگردزدایی اکسایشی انجام شده است. بر اساس تحقیقات قبلی و مقالات موجود، نانوکاتالیست‌های مورد استفاده در فرآیند اکسیداسیون را می‌توان به پنج گروه طبقه‌بندی کرد: پلی اکسومتالات‌ها، اکسید فلزات واسطه، مواد کربنی، مایعات یونی و چارچوب‌های فلزی-آلی (MOF). همچنین نانوکاتالیست‌ها و اکسیدکننده‌های مختلف و شرایط بهینه برای دستیابی به بالاترین درصد تبدیل برای حذف ترکیبات گوگردی مورد بررسی قرار گرفت.

واژگان کلیدی: نانوکاتالیست، گوگردزدایی اکسایشی، نفت کوره

بهینه‌سازی انرژی واحد شیرین‌سازی گاز طبیعی پالایشگاه گچساران با استفاده از روش تراکم بخار

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چکیده

ایران دارای ششمین جایگاه در تولید گاز طبیعی در جهان به شمار می‌رود. پالایشگاه گاز گچساران با تولید بیش از یک میلیارد فوت مکعب گاز خشک در روز سهم عمده‌ای در تأمین درآمدهای اقتصادی کشور دارد. شیرین‌سازی گاز ترش که به صورت مایع وجود دارد، همواره جهت تأمین بخشی از خوراک مجتمع‌های پتروشیمی بندر امام، یکی از مهم‌ترین اهداف پالایشگاه نفت و گاز گچساران بوده است. به طوری که روزانه ده‌ها هزار بشکه به پتروشیمی بندر امام ارسال می‌شود. گاز ترشی که به عنوان خوراک ورودی مورد استفاده قرار می‌گیرد، دارای مقداری سولفید هیدروژن و دی‌اکسید کربن است. به دلیل انرژی مصرفی بالای شیرین‌سازی، بهینه‌سازی انرژی این فرآیند از اهمیت بالایی برخوردار است. در این مطالعه، از روش تراکم بخار به منظور بهینه‌سازی انرژی فرآیند شیرین‌سازی واحد گاز گچساران استفاده شده است. در این روش به کمک کمپرسور، بخار بالای برج تقطیر فشرده می‌شود و این امکان را پیدا می‌کند که انرژی گرمایی خود را به جریان پایین برج منتقل کنند. نتایج نشان می‌دهد که روش تراکم بخار نسبت به فرآیند مرسوم ۵۷ درصد کاهش مصرف انرژی داشته است که مهم‌ترین دلیل آن کاهش مصرف یوتیلیتی گرم و یوتیلیتی سرد است. البته در این فرآیند یک کمپرسور اضافه می‌شود که فشار خروجی آن به طور دقیق محاسبه شده است. چنانچه فشار خروجی کمپرسور بیش از حد افزایش یابد، این روش کارایی خود را از دست می‌دهد و غیراقتصادی می‌شود.

واژگان کلیدی: شیرین‌سازی گاز ترش، گاز طبیعی، تراکم بخار، بهینه‌سازی انرژی

ارزیابی مخازن گاز طبیعی غیرمتعارف

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چکیده

در قرن بیست و یکم، حجم بزرگی از نفت و گاز در صنعت پتروشیمی مصرف می‌شود که با در نظر گرفتن جمعیت رو به رشد تقاضای انرژی جهانی رو به افزایش است. گاز طبیعی، پاک‌ترین منابع غیرقابل تجدید است که در مقایسه با دیگر هیدروکربن‌ها، به‌عنوان یک منبع انرژی مهم در نظر گرفته می‌شود. به‌طور کلی با توجه به حجم بزرگی از شیل گازی، ماسه‌ای متراکم گازی و بسترهای زغالی و هیدرات گازی، مخازن گاز غیرمتداول به‌عنوان یک منبع عظیم هیدروکربن شناخته شده است. دامنه این مطالعه شامل تأثیرات زیست‌محیطی، ویژگی‌های زمین‌شناسی، موانع و چالش‌های فنی استخراج از مخازن غیرمتعارف از جمله تقاضای انرژی، مصرف و تولید انرژی، آلودگی آب، انتشار گاز گلخانه‌ای و ویژگی‌های زمین‌شناسی مخزن است. این مقاله به بررسی روش‌های نوظهور در توسعه گاز غیرمتعارف در کشورهای مختلف با تمرکز بر ایالات متحده می‌پردازد. نتایج نشان می‌دهند که امکان توسعه گازی غیرمتعارف در کشورهای مختلف وجود دارد، اما آینده آن به مسائل زیست‌محیطی، سرمایه‌گذاری در انرژی‌های تجدیدپذیر و بازارهای جهانی گاز بستگی دارد.

واژگان کلیدی: گاز غیرمتعارف، شیل گازی، ماسه‌ای متراکم گازی، بسترهای زغالی متان، هیدرات گازی

استفاده از روش شکستن خوراک در بهینه‌سازی انرژی واحد شیرین‌سازی گاز طبیعی پالایشگاه ایلام

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چکیده

واحد شیرین‌سازی پالایشگاه گاز ایلام نقش اصلی در تأمین خوراک الفین دارد و در حال حاضر استان‌های ایلام، کرمانشاه، بخش‌هایی از همدان، کردستان و لرستان مصرف‌کننده‌ی گاز تولیدی این پالایشگاه هستند. واحد شیرین‌سازی گاز پالایشگاه ایلام دارای یک برج جذب و یک برج تقطیر است. در برج جذب به کمک حلال دی اتانول آمین، CO_2 و H_2S از گاز طبیعی حذف می‌شوند و در برج تقطیر نیز حلال استفاده شده، بازیابی می‌شود. مشکلی که وجود دارد این است که مصرف انرژی این فرآیند به‌ویژه برج تقطیر، بسیار بالا است. در این مقاله از روش Feed Splitting برای انتگراسیون حرارتی برج تقطیر واحد شیرین‌سازی گاز پالایشگاه ایلام استفاده شده است. به این صورت که خوراک ورودی به برج تقطیر قبل از ورود به برج به دو قسمت تقسیم می‌شود. سپس بخش پایینی آن به کمک محصول پایین برج پیش گرم می‌شود. پیش گرم کردن بخش پایینی خوراک باعث کاهش Heat Duty ریبویلر و کندانسور می‌شود. نتایج نشان می‌دهد که روش پیشنهادی میزان مصرف انرژی را ۱۷ درصد کاهش می‌دهد.

واژگان کلیدی: شیرین‌سازی گاز، دی اتانول آمین، پالایشگاه ایلام، تقسیم خوراک



JOURNAL OF GAS TECHNOLOGY

VOLUME 7 • ISSUE 2 • WINTER 2022

EISSN: 2588-5596

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