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Review Article

# Natural gas origin, composition, and processing: A review

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## ABSTRACT

Natural gas (NG) is a naturally gaseous hydrocarbon mixture that is formed under the earth's surface. NG is considered to be the cleanest fossil fuel and is a safe source of energy when transported, stored and used. The primary constituent of NG is methane, it may also contain ($C_2$+ hydrocarbons, $N_2$, $CO_2$, He, $H_2S$, and noble gases) according to its origin. Different gas processing technologies can be employed to remove constituents other than methane.

Due to importance of NG as a fuel and the increasing global demand of it, this article reviews the fundamentals of NG origin, composition, and processing.

**Contents**

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## 1. Introduction

The term natural gas refers to hydrocarbon-rich gas; it is a gaseous fossil fuel that is found in oil fields, natural gas fields, and coal beds (Carroll, 2010; Speight, 2007).

The first recorded natural gas well was drilled by William Hart, who is considered to be America's "father of Natural Gas," in 1821 in Fredonia, United States. More recently, natural gas was discovered as a consequence of prospecting for crude oil drilling. Throughout the 19th century, natural gas was used locally as a source of light due to the lack of a safe structure for long-distance gas transport. After World War II, natural gas was extensively utilized due to the advances in engineering that allowed the construction of safe, reliable, long-distance pipelines for gas transportation (Kidnay et al., 2011; Speight, 2007, 1993).

In its pure state, natural gas is colorless, shapeless, and odorless. It is a combustible gas, and it gives off a significant amount of energy when burned (Speight, 2015a). It is considered to be an environmentally friendly clean fuel when compared with other fossil fuels (coal and crude oil). The combustion of fossil fuels other than natural gas results in the emission of enormous amounts of compounds and particulates that have negative impacts on human health (EIA, 1999). However, during natural gas combustion, the emissions of sulfur dioxide are negligible and emissions of nitrous oxide and carbon dioxide are lower, which consequently helps to reduce problems associated with acid rain, the ozone layer, or greenhouse gases (BP Technology Outlook, 2015; Ramanathan and Feng, 2009). The global shift from fossil fuel to natural gas for power improves the energy efficiency and represents a future of lower carbon emissions. That may be achieved through the development of carbon capture and storage technology that permits the mitigation and utilization of carbon dioxide (BP Technology Outlook, 2015; EIA, 2013; Speight, 2007).

According to the BP Statistical Review of World Energy (2015), the total worldwide proved reserves of natural gas were 187.1 trillion cubic meters (tcm) at the end of 2014, with a growth of approximately 0.3% compared with the end of 2013 (186.5 tcm), Fig. 1.

In 2014 (BP Statistical Review of World Energy, 2015), the production of world natural gas is increased by 1.6%, which is higher than the global consumption growth rate by about four times (+0.4%). Production and consumption growths were below the average in all regions, except North America for the former and Middle East and North America for the later, Fig. 2.

Natural gas is a very safe source of energy when transported, stored, and used. It has been used for residential, commercial, and industrial heating. Additionally, it is used for generation of heat and electricity. In the petrochemical industry, it is used as a feedstock or raw material, e.g., in the production of ethylene. In the fertilizer industry, it is used for ammonia production. Hydrogen, sulfur and carbon black can be produced using natural gas (Mokhatab et al., 2006; Schoell, 1983; Tabak, 2009).

Globally, natural gas accounts for 23.7% of primary energy consumption (BP Statistical Review of World Energy, 2015). The expected growth of the global natural gas demands is 1.9% per annum over the BP Energy Outlook (2015). The usage by the power and industrial sectors accounts for over 80% of the growth in the global demand for natural gas, Fig. 3.

## 2. Natural gas origin

Natural gas originates from any one or more of three major processes: thermogenic, biogenic, and abiogenic processes (Gold, 1985; Pusey, 1973).

### 2.1. Thermogenic process

This process involves the relatively slow decomposition of organic material that occurs in sedimentary basins under the influence of the temperature and pressure with associated with increased depth. As a result of this decomposition reaction, natural gas (also called *thermogenic* methane) and petroleum are presumed to be formed (Speight, 2007).

Living organisms degrade debris from organisms. In an anaerobic environment, the degradation is slow and incomplete. The residues accumulate in the sediments as complex macromolecules structures known as kerogen (Durand, 1993). The thermal degradation of kerogen generates hydrocarbons, non-hydrocarbon compounds such as $CO_2$, $H_2S$, $H_2$, $H_2O$ and $N_2$, and a residue called pyrobitumen, which is very rich in carbon (Tissot and Welte, 1984). The process of kerogen conversion resulting in the formation of oil followed by thermal gas is called *maturation*.

Gas is derived from two types of kerogen (Clayton, 1991):

a. *Labile kerogen*, which can generate both gas and oil with mass ratio of ~0.2 in the temperature range between 100 and 150 °C.
b. *Refractory kerogen*, which generates gas at temperatures between 150 and 220 °C.

### 2.2. Biogenic process

In this process, methane is formed by the action of living organisms (methanogenic bacteria) on organic materials during the

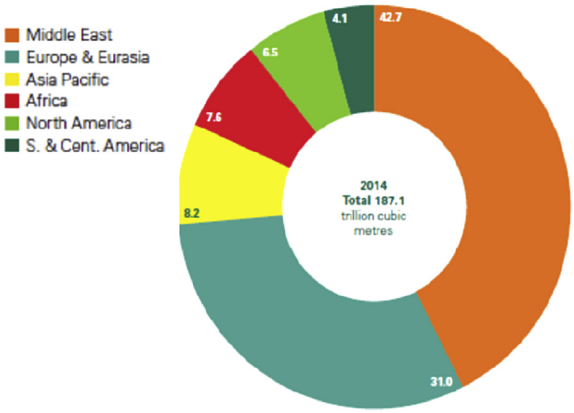

**Fig. 1.** Distribution of world natural gas proved reserves (source:BP Statistical Review of World Energy, 2015).

deposition of the sediments and in the early part of their burial (Gold, 1985; Ourisson et al., 1984; Rice, 1992). The methanogens are abundant in habitats where electron acceptors such as $O_2$, $NO_3^-$, $Fe_3^+$, and $SO_4^{2-}$ are limiting. Common habitats of methanogens include anaerobic digesters, anoxic sediments, flooded soils, and gastrointestinal tracts (Speight, 2007; Whitman et al., 2006).

The methanogenesis from oil or coal involves different process through the action of various groups of micro-organisms (Aitken et al., 2004; Schink, 1997; Zengler et al., 1999):

1 Acidogenesis: through the action of the heterotrophic bacteria that hydrolyze the large, complex organic polymers to produce smaller and simpler substrates, e.g., sugars, volatile fatty acids, and alcohols.

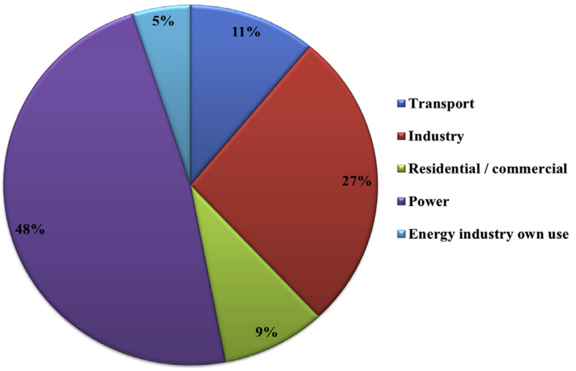

**Fig. 3.** Global gas demand by sector (source: IEA, 2015c).

2 Acetogenesis: through the fermentation of the produced simple substrates by the action of syntrophic bacteria to produce acetate, format, $H_2$, and $CO_2$.
3 Methanogenesis: through the formation of methane from the fermented product by the action of methanogenic Archaea.

For petroleum exploration; the distinction between thermal and bacterial gas is necessary. In a thermal gas basin, oil must form at first, but this is not the case in a bacterial gas basin. Therefore, the exploration techniques must be planned differently (Rojey et al., 1997).

### 2.3. *Abiogenic process*

In this process, the starting material is the volcanic gases (not the organic matter). Methane is formed by the reduction of carbon

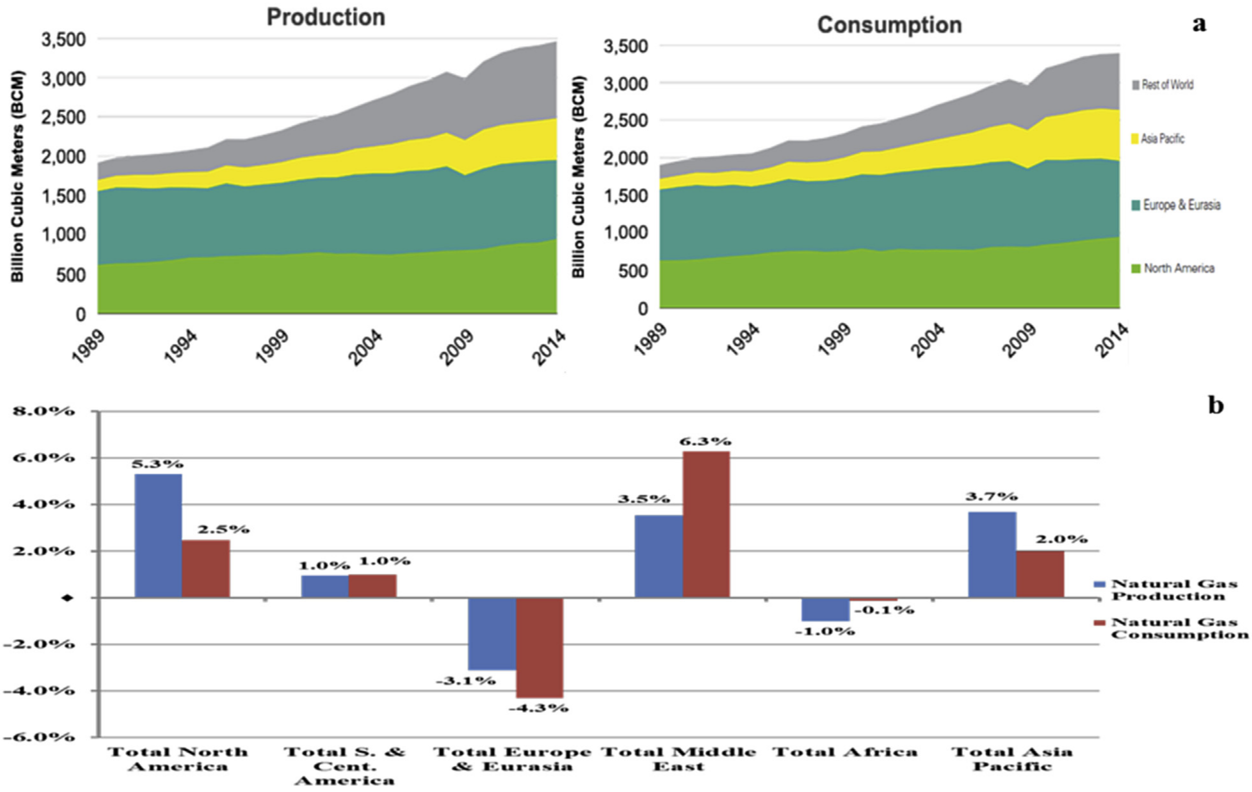

**Fig. 2.** (a) World natural gas production and consumption by region, (b) changes of production and consumption in 2014 over 2013 (source: BP Statistical Review of World Energy, 2015).

dioxide during magma cooling, commonly in hydrothermal systems during water-rock interaction (Gold and Soter, 1982; Rojey et al., 1997; Sherwood Lollar et al., 2002).

## 3. Natural gas reservoirs

A gas reservoir is a naturally occurring storage area; it consists of permeable and porous rocks (often sandstone) surrounded by impermeable materials. Natural gas is formed underneath the surface; it migrates through the underground faults and fissures until reaching the reservoir (Speight, 2007; Wang and Economides, 2009). The porous rocks in the reservoir contain the gas, and it is prevented from escaping upward or laterally by the impermeable rocks that form an effective seal (Speight, 2007). Natural gas reservoirs exist in many forms, such as a dome (syncline-anticline) structure (Speight, 2007); Fig. 4.

## 4. Classification of natural gas

Natural gas can be classified according to its origin and chemical composition (Rojey et al., 1997; Kidnay et al., 2011; Speight, 2007; Tagliabue et al., 2009), Fig. 5.

### 4.1. Classification according to the origin

#### 4.1.1. Conventional gas

Conventional gas (Speight, 2007) occurs in deep reservoirs that are either associated with crude oil (*associated gas*) or contain little or no crude oil (*non-associated gas*).

- ***The associated gas*** coexists in the reservoir rock with an oil reservoir. It may be present in different forms as *solution gas* in the oil (*dissolved gas*) or as *gas-cap gas*, lying above the oil reservoir (*casing head gas*).

Associated gas (also called *wet gas*) is usually leaner in methane and richer in higher molecular weight paraffinic constituents. The gas stream traditionally (*rich gas*) has high proportions of *natural gas liquids* (NGLs), which contain ($C_2$+ product). The ($C_5$+ product) constituents are commonly referred to as *natural gasoline* or *gas condensate*.

- ***The non-associated gas*** (also called gas well gas or dry gas) is produced from a geological formation that typically does not contain much, if any, crude oil or hydrocarbons (gas liquids) that are higher-boiling than methane. This gas is usually richer in methane and markedly leaner regarding the higher molecular weight hydrocarbons and condensate materials. It also may contain non-hydrocarbon gases, such as carbon dioxide and hydrogen sulfide (Speight, 2015b). It should be noted that, after gas processing, methane will be produced in a pure state regardless of whether the raw gas state was associated or non-associated (Mokhatab et al., 2015).

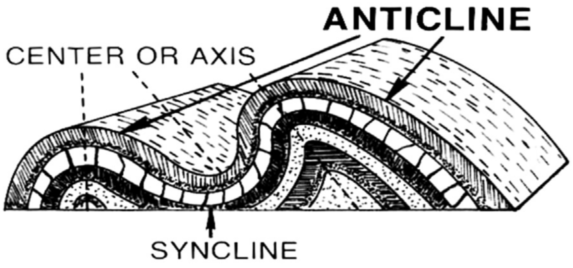

**Fig. 4.** Syncline-anticline structure diagram (source: http://en.wikipedia.org/wiki/File:Antecline_%28PSF%29.png).

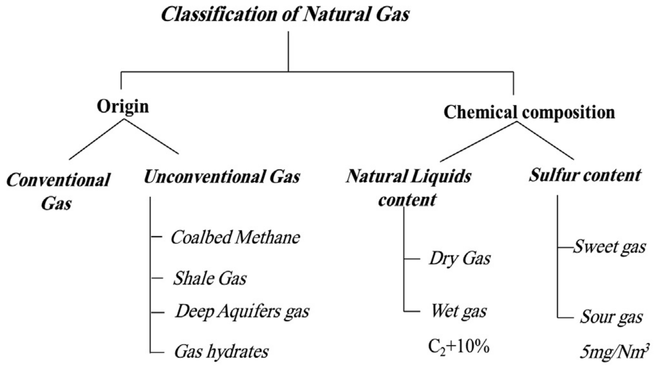

**Fig. 5.** Natural gas classification schematic diagram.

#### 4.1.2. Unconventional gas

Several types of unconventional gas are found, such as, shale gas, coal-bed methane, deep aquifer gas, and gas hydrates.

- ***Shale gas*** is found in low-permeability shale, impermeable (tight) sandstone, siltstones, sandy carbonates, limestones, dolomite, and chalk reservoirs. The methane produced from these reservoirs is not associated with oil (Speight, 2013).

Shale gas can be originated from thermogenic, biogenic and/or mixture between the pathways (Prinzhofer and Battani, 2003). This is as in the cases of Upper Devonian New Albany Shale in the Illinois Basin (Martini et al., 2008; Schlegel et al., 2011a, 2011b) and shallow aquifers, southwestern Ontario, Canada (Hamilton et al., 2015; McIntosh et al., 2014). The origin of the natural gas in the shale basins have been approved using the stable isotopes combined with hydrogeochemistry characteristics. Understanding the gas origin may result in the development of methane production and exploration and some cases stimulation (Martini et al., 2008; Schlegel et al., 2011a, 2011b).

Stimulation techniques or enhancing microbial methane production may be applied for the areas of low biodegradable organic matter (McIntosh et al., 2002; Schlegel et al., 2011a, 2013, 2011b; Strąpoć et al., 2010). Although, stimulation techniques of methane production can be applied to deep or thin unmineable coal deposited, gas-depleted from shales and coal waste materials (Ritter et al., 2015). Meslé et al. (2012) stated that biostimulation techniques are a reliable method that can be used for the detection of methanogenic consortia in organic-rich rocks. They reported the presence of live methanogenic consortia in shale rocks and their ability to produce methane.

- ***Coalbed methane*** (also known as coal mine methane) is found in coal seams and is formed during the coalification process. *Thermogenic coal-bed methane* is formed by the action of increasing temperature and pressure in the buried organic matter that is slowly transformed into coal. Bacterial processes form another type known as biogenic coal bed methane in the thermally immature coals; Fig. 6. The major constituent of the gas produced from the coal bed is methane, with minor amounts of ethane, carbon dioxide, nitrogen, hydrogen sulfide, and sulfur dioxide (Flores, 1998; Moore, 2012; Speight, 1993).

A case studied is the Velenje Basin (Kanduč and Pezdic, 2005;

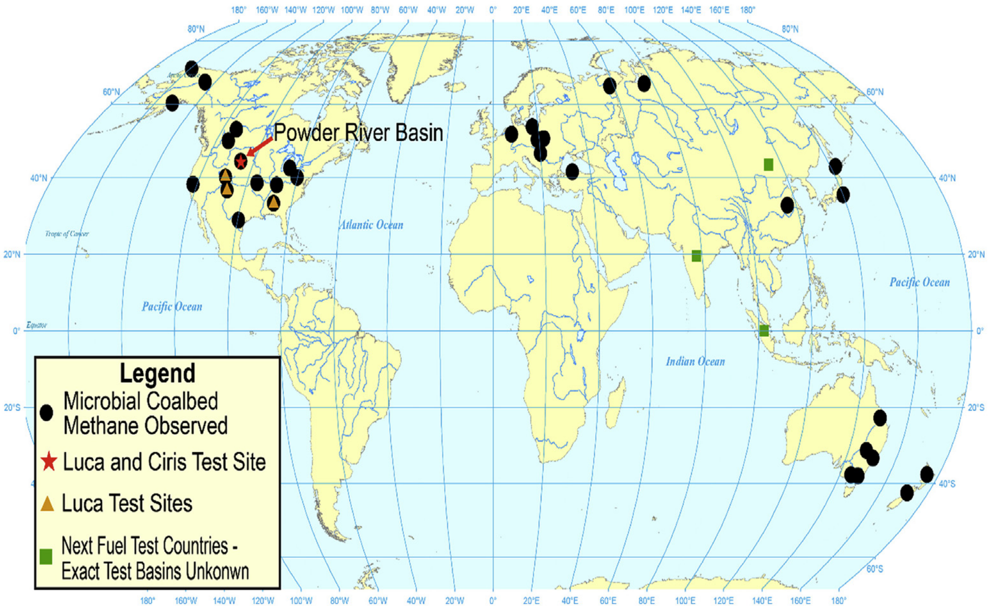

**Fig. 6.** Map showing global microbial coal bed methane production (for more details see (Strąpoć et al., 2011)), and pilot test locations (Ritter et al., 2015), (reproduced from Ritter et al., 2015; under the licenses of Elsevier).

Lazar et al., 2014; Kanduč et al., 2012); the authors used the stable isotopes, and carbon dioxide-methane index (CMDI) to decipher the origin of gases in this basin (see Section 4.1.3.1). For methane in this dynamic coalbed system, several aspects are considered such as distance from the longwall, rate of advancement of the longwall, depth of the excavation field, pre-mining area and stress state (Lazar et al., 2014).

Each excavation filed in the Velenje Coal Mine has its own gas characteristics (both methane and $CO_2$ origin and concentration). Since it migrates faster than $CO_2$, methane can accumulate as a free gas at the subsurface within the water-saturated layers of the basin, while $CO_2$ is retained in the coal bed structure or dissolved in water. Also, both methane and $CO_2$ can be adsorbed on the microporous structure of the coalbed (Kanduč and Pezdic, 2005). It is essential to monitor the concentration of methane and $CO_2$ at the working faces to prevent the possible risk of hazardous explosions, as they are considered as powerful greenhouse gases. Although, gases monitoring allows the reduction of methane emission as it can be utilized and used as an energy source (Kanduč et al., 2012). In conclusion; CBM exploration and production depend mainly on the accurate estimation of reservoir characteristic; percent of gas saturation, coal permeability, and continuing of the primary seam (Moore, 2012).

- ***Deep aquifers gas*** is found during gas migration through the aquifers to the reservoir rocks; the aquifers are then largely saturated with methane. The solubility of methane in water is low, so the aquifer gas content is influenced greatly by the pressure, salinity and temperature.
- Gas hydrates

Clathrate hydrates are crystalline cell of hydrogen-bonded water molecules (ice-like water lattice) in which gas molecules are trapped in their cages. At different conditions of temperature and pressure, all gases can form hydrates (Makogon, 2010).

The hydrate crystals are formed through the nucleation step followed by crystal growth from the nuclei. In the first step, a nucleation seed is formed and is unstable until it reaches its critical size. Nuclei are represented by seeds that have a particular size. The time required for the nuclei formation is called the incubation time. Once the nuclei are formed, the growth of gas hydrate crystals can be developed (Rojey et al., 1997). Many factors affect the formation and dissociation of natural gas hydrates, such as gas composition, temperature, pressure, the salinity of the water reservoir, and the nature of the porous medium in which they have formed (Makogon, 2010). Methane hydrate is mainly formed by the microbial reduction $CO_2$ from organic matter in the shallow sedimentary basins (Kvenvolden, 1995). In some cases, a mixed (thermogenic and biogenic) origin could be obtained (Moritz et al., 2015).

Methane hydrate, which is known as "***the ice that burns***," is commonly found in marine environments (deep-sea sediments), terrestrial deposits in Polar Regions hosted in sediments within and beneath the permafrost, and sometimes in deep lake sediments. Different resources found for the production of methane hydrate are represented by the *"Methane Hydrate Resource Pyramid"* (Boswell and Collett, 2006; DOE/NTEL, 2011; Speight, 2007; Wuerthner, 2012); Fig. 7.

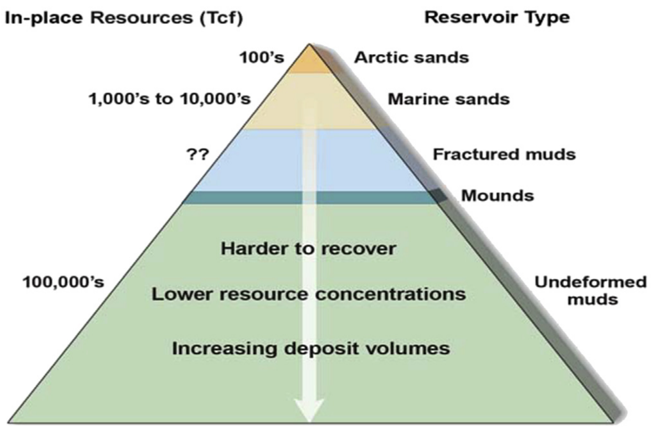

**Fig. 7.** The methane hydrate resource pyramid; (source: DOE/NETL, 2011).

According to BP Technology Outlook (2015), methane hydrate recovery may account for 5% or more of world gas production by 2050. This can be achieved if private and public sectors working on the development of the extraction technology make it safer and more profitable.

### 4.1.3. *Gas origin characterization methods*

Different methods are proposed to characterize and differentiate between the different sources of the produced methane. Some of these methods are listed below.

*4.1.3.1. Stable isotopes.* Stable isotope techniques can be used to distinguish the origin of gas.

- ***Carbon isotopes***

The carbon isotopic ratio of natural gas is related to its formation processes and the degree of maturation of the organic matter, but it is not affected by gas migration. Migrated gas from a more mature source has higher $^{13}C$ concentrations compared with indigenous methane. Using $^{13}C$ contents, gas types can be distinguished as follows (Schoell, 1983):

a Bacterial gas has $\delta^{13}C$ values that are more negative than $-60‰$ (‰ is per-mille) on the PDB (Pee Dee Belemnite) scale.
b Thermogenic gas has $\delta^{13}C$ values that are more positive than $-60‰$.
c Gas with a mixed origin has $\delta^{13}C$ values between $-60$ and $-50‰$.

- *Nitrogen Isotopes*

Nitrogen is one of the proteins constituents in microorganisms and marine water plants. Sediments are enriched in nitrogen as a result of metabolism and microorganisms' death. Nitrogen stable isotopes ($\delta^{15}N$) values are indications of the organic matter mineralization. It could be used to interpret the origin of nitrogen formation in natural gas, Table 1 (Zhu et al., 2000).

Many researches had been used nitrogen stables isotopes to interpret the origin of gases in natural gas (e.g. Kanduč et al., 2012; Kotarba and Keisuke Nagao, 2015; Lazar et al., 2014; Liu et al., 2012b; Quan et al., 2013; Zhu et al., 2000). For Velenje Basin (Kanduč et al., 2012) as an example, the value of $\delta^{15}N$ ranged from 1.8 to 4.6‰ indicate that gas formation and early diagenesis of the Velenje lignite are greatly influenced by biogeochemical process and original floristic ingredients.

- Noble gas isotopes

Measurements of stable isotopes and noble gas isotopes provide valuable information about the gas origin as well as its dynamic behavior from generation in the source rock to accumulation in the reservoir. Due to their chemical inertness (Ballentine and O'Nions, 1994), noble gas isotopes can be used as precise tracers for source and physical processes associated with segregation in the reservoir systems.

Nobel gases can be classified as (Prinzhofer and Battani, 2003).

- **Fossil isotopes**, which were generated during the formation of the solar system. They can be transferred from the atmosphere to the hydrocarbon fluid by solubilization in water recharge and then exchanged and fractionated between crustal fluids (gas, oil and water).
- **Radiogenic isotopes**, which are formed during the radioactive decay of radioactive material.
- **Nucleogenic isotopes**, which are formed through nuclear reactions as $(\alpha,n)$ or $(n,\alpha)$ on nuclei of Li, Mg, F, O, etc.

Some isotopes produced by natural radioactivity represent geological "clocks" (e.g., $^{4}He$ and $^{40}Ar$). Hydrocarbon residence time in the reservoir can be quantified using the ratio of radiogenic (or nucleogenic) concentration to fossil concentration (Prinzhofer and Battani, 2003).

Nobel gas isotopes can also be used as inert tracers for leakage from the reservoir either through caprocks or aquifers. Because noble gases form a series of different sizes from lighter (helium) to heavier (xenon), trace leakage phenomena can be followed. This can be followed by either measuring the concentrations of different noble gases or by the ratio of the contents of two noble gases of different sizes (heavy compound/light compound). Thus, in a leaking system, a decrease in (e.g., He) concentration will be noticed, and the ratio (e.g., Xe/He) will increase (Prinzhofer and Battani, 2003).

For a mixed gas origin (biogenic and thermogenic) due to migration, the use of carbon isotope techniques by themselves will not provide an accurate prediction of the migration process. However, because noble gases will not be affected by hydrocarbon mixing processes, they may provide a precise direction of migration (Prinzhofer and Battani, 2003). Hunt et al. (2012) stated that the noble gas technique is a powerful tool for geochemical fingerprinting and post-genetic processing of natural gas. Additionally, it represents a unique tool that can be used for monitoring and evaluating fugitive gases in shale gas production.

- ***Clumped isotopes***

For systems where gas has migrated, resulting in a mixture of gases with different environments, Stolper et al. (2014a, 2014b) were the first who developed the combined clumped isotopes technique for methane. Clumped isotopologues are molecules that contain more than one rare isotope (Eiler, 2007, 2013), each having its own physical and chemical characteristics.

Moritz et al. (2015) stated that, to define the exact source of the gas, additional analysis should include the $\delta^{13}C$ signatures of ethane and propane and the $\delta^{2}H$ signature of methane. By examining different resources of shale gas, they stated that methane levels are controlled by bedrock composition, redox conditions, water flow

**Table 1**
Nitrogen stable isotopes ($\delta^{15}$ $N_{N2}$) values as an indication of $N_2$ formation origin (Zhu et al., 2000).

| $\delta^{15}N_{N2}$ values | $N_2$ origin |
|---|---|
| $-19‰ \le \delta^{15}N_{N2} \le -10‰$ | Sedimentary organic matter at the immature and the early mature stage (*Ro**<0.6%). |
| $-10‰ \le \delta^{15}N_{N2} \le -2‰$ | Mature (including high mature) sedimentary organic matter (*Ro* ≈ 0.6–2.0%). |
| $-2‰ < \delta^{15}N_{N2} < +1‰$ | The deep crust or mantle. |
| $\delta^{15}N_{N2} = 0‰$ and $N_2/Ar = 38-84$ | The atmosphere is the origin. |
| $+1‰ \le \delta^{15}N_{N2} < +4‰$ | The ammonium clay minerals in shales and mudrocks during metamorphism. |
| $\delta^{15}N_{N2} = +4‰$ | Saltpeter in evaporates. |
| $+4‰ < \delta^{15}N_{N2} \le +18‰$ | Post-mature sedimentary organic matter (*Ro*>2.0%). |

* Ro is the Vitrinite reflectance (see Section 4.1.3.7).

patterns, and residence time. Natural faults could be preferred pathways for gas migration.

- ***Carbon and hydrogen isotope fractionation***

Methane can be generated by the action of methanogens, either via acetate formation or via $CO_2$ reduction. Methanogens are thought to fractionate carbon and hydrogen isotopes differently during these two metabolic pathways. Metabolic pathways can be distinguished using the carbon isotope approach through the comparison of fractionation values between $CO_2$ and $CH_4$, which is written as $\delta^{13}C_{CO2-CH4}$ (Schoell, 1980; Whiticar, 1999; Whiticar et al., 1986).

The origin of $CO_2$ in coalbed methane can be interpreted by isotopic composition of $CO_2$ combined with carbon dioxide-methane index (CDMI) $[(CO_2/CO_2 + CH_4)\cdot 100\%)]$ (Kotarba, 2001; Kotarba and Rice, 2001; Smith and Pallasser, 1996). The illustrated types of $CO_2$ are (Lazar et al., 2014; Kanduč and Pezdic, 2005):

1. Endogenic $CO_2$; typical values of $\delta^{13}C_{CO2}$ around −7.0‰ and CDMI index (>90%).
2. $CO_2$ from carbonate mineral dissociation; where $\delta^{13}C_{CO2}$ value between −10.0 and −6.0‰, depending on the $\delta^{13}C$ value of the carbonates and its degradation temperature.
3. $CO_2$ from biodegradation of organic matter; characterized by low CDMI index due to the low $CO_2$ content (>about 5.0. %), and the $\delta^{13}C$ value is up to around +18.0‰.
4. $CO_2$ from headwaters recharging the basin (Kanduč and Pezdic, 2005). A wide range of $\delta^{13}C_{CO2}$ is obtained if the gas of mixing origin and if the gas is migrated from coal microporous structure (Smith and Gould, 1980).

*4.1.3.2. Hydrocarbon gas concentrations.* The ratio of methane to the sum of higher hydrocarbons (e.g., C1/(C2+C3)) can be used as a source indicator related to gas wetness. Thus, this ratio can be used to differentiate between thermogenic and biogenic gases. This is because thermogenic gas contains higher amounts of hydrocarbons (ethane, propane, and other hydrocarbon gases), whereas biogenic gas contains mainly methane. Thus, for a biogenic gas source, (C1/(C2+C3)) > 1000, whereas for a thermogenic source, (C1/(C2+C3)) < 100 (Golding et al., 2013; Schoell, 1980; Strąpoć et al., 2008; Whiticar, 1999), Fig. 8.

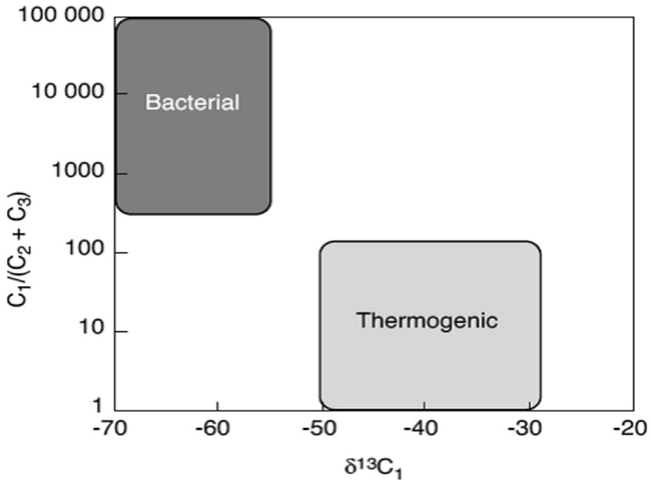

**Fig. 8.** Distribution of genetic signature of natural gas (bacterial *versus* thermogenic) (source: Prinzhofer and Battani, 2003).

The gas wetness and/or $\delta^{13}C$ signature of methane can be varied through three processes:

a. Methane oxidation by methanotrophs results in increased $^{13}C$ in the produced gas and a decrease in the C1/(C2+C3) ratio.
b. Gas migration results in the diffusion of the gas through the bedrock. Methane is lighter than higher hydrocarbons, so it can diffuse faster through the bedrock, resulting in an increase in (C1/(C2+C3)) and a slight effect on the $\delta^{13}C$ signature of methane.
c. Mixing of different sources.

*4.1.3.3. Microbial identification characterization.* To characterize the metabolic process in a complex microbial system, a combination of analytical chemistry, physiological, and molecular biology experiments must be integrated. Some of the powerful techniques listed for identifying the microbial constraints are 16S rRNA phylogenetic surveys and functional gene detection in community DNA (Strąpoć et al., 2011).

*4.1.3.4. Formation temperature.* Gas formation processes are kinetically controlled by the composition of organic matter, time, and temperature. The thermogenic gas formation temperature is between 157° and 221 °C within a nominal gas window, whereas the temperatures of biogenic gas formational environments are <50 °C (Clayton, 1991).

*4.1.3.5. Crushed core analysis.* Exploration strategies for methane production from coalbed and shale basins are affected by the early identification of methane formation processes. These processes could be predicted even before the formation of fluids and the availability of produced gas samples through the markers obtained in crushed core analysis. This analysis includes the composition of crushed gas, especially contents of $CO_2$, $\delta^{13}C_{CO2}$, $\delta^{13}C_{CH4}$ and $\delta^{13}C_{C2H6}$, and coupled total organic carbon (TOC) and total gas content (TGC) analyses. High $\delta^{13}C_{CO2}$ values (>5‰) from elevated $CO_2$ contents in crushed core gases are the most useful markers for microbial gas. Despite the sample depth and organic carbon content, microbial gas cores have more total gas absorbed compared with thermogenic gas cores (Martini et al., 2008).

The hydrogeological data recharge history, and salinity patterns of fluids in fractured black shale and coalbeds may provide a guide to areas that are enriched in microbial methanogens, and they may also guide future drilling efforts (Martini et al., 2008).

*4.1.3.6. Hydrochemistry.* Formation water is naturally occurring water present in large volumes in oil and gas reservoirs, it is associated with the process of oil and gas formation (Satter et al., 2008). The myriad amount of organic matter present in the formation water in both coalbed and shale may act as substrates for methane production via microbial methanogenesis (Jones et al., 2010). Specifying the type of formation water organic matter that drive the microbial methanogenesis to produce, may predict the places of gas accumulation, and provide insight of microbial methane production pathway (Orem et al., 2010, 2014).

High concentrations of chloride and sulfate in coalbed methane (CBM) produced waters are major factors of inhibiting the extent of methanogenesis (Lovley and Klug, 1982). Typically, total dissolved salts (TDS) and salinity values in CBM-produced water increase with depth and distance from recharge zones (Bates et al., 2011; Cheung et al., 2009; Draper and Boreham, 2006; Kinnon et al., 2010; Rice et al., 2008).

Dissolution of carbonate and organic matter degradation are the main sources of dissolved inorganic matter (DIC) in ground water.

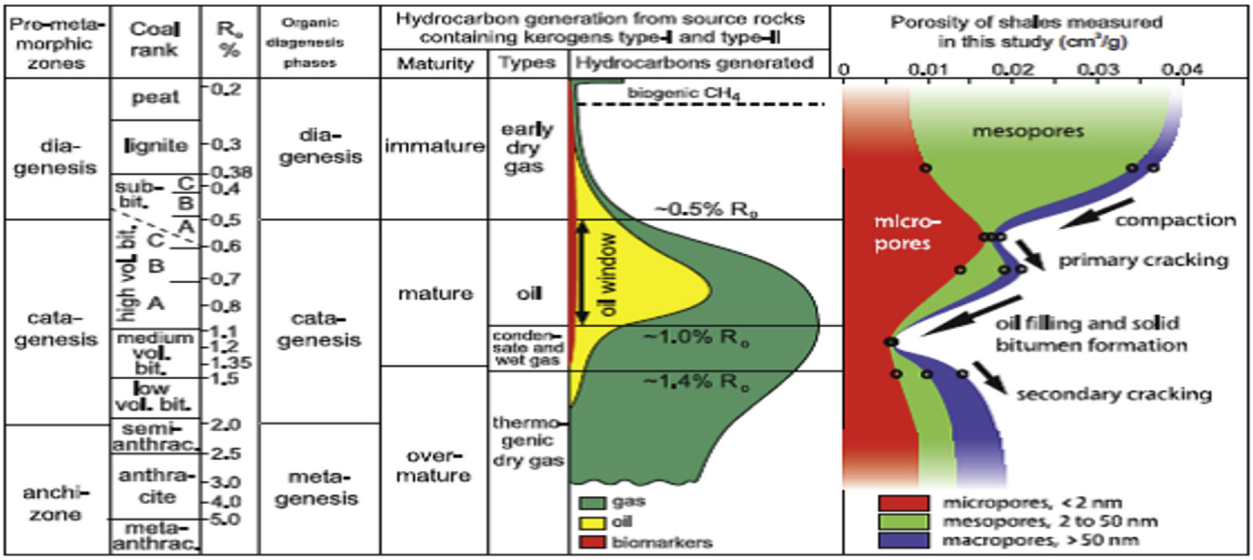

**Fig. 9.** Schematic diagram represents the effect of source rock porosity on the maturation and hydrocarbon generation (Mastalerz et al., 2013).

**Table 2**
General composition of wet and dry natural gas (adapted from Speight, 2015a).

| Constituents | Composition (vol%) | |
|---|---|---|
| | Wet | Dry |
| **Hydrocarbons** | | |
| Methane | 84.6 | 96.0 |
| Ethane | 6.4 | 2.00 |
| Propane | 5.3 | 0.60 |
| Isobutane | 1.2 | 0.18 |
| n-butane | 1.4 | 0.12 |
| Isopentane | 0.4 | 0.14 |
| n-Pentane | 0.2 | 0.06 |
| Hexanes | 0.4 | 0.10 |
| Heptanes | 0.1 | 0.80 |
| **Non-hydrocarbons** | | |
| Carbon dioxide | $\leq$5 | |
| Helium | $\leq$0.5 | |
| Hydrogen sulfide | $\leq$5 | |
| Nitrogen | $\leq$10 | |
| Argon | $\leq$0.05 | |
| Radon, Krypton, Xenon | Traces | |

These actions produce typically negative $\delta^{13}$C-DIC values $-10$‰ (Carothers and Kharaka, 1980; Clark and Fritz, 1997; Golding et al., 2013; Osborn and McIntosh, 2010; Sharma and Baggett, 2011; Sharma and Frost, 2008; Whiticar et al., 1986). If methanogenesis in coal and shale systems is active, isotopically light $CH_4$ and $^{13}$C-enriched $CO_2$ are produced, resulting in positive $\delta^{13}$C-DIC values (Harrison et al., 2006). Therefore, the presence of microbial methanogenesis in organic-rich gas reservoirs can be detected through an increase in $\delta^{13}$C-DIC with the alkalinity of the produced water (Golding et al., 2013; Rice and Claypool, 1981; Schlegel et al., 2011a).

*4.1.3.7. Thermal maturity.* The thermal maturity (Strąpoć et al., 2011) of the source rocks is the degree of degradation of organic matter under geothermal conditions. It can be measured by vitrinite reflectance (*R*o), which is a percentage of the incident light reflected from a polished surface of maceral vitrinite measured with a reflected light microscope using an oil immersion objective. In addition, the **transformation ratio (TR)** is the level of conversion of organic matter into hydrocarbons during thermal maturation. It can be expressed as a fraction (values from 0 to 1), where a value of 1 designates complete conversion.

Thermal maturity can be divided into (Schimmelmann et al., 2006; Strąpoć et al., 2011; Waples and Marzi, 1998).

1. *R*o~0.5%, associated with early thermogenic gas generation (immature rock)
2. *R*o~0.7%, when thermogenic gas production from coal reaches 0.1 times the transformation ratio (TR) (mature rock)
3. *R*o between ~0.7% and 1.6%, when major thermal cracking to gaseous hydrocarbons in coal reaches a TR of 0.8
4. *R*o between 2.5 and 5%, when gas production continues well into the anthracite (over-mature)

Fig. 9 shows the effect of source rock porosity on the maturation and hydrocarbon generation. Mastalerz et al. (2013) reported that increasing maturity changes the total porosity and total pore volume, consequently changing the pore size distribution and relative proportions of micropores, mesopores, and macropores in the source rock.

### *4.2. Classification according to chemical composition*

#### *4.2.1. Hydrocarbon content*

Natural gas may be classified according to the hydrocarbon content of the produced gas. *Dry gas* (*unassociated gas*) consists of methane as the major constituent with little or no $C_2+$ component, whereas *wet gas* (*associated gas*) contains $C_2+$ constituents higher than 10 vol% (Rojey et al., 1997).

#### *4.2.2. Sulfur content*

Natural gas can also be classified according to the amount of sulfur content (generally $H_2S$) in the produced gas (Carroll, 2010; Kidnay et al., 2011; Rojey et al., 1997; Speight, 2007, 2015b). In this classification, the natural gas could be sweet or sour. Sweet gas contains no or a negligible amount of $H_2S$, whereas sour gas contains unacceptable quantities of $H_2S$ (more than 5 (mg/Nm$^3$)) (Maddox, 1974).

## 5. Natural gas composition

According to the reservoir from which the natural gas is extracted, its composition will vary. Natural gas may contain different hydrocarbon and non-hydrocarbon constituents; consequently, the gas composition is never constant. Table 2, illustrates the typical natural gas composition (Speight, 2015a).

### 5.1. Hydrocarbon constituents

Methane may associate with paraffinic hydrocarbons such as ethane, propane, the butanes and a small proportion of $C_5+$ hydrocarbons. It also may contain some aromatics such as benzene, toluene, and xylenes (Mokhatab et al., 2006).

### 5.2. Non-hydrocarbon constituents

The non-hydrocarbon constituents of natural gas can be classified as diluents, contaminants and solid matter (Kidnay et al., 2011; Rojey et al., 1997; Speight, 1999).

**The diluents** are noncombustible gases (such as $CO_2$, $N_2$, He) that reduce the heating value of the gas (Speight, 2014). It could be used as fillers when it is necessary to reduce the heat content of the gas (Kidnay et al., 2011).

- ***Different mechanisms that can produce carbon dioxide***:
  - During sedimentation, by the action of anaerobic bacterial degradation of organic debris in recent sediments through a biochemical mechanism (Tissot and Welte, 1984; Strąpoć et al., 2011).
  - The organic mechanism, involving the reaction between the residues resulting from kerogen degradation (hydrocarbons and carbonaceous) with water at extreme depth. It could also be produced at very great depth during the reduction of sulfates by hydrocarbons (Machel, 2001).
  - The inorganic mechanism, involving thermal decomposition of carbonates at temperatures above 200 °C (Hunt, 1979).
- ***Nitrogen*** may be produced in natural gas in different ways:
  - Through bacterial reduction of nitrates dissolved in water (present in soils and sediments).
  - Through thermal degradation of organic matter.
  - From trapped air, which is the main source of nitrogen in recent sediments (Rojey et al., 1997).
- ***Helium*** has two isotopes, $^3$He and $^4$He, and it has an inorganic origin. As the depth of the helium source increases, its average quantity in the soil increase. $^3$He is produced from the outgassing of the mantle, a layer between the crust and the outer core of the Earth. In contrast, $^4$He is formed through the disintegration of radioactive minerals present in Earth's crust. Gas containing more than 0.3% helium is defined as helium-rich gas (Johnson and Rydjord, 2001).
- ***Hydrogen*** is thought to be produced during the thermal cracking of kerogens and oils at a great depth because the energy required is greater than that of methane formation. Hydrogen levels in the produced gas are not high enough to cause a problem (Kidnay et al., 2011).
- ***Water*** is frequently produced from gas and oil reservoirs (Ray and Engelhardt.R, 1992). Depending on the thermodynamic conditions prevailing in the reservoir and the chemical species present; the gas may be dissolved in the water or the oil. The water concentration of gas ranges from trace amounts to saturation (Rojey et al., 1997).
- ***Oxygen*** is considered as the only component that is not naturally produced. The leaking valves and the piping in the gathering systems that operate at atmospheric pressure are the primary sources of oxygen. Oxygen ingress is responsible for a significant amount of corrosion in the gas processing system (Kidnay et al., 2011).
- ***Inert gases,*** such as argon, krypton, neon and xenon, may be present in the produced gas, where its source could be the trapped air. These gases could be produced when the oxygen in the trapped air in the sediments is consumed by bacteria leaving the inert gases (Rojey et al., 1997).

**The contaminants** are gases that are detrimental to production and transportation equipment in addition to being obnoxious pollutants. These contaminants include:

- ***Sulfur species:*** hydrogen sulfide ($H_2S$) can be formed during the reduction of sulfate ions in sulfates dissolved in water by sulfur-reducing bacteria in recent sediment by a biochemical mechanism. It can also be formed by thermal degradation of sulfur-rich kerogen at depth. Different sulfur species may be present in the produced gas, such as carbonyl sulfide (COS), carbon disulfide ($CS_2$), elemental sulfur, and mercaptans (RSH, where R represents an alkane group e.g. mehyl mercaptan $CH_3SH$, ethyl mercaptan $C_2H_5SH$,etc (Younger, 2004).) if the $H_2S$ concentration is greater than 2–3% (Kidnay et al., 2011).
- ***Mercury*** is thought to be formed through the reduction or thermal decomposition of mercury sulfide (cinnabar) in contact with hydrocarbons. It was mentioned that mercury has a high affinity for carbon as well as sulfides. Mercury may be present in different forms as elemental, organometallic compounds, such as dimethylmercury, methylethylmercury, and dimethylmercury, or inorganic mercury such as HgCl or $HgCl_2$ (Fitzgerald and Lamborg, 2003; Rios et al., 1998).
- ***Arsenic*** can be found in oil and gas operations, and it is believed to be as a result of the formation of geological gas. It has been found in different forms in natural gas and gas condensate. It not only exists as arsine ($H_3As$) but also as trialkylarsines, such as trimethylarsine ($Me_3As$), dimethylethylarsine ($Me_2EtAs$), methyldiethylarsine ($MeEt_2As$), triethylarsine ($Et_3As$), and triphenylarsine ($Ph_3As$). In sour natural gas systems, arsenic sulfide minerals could be found (Caumette et al., 2009; Trahan, 2008).

It is reported that arsenic levels can range from parts per billion levels up to high parts per million (Trahan, 2008). The trialkylarsines are a less reactive group than arsine itself and are more difficult to remove from natural gas.

- ***Naturally Occurring Radioactive Material (NORM)***

In the produced gas, most of the radioactivity in NORM is derived from the decay of uranium (U-238) and thorium (Th-232) present in the subsurface formations. Different concentrations of uranium and thorium may be present in limestones and evaporates, and they tend to be the highest in clay-rich formations (e.g., shales, granites, and some sandstones). Uranium also may be present in carbonaceous materials such as bitumen, pyrobitumen, and gilsonite. U-238 and Th-232 have very long half-lives; if present, they are not mobilized from the reservoir rock. Radioactive decay of these elements produces several series of daughter radioisotopes of different elements and different physical characteristics (IAEA, 2003; Smith, 1992).

One of the radionuclides resulting from the decay of U-238 and Th-232 is radon-222 (Rn-222) which has a short-lived ($t_{1/2} = 3.8$ days) radioactive noble gas as progeny (IAEA, 2003; Rowan and Kraemer, 2012). It may be released from natural gas reservoirs and transported with the produced gas to the processing plants

(Organo, 2005). The highest radon levels are found in equipment for ethane/propane processing, as it has a boiling point between those of ethane and propane (Summerlin and Prichard, 1985). However, deposition of thin, active lead (Pb-210) and polonium (Po-210) films on the internal surfaces of production equipment and transport facilities may be present as a result of Rn-222 decay (IAEA, 2003).

In the gas and oil industry, accumulation of NORM (Fig. 10) may be present in the form of scale at the wellheads, in the form of sludge at Gas/Oil Separation Plants (GOSP), or in the form thin films as the result of radon gas decay in gas plants (International Association of Oil and Gas Producers, 2008).

***Solid matter*** may be present in the form of fine silica (sand) and black powder resulting from the scaling in the pipe (Speight, 2015b). The black powder mainly consists of iron oxides and iron sulfides. However, it may also contain metallic lead, lead oxides, lead sulfide, zinc sulfide, barium sulfate, calcium carbonate, as well as polonium (Po-210) deposits (Godoy et al., 2005).

### *5.3. Natural gas composition test methods*

The determination of natural gas composition is performed through different standard methods, as listed in Table 3. Gas chromatographic techniques are an essential tool for natural gas characterization. For example, they are used in the determination of hydrocarbon gases, inorganic gases, arsenic species (Pantsar-Kallio and Korpela, 2000), mercury species (Tao et al., 1998), and isotope ratios (Hayes et al., 1990; Sessions, 2006; Yürüm and Levy, 1985).

## 6. Natural gas processing

Different processes are necessary for cleaning of the raw natural gas to meet the specification of the pipeline (Pipeline-Quality Natural Gas) and for environmentally clean-burning gas (EIA, 2006; Speight, 2007).

Gas processing is applied to (Kidnay et al., 2011) the raw natural gas to achieve the following:

- Purification of the raw gas from materials that inhibit the use of the gas as fuel (residential or industrial).
- Separation of valuable components from the raw gas that can be used as petrochemical feedstocks, fuels (e.g., propane), or industrial gases (e.g., ethane, helium).
- Liquefaction of the natural gas to be transported or stored.

In the gas plant (Fig. 11); the unit operations will be dependent on the gas composition, the type of facility, and the product specifications.

The following section illustrates the different types of unit operations in the gas plant.

### *6.1. Removal of liquid hydrocarbon*

Natural gas liquids (NGLs) are valuable products. They can be separated from the raw natural gas, recovered, and fractionated as natural gasoline or condensate, liquefied petroleum gas (LPG) and liquefied natural gas (LNG). The NGLs can be separated from the raw gas by cooling (refrigeration), oil absorption, adsorption (such as by activated carbon or silica gel) or membrane processes (Kidnay et al., 2011; Rojey et al., 1997; Speight, 2007).

### *6.2. Removal of water*

The produced gas may contain water, which is a common impurity. It must be removed from the gas stream for the following reasons (Speight, 1993; Mokhatab et al., 2006):

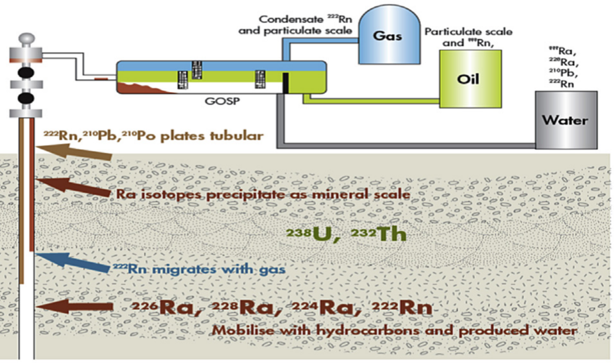

**Fig. 10.** The origin of Naturally Occurring Radioactive Material (NORM) in oil and gas industry, (adapted from: International Association of Oil and Gas Producers, 2008).

- Decreasing the heating value of the produced gas, consequently increasing its volume.
- Condensation of water in the pipelines causing slug flow.
- Possible erosion and corrosion of the pipelines, especially when present with carbon dioxide and hydrogen sulfide (acid gases).
- Hydrate could be formed under specific conditions that plug valves, fittings or even pipelines (Carroll, 2014).

The removal of water associated with natural gas could be accomplished by a simple separation method at or near the wellhead, or the water could simply be removed by cooling (Engineering Data Book, 2004a; Wilson and Yuvancic, 2004). However, the removal of water vapor from natural gas requires a more complicated dehydration process. The dehydration of natural gas usually involves the following operations:

- ***Absorption process*** (Hicks and Senules, 1991; Speight, 1993), which can be carried out by using:
  - Organic liquids (e.g., diethylene or triethylene glycol)
  - An aqueous solution of salts (e.g., lithium chloride)
  - Solid absorbents (e.g., fused anhydrous calcium sulfate, lime, and magnesium perchlorate)
  - Deliquescent absorbent (e.g., calcium chloride and potassium hydroxide)

The solid absorbent removes water vapor by chemical reaction, whereas the deliquescent absorbent removes water vapor by chemical reaction and dissolution.

- ***Adsorption Process***, which can be carried out by using solid adsorbents such as activated alumina, silica gel or molecular sieves (Campbell, 1992).
- ***Gas Permeation***, which involves dehydration of natural gas achieved using membranes. This process applies to plants that use natural gas fuel at low pressure (Engineering Data Book, 2004a).

### *6.3. Removal of mercury*

The presence of mercury traces in the gas processing plant may corrode the aluminum heat exchanger, causing system failure. However, mercury sorbent materials and sludge containing mercury resulting from different treatment processes represent toxic

**Table 3**
Some listed standard test methods for natural gas analysis.

| Standard test methods for natural gas analysis | |
|---|---|
| GPA[a] 2261 | Analysis of Natural Gas and Similar Gaseous Mixtures by Gas Chromatography |
| GPA 2199 | Determination of Specific Sulfur Compounds by Capillary Gas Chromatography and Sulfur Chemiluminescence Detection |
| GPA 2286 | Tentative Method of Extended Analysis for Natural Gas and Similar Gaseous Mixtures by Temperature Programmed Gas chromatography. |
| ISO[b] 13443 | Natural gas—Standard reference conditions |
| ISO 6141 | Gas analysis—Requirements for certificate for calibration gases and gas mixtures |
| ISO 6143 | Gas analysis—comparison methods for determining and checking the composition calibration gas mixture. |
| ISO 19739 | Natural gas—Determination of sulfur compounds using gas chromatography. |
| ISO 6326 | Natural gas—Determination of sulfur compounds. |
| ISO 6327 | Gas analysis—Determination of the water dew point of natural gas- cooled surface condensation hygrometer. |
| ISO 6974 | Natural gas—Determination of composition with defined uncertainty by gas chromatography |
| ISO 6975 | Natural gas—Extended analysis-Gas chromatographic method. |
| ISO 6976 | Natural gas—Calculation of calorific values, density, relative density and Wobbe index from composition. |
| ISO 6978 | Natural gas—Determination of mercury |
| ISO 7941 | Commercial propane and butane—Analysis by gas chromatography. |
| ISO 10715 | Natural gas—Sampling guidelines. |
| ISO 12213 | Natural gas—Calculation of compression factor. |
| ISO 11150 | Natural gas—Hydrocarbon dew point and hydrocarbon content. |
| ISO 23874 | Natural gas—Gas chromatographic requirements for hydrocarbon dewpoint calculation. |
| ISO 14749 | Natural gas—Online gas chromatograph for upstream area. |
| ASTM[c] D1945 | Standard Test Method for Analysis of Natural Gas by Gas Chromatography. |
| ASTM D5504 | Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence. |
| ASTM D6228 | Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection. |
| ASTM D5954 | Standard Test Method for Mercury Sampling and Measurement in Natural Gas by Atomic Absorption Spectroscopy. |
| ASTM D6350 | Standard Test Method for Mercury Sampling and Analysis in Natural Gas by Atomic Fluorescence Spectroscopy. |
| ASTM D6849 | Standard Practice for Storage and Use of Liquefied Petroleum Gases (LPG) in Sample Cylinders for LPG Test Methods. |

[a] Gas processor association.
[b] International organization for standardization.
[c] American society for testing and materials.

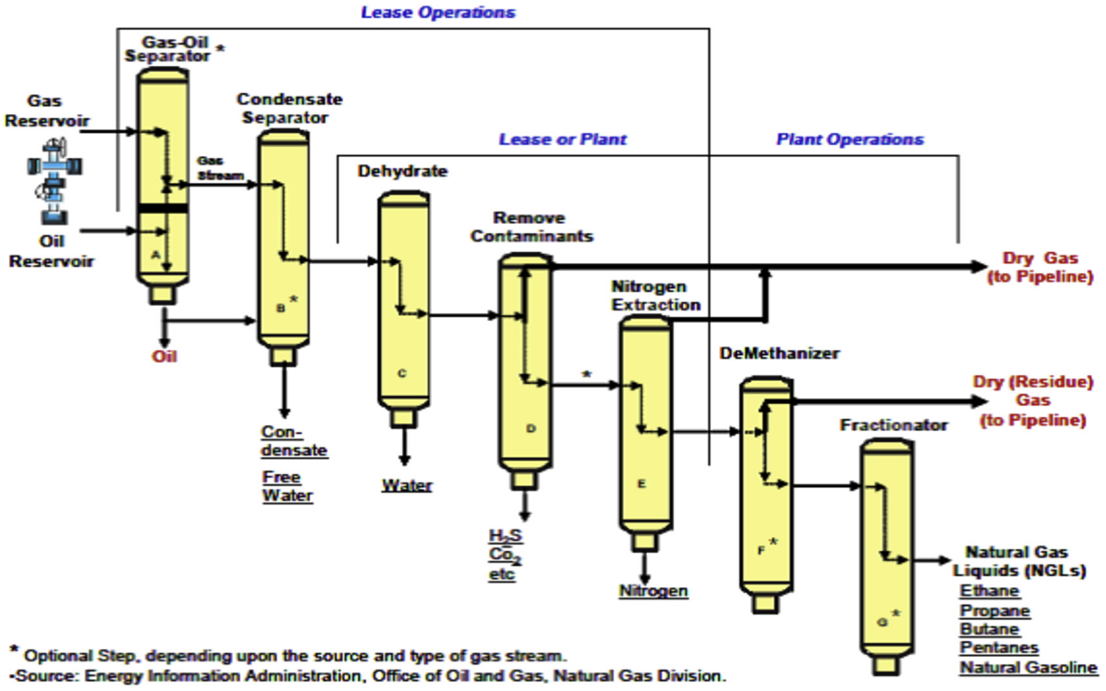

**Fig. 11.** Schematic diagram represents the general gas processing units (EIA, 2006).

hazardous wastes that are difficult to store or process for disposal (Kozin and Hansen, 2013). Elemental mercury has a poisoning effect on many catalysts. Mercury compounds are toxic to humans, and most biological systems can absorb it. These compounds can pose environmental and safety hazards (Wilhelm and Bloom, 2000).

Removal of mercury from gas and liquid streams can be carried out by both non-regenerative and regenerative processes (Kidnay et al., 2011; Mokhatab et al., 2006).

- ***Non-regenerative Processes***:

Most of these processes use sulfur in the form of metal sulfide or as sulfur impregnated on a support such as activated carbon or metal oxides (e.g., alumina). In this process, mercury reacts with sulfur, forming a stable compound. In a few cases, potassium-iodide-promoted activated carbon has been used (Bourke and Mazzoni, 1989; Eckersley, 2010; Engineering Data Book, 2004b; Rios et al., 1998).

- ***Regenerative Process***:

In this process, a silver-promoted molecular sieve is used, where mercury reacts with silver forming an amalgam. This amalgam decomposes through a regeneration process (Eckersley, 2010; Stiltner, 2002).

### 6.4. *Removal of trace components*

- **Nitrogen** must be removed from the produced gas because a high nitrogen concentration reduces the heating value of the natural gas. It can be removed by either cryogenic distillation (Howard, 1998), pressure swing adsorption (Cheng and Hill, 1985; Mitariten, 2001), or membrane separation (Hoffman, 2003).
- **Helium** is a valuable product from natural gas processing. Unlike the other trace component, a high concentration of helium is desirable. It can be removed by nitrogen injection (Kidnay et al., 2011).
- **Oxygen** can be removed by the use of non-regenerative scavengers when it exists at low concentrations. At higher concentrations, it can be withdrawn from the gas by a catalytic reaction to produce water, which is then eliminated in the dehydration process (Kidnay et al., 2011).
- **Arsenic compounds,** if present in natural gas, must be removed due to the following reasons (Krupp et al., 2007; Trahan, 2008):
  - Environmental pollution through burning.
  - Health and safety hazards.
  - The poisoning of the catalysts in a subsequent processing plant (e.g., palladium and platinum catalysts).

Arsenic compounds can be removed from the gas by the use of a non-regenerative adsorption process (Hennico et al., 1991; Sarrazin et al., 1993). They can also be removed by cleaning the pipelines to remove the deposits, which are typically iron sulfide (Trahan, 2008).

- **Naturally Occurring Radioactive Material (NORM)** emissions are inhibited (Organo, 2005) by using filter assemblies in gas lines to remove radon decay products. Another method is by the injection of scale inhibitors in the system when formation water begins to be produced.

### 6.5. *Removal of acid gases*

The term “acid gases” is related to the presence of both hydrogen sulfide and carbon dioxide, which form weak acids when present with water. These acidic solutions are very corrosive, and their removal requires special treatment. However, hydrogen sulfide has high toxicity and strong offensive odor, whereas carbon dioxide has no heating value (Carroll, 2010). On the other hand, under certain conditions of pressure and temperature, solid hydrate can be formed due to the presence of $CO_2$ or $H_2S$ and water mixture. The temperature required for hydrate formation increases with increasing content of $H_2S$, and the case with $CO_2$ is the opposite (Song and Kobayashi, 1989).

The process of removal of acid gases is greatly dependent on the specification required for the residue gas, the quantity of gas processed, and the composition of the raw gas being treated (Younger, 2004). There are two general processes used for acid gas removal: adsorption and absorption (Speight, 1993).

#### 6.5.1. *Absorption processes*

*6.5.1.1. Chemical solvent processes.* In these processes, $H_2S$ and $CO_2$ can be removed from the gas stream by chemical reaction with a material in the solvent solution. This reaction may be reversible or irreversible (Engineering Data Book, 2004b).

- ***Amine process***

This process is known as amine washing of natural gas, in which acid gases ($H_2S$ and $CO_2$) chemically react with amine compounds. Commercial amine-derivative compounds have been used, such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), methyl diethanolamine (MDEA), di-isopropanolamine (DIPA), and diglycolamine (DGA) (Kohl and Riesenfeld, 1985; Mokhatab et al., 2006; Speight, 1993). Different amines can be selected, depending on the composition and operating conditions of the feed gas, to meet the specification for the produced gas.

The selectivity of $H_2S/CO_2$ can be improved by using sterically hindered amines. When these amines react with $CO_2$, the formation of carbamate (a product of the reaction between $CO_2$ and the amine compound) is prevented due to the steric hindrance in the amine structure. Consequently, the absorption of $CO_2$ is slowed down without preventing the reaction with $H_2S$ (Weinberg et al., 1983).

- ***Carbonate washing and water washing***

In this process, the acid gases are removed by washing with potassium carbonate, which is a mild alkali. This process was originally used for $CO_2$, but $H_2S$ is also absorbed (Speight, 1993; Rojey et al., 1997).

- ***Caustic wash***

$CO_2$, $CS_2$, $H_2S$, and mercaptans (RSH, where R is an alkyl group) can be removed from the natural gas by using caustic (NaOH) scrubbing systems. Natural gas is usually washed with water after a caustic wash process to remove any caustic substances entrained in the gas before dehydration (Engineering Data Book, 2004b).

*6.5.1.2. Physical solvent processes.* Physical absorption is the basis of these processes. Some of these processes are listed below:

1 Methanol-based process

The first commercial organic, physical solvent used was methanol. It has been used for hydrate inhibition, dehydration, gas sweetening, and liquid recovery (Kohl and Nielsen, 1997; Mokhatab et al., 2006). In this process, also called Rectisol, pure refrigerated methanol is used as a solvent. Lurgi Oel Gas Chemie GmbH and Linde AG have developed and licensed this process (Engineering Data Book, 2004b).

2 Selexol process

The solvent used in this process is polyethylene glycol dimethyl ether. This process was developed by Allied Chemical Corporation (Johnson and Homme, 1984).

3 Purisol® Process

The solvent used in this process is N-methyl-2-pyrrolidone

(NMP or N-Pyrol), which has a high boiling point and exhibits a high selectivity for $H_2S$. Lurgi Oel Gas Chemie has developed and licensed this process (Engineering Data Book, 2004b).

4 Fluor Solvent

In this process, anhydrous propylene carbonate has been used. It is mainly used for high carbon dioxide concentrations. This process was patented by the Fluor Corporation (Rojey et al., 1997).

*6.5.1.3. Hybrid solvent processes.* Sulfinol® process (Kohl and Nielsen, 1997): This process can be used for the removal of $H_2S$, $CO_2$, COS, $CS_2$, mercaptans and polysulfides from natural and synthetic gases. Sulfinol consists of a mixture of a physical solvent (Sulfolane), water and chemical solvents (Diisopropanolamine (DIPA) or Methyldiethanolamine (MDEA)). The Sulfinol® Process is licensed by Shell Global Solutions (Engineering Data Book, 2004b; Kidnay et al., 2011).

### *6.5.2. Adsorption processes*

Adsorption processes can be used for the purification of natural gas from $H_2S$, $CO_2$, and other sulfur contaminants (Speight, 1993). The adsorbents used are either regenerative, such as molecular sieves, or non-regenerative, such as impregnated activated carbon.

- *Molecular Sieves*

Molecular sieves are highly selective for the removal of hydrogen sulfide (as well other sulfur compounds) from gas streams (Manning and Thompson, 1991).

- *Oxorbon*

This solid adsorbent consists of activated carbon impregnated with potassium iodide (Abatzoglou and Boivin, 2009; Marsh and Rodriguez-Reinoso, 2006). *Donau Carbon* markets such a carbon product for the removal of $H_2S$ and mercaptans (Engineering Data Book, 2004b).

- *Membrane Process*

The use of membranes for gas separation has been limited to carbon dioxide removal (Mokhatab et al., 2006). The main disadvantages of using the membrane process in natural gas sweetening are plasticization, which is due to the exposure to high pressure or temperature in the operating conditions, and weak mechanical strength. Attempts have been made to produce a high-performance membrane system. These attempts suggested that membrane plasticization can be overcome by crosslinking of membrane material, whereas the mechanical strength of the membrane can be improved by adding inorganic fillers to the polymer matrix (Adams et al., 2011; He and Hägg, 2012; Wind et al., 2002).

### *6.5.3. Hydrogen sulfide scavenger processes*

These processes scavenge $H_2S$ and organic sulfur compounds (mercaptans) from gas streams through reaction with solid-based media (Javaherdashti et al., 2013; Kelland, 2014). The main metal oxides used in this process are iron oxide and zinc oxide (Houghton and Bucklin, 1994; Kohl and Nielsen, 1997). A continuous process such as the *Ferrox process* or the *Stretford process* is required for the removal of high $H_2S$ concentrations from the gas stream (Speight, 2007).

### *6.5.4. Biological process*

This process consists of two steps. The first is the absorption of $H_2S$ from the gas stream by mild alkaline solution. The second step is the oxidation of the adsorbed sulfide to produce elemental sulfur by naturally occurring microorganisms (Cline et al., 2003).

## 7. Carbon dioxide

All living microorganisms (animals or vegetables) produce carbon dioxide, but the main source of $CO_2$ release is the combustion of fossil fuels (coal, oil, and gas) for energy production purposes. The carbon cycle is capable of naturally recycling approximately 203 gigatons (Gt) of $CO_2$ each year. Although, anthropogenic (humane activity) $CO_2$ release represents ~3.4% (~7 Gt per year) of the total $CO_2$ converted in the natural cycle, it has no ability to be recycled naturally. As a result, $CO_2$ (greenhouse gas) is accumulated in the atmosphere, consequently leading to the global warming phenomenon (Aresta, 2010).

According to IPCC (2014), annual GHG (greenhouse gases) emissions grew by ~ 2.2% per year (1.0 gigaton carbon dioxide equivalent ($GtCO_2eq$)) from 2000 to 2010, which is large compared with the growth of 1.3% per year (0.4 $GtCO_2eq$) from 1970 to 2000. This occurred despite the growing number of climate change mitigation policies. Without additional efforts to mitigate GHG emissions, it is expected that the increase in global temperature in 2100 will be from 3.7 °C to 4.8 °C compared with pre-industrial levels. $CO_2$ emissions contributed to approximately 78% of the total GHG emissions from fossil fuel combustion and industrial processes. $CO_2$ emissions from fossil fuels grew by approximately ~3% from 2010 to 2011 and by ~1–2% from 2011 to 2012. Fig. 12; represents a schematic diagram for GHG emissions according to economic sector (IPCC, 2014).

One of the most significant challenges facing the energy sectors is the orientation of the global energy systems to be consistent with global climate goals (IEA, 2015a). Multiple scenarios related to technological and behavioral options have been proposed in order to mitigate the GHG emissions (IPCC, 2014). According to IEA (2015a), the rate of emissions from global energy and related processes deceased by considerably slowing down the growth of fossil fuel demands and increasing the share of low-carbon fuels (natural gas).

Natural gas fields produce up to 20% $CO_2$, whereas $CO_2$ concentrations in other fields reach more than 50%. A powerful

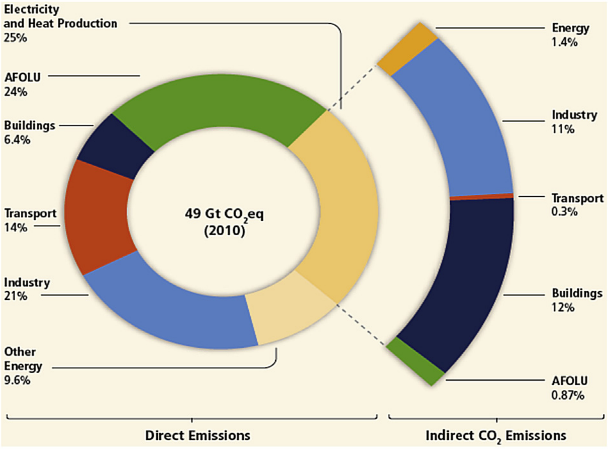

**Fig. 12.** Schematic diagram indicate the total anthropogenic greenhouse gases (GHG) emissions by economic sector. Direct GHG emissions shares are represented by the inner circle. The indirect $CO_2$ emission shares from final energy use sectors are indicated by pull out by Section. AFOLU symbol indicate Agriculture, Forestry and Other Land Use sector (source: IPCC, 2014).

example of that is Indonesia's Natuna field, which contains 71% $CO_2$ (Rackley, 2010). In natural gas streams, excess $CO_2$ must be removed from the gas stream before it can be sold. Instead of being vented to the atmosphere, $CO_2$ can be stored, giving raise to the development of carbon capture and storage strategies. According to IEA (2015b), the Australian Gorgon Project for natural gas production, a project by both Norway and Australia, is set to become the world's largest $CO_2$ storage project in 2016, storing more than 3 $MtCO_2$ per year.

### 7.1. General features of carbon dioxide

$CO_2$ has an essential role in the life cycle of plants and animals in Earth's environment. It is a colorless gas that has a slightly irritating odor and is denser than air. $CO_2$ is harmless if it exists in air as a minor component, but it is dangerous at higher percentages (IPCC, 2005).

The thermodynamic and kinetic stability of $CO_2$ is the main cause of its chemical inertness. To overcome its kinetic barrier, it can be activated over the surfaces of metals, metal oxides, metal complexes and enzymes. $CO_2$ can also be activated by photooxidation and electrochemical pathways (Ratnasamy and Srinivas, 2008). In the aqueous phase, $CO_2$ exists in three forms: molecular $CO_2$ and two ionic forms, including the bicarbonate ($HCO^{-}{}_{3(aq)}$) and carbonate ($CO_3^{2-}$) ions (Carroll, 2010).

### 7.2. Uses of carbon dioxide

Carbon capture and storage is a process in which $CO_2$ is separated from industrial and energy-related sources, transported, and stored to for long-term isolation from the atmosphere. Under specific conditions, $CO_2$ can be stored in deep offshore or onshore geological formations of oil and gas fields (IPCC, 2005). Additionally, large amounts of $CO_2$ can be stored over a long term in the form of safe chemicals through the $CO_2$ "*inorganication*" process. In the process, residual inorganic oxides and sludges from industrial materials can be used (Aresta, 2010).

Uses of $CO_2$ (utilization) (Centi and Perathoner, 2014) provide a major contribution to reducing its accumulation in the atmosphere. Thus, it can be used as a technological fluid, as a raw material in the chemical industry, or in biotechnological applications (biological fixation) (Ratnasamy and Srinivas, 2008). One of the most promising technologies is carbon fixation on microalgae, and it can then be converted to biofuel under suitable conditions (Kumar et al., 2010).

$CO_2$ can be used as a raw material in industrial manufacturing processes such as (Ratnasamy and Srinivas, 2008; IPCC, 2005):

- urea synthesis
- the manufacture of salicylic and *para*-benzoic acids
- cyclic and polycarbonate synthesis
- production of methanol
- manufacture of polyurethane

In the oil and gas industry, $CO_2$ can be used as a technological fluid in enhanced oil recovery (EOR) technology through its injection in oil reservoirs (Rackley, 2010).

### 7.3. Carbon dioxide removal from natural gas

During separation of $CO_2$ from natural gas in both on/offshore natural gas wells, it can be separated from the gas steam and reinjected into geological formations. Then, it can be compressed and transported (IEA, 2006).

#### 7.3.1. Chemical and physical absorption

Processes for capturing $CO_2$ based on absorption process are distinguished depending on whether the solvent either reacts chemically (chemical absorption) with $CO_2$ to form chemical compounds from which the $CO_2$ can be recovered or the solvent is chemically inert (physical absorption) and absorbs the $CO_2$ without a chemical reaction (Rackley, 2010).

*7.3.1.1. Conventional chemical absorption.* Amine or carbonate solutions can chemically absorb $CO_2$ at low partial pressure. This method is preferred at low partial pressure (Rackley, 2010).

- ***Amine-Based Absorption***

$CO_2$ reacts with amines at ~40 °C through a zwitterion mechanism to form carbamates (Vaidya and Kenig, 2007). After absorption, the $CO_2$-rich liquid amine passes through a stripping tower in which the mixture was heated with steam to desorb $CO_2$. The chemical solvent is regenerated at high temperature (100–140 °C) and pressure (D'Alessandro et al., 2010).

Industrially, primary amines (monoethanolamine (MEA)) have been used for absorption of CO2 from natural gas. However, MEA has low CO2 absorption capacity. In addition, its regeneration process is costly, and it can constitute up to approximately 70% of the total operating costs in $CO_2$ capture plants (Idem et al., 2006). Secondary amines (e.g., diethanolamine (DEA)) absorb $CO_2$ at a lower heat of reaction compared with primary amines. The regeneration step is more economical due to the lower stability of the formed carbamate tertiary amines (e.g., N-methyldiethanolamine (MDEA)), which exhibit lower degradation rates and lower solvent regeneration energy (D'Alessandro et al., 2010). To maximize the qualities of individual amines, mixed amines can be used. These could contain a mixture of primary and tertiary amines or tertiary and secondary amines (Kohl and Nielsen, 1997; Yang et al., 2008).

Another type of amine has been used in the gas industry, namely sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP). They contain bulkier substituent groups, where the carbamation reaction is hindered by the physical structure of the large amine molecules. The energy required for regeneration of hindered amines is lower than that of individual amines. This is compensated by the slow overall reaction rate (D'Alessandro et al., 2010; Rackley, 2010). Commercial FLEXSORB® solvents are examples of the strictly hindered amines, and they are marketed by the Exxon Mobil Research and Engineering Company (Engineering Data Book, 2004b).

The main disadvantages of amine absorption processes are (Rojey et al., 1997):

- Corrosion, which may occur during the absorption process. Consequently, corrosion inhibitors must be added.
- Degradation processes, which occur if oxygen or air are in contact with amine solutions. This results in a slow oxidation process, which generates corrosive degraded species.
- Foaming, which occurs as a result of condensed hydrocarbons, suspended solids, impurities, from corrosion inhibitors, and amine degradation products.

- ***Carbonate-based absorption***

$CO_2$ can be chemically absorbed by inorganic solvents such as aqueous potassium and sodium carbonates, or as an aqueous ammonia solution and its derivatives. The advantages of this treatment are that the solutions are regenerable and require low desorption energy compared with amine-based treatments. The lower rate of $CO_2$ absorption at low pressure is the main disadvantage of the alkali carbonate systems. However, addition of a piperazine compound can enhance the absorption capacity and increase the rate of absorption (Cullinane and Rochelle, 2004). Piperazine is a cyclohexane ring with two opposing carbon atoms replaced by amine functional groups (Rackley, 2010).

- ***Sodium hydroxide-based absorption***

In this process, the gas stream is passed through a packed or trayed column filled with caustic solution. In the absorption process, $CO_2$ forms a non-regenerable product ($Na_2CO_3$) with the solution, and this must be removed. The wastes of the used caustic solution are considered to be hazardous (Engineering Data Book, 2004b).

Lime (CaO) can be added to the carbonation products to regenerate sodium hydroxide, but it requires high energy. Solid-state reaction between sodium trititanate ($Na_2O.3Ti_2$) and sodium carbonate has been investigated as an alternative route (Rackley, 2010).

*7.3.1.2. Physical absorption.* In contrast with the chemical solvent, physical solvents are chemically inert and do not form heat-stable salts when reacted with $CO_2$. This process is preferred at high partial pressure and high $CO_2$ concentration. $CO_2$ binds with physical solvents at low temperature and high partial pressure. In natural gas processing plants, physical solvents such as Selexol (polyethylene glycol dimethylether) and Rectisol (methanol chilled to −40 °C) have been used (D'Alessandro et al., 2010); IEA, 2004; Rackley, 2010).

***Ionic liquids***

Recently, studies have shown that $CO_2$ capture using ionic liquids (ILs) has potential advantages compared with amine-based solvents (Wappel et al., 2010; Karadas et al., 2010). Therefore, many types of ILs, such as 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF4]), 1-butyl-3-methylimidazolium-hexafluorophosphate ([Bmim][PF6]), tetrabutylphosphonium amino acid ILs ([P(C4)4][AA]) (Zhang et al., 2006) and dual amino-functionalized phosphonium ILs (Zhang et al., 2009), were synthesized to capture $CO_2$ from gaseous mixtures (Shiflett and Yokozeki, 2005; Zhang et al., 2008), and they exhibited excellent properties, including low energy consumption, easy recycling, a lack of contamination, functionality, and high $CO_2$ scrubbing efficiency (Visser et al., 2001).

However, IL solvents are high-cost materials when used industrially for $CO_2$ capture, and they have relatively high viscosity compared with amine-based solvents (Camper et al., 2008; Ramdin et al., 2012; Shannon and Bara, 2012). Attempts were made to obtain effective and low-cost ionic liquid solvents, such as novel alkaline ionic liquids (e.g. Anderson et al., 2015; Pinto et al., 2014; Zhao et al., 2011).

*7.3.2. Adsorption processes*

Adsorption processes by solid sorbents have many potential advantages when compared with absorption processes using liquid sorbents. Adsorption processes can be operated at a very wide range of temperatures, but they are characterized by lagoons of liquid and/or solid wastes that pose problems for disposal and are environmentally unacceptable (Olivares-Marín, 2012; Rackley, 2010).

According to (Rackley, 2010; Wang et al., 2011), the adsorbents used for $CO_2$ capture are classified as either low or high-temperature $CO_2$ sorbents.

*7.3.2.1. Low-temperature $CO_2$ sorbents.* These low-temperature sorbents are typically applied at temperatures from ambient up to ~100 °C.

- ***Microporous and mesoporous materials***
  - *Zeolites* are crystalline microporous (pore size below 20 Å, according to the IUPAC) aluminosilicates based on an infinitely extending three-dimensional connected framework of AlO4 and SiO4 tetrahedra linked to each other by sharing oxygens (Diaz and Mayoral, 2011). Small numbers of natural zeolites may be potentially used for gas separation, such as clinoptilolite, chabazite, mordenite, erionite, ferrierite and phillipsite. Despite their abundance and low cost, natural zeolites have low purity and variable compositions, and they may have low separation efficiency compared with synthetic zeolite (Ackley et al., 2003). *Examples* of zeolite materials used in gas purification are $\beta$-zeolite (Li and Tezel, 2007), synthetic FAU (Cavenati et al., 2006; Ghoufi et al., 2009), alkali-modified zeolites (Walton et al., 2006; Xu et al., 2008; Tagliabue et al., 2012) and composite of 5A zeolite with ultrathin porous $TiO_2$ coating (Song et al., 2015).

Zeolites are typically operated at elevated pressures (above 2 bar), and their adsorption capacities are greatly reduced by the presence of moisture in the gas stream. Regeneration of zeolite requires very high temperatures (often in excess of 300 °C) (Chue et al., 1995; Harlick and Sayari, 2006; Yu et al., 2012).

- *Ordered mesoporous materials (molecular sieve (OMS))*

These types of materials are amorphous silicate materials with ordered arrangements of pores (channels or cages) in the mesoscale range (Diaz and Mayoral, 2011). OMS have been used for $CO_2$ adsorption because of high porosity, which permits rapid gas diffusion.

Functionalization of the OMS material surfaces with amine groups has been proposed to overcome the disadvantages of the conventional amine solvents. The amine-functionalized OMS are thermally stable, and they include silica (Knowles et al., 2005, 2006), SBA-1 (Yoshitake et al., 2002), SBA-15 (Gray et al., 2005), MCM-41 (Song, 2006; dos Santos et al., 2015; Heydari-Gorji et al., 2011; Serna-Guerrero and Sayari, 2010; Sayari and Belmabkhout, 2010), MCM-48 (Huang et al., 2003) and MCM-36 (Cogswell et al., 2015). The "molecular basket" adsorbent, which is formed by the impregnation of MCM-41 with polyethylenimine (PEI), exhibits a high $CO_2$ adsorption capacity (Xu et al., 2002; Song, 2006).

OMS materials have low hydrothermal stability due to the hydrolysis of Si—O—Si bonds when silanol groups are subjected to water adsorption (Park et al., 2001). Numerous studies have reportedly improved the hydrothermal stability of mesoporous materials (Chew et al., 2010).

- *Carbon molecular sieve (CMS)*

CMS materials for large-scale applications are obtained from coals. These materials are characterized by very narrow pore size distributions (generally centered on 5 Å) and very high surface areas. CMS provides molecular separation on the basis of rates of adsorption. Carbon dioxide separation from natural gas by CMS-based systems has been extensively studied (Kapoor and Yang, 1989; Jayaraman et al., 2002; Cavenati et al., 2005). Nitrogen doped carbon have been reported for $CO_2$ adsorption (Li and Zhoa, 2013; Sethia and Sayari, 2014; Wickramaratne et al., 2014).

- *Metal organic frameworks*

These microporous crystalline solids are composed of organic bridging ligands or "struts" coordinated to metal-based nodes to form a three-dimensional extended network with uniform pore diameters, typically in the range 3–20 Å (Eddaoudi et al., 2001; Yaghi et al., 2003; Rosi et al., 2005; Natarajan and Mandal, 2008; Tranchemontagne et al., 2008; O'Keeffe et al., 2008). The nodes generally consist of one or more metal ions (e.g., $Al^{3+}$, $Cr^{3+}$, $Cu^{2+}$, or $Zn^{2+}$) to which the organic bridging ligands coordinate through a specific functional group (e.g., carboxylate, pyridyl).

Carbon dioxide and methane adsorbs on carboxylate-based MOFs such as MIL-53 (Loiseau et al., 2004; Llewellyn et al., 2006) and imidazolate-based MOFs (also called ZIFs (Hayashi et al., 2007; Banerjee et al., 2008; Banerjee et al., 2009). The adsorption mainly proceeds by van der Waals and quadrupole interactions. The use of MOF for $CO_2$ capure have been reviewed elsewhere e.g. (Liu et al., 2012a,2012d; Zhang et al., 2014; Sumida et al., 2012).

The regeneration step decreases the selectivity values for CO2, also permitting the adsorption of methane. Therefore, a new generation of MOF adsorbents will be developed to enhance the selectivity towards CO2 uptake. Before it can be applied industrially for capture processes, many requirements must be fulfilled (Tagliabue et al., 2009; D'Alessandro et al., 2010; Li et al., 2011).

*7.3.2.2. High-temperature $CO_2$ sorbents.* These are sorbents that have been developed with high capacities at high operating temperatures (400–600 °C), which are typical of hot flue gas applications. The adsorbents used include metal oxides (e.g., CaO and MgO (Choi et al., 2009; Feng et al., 2007; Liu et al., 2012c; Kierzkowska et al., 2013), activated carbon (Maroto-Valer et al., 2005), lithium compounds (zirconate (Fauth et al. (2005)), silicates (Essaki et al., 2004; Kato et al., 2005), dry carbonates (e.g., $Na_2CO_3$ or $K_2CO_3$) (Nelson et al., 2009), and hydrotalcite.

### *Hydrotalcite (HTlcs)*

Hydrotalcite-like compounds (HTlcs), or layered double hydroxides (LDHs), are a type of anionic or basic clays. These compounds are constituted by a stacking of positively charged sheets (brucite-like layers) separated by intercalated anions. The formula of these compounds can be generalized (Cavani et al., 1991) to:

$$[M_{(II)1\text{-}x}M_{(III)x}(OH)_2]^{x+}(A^{n\text{-}}x/n).mH_2O$$

where $M_{(II)} = Mg^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Cu^{2+}$, $Mn^{2+}$; $M_{(III)} = Al^{3+}$,$Fe^{3+}$, $Cr^{3+}$, $A^{n-} = CO_3^{2-}$, $SO_4^{2-}$, $NO_3^-$, $Cl^-$, $OH^-$, and x is normally between 0.17 and 0.33, but there is no limitation.

LDHs are characterized by the "memory effect" phenomenon. When LDHs are calcined, they form an amorphous mixed oxide phase that retains its original structure if exposed to water and suitable anions (Marchi and Apesteguía, 1998; Rocha et al., 1999; Stanimirova et al., 2001; Erickson et al., 2005).

Hydrotalcites were used as $CO_2$ adsorbents by (Yamamoto et al., 1995; Yong et al., 2002; Yong and Rodrigues, 2002). They reported that:

- The larger and/or higher the charge of the anion, the greater the adsorption capacity of carbon dioxide (e.g., $CO_3^{2-}/Fe(CN)_6^{4-}$ shows a higher adsorption capacity than $OH^-/NO^3$).
- A low content of water/steam can improve the adsorption capacity.
- Increasing aluminum content (optimum content) increases the adsorption capacity.

Additionally, calcined LDHs have been used for $CO_2$ adsorption (Ram Reddy et al., 2006; Ram Reddy et al., 2008). The adsorption capacity of carbon dioxide onto hydrotalcites can be enhanced by chemical modification (such as $K_2CO_3$) (Lee et al., 2007; Ebner et al., 2006; Yang and Kim, 2006). Alkali (K and Cs) modified hydrotalcites were tested for $CO_2$ sorption (Oliveira et al., 2008). When coated on commercial zeolites, hydrotalcites showed an increase in $CO_2$ adsorption Othman et al. (2006). Although, recent work has demonstrated that the substituted hydrotalcites, such as those containing $Ga^{3+}$ substituted for some fraction of the $Al^{3+}$, exhibit enhanced $CO_2$ adsorption properties (Yavuz et al., 2009).

**Amin modified LDHs have been reported** (Wang et al., 2012 a; 2012b). Our previous work focused on the removal of $CO_2$ from natural gas streams under normal conditions of temperature and pressure using Zn–Al LDHs intercalated with nitrogen-containing anions (Sakr et al., 2013). We reported that, by controlling the synthesis temperature of homogenous precipitation of LDHs, different nitrogen-containing anions can be intercalated, and these groups greatly enhance the capture of $CO_2$ from gas streams.

## 8. Conclusion

Natural gas is a hydrocarbon-rich gas consisting primarily of methane. The high energy resulting from burning of natural gas makes it useful as a fuel. However, it is considered to be a clean fuel compared with other fossil fuels because of low emissions of gases that could harm the environment. The global shift from fossil fuels to natural gas represents a path toward a future with lower carbon emissions.

Natural gas is considered to be the cleanest fossil fuel. It is easy to be transported, used and stored. Thus, it is considered to be a safe source of energy. Natural gas is also used industrially for heating, electricity generation, fertilizers, and production of petrochemicals.

The exploration techniques of natural gas are mainly dependent on its origin. Natural gas can originate through different pathway process, such as thermogenic, biogenic, or abiogenic processes. Different methods have been proposed to distinguish the origin of natural gas, such as stable isotope measurements (e.g., $\delta^{13}C$, $\delta^{15}N$, $\delta^2H$, noble gas and clumped isotopes), hydrocarbon gas concentrations, hydrochemistry, core maturity, and genetic identification of microbes. In some basins, mixed biogenic and thermogenic origins can be obtained. For example, using $\delta^{13}C_{CH4}$ values can distinguish between biogenic methane ($\delta^{13}C_{CH4}$-60‰), thermogenic ($\delta^{13}C_{CH4} > -60$‰), and mixed origin ($\delta^{13}C_{CH4}$ between −60 and −50‰). Thus, defining the gas source determines how it could be explored.

Natural gas can be classified according to its origin as conventional or unconventional gas. Conventional gas can be associated (with crude oil) or non-associated gas (with little or no crude oil). Unconventional gas includes coal-bed methane, shale gas, deep aquifer gas, and gas hydrates (with crude oil). Recently, significant unconventional gas reserves have been proved. Another classification of natural gas can be carried out according to its chemical composition. The gas can be dry or wet (according to its hydrocarbon content), or it could be sour or sweet (according to its sulfur content).

Methane is the major component of natural gas, but it may contain different hydrocarbon and non-hydrocarbon constituents according to its formation process. The natural gas composition is never constant. It may contain valuable components (such as higher hydrocarbons, He gas), diluents (such as $CO_2$ and $N_2$), contaminants (such as sulfur, Hg, As components, and naturally occurring radioactive materials (NORM)), or solid matter. Natural gas composition could be determined using different listed standard methods stated by e.g. Gas Processor Association (GPA), International Organization for Standardization (ISO), and American Society for Testing and Materials (ASTM).

Processing of the raw gas must be performed to produce a gas having a composition compatible with the pipeline specification and meeting the environmentally accepted limits (when used as a fuel). Natural gas processing is applied for the separation of the valuable component, removal of any component preventing its use as a fuel, and liquefaction of the gas to be transported or stored. The unit operation of the processing plant will depend on gas composition, the specification required for the produced gas, and the type of facilities. The separation or removal processes depend on the type of component that must be separated or removed, as well as its concentration. These processes could be adsorption, absorption, gas permeation, biological action, or through the combination between different processes. It is worth noting that the components that are separated and removed from the raw gas stream can be recovered and reused. Valuable products could obtain in the technological processes, for example, natural gas liquids, sulfur, hydrogen, and helium.

Carbon dioxide is the produced from all types of natural gas fields (either conventional or unconventional). In some fields it could be accounted for more than 70% of the produced gas. $CO_2$ is considered as a diluent of natural gas because it has no heating value; consequently, it must be removed from the gas stream. Also, the release of $CO_2$ into the atmosphere contributes to the global warming. The global challenge is to reduce its emission, through the development of $CO_2$ capture, storage, and utilization technologies.

Large amounts of $CO_2$ can be stored and used as a technological fluid (as in enhanced oil recovery (EOR). Although $CO_2$ is a thermodynamically and kinetically stable component, it could be activated by a different process, and used as a raw material a raw material in the chemical industry, or in biotechnological applications (biological fixation).

$CO_2$ can be removed from the natural gas by absorption or adsorption processes. Absorption process could be chemical using (e.g. amine, carbonate, and sodium hydroxide-based absorption), or physical (using physical solvents such as Selexol, and ionic liquids). Adsorption processes could be low-temperature sorbents (from ambient up to ~100 °C e.g. microporous and mesoporous materials) and high-temperature sorbents (form 400–600 °C, e.g. metal oxides, and hydrotalcite).

In our previous study, we used hydrotalcite (layered double hydroxides) to capture $CO_2$ from the natural gas stream at ambient temperature and pressure. Higher $CO_2$ adsorption capacity was obtained through the intercalation nitrogen containing anions in the layered structure (Sakr et al., 2013).

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