MATHEMATICAL MODELING FOR CRYOGENIC UPGRADING OF BIOGAS AND CARBON CAPTURE

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Abstract. Biogas is used for various energetic purposes: Electricity generation, thermal purposes, replacement of fossil fuels in vehicles, injection into natural gas distribution networks and injection into blast furnaces to replace coke and pulverized coal. However, for the various uses, it is necessary to purify the biogas. The purification of biogas essentially involves the removal of CO_2. When the CO_2 is removed, the relative density of the gas decreases and the calorific value increases. Technologies for purifying biogas are commercially available, such as: Amine scrubbing, water scrubbing, pressure swing adsorption (PSA), membrane separation, and organic solvent washing. The use of cryogenics for biogas purification is still an emerging technology. In this context, the mathematical modeling of a cryogenic upgrading plant for the production of biomethane using Aspen Plus was carried out in this paper. The final results of the mathematical modeling show that it is possible to produce biomethane with a purity of 99.6% and to store CO_2 with a purity of 92.3%, which could be used for the production of microalgae in photobioreactors and in MAG welding processes.

Keywords: biogas, biomethane, carbon capture, blast furnace injection, cryogenic ugrading

1 Introduction

The increase in world population leads to an increase in demand, which in turn leads to an increase in the number of industries, focusing on the period after Industrial Revolution when this number increased significantly. Developed countries need to maintain their consumption levels and also cater to the foreign market which is also craving for products and services. However, with this large number of industries comes a large amount of pollutants that are produced during the production process [1, 12].

The leading role of the countries with the largest economic power is accompanied by the responsibility to emit the largest amount of polluting gases. As the amount of greenhouse gases (GHG) emitted into the atmosphere is increasing, the concern about the consequences of these emissions is growing day by day [2-3, 12].

More and more studies are being conducted on how to reduce the losses caused by these gases and the amount of gases released into the atmosphere, and there are several alternatives to reduce GHG emissions. A recent solution to the problem is the use of material from organic sources that can be recycled and is commonly referred to as biomass. The major global challenge in combating climate change is leading to the increasing use of renewable energy sources. In addition to environmental problems, the dominance of fossil fuels is increasingly encountering obstacles such as price volatility and the medium and long-term trend of diminishing supply. Biogas is a combustible gas mixture mainly composed of methane and carbon dioxide, which is produced during the decomposition of organic waste in an anaerobic environment [3, 5, 7].

The composition of the biogas varies depending on the substrate being decomposed and the physical and chemical conditions affecting the process of anaerobic biological digestion. The typical volumetric composition of biogas is about 60%CH_4, 35%CO_2 and 5% other gases: Nitrogen, ammonia, hydrogen sulphide, carbon monoxide, and oxygen, to name a few. Table 1 shows the chemical composition of industrial gases such as biogas, natural gas and syngas used in industrial applications [6-7].

Table 1. Composition of combustible gas mixtures

Component	Concentration		
	Biogas	Natural gas	SynGas
Methane (CH_4)	55-70	70-91	0-15
Ethane (C_2H_6)	-	5.1	-
Propane (C_3H_8)	-	1.8	-
Butane (C_4H_{10})	-	0.9	-
Pentane (C_5H_{12})	-	0.3	-
Carbon dioxide (CO_2)	25-40	0,61	25-35
Hydrogen (H_2)	-	-	20-40
Hydrogen sulfide (H_2S)	0.5-1	< 0.001	0
Oxygen (O_2)	< 0.2	-	-
Nitrogen (N_2)	< 0.001	0.32	2-5
Ammonia (NH_3)	< 0.01	< 0.001	< 0.001
Carbon monoxide (CO)	< 0.01	-	35-40
Water (H_2O)	< 0.5	-	-

Syngas is a combustible gas mixture produced by gasification processes, i.e. by the incomplete combustion of solid fuels. These processes use, for example, wood, coal, or other fuels that are generally rich in carbon and do not contain enough oxygen for complete combustion, and in some cases water vapor [3].

Natural gas is an energy source that occurs naturally, usually in deep underground reservoirs. Generally, it is obtained by the decomposition of organic plant and animal matter accumulated over millions of years in natural underground deposits [3, 11].

Natural gas is odorless, colorless and cleaner to burn than other fuels. It is the result of the combination of gaseous hydrocarbons under normal atmospheric pressure and temperature conditions that have not undergone any significant industrial conversion process, and is used essentially as it occurs underground. Natural gas consists of a variable gas mixture in which methane (CH_4) predominates with a proportion greater than 70% and which remains in a gaseous state at ambient temperature and atmospheric pressure [3, 11].

In this context, biogas proves to be one of the most sustainable alternatives and represents a technology that is at an advanced stage of industrial scaling. However, it is still in the early stages of a growth that could be exponential. Germany, Italy, France, the United States and United Kingdom inject 100% of the biomethane produced into the natural gas grid, while Norway and Sweden prefer its use by vehicles.

In Brazil, biogas production technology is not yet widespread and the priority use of biogas is the production of heat and electricity [8, 9, 13, 14]. In fact, biogas offers exceptional conditions to reduce the release of organic methane and CO_2 into the atmosphere. Its production involves limited, controlled and optimized processes that are commercially viable and produce a biofuel that can be used both for electricity generation and for vehicles as a substitute for diesel [10]. When biogas is burned, methane is converted to CO_2 and water, which reduces the negative impact on the climate and makes the processing of waste profitable [5, 9, 21].

Moreover, with some upgrading, it can be used as an alternative to natural gas in all its applications. One of the most widely used techniques in industries focused on steel production is the injection of fuel through the blast furnaces of Blast Furnaces. This technique is advantageous from an environmental point of view and due to the scarcity of high-quality raw materials to be injected into the blast furnace, as well as the high competitiveness of the steel sector [4, 17, 23-24].

In addition to the injection of pulverized coal into the blast furnaces of Blast Furnaces, fuel gasses are also injected. Currently, the most common gas used for injection in Blast Furnaces is natural gas. Studies are currently underway to use a new gas as an additional fuel, namely biogas.

The injection of biogas together with the pulverized fuel leads to a reduction in coke consumption as some carbon is added from the nozzles, which leads to a direct reduction in the production cost of cast iron. However, the biogas needs to be purified, which increases its heating power and improves the final quality of the product [4, 9, 17, 23-24].

Purification or upgrading of biogas is necessary when the intended use is injection into the natural gas distribution network, injection into blast furnaces or use in vehicles. Purification of biogas essentially involves the removal of CO_2, because as CO_2 is removed, the relative density of the gas decreases and the heating value increases [15-16, 18-20].

Technologies for purification of biogas are commercially available such as: Amine scrubbing, water scrubbing, pressure swing adsorption (PSA), membrane separation, and organic solvent scrubbing. They are all primarily recommended for the removal of CO_2, but they also remove other components [2, 11-12, 21]. The use of cryogenics for biogas purification is still a young technology. Cryogenic separation is based on the difference between the boiling points of CH_4 and CO_2, as shown in Figure 1

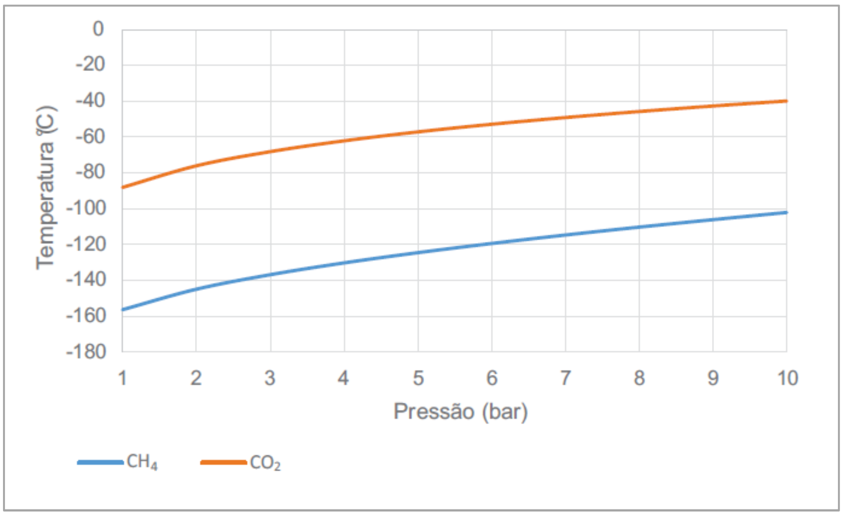

Figure 1. Boiling temperatures of methane and carbon dioxide indifferent pressures.

In cryogenic upgrading, the biogas is dried to avoid the formation of ice, pressurized to 40-80 bar, and cooled to at least -45°C, as the CO_2 begins to liquefy under these conditions. The gas is then cooled to -55°C and expanded to 8-10 bar. Upon further cooling, the gas reaches -110°C and a solid-gas mixture (CO_2/CH_4) forms at equilibrium. The solid phase is rich in CO_2 and the gas phase is rich in methane with contents between 90 and 98% methane [1, 3, 7-8].

When the gas is compressed to 17 to 26 bar and cooled to -25°C, with subsequent cooling in the order of -50 to -60°C, the CO_2 liquefies and can be removed at the bottom of the column. When cooling to -165°C, the methane contained in the biogas liquefies [10-11, 14].

Also in this case, it is necessary that impurities such as H_2S and H_2O are removed beforehand. However, it is also possible to separate the phases without solidifying the CO_2, thus saving energy and obtaining a purer biomethane since impurities such as H_2S in the liquid phase have been diluted in the CO_2 [15, 19, 21-22].

Although it is possible to produce high quality biomethane in cryogenic plants, several authors point out that the cost of installing and operating this technology is quite high, so cryogenic processing is still considered a developing technology [24-25].

However, recent studies indicate the possibility of producing biomethane in integrated steel mills, which makes the cost cheaper, as one could use the same equipment for gas separation as nitrogen and oxygen, which are also injected into the blast furnace nozzles to make the process more productive.

Biogas, for example, can be used as fuel for motor vehicles and for injection into blast furnaces to replace coal, which is a non-renewable natural resource. Moreover, the CO_2 that is not directly released into the atmosphere could be reused in MAG welding processes and in the production of microalgae in photobioreactors. In this sense, the main objective of this work was to mathematically model a cryogenic system for biogas upgrading for the production of high purity biomethane that can be used in nobler future applications.

2 Materials and methods

In cryogenic upgrading, biogas is cooled under high pressure and low temperature to separate the methane (CH_4) and carbon dioxide (CO_2) in liquid form. However, this process is very complex and requires prior desulfurization (H_2S removal) and drying of the gas (H_2O removal). The main drawback is the high energy consumption; however, it is possible to produce high quality biogas (99% CH_4).

The mathematical process simulation procedure was carried out by combining information about the process equipment. This procedure is influenced by linking the variables that are the output of one equipment and used as input for other equipment.

The modeling mainly used absorption columns, heat exchangers, coolers, compressors and centrifugal pumps for biogas upgrading process. The logarithmic temperature difference method was used to calculate the temperature differences in the heat exchangers.

The efficiency of the distillation columns depends on the chemical composition and flow rate of the biogas. In most cases, the distillation columns are operated under pressure to achieve a higher mass transfer classification and a larger capacity. The solute partial pressure depends only on the liquid composition and temperature.

The mathematical modeling of the cryogenic model was performed in Aspen Plus software using as input parameters a flow rate of 20 kmol/h, a pressure of 2 bar, a temperature of 23°C, and the chemical composition of the biogas as shown in Table 2 by the modular sequential method (Aspen Technology) with algorithm to solve the system of equations.

Table 2. Mole fraction composition of biogas

Component	Nomenclature	Mole fraction
Methane	CH_4	62.4%
Carbon dioxide	CO_2	36.9%
Oxygen	O_2	0.2%
Nitrogen	N_2	0.8%
Water	H_2O	0.1%
Ammonia	NH_3	0.005%
Hydrogen sulfide	H_2S	0.015%

The proposed flowchart for the simulation of cryogenic upgrading of biogas, as shown in Figure 2, aimed to achieve the highest methane concentration in the outgoing biogas stream, i.e. all operating conditions were designed to maximize the purity of the biogas produced.

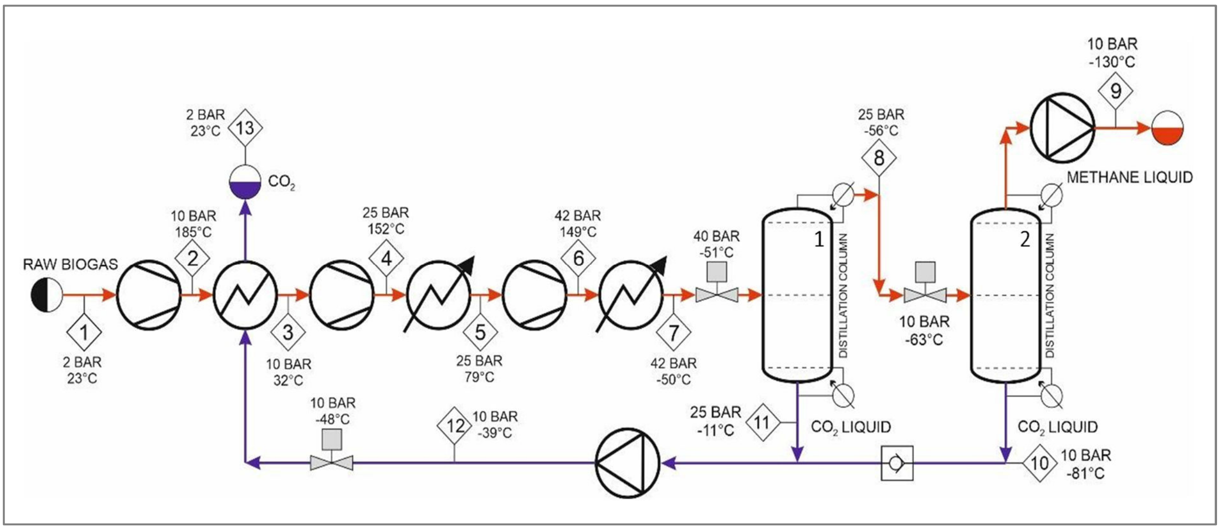

Figure 2. Upgrading cryogenic biogas

3 Results and discussion

According to Figure 2, the raw biogas (stream 1) with the chemical composition as shown in Table 2, a temperature of 23°C and a pressure of 2 bar is fed into a 3-stage compressor while the pressure increases from 2 bar to 42 bar (streams 1-7) and the temperature decreases to -50°C in 2 coolers and 1 heat exchanger.

Stream 7 is directed to an expansion valve and the pressure and temperature drop to 40 bar and -51°C. Stream 7 then enters the first distillation column.

After separation, stream 8 flows out of the separator through the top of separator 1 at a pressure of 25 bar, a temperature of -56°C and a concentration of 83.3% mol methane in the vapor phase.

At the bottom of separators 1 and 2 (streams 10 and 11), the liquid carbon dioxide is extracted and used to cool the raw biogas in the initial phase. The composition of separator 1 is shown in Table 3.

Table 3. Mole fraction composition of separator 1

Component	Nomenclature	TOP 15 kmol/h	BOTTOM 5 kmol/h
Methane	CH_4	83.3%	-
Carbon dioxide	CO_2	16.4%	98.4%
Oxygen	O_2	0.2%	-
Nitrogen	N_2	0.1%	-
Water	H_2O	-	0.8%
Ammonia	NH_3	-	0.2%
Hydrogen sulfide	H_2S	-	0.6%

In the last step, stream 8 is directed to methane liquefaction and pressure reduction in an expansion valve (from 25 bar to 10 bar). The liquid biomethane is taken from the upper part of the separator 2, while the liquid CO_2 is taken from the lower part. The compositions of the separator 2 are listed in Table 4.

Table 4. Mole fraction composition of separator 2

Component	Nomenclature	TOP 12 kmol/h	BOTTOM 3 kmol/h
Methane	CH_4	99.6%	18.0%
Carbon dioxide	CO_2	-	82.0%
Oxygen	O_2	0.3%	-
Nitrogen	N_2	0.1%	-
Water	H_2O	-	-
Ammonia	NH_3	-	-
Hydrogen sulfide	H_2S	-	-

In this modeling, the liquid CO_2 (streams 10 and 11) is pumped to the initial stage to exchange heat with the raw biogas in the 3-stage compressor (streams 12 and 13) to reduce energy consumption. The composition of the carbon dioxide, stream 13, is shown in Table 5.

Table 5. Mole fraction composition of separator 2

Component	Nomenclature	Flow rate 8 kmol/h
Methane	CH_4	6.7%
Carbon dioxide	CO_2	92.3%
Oxygen	O_2	-
Nitrogen	N_2	-
Water	H_2O	0.5%
Ammonia	NH_3	0.1%
Hydrogen sulfide	H_2S	0.4%

4 Conclusions

In this paper, the modeling of a cryogenic system was presented, focusing on phase equilibrium. Some conclusions can be drawn as follows:

- The purity of the produced biomethane was 99.6% in the liquid phase;
- The CO_2 produced had a purity of 92.3% in the gas phase according to the data of this model;
- The captured CO_2 can be used for the production of microalgae in photobioreactors and also in MAG industrial welding processes;
- Cryogenic purification of biogas is a very expensive technique, but it is possible to produce high purity biomethane as shown in this study;
- Cryogenic production of biomethane can be a viable alternative in integrated steel plants;
- Although not elaborated in this study, we know that biomethane (high purity biogas) has a higher calorific value than raw biogas, which makes biomethane injection in blast furnaces a new global trend;
- Regarding technologies for biomethane production, it was found that there are technologies in commercial stage, such as washing processes with water and solvents, PSA and membranes, which are used in other processes besides biomethane production;
- In terms of production and end use, the figures show that the largest end use is the production of electricity and heat;
- Germany, France, the United States and United Kingdom feed 100% of the biomethane produced into the natural gas grid, while Norway and Sweden give priority to use by vehicles;
- In Brazil, biogas production technology is not widespread and the priority use of biogas is the production of heat and electricity;
- As for new applications, the injection of biogas into blast furnaces is becoming a global trend, but this new technology is not yet widely developed;
- Feeding biomethane into blast furnaces is interesting because it can reduce the use of coal, a non-renewable natural resource;
- For future research, it is proposed to validate the simulation results with a more comprehensive set of industrial data for different operating conditions.
- It is also proposed to further investigate the gasification process and perform a detailed analysis of the different energy integration scenarios.

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Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authorship contribution statement
Wandercleiton S. Cardoso: methodology, writing - original draft, data interpretation, results, interpretation, recommendations, writing manuscript draft, investigation, results interpretation, reading manuscript and revision.
Raphael C. Baptista: formal analysis, data curation, laboratory operations, laboratory physico-chemical analysis, analysis and data interpretation, reading manuscript, and revision.
Renzo di Felice: reading manuscript, critical review of the article for intellectual content, methodology, and revision.

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