Master Thesis

Separation, purification and upgrading of biogas from supercritical water gasification

Author: Guillermo Jesús Rey Gutiérrez [1]
Supervisor: Raúl Robledo Cabezuela [2 3]

[1] Universidad Pontificia de Comillas (ICAI); 201801802@alu.icai.comillas.edu
[2] Universidad Pontificia de Comillas (ICAI); rrobledo@comillas.edu
[3] CADE Soluciones de Ingeniería S.L.; rrobledo@cadesoluciones.com

Abstract: The objective of this study is to select a process for obtaining biomethane from syngas, produced by supercritical water gasification (SCWG), with the necessary purity to be supplied to the natural gas network in Spain. The methodology used in this study is a simulation in CHEMCAD to determine the proper operation conditions to purify the syngas from three different scenarios of temperature and initial composition of the stream produced by SCWG. The selected technologies used in the simulation correspond to flash distillation as the liquid-gas separation process, absorption using amines has the gas separation process and methanation as the upgrading process. It was concluded that under the operating conditions used in the simulation, it is possible to obtain the conditions for injection of gas into the Spanish natural gas network.

Keywords: Supercritical Water Gasification, Upgrading, Bio-Syngas, Methanization, CHEMCAD.

1. Introduction

Energy production is undergoing a profound transformation in order to adapt to ever-growing energy needs. This transformation is driven by research into energy production technologies that have a positive or neutral impact on the environment.

Among the numerous alternatives for generating renewable energy, this study focuses on biomethane, a versatile energy product that can be stored, burned to generate electricity, or used as a source of heat for both industrial and residential purposes. As can be seen in Figure 1, electricity demand from thermal sources or sources that involve combustion for energy release accounts for 23.2% of Spain electricity needs in 2024, demonstrating the potential for gas-based energy in Spain [1].

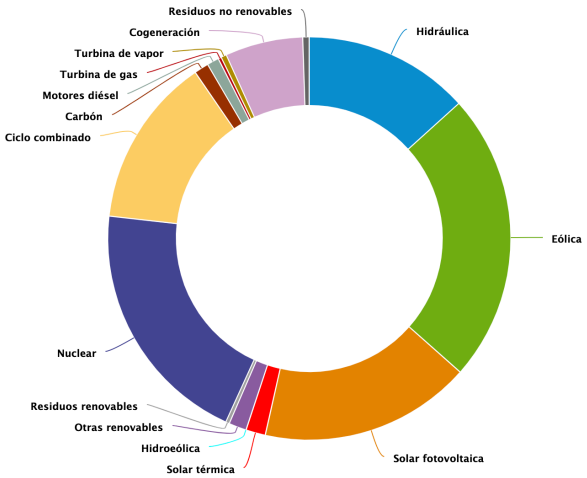

Figure 1: Electricity demand coverage 2024. Spanish Electricity Network [1]

This biomethane can come from various organic wastes treated by multiple transformation processes, such as anaerobic digestion, pyrolysis, or classic gasification. Among the many

alternatives for gas production, supercritical water gasification (SCWG) stands out, a technology currently in the research and development phase due to its potential to valorize organic matter with high moisture content (more than 60%) [2, 3]. The operating conditions for this process involve using water in supercritical conditions, at temperatures above 374 ºC and pressures above 221 bar [2], these conditions are kept after the reaction leading to the separation, purification and upgrading processes stages.

Among the main countries studying supercritical gasification are Spain, Germany, the Netherlands, the United States, Switzerland, and France [2]. In Switzerland, research is led by the Paul Scherrer Institute (PSI), while in France it is led by the Commissariat à l'Énergie Atomique (CEA) and in Spain its current researchers work for CADE Soluciones de Ingeniería, S.L. [2, 3].

Currently there are two main categories for the process, catalytical and high temperature supercritical water gasification processes, differing by the use of catalysts, the concentration of different gasses produced and the temperature of gas production [2]. Since this process produces syngas, a mixture of H_2, CO_2, CO and CH_4, dissolved in water it needs further separation processes to obtain the CH_4 produced [2].

2. Objectives

The main objective of this study is to obtain a process for obtaining biomethane from syngas produced by supercritical water gasification (SCWG), with the necessary purity to be supplied to the natural gas network in Spain. To meet the main objective of this work, the following sub-objectives are established:

- Evaluation and study of different liquid-gas separation technologies.

Since the supercritical gasification process is used on biomass with a minimum moisture content of 60% of the total mass content, research is needed on the separation of liquid and gas from the water stream containing the produced syngas.

- Evaluation and study of different gas separation technologies.

Once the processes for separating excess liquid from the gas mixture have been studied, we move on to studying technologies for separating process gases, since methane is the gas of great interest in this work.

- Evaluation of gas purification and upgrading methods to meet purity requirements for injection into the Spanish natural gas grid, with renewable guarantees of origin.

Since gas separation does not necessarily achieve the desired final gas qualities, processes that are considered exclusive to gas upgrading are studied. Some of those already seen in the previous section can be considered part of this study.

3. State of the art for methane recovery

The following technologies have been studied due to their common usage in chemical, petrochemical and engineering fields for chemical separation, except for the upgrading methods.

3.1. Liquid-gas separation technologies

Different technologies were studied for liquid-gas separation due to the grand amount of water present in the product stream following the SCWG process (more than 60% in mass). Among the technologies three showed promise due to the reported efficiencies of operation, those being flash distillation with a reported efficiency of 99% for Liquid-gas separation, desorption with a variable efficiency of 30% for CH_4 [4] to CO_2 89% [5] and liquid-gas membranes with a 92.6% gas recovery efficiency [6].

3.2. Gas mixture separation technologies

Just like the different technologies studied for liquid-gas separation there are multiple technologies suitable for methane separation from the syngas recover from the water rich product stream. Among the different technologies available three showed promise due to the reported efficiencies of operation and implementation across the chemical and gas industries, those being absorption with reported efficiencies has high has 99%, adsorption and membranes for gas separation with also a 99% CH_4 recovery efficiency [7].

3.3. Upgrading technologies

Since some of the technologies used for gas mixture separation can also be used for upgrading of biomethane, only two alternatives were studied for the specific purpose of upgrading biomethane. These two technologies are cryogenic distillation which allows the reduction of impurities in CH_4 streams due to condensation, with the reported capability of producing CH_4 with 97.12% molar purity and methanation, which allows for extra methane production with a theoretical 78% efficiency.

3.4 Selected technologies

After a review process of different liquid-gas separation, gas separation, and gas upgrading technologies, the following technologies were selected for simulation.

- Flash distillation as the liquid-gas separation process, due to the simplicity of the technology and the reported 99% efficiency purification of gas mixtures from water.
- Absorption using amines has the gas separation process, due to market share in the European union of more than 65% biogas purification.
- Methanation as the upgrading process, due to the interest in increasing the overall amount of biomethane, which improves its properties such as its calorific value.

3.4.1. Flash distillation

Distillation is a unit operation widely used in the chemical industry to separate liquid mixtures based on the difference in volatility between their components. The term distillation is very broad and encompasses multiple types of distillation used in the chemical industry, in this thesis we mainly focus flash distillation. This process consists of continuously feeding a mixture in thermodynamic equilibrium into a tank, which, by means of instantaneous pressure and/or temperature variation, separates into two phases: a vapor phase and a liquid phase. Among current flash distillation technologies, there are patents that demonstrate the efficiency of separating CO_2 from a water-based stream with an efficiency of over 99% in the purification of both water and CO_2 [8]. In the case of CH_4, it is assumed that, as it has a lower solubility in water than CO_2 approximately 26 times lower [9], the same separation efficiencies can be achieved with respect to the water-rich liquid phase.

3.4.2. Absorption/Scrubbing

Absorption is based on contact between a gas mixture and a liquid in order to selectively dissolve one or more components by transferring mass from the gas to the liquid [10]. Among the most common absorbents used in CO_2/CH_4 separation are water and amines. This technology dominates 65% of the European biomethane purification market in 2018, with 40% of the European market using water as an absorbent agent and 25% using chemical methods (amines) [11].

Studies have been found that claim carbon dioxide reduction efficiencies of up to 95%. One of them used a combination of amines: 40% methyldiethanolamine (MDEA), 3% diethanolamine (DEA), 7% diethylenediamine (PZ) together with additives managed to reduce the CO_2 content in a gas stream by more than 99.5% [12]. The stream in this study was a mixture of 62% CH_4 and 37% CO_2 [12]. Another study, in this case simulating amines, used a stream similar to the previous experiment, in this case 60% CH_4 and 40% CO_2 with temperature variation in the operating

temperature during the simulation [13]. In this simulation, the amine used was aminomethylpropanol (AMP). In these simulations of CO_2 separation in the biogas stream studied, the process achieved 97% efficiency [13].

3.4.3. Methanation

Since CO_2 has no energy value, the previous sections on gas separation and cryogenic distillation have analyzed various technologies focused on its separation for other uses, with the aim of obtaining biomethane suitable for injection into natural gas networks. However, there is the possibility of converting CO_2 into CH_4 through methanation, in order to improve the concentration and purity of biomethane without losing carbon that can still acquire value. Methanation is a process that allows a large part of the impurities that make up syngas to be converted into CH_4, which increases the final amount of CH_4 in the overall process, improving its quality and properties of use. Since it is not used directly as a CO_2 or H_2 separation process, as both gases are necessary for the process, it is classified as an upgrading study. Methanation chemical equation, also known as the Sabatier reaction, is as follows:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$$

This exothermic thermodynamic equilibrium reaction is favored at lower temperatures, but the total conversion of CO_2 to CH_4 still has major limitations due to kinetic constraints, which is why there is growing interest in studying potential catalysts that improve its overall efficiency [14]. Currently, it is believed that the maximum theoretical efficiency that can be achieved in the conversion of CO_2 and H_2 is 78%, based on the lower calorific values of CH_4 and H_2 [15]. In addition to the energy requirements due to it being an exothermic reaction, it has also been found that CO_2 selectivity in the formation of CH_4 is favored by varying the pressure between 1 and 100 atm. However, this pressure variation can be very costly, so the aim is to improve the efficiency of the process to operate in an ideal range of 8 to 16 bar. Regarding temperatures of those studied, the highest efficiency is between 200 and 400ºC, when highest efficiency of CO_2 conversion towards CH_4 is achieved [16].

4. Spanish gas network grid purity conditions

Due to the interest in supplying biomethane to the grid, the maximum amounts of impurities and the properties of biomethane are stipulated in Spanish Official Bulletin, BOE (*Boletin Oficial del Estado)*, specifically in the 3873 BOE's disposition, number 50 of 2025 **[17]**. In section 2.5.2.2 de *'especificaciones de biometano' (biomethane specifications)*, the following impurity compositions and thermal properties for injection into the network are established.

Table 1. Properties of biogas for injection of biomethane into the natural gas network in Spain [17].

Property	Unit	Minimum	Maximum
CO_2	% molar	-	2.5%
H_2	% molar	-	2%
CO	% molar	-	0.1%
O_2	% molar	-	0.01%
H_2O (dew point)	ºC at 70 bar	-	2
Higher calorific value (PCS)	kWh/m³	10.26	13.26
Wobbe index	kWh/m³	13.403	16.058
Relative density	-	0.555	0,.7

Among the considerations considered in this work is that the only gases formed in the supercritical gasification process of organic matter are CO, CO_2, CH_4, and H_2. Of these gases, the amount of CO formed has been considered insignificant, as has the amount of water present after the simulations, where in the most unfavorable case did represent 0.04 molar of the simulated mixture.

The CO could have been used in the proposed methanation reaction with two independent methanation reactors, although this could increase the need to supply H_2.

5. Simulation study of methane recovery

Once the technologies that enable the separation of biosyngas from the liquid stream after passing through the SCWG reactor, as well as the separation of biomethane from the other gases produced, have been analyzed and selected, a simulation was prepared based on the intrinsic need for each of the operations. Since the first problem found with the SCWG is the abundance of water the first operation that was carried out was the flash distillation followed by a methanation reactor to take advantage of the amount of CO_2 and H_2 already present in the biosyngas mixture. Since the methanation process produces water alongside CH_4, a second flash operation was included before the final operation of gas separation using absorption to reduce the remaining CO_2 present in the mixture.

The simulation was carried out by using the chemical process simulation software CHEMCAD, employing the Benedict-Webb-Rubin-Starling (BWRS) thermodynamic calculation model, due to its ability to calculate under supercritical conditions, as well as being used for natural gas and CO_2 simulation processes, due to the supercritical initial conditions of both the water and carbon dioxide present in the mixture to be treated, and its ability to accurately simulate the process chemical and physical interactions. The following simulation is used to evaluate the combination of the selected technologies.

The following simulation design was developed entirely for this study, own authorship from CHEMCAD, using has reference the items available in the simulation software.

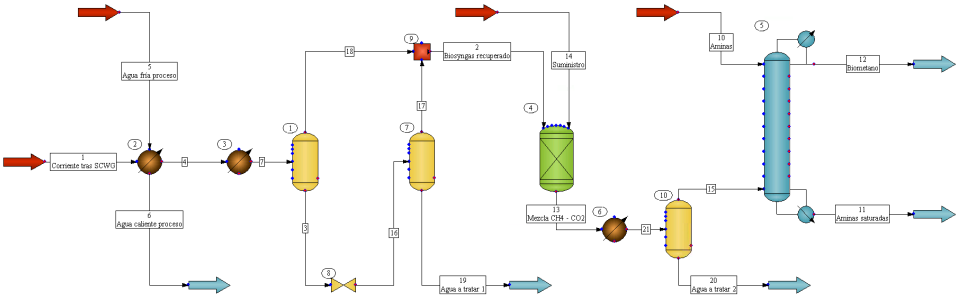

Figure 2: Simulated process designed in CHEMCAD simulation, own authorship from CHEMCAD, using has reference the items available in the simulation software.

5.1. Simulation equipment

- Heat exchangers marked as brown spheres. These are the elements that are employed prior to flash distillations. The Heat exchangers in the simulation include element **2** has a heat recovery unit which transfers excess heat to water inlet stream for SCWG; element **3** which reduces the temperature of mixture to 25ºC; and finally, element **6** which also reduces the temperature of mixture to 20ºC or 5ºC depending on simulation scenario. The temperature of 25ºC before elements **1** and **7** was selected due to low solubility of gas in water at that temperature.

- Flash drums units marked as yellow tanks. These units are used for recovery of gas contained in water rich streams. The Flash drums in the simulation are element **1**, which separates gas mixture from water at 250 bar 25ºC; element **7**, which separates gas mixture from water at 1 bar 25ºC; and element **10**, which separates gas mixture from water at 30 bar. It was decided to employ a multi-stage flash distillation unit to recover the highest amount of gas from the water at the first part of the simulation due to high pressure and a second flash distillation unit was added after the methanation reactor due to the formation of water.

- Pressure reduction valve, between equipment, marked as element **8**.

- Steam mixer, element **9**, in which the vapor phases rich in syngas obtained from flash distillation are mixed. Its pressure is adjusted to match the pressure of the next equipment, 30 bar and its temperature corresponds to the temperature of the gas, which is 25ºC.

- Methanation unit marked as element **4**. Third piece of equipment that allows gas treatment. It operates at 400ºC in order to simulate the reaction temperature with the use of a catalyst. It was decided that it operates at 30 bar, since it favors the reaction selectivity towards CH_4 formation with a reaction efficiency of 78%.

- Absorption column marked element **5**. Last piece of equipment in the process, after which the gases leave the simulation, it employs an amine solution of that enters from the top and interacts with the gas mixture in order to capture CO_2. It operates at 30 bar and with an amine temperature of 25ºC.

5.2. Simulation conditions

Since the simulation evaluates the capability of the original stream to be purified, three simulation scenarios are evaluated based on the different supercritical condition has it changes its chemical composition and temperature to resemble 1 theoretical catalytical SCWG stream, 2 theoretical high temperature SCWG stream and 3 experimental SCWG stream. The three compositions and temperatures of the incoming aqueous currents 1 that define each simulation performed are shown below in table 2. Each simulation uses a supercritical stream flow of 25 kg/h at 250 bar.

Table 2. Supercritical inflow streams mass compositions and temperatures

Simulation	Type of stream	Temperature	H_2	CH_4	CO_2	H_2O
1	Theoretical catalytical SCWG stream	480ºC	0,21%	10,63%	9,16%	80%
2	Theoretical high temperature SCWG stream	625ºC	1,78%	10,39%	7,83%	80%
3	Experimental data SCWG stream	525ºC	0,38%	3,4%	29,22%	67%

The Experimental data SCWG stream was acquired for simulation since this master thesis was elaborated while an internship at CADE Soluciones de Ingenieria, S.L. Some of the parameters in this simulation like pressures of equipment and the inclusion of the heat recovery unit are also selected to match some of the design choices of CADE's experimental facility.

Additional to the supercritical streams two other inflow streams are used for the simulation, a supplementary stream for the methanation reaction and an amine rich stream. The supplementary stream operates at 30 bar at 25ºC and complements the amount of CO_2 or H_2 needed for the methanation reaction in order to reduce the amount of CO_2 present in the syngas mixture.

In the case of the amine inflow a solution the mixture is defined that has 45,72% Ethylene glycol, 32,37% n-propanol and 21,91% of mixture of Aminomethylpropanol, for a total flow of 5 kg/h at 25 ºC and 30 bar. This mixture was selected due to it 97% efficiency for CO_2 extraction.

5. Results

The results shown below show the composition of the gases in the three simulations. Starting with the theoretical simulations and ending with the experimental data simulation. To simplify the amount of raw data obtained from the simulations, only main gas mixture streams are showcased after each separation stage.

The efficiency of the separation process where calculated cording to the reduction of impurity of present in the gas, for the flash distillation units it measures the amount of H_2O extracted from the stream, for the methanation reactor the amount of CO_2 reduced due to form CH_4 and for the absorption the decrease of CO_2 from the stream.

5.1. Theoretical catalytical SCWG stream simulation

Table 3. Streams compositions in mass after it pass through the separation process in simulation 1

Separation process	Efficiency	H_2	CH_4	CO_2	H_2O
multi-stage flash distillation	94.87%	1%	45%	35%	18%
Methanation reactor	78%	0%	53%	7%	39%
flash distillation after methanation (20ºC)	99.94%	0%	95%	5%	0%
flash distillation after methanation (5ºC)	99.98%	0%	98%	2%	0%
Absorption column	10.39%	0%	98%	2%	0%

5.2. Theoretical high temperature SCWG stream simulation

Table 4. Streams compositions in mass after it pass through the separation process in simulation 2

Separation process	Efficiency	H_2	CH_4	CO_2	H_2O
multi-stage flash distillation	95.14%	8%	44%	31%	17%
Methanation reactor	60.46%	0%	48%	10%	42%
flash distillation after methanation (20ºC)	99.,95%	0%	94%	6%	0%
flash distillation after methanation (5ºC)	99.99%	0%	97%	3%	0%
Absorption column	10.14%	0%	97%	3%	0%

5.3. Experimental data SCWG stream simulation

Table 5. Streams compositions in mass after it pass through the separation process in simulation 3

Separation process	Efficiency	H_2	CH_4	CO_2	H_2O
multi-stage flash distillation	95.03%	1%	10%	78%	10%
Methanation reactor	78%	0%	30%	16%	55%
flash distillation after methanation (20ºC)	99.98%	0%	91%	9%	0%
flash distillation after methanation (5ºC)	99.99%	0%	96%	4%	0%
Absorption column	12.31%	0%	96%	4%	0%

5.4. Biomethane properties after absorption column

Table 6. Biomethane properties after absorption column

Property	Unit	Theoretical catalytical SCWG stream simulation	Theoretical high temperature SCWG stream simulation	Experimental data SCWG stream simulation
CO_2	% molar	0.898	1.130	1.580
H_2	% molar	0.019	0.016	0.050
Higher calorific value (PCS)	kWh/m³	10.863	10.834	10.781
Wobbe index	kWh/m³	14.536	14.470	14.347
Relative density	-	0.558	0.561	0.565

5.5. Biomethane properties after flash distillation at 20ºC

Table 7. Biomethane properties after flash distillation at 20ºC

Property	Unit	Theoretical catalytical SCWG stream simulation	Theoretical high temperature SCWG stream simulation	Experimental data SCWG stream simulation
CO_2	% molar	1.801	2.310	3.500
H_2	% molar	0.018	0.015	0.043
Higher calorific value (PCS)	kWh/m³	10.834	10.778	10.643
Wobbe index	kWh/m³	14.338	14.202	13.889
Relative density	-	0.571	0.576	0.587

6. Discussion of results

The liquid-gas separation achieved by using the two flash distillation units to reduce the water content at the beginning showcase an average 95% efficiency. This makes sense, since these operating temperatures allow the mixture to be in a two-phase state at the unit inlet, and CH_4 and H_2 are insoluble in water, which facilitates good separation. It should be noted that of the three gases that make up the biosyngas, the one that is most reduced at this stage for the three simulations is CO_2, which makes sense since it is the most soluble in water.

Regarding the methanation process, the average CO_2 reduction efficiency for the simulations is 72.15%, which is acceptable given that the reaction has a 78% yield. The fact that it does not deviate significantly from this percentage is promising for this stage. It should be noted that for the theoretical catalytic current and experimental data current scenarios, this 78% maximum theoretical yield is achieved, while for the high-temperature theoretical current scenario it is not. This may be due to the difference in the supply of gases used in this stage, since the high temperature current is the only simulation in which CO_2 is supplied instead of H_2.

As mentioned before, in the structure of the process, the stage following methanation corresponds to the amine absorption process. However, due to the formation of water after the previous operation, an additional flash distillation process has been included, which establishes the pressure and temperature conditions under which the CO_2 and CH_4 rich stream interacts with the amines. Just like the previous flash operation, the mixture is cooldown in order to facilitate the liquid-gas separation process. During the simulations, it was observed that after leaving the flash distillation unit after methanation reaction, the biomethane in some scenarios already meets the conditions for injection into the natural gas network. Because of this in the results appear has flash distillation after methanation (20ºC) and flash distillation after methanation (5ºC), the scenario of 20ºC in some cases meets the conditions established for gas to be transport in the Spanish national gas network.

Two temperature ranges were used for different reasons. In the case of 5 °C, this condition was selected due to the difficulties in properly managing the final stage of separation by absorption with amines, since it was of interest to be studied. This process was only efficient when the amines were kept relatively warm and at high pressure, with their performance being sensitive to the temperature of the syngas stream at the inlet. Iteratively, it was determined that the optimum temperature for the operation of the amine absorption was for the syngas mixture to enter the scrubber at 5 °C.

As for 20 °C, it was observed that, although a gas stream suitable for recovery was already obtained at 5 °C, in some cases without the need for the amine stage, such a drastic reduction in temperature was not always operationally convenient. Through iterative simulations, it was verified that, in two of the three scenarios evaluated, maintaining the final flash distillation unit at 20 °C also allowed gas to be obtained in conditions suitable for injection into the natural gas network.

Regardless of the condition studied in the simulation, the flash distillation process after the methanation process shows an overall efficiency of 99.9%, in separating the excess water present in the gas mixture.

The operation with amines proved to be problematic, since with the small amount of CO_2 remaining in the mixture, it was observed that after the process it also retained part of the CH_4 and the remaining water, which is reflected in an overall efficiency of 10.95% in terms of reducing the CO_2 content. This can be seen in the extreme decrease in the performance of the flash distillation drum prior to this operation.

7. Conclusions

Based on the simulation results, it can be concluded that the use of most of the technologies selected to treat biomethane from supercritical water gasification was appropriate. Those been liquid-gas separation a flash distillation, the upgrading operation with methanation, and a second flash distillation after the upgrading process, under the right conditions, would be sufficient to obtain biomethane of a quality suitable for injection into the natural gas network in Spain.

This however can't be said about the amins used in this study, based on their average efficiency 10.95%, in addition to the loss of biomethane resulting from the use of the amines in the simulation. The amines used for the simulation were selected based on their theoretical efficiency in the study of reference, but the very low amount of CO_2 present in the final gas mixture and the operating conditions of this stage are different. Their potential for industrial use is not denied, since the use of amines dominates 25% of the European market as a gas separation agent. They would probably be more efficient if the mixture contained a higher amount of CO_2 in the absence of a methanation unit that drastically reduces the amount of CO_2. As a future study, it is considered appropriate to evaluate comparatively the use of the methanation unit and the amine absorption unit as final stages of the process after the first flash distillation.

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