

Ministry of Education and Science of Ukraine
Black Sea Universities Network

ODESA NATIONAL UNIVERSITY OF TECHNOLOGY

International Competition of
Student Scientific Works

BLACK SEA SCIENCE 2022 PROCEEDINGS



ODESA, ONUT 2022

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BLACK SEA SCIENCE 2022

Proceedings

Odesa, ONUT 2022

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INTRODUCTION

International Competition of Student Scientific Works “Black Sea Science” has been held annually since 2018 at the initiative of Odesa National University of Technology (formerly Odesa National Academy of Food Technologies) with the support of the Ministry of Education and Science of Ukraine. It has been supported by Black Sea Universities Network (the Association of 110 higher education institutions from 12 countries of the Black Sea Region) since 2019, and by Iseki-FOOD Association (European Integrating Food Science and Engineering Knowledge into the Food Chain Association) since 2020.

The goal of the competition is to expand international relations and attract students to research activities. It is held in the following fields:

- Food science and technologies
- Economics and administration
- Information technologies, automation and robotics
- Power engineering and energy efficiency
- Ecology and environmental protection

The jury includes both Ukrainian and foreign scientists. In the 4 years that the competition has been held, the jury included scientists from universities of 24 countries: Angola, Azerbaijan, Benin, Bulgaria, China, Czech Republic, France, Georgia, Germany, Greece, Israel, Italy, Kazakhstan, Latvia, Lithuania, Moldova, Pakistan, Poland, Romania, Serbia, Slovakia, Switzerland, Turkey, USA.

At the same time, every year the geography has expanded and the number of foreign jury members has increased: from 46 jury members representing 25 universities from 12 countries in 2018, to 73 jury members of the 46 universities from 19 countries in 2022.

More than a thousand student research papers have been submitted to the competition from both Ukrainian and foreign institutions from 25 countries: China, Poland, Mexico, USA, France, Greece, Germany, Canada, Costa Rica, Brazil, India, Pakistan, Israel, Macedonia, Lithuania, Latvia, Slovakia, Romania, Kyrgyzstan, Kazakhstan, Bulgaria, Moldova, Georgia, Turkey, Serbia.

The interest of foreign students in the competition grew every year. In 2018, the students representing 15 institutions from 7 countries have submitted 33 works. In 2021 the number of submitted works increased to 73, authored by the students of 40 institutions from 18 countries.

The competition is held in two stages. In the first stage, student research papers are reviewed by members of the jury who are experts in the relevant fields. In the second stage of the competition, the winners of the first stage have the opportunity to present their work to a wide audience in person or online.

All participants of the competition and their scientific supervisors are awarded appropriate certificates, and the scientific works of the winners are included in the electronic proceedings of the competition. Every year the competition receives a large number of positive responses from Ukrainian and foreign colleagues with the desire to participate in the coming years.

4. POWER ENGINEERING **AND ENERGY EFFICIENCY**

HELIUM PRODUCTION FROM NATURAL GAS AND MARKET ANALYSIS

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Abstract: *Helium is a non-renewable gas used in emerging applications as well as in well-established industries of more than 5 decades. Because it has such unique properties, it is difficult to replace it with another element.*

Helium is obtained as a by-product natural gas purification via cryogenic distillation, therefore its production is tied to that of methane. Helium as a by-product of this process is only profitable depending on the percentage that the natural gas carries. One part of the market is supplied by natural gas producers such as Gazprom, Exxon-Mobile and Qatar gas and the other part by annual auctions of the United States Federal Helium Reserve, which sells crude gas to refineries of Linde, Air Liquide, Praxair, Air Products and Messier. This scenario is about to change due to the total privatization of the reserve in Amarillo Texas and the sale of the last public reserves.

On the other hand, electromagnetic resonances always accounted for most of the helium demand, but the machines have been modernized and consume less without sacrificing efficiency. Experts suggest that helium consumption for the production of semiconductors and optical fibers in electronics will exceed that of MRIs in the coming years.

The helium market is volatile not only due to supply and demand but also due to logistics and storage complexities: in the past 15 there were three Helium Shortages that is 6 years in which supply could not meet demand. With inelastic economic characteristics and production methods that present adversities to supply the demand, this research opts for a better understanding of the elements that influence the second most common element in the universe but of limited quantities on Earth.

Keywords: *Helium, natural gas, cryogenics, MRI, BLM, Amur.*

I. INTRODUCTION

The work that follows aims to understand technical and economic elements that influence helium as a gas for industrial and technological use. First, a detailed description of helium's unique characteristics and specific applications is described, followed by an understanding of why it is such a unique element.

Then an economic analysis based on demand, supply and the largest traders in the world is conducted. Based on historical facts, information collected by experts, relevant news and market data related to helium as a product, an attempt is made to identify the forces that affect the price and quantity in the market.

From a better perception of the market the production process is described. The different technologies that allow obtaining high purity helium from natural gas are demonstrated to obtain a summary of the critical points for its purification and liquefaction.

II. Helium

2.1. Properties

The symbol for Helium is He, it has an atomic number of 2. It is an inert gas with no color or odor [Meyer, 1926]. Its two most important isotopes are ^3He with a natural occurrence of 0.000137%, and ^4He with a natural occurrence of 99.99% both stable. Its density at 298 K is 0.1785 kg/m³. This element has a boiling point of 4.15K (-269°C) [Sicius, 2016].

For pressures below about 2.5 MPa, helium remains liquid down to absolute zero [Leyarovski et al., 1986]. Under standard conditions, helium behaves almost like an ideal gas. The weight of one m³ of helium is 179g under standard conditions. Helium as an ideal gas has a heat capacity of 5.238 kJ / (kg K). And as a gas at atmospheric pressure a thermal conductivity of 0.143 W/(m K) [Langeheinecke et al., 2020], [Winnacker et al.,]. It has a boiling point of -269°C (4.15K), a heat of vaporization of 0.084 (kJ / mol), its triple point is -270°C at 5.043kPa and its critical point is -267.96°C and 227.5 MPa [Dohmann,].

In 1895, Ramsay produced helium by adding acid to uranium and isolating the gas that formed in the subsequent reaction. [Meyer, 1926]. Helium recorded the yellow line D3, which was characteristic of helium and was already known at the time, having previously separated nitrogen and oxygen. Almost simultaneously, Crookes and Cleve Langlet carried out a similar experiment. They recovered a sufficient quantity to determine the atomic mass of the gas [Sicius, 2016]. A little later, an oil well operated in Kansas delivered a natural gas that contained up to 12% by volume of an as yet unknown gas. Cady and McFarland proved in 1905 that it was helium. Almost simultaneously, Rutherford and Royds showed that alpha particles are helium nuclei [Sicius, 2016].

2.2. Sources

The first detection of He in air is based on the lines of the spectrum of crude argon. A He-Ne mixture was prepared using liquid hydrogen. The content in air was first determined by Ramsay in 1905 and then in 1908 at 0.0004% by volume. Subsequent determinations showed 0.0005% volume by Claude [Meyer, 1926]. A newer study shows that the amount of Helium in the air is close to 0, according to B.M. Oliver Measurements in 1981 of the helium content of the Earth's lower atmosphere have given a value of 5.222 ± 0.017 ppm by volume [Oliver et al., 1984]. Even though it is one of the most abundant elements in the Earth's air its quantities are still low compared to natural gas deposits [Littlejohn, 1993].

The helium that accumulates in the atmosphere could be the result of venting the helium separated in natural gas production but according to the study it is not really quantifiable. Helium II moves up against gravity on surfaces this phenomena is known as Onsager effect [Westphal, 2013]. Helium can be obtained from liquefied atmospheric air by fractional distillation, this was done for the first time in 1900 by Ramsay and Travers. They obtained a mixture of HeNe from which pure Neon is generated, but even after laborious fractionation and the use of very low temperatures, they did not obtain pure helium [Meyer, 1926]. This shows how energy intensive and complicated

it is to extract Helium from air in comparison to its major source is: Natural Gas. Helium is separated from methane and other gases by using their physical properties of adsorption like in air separation processes. [Van Sciver, 2013]. Therefore, helium is obtained from natural gas by fractional distillation. By cooling natural gas, it is possible to separate helium from hydrocarbons and nitrogenous compounds contained in crude natural gas [Timmerhaus, 2013].

Helium is formed during radioactive atomic decay. On earth, $4\text{ }^2\text{He}$ (Alpha-particles) is formed during Alpha-decay of various radioactive elements such as uranium or radium. Most of the Helium on earth comes from radioactive decay [Sicius, 2016]. From 1 Curie of Radium emanation in equilibrium with Radium-A, Radium-B and Radium-C, Danysz and Duane in 1912 calculated the formation of Helium of for 1g of Radium per year [Meyer, 1926]. Helium formation from Uranium. Helium can also be formed by alpha elements decay from Uranium and Thorium [Grynja and Griffin, 2016]. It is certainly a decay product of Uranium [Grynja and Griffin, 2016], [Meyer, 1926], [Yakuceni, 2009]. For 1g Uranium, a Helium formation of 2 to 4.5×10^{-12} g per year was calculated.

III. Application

Helium is now used in a great many applications [Sicius, 2016]. In welding technology, helium is used as an inert gas to protect the welding point from oxygen entering [Mohler, 1983]. In the food processing industry it is used as a packing gas [Kuhnert, 2014].

For analyzing critical products, which need to be totally hermetic, the use of gases in leakage tests has been implemented in several areas. Helium is used also for quality control of oral drug container products. If a leak is detected then the part is defective [Kossinna and Meyer, 2010] and needs a replacement or has to be fixed. In intensive care medicine, a helium-oxygen mixture (80:20) is used as breathing gas, which flows through constrictions with less resistance [Gupta and Cheifetz, 2005]. When diving, it is used as breathing gas: Trimix (oxygen, nitrogen, helium), Hydrex (hydrogen, helium, oxygen) and Heliox (helium, oxygen) [Lettnin, 2012].

There are two ways to decrease the ohm resistance of a conductor. The first option is to change the thickness and the length of the cable. The larger the diameter of the cable and the shorter it is, the smaller the electrical resistance, but short and thick cables are not so convenient or practical. The second dependence of the resistance is on the temperature of the conductor. The colder the temperature, the lower the resistance of the conductor [Lemmer et al., 2017]. In 1911 Heike Kamerlingh Onnes examined the electrical resistance of mercury with liquid helium at 4K and the resistance came down to zero. So he discovered the phenomenon of superconductivity [Huebener, 2017]. Helium plays a central role in superconductivity.

Regardless of improvement in high temperature superconductors, helium is still chosen as a coolant [Glowacki et al., 2013]. If superconductors are used, the helium used as a coolant helps to keep them below their transition temperature, e.g. in magnetic resonance imaging (MRI) [Sicius, 2016].

Nuclear magnetic resonance tomographies have shown high-resolution images from the body inside for the past decades using Helium to reduce the temperature of

the magnets [Lvovsky et al., 2013], [Heil, 1997]. This technology has been developed further the past years, for example it is possible super fast lung ventilation magnetic resonance imaging using hyperpolarized Helium-3 [Schreiber et al., 2000]. The MRI with hyperpolarized 3-He enables a detailed representation of the body morphology as well as organ and internal functions. [Morbach et al., 2006].

Aside from medical applications like MRI, superconductors are also used in nuclear magnetic spectroscopy. For alloys in the magnets to even reach superconductivity they have to be cooled down at cryogenic temperatures [Styles et al., 1984]. NMR-spectroscopy has been used in chemical analysis for determining and checking the structure of small molecules. The reason Helium plays a big role in superconductivity is because when the coil is completely wound, the wire can become superconducting once the materials lowered to a temperature of 2K. The magnet is hung on a Dewar Vessel with liquid Helium and such a low temperature can be reached [Rüterjans et al., 1996]. Nevertheless MRI technology has improved since it was invented and a lot of hospitals have transitioned from consuming one thousand liters of liquid helium per year for every machine to newer Zero boil off machines, which according to [Cockerill, 2021a] have shrunk in size and consume therefore less liquid helium than before.

In the Large Hadron Collider at the CERN research center in Geneva, two opposing beams with protons are accelerated into a 26.7 km tube. The rays cross in four places and are brought to collision after reaching the final energy. 9300 magnets keep the particle beams on the path. The magnets at CERN, which are necessary to focus the particle beams, are operated at a temperature of 1.9K, the rest of the accelerator at 4.5K. 700,000 liters of liquid helium are required to cool the material down [Müller, 2008].

According to [Scholes, 2011] NASA and the USA Military are the biggest consumers of helium to cool hydrogen and oxygen propulsion rockets down. In chemical rockets fuel-tank systems, two propellants are fed liquid fuel from two tanks via double injection. In case of liquid propulsion the fuel tanks must have a higher pressure than the combustion chamber. The fuels are injected by over pressure [Messerschmid and Fasoulas, 2011]. One method to deliver propellants the fuel is with pressurized gas. Neutral gases such as Helium or Nitrogen are used to push the fuel into the engine. Helium dissolves less in liquid oxygen, therefore it is the favored option [Sutton and Biblarz, 2016]. When using a pressurized gas the helium is fed into the fuel tanks and presses the fuel into the combustion chamber. Pressurized Helium can also be carried in gas phase in the same tank as the liquid fuels and be in contact with the liquids to pump them out. Another method is to use pumps to push fuels to the combustion chamber. In this case Helium replaces liquid fuel from the tank to maintain it pressurized [Ingenbergs, 2002]. Besides using He in Propulsion Systems, it is used to remove any remaining air from the engines to prevent that it freezes in the ducts [Sutton and Biblarz, 2016]. In laser technologies Helium is used as a buffer gas in Helium-Neon Excimer lasers in a range of 157nm-351nm wavelength [Svelto and Hanna, 1998].

In high temperature nuclear reactors HTR that use graphite as main material in the reaction chamber, helium has two important roles in the process. It cools the

reaction chamber down [Wu et al., 2002] and functions as a heat carrier for generating the steam. Helium is first heated up to 700°C and carries the heat to produce 530°C steam [Kugeler, 2001]. When using helium for this purposes it has the advantages of being inert and having the highest thermal conductivity of all gases after Hydrogen [Van Sciver, 2013], [Sicius, 2016].

A specialized use of helium is for the manufacture of optical fibers. The gas is injected in process cooling unit after the furnace and provides sufficient cooling so that the glass fibers do not break this way the drawing speed of the fibers is increased [Park et al., 2014].

A market that might grow is the use of helium in electronics [Cockerill, 2021a]. For instance in semiconductors production the gas is used to create an inert environment around the silicon to avoid undesired reactions [Filtvedt et al., 2010]. According to [Jelinek, 2018] the revenue of the semiconductor industry is expected to keep growing in the following years and after COVID-19 the semiconductor market could rise stronger like other electronic technology materials [Bauer et al., 2020] see Fig. 1.

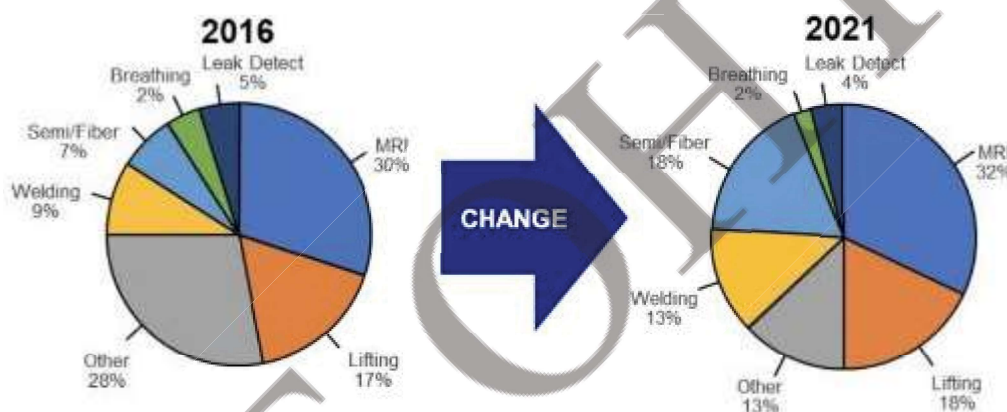


Fig. 1 Helium Transition: *High-tech usage in the semiconductor and fiber-optic segments has increased dramatically. It is expected that helium will play a significant role in the global refrigeration and transportation of COVID vaccines.* [Garvey , 2021]

IV. Supply and Demand

The helium supply chain starts with the radioactive decay and the helium mixed in the raw natural gas reserves. The first level of helium flow in the industrial supply chain consists of the natural gas extraction and processing. Helium is treated as a byproduct and is separated from the other components such as carbon-oxide and carbon-dioxide, hydrogen, nitrogen and hydrocarbons by cryogenic processes [Wilson and Newsom, 1968]. After this step crude helium is obtained with purities between 60 to 80 percent [Snyder and Bottoms, 1930].

Unpurified helium contains high amounts of nitrogen, the separation of the gases and components of crude helium to obtain high purity comprises the second level of the supply chain [Hamedi et al., 2019]. Helium refiners produce Grade-A Helium (high purity helium), they process crude helium and sell it for higher pices [Anderson, 2018], see Fig 2. This “high quality” helium can have a purity up to 99,99% purity with very low percentages of other components like hydrogen, oxygen and water [Sifrig et al., 2021].

After extraction, production and purification: the gas can be liquefied for special applications or stored as a gas at high pressures. When helium can be transported in liquid state in containers with volumes of 25000nm^3 . Liquid helium distribution has technical complications and significant losses due to temperature increase during transportation it boils. The other option to store and transport helium is as gas under high pressures [Smith et al., 2004]. In the third level of the chain, helium is sold to end users by refiners and non-refiners [Bell et al., 1983] or to smaller gas distributors that commercialize the gas and transport helium with trucks and storage tanks [Dong et al., 2014].

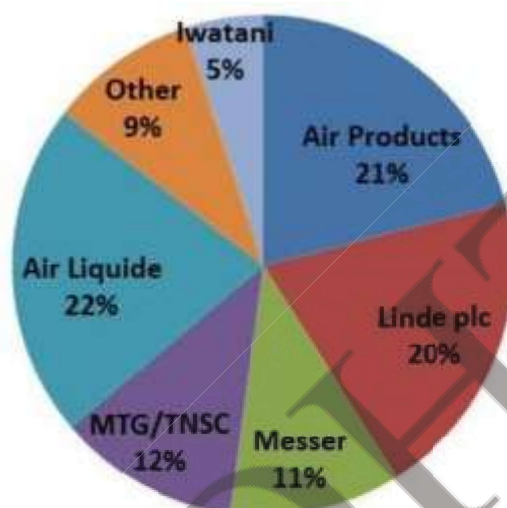


Fig. 2 World Wide refiners Share of Supply (Production)-2021: 2021 World Wide Helium Production 5.9 Billion Cubic Feet. [Garvey, 2021]

For years helium has been squandered because it is treated as an undesired byproduct from natural gas production facilities. Methane producers vent helium into the atmosphere [Nuttall et al., 2012b], which is counterproductive since purifying the gas from the air is more expensive than methane. Regularly increase on Helium consumption and demand will presumably continue [Olafsdottir and Sverdrup, 2020].

According to [Anderson, 2018] the helium market is complex due to inelastic demand, production of the gas only as a byproduct plus only a few big helium producing companies. Since the demand is uncertain, producers only separate helium from natural gas if they have storage facilities where the gas does not leak [Council et al., 2010]. For example refineries with access to the National Helium Reserve in Amarillo Texas. If they don't have easy access to any storage it is cheaper sometimes for the companies to vent it or leave it in a low percentage mixed with the natural gas [Clarke et al., 2013] because it is a harmless and an inert element.

After the Federal Helium Reserve (FHR) facility was completed in the 60's the governmental consumption of helium in the United States for military rockets and space exploration increased [Sears, 2012]. Apart from these consumption increases there was not enough demand to justify the investment in another storage facility like the FHR [Anderson, 2018].

An important transition use in Helium markets according to Global Helium [Garvey and Associates, 2021] and J.R. Campbell and Associates [Garvey, 2021] took place in the past four years: semiconductors and fiber optic share of the helium users

increased from 7% in 2016 to 18% in 2021. This could influence the helium consumption regions depending on fiber optic or electrical semiconductors producers and shift the demand of helium to Asian regions [Gravey, 2021].

Another key factor on Helium demand according to Phil Kornbluth, President of Kornbluth Helium Consulting LLC, is the role that private aerospace companies such as SpaceX and Blue Origin could play in the future if they use helium for space exploration and propulsion rockets [Kornbluth, 2020b]. Other ideas like Project Loon from Alphabet to use helium to suspend balloons and have a Balloon-base communications infrastructure could influence the demand in the future [Zindel, 2020].

V. Shortages

Possible helium supply disturbances are likely to happen as they happened in the past [Cockerill, 2021b]. In the beginning of the XX century the US government developed a Helium Reserve since it was considered a crucial element for national defence and it was used for airships until the 50s [Burton, 2016]. Later in 1960 an Act was created which allowed the stored helium to be commercialized to use helium for space exploration and to buy helium from natural gas producers [Nekuda Malik, 2013].

After years in 1995 when the Bureau of Mines was not able to pay its debt to the government the U.S. Congress passed another Act to privatise helium. In 1996 they ordered BLM (Bureau of Land Management US. to sell Helium at a prize depending on the stored amount and to keep 600 million cubic feet of the crude gas in storage and the remaining debt [Lance, 2014]. The first Helium Shortage happened in 2006 because helium sources were not being developed [Kaplan, 2007]. Prices doubled due to high helium demand for supercoils of magneric resonance imaging devices during that year [Yam, 2007].

In 2010 helium shortage 2.0 lasted until 2013, the price increased particularly sharply in the following three years [Ehrensberger, 2013], due to allocation of large quantities of helium as a reserve only for Federal consumption [Lance, 2014]. Obama signed in 2013 a new helium Act to end Federal helium operations by 2021 with low market disturbance and to continue founding of the Federal Helium Reserve [US. Government, 2013].

The first helium auction conducted by the BLM took place in 2014 and the planned disposal of the Federal Helium System was scheduled for 2021 [Jolley, 2016]. Ever since the first auction in 2014 the U.S. Federal Helium Reserve has published the yearly sold quantities and prices see Appendix: A1. The average price from the first auction was 161\$ per Mcf (thousand cubic feet), from 2015 to 2016 the market faced slight oversupply at a price of 106\$ per Mcf. Later in 2017 the market tightened at a price of 119\$ per Mcf. The next Helium Shortage (Helium Shortage 3.0) hit from 2018 to 2019 with a 144% price increase from the previous year at 290\$ per Mcf [Burton, 2022]. The shortage was a market reaction to the Qatar embargo which stopped helium trading in 2017 from a source that was responsible of 30% of the world supply [Anderson, 2018].

On 2020 a lot of change was expected in the market since the BLM reserve was planned to be privatised starting September 2021 [Nick Parkinson, 2020]. That same year Covid-19 hit and helium manufacturing was reduced same way other sectors did

[Nick Parkinson, 2020]. The world helium market was impacted by Covid-19 in several ways, the demand dropped after the second largest consumer of the gas, China went on lockdown. World wide social distancing impacted the balloon industry negatively, in total the market was reduced by at least 10% according to [Kornbluth, 2020a]. Helium experts suggest Covid-19 in 2020 events caused an early termination of Shortage 3.0 [Kornbluth, 2020a], [Garvey and Associates, 2021], [Cockerill et al., 2020].

In the first quarter of 2021 the helium market recovered and the demand returned, some applications like MRI and balloons had not recovered completely but others like electronics and aerospace returned stronger [Kornbluth, 2021]. Like other industries helium faced logistics and supply-chain problems [Dyatkin, 2020]. On the other side of the market, supply was also influenced that year by two key factors: first Qatar 3, Bazar's gas plant even though uncertain wanted to produce 432MMCF per year, second the long planned Gazprom's project Amur in Russia first production train started operating with 700MMCF (million cubic feet) per year [Quader, 2020], [Kornbluth, 2021], [Abdul Quader et al., 2018].

Qatar's embargo was lifted by Saudi Arabia that year [Adela Suliman, 2021] and was able to sell helium produced from extracted natural gas [Danabalan et al., 2022]. Since Amur's helium production plant-startup in September Gazprom was able to produce some helium before a planned shutdown in October 2021 which got prolonged because of a fire [Soldatkin, 2021]. Amur wanted to start production and include the second production train of the helium plant at the beginning of 2022 but there was an explosion and now the Natural Gas plant will shut down for at least 6 months [Kornbluth, 2022] which puts helium supply in uncertainty.

VI. Production

Helium is obtained from liquefied atmospheric air or from natural gas by fractional distillation [Gmelin et al., 1978]. In this way, a He-Ne mixture is obtained from which pure Ne is obtained and after laborious fragmentation and the use of very low temperatures high helium concentrations can be obtained using the different boiling points of the gases: -161°C for Methane and -268.93°C for Helium [Liquide, 2017]. Since producing Helium from air costs of 1600 \$ MCF (50450 e MCM) is harder than extracting it from natural gas at a cost of 7 \$ MCF (220,71 e MCM helium production out of natural gas predominates in the market [Anderson, 2018] , [Nuttall et al., 2012b].

6.1. Sources

From the Earth's crust radioactive decay helium accumulates in a "natural reserve" where is mixed with natural gas. If natural gas is processed and purified, raw helium with a 40 to 50% purity is obtained [Nuttall et al., 2012a]. In natural natural gas, helium accumulates in a relatively large proportion compared to air. By cooling the natural gas, it is possible to separate helium from the hydrocarbons and nitrogen compounds contained in the natural gas [Sicius, 2016].

Natural gas is processed before being transported, raw natural gas contains a number of hydrocarbons as well as water vapor, hydrogen carbon dioxide nitrogen and helium [Devold, 2013], [Bahadori, 2014]. Nitrogen rejection is a methane purification

crucial step, it is done by cryogenic distillation which allows helium production afterwards [Jahromi et al., 2018]. Without this step separating helium from natural gas very difficult [Grynja and Griffin, 2016]. After nitrogen rejection helium is pre-treated, refined and liquefied, some LNG plants do not have such units and helium is vented into the atmosphere [Nuttall et al., 2012b].

6.2. Process

Helium removal from natural gas consists of several steps: first the gas is fed and compressed, then a sequence of acid gas, water and mercury extraction takes place before liquefying through the main heat exchanger where the heavies are removed and LNG is separated from the flow stream containing 1-3-% helium that enters the Nitrogen rejection unit [Rufford et al., 2014]. From there Helium is recovered, purified to remove the remaining N₂ to reach a 99+-% purity and liquefy it (see Fig. 3)

The guideline to know if the helium recovery should be included in the natural gas processing is the amount of helium contained in the reservoir, the minimum percentage of helium on a stream that was purified so far is 0.05mol% due to high amounts of liquefied natural gas production [Hwang et al., 2000]. Other concentrations of helium in natural gases vary between 0.05 and 4vol% [Conference, 1960].

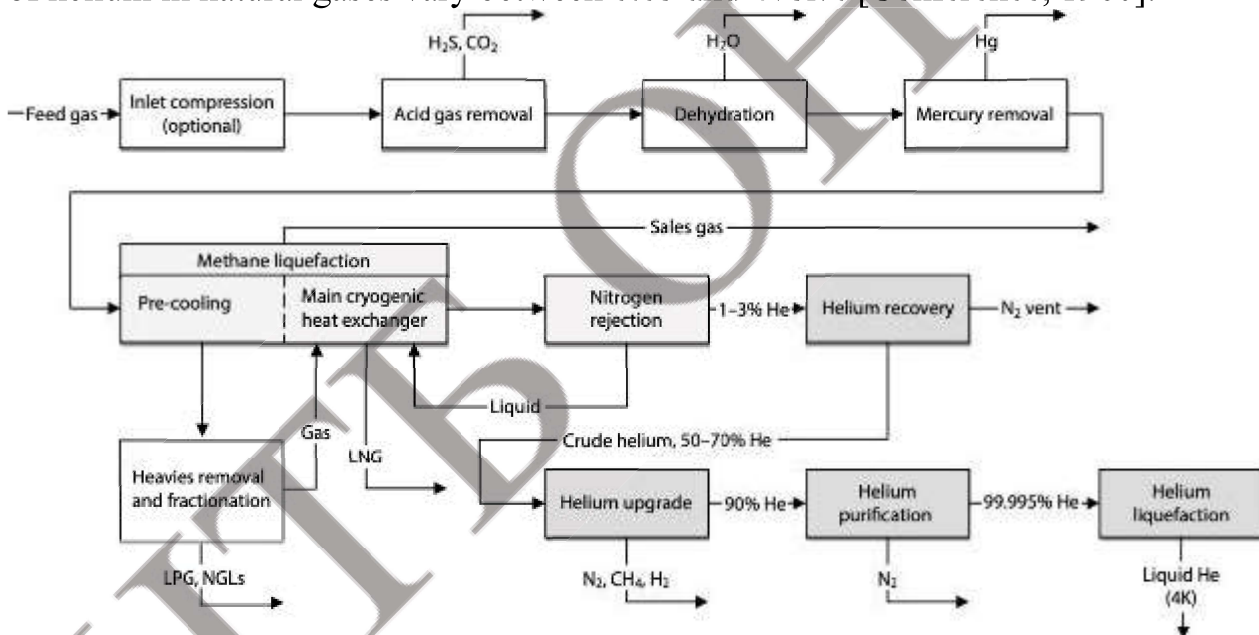


Fig. 3 LNG production with Nitrogen Rejection Schematic [Grynja and Griffin, 2016]

6.2.1. Cryogenics

Cryogenic technologies refers as engineering processes and technical applications that happen below 120K [Hwang, 2004]. The liquefaction of natural gas happens around that temperature. Cryogenic technology is used to refrigerate or cool down in processes. Another important role of cryogenics is to produce high purity gases [Agrawal et al., 2000]. Distillation has been used to process natural gas and remove nitrogen and helium. Two standard processes are single-column and double-column [Agrawal et al., 2000].

A stream of gas is cooled and fed to a high pressure column (2-2.8 MPa). Gaseous nitrogen is extracted at the top of the column and LNG at the bottom. The natural gas

is reheated in a Flash unit with previously separated nitrogen to recover refrigeration [De Guido et al., 2019].

In the double column process (see Fig. 4) the gas is fed to a high pressure column (1-

2.5 MPa). The nitrogen from the upper part of the column and a part of the crude LNG from the lower part continue to a second low pressure 150kPa column where the nitrogen is processed to complete the separation. The energy provided by the low pressure column reboiler is provided by condensation of nitrogen at the top of the high pressure column. As in the single-column process, liquid natural gas is mixed with nitrogen for nitrogen recovery [Bauer and Linde, 2009]. If the double-column process uses partial condenser crude helium can be purified and liquefied [MEHRA, 2017].

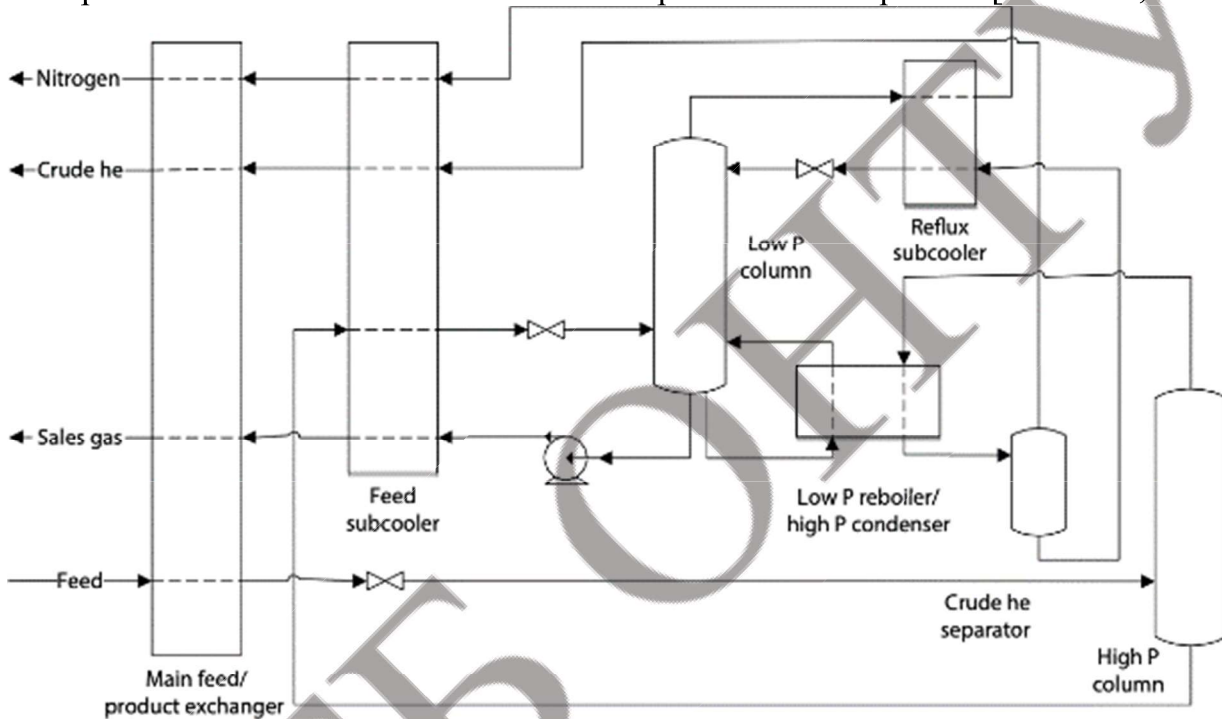


Fig. 4: Double-Column Process for Helium Processing example [Grynja and Griffin, 2016]

6.2.Purification

Helium's boiling temperature is at 4.2K, its critical temperature is at 5.2K and at some conditions it shows properties of a superfluid [Van Sciver, 2013]. To Purify helium several steps are necessary in order to remove hydrogen and neon which are not possible to remove in the Pressure Swing Adsorption process (PSA). Therefore a cryogenic process is combined with the PSA.

Crude Helium is cooled down and combined with recycled purge gas from the PSA unit to obtain a partial-condensed flow at a purity of 90% helium. This stream goes is mixed with air so hydrogen can be removed at a catalyst [200, 2006]. Afterwards the stream is cooled down again to separate the water. Once water is removed the stream enters the PSA unit where high purity helium is obtained and can be liquefied or sold as commercial pure gas [Das et al., 2008], [Das et al., 2012], [Rufford et al., 2014].

VII. CONCLUSIONS

Since the beginning of its commercialization, helium has shown to have unique characteristics and specific properties. This attributes to helium an economic value and also to its specific applications.

The main consumers of helium choose to optimize their technologies to reduce their consumption. The market is known as a "little transparent" and with limitations such as: a low number of suppliers, logistics complications due to the reduced number of commercial sources and the volatility of gas when it comes to being transported and due to its high price.

On the other hand, helium producers are tied to the amount of helium in the natural gas field, which leads them to question whether production is profitable, knowing that its management involves highly complex technology.

The fact that the market will no longer have the Federal Helium Reserve from the BLM in the United States in the coming years causes uncertainty whether there will be enough supply or of the prices will double like they did two years ago. This causes complications and responsibilities for the refiners and commercializers of this product since they will have to buy the gas directly from a natural gas processor.

The processes for helium purification and liquefaction involve a series of devices and technologies with a high number of investment and energy consumption. That is why the price of this specialty gas could remain high in the near future, taking into account that it is a non-renewable resource and consumption increases annually.

VI. References

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Appendix A1

5th Annual BLM Crude Helium Auction August 31, 2018				
Lot Number	Volume (MMcf)	High Bid	Bidder	Amount
Lot Number 1	25	\$233	Air Products - 107	\$5,825,000
Lot Number 2	25	\$308	Air Products - 107	\$7,700,000
Lot Number 3	25	\$334	Air Products - 107	\$8,350,000
Lot Number 4	25	\$337	Air Products - 107	\$8,425,000
Lot Number 5	25	\$271	Air Products - 107	\$6,775,000
Lot Number 6	15	\$272	Air Products - 107	\$4,080,000
Lot Number 7	15	\$259	Air Products - 107	\$3,885,000
Lot Number 8	15	\$250	Air Products - 107	\$3,750,000
Lot Number 9	15	\$260	Air Products - 107	\$3,900,000
Lot Number 10	15	\$236	Air Products - 107	\$3,540,000
Lot Number 11	5	\$251	Air Products - 107	\$1,255,000
Lot Number 12	5	\$261	Air Products - 107	\$1,305,000
	210	\$280	TOTAL	\$58,790,000

Average per Mcf

The average per Mcf bid is not intended to serve as a benchmark price for helium sales contracts.

4th Annual BLM Crude Helium Auction July 19, 2017					
Lot Number	Lot Number	Volume (MMcf)	High Bid	Bidder	Amount
Lot Number 1	1	25	\$112	274 - Linde	\$2,800,000
Lot Number 2	2	25	\$112	271 - Air Products	\$2,800,000
Lot Number 3	3	25	\$113	271 - Air Products	\$2,825,000
Lot Number 4	4	25	\$114	271 - Air Products	\$2,850,000
Lot Number 5	5	25	\$116	271 - Air Products	\$2,900,000
Lot Number 6	6	25	\$118	271 - Air Products	\$2,950,000
Lot Number 7	7	25	\$113	271 - Air Products	\$2,825,000
Lot Number 8	8	25	\$119	271 - Air Products	\$2,975,000
Lot Number 9	9	25	\$121	271 - Air Products	\$3,025,000
Lot Number 10	10	25	\$121	271 - Air Products	\$3,025,000
Lot Number 11	11	25	\$122	271 - Air Products	\$3,050,000
Lot Number 12	12	25	\$119	271 - Air Products	\$2,975,000
Lot Number 13	13	25	\$124	271 - Air Products	\$3,100,000
Lot Number 14	14	15	\$121	279 - Weil	\$1,815,000
Lot Number 15	15	15	\$122	271 - Air Products	\$1,830,000
Lot Number 16	16	15	\$122	271 - Air Products	\$1,830,000
Lot Number 17	17	15	\$122	271 - Air Products	\$1,830,000
Lot Number 18	18	15	\$124	271 - Air Products	\$1,860,000
Lot Number 19	19	15	\$124	278 - Uniper	\$1,860,000
Lot Number 20	20	15	\$122	278 - Uniper	\$1,830,000
Lot Number 21	21	15	\$123	277 - Praxair	\$1,845,000
Lot Number 22	22	15	\$125	276 - Matheson	\$1,875,000
Lot Number 23	23	5	\$123	277 - Praxair	\$615,000
Lot Number 24	24	5	\$123	276 - Matheson	\$615,000
Lot Number 25	25	5	\$122	277 - Praxair	\$610,000
Lot Number 26	26	5	\$125	271 - Air Products	\$625,000
Lot Number 27	27	5	\$125	271 - Air Products	\$625,000
Lot Number 28	28	5	\$125	271 - Air Products	\$625,000
Lot Number 29	29	5	\$125	271 - Air Products	\$625,000
Lot Number 30	30	5	\$128	271 - Air Products	\$640,000
		500	\$119	TOTAL	\$59,655,000

Average per Mcf

Bureau of Land Management Amarillo, Texas
2nd Annual BLM Crude Helium Auction
August 26, 2015, 1:00 PM Central

Lot Number	Volume (MMcf)	High Bid	Bidder	Revenue Generated
Lot Number 1	25	103	Air Products	\$2,575,000
Lot Number 2	25	105	Air Liquide	\$2,625,000
Lot Number 3	25	102	Air Products	\$2,550,000
Lot Number 4	25	104	Air Products	\$2,600,000
Lot Number 5	25	106	Air Products	\$2,650,000
Lot Number 6	25	100	Air Products	\$2,500,000
Lot Number 7	25	0	No Bid	\$0
Lot Number 8	25	103	Praxair	\$2,575,000
Lot Number 9	15	105	IACX	\$1,575,000
Lot Number 10	15	104	Praxair	\$1,560,000

Lot Number 11	15	104	Praxair	\$1,560,000
Lot Number 12	15	105	Praxair	\$1,575,000
Lot Number 13	15	105	Praxair	\$1,575,000
Lot Number 14	5	104	Praxair	\$520,000
Lot Number 15	5	106	Matheson	\$530,000
Lot Number 16	5	105	Air Liquide	\$525,000
Lot Number 17	5	105	Matheson	\$525,000
Lot Number 18	5	105	Matheson	\$525,000
TOTAL				\$28,545,000

Average per Mcf = \$104.18

Bureau of Land Management Amarillo, Texas

Helium Phase B Auction

July 30, 2014, 2:00 PM Central

Lot Number	Volume (MMcf)	High Bid	Bidder	Revenue Generated
Lot Number 1	10	161	Air Products	\$1,610,000
Lot Number 2	10	171	Air Products	\$1,710,000
Lot Number 3	10	180	Air Products	\$1,800,000
Lot Number 4	10	171	Praxair	\$1,710,000
Lot Number 5	10	178	Air Products	\$1,780,000
Lot Number 6	10	171	Praxair	\$1,710,000
Lot Number 7	5	156	Air Products	\$ 780,000
Lot Number 8	5	150	Air Products	\$ 750,000
Lot Number 9	5	142	Air Products	\$ 710,000
Lot Number 10	5	130	Air Products	\$ 650,000
Lot Number 11	5	140	Air Products	\$700,000
Lot Number 12	7.813	136	Air Products	\$1,062,568
TOTAL				\$14,972,568

Average per Mcf = \$161.32

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