A Review on the Use of Natural Gas Purification Processes to Enhance Natural Gas Utilization

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Abstract: The necessity for the adoption of clean and sustainable energy sources that would result in the diversification of Nigeria's energy mix has arisen as a result of the significant area of concern surrounding climate change caused by CO_2 emission. It's interesting to note that Natural Gas (NG), a readily accessible alternative energy source in Nigeria with a wealth of approximately 187 trillion cubic feet (Tcf) of proven gas reserves, has remained a crucial part of the energy mix, providing adequate energy with high energy quality and low CO_2 emission. However, natural gas naturally contains some acid gases and small amounts of CO_2, which act as impurities. This has posed a limitation to its effective utilization due to the bottlenecks in pipeline and equipment corrosion during transportation, storage, distribution, etc. To tackle this challenge, numerous researches have been conducted on the purification of natural gas through available technologies, including the cryogenic, membranes, absorption, and adsorption methods. Additionally, the independent use of these technologies has consistently been proven to be less economical and financially demanding with longer purification time, leading to low product recovery and high energy intensity for regeneration in the NG purification processes, which leaves them uniquely challenged. In order to improve natural gas consumption, this study reviews technological techniques in the use of various natural gas purification procedures and hybrid natural gas purification processes. Membranes are used in the purification process for both the gas-absorption and bulk separation of gaseous pollutants. These strategies, created to strike a compromise between the shortcomings of membrane and absorption processes, demonstrated a better separation that contributed to long-term process improvement.

Keywords: Gas Technology, Utilization, Emission Purification, Energy-Mix

1. Introduction

Shimekit and Mukhtar [1] assert that it is crucial to look for potential energy alternatives as the globe works to meet the expanding demand for energy while simultaneously reducing the consequences and direct impact of such global greenhouse gas (GHG) emissions. According to Shimekit et al. [12], the challenge of creating an adequate amount of

high-quality energy that is environmentally sustainable and commercially feasible has emerged as a current concern. This is the baseline for most techniques. Natural gas is one of the parts of the global energy supply that already meet the aforementioned condition. According to Khalilpour and Karimi [2], the demand for primary energy is rising at an accelerating rate, and this has motivated extensive research on finding and developing new and better energy sources. Oil, gas, and coal continue to reign supreme as the main energy sources for at least a few decades, despite the possibility that unconventional energy sources like renewables may help gradually lessen the world's dependency on fossil fuels. More than 85% of the world's energy needs are currently met by these three resources. The cleanest of the three main energy sources is NG (natural gas), according to Khalilpour and Karimi [2]. Natural gas is particularly appealing from an environmental standpoint due to its lower C/H ratio, which results in lower carbon emissions as compared to oil and coal, as well as its lower emissions of oxides (nitrogen and sulfur) and particulates. More crucially, compared to coal and oil, the cost of natural gas-based processes, including power generation, is far cheaper. The most significant use of natural gas is as a fuel, and it also serves as a supply of hydrocarbons for petrochemical feedstocks. It has been shown that natural gas' significant methane component can produce additional potential byproducts, such as syngas and high purity hydrogen [1].

According to Shimekit and Mukhtar [1], the main component of natural gas is methane. However, it also contains sizable amounts of polluting substances as CO_2, N_2, Hg, He, H_2S, and light and heavy hydrocarbons. In order to satisfy pipeline impurities, boost natural gas's calorific value, reduce pipeline and equipment corrosion, and address related process bottlenecks, the impurities must be removed from natural gas in order to meet international pipeline quality standard standards as a consumer fuel. The natural gas market has undergone a significant transformation over the past 13 years, with prices decreasing and output rising. The discovery of unconventional resources, primarily in the US, has led to the supply of natural gas expanding; by 2040, the US is predicted to produce approximately one-fourth of the world's gas [3]. According to Economides and Wood [4], taking into account the demands of cutting-edge green technology for promoting low- and zero-emissions through the prudent use of natural resources for available reserves, natural gas has emerged as one of the most alluring, fastest-growing, and premium-growing fuels of the world's primary energy consumption. Shimekit and Mukhtar [1] predict that the increase in natural gas usage will slacken to an average annual growth rate of 0.9 percent as a result of the high cost of the resources and products provided to the worldwide market. According to Oluwatobi Ajagbe [3], the introduction of LNG as a fresh option for using natural gas has actually greatly boosted international natural gas trade.

Furthermore, it is anticipated that government regulations and decision-makers will support the use of natural gas to at least reduce GHG emissions because it produces less CO2 when burned than other fuels like coal or petroleum [4]. Intriguingly, the use of gas from offshore and/or stranded gas fields has aroused enormous attention due to the increasing demand and new market opportunities, and the emergence of LNG as a new NG usage alternative has considerably aided the worldwide NG trade [2, 5].

Oluwatobi Ajagbe [3] underlined that natural gas is currently the energy source with the quickest rate of growth, and that by 2025, consumption will have increased from roughly 92 trillion cubic feet to 156 trillion cubic feet. About half of the increase in global natural gas demand over this time period is accounted for by the electric power sector. The demand for natural gas is anticipated to rise most significantly in emerging economies.

This study examines technological methods for using various natural gas purification techniques and hybrid natural gas purification processes in an effort to enhance natural gas utilization.

2. Literature Review

It is worthwhile looking at prospective energy alternatives in an effort to meet the expanding worldwide demand for energy and, at the same time, address environmental effects such global greenhouse gas (GHG) emissions. The production of appropriate amounts of high-quality energy while being economically viable and environmentally sustainable serves as the baseline for the majority of approaches [1]. Natural gas is one of these essential parts of the global energy supply that has met the aforementioned condition. Natural gas serves primarily as a fuel, but it also provides hydrocarbons for petrochemical feedstocks. Many studies have been conducted in the natural gas industry since methane, which makes up a large portion of natural gas, helps to produce other potential products including syngas and high purity hydrogen [6]. The contaminants must be eliminated in order for the pipe-line quality standard standards for consumer fuel to be met, for the natural gas to have a higher calorific value, to prevent equipment and pipeline corrosion, and to further circumvent related process bottlenecks [1].

2.1. Natural Gas Source / Composition

According to Shimekit and Mukhtar's research, natural gas is mostly created by the putrefaction of once-living things like plants, animals, and bacteria that evolved into an inanimate combination of gases millions of years ago. According to the most widely accepted hypothesis of how fossil fuels are formed, they are created when organic matter decomposes while being squeezed under high pressure for an extended period of time beneath the earth's crust. This kind of generation is referred to as "thermogenic methane". This type of natural gas is produced by the decomposition of stacked and compressed organic matter that is covered in muck, sediment, and debris at a high temperature beneath the earth's crust. Technically known as biogenic methane, natural

gas can also be created by tiny methane-producing bacteria. In this case, methane creation takes place close to the earth's surface, and the resulting gas is typically released into the atmosphere. A third hypothesis states that natural gas is produced via abiogenic processes, which take place deep inside the earth's crust and are dominated by carbon and hydrogen-rich gases.

Table 1. *Emissions from Natural Gas and Fossil Fuels [7].*

	CO_2	CO	NO	SO	Particulate
Coil	208,000	208	457	2,951	0.016
Oil	164,000	33	448	1,1222	0.007
Natural gas	117,000	40	92	1	0.00

2.2. Natural Gas Composition

Natural gas that is produced from oil wells is classified as either associated with (dissolved in) crude oil or non-associated, according to Shimekit and Mukhtar [1]. When tiny hydrocarbon molecules (two to eight carbons) and methane, which was in a gaseous state at deep pressures, become liquid (condense) in the reservoir at standard atmospheric pressure, the composition of the gas produced from a certain reservoir may change with time. Common names for them include condensates and natural gas liquids (NGLs). This is standard procedure in a retrograde condensate reservoir ([6, 8]).

Table 2. *Natural gas reservoir composition in volume% in various parts of the world. ([6, 9, 10]).*

Reservoir					
Component	Groningen (Netherlands)	Laeq (France)	Uch (Pakistan)	Uthmaniyah (Saudi Arabia)	Ardjuna (Indonesia)
CH_4	81.3	69	27.3	55.5	65.7
C_2H_6	2.9	3	0.7	18	8.5
C_3H_8	0.4	0.9	0.3	9.8	14.5
C_4H_{10}	0.1	0.5	0.3	4.5	5.1
C_{5+}	0.1	1.5	-	1.6	0.8
N_2	14.3	15.3	25.2	0.2	1.3
H_2S	-	15.3	-	1.5	-
CO_2	0.9	9.3	46.2	8.9	4.1

Dortmundt and Doshi [11] contend that carbon dioxide must be eliminated as effectively as possible since it reduces the energy content of natural gas and raises the cost of sale. Moreover, it turns acidic and corrosive when there is water present, harming the equipment system and pipeline. Moreover, liquefied natural gas (LNG), gas to liquid (GTL), and chemicals are thought of as alternatives when transporting natural gas over very long distances is a worry since pipelines will be too expensive. In an LNG processing facility, the CO_2 may freeze, obstruct pipelines, and affect transportation while the natural gas is being cooled to an extremely low temperature. As a result, the presence of CO_2 in natural gas remains one of the most difficult gas separation difficulties in CO_2/CH_4 systems. As a result, one of the most challenging gas separation challenges in CO_2/CH_4 systems continues to be the presence of CO_2 in natural gas. As a result, boosting product quality requires the removal of CO_2 from natural gas through purifying processes. Natural gas, a gaseous fossil fuel, has a comparatively low energy content per unit volume and emits fewer greenhouse gases (GHG) than other fossil fuels, according to Pascoli, Femia, and colleagues [12]. Nonetheless, it is the most hydrogen-rich and has greater energy conversion efficiency when compared to other hydrocarbon energy sources [4].

Table 3. *U.S Pipeline Specifications for Natural Gas Delivery [13].*

Components	U.S. pipeline specification
C_{3+}	950 – 1050 Btu/scf dew point -20°C
H_2S	< 4 ppm
CO_2	< 2 mol%
H_2O	< 0.1 g/cm³ (<120 ppm)
Total inerts (N_2, He, Ar, etc.)	< 4 mol%

The following specifications are frequently used for natural gas in pipeline systems [14]. Natural gas ought to be:

Within a specific Btu content range (1,305 Btu per cubic feet, +/- 50 Btu), at a predetermined hydrocarbon dew point temperature, with only trace amounts of hydrogen sulfide, carbon dioxide, nitrogen, water vapor, and oxygen, and free of particles and liquid water that could damage the pipeline or its associated operational equipment.

Table 4. *Composition of Natural Gas by Volume, V%. [15].*

Component	Composition by volume
CH_4	0.9586
C_2H_6	0.0154
C_3H_8	0.0017
C_4H_{10}	0.0062
C_5H_{12}	0.0006
C_6H_{14}	0.0003
N_2	0.0113
CO_2	0.0119

2.3. Liquefied Natural Gas

Liquefied natural gas (LNG) is one of the many ways to transport and profit from natural gas assets, according to Oluwatobi Ajagbe [3], particularly when it involves delivering natural gas to a location more than 2500 miles from the source where other methods of transporting gas become less desirable. Using cryogenic temperatures, natural gas is physically transformed into a liquid for LNG, which is then transported to the target markets typically by specially built ocean liners.

2.4. Compressed Natural Gas (CNG)

The fundamental idea of compressed natural gas (CNG), according to Oluwatobi Ajagbe [3], is to compress the natural

gas at pressures between 1,500 and 3,000 psi (about 100-200 atmospheres), and occasionally chill it to lower temperatures (up to - 40°F, -40°C). CNG technology is simple to use and simple to integrate into commercial environments. The two main goals that CNG schemes want to achieve are monetizing modest reserves and catering to niche markets. This would release reserves that would otherwise stay stranded and service several minor markets that could not be supplied via pipeline or LNG due to economic reasons. This idea is made even more appealing by the CNG sea transport system's scalability and the chance to reuse its main assets (the carrier vessels) [16]. It's common to use the phrases compressed natural gas (CNG) and liquefied natural gas (LNG) interchangeably. While both CNG and LNG are natural gas storage methods, the main difference between the two is that CNG is kept (as a gas) at high pressure whereas LNG is stored (as an uncompressed liquid) at extremely low pressure (cryogenic temperatures). As CNG doesn't need cryogenic tanks or an expensive cooling procedure, it is less expensive to produce and store than LNG. As compared to alternative natural gas types, like LNG, CNG is relatively cost-competitive. CNG is perfect for smaller vehicles traveling shorter distances as well as storing and extending limited gas resource amounts, but LNG is better suited to longer-distance and larger vehicles [17].

2.4.1. Advantages of Compressed Natural Gas (CNG)

There are strong justifications for the expansion and use of CNG. Finally, there are five immediate benefits of CNG that stick out. These are emissions, flexibility, gas reserves, cost, abundant gas reserves and safety record.

First off, CNG is the best fuel for automobiles in terms of pollution. This recognizes natural gas as the cleanest-burning fossil fuel due to its low emissions. Compared to coal and oil, CNG releases about 80% less CO_2 during combustion.

2.4.2. Disadvantages of Compressed Natural Gas (CNG)

The following drawbacks must to be taken into account (Consumer gas cooperative, 2023) [18]:
1) Because it is combustible, natural gas must be handled carefully.
2) Like all fossil fuels, natural gas is not a renewable energy source.
3) Greenhouse gases are produced in part by natural gas. The principal gas found in natural gas, methane, is a potent greenhouse gas, however it doesn't linger in the atmosphere as long as carbon dioxide (CO_2). In 2014, it made up around 11% of all greenhouse gas emissions from human activities, making it the second most common greenhouse gas after CO_2. Across the world, human activity is responsible for more than 60% of all methane emissions, of which the natural gas and petroleum industries are responsible for 33% [19].

2.5. Natural Gas Processing

Tobin J., Shambaugh P., et al. [14] state that the following operations make up the majority of a typical natural gas processing plant:
1) gas oil separator (treatment unit);
2) condensate separator;
3) dehydrator;
4) acid gas removal unit;
5) Nitrogen rejection unit (NRU) or nitrogen extractor and
6) fractionator.

Using pressure at the wellhead, where gravity separates the lighter gas hydrocarbons from the heavier oil, gas-oil separators are used to separate the gas stream from crude oil at the top and bottom of the cylindrical shell, respectively. Mechanical separators at the wellhead use condensate separators to separate condensates from the gas stream. The two main procedures carried out in the condensate treatment section are water washing and condensate stabilization. Condensate may need to be rinsed with water to remove salts and additives [14]. Dehydrators: These devices employ the dehydration process to remove water vapor from natural gas, which prevents hydrate formation, corrosion issues, and dew points. The method of absorption utilizing ethylene glycol is employed in this treatment to take out water and other impurities from the feed stream. Dehydration towers with dry beds can also be used as an alternative to remove water using the adsorption technique [14]. Acid gas removal units are employed to efficiently remove contaminants from dry gas, including CO_2, H2S, lingering water vapor, and inert gases like helium and oxygen. Alkanolamines or Benfield solution techniques are frequently employed to absorb CO_2 and H_2S from the input gas [14]. There are two ways to remove nitrogen from a stream: nitrogen extractors and nitrogen rejection units. Due to the distinction in their boiling points, nitrogen in the first kind is cryogenically separated from the gas stream. In the second type, a physical absorption mechanism separates methane from nitrogen. Regeneration is often performed by reducing pressure. A pressure swing adsorption device can be used to remove inert gases like helium if there are even minute amounts of them in the gas stream [14].

Demethanizer: This device uses absorption or cryogenic processing to extract methane from NGLs. The process of demethanization can take place inside the plant or as a way to extract nitrogen. The cryogenic approach is more effective than the absorption method for separating lighter liquids like ethane [14].

Fractionators: By changing the volatility of the hydrocarbons in the stream, fractionators are used to separate the NGLs from the gas stream. In fractionation, the NGLs are allowed to rise through the towers while being heated to gradually raise the gas stream's temperature. By doing this, the vapor and liquid phases are helped to fully contact one another, facilitating the components' easy vaporization, condensation, and separation into separate holding vessels [14].

Natural gas (NG) is also the energy source that is expanding the fastest globally, according to Aspelund and Gundersen's research [20]. Throughout the past two decades, the output of liquefied natural gas (LNG) has risen by 7% annually.

2.6. Natural Gas Utilization

When building infrastructure to bring associated natural

gas to the market is technically or financially impractical, it is typically flared or vented as a byproduct of oil production. Huge volumes of greenhouse gases are released into the atmosphere as a result of the accompanying gas flaring and venting, causing catastrophic global warming and energy waste. Since 2002, significant efforts have been made to effectively utilize natural gas in order to reduce the incidence of gas flaring and venting [21].

Regarding the consumption of natural gas ([22, 23]), a number of natural gas utilization techniques, including:
  a) Gas re-injection.
  b) Liquefied natural gas (LNG).
  c) Compressed natural gas (CNG).
  d) Gas to wire (GTW).
  e) Gas to liquids (GTL).
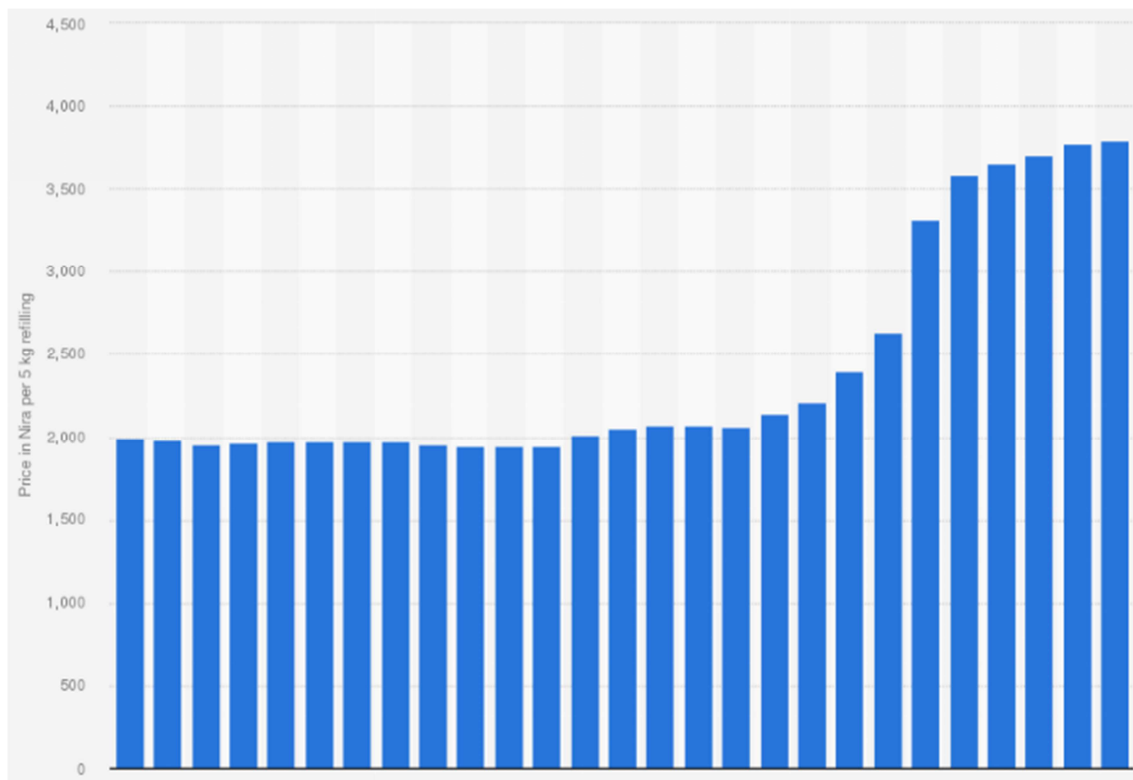 f) Gas to Chemicals (GTC).
  g) Gas to solids (GTS).

Furthermore, the substantial (>400 MMSCFD) and moderate (>200 MMSCFD) gas reserves are often required for LNG and CNG, respectively. In contrast, minor gas reserves (200 MMSCFD) are often suited for gas re-injection, GTW, and GTL. While gas re-injection also necessitates substantial infrastructure expenses for the drilling of deep re-injection wells without producing money, GTW required gas reserves with a nearby electricity market.

To maximize the processes, a reliable purification technique must be used before natural gas may be used. Thus, before using natural gas for a variety of applications, purification is necessary. According to Khalilpour et al. [24], the large expenditure needed for pipelines and LNG makes it uneconomical to use the gas from such fields. Moreover, for oil fields having associated gas, using natural gas is a "necessity" rather than an "option". The accompanying gas has typically been flared and/or reinjected. However, the oil and gas industry has reached a point where it is hard to build a new field without addressing the related gas problem as public awareness of the environmental impact of flaring develops. Because to this, intensive research is being conducted to create alternate gas consumption solutions for remote NG monetization. At roughly -161°C and 1 atm, LNG is liquefied natural gas, according to Rojey et al. [9]. Transporting a stranded resource to market is substantially less expensive because to liquefaction, which reduces volume by a factor of almost 600. It is moved in LNG tankers and kept in atmospheric tanks. But CNG is Extremely compressed—typically between 1500 and 4000 psi. Other than through a pipeline, it is kept and moved in pressure vessels in a variety of methods. The ease of its producing method gives CNG an edge over LNG. However, it requires a greater cargo capacity because the volume reduction is less than with LNG [25].
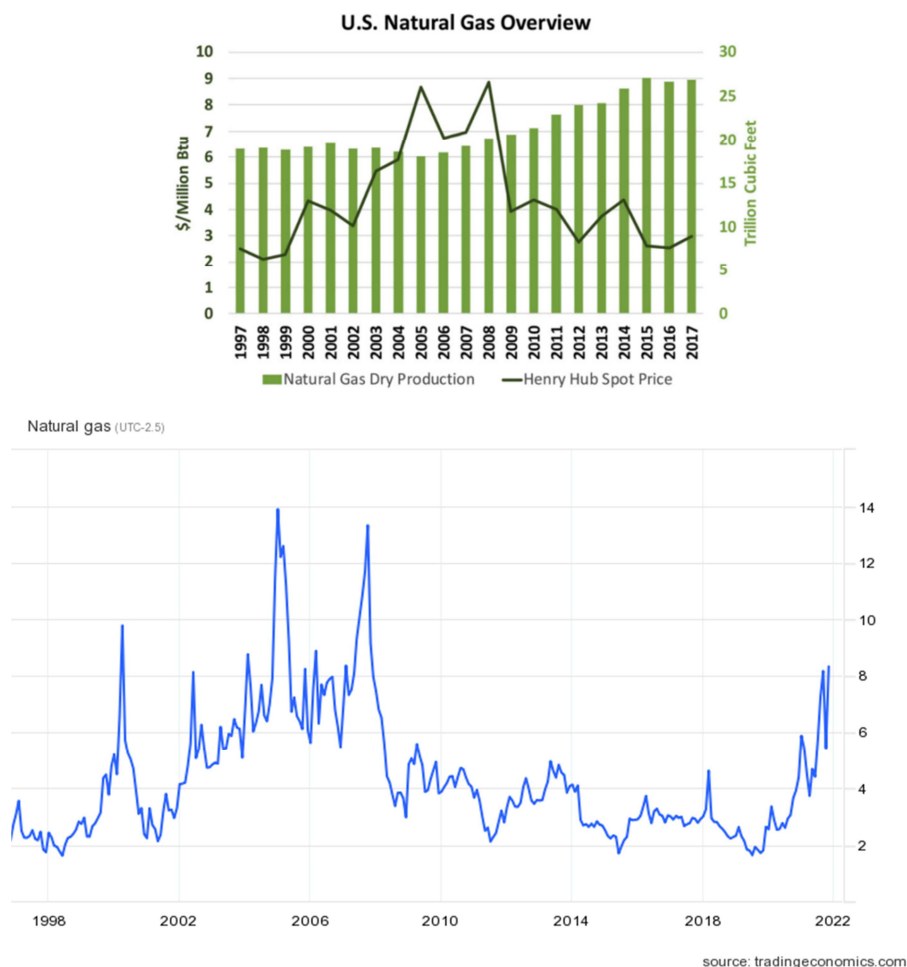
Figure 1. *Trading economics for natural-gas [25].*

Important information regarding the trading of particular items' merchandise is provided through trade profiles. In regard to this research project, Figure 1 shows the trade profile for natural gas during a twenty-four (24) year period, from 1998 to 2022. This zigzag pattern in natural gas trading shows that no certain trade is assured to happen within a particular time range. Nonetheless, the graph reveals that the years with the biggest volumes of natural gas trade were 2001, 2005, and 2008, with 2008. The profile indicates that recent declines in methanol trade. So, it's critical to actively encourage the usage of natural gas rather than fossil fuel for both home and commercial applications.

Figure 2 displays the average price of cooking gas in Nigeria during the previous 27 months per 5 kg of natural gas. A value of roughly 2,000 naira was reported during the first thirteen (13) months; thereafter, a steady price increase was noted each month. This demonstrates that the commodity's price has gone up, which has an impact on whether or not natural gas is used as a fuel source for homes or businesses. This might lead to a preference for fossil fuels over natural gas, despite the latter's detrimental impact on the environment. Thus, there is a need for a review and management of natural gas prices.

Figure 2. Average Cooking Gas-Price in Nigeria [27].

The CNG value chain, according to Friis et al. [28], similarly consists of three stages: compression, transportation, and decompression. During compression, feed NG is chilled to a lower temperature and compressed to a higher pressure. The cold CNG is transported using specially built vessels with containment systems comprised of stacked horizontal or vertical pipes. Furthermore, the high-pressure CNG is decompressed to the necessary pressure (pipeline specification) for feeding the target market once it arrives at the delivery terminal.

According to Tso, Demirhan, et al. [29], natural gas utilization can be accomplished through;

1) Heat and Power Generation.
2) Feedstock for catalysis.

2.7. Natural Gas Purification Technologies

Natural gas must first be sufficiently purified before it can be used for a variety of applications. The technologies used for natural gas purification, which are now accessible, are key. It is important to keep in mind that sweetening natural gas requires the removal of acid gas. Acid gases like CO_2 and H_2S are removed from natural gas using techniques known as acid gas removal or natural gas sweetening. The methods and procedures utilized to treat natural gas include membranes, cryogenic condensation, adsorption procedures, and absorption procedures [1]. The "Membrane Process [1]" is one of the natural gas separation methods that is a practical alternative gas separation method that saves energy and does not require any phase change.

2.8. Effective Selection of Natural Gas Purification Technologies

Because each technique has different benefits and drawbacks, it is crucial to choose the right natural gas purification method. As a result, Dortmundt and Doshi [11]

claimed that the selection of Natural Gas Purification Technologies might be based on fewer considerations, which include the following:

1) The quantity and kind of impurities in the supply gas.
2) The quantity of each impurity in the feed gas and the intended removal capacity.
3) Specifying the pipeline.
4) Operating and capital expenses.
5) How much gas needs to be treated.
6) The preferred selectivity.
7) The gas's hydrocarbon content.
8) The process conditions under which the feed gas is processable.

These important factors listed above should be taken into account when choosing a natural gas purification technology.

3. Natural Gas Purification Processes

Natural Gas Purification Processes includes the following;

1) Absorption Process.
2) Adsorption Process.
3) Cryogenic Process.
4) Membrane Process.

3.1. Absorption Process

According to Shimekit and Mukhtar [1], one of the basic unit activities in the process of purifying natural gas is the absorption process, which involves coming into contact with a liquid in which a component of a gaseous phase is selectively soluble. In a countercurrent tower (column), where liquid descends and gas ascends, absorption is frequently carried out. High gas solubility, high chemical stability, high volatility, high solvent selectivity, low effects on products and the environment, low cost, greater availability, low viscosity, non-corrosive, non-flammable, and low freezing point are the main characteristics of a suitable solvent for the absorption process that satisfy the following general selection criteria. For physical absorption, solubility and mass transfer are essential fundamental concepts, whereas reaction equilibria and reaction kinetics apply to chemical absorption. Using a hot carbonate solution or one of the physical solvents is preferable for situations when CO_2 removal is only needed in large amounts or when only partial removal is needed for economic reasons.

3.2. Physical Absorption

The majority of physical solvent systems are used when the supply gas has a high CO_2 partial pressure and low temperatures, according to Ebenezer and Gudmunsson [30].

Heavy hydrocarbons restrict the use of physical solvents, but they have a higher absorption capacity than chemical solvents. Physical solvent application may also be hampered by low CO_2 partial pressures and low product stream output pressure. The solubility of CO_2 in the solvents is necessary for the physical solvent absorption method of removing CO_2 from the supply gas.

It is possible to remove CO_2 from natural gas using a variety of physical solvent approaches, but not all of them are capable of doing so to the level required by LNG, which is between 50 and 100 ppmv or less than 2.5% CO_2 in the product stream. Physical absorption has a lesser interaction between CO2 and the absorbent than chemical solvents, which reduces the energy needed for regeneration. Heating, pressure reduction, or a mix of the two are all beneficial for solvent regeneration.

3.3. Chemical Absorption

According to Shimekit and Mukhtar [1], chemical absorption techniques are used in natural gas purification plants to remove acid gases like CO_2 from the gas stream through the action of an exothermic reaction of the solvent with the gases. Many alkanolamines are most frequently used as the chemical solvent gas treatment technique for acid gas removal in the natural gas and petroleum processing industries. These approaches use an alkanolamine or an alkali salt in an aqueous solution (hot potassium carbonate processes). Monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) are popular amine-based solvents used in the absorption process. These solvents react with the acid gas (CO_2 and H_2S) to produce a complex or bond. H_2S, CO_2, or SO_2 dissociate when they come into contact with water or an aqueous solution to produce a mild acidic solution that is known as an acid gas. Weak organic bases are what these amines are referred to as. Aqueous alkanolamine solution is routed to the top of the absorber in a typical operation, and a sour gas (H_2S and/or CO_2) is injected into the absorber at high pressure from the bottom and rises up to countercurrently contact it. The amine solution that results, which contains a lot of CO_2, is then moved via heat exchangers to be heated. In order to achieve countercurrent contact with steam at a high temperature and low pressure, the water is then transported to the top of a regenerator (stripper). The lean alkanolamine solution is then passed via the heat exchanger, where it is cooled and then reintroduced at the top of the absorber after the steam has removed the CO_2 and H_2S from the solution [13]. In general, the relatively high heat of acid gas absorption and the requirement for a sizable quantity of heat for regeneration are characteristics of chemical solvent processes.

Table 5. *Comparison of the major acid gas absorption processes* [31].

| | Chemical Absorption | | Physical Absorption |
	Alkanolamine	Inorganic Carbonate	
Type of absorbents	MEA, DEA, DGA, MDEA, DIPA	K_2CO_3, K_2CO_3-MEA, K_2CO_3-DEA	Selexol, Rectiaol, Purisol
Operating gauge pressure, mmHg	Insensitive to pressure	> 10,337.76	12,922.2 – 51,688
CO_2 absorption mechanism	Chemical reaction CO_2: $2RNH_2 + CO_2 + H_2O = 2RNH_3HCO_3$	Chemical reaction CO_2: $Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$	Physical dissolution

	Chemical Absorption		Physical Absorption
	Alkanolamine	Inorganic Carbonate	
Operating temperature, °C	37.78 – 204.44	98.33 – 121.11	Ambient temperature
Absorbent Recovery	Reboiled Stripper	Stripper	Flash, Reboiler, Steam Stripper
Utility Cost	High	Medium	Low to medium
Swing variables (Temperature or pressure)	Temperature principally	Both, but pressure principally	Pressure principally
Selectivity CO_2 vs. ppmv H_2S	Only MDEA selective for H_2S	May be selective for H_2S	Some selectivity of H_2S
Meets ppmv CO_2	Yes	Yes	Yes

3.4. Adsorption

The adsorption process in gas separation operations is described as the adhesion or retention of specific feed gas stream constituents that come into contact with a solid adsorbent's surface due to the force of field at the surface [1]. Yang [32] claims that kinetics-based adsorption systems have been used in the USA to recover methane from landfill gas despite the fact that the adsorption process is rarely used for the bulk separation of CO_2 from CH_4. Methane (50–65%), carbon dioxide (35–50%), carbon monoxide, and trace amounts of sulfur and nitrogen compounds make up the majority of these gases. The adsorbent in this procedure is carbon molecular sieves. With this method, it may be able to recover more than 90% of methane with a purity of 87-89%. The majority of adsorption techniques employ physical adsorption. Compared to chemisorption, physical adsorption uses weaker forces (a combination of Van der Waals and electrostatic forces), which results in lower temperatures and easier regeneration of the adsorbent because no covalent bonds are created. Adsorbed CO_2 has a lower chemical potential than CO_2 that was present in the gas mixture during capture. Physical adsorption occurs at surfaces very quickly, and rather than being governed by the intrinsic rate of the surface process, its kinetics are mostly determined by mass or heat transfer. The surface area to volume ratio of an adsorbent should be high because adsorption is a surface phenomenon. The primary advantage of physical adsorption systems is the low energy need for rapidly replenishing the sorbent material in response to a pressure change. Adsorption techniques have a number of advantages, including simplicity of usage, the relative resistance of molecular sieve beds to mechanical degradation, and the ability to concurrently dehydrate gases and remove acids [33].

Table 6. Showing Typical CO_2 loading capacities of some adsorbents at operating conditions, with CO_2 adsorbate [31].

Adsorbent	T (°C)	P (mmHg)	Loading (mol/kg)	Regeneration Method
Activated carbon	25 – 300	500	1.5 – 2.0 @ 25°C 0.1 - 0.2 @ 250°C	PSA
5A zeolite	25 - 250	500	≈ 3.0 @ 25°C 0.2 @ 250°C	PSA
Titanosilicates	25 - 200	$760 – 6 \times 10^5$	-	PSA
Alumina (doped w/Li_2O)	400	500	0.52	PSA
Alumina (basic)	300	500	0.3	PSA
Li zirconate	500	760	3.4 – 4.5	TSA
CaO	500	150	4 – 8 @ 500°C 7 @ 500°C	TSA
HTlc (K-promoted)	300 - 400	200 - 700	0.4-0.7	PSA
Solid Amine (Supported PEI)	75	760	1.5 – 3.0	PSA
Double-layer hydroxides	375	230	1.5	PSA
Alumina (un-doped)	400	500	0.06	PSA

Other adsorption techniques include;
a) Thermal Swing adsorption.
b) Pressure Swing adsorption.
c) Displacement Desorption.

3.5. Cryogenic Process

According to Ebenezer and Gudmunsson [30], cryogenic separation (also known as low-temperature distillation) uses a very low temperature (-73.30°C) to purify gas mixtures in the separation process. In comparison to the alternative absorption technique, the cryogenic approach is superior at extracting lighter liquids like ethane. The term "cryogenic" describes the process of bringing a gas stream's temperature down to roughly -84.44°C. Although there are various ways to accomplish this work, the turboexpander procedure—which cools the gas stream using external refrigerants—is the most effective. The hydrocarbons in the gas stream are condensed by the expander's capacity to quickly lower temperature while keeping methane gaseous [16]. In order to separate CO_2 from other gases and produce solid or liquid CO_2 particulate matter as well as remove other pollutants, cryogenic separation is used. The core idea behind cryogenics is the condensation of gases. CO_2 splits into liquid and condenses when cooled below its boiling point. When each gas boils into a liquid at a different temperature, differences in boiling points cause the gases to separate; however, the composition of the gas being cooled can also affect separation into pure components [16]. Gas separation membranes are thin films, according to Stern [34], Burggraaf [35], Shekhawat, Luebke et al. [36], that transport gases preferentially across the membrane based on variations in the permeabilities of the species flowing through the membrane. A

membrane's physical and chemical structure, the characteristics of permeant species (such as size, shape, and polarity), and interactions between permeant species are what determine a membrane's gas permeability. High selectivity and high permeability are required of separation membranes. The higher the permeability, and hence the cheaper the cost of the membrane, the less membrane area is needed for a given separation. More product may be recovered as a result of the lower methane waste and improved selectivity ([36, 37]).

Shimekit and Mukhtar [1] claim that membranes and a solvent may be used in another dimension to absorb desired gases such as CO_2, a procedure known as membrane gas absorption. CO_2 diffuses through the membrane's pores in this process and is absorbed by the solvent. The membrane keeps the surface area between the liquid and gas phases constant. This type of membrane is employed when the partial pressure of CO_2 is low, such as in flue gases, because the gas separation driving power is so low. The membrane gas absorption method, in contrast to the gas separation membrane previously described, does not separate CO_2 from other input gases; instead, it serves as a barrier between the liquid and gas with permeability through the pores.

The selection of membranes is based on crucial factors;

A valuable asymmetric morphology with high mechanical strength can be produced from membrane material under challenging thermal and feed mixture conditions. These conditions include:

(a) an intrinsic membrane permselectivity;

(b) the ability of the membrane material to resist swelling-induced plasticization (chemical resistance, which is relatively uncommon but mostly achieved by an inorganic membrane); and

(c) the ability to process the membrane material into such a morphology.

Some other membrane technologies are:

1) Polymeric membranes.

2) Inorganic membranes.

3) Mixed matrix membranes.

Table 7. Technology comparisons for natural gas purification [1].

Process	Advantages	Disadvantages
Absorption	Often used technique for (50–100%) effective acid gas removal (CO_2 and H_2S)	Physical solvents require a high partial pressure, which is not cost-effective.
Adsorption	a. Achieving high product purity is possible. b. The simplicity of moving adsorbents to distant regions when equipment size becomes an issue	a. Product recovery is lower b. Often one pure product
Membrane	a. Simple, adaptable, low-cost operation; b. Stability under high pressure; c. High product recovery; d. Good weight and space efficiency e. Minimal environmental effect	a. Recompression of permeate b. Moderate purity
Cryogenic	a. Comparatively greater recovery than other procedures b. Products with a relatively high purity	a. High energy requirements for regeneration b. Scaling down to a very tiny size is not economically feasible. c. The difficulty of operating under various feed streams because it is an enclosed, highly integrated system.

4. Hybrid Separation Processes for Effective Natural Gas Utilization

In order to effectively utilize natural gas, it is essential to apply hybrid methodologies, and the hybrid natural gas separation process combines one or two natural gas utilization technologies and procedures. Bernardo, Drioli, et al. [38] claim that hybrid separation methods use integration of one process with other separation processes or procedures in which the basic functioning of one process is associated with another physical or chemical process in a single unit operation. A properly built hybrid approach, according to Bernardo et al. [38], will effectively balance the drawbacks of each particular method while amplifying its advantages. Better separation is anticipated as a result, which will enable lower investment and operational costs and ultimately lead to long-term process improvement.

Some Natural Gas Hybrid Separation processes;

1) Membrane-amine hybrid system.

2) Membrane-Cryogenic distillation hybrid system.

3) Membrane integration with other separation processes, such as PSA.

4) A hybrid system comprising Cynara membranes and amine absorption.

Although bulk CO_2 removal with membranes in high-pressure natural gas streams with high CO_2 content has greater economic potential, the technology has a number of disadvantages as compared to other methods, especially when the CO_2 concentration is low. Further procedures (such an amine-based or cryogenic system) might be needed in order to build a hybrid system [39]. As a result, scientists are urged to look for an alternate technology that uses a hybrid separation method to close technological gaps. Some researchers, such as Bhide, Voskericyan, et al. [40], believe that a membrane-amine hybrid would be more cost-effective than an amine system or a membrane system on its own for a variety of situations, including low CO_2 compositions. Furthermore, recent research has shown that another membrane-amine system architecture is commercially viable [41]. For bulk CO_2 removal, membrane techniques paired with another method—most typically amine units—offer a more cost-effective solution than amine technologies. However, because it combines two processes, this method

also has the drawback of being complex [10]. Vu's [42] earlier research included a study using a hybrid membrane-cryogenic distillation system that demonstrates favorable economics as well. A conventional PSA process can benefit from membrane permeation throughout the pressurization and high-pressure adsorption stages because the pressure differential created by the PSA can be used to power the membrane in the PSA cycle's blowdown step [43].

5. Conclusion

According to the study's findings, membrane integration with PSA is typically considered for H_2 separation. Whereas hybrid membranes plus amine absorption are utilized for CO_2 separation. However, it was found that for CO_2 feed concentrations of 5–40 mol%, the membrane process is more cost–effective when compared to the absorption (diethanolamine) method. It is also true that the cost of removing other gases, such H_2S, for single-separation separation processes. In these circumstances, hybrid membrane methods (membranes for bulk separation of CO_2 and H_2S and gas-absorption techniques for purification) are economical. Hence, the cost-effectiveness and extremely efficient operability of the hybrid processes are revealed.

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