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Analysis of Negative Emission Ammonia Fertilizer (urea) Process

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Abstract

As the world population keeps increasing, ammonia-based fertilizers like urea are essential to provide food security. However, the current fertilizer industry is based on fossil fuel feedstock (mainly natural gas), making the production process CO₂ emission-intensive. More specifically, besides the CO₂ emitted during the process, the CO₂ captured in urea is also released into the atmosphere after the fertilizer is applied to agricultural soils. Thus, positioning the fertilizer industry among the top four industrial emitters globally. Hence, in order to meet the target of limiting global warming to 1.5 °C and achieve net-zero emissions by 2050, it is necessary to strengthen the carbon mitigation efforts in the current fertilizer industry. This can be achieved in different ways, such as using renewable biofuels and implementing technologies that can lead to zero/negative CO₂ emissions.

For that reason, the present study presents pathways to achieve a more environmentally friendly fertilizer production process. An overall analysis is performed if negative emissions can be achieved by replacing different fractions of natural gas (used as both feedstock and fuel) with biogas and biomethane and by capturing and storing the CO₂ emitted from the process using chemical solvents as activated MDEA and MEA. The results obtained from the study revealed that negative emissions in fertilizer plant can be achieved by retrofitting an existing ammonia plant with a MEA based CO₂ capture system (with a carbon capture rate of 90%) for the SMR burner flue gas, and by introducing 50% of biogas in the feedstock (alongside Natural gas), and 75% of biogas in the SMR burner fuel (alongside Natural gas). This initial approach would result in net negative emissions from urea's production and application and require approximately 0.5 kg of biogas per kg of urea produced in this case. Furthermore, the equivalent energy intensity for the negative emission urea plant would be 0.32% and 3.37% lower compared to the fossil fuel-based case without/with CCS, respectively. Ultimately, it is even possible to produce approximately 6% more urea product by replacing a particular fraction of natural gas with biogas. The reason for this increased production is due to the surplus of carbon dioxide by the introduction of biogas. It can be used along with the ammonia product going to storage in the fossil fuel-based case, where there was not enough CO₂ to keep the feedstock molar ratio at the urea plant's inlet.

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Nomenclature

<i>Symbol</i>	<i>Definition</i>
<i>ATR</i>	<i>Autothermal Reformer</i>
<i>BECCS</i>	<i>BECCS bio energy carbon capture and storage</i>
<i>BECCUS</i>	<i>BECCUS bioenergy carbon capture utilization and storage</i>
<i>BG</i>	<i>Biogas</i>
<i>BM</i>	<i>Biomethane</i>
<i>BRC</i>	<i>Biogas Research Centre</i>
<i>CCS</i>	<i>Carbon Capture and Storage</i>
<i>CHS</i>	<i>Chemical Scrubbing</i>
<i>CRY</i>	<i>Cryogenic separation</i>
<i>EU ETS</i>	<i>European Union Emission Trading System</i>
<i>GDP</i>	<i>GDP gross domestic product</i>
<i>GHG</i>	<i>Greenhouse Gas</i>
<i>HHV</i>	<i>High Heating Value</i>
<i>HT</i>	<i>High Temperature</i>
<i>HVO</i>	<i>Hydrogenated Vegetable Oil</i>
<i>HyCO</i>	<i>Hydrogen and Carbon Monoxide Plant</i>
<i>IAMs</i>	<i>Integrated Assessment Models</i>
<i>IEA</i>	<i>International Energy Agency</i>
<i>IFIA</i>	<i>International Fertilizer Industry Association</i>
<i>IPCC</i>	<i>Intergovernmental Panel on Climate Change</i>
<i>LHV</i>	<i>Lower Heating Value</i>
<i>LNG</i>	<i>Liquified Natural Gas</i>
<i>LPG</i>	<i>Liquified Petroleum Gas</i>
<i>LT</i>	<i>Low Temperature</i>
<i>MDEA</i>	<i>Methyl Diethanolamine</i>
<i>MEA</i>	<i>Monoethanolamine</i>
<i>MEM</i>	<i>Membrane Separation</i>
<i>NET</i>	<i>Negative Emission Technology</i>
<i>NGCC</i>	<i>Natural Gas Combined Cycle</i>
<i>PHS</i>	<i>Physical Scrubbing</i>
<i>PSA</i>	<i>Pressure Swing Adsorption</i>
<i>R&D</i>	<i>Research and Development</i>
<i>RSM</i>	<i>Response Surface Methodology</i>
<i>SCR</i>	<i>Selective Catalytic Reduction</i>
<i>SDG</i>	<i>Sustainable Development Goals</i>
<i>SER</i>	<i>Sorption Enhanced Reforming</i>
<i>SMR</i>	<i>Steam Methane Reformer</i>
<i>SNCR</i>	<i>Selective non-Catalytic Reduction</i>
<i>SRD</i>	<i>Steam to Reboiler Duty</i>
<i>TRL</i>	<i>Technology Readiness Level</i>
<i>WAS</i>	<i>Water scrubbing</i>
<i>WGS</i>	<i>Water-gas Shift</i>

1. Introduction

During the last decades, the world population has continued growing at an increased rate, such that Food security has become a significant concern nowadays. According to the *World Health Organization* (WHO), *Food security* is defined as the sufficient availability, access, and utilization of food and nutrients in a way that the survival and growth of the human population are assured (Peng and Berry, 2019). For that reason, ammonia-based fertilizers are essential and play an important role in achieving the desired objective of food security because they stimulate plant growth by supplementing nutrients extracted from the soil during crop growth. This replenishment of nutrients for sustainable crop production has been a constant preoccupation of farmers for many years (Nexant, 2014).

Historically, during the 19th century, European scientists' interest in investigating different plant growth manures increased. In the early 1800s, the first mineral fertilizers rich in phosphate were used in Europe. The application of these fertilizers in the form of bones led to the phosphate fertilizer industry's development (Nexant, 2014). Then, a main technological breakthrough within the fertilizer industry came in the early 20th century when the "*Haber-Bosh*" process was developed. The mentioned process uses a catalyst and operates at a high temperature and high pressure to fix hydrogen with nitrogen, thus producing liquid ammonia. This process currently constitutes the basis for the global production of fertilizers (Nexant, 2014). Furthermore, according to the European Commission report "*Fertilizers in the EU*," around 450 million tons of nitrogen-based fertilizers are produced with the *Haber-Bosch* process every year, and approximately 48% of the global population is fed thanks to the deployment of fertilizers (European Commission, 2019). This way, making the fertilizer industry one of the most important contributors for proper human population development, providing not only more and better food, but economic wealth, human health, and socio-economic stability (European Commission, 2019).

However, a new problem arose with the current fertilizer production process. It is based on fossil fuel feedstock. The hydrogen feedstock used in the *Haber-Bosch* process is generally obtained through natural gas steam reforming. Thus, making the natural gas feedstock account for up to 70 to 85% of the total production cost (Martinez et al., 2017). The use of natural gas makes the current fertilizer industry CO₂ emission-intensive and accounting for one of the top four industrial emitters globally (European Climate Foundation, 2019). In the current urea fertilizer production, not only the process is CO₂ emission-intensive with approximately 0.325 t-CO₂/t-urea (Santos et al., 2017) due to the use of natural gas as feedstock for the production of ammonia, but the final product of granulated urea also produces large CO₂ emissions when applied on the soil. Around 98% of the bounded carbon in urea evaporates within eight days (Tierling, 2016), which would correspond to 0.7 ton of CO₂ per kg of urea applied (European Climate Foundation, 2019). For that reason, besides fulfilling the objective of food security, it is also crucial to address the problem of the carbon dioxide emitted during the process.

The Intergovernmental Panel on Climate Change (IPCC), in their report "*Global Warming of 1.5 °C*," advises that it is crucial to mitigate the greenhouse gas emissions to limit the global temperature increase by 1.5 °C. For that reason, in the report is recommended that by 2030 the anthropogenic carbon dioxide emissions would need to decrease by 45% compared to the levels registered in 2010, this way towards the ultimate and ambitious objective of reaching zero net emissions by 2050 (Jiang et al., 2020). Hence, to mitigate the anthropogenic carbon dioxide emissions, different technologies were developed to capture and reduce the CO₂ emissions from fossil fuel combustion processes (Bui et al., 2018a).

These capture technologies can be set in different configurations such as pre-combustion capture, post-combustion capture, oxy-fuel combustion capture, and chemical looping combustion (Khan et al., 2017). Post-combustion technology is the most appropriate from the mentioned technologies since it can be fitted to an already existing plant (Davison, 2007). The mentioned technology covers several methods to capture CO₂, such as chemical absorption, physical adsorption, cryogenic separation, membrane-based separation, and biological separation. From the mentioned methods, amine-based post-combustion capture is the most mature and widely dominant technology to reduce carbon dioxide emissions due to its selective capacity to capture CO₂ at low partial pressures and large volumes of exhaust gas (Khan et al., 2017). Additionally, the addition of biofuels to the process along with carbon capture (BECCS) is considered a key combination in the pathway to mitigate climate change and thus limit global warming to 1.5 °C (Hanssen et al., 2020) (Azar et al., 2006) (Bui et al., 2018b).

Biofuels initially emerged as an alternative energy source to meet the global energy demand, reducing the amount of greenhouse gas emissions to the atmosphere and thus combating global warming in the process. Biofuels are classified in different generations, from the first to fourth generation, each of them with the same objective to reduce greenhouse gas emissions (Mat Aron et al., 2020). As previously mentioned, the combination of biofuels with carbon capture is key and can act as a negative emission technology. However, this approach has to be rigorously assessed, and an early deployment with the right policies would increase the mitigation potential of this combination (Hanssen et al., 2020). Among the biofuels that can be used in this approach, biogas has received increased attention due to its potential to replace fossil fuels for power and heat generation (García et al., 2020).

Nevertheless, biogas was not considered a common energy source early on, primarily due to its high carbon dioxide content, which decreases the heating value and the flame stability of the gas mixture (García et al., 2020). However, it has been considered for power production and mainly as transportation fuel after an upgrading process, resulting in biomethane. As an alternative methane source, some studies found that synthesis gas can be produced from biogas by conventional steam reforming, providing in this way significant amounts of renewable hydrogen (García et al., 2020) and opening new possibilities for ammonia production in the *Haber-Bosch* process.

Furthermore, efforts were made among the scientific community to improve the synthesis gas generation, reduce the emissions from the current ammonia production process, or make it more environmentally friendly. Different studies propose methods to improve the overall process, such as:

- (Martínez et al., 2017) study, where the implementation of calcium and copper (Ca-Cu) process within a state-of-the-art ammonia plant was proposed. Their study's challenges were to reduce the emissions, and the primary energy needs in generating and purifying syngas (Martínez et al., 2017). The primary outcomes from the study about the integration of the Ca-Cu process in the ammonia synthesis loop were: fewer emissions due to the higher CO₂ capture efficiency (with approximately 97%), lower specific and equivalent energy consumption, and the conditions of the captured CO₂ in the MDEA section of high purity made the captured CO₂ ready to be compressed and sent to storage. Thus, from an environmental point of view, proving the potential of using the Ca-Cu process as a reliable route for syngas generation in actual ammonia plants (Martínez et al., 2017).

- Cloete et al. (2021) study proposed the improvement of the ammonia production process through the implementation of a membrane-assisted auto thermal reforming process. This membrane implementation would replace other syngas treatment units standard in ammonia plants such as the fired tubular reformers, auto thermal reformers, water gas shift reactors, etc (Cloete et al., 2021). Thus, with a carbon and capture section, a high-purity hydrogen and nitrogen mixture can be achieved along with other simplifications in the ammonia production loop and overall higher efficiencies. The study results showed that hydrogen generation for ammonia production could achieve a 10.7% greater efficiency along with a 14.9% reduction in ammonia production cost and a 16.5% greater in CO₂ avoidance (Cloete et al., 2021).
- Gilbert et al. proposed an approach to decarbonize and achieve a more sustainable fertilizer production process by using biomass gasification instead of natural gas for ammonia production (Gilbert et al., 2014). This replacement aimed to reduce greenhouse gas emissions during the production process. The study's primary outcome was the economic viability of using biomass as feedstock, leading to greenhouse reductions of approximately 65% compared to a conventional ammonia production process using natural gas as feedstock (Gilbert et al., 2014).

Hence, the inclusion of technologies and renewable fuels that can significantly reduce the use of fossil fuels and their respective carbon dioxide emissions is of paramount importance. For that reason, this study aims to present a sustainable and environmentally friendly ammonia-based fertilizer process production through (i) the implementation of biofuels such as biogas and biomethane, as a complement to the natural gas feedstock used for fertilizer production and to the fuel used to provide heat to the endothermic reactions of the process, and (ii) the capture of the carbon dioxide present in the syngas using an absorber unit based on with piperazine as the active component with a carbon capture rate of 98.5%, and an absorber unit based on Monoethanolamine (MEA) for the flue gas coming out from the primary reformer with a carbon capture rate of 90%. In this manner, sending the surplus amount of CO₂ captured in the ammonia production process to the urea plant to produce more fertilizer or store it underground. Ultimately, this study aims to present the potential of replacing fossil-based feedstock with biogas and biomethane from a sustainability point of view.

2. Research questions

The research questions proposed for the present study are the following:

- Can ammonia fertilizer (urea) plant be a negative emission plant?
- Can ammonia fertilizer (urea) plant be a negative emission plant if CO₂ from urea is also released to the atmosphere after its application?
- What will be the energy intensity of negative emission urea plant compared to a fossil fuel-based urea plant with/without capture?
- How much bio-feedstock we need to achieve negative emissions in urea production and use?
- Can we produce more urea by using bio-feedstocks?

With the results and discussion section, it will be possible to comprehensively and concisely address the questions above. Before arriving at the mentioned section, it is essential to describe the ammonia fertilizer plant's overall process, first for the fossil-fuel-based case and then addressing how the different biofuel streams will be integrated with the existing process.

3. Process Description

Ammonia and carbon dioxide are the pillars and principal components for the production of urea fertilizer. At the beginning of the process, the steam methane reformer (SMR) and auto thermal reforming (ATR) reactors reform the natural gas feedstock into synthesis gas (syngas), which is treated along different processes to produce a syngas stream consisting of N_2 , H_2 , and CO_2 . Then, an absorber column based on activated methyl diethanolamine (MDEA) (piperazine being the active component) separates the carbon dioxide from the syngas stream. The captured CO_2 in the process is regenerated in a downstream process in a stripper column, compressed, and sent to the urea synthesis and granulation plant. As a result, the syngas stream consisting principally of N_2 and H_2 was ready to be used for the production of ammonia through the Habers-Bosch process reactor. The syngas stream's unreacted components are sent to recirculation to achieve a higher conversion pass, and the final ammonia product stream is sent as feedstock to the urea plant along with the CO_2 stream from the absorption process.

Throughout the entire process, the whole process's principal carbon dioxide emissions come from the SMR reactor, where natural gas fuel is combusted to provide the necessary amount of heat to the endothermic reactions and, thus, emitting CO_2 directly to the atmosphere from the exhaust flue gas. For that reason, a post-combustion Monoethanolamine (MEA) based model provided by *SINTEF Energy* for capturing carbon dioxide with a 90% carbon capture ratio and predicting the steam to reboiler duty (SRD) and specific auxiliary power consumption was used.

As mentioned previously, in the present study, major focus and emphasis are given to biogas due to its increased production in the last years and its particular role in the circular economy, leading to important socio-economic benefits for the local community. For that reason, retrofitting an existing ammonia fertilizer plant with CO_2 capture systems and replacing natural gas feedstock with biofuels were studied. The cases considered for this study covered the following:

- Replacement of different fractions (25, 50, 75, and 100%) of Natural gas feedstock, used in the reforming process for syngas production, with biogas. Therefore, making the urea production process less emission-intensive as biogenic CO_2 is considered neutral.
- Replacement of different fractions (25, 50, 75, and 100%) of Natural gas fuel feedstock, used in the SMR burners, with biomethane and biogas. Then by capturing the CO_2 from the exhaust gas, we identify the point at which overall negative emissions are achieved.

The definition and set of proper operating conditions and a suitable feedstock are essential for the rest of the ammonia fertilizer production process. For that reason, and in order to validate the results obtained from the ammonia plant process simulation, initial data regarding feedstock streams used in a real ammonia plant was gathered from the International Energy Agency Greenhouse Gas programme (IEAGHG) in their technical report “*Techno-Economic Evaluation of HYCO Plant integrated to Ammonia/Urea or Methanol Production with CCS*” (Santos et al., 2017). Whereas the operating conditions for the production of Ammonia were obtained from “*Integration of the Ca-Cu Process in Ammonia Production Plants*” (Martínez et al., 2017), “*European best practice guidelines for the assessment of CO_2 capture technologies*” (Anantharaman et al., 2018), and “*Efficient hydrogen production with CO_2 capture using gas switching reforming*” (Nazir et al., 2019).

A basic diagram for the ammonia production process is shown in **Figure 1**. The process is divided into different process blocks: Feedstock pretreatment, Primary reformer (SMR), Secondary reformer (ATR), High and low-temperature water-gas shift reactors (WGS), Bulk removal of CO₂, methanation reactor, synthesis gas compression train, and ammonia synthesis reactor. The specific function of each process block principle is explained in the following section.

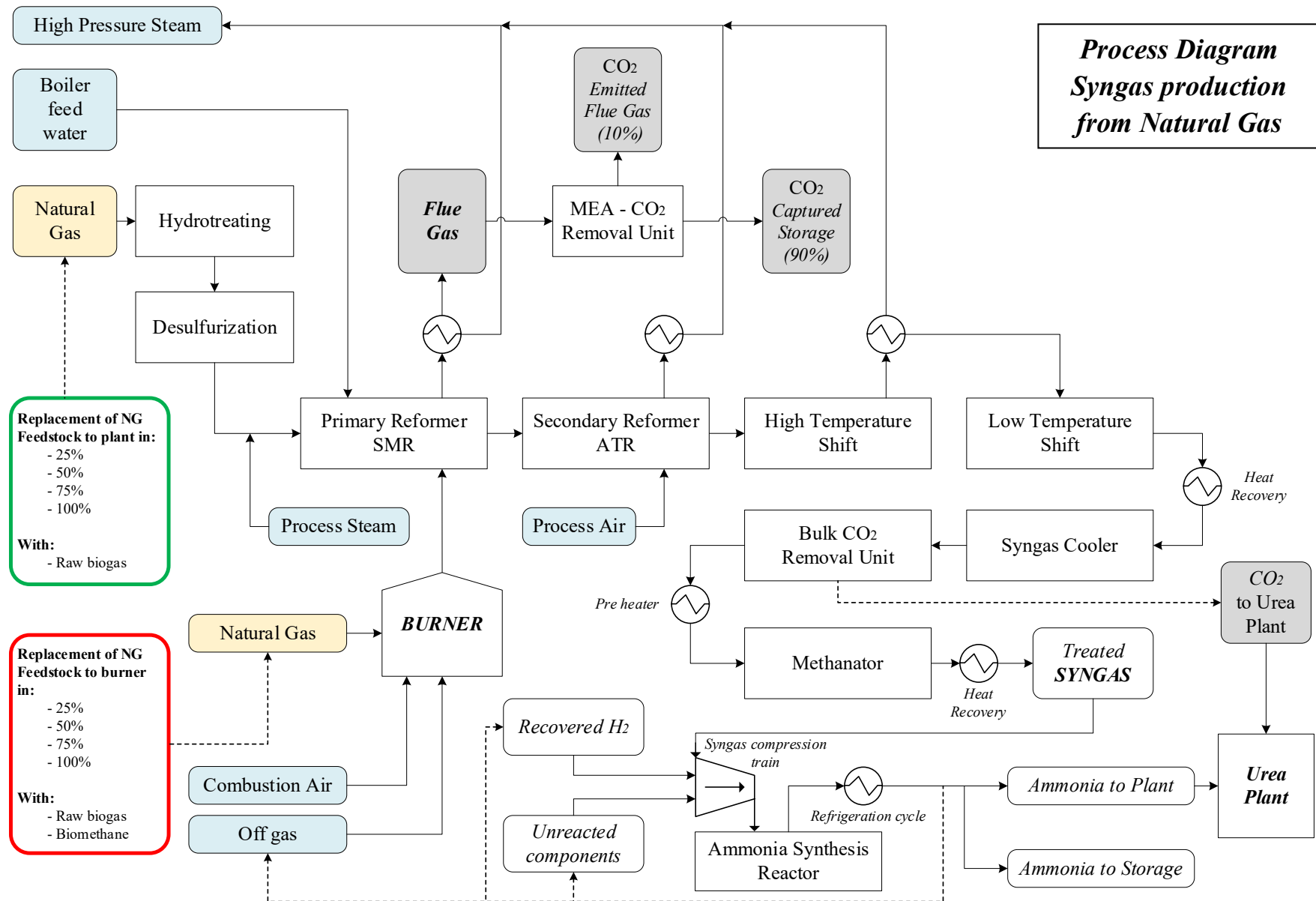


Figure 1. Syngas generation process diagram along with the cases proposed for the study case.

3.1. Synthesis gas generation

3.1.1. Introduction

Synthesis gas or Syngas is a term used to describe mixtures of hydrogen and carbon monoxide ($\text{H}_2 + \text{CO}$) in various ratios. The mixture of nitrogen and hydrogen ($\text{N}_2 + \text{H}_2$) is also referred to as synthesis gas. This mixture of gases can be produced from a fossil or renewable source. The selection of a specific source depends entirely on its cost and feedstock availability (Moulijn, 2013). Syngas can be produced by one of the following processes:

- **Steam reforming of light hydrocarbons**

This first method of steam reforming is a process where a chemical reaction is performed between a light hydrocarbon compound and steam over a catalyst in the presence of oxygen-containing compounds such as H_2O , CO_2 , and O_2 . The chemical reaction of steam reforming is endothermic, meaning that the reaction needs a heat source to occur. In addition to this reaction, the amount of steam used in the process gives rise to a simultaneous equilibrium reaction, known as *Water Gas Shift* reaction.

- **Partial Oxidation of heavy hydrocarbons**

In this partial oxidation method, a non-catalytic chemical reaction takes place between a heavy hydrocarbon compound with oxygen and usually also steam. The chemical reaction of partial oxidation is exothermic, meaning that the reaction releases heat.

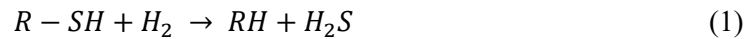
The combination of steam reforming and partial oxidation leads to a couple of both endothermic and exothermic reactions, resulting in a process known as auto thermal reforming (Moulijn, 2013).

The most common feedstock used nowadays for industrial syngas generation are light hydrocarbons such as methane CH_4 , present in natural gas. The gasification process of methane is also known as *Steam Methane Reforming* (SMR) (Appl, 2011a). However, before utilizing natural gas as feedstock for syngas generation, a pretreatment process is required to ensure a proper syngas production process without any operational problems such as catalyst poisoning within the reformer reactors. More details about the pretreatment process and posterior processes are presented in the following section.

3.1.2. Feedstock Pretreatment

Natural gas usually contains up to 5 ppm (v/v) of sulfur compounds, which can poison the catalysts used in the primary reformer and the posterior low-temperature water gas shift reactor due to the materials used in the respective catalysts which are susceptible to sulfur compounds (Santos et al., 2017). Hence, the process of feedstock pretreatment takes place in two stages: Hydrotreatment and Desulphurization.

Hydrotreatment process is usually performed by catalytic hydrogenation over a cobalt-molybdenum catalyst (Appl, 2011a) according to the following reaction:



Followed by the desulphurization process, where ZnS is formed by the adsorption of H₂S on ZnO pellets. The mechanism of adsorption is the following (Appl, 2011a):



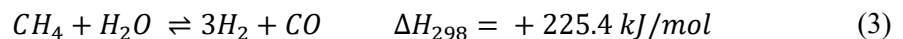
ZnO pellets have to remove most H₂S compounds, thus reducing their concentration to less than 0.05 ppm (v/v) (Santos et al., 2017).

The main advantage of a pretreatment process is that it has no direct influence on energy consumption, and its application leads to other energy-saving measures in the following reforming and shift conversion processes (Appl, 2011b). Once the feedstock has been pretreated, the desulphurized feedstock is then reformed in the subsequent primary and secondary reformer reactors.

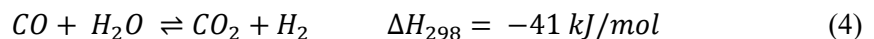
3.1.3. Primary Reformer

The Primary reformer reactor is based on the principle of Steam Methane Reforming (SMR), where the heat required for the reaction is supplied by the combustion of part of the feedstock as fuel for the SMR furnace (Santos et al., 2017). As mentioned previously, the most common feedstock for syngas generation is natural gas, and methane as the primary constituent element is considered the most valuable compound to produce a rich mixture of hydrogen and carbon monoxide. Thus, the reactions involved inside the primary reforming reactor are the following (Vozniuk et al., 2019):

Steam Methane Reforming (SMR)



Water Gas shift reaction (WGS)



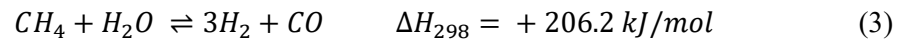
Regarding the equipment used in the process, a conventional steam reformer unit usually consists of several hundred fixed-bed reactor tubes filled with a catalyst that can vary in size and geometry. As for the process conditions, high temperatures above 600 °C and low pressures favor the formation of hydrogen and carbon monoxide products. However, at an industrial scale, the steam reformer reactor is operated under pressures of 20 to 30 atm for kinetic reasons along with an exit temperature of 800 to 870 °C, where methane and steam are converted into synthesis gas (Vozniuk et al., 2019). The selection of a suitable catalyst depends entirely on its properties and its capacity to work at severe operating conditions. These properties are already established for the primary reformer to temperatures up to 950 °C and pressures up to 30 bar.

Finally, in a conventional steam methane reforming (SMR) method, the primary reformer's operation is controlled to achieve a partial conversion only. Since the process is less intensive, it allows a higher methane slip up to 10% vol (Santos et al., 2017). The term “methane slip” is a reference to the percentage of unreacted methane.

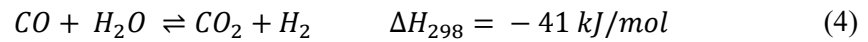
3.1.4. Secondary Reformer

Compared to the primary reformer reactor based on the principle of *Steam Methane Reforming* (SMR), the secondary reformer is based on the principle of air blown *Auto Thermal Reforming* (ATR). In this reformer, the feedstock gas is mixed with a controlled amount of air introduced through a nozzle (burner) (Appl, 2011a). The implementation of air to the reactor provides the required nitrogen for the synthesis of ammonia in a later stage (Santos et al., 2017). Haldor Topsøe initially developed this method to perform a partial oxidation along with the steam reforming process in a single ATR reactor. Hence, the essence of the concept is to combine both noncatalytic partial oxidation and adiabatic catalytic steam reforming (Vozniuk et al., 2019). The temperature and heat required for the reactor are supplied by the combustion process of the gas mixture obtained from the primary reformer with air (Santos et al., 2017). The reactions taking place in the secondary reformer reactor, using methane as the main hydrocarbon component and the steam added to the process, are the following:

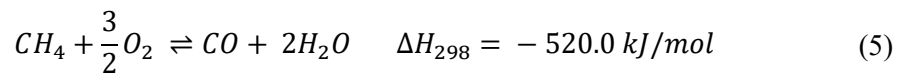
Steam Methane Reforming



Water Gas shift reaction



Combustion reaction

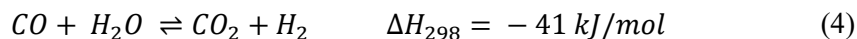


Within the ATR reactor, the combustion process, which provides the necessary heat for the endothermic reactions, occurs at the reactor's upper section, known as the combustion chamber. The combusted gas mixture passes to the lower section of the reactor, composed of a catalyst bed, and reforms the gas mixture into hydrogen. Due to the higher operating temperature of this process, methane slip is reduced to less than 0.8 % vol (Santos et al., 2017).

For the posterior ammonia synthesis process, the syngas generated during this stage must be composed of mainly nitrogen and hydrogen in a molar ratio of 1:3, respectively. For that reason, the amount of air introduced to the ATR reactor has to be fixed, and the ammonia slip is controlled by adjusting the temperature in the SMR reactor by changing the firing. Thus, the resultant syngas leaves the ATR reactor at approximately 1000 °C, and through heat recovery steam generators, heat is recovered and used to produce high-pressure steam (Santos et al., 2017).

3.1.5. Water-gas Shift Reactors (WGS)

The syngas stream leaving the secondary reformer contains a non-negligible amount of CO produced during steam reforming and methane combustion. Hence, a conversion from CO to CO₂ is crucial for further downstream processes and can be achieved through the following reaction:



The water gas shift conversion has two stages. The first one is performed in one reactor at operating conditions of high temperature (HT), and the other one in the following reactor at operating conditions of low temperature (LT) (Santos et al., 2017).

- **High temperature Shift reactor (HT)**

The high-temperature shift reactor (HT) is usually loaded with an iron-chromium catalyst and operates at a temperature range of 320 – 350 °C. This process leads to a residual CO content of around 3.0 vol%, and the gas mixture product is cooled again for heat recovery and production of high-pressure steam before entering the low-temperature shift reactor (Appl, 2011a).

- **Low-temperature Shift reactor (LT)**

Within the low-temperature shift reactor (LT), after the HT reactor, the resultant gas mixture has been cooled to around 180 – 210 °C, the conversion of CO to CO₂ takes place over a copper-zinc-aluminum catalyst, leading to a decrease of CO concentration from 3% to 0.1 – 0.3 % vol (Appl, 2011a).

The HT and LT shift conversions' main outcome is that approximately 95% of the total CO content of the initial syngas produced from the primary and secondary reformers is converted into CO₂. The resultant gas mixture from the LT shift reactor is then cooled down to a temperature around 50 °C and sent to the Bulk CO₂ removal section (Santos et al., 2017).

3.1.6. Bulk CO₂ removal section

The traditional method to remove CO₂ gas is to scrub the synthesis gas stream with a solvent capable of dissolving the gas at a sufficient rate and quantity. This process is usually done under pressure and in countercurrent within a column equipped with trays or packings (Appl, 2011a). Once the solvent was loaded with CO₂, the process to release the dissolved gas was to flash the solvent under atmospheric temperature conditions. The solvent used in the process is then heated and regenerated in a stripping column before being sent to the absorption column for recirculation (Appl, 2011a).

Nowadays, there is a variety of solvents used in the industry classified as physical and chemical solvents. The principle of physical solvents is that carbon dioxide is dissolved into the employed solvent without forming a chemical compound, making the recovery process more straightforward by flashing (Appl, 2011a). Whereas the principle of chemical solvents is that carbon dioxide is dissolved in the employed solvent through fixation as a chemical compound. Hence, in order to be released, a solvent regeneration process using a specific amount of heat is required (Appl, 2011a).

According to the literature review, there are several advantages and disadvantages when using one type of solvent or another. Appl (2011a) specifies that selecting a proper type of solvent is based mostly on the process's operating conditions. For example, when the carbon dioxide partial pressure is low, chemical solvents have the characteristic to absorb a major quantity of gas than physical solvents. However, when carbon dioxide partial pressure is higher, Henry's Law states that the loading property is approximately proportional to the CO₂ partial pressure. Hence, physical solvents would be more suitable for the process due to their higher loading capacity than chemical solvents (Appl, 2011a). The CO₂ loading of different type of solvents is presented in **Figure 2**:

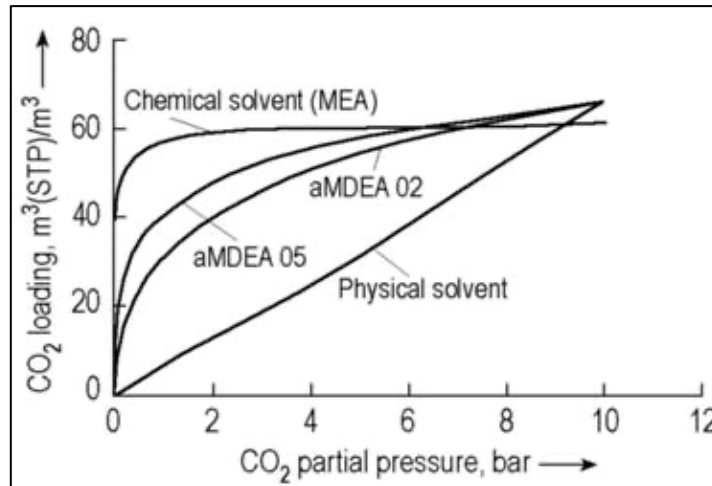


Figure 2. CO₂ loading capacity of different solvent. Source: (Appl, 2011a)

For the specific case of a steam reforming plant and where the partial pressure of CO₂ is between the range of 4 to 7 bar, the following types of chemical solvents are preferred:

- Aqueous solutions of Potassium Carbonate K₂CO₃
- Alkanolamines containing additional activators.
- Amines

The addition of activators in alkanolamines enhances the chemical solvent by increasing the mass transfer rate for CO₂. In some cases, these activators are accompanied by inhibitors in order to avoid or limit any corrosion process that could occur during the process (Appl, 2011a).

The most common chemical solvents used in the industry are *Primary* and *Secondary amines*. Some examples of these solvents that demonstrated a high mass transfer rate for carbon dioxide are Monoethanolamine (MEA) and Diethanolamine (DEA). However, their application's main disadvantage is that these solvents require a high energy demand for their regeneration, directly affecting the economic part of the process. For that reason, another preferred option commonly used in the industries nowadays are *Tertiary amines*. An example of this type of solvent application is the BASF's *aMDEA* process, which uses an aqueous solution of methyldiethanolamine (MDEA) and piperazine as the active component (Appl, 2011a). Also according to Appl, (2011a) The main advantage of MDEA use is that no solvent degradation is detected, and hence no recovery installations are needed.

Regarding the mechanism in which carbon dioxide dissolves in MDEA, thanks to the activator's addition, carbon dioxide binds much less strongly to it compared to MEA. This weak binding is advantageous for the process since a substantial amount of carbon dioxide can be separated by simply flashing the mixture to low pressure, and the remaining amount of CO₂ is recovered by stripping. This way, resulting in a very versatile process (Appl, 2011a).

As for physical solvents used in a steam reforming plant, there are several processes examples such as:

Table 1. Examples of solvent applications for different processes. Reproduced from (Appl, 2011a)

<i>Name of Process</i>	<i>Solvent used</i>
Selexol Process	Polyethylene glycol dimethyl ether
Sepasolv MPE process	Polyethylene glycol methyl isopropyl ether
Fluor Solvent process	Polypropylene carbonate

An advantage of the solvents mentioned in the table above is that they are stable, non-corrosive, non-toxic, and have very low volatility. However, the main disadvantage is their water adsorbing capacity, and for that reason, the syngas entering the process must be dry. This requirement is achievable by operating at lower temperatures, and the CO₂ captured is separated through a simple flash operation requiring no heat (Appl, 2011a).

In summary, for a specific application like steam reforming for ammonia production, during the comparison of energy consumption between a physical or chemical solvent, not only the heat required for solvent regeneration must be considered but also the mechanical energy for the posterior recirculation of the regenerated solvent (Appl, 2011a).

3.1.7. Methanator

Finally, after the bulk removal of CO₂, the final syngas purification process is known as the methanation process. The CO and CO₂ content present in the syngas after the bulk CO₂ removal section is about 0.2 – 0.5% vol. for CO and 0.005 – 0.2% vol. for CO₂. All oxygen-containing compounds are poisons for the ammonia synthesis catalyst. For that reason, these components must be removed (along with any remaining trace of water) down to a very low parts-per-million level (ppm). In this manner, and to achieve these very low ppm levels, a process of methanation is required (Appl, 2011a).

Methanation is a widely used process in steam reforming plants. It is considered the simplest method to decrease carbon oxide concentrations to levels below 10 ppm. The mechanism in which this method achieves those levels is by a reverse reaction of methane steam reforming (Appl, 2011a):



The reactions take place on a relatively small nickel catalyst, under operating conditions of pressure around 25 to 35 bar, and a temperature in the range 250 to 350 °C. The advantages of this purification process are based on simplicity and low-cost operations. Simultaneously, they outweigh the disadvantages of hydrogen consumption and the production of additional inert compounds in the make-up gas to the synthesis loop (Appl, 2011a).

Finally, the purified syngas stream sent to the ammonia synthesis loop is composed mainly of N₂ and H₂, approximately 1% mol of argon and methane, and less than 5 ppm of CO₂ and CO (Santos et al., 2017).

3.1.8. Syngas specifications

The requirements and specifications that the gas stream needs to have before entering the different reactors are summarized in the following table:

Table 2. Stream specifications and requirements. Source: Reproduced from (Santos et al., 2017)

<i>Stage</i>	<i>Compound</i>	<i>Content</i>	<i>Reason</i>
Feedstock before entering Primary Reformer (%v dry basis)	Sulphur	< 0.05 ppm	Catalyst poison
	Chloride	< 0.05 ppm	Catalyst poison
	As, V, Pb, Hg	< 5 ppb	Catalyst poison
	Olefin	< 1 – 2 %	Carbon formation
Syngas from Secondary reformer to LT shift reactor (%v dry basis)	Sulphur	< 0.1 ppm	Catalyst poison
	Chloride	< 5 ppb	Catalyst poison
Syngas from Bulk CO ₂ removal section to Methanator	K ₂ CO ₃	-	Methanator pore blockage
	As (as As ₂ O ₃)	< 5 ppb	Methanator catalyst poison
	Sulpholane	-	Methanator catalyst poison
Syngas to Ammonia Synthesis Reactor	CO ₂ + CO	< 5 ppm	Ammonia catalyst poison

3.2. Ammonia Synthesis

3.2.1. Introduction

Ammonia is considered the second largest synthetic chemical product globally, where around 90% is manufactured from a catalytic process of nitrogen and hydrogen. Fritz Harber and Carl Bosch developed the initial ammonia synthesis process, which has not drastically changed compared to today's industrial production. The synthesis process begins with a synthesis gas (composed principally of hydrogen and nitrogen) reacting over an iron catalyst at an elevated temperature (400-500 °C) and high pressure (above 100 bar). Unreacted elements from the reaction are recycled back, and ammonia's separation process is usually performed under high pressure. Nevertheless, the only minor change the ammonia synthesis process has suffered is related to the synthesis gas generation, preparedness, and purification (Appl, 2011a). Once the synthesis gas is purified, it consists primarily of nitrogen and hydrogen. Although these elements are abundant in nature, they can also be obtained from fossil sources. For example, methane (CH₄), the major component in natural gas, is a valuable hydrocarbon source to obtain hydrogen due to its high hydrogen compound structure (Appl, 2011a).

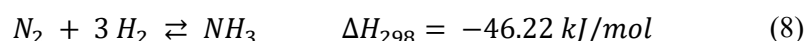
Throughout the following sections, an evaluation is performed on the most relevant aspects for ammonia production, such as chemical reaction, thermodynamics, the most common feedstock used in the process, etc.

3.2.2. Applications

Ammonia itself is an essential source of nitrogen needed by plants and animals. For that reason, around 80% of the ammonia produced by the industry is employed as fertilizer in the agriculture field. However, it can also be extensively used as fuel, refrigerant gas, household, industrial-strength cleaning solution, critical compound to purify water supplies, manufacture of plastics, explosives, textiles, pesticides, paints, dyes, and other chemicals (National Center for Biotechnology Information, 2020).

3.2.3. Ammonia synthesis process

Ammonia synthesis is performed through the following reaction:



The molar ratio required for ammonia synthesis is 1:3, 1 mol of nitrogen per 3 mol of hydrogen. Also, releasing heat in the process since the reaction is exothermic (Appl, 2011a).

3.2.4. Synthesis process conditions

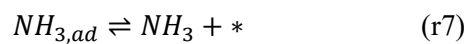
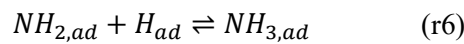
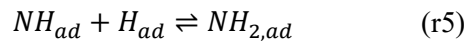
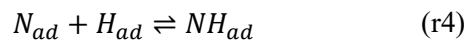
According to Appl (2011a), any system with an exothermic reaction involved should usually react spontaneously. However, in the case of ammonia synthesis with nitrogen and hydrogen molecules, significant energy input is required for nitrogen due to its high dissociation energy of 941 kJ/mol, considerably higher compared to hydrogen requiring only 439 kJ/mol. Furthermore, the gas phase's synthesis reaction requires an activation energy of 230 to 420 kJ/mol. Hence, an operating temperature in the range of 800 to 1200 K is required to surpass that activation barrier. For that reason, Appl (2011a) also states that ammonia's theoretical yield is extremely small at high temperatures and moderate pressures at an industrial scale due to the thermodynamic equilibrium's unfavorable position (Appl, 2011a).

Some interesting aspects associated with the process conditions are that, at high pressures above 2000 bar, ammonia synthesis occurs without any specific catalysts. At such extreme pressures, the vessel walls are presumed to catalyze the formation of ammonia. If a catalyst is employed in the process, during the combination of nitrogen and hydrogen, both of them lose their translational degrees of freedom by fixating on the catalyst surface. The addition of a particular catalyst to the process drastically reduces the required energy of activation. For example, if an iron catalyst is employed, the energy required would be 103 kJ/mol, and the temperature for the reaction to take place would range between 250 to 400 °C. For that reason, iron catalysts are commonly used today in the commercial production of ammonia.

During the catalytic gas-phase reaction, the ammonia synthesis process mechanism is divided into the following steps: transportation of the reactants by diffusion and convection through a laminar boundary layer to the outer surface of the catalyst particles, adsorption of the reactants on the inner surface, the reaction of the absorbed species and the formation of intermediate compounds, desorption of ammonia into the gas phase, and transport of ammonia through a pore system into a bulk gas stream.

3.2.5. Reaction mechanism

The reaction mechanism sequence of ammonia on the catalyst would be the following:



Where: * denotes a surface site of the catalyst

3.2.6. Catalyst specifications

The catalyst is considered the process' heart due to its several effects on the overall production process (Appl, 2011b). Appl (2011b) mention that it determines the operating temperature range at a specific operating pressure, the recycle gas flow, refrigeration requirement, the vessel and exchanger design in the synthesis loop, capital cost, and energy consumption. Hence, although the catalyst's cost is negligible compared to an actual ammonia plant's total cost, the correct selection of an adequate catalyst is crucial since it will dictate the entire process's economic results based on its performance (Appl, 2011b).

According to Appl (2011b), the characteristics to select a specific catalyst for an industrial ammonia synthesis are the following:

1. High catalyst activity

It is essential to have a high catalyst activity at the lowest possible reaction temperatures to take advantage of the favorable thermodynamic equilibrium situation present at low temperatures.

2. Resistance to catalyst poisons

The selected catalyst should be resistant to oxygen and chlorine-containing compounds, which may be present in even very effectively purified synthesis gas. The effect of poison from oxygen compounds becomes more severe as temperature declines.

3. Long lifespan

A catalyst's lifespan is determined by the following properties: its thermal degradation resistance and irreversible poisoning resistance. An iron catalyst's lifespan can reach up to 14 years of life service in modern ammonia plants.

4. Mechanical Strength

Catalyst abrasion resistance and insufficient pressure may lead to an excessive pressure drop inside the converter, leading to a premature plant shutdown.

5. Availability of raw material

Due to the increasing demand for ammonia in the market and the world, selecting an adequate catalyst made with materials available as a reliable primary raw material source is crucial.

BASF A., for example, performed diverse ammonia synthesis experiments with almost all periodic table elements to find an adequate catalyst (Appl, 2011b). After that, it was concluded that most metals and metal alloys are suitable as ammonia catalysts in principle. Metals and metal compounds for which the chemisorption energy of nitrogen is neither too high nor too low show the greatest effectiveness. For that reason, a magnetite-based catalyst proved to be suitable for industrial use (Appl, 2011b).

3.2.7. Catalyst poisons

According to Appl (2011b), an ammonia synthesis catalyst's performance may be affected by certain substances. These substances, usually known as catalyst poisons, are minor gaseous constituents present in the synthesis gas. They can be divided into permanent and temporary poisons. Permanent poisons are responsible for producing irreversible damage to the catalyst, while temporary poisons are responsible for lowering the catalyst activity (Appl, 2011b). Among the temporary poisons, the most common in ammonia synthesis are oxygen-containing compounds such as H_2O , CO , CO_2 , and O_2 . Meanwhile, sulfur and chlorine compounds are known as permanent poisons.

- **Oxygen compounds**

In the case of oxygen compounds, the advantage of facing temporary poisons is that the damaged catalyst activity can be completely restored by reduction with more clean synthesis gas. However, irreversible damage to the catalyst activity is also possible due to continuous exposure to oxygen compounds and the consequent growth of primary iron crystallite (Appl, 2011b). This irreversible damage has been cataloged as one of the main causes of the catalyst's performance decrease throughout its operating lifetime. The damage depends initially on the water vapor pressure, and it is inherently serious compared to reversible poisoning at process conditions of high temperature. Thus, the higher the temperature, the greater the harmful effect of oxygen compounds will be. For that reason, Appl et al (2011b) advise that operating temperatures above 500 to 520 °C must be avoided to achieve a converter's good life operating period. However, with today's treatment processes that generate highly purified synthesis gas, such as the methanation process, even longer service operating periods up to 14 years can be achieved without any significant loss of activity (Appl, 2011b).

- **Sulfur, Phosphorus, and Arsenic compounds**

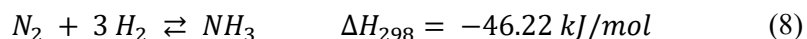
Even if phosphorus and arsenic are not generally present in industrial syngas, sulfur compounds are usually present to some extent in synthesis gas produced from carbon or heavy fuel oil. The principal characteristic of sulfur compounds as catalyst poisons is that they are more tightly bound on iron catalysts than oxygen (Appl, 2011b). Appl et al. mention that catalysts poisoned with hydrogen sulfide, even in a partial grade, cannot be generated under the process conditions of industrial ammonia synthesis. However, in modern ammonia plants, the sulfur content is extremely low, with around 0.5 – 1 ug S/m³ (STP) thanks to a very effective synthesis gas purification process. Hence, the aspect of sulfur poisoning is less important compared to carbon monoxide and chlorine poisoning.

- **Chlorine compounds**

The harmful effect of chlorine compounds results in permanent poisoning, and the magnitude of poisoning is far worse compared to the poisoning of oxygen compounds. Recommendations about the permitted concentration of chlorine compounds are about 0.1 ppm (Appl, 2011b). According to Appl (2011b), this lower value is the uppermost allowable limit value that does not affect ammonia catalysts' operating lifetime. The manner in how the deactivation effect occurs on the catalyst surface is based partially on the formation of alkali chlorides, volatile compounds at upper synthesis temperatures.

3.2.8. Process steps for Ammonia production

The ammonia synthesis process, as mentioned previously, takes place in the converter according to the following reaction:



Inside the reactor, around 25 – 30% of the N_2 and H_2 present in the feedstock is converted into NH_3 . The unconverted compounds are sent for recirculation after liquid ammonia has been separated (Santos et al., 2017).

Regarding proper operating conditions for the converter, ammonia formation is favored with high pressures and low temperatures. Because the reaction is exothermic, selecting a proper operating temperature is based on a compromise between the equilibrium approach theoretical conversion (Santos et al., 2017) and the catalyst's load and activity used in the converter. Therefore, a typical operating temperature for the synthesis process ranges between 370 – 500 °C, with an operating pressure ranging between 130 and 220 bar at the inlet of the converter (Santos et al., 2017).

In modern ammonia plants, the heat released from the ammonia synthesis reaction is recovered and used for high-pressure steam generation. This steam is sent to other sections of the plant and is used to pre-heat the boiler feed water and the synthesis gas (Santos et al., 2017). After the synthesis process, the effluent gas must be cooled down to temperatures near 0 °C. At these low temperatures, ammonia's condensation process takes place, and liquid ammonia is separated from the rest of the unreacted compounds in the effluent gas. After the separation process, the unreacted compounds are sent to the converter reactor. This recirculation process is an integral part of the syngas compressor train, where the syngas coming from the methanator is compressed to the synthesis loop pressure (Santos et al., 2017).

3.2.9. Inert Gases Removal

After the methanator section, the resultant synthesis gas contains small traces of methane and argon. These inert gases accumulate due to the recycling process to the converter and cause problems such as inhibit the formation of ammonia, leading to a requirement of a larger volume of catalyst or higher operating pressures. Thus, to avoid this problem, inert gases are removed through a continuous purge gas system from the synthesis loop and sent to ammonia and hydrogen recovery units. The recovered ammonia is sent back to the ammonia synthesis loop, and the recovered hydrogen is used as feedstock for the hydrotreatment reactor. The remaining compounds present in the stream, known as tail gas, are sent as fuel to the SMR reactor. However, there is also the possibility that inert gases are dissolved in the liquid ammonia stream, but these are released during the let-down of the liquid product in the ammonia separator. The quantity of inert gas leaving the loop during the whole process is proportional to the inert gases' partial pressure (Santos et al., 2017).

3.2.10. Refrigeration

As mentioned previously, implementing a refrigeration circuit is required to perform different cooling duties throughout the ammonia synthesis loop, such as condense ammonia, and to cool down the purged gas and inert gas streams. The following equipment commonly composes this refrigeration circuit: four chillers that operate at different pressure levels, refrigeration compressor, ammonia booster compressor, ammonia condenser, ammonia accumulator (Santos et al., 2017). The production of liquid ammonia can be performed at different pressure and temperature conditions depending on the final use. If ammonia is destined for other processes, it shall be stored in cryogenic atmospheric tanks at temperatures around -33 °C (Santos et al., 2017).

3.3. Carbon dioxide capture

Carbon capture and storage (CCS) plays an important role in mitigating climate change and meet specific targets such as the objective to keep global warming less than 2 °C during this century. Furthermore, it has the potential to decarbonize the industry, and in recent years, the ability to remove carbon dioxide directly from the atmosphere. For that reason, in the present section, an initial introduction to CCS and a subsequent review of the state of the art of these technologies and the possibilities of integration to this study case are performed.

3.3.1. Introduction

A negative carbon dioxide emission project aims to integrate a viable technology that enables CO₂ capture and leads to negative CO₂ emissions, all of these actions with the lowest possible cost and energy penalty possible. First, it is important to define the term of negative emissions and how we can achieve them. Negative emission term refers to reducing the amount of carbon dioxide by capturing it, extracting it from the environment or process, and storing it safely. These three steps are known as Carbon Capture and Storage (CCS) (Envirotech, 2020).

3.3.2. Carbon Capture and Storage (CCS)

Carbon Capture and Storage comprehend different methods and technologies capable of capturing up to 90% of the total carbon dioxide emissions produced from fossil fuels and industrial processes. Thus, preventing carbon dioxide from entering the atmosphere. In conjunction with renewable biomass, CCS's application is one of the few carbon abatements technologies that can enable a carbon-negative mode (Carbon Capture & Storage Association, 2020). CCS consists of three steps:

- **Capturing carbon dioxide**

The first stage in the CCS technology process, where carbon dioxide is produced from burning fossil fuels or other industrial processes, is captured (Carbon Capture & Storage Association, 2020). This step can be performed in the following ways:

- **Pre-combustion capture:**

The pre-combustion system initially converts a solid, liquid, or gaseous fuel into a mixture of hydrogen (H₂) and carbon dioxide (CO₂) through gasification or reforming. The most common process used nowadays is gas reforming since it is a well-established technology used for many years at refineries and chemical plants worldwide. The main application for the hydrogen produced from these processes is to produce electricity with near-zero emissions (Carbon Capture & Storage Association, 2020).

- **Post-combustion capture:**

Carbon dioxide can be directly captured from the exhaust of a combustion process by absorbing it with a suitable solvent. The absorbed gas can then be liberated from the solvent and be compressed for its respective transportation and storage. Other technologies for post-combustion capture involve high-pressure membrane filtration, adsorption/desorption processes, and cryogenic separation (Carbon Capture & Storage Association, 2020).

- **Oxy-fuel combustion:**

Before the combustion process, the oxygen required is separated from air, and the fuel is then combusted in the presence of pure diluted oxygen with recycled flue-gas, rather than by pure air. This method yields flue gases consisting mainly of CO₂ and H₂O thanks to the oxygen-rich and nitrogen-free conditions. Thus, producing a more concentrated CO₂ stream and a consequent more straightforward purification process (Carbon Capture & Storage Association, 2020).

- **Transporting carbon dioxide**

Once carbon dioxide has been captured, it must be transported using different mediums such as pipelines or ships to its respective storage at a designated and suitable site. The technology involved in pipeline transportation is the same as the one used nowadays to transport natural gas, oil, and many other fluids around the world. In the particular carbon dioxide case, it is currently transported for commercial purposes by road tankers, ships, and pipelines. However, each project shall choose the most appropriate method for transporting carbon dioxide according to its planning, health, and safety regulations (Carbon Capture & Storage Association, 2020).

- **Storing carbon dioxide**

Finally, CO₂ can be stored in porous geological formations typically located several kilometers under the earth's surface with pressure and temperature conditions where carbon dioxide would be in the liquid or "*supercritical*" phase. Some suitable sites for the storage of CO₂ include former gas and oil fields, deep saline formations (referred to porous rocks filled with very salty water), or depleted oil fields, where CO₂ can be used to, once injected, increase the amount of oil recovered. Depleted oil and gas reservoirs would be chosen first since extensive information about geological and hydrodynamic assessments would be available. However, deep saline aquifers represent the largest potential for carbon dioxide storage capacity in the long term (Carbon Capture & Storage Association, 2020).

The storage mechanism is called "Structural storage," where carbon dioxide, once injected underground, moves up until reaching an impermeable layer of rock. By overlaying the storage site, carbon dioxide is trapped in the storage formation. Structural storage is the primary storage mechanism in CCS technology. The same process has kept oil and natural gas safely trapped underground for millions of years (Carbon Capture & Storage Association, 2020).

In each step from production to storage, all industries have at their disposition a number of methods that are well studied and have excellent health and safety records. Hence, Carbon capture and storage (CSS) 's commercial deployment would benefit from adopting one of these methods, along with a robust monitoring technique and a strong government regulation (Carbon Capture & Storage Association, 2020).

3.3.3. CCS State of the art

Carbon capture and storage, as previously mentioned, plays an essential role in meeting the global warming targets presented by the Intergovernmental Panel on Climate Change (IPCC) and the 2015 United Nations Climate Change Conference (COP21) held in Paris, France (Bui et al., 2018a). Before integrating any CCS technology, it follows a scheme of several scale-up steps, also known as the “*Technology Readiness Level*” (TRL). This system measures the technology maturity level and provides a status tracking tool throughout the different Research and Development (R&D) stages (Bui et al., 2018a). The scale-up steps are the following:

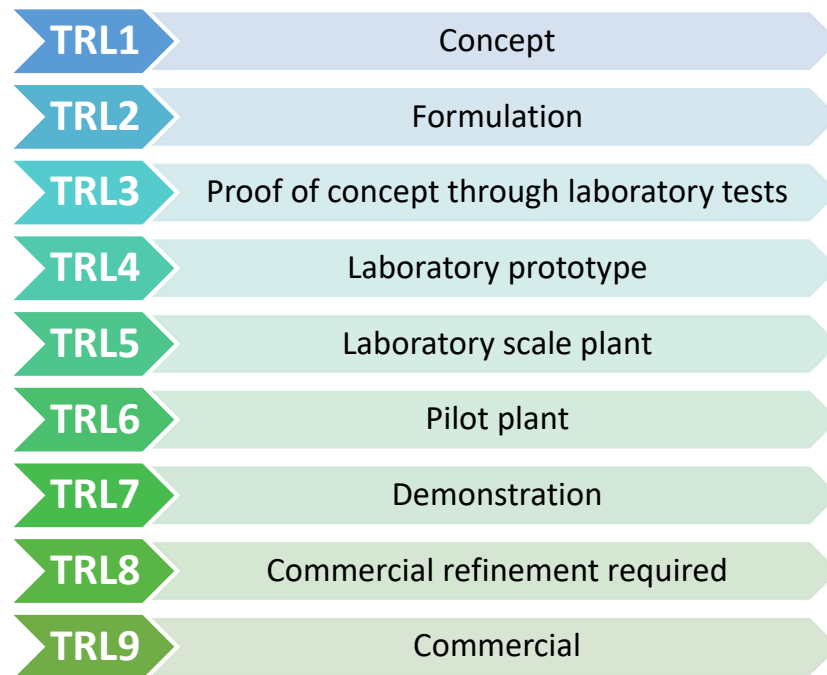


Figure 3. Technology readiness levels. Source: (Bui et al., 2018a)

CCS technologies that are reaching or have already reached the commercial-scale are the following:

- **CO₂ Capture:**

Throughout the years, a carbon capture technology that reached a commercial scale based on chemical adsorption, using different aqueous amine solutions, has always been the industry's preference. However, there have been recent developments regarding polymeric membranes. An example is Polaris membrane, developed at NTNU, that reached the demonstration-scale TRL7 and is used to separate CO₂ from syngas (Chemical Processing, 2017). Another example of a technology that reached the demonstration-scale is oxy-combustion coal power plants. This technology is expected to reach commercial status in the near future (Bui et al., 2018a).

- **CO₂ Transport:**

The technologies for CO₂ transportation are well studied and established. In the case of pipe transportation, currently, there is more than 6500 km of pipelines worldwide that transport this gas. Another technology that is also very well established and relatively mature is the transportation of CO₂ using ships. These technologies have reached TRL9 and are nowadays used in many commercial applications (Bui et al., 2018a).

- **CO₂ Storage:**

Finally, regarding the storage of carbon dioxide in a commercial scale project, saline formations have been the preferred option, including other storage technologies such as *Sleipner CO₂ storage* and *Snøbit CO₂ storage*. Despite mentioning before that depleted oil and gas fields would represent an optimum storage site due to the immediate information available about geological and hydrodynamic assessments, they have not yet reached a commercial scale stage. They are still in a demonstration phase TRL7. In the case of ocean storage and mineral storage, these technologies are also still in an early phase of development (Bui et al., 2018a).

- **CO₂ Utilization:**

The usage of CO₂ in various applications is well established and positioned in a commercial stage since several industries use CO₂ in various processes. For example, the main industries that use CO₂ extensively are the food and beverage industry, and the chemical industry for the production of urea or methanol. The CO₂ used in each industry generally comes from industrial processes (such as in the production of fertilizers, ammonia and ethylene glycol) and in some cases from power plant flue gases (Bui et al., 2018a).

3.3.4. Role of CCS in climate change mitigation

According to *Bui et al.* in order to keep the average global warming of earth less than 2 °C during this century, Integrated Assessment Models (IAMs) have been the core and at the same time the key to achieve this objective. These assessment models are capable to explore the future role of particular technologies in charge to meet climate targets. Hence, CCS technologies by being an essential part of the climate change mitigation portfolios, show several advantages and benefits as for their implementation. The first advantage is that CCS technologies can be integrated to the actual energy systems without requiring larger modifications to the system itself. The second advantage refers to the fact that these technologies are a viable option to decarbonize current emission intensive industries such as the case of the industry of cement production. Finally, the third advantage is that these technologies when combined with low carbon or carbon neutral bioenergy (BECCS) enables the possibility to generate negative emissions. Additionally, the combination with BECCS has a double benefit which is to mitigate emissions and generate energy, by this manner making it an attractive cost – optimization perspective from an IAM connected to the possibility to substitution for coal and natural gas over time. The role of CCS and specifically the combination with BECCS become even more important in the light of the increased level of ambition of the 2015 Paris COP (Bui et al., 2018a).

However, even though the implementation of CCS technologies plays an important role in the IAM climate change mitigation portfolios, the respective deployment and application of these technologies has barely reached the indicated levels, estimations and roadmaps proposed by the International Energy Agency (IEA). Moreover, a recent report “*20 Years of Carbon Capture and Storage*” presented by the IEA reached to a conclusion that the rate of progress and implementation of these CCS technologies is falling short respect to what is required to achieve the climate targets, and additionally an opposition against the implementation of these technologies due to the uncertainties, lack of experience and fear for safety regulations will mostly lead to a prolonged dependence on fossil fuels and at the same time, creating a barrier that will impede the utilization of renewable sources (International Energy Agency, 2016). Yet, it has been found that CCS technologies will not have a decreasing role over time and in the current integrated assessment models, a negative emission result is obtained through the deployment of BECCS (Bui et al., 2018a)

3.4. Urea Fertilizer

3.4.1. Introduction

The overall yield usually obtained in agriculture can be increased through different approaches, the utilization of fertilizers, herbicides, pesticides, and minerals among them as an example. The nitrogen-based fertilizer, urea, is considered as one of the most energy intensive industries with environmental and global warming implications due to the utilization of fossil sources for its production, and the emission of greenhouse gases to the atmosphere through volatilization once the fertilizer is applied to the soil. Thus, having a great impact on climate policies.

Hence, the development of a successful generation of new agricultural technologies requires not only a proper understanding about the environmental aspect, but the acknowledgment of other technical aspects interplay too. For that reason, is that the leading world fertilizer companies have decided to make a future concerned with energy and climate road map up to 2050. The environmental challenges involved in this roadmap can only be resolved if the major economic country contributors, such as the USA and China, give their full attention on the sustainability and technical aspects, such would be the control of the volatilization effect through an efficient coating technology, which would lead to slow release properties and thus reducing the volatilization and denitrification effect (Yahya, 2018).

3.4.2. Consumption and demand

As previously mentioned, fertilizers play an important role in ensuring crop production and food security. For that reason, and connecting to the world population increase, it is important to acknowledge the current fertilizer production and consumption from the major countries in order to predict the trends in the following years and reach a more sustainable fertilizer production. Currently, according to the International Fertilizer Industry Association (IFIA), more than 70% of the fertilizer consumption is dominated by China, India and USA (Yahya, 2018).

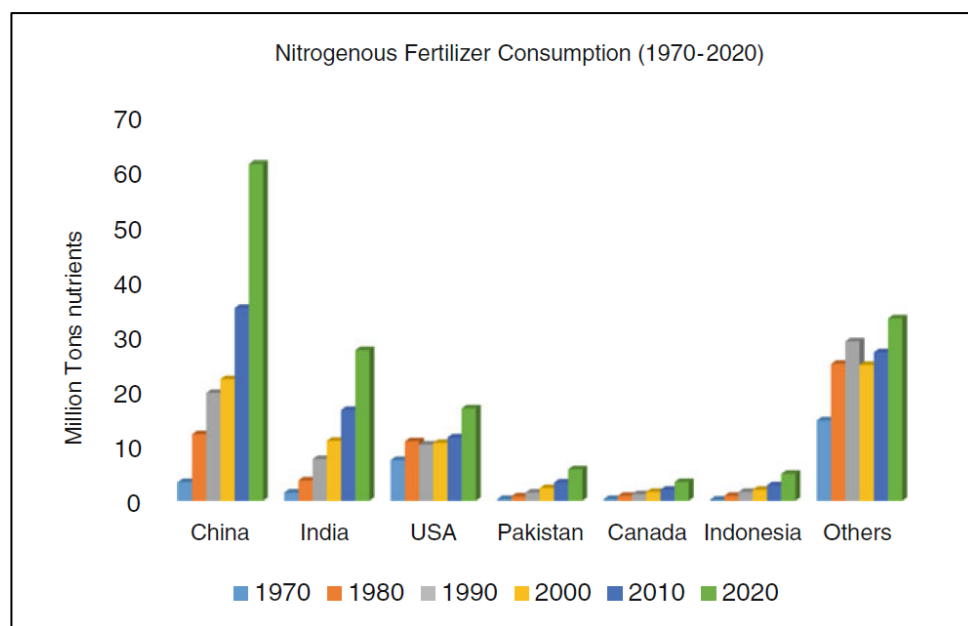


Figure 4. Nitrogenous Fertilizer Consumption during the period 1970 – 2020. Source: (Swedish Gas Association, 2018).

A Response Surface Methodology (RSM) performed by (Yahya, 2018) evaluated the nitrogenous world fertilizer production and consumption from 1970 to 2020 to predict the trends for the following years 2030 and 2050, and the results obtained in the evaluation shown that the trend in production and consumption is going to increase year by year in the whole world. More specifically for the mentioned fertilizer consumption dominating countries, the trend would be the following:

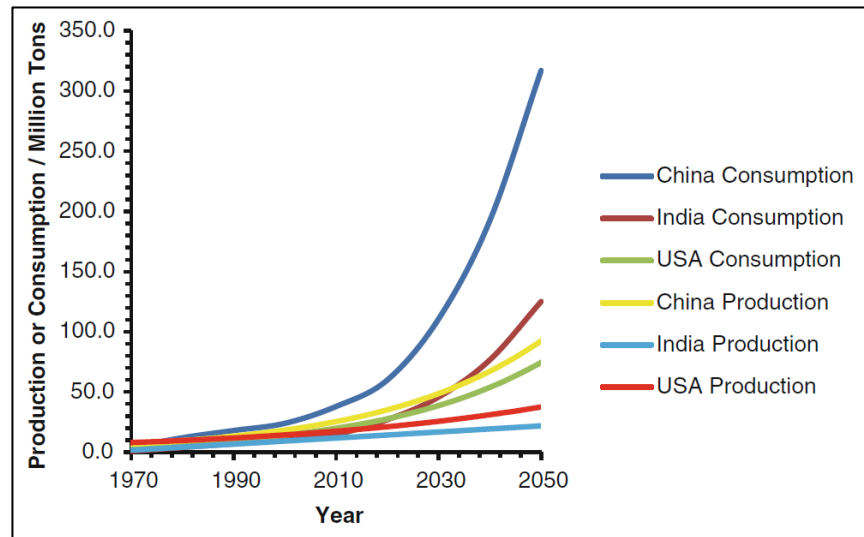


Figure 5. RSM prediction for 2050 for fertilizer consumption. Source: (Swedish Gas Association, 2018).

As seen in **Figure 5**, the following can be inferred for the dominating countries:

- **China:**

In the year 2050, the nitrogenous fertilizer consumption is three times higher than the predicted consumption for 2030, and it will be five times higher than its production.

- **India:**

In the year 2050, the nitrogenous fertilizer consumption is 2.7 times higher than the predicted consumptions for 2030, and it will be 6.2 times higher than its production.

- **USA:**

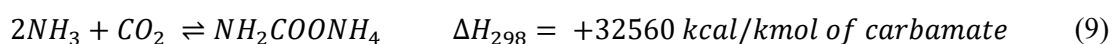
In the year 2050, the nitrogenous fertilizer consumption is 3.44 times higher than the predicted consumption for 2030, and it will be 1.8 times higher than its production.

Hence, the utilization of renewable sources needs to be addressed in order to meet these future predictions and moreover, successfully achieve worldwide food supply.

3.4.3. Urea Synthesis Process

The process of urea synthesis is performed with liquid ammonia NH_3 and gaseous carbon dioxide CO_2 . Both elements were obtained in the previous section of ammonia production. These elements are sent and mixed inside a reactor, producing ammonium carbamate, an intermediate product that is dehydrated in a downstream process to produce urea and water (Santos et al., 2017). The reactions involved in these processes are:

Ammonium Carbamate formation



Urea obtention through dehydration

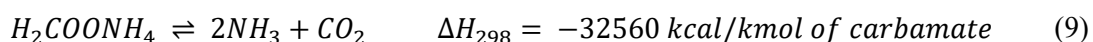


The first reaction of ammonium carbamate formation is fast and takes place until completion, while in contrast, the second reaction of dehydration is slow and, at the same time, establishes the volume of the reactor to be used.

A urea plant is commonly composed of a synthesis reactor, stripper column, carbamate condenser, decomposer, vacuum concentrator, evaporator, and granulation plant. Regarding the processes and operating conditions for the production of urea. The reactor where the blending process between ammonia and carbon dioxide occurs is operated at the following conditions: a temperature of 190 °C and pressure between 150 – 160 bar. For that reason, the carbon dioxide coming from the Bulk CO_2 removal section with a purity of at least 98.5% vol. and a pressure of 0.5 to 0.75 bar, is compressed up to 160 bar.

Then, once ammonium carbamate has been formed within the reactor, the dehydration percentage in the subsequent process is determined by the following aspects: the various reagents ratio, operating temperature and pressure, and the residence time inside the reactor. In addition to this intermediate process, it is essential to acknowledge that the recently formed ammonium carbamate in a downstream process is prone to decomposition due to the reverse reaction into ammonia and carbon dioxide.

Ammonium Carbamate decomposition reaction:



These compounds along with the unconverted chemical reagents, are recovered in different steps at lower pressures in a subsequent process. However, this decomposition process can be avoided by operating at a reduced pressure or adding more heat (Santos et al., 2017).

Afterward, in order to granulate urea, it is necessary to concentrate the solution of urea up to 96% wt. This process is usually achieved through several vacuum concentration stages. Initially, the solution coming from the decomposer bottom (at low pressure with a concentration of 70% wt. of urea) is sent to a vacuum pre concentrator. The resultant solution is then sent through a pump to the following vacuum concentrator, where saturated steam at low pressure is added to concentrate the urea solution. The resultant mixed phase from this stage is sent to the gas-liquid

vacuum separator, where the vapors are extracted. The resulting urea concentrated solution (around 96%) is sent to the granulation unit.

The process water coming from the vacuum system usually contains ammonia, carbon dioxide, and urea. For that reason, in order to achieve an almost $\text{NH}_3\text{-CO}_2\text{-urea}$ free process condensate that can be used as boiler feedwater, these elements are collected and sent to a urea hydrolyzer reactor where urea is decomposed into carbon dioxide and ammonia.

Finally, the concentrated urea solution in the granulation unit is atomized and assisted by air fluidization, where air flows through the product layer to create a fluid bed which is discharged at the top of the granulator. The granulated urea is then sent to a cooler and subsequently to a screening section where the fine fraction is recycled and sent to the granulator again, while the coarse material is crushed before being sent to the granulator. The final product is then finally sent to a warehouse.

3.4.4. Negative emission assessment

Carbon Capture and Storage (CCS) plays an essential role in meeting the climate change targets by decarbonizing the fertilizer industry, and the integration of bioenergy with carbon capture and storage (BECCS) and carbon capture and utilization (BECCUS) results in a CO_2 mitigation technology (Bui et al., 2018a). In the BECCS concept, the CO_2 released from the biomass is captured and stored in geological formations. In contrast, in the BECCUS concept, the captured CO_2 is temporarily fixed into products, such as fuels, construction materials, chemicals, fertilizers, etc. In essence, fossil CCS takes carbon from the geosphere and returns it there, while BECCS takes carbon from the atmosphere, puts it in the biosphere temporarily, and finally stores it in the geosphere permanently.

More specifically, the concept of BECCS relies on the assumption that carbon dioxide from the atmosphere binds to biomass while growing. Once biomass has undergone a conversion process, the CO_2 released is captured and stored. Resulting in this manner in the net removal of CO_2 from the atmosphere and leading to the referred Negative Emission Technologies (NETs). The biomass feedstock's characteristics and carbon neutrality play a decisive factor in reducing negative emissions.

Hence, industrial processes that take the carbon component from either the geosphere or biosphere and transfer it to the atmosphere result in carbon-neutral to some extent. In contrast, the processes that make use of carbon from fossil sources result in net positive emissions. Thus, one of the advantages of BECCS is that it allows the offsetting of emissions from difficult sectors where the CO_2 reduction is hard to achieve due to economic or technical constraints. Another advantage is that fossil CCS plants have the potential to become BECCS by only switching the fuel feedstock. For example, in coal-powered plants, the partial integration of biomass feedstock as fuel would do the trick (Bui et al., 2018a).

Nowadays, in a more deep analysis about when negative emissions can occur, it has been found that system boundary choices have a significant impact on the estimated emissions of a NET system (Tanzer and Ramírez, 2019). To illustrate how the selection of these boundaries has a significant impact on the estimated GHG emissions of a NET system, Tanzer and Ramírez (2019) present in the figure below the example of a steel mill with BECCS.

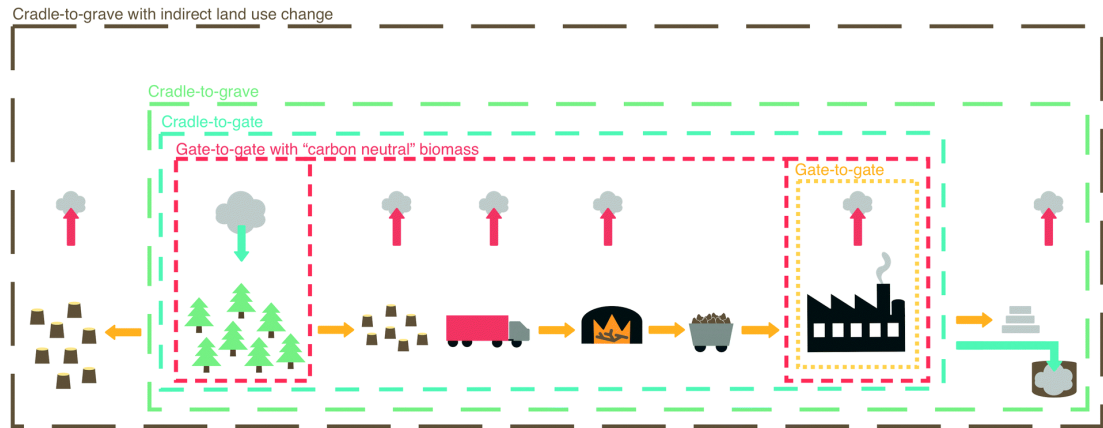


Figure 6. Boundaries applied to a steel mill implementing BECCS. Source: (Tanzer and Ramirez, 2019).

A brief explanation to understand the system boundaries in the figure above is the following:

- **“Gate to Gate”**
In this system, only the processes and emissions within the plant are considered. Bioenergy studies based on this boundary assume that the amount of CO₂ removed by biomass is equal to the amount of CO₂ released during the combustion, making the bioenergy used “carbon neutral.”
- **“Cradle to Gate”**
In this system, the previous “Gate to Gate” system is considered along with the upstream emissions produced from land use, cultivation, harvesting, biomass transport, and others. However, this system does not consider other downstream emissions, such as the final product or waste treatment emissions.
- **“Cradle to Grave”**
In this system, the previous system boundaries are considered along with the downstream emissions.
- **“Cradle to Grave with indirect land-use change”**
This last system considers the previous systems along with the emissions involved in land-use changes from the cultivation and harvesting of biomass.

Hence, negative emissions cannot be determined without accounting for all the emissions and removal of greenhouse gases. Thus, it is essential to be aware of the system boundaries and their limitations to determine the quantities of negative emissions that can be achieved in any case, keeping in mind the main objective, which is to reduce the atmospheric level of greenhouse gases (Tanzer and Ramírez, 2019).

3.5. Biofuels

3.5.1. Introduction

On September 25th of 2015, the United Nations set 17 global sustainable development goals (SDGs) for the 2030 agenda. These goals were set to balance the following dimensions: economic, social, and environmental. These dimensions are essential since they constitute and lead to a solid and sustainable development, and aim for peace and prosperity for people and the planet (United Nations, 2020).



Figure 7. United Nation's 17 global goals for sustainable development. Source: (United Nations, 2020)

Biofuels relate to these goals since they currently play an essential role in the global economy and contribute to approximately 13% of the global energy needs. Furthermore, biofuels are also considered as a critical element in future low carbon scenarios, and for the reduction of greenhouse gas (GHG) emissions from the transport sector and the industry in general (IEA, 2020). According to the report made by the International Energy Agency, decarbonizing the industry will require a range of bio-based fuels and advanced low carbon fuels. Within the range of bio-based fuels is situated biogas.

According to the Linköping-based Biogas Research Centre (BRC), biogas plays an important role in achieving these 17 goals by contributing directly and indirectly to all of them (Hagman and Eklund, 2016). For the reason that the production and use of biogas carry economic, social, and climate benefits with it. Such as increased energy, ensure food security, waste management, reduced dependency on the importation of mineral fertilizers, improved air quality, increased employment. Etc (Swedish Gas Association, 2018). For that reason, in the following section, a more detailed explanation is given about how biogas contributes directly and indirectly to these 17 goals.

3.5.2. Biogas

Among the biofuels group, biogas itself is considered as a unique asset for society because it forms part of a closed cycle. More specifically, the food waste, wastewater, and other residues from the agriculture, forestry, and industry sectors are used to produce heat, electricity, and raw materials for the industry, and biofertilizer for the agriculture sector. Hence, producing biogas and using it leads to an efficient use of society's resources (Swedish Gas Association, 2018).

Furthermore, the biogas industry, besides taking the lead with the current climate problems and helping achieving climate targets, is capable to create new jobs and open new opportunities for the development of a country, such as by ensuring the domestic fuel supply security for the industry and the automobile sector, providing biofertilizer for the agriculture sector, etc. For that reason, biogas currently constitutes an important part of a country's circular business development (Swedish Gas Association, 2018).

For the specific case of Sweden, a consultancy company performed studies regarding the social benefit of biogas, based on 2 TWh's production in 2016. The results were that the country produced in gross domestic product (GDP) near to 4 billion SEK per year, and by just implementing some measure the biogas production could go up to 7 TWh per year along with a GDP of 14 billion SEK per year. Furthermore, the Swedish Gas Association in collaboration with the biogas industry, developed an initial proposal to achieve the production of biogas up to 15 TWh by the year 2030, where 12 TWh would be destined for transportation purposes meanwhile the rest would be destined to the industry. In addition, the 15 TWh biogas production by 2030 would also mean the production of 30 billion SEK in GDP. However, the Swedish Gas Association mentions that in order to achieve such development, requires the participation of different parties such as the government and parliament, authorities, municipalities and regions and specially the industry sector (Swedish Gas Association, 2018).

In order to achieve the mentioned objective, currently there are particular instruments that would provide the boost and help for the mentioned objective for 2030, such is the tax exemption for customers which is planned to settle the boost in the conditions for biogas production in the following 10 years, from 2021 to 2030. This measure also ensures that the Swedish produced and imported biogas can compete on equal terms compared to other European countries (Swedish Gas Association, 2018). By 2020, the biogas sector did not count with long term rules in place and the funding plan for the sector by the government was also unclear, however thanks to the European Commission on June 29th of 2020, the initial tax exemption measure was approved for its prolongation for the next 10 years for non-food-based biogas and bio-propane used for heating and as motor fuel.

The principal aim of this tax exemption measure is to increase the use of biogas and bio-propane in the country, reduce the use of fossil sources and avoid the emission of greenhouse gases to the atmosphere. The effective implementation and accomplishment of this tax exemption measure will settle the ground to a consequent transition to a society based on advanced biofuels in the future. According to Maria Malmkvist, CEO of the Swedish Gas Association, the approval of the tax exemption measure was an appropriate and necessary action to stimulate the production and consumption of domestic and imported biogas and bio-propane in the country and will contribute to the efforts of both Sweden and the European Union to meet the objectives set by the Paris agreement and move towards a fossil free society (Bioenergy International, 2020).

3.5.3. Applications

The employment of biogas in the market depends on various factors, such as the availability, price, taxes, and the overall competition (Swedish Gas Association, 2018). According to the Swedish Gas Association, in Sweden's particular case, biogas is used in different sectors, with the major application found in the vehicle marker. Other applications can be found in the following *Figure 8*:

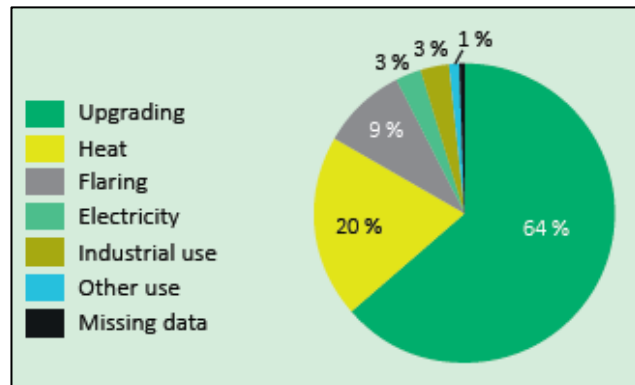


Figure 8. Applications to biogas produced in Sweden in 2016. Source: (Swedish Gas Association, 2018)

As seen in the figure, most of the biogas produced is used for upgrading and thus used as vehicle fuel. The amount of biogas used in vehicles has steadily increased in recent years in proportion and absolute volume thanks to a heavy taxation policy on fossil fuels (Swedish Gas Association, 2018). This measure has made it relatively easy for the vehicle sector to prioritize biogas and other renewable products. However, in terms of only biogas application, there is still a tougher competition from other renewable fuels, such as hydrogenated vegetable oil (HVO), which has had a strong increase within the public transport as well (Swedish Gas Association, 2018). Biogas in Sweden is currently created from different substrates as seen in *Figure 9*:

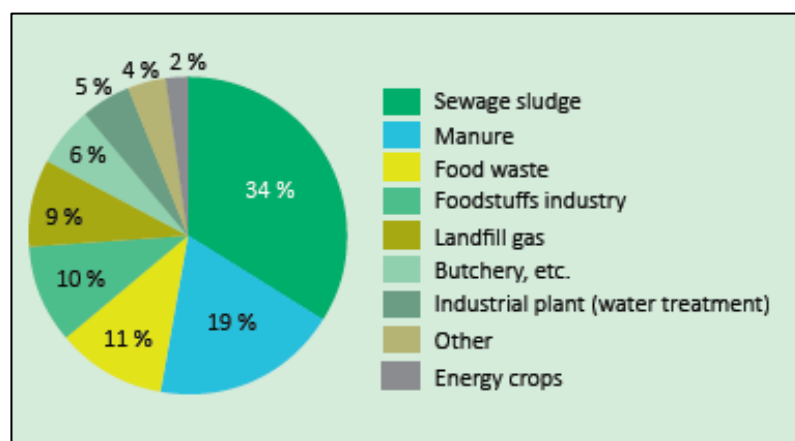


Figure 9. Substrates used in Sweden for the production of Biogas. Source: (Swedish Gas Association, 2018).

According to the Swedish Biogas Association, the following substrates are considered as the best source for biogas production: Manure, waste from food industry, cultivation residues, food waste and sewage sludge. By having different substrates for biogas production, the production in Sweden during the past few years has increased in a slow but steady rate, being co-digestion plants the main responsible for this increase (Swedish Gas Association, 2018).

3.5.4. Specifications

Biogas is usually produced from the decomposition of organic matter by different types of microorganisms in anaerobic conditions. It is mainly composed by methane and carbon dioxide, and several other minor components. However, its composition usually varies and depends on a number of factors such as the nature of the substrate used in the process and the process design for its production (Svensk Gastekniskt Center AB, 2012). The following *Table 5* represents the general composition of biogas produced in Sweden from anaerobic digestion.

Table 3. Biogas characteristics from anaerobic digestion. Reproduced from (Svensk Gastekniskt Center AB, 2012).

<i>Composition of Biogas in Sweden</i>		
		<i>Anaerobic digestion</i>
Lower Calorific Value	<i>MJ / Nm³</i>	23
	<i>kWh / Nm³</i>	6.5
	<i>MJ / kg</i>	20
Density	<i>kg / Nm³</i>	1.1
Relative density	-	0.9
Wobble Index, upper	<i>MJ / Nm³</i>	27
Methane number		> 135
Methane	<i>Vol - %</i>	65
Methane, range	<i>Vol - %</i>	60 – 70
Heavy hydrocarbons	<i>Vol - %</i>	0
Hydrogen	<i>Vol - %</i>	0
Carbon dioxide	<i>Vol - %</i>	35
Carbon dioxide, range	<i>Vol - %</i>	30 – 40
Nitrogen	<i>Vol - %</i>	0.2
Nitrogen, range	<i>Vol - %</i>	-
Oxygen	<i>Vol - %</i>	0
Oxygen, range	<i>Vol - %</i>	-
Hydrogen sulphide	<i>ppm</i>	< 500
Hydrogen sulphide, range	<i>ppm</i>	0 – 4000
Ammonia	<i>ppm</i>	100
Total Chlorine as Cl-	<i>mg / Nm³</i>	0 – 5

The upgrade process removes most of the carbon dioxide and other minor components present in biogas with the aid of different technologies. This process is generally performed with the main objective to increase the energy density of biogas.

Table 4. Different carbon dioxide removal technologies. Reproduced from (Svensk Gastekniskt Center AB, 2012)

<i>Technology</i>	<i>Function</i>
<i>Pressure Swing Adsorption (PSA)</i>	Adsorption of carbon dioxide on materials such as activated carbon
<i>Water Scrubber</i>	Absorption of carbon dioxide in water
<i>Chemical Absorption</i>	Absorption of carbon dioxide and amine-based solvents through a chemical reaction
<i>Membrane</i>	Separation of carbon dioxide through a CO ₂ permeable membrane
<i>Cryogenic Separation</i>	Separation of carbon dioxide through cooling it until condensation or sublimation.

Moreover, it is even possible to upgrade the biogas to a degree to condense it and obtain liquefied biogas, commonly abbreviated (LGB).

As mentioned previously, in Sweden biogas is generally upgraded to be used as a vehicle fuel (generally referred as biomethane) and must meet a standard imposed by the Swedish Standard Institute (SIS). There are two types of biogas, the first one is called “*Biogas type A*” and is aimed to “lean-burn” engines without lambda regulation, usually found in heavy vehicles such as trucks and buses. Meanwhile the other type “*Biogas type B*” is aimed to engines with lambda regulation for stoichiometric combustion (Svensk Gastekniskt Center AB, 2012). The following table summarizes the characteristics that both types of biogas must meet:

Table 5. Composition of upgraded biogas in Sweden. Reproduced from ((SSI), 2018).

<i>Composition of Upgraded Biogas in Sweden</i>			
	Unit	<i>Biogas Type A</i>	<i>Biogas Type B</i>
<i>Wobbe index</i>	<i>MJ / Nm³</i>	44.7 – 46.4	43.9 – 47.3
<i>Methane content</i> (* at 273.15 K and 101.325 kPa)	<i>Vol - %*</i>	97 +- 1	97 +- 2
<i>Water dew point at the highest storage pressure</i> (** lowest average daily temperature)	<i>C</i>	T-5**	T-5**
<i>Maximum water content</i>	<i>mg / m³</i>	32	32
<i>Maximum CO₂ + O₂ + N₂</i>	<i>Vol - %</i>	4.0	5.0
<i>Maximum O₂</i>	<i>Vol - %</i>	1.0	1.0
<i>Total Sulphur content, maximum</i>	<i>mg / m³</i>	23	23
<i>Total content of nitrogen compounds (excluding N₂)</i>	<i>mg / m³</i>	20	20
<i>Maximum size of particles</i>	<i>um</i>	1	1

According to *Energigas Sverige*, in 2018 around 63% of the total produced biogas was upgraded to biomethane, of which around 67% was used as transportation fuel (Klackenberg, 2019). However, upgraded biogas besides its utilization as transportation fuel, it can also be injected into natural gas grids. From the 1.25 TWh of biomethane produced in 2018 with the aid of 69 biomethane upgrading units, around 0.5 TWh of the total were injected into the south-western gas grid (which is connected to the European gas grid) and in the Stockholm gas grid. As for the rest 1.20 TWh, it was used locally or to fill truck stations (Klackenberg, 2019).

4. Modeling and Simulation

4.1. Research Methodology

For the present study, a modeling and simulation approach was considered with the aim to simulate an actual ammonia fertilizer plant and estimate its performance by the implementation of different biofuels in order to achieve both, a sustainable fertilizer process production and achieve negative emissions. The main reason why a model and simulation approach were used for the development of the present study is that due to its flexibility, it allowed us to observe the performance of the actual plant based on real quantitative data. Hence, after modeling the actual plant with a proper simulation software tool, it was possible to evaluate the different biofuel integration cases. Once the different cases were evaluated, it led to the opportunity to analyze how different configurations within the plant would affect and what influence they would have on the set objectives.

Regarding data collection, the quantitative data about the amount of feedstock used in the process was obtained from an actual ammonia fertilizer plant presented by the International Energy Agency Greenhouse Gas programme (IEAGHG) in their technical report “*Techno-Economic Evaluation of HYCO Plant integrated to Ammonia/Urea or Methanol Production with CCS*” (Santos et al., 2017), the quantitative data about the operating conditions normally used in a state of the art ammonia fertilizer plant was obtained from the study “*Integration of the Ca-Cu Process in Ammonia Production Plants*” (Martínez et al., 2017), “*European best practice guidelines for the assessment of CO₂ capture technologies*” (Anantharaman et al., 2018), and “*Efficient hydrogen production with CO₂ capture using gas switching reforming*” (Nazir et al., 2019), and the quantitative data regarding the process conditions used in the Urea plant were obtained from the template document “*Aspen plus Urea synthesis loop model*” (Aspen Technology Inc., 2011).

The results for each study case were gathered, analyzed and compared with the base case with the aim to understand if each one of them improved the performance of the ammonia fertilizer plant and if they fulfilled the expectations that would directly contribute to the set objectives of sustainable development and negative emissions.

4.2. Assumptions and limitations

The following limitations were considered for the development of the present case study:

Urea Plant:

- The aspen plus process template describes a steady-state simulation of a high-pressure synthesis loop urea plant with a capacity of 1,100 metric tons of prilled urea per year. Half the capacity of the actual urea produced in the HyCO report.
- The provided process template describes the Stamicarbon CO₂ stripping process, which initial results proved the applicability of Aspen Plus to the actual results from the ammonia plant in Aspen Hysys.
- The side reaction product, Biuret, is not considered during the synthesis in the simulation.

4.3. Process simulation software used

The process simulation software used for the project was provided by Aspen Tech, for the production of ammonia the programme used was Aspen Hysys v11, meanwhile for the production of urea the software used was Aspen Plus v11.

4.4. Modelling of Ammonia Plant

The simulation of the ammonia plant begins by setting the conditions for different streams, such as:

- **Mass/molar flow:**

The conditions of mass and molar flows for diverse material streams were taken from the International Energy Agency Greenhouse Gas programme (IEAGHG) report “*Techno – Economic evaluation of HYCO plant integrated to Ammonia / Urea or Methanol Production with CCS*” (Santos et al., 2017) as a base for a later validation process.

- **Temperature & Pressure:**

Other conditions such as temperature, pressure for the production of ammonia, were taken from the article “*Integration of the Ca – Cu process in Ammonia production plants*” (Martínez et al., 2017).

- **Streams compositions:**

Finally the composition of different streams such as natural gas, air, and others were taken from the report “*CESAR – CO₂ Enhanced separation and recovery*” (Anantharaman et al., 2018).

- **Equipment process conditions:**

Process conditions such as pressure drop for the different reactors (1% from the inlet pressure) and heat exchangers (2% from the inlet pressure), efficiencies of the syngas compressors (80%), air compressors (92.5%), pumps (80%), and hydrogen recovery rate in the ammonia plant were taken from the article “*Efficient hydrogen production with CO₂ capture using gas switching reforming*” (Nazir et al., 2019)

Then, once the conditions for different streams have been defined, the simulation of the base case ammonia plant begins by initially introducing all the chemical compounds involved in the whole process in the component list section. Hence, the elements introduced for the production of ammonia are summarized in the table below:

Table 6. Component list used in the simulation of ammonia plant.

<i>Component name</i>	<i>Formula</i>
<i>Methane</i>	CH ₄
<i>Ethane</i>	C ₂ H ₆
<i>Propane</i>	C ₃ H ₈
<i>i – butane</i>	C ₄ H ₁₀
<i>n – butane</i>	C ₄ H ₁₀
<i>i – pentane</i>	C ₅ H ₁₂
<i>n – pentane</i>	C ₅ H ₁₂
<i>Hydrogen</i>	H ₂
<i>Carbon dioxide</i>	CO ₂
<i>Carbon monoxide</i>	CO
<i>Urea</i>	CH ₄ N ₂ O
<i>Ammonia</i>	NH ₃
<i>Oxygen</i>	O ₂
<i>Water</i>	H ₂ O
<i>Argon</i>	Ar
<i>Nitrogen</i>	N ₂
<i>MDEAmine</i>	CH ₃ N(C ₂ H ₄ OH) ₂
<i>Piperazine</i>	C ₄ H ₁₀ N ₂
<i>Hydrogen Sulfide</i>	H ₂ S

Once the totality of the elements to be used in the simulation have been introduced in the component list, the subsequent streams for each section of the process are defined. For the initial section of ammonia production, the streams of natural gas, steam and process air are set. The composition of natural gas is the following:

Table 7. Composition of Natural gas. Reproduced from (Anantharaman et al., 2018).

<i>Natural Gas Composition</i>	
<i>Component</i>	<i>Volume %</i>
CH ₄ – <i>Methane</i>	89.00
C ₂ H ₆ – <i>Ethane</i>	7.00
C ₃ H ₈ – <i>Propane</i>	1.00
C ₄ -i – <i>i-butane</i>	0.05
C ₄ -n – <i>n-butane</i>	0.05
C ₅ -i – <i>i-Pentane</i>	0.005
C ₅ -n – <i>n-Pentane</i>	0.004
CO ₂	2.00
N ₂	0.89
S	< 5 ppm
HHV (MJ / kg)	51.473
LHV (MJ / kg)	46.502
CO ₂ emissions g / kWh LHV	208

The stream conditions of the desulfurized natural gas feedstock are an initial temperature and pressure of 10° C and 7 MPa respectively, and a molar flow of 1500 kmol/hr (Santos et al., 2017). Before entering the pre-reformer reactor, the NG feedstock stream is mixed with a stream of high-pressure steam coming from the plant itself. In the blending process, the steam to carbon (S/C) ratio generally varies from 2.5 to 3.6 in existing ammonia production plants (Martínez et al., 2017). However, according to (Martínez et al., 2017), a lower value is desired for modern plants. For that reason, an intermediate S/C ratio value of 2.77 was chosen for this work. Hence, the stream conditions for the process steam are an initial temperature and pressure of 375°C and 4.2 MPa respectively, and a molar flow of 3750 kgmol/hr (Santos et al., 2017).

Then, the resultant mixed feedstock is heated up to a temperature of 490 °C before entering the pre-reformer, where it is heated up to 620 °C (Martínez et al., 2017). Martínez et al. (2017) mentions that this previous step of pre-reforming enables the partial decomposition of higher hydrocarbons present in the feedstock mixture stream into carbon monoxide and hydrogen before entering the primary reformer reactor and the integration of this step is beneficial for the process since it reduces the reforming duty necessary in the reforming process section. Then, the resulting stream from the pre-reforming reactor is sent to the Primary fired tubular reformer (FTR) where the mixture is heated up to 820 °C due to the fact that the reactions involved at this initial stage are endothermic. The heat necessary for this initial reforming process comes from burning part of the natural gas total feedstock and from other streams from other processes in the plant.

Martínez et al. (2017) also mentions that this primary reforming stage leads to a methane conversion within the range of 55 – 65%, for the present study case and due to the previous established stream conditions, a methane conversion of 52% was obtained. Regarding the concentration of methane in the resulting reformed product stream is expected to be within the range of 10 – 15% on a dry basis, in this study case the concentration obtained was 15.69% on a dry basis. Then, the resultant stream is sent to the secondary reformer reactor (ATR) where an additional stream of process air is attached. The composition for the air used in process is the following:

Table 8. Process Air composition. Reproduced from (Anantharaman et al., 2018).

<i>Air Composition</i>		
<i>Component</i>	<i>Volume Fraction Dry</i>	<i>Volume fraction at 60% Relative humidity</i>
<i>N₂</i>	78.09	77.30
<i>CO₂</i>	0.03	0.03
<i>H₂O</i>	0.00	1.01
<i>Argon</i>	0.932	0.923
<i>Oxygen</i>	20.95	20.74
<i>Gas constant [J/(kg*K)]</i>	287.06	288.16
<i>Molecular weight</i>	28.964	28.854

The stream conditions for the Air process stream are an initial temperature, pressure of 540 °C, and 3.3 MPa, and a molar flow of 2286 kmol/hr. In order to reach the mentioned conditions, Process air is initially compressed in a three-stage intercooled compressor with a polytropic efficiency of 92.5%. The reactions involved within the secondary autothermal reformer reactor (ATR) are highly exothermic and lead to outlet temperatures around 1000 °C with a methane concentration lower than 0.5% in a dry basis. In the present case study, an outlet temperature of 992.4 °C was obtained with a reformed product stream with a methane content of 0.55%. The process air introduced to the reactor provides the nitrogen necessary for the posterior downstream ammonia synthesis reactor, which as mentioned before, should be fed with a synthesis gas containing merely hydrogen and nitrogen in a ratio 3:1 respectively. The product from the reforming section is a raw syngas stream expected to contain around 15% of CO in a dry basis, in the present case study a raw syngas stream was obtained with a concentration of CO of 15.11%. The content of CO present in the raw syngas stream is later on converted to CO₂ and H₂ through the water gas shift reaction.

The raw syngas stream obtained from the reforming process section is cooled down to a temperature around 350 °C before entering the water gas shift (WGS) section, which is composed by two reactors, one that operates at a higher temperature and other one at a lower temperature. Once the raw syngas stream has been cooled down to the mentioned temperature it is then sent to the High temperature WGS reactor, where due to the exothermic nature of the equilibrium reactions involved in the conversion process, the temperature of the initial produced stream reaches up to 436.9 °C. This heat produced in the first process is recovered and the produced stream is once again cooled down to a temperature around 200 °C before entering the subsequent reactor. Within the low temperature WGS reactor, again due to the equilibrium reactions involved in the process, the temperature of the produced stream reaches up to 235 °C. According to (Martínez et al., 2017), the resultant stream from the WGS section is expected to contain a CO and CO₂ concentration of 0.4% and 18% respectively in a dry basis. The concentrations obtained in the present case study were 0.47% for CO and 18.15% for CO₂ in a dry basis. Hence, after the concentrations of CO and CO₂ have been validated, the resultant stream from the WGS section is cooled down to 35 °C before being sent to the Bulk CO₂ removal section. The cooling down and heat recovery process condensates the water present in the stream, which is subsequently recovered with the aid of a separator, leaving as a result an untreated syngas stream containing mainly hydrogen, carbon dioxide, nitrogen, and some traces of carbon monoxide.

The bulk CO₂ removal section is composed by an absorber, a flash column, a rich lean heat exchanger and regeneration columns. Firstly, the untreated syngas stream is sent to the absorber where it enters from the bottom part and a MDEA stream is fed from the upper section. The composition for the MDEA stream is the following:

Table 9. MDEA set conditions in Hysys.

MDEA Conditions	
Component	Mass fraction %
CO ₂	0.05
Piperazine	0.05
MDEA	0.45
H ₂ O	0.45
Temperature (°C)	35
Pressure (kpa)	2420
Mass flow (kg/hr)	1.034e+006

Hence, with a 98.5% carbon capture rate, carbon dioxide is recovered from the syngas stream, compressed at a specific pressure and sent to the urea plant. Following the CO₂ removal section, the content summation of CO₂ and CO present in the syngas stream is expected to be 0.6% vol. The content of CO₂ and CO in the base case simulation was of 0.01%. Then, the treated syngas stream is sent to the methanation reactor, where CO₂ and CO are converted into methane. This way, reducing the amount of oxygen containing compounds that could deactivate the catalyst in the ammonia synthesis process. Thus, the treated syngas stream is heated up to 280 °C before being fed to the Methanator, methane is formed and due to the exothermic reaction, the temperature of the syngas stream is expected to increase in a range of 50 to 70 °C, in the base case an increase of 42.9 °C was observed. Then, the rest of oxygen containing compounds, namely H₂O, is subsequently removed by condensation and cooling down the Methanator resultant stream to 35 °C.

The resultant syngas stream is then sent to the syngas compression train, which is composed by a three-stage intercooled compressor with a polytropic efficiency of 80%. The syngas stream is first mixed with the hydrogen recovered from a downstream PSA recovery process, and second with a stream of unreacted components from the ammonia synthesis loop. Hence, the overall stream is compressed to the required conditions at the inlet of the ammonia synthesis reactor, which are a pressure range of 150-250 bar and a temperature range of 350-550 °C. For the base case, the conditions at the inlet of the ammonia synthesis reactor were set to 199 bar and 320 °C. Given the operating conditions, the reaction rate of ammonia formation is limited, giving as a result an ammonia conversion pass of 34% according to a calculation of ammonia conversion at chemical equilibrium at 465 °C (Martínez et al., 2017). In the base case, the observed conversion of ammonia per pass was of 37.99%. Due to the lower conversion per pass, the unreacted components from the ammonia synthesis reaction are sent back for recirculation after a downstream ammonia condensation process. However, before being recirculated, it is necessary to avoid the accumulation of inert components such as methane and argon at the inlet of the ammonia synthesis process, for that reason a fraction of the recirculation stream, about 1 to 2% of the total, is purged. For the base case, a fraction of 2% is purged. The purged stream is sent to scrubber unit where it is scrubbed with water in order to remove any amount of ammonia present in the stream. Then it is sent to the Pressure Swing Adsorption (PSA) unit where hydrogen is recovered. The amount of hydrogen recovered in PSA was determined according to the following formula (Nazir et al., 2019), Where P₁ and P₂ are the pressures of the PSA feed and off-gas streams respectively:

Amount of hydrogen recovered in PSA:

$$H_2 \text{ recovery in PSA (\%)} = 100 - \frac{100}{0.2521 \left(\frac{P_1}{P_2} \right) + 1.2706} \quad (11)$$

Hydrogen recovered from the PSA process is sent to recirculation, and the off-gas composed of H₂, CH₄, and N₂ is sent as fuel to the SMR burner. Hence, the ammonia produced has to be separated from the syngas stream with a refrigeration cycle. First, the product from the ammonia synthesis reactor is cooled down to around 30 – 45 °C. For the present base case, the product was cooled down to 30 °C and sent to the refrigeration cycle, which uses ammonia as the refrigerant fluid and operates between 1.5 and 1.8 bar (Martínez et al., 2017). The syngas is then cooled down to -20 °C condensing the ammonia present in the stream. The liquid ammonia is separated by flashing the stream to around 20 bar, releasing the unreacted gases dissolved in the stream.

Finally, for the base case a fraction of the liquid ammonia is sent to storage meanwhile the rest is compressed and sent to the urea plant with the following conditions: 34 °C and 156.9 bar, along with the compressed carbon dioxide stream from the bulk removal section with the following conditions: 100 °C and 138.3 bar.

Regarding the heat integration in the base case, a large amount of energy is available in the following: the flue gas stream from the SMR burner, the syngas stream from the ATR reformer reactor, and the products from the WGS section and the ammonia reactor. Hence, energy is recovered from the mentioned sections by cooling them down and producing steam at 318 °C and 112.3 bar, and high pressure steam at 510 °C and 110 bar. Energy is recovered from the total high pressure steam stream by sending it to the turbine section for the production of electric power. However, first a fraction of the high pressure steam is sent to the ammonia plant in order to meet the steam to carbon ratio requirement, and the electricity produced in the turbine section will be used for the syngas compression train, the refrigeration cycle, the air compressor for the ATR reactor, and other components in the urea plant.

4.5. Modelling of Urea Plant

The ammonia and carbon dioxide streams obtained from the ammonia plant are sent to the urea and granulation plant. As mentioned in the assumptions and delimitations section, the production of urea is based on a flowsheet provided by Aspen Tech that describes a steady state model of a high-pressure synthesis loop of a urea plant. In essence the urea production process in the flowsheet is based on the Stamicarbon CO₂ stripping process. Hence, the urea production process follows the following sequence:

- **CO₂ stripper column:**

The carbon dioxide stream is fed to the CO₂ stripper column in counter current to the urea solution coming down from the urea synthesis reactor. Then within the stripper column, the ammonium carbamate formed in the reactor and present in the falling down urea solution is decomposed into ammonia (NH₃) and carbon dioxide (CO₂), which are stripped out. During this process, heat is provided in the form of steam injection through the shell side of tubes, the steam entering at almost 20 bar is condensed while the urea solution falls down inside the tubes in counter current to the rising carbon dioxide stream. The result of this process is a liquid solution coming from the bottom of the stripper column rich in urea, and it is sent to a downstream urea purification process.

- **Urea reactor:**

First, the urea reactor's design is modeled in a manner that the residence time is enough for urea formation and thus minimize any back-mixing process. Then ammonia, carbon dioxide (most of it in the form of ammonium carbamate), and other vapors flow upward within the reactor. Thus, vapors condensate and ammonium carbamate decompose, releasing heat in the process. The heat released provides the necessary energy required for the slight endothermic reaction of ammonium carbamate to urea. Hence, urea is formed, and the overall solution overflows from the top of the reactor going back to the CO₂ stripper column.

- **Scrubber unit:**

The unreacted gases leaving the urea reactor are sent to a scrubber unit, where ammonium carbamate coming from the evaporation and recirculation section is recycled. During this process, the unreacted gases enter from the bottom of the scrubber column and flow upward in counter current to the ammonium carbamate falling down from the inner tubes. Ammonium carbamate solution while falling down in counter current, absorbs the ammonia and carbon dioxide present in the unreacted gases stream, thus the remaining gases such as nitrogen, oxygen and other leave from the top of the scrubber unit. Then at the bottom of the scrubber unit, the heat released from the absorption process is cooled down with cooling water.

- **Carbamate Condenser:**

The vapors and the stream coming out from the top of the CO₂ stripper column are fed into the carbamate condenser along with the ammonium carbamate stream coming from the scrubber unit. In this unit, ammonium carbamate is formed, and the heat released during this process is recovered throughout the generation of 3.5 bar steam on the shell side. Finally, the mixture stream formed during this process is sent to the bottom of the reactor to produce urea.

Thereafter, the final product of urea from the urea purification section is sent to the granulation plant.

4.6. Natural gas feedstock and fuel replacement cases

For the present case study, the replacement of different fractions of natural gas in different proportions such as 25, 50, 75, and 100% for both the feedstock and SMR burner fuel, was calculated considering the low heating value that was being removed from the total inlet stream of natural gas. Then, once noted the amount of natural gas that is being removed from the inlet stream of natural gas for the feedstock and for the burner fuel, it is possible to calculate the total amount of energy that is being removed by simply multiplying the amount of natural gas that is being removed by natural gas's low heating value. Thus, we are able to calculate, with the calculated total amount of energy that is being removed, the amount of biogas (BG) and biomethane (BM) that is required in each case. Hence, the biogas and biomethane replacement cases with biogas and biomethane are the following:

- *Cases: Replacing NG feedstock with biogas*

<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
Feedstock: 75% NG - 25% BG	Feedstock: 50% NG - 50% BG	Feedstock: 25% NG - 75% BG	Feedstock: 0% NG - 100% BG
SMR Burner fuel: 100% NG	SMR Burner fuel: 100% NG	SMR Burner fuel: 100% NG	SMR Burner fuel: 100% NG

- *Cases: replacing NG in SMR Burner fuel with biogas or biomethane:*

<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>
Feedstock: 100% NG	Feedstock: 100% NG	Feedstock: 100% NG	Feedstock: 100% NG
SMR Burner fuel: 75% NG - 25% BG	SMR Burner fuel: 50% NG - 50% BG	SMR Burner fuel: 25% NG - 75% BG	SMR Burner fuel: 0% NG - 100% BG

<i>I</i>	<i>J</i>	<i>K</i>	<i>L</i>
Feedstock: 100% NG	Feedstock: 100% NG	Feedstock: 100% NG	Feedstock: 100% NG
SMR Burner fuel: 75% NG - 25% BM	SMR Burner fuel: 50% NG - 50% BM	SMR Burner fuel: 25% NG - 75% BM	SMR Burner fuel: 0% NG - 100% BM

4.7. Combination of feedstock and fuel replacement cases

The results obtained from the feedstock and SMR burner fuel replacement cases are combined in different arrangements in order to evaluate the potential that represents combining both replacement cases in the pathway to achieve negative emissions. Thus, the combination of the feedstock and SMR burner fuel cases were the following:

Cases: Replacing NG in Feedstock and SMR Burner fuel with biogas

<i>AE</i>	<i>AF</i>	<i>AG</i>	<i>AH</i>
<i>Feedstock:</i> 75% NG - 25% BG	<i>Feedstock:</i> 75% NG - 25% BG	<i>Feedstock:</i> 75% NG - 25% BG	<i>Feedstock:</i> 75% NG - 25% BG
<i>SMR Burner fuel:</i> 75% NG - 25% BG	<i>SMR Burner fuel:</i> 50% NG - 50% BG	<i>SMR Burner fuel:</i> 25% NG - 75% BG	<i>SMR Burner fuel:</i> 0% NG - 100% BG

<i>BE</i>	<i>BF</i>	<i>BG</i>	<i>BH</i>
<i>Feedstock:</i> 50% NG - 50% BG	<i>Feedstock:</i> 50% NG - 50% BG	<i>Feedstock:</i> 50% NG - 50% BG	<i>Feedstock:</i> 50% NG - 50% BG
<i>SMR Burner fuel:</i> 75% NG - 25% BG	<i>SMR Burner fuel:</i> 50% NG - 50% BG	<i>SMR Burner fuel:</i> 25% NG - 75% BG	<i>SMR Burner fuel:</i> 0% NG - 100% BG

<i>CE</i>	<i>CF</i>	<i>CG</i>	<i>CH</i>
<i>Feedstock:</i> 25% NG - 75% BG	<i>Feedstock:</i> 25% NG - 75% BG	<i>Feedstock:</i> 25% NG - 75% BG	<i>Feedstock:</i> 25% NG - 75% BG
<i>SMR Burner fuel:</i> 75% NG - 25% BG	<i>SMR Burner fuel:</i> 50% NG - 50% BG	<i>SMR Burner fuel:</i> 25% NG - 75% BG	<i>SMR Burner fuel:</i> 0% NG - 100% BG

<i>DE</i>	<i>DF</i>	<i>DG</i>	<i>DH</i>
<i>Feedstock:</i> 0% NG - 100% BG	<i>Feedstock:</i> 0% NG - 100% BG	<i>Feedstock:</i> 0% NG - 100% BG	<i>Feedstock:</i> 0% NG - 100% BG
<i>SMR Burner fuel:</i> 75% NG - 25% BG	<i>SMR Burner fuel:</i> 50% NG - 50% BG	<i>SMR Burner fuel:</i> 25% NG - 75% BG	<i>SMR Burner fuel:</i> 0% NG - 100% BG

As stated previously, the present study emphasizes the integration of biogas to the plant feedstock and SMR burner fuel due to all the positive benefits for society, the economy, and the environment. For that reason, only biogas combination cases will be addressed.

4.8. Negative emission assessment

For the respective negative emissions calculations for each case, the following boundaries were defined:

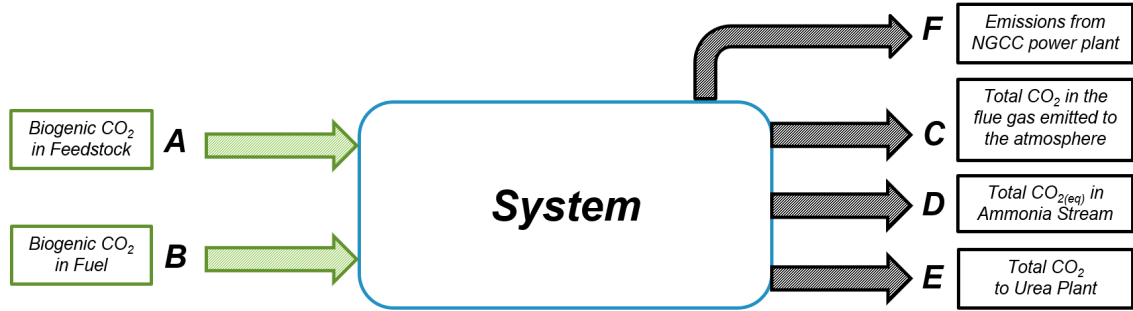


Figure 10. Limitations for the present study system.

Where:

- **A** refers to the biogenic CO₂ present in the *Feedstock* entering the ammonia fertilizer plant
- **B** refers to the biogenic CO₂ present in the *SMR burner fuel* entering the ammonia fertilizer plant
- **C** refers to the total CO₂ that is being emitted to the atmosphere through the flue gas
- **D** refers to the total equivalent CO₂ (in the form of methane) leaving the plant along with the ammonia product
- **E** refers to the total CO₂ that was sent to the urea plant
- **F** refers to the emissions of CO₂ produced from the natural gas combined cycle power (NGCC) plant to provide the necessary energy to the ammonia fertilizer plant.

Hence, the following scenarios were considered:

- **Scenario 1: CO₂ emitted from the urea plant only**
Considers the summation of the emissions to the atmosphere from the CO₂ present in the flue gas to stack and the equivalent CO₂ present in the ammonia product (in the form of methane), minus the summation of the equivalent biogenic CO₂ that enters the ammonia fertilizer (urea) plant present in the feedstock and SMR burner fuel. The formula to calculate the resultant emissions is the following:

$$\text{Scenario 1: } (C+D) - (A+B) \quad (12)$$

- ***Scenario 2: CO₂ emissions from urea plant and electricity plant (NGCC)***

Considers the summation of the emissions to the atmosphere from the CO₂ present in the flue gas to stack, the equivalent CO₂ present in the ammonia product (in the form of methane), and the emissions from the natural gas combined cycle (NGCC) power plant. All of that minus the summation of the equivalent biogenic CO₂ that enters the ammonia fertilizer (urea) plant present in the feedstock and SMR burner fuel. The formula to calculate the resultant emissions is the following:

$$\text{Scenario 2: } (C+D+F) - (A+B) \quad (13)$$

- ***Scenario 3: CO₂ emissions from urea plant, electricity plant and from urea use***

This last scenario considers the summation of the emissions to the atmosphere from the CO₂ present in the flue gas to stack, the equivalent CO₂ present in the ammonia product (in the form of methane), the emissions from the natural gas combined cycle (NGCC) power plant, and the CO₂ emissions from the urea product. All of that minus the summation of the equivalent biogenic CO₂ that enters the ammonia fertilizer (urea) plant present in the feedstock and SMR burner fuel. The formula to calculate the resultant emissions is the following:

$$\text{Scenario 3: } (C+D+F+E) - (A+B) \quad (14)$$

In order to compare the emissions from each of the proposed cases with each other, the results obtained from the previously described scenarios will be divided by the total amount of urea produced in each case. Resulting in this manner the “*Specific CO₂ emissions*”.

5. Results and Discussion

The results and discussion section begin with the base case simulation, presenting the results obtained in Aspen HYSYS of an actual ammonia plant. Subsequently, the feedstock and SMR burner fuel replacement cases are presented. Ultimately, the different combinations of the feedstock and fuel biogas replacement cases are presented.

5.1. Base Case

The current section presents the results obtained from the simulation of an actual ammonia plant. As previously set, the data of the natural gas inlet streams used in the simulation were obtained from the International Energy Agency Greenhouse Gas programme (IEAGHG) in their technical report “*Techno-Economic Evaluation of HYCO Plant integrated to Ammonia/Urea or Methanol Production with CCS*” These natural gas streams were used both as feedstock to produce ammonia and as fuel to provide the necessary energy required by the endothermic reactions involved in the ammonia production process.

The following table presents the mass flow of the natural gas feedstock and the fuel used in the ammonia plant:

<i>Mass flow - Inlet streams</i>		<i>Base Case</i>
Natural gas (as Feedstock)	kg/hr	27028.34
Natural gas (as Fuel)	kg/hr	10631.15
Natural gas total Consumption	kg/hr	37659.49
Biogas (as Feedstock)	kg/hr	0.00
Biogas (as Fuel)	kg/hr	0.00
Biogas Total Consumption	kg/hr	0.00
Biomethane (as Feedstock)	kg/hr	0.00
Biomethane (as Fuel)	kg/hr	0.00
Biomethane Total Consumption	kg/hr	0.00
Total Feedstock	kg/hr	27028.34
Total Fuel	kg/hr	10631.15

The following table presents the total energy input per inlet stream at the beginning of the process. The lower heating value (LHV) of natural gas is multiplied by its respective streams entering the ammonia plant.

<i>Total Energy Input</i>		<i>Base Case</i>
Natural Gas LHV	MJ/kg	46.50
Biogas LHV	MJ/kg	20.14
Biomethane LHV	MJ/kg	45.67
Natural Gas (Feedstock) Energy input	MJ	1256750.78
Natural Gas (Fuel) Energy input	MJ	494321.97
Biogas (Feedstock) Energy input	MJ	0.00
Biogas (Fuel) Energy input	MJ	0.00
Biomethane (Feedstock) Energy input	MJ	0.00
Biomethane (Fuel) Energy input	MJ	0.00
Total Energy input	MJ	1751072.75
Total Energy input	MW	486.41

The total energy input provided by the natural gas used both as feedstock and fuel is ***1.75E+06 MJ*** or ***486.41 MW***. This information is essential in the following natural gas replacement cases since the amount of energy removed must be compensated with a specific amount of biogas and biomethane.

The outlet streams and products obtained from the base case are summarized in the following table:

<i>Outlet Streams</i>		<i>Base Case</i>
Ammonia Product to Urea Plant	<i>kg/hr</i>	53440,31
Ammonia Product to Storage	<i>kg/hr</i>	2657,20
<i>Total Ammonia</i>	<i>kg/hr</i>	<i>56097,51</i>
CO ₂ stream Product to Urea Plant	<i>kg/hr</i>	70088,00
CO ₂ stream Product to Storage	<i>kg/hr</i>	0,00
<i>Total CO₂ stream</i>	<i>kg/hr</i>	<i>70088,00</i>
<i>Urea Product</i>	<i>kg/hr</i>	<i>94082,40</i>

Table 10. Results obtained from an existing ammonia plant. Reproduced from (Santos et al., 2017)

<i>Outlet Streams</i>		<i>HyCO Plant</i>
Ammonia Product to Urea Plant	<i>kg/hr</i>	53400,0000
Ammonia Product to Storage	<i>kg/hr</i>	2850,0000
<i>Total Ammonia</i>	<i>kg/hr</i>	<i>56250,00</i>
CO ₂ stream Product to Urea Plant	<i>kg/hr</i>	70593,00
CO ₂ stream Product to Storage	<i>kg/hr</i>	0,00
<i>Total CO₂ stream</i>	<i>kg/hr</i>	<i>70593,00</i>
<i>Urea Product</i>	<i>kg/hr</i>	<i>94170,00</i>

Comparing the results obtained from the base case simulation with the results from the (Santos et al., 2017) report, we can appreciate a percent error of approximately ***0.27%*** for the total ammonia produced, ***0.71%*** for the total CO₂ stream captured in the process, and ***0.1%*** for the total amount of Urea produced. Hence, the results obtained from the base case are within an acceptable error range and can be considered as acceptable.

The specific energy consumption per kilogram of urea produced was the following:

<i>Specific Consumption Per kilogram of Urea</i>		<i>Base Case</i>
Natural Gas (as Feedstock)	<i>MJ/kg Urea</i>	13,36
Natural Gas (as Fuel)	<i>MJ/kg Urea</i>	5,25
Biogas (as Feedstock)	<i>MJ/kg Urea</i>	0,00
Biogas (as Fuel)	<i>MJ/kg Urea</i>	0,00
Biomethane (as Feedstock)	<i>MJ/kg Urea</i>	0,00
Biomethane (as Fuel)	<i>MJ/kg Urea</i>	0,00
<i>Feed + Fuel</i>	<i>MJ/kg Urea</i>	<i>18,61</i>

The specific energy consumption to produce one kilogram of urea for the base case is ***18.61 MJ/kg urea***. This result will be useful for comparison in the following biogas and biomethane replacement cases since it can be used as an energy performance indicator.

Now the base case emissions can be addressed. In order to make the respective calculations, the following information is necessary:

- The results regarding the total carbon dioxide captured during the process. In the following table, the *Feedstock* section covers the amount of CO₂ released from the stripper column, the amount sent to the urea plant, and storage. Meanwhile, the *SMR burner fuel* section covers the total amount of CO₂ captured and the amount released through the flue gas to stack. In the base case simulation, no capture process was considered for the flue gas.

Table 11. Results obtained from an existing ammonia plant and base case. Reproduced from (Santos et al., 2017)

Specific Emissions		HyCO Plant <i>Reproduced from (Santos et al., 2017)</i>	Base Case
Feedstock			
Total Only CO ₂ Released from Stripper	kg/hr	68988,48	69080,07
Captured Only CO ₂ to PLANT	kg/hr	68988,48	69080,07
Captured Only CO ₂ to STORAGE	kg/hr	0,00	0,00
SMR Burner fuel			
Total Only CO ₂ produced	kg/hr	30512,26	29808,62
Total Only CO ₂ captured to STORAGE	kg/hr	0,00	0,00
Total Only CO₂ in flue gas to stack	kg/hr	30512,26	29808,62

* ONLY CO₂ refers to the component CO₂ present in the stream only, not counting other components within the complete stream.

- The equivalent molar flow of CO₂ from the natural gas streams entering and leaving the ammonia fertilizer plant, which is presented in the table below. It is worth mentioning that the equivalent molar flow of CO₂ in the inlet varies from the values reported in the outlet streams. This is due to the existence of a small quantity of unconverted CO₂ in the form of methane or carbon monoxide.

Table 12. Results obtained from an existing ammonia plant and base case. Reproduced from (Santos et al., 2017)

Inlet - Equivalent Molar Flow of CO₂		HyCO Plant <i>Reproduced from (Santos et al., 2017)</i>	Base Case
Natural Gas feedstock	kmol/hr	1626,75	1626,75
Natural Gas fuel	kmol/hr	639,86	639,86
biogas feedstock	kmol/hr	0,00	0,00
biogas fuel	kmol/hr	0,00	0,00
Biomethane feedstock	kmol/hr	0,00	0,00
Biomethane fuel	kmol/hr	0,00	0,00
Total Inlet	kmol/hr	2266,61	2266,61
Outlet - Equivalent Molar Flow of CO₂		HyCO Plant <i>Reproduced from (Santos et al., 2017)</i>	Base Case
Urea Carbon Content	kmol/hr	1567,57	1569,66
Total CO ₂ to STORAGE	kmol/hr	0,00	0,00
Total not emitted	kmol/hr	1567,57	1569,66
Flue gas to stack	kmol/hr	693,31	677,32
Vents	kmol/hr	0,00	0,00
Emission	kmol/hr	693,31	677,32
Total Outlet	kmol/hr	2260,88	2246,97

With the results from the tables above, it is then possible to calculate the emissions for the base case.

Thus, with the formulas described in the previous section, the results obtained from the calculations were the following:

Table 13. Results obtained from an existing ammonia plant and base case. Reproduced from (Santos et al., 2017)

Emission Calculations		HyCO Plant <i>Reproduced from</i> (Santos et al., 2017)	Base Case
Specific CO ₂ Emission	kg/kg Urea	0,3240	0,3168
Equivalent CO ₂ in Urea Product	%	69,1596	69,2514
Captured CO ₂ to Storage	%	0,0000	0,0000
Overall CO ₂ not emitted	%	69,1596	69,2514

From the results obtained, the specific CO₂ emission for the base case is **0.3168 kg/kg urea**, approximately the same as the HyCO plant of **0.3240 kg/kg urea** with a percent error of approximately **2.22%**. Furthermore, the reason for the specific CO₂ emission value to be high in both cases is because no capture process was considered for the flue gas coming out from the SRM burner. This value will be significantly reduced once the MEA capture system is attached to the process in the following biogas and biomethane replacement cases.

Finally, the negative emissions are analyzed for the base case simulation. The table below presents the information required to determine the emissions of CO₂ for the base case:

CO₂ emissions from Base Case		
(A) Biogenic CO ₂ in Feedstock	kg/hr	0.00
(B) Biogenic CO ₂ in Fuel	kg/hr	0.00
(C) Total CO ₂ in the flue gas emitted	kg/hr	29808.62
(D) Total CO ₂ in Ammonia Stream	kg/hr	735.18
(E) Total CO ₂ to Urea Plant	kg/hr	69086.01
(F) Emissions from NGCC power plant	kg/hr	2007.68
Amount of urea produced	kg/hr	94082.40
Scenario 1: (C+D)-(A+B)	kg/hr	30543.80
Scenario 2: (C+D+F)-(A+B)	kg/hr	32551.48
Scenario 3: (C+D+E+F)-(A+B)	kg/hr	101637.49
Specific CO₂ emissions for Scenario 1	kg CO ₂ / kg urea	0.3246
Specific CO₂ emissions for Scenario 2	kg CO ₂ / kg urea	0.3460
Specific CO₂ emissions for Scenario 3	kg CO ₂ / kg urea	1.0803

As seen in the table, the base case's specific CO₂ emissions are net positive for all the scenarios since there is no MEA carbon capture system for the flue gases in the base case.

The respective calculations are performed for the feedstock and SMR burner fuel replacement cases with biogas and biomethane in the following section.

5.2. Feedstock replacement cases

As previously set, in the feedstock replacement cases, the natural gas feedstock used for the production of ammonia is replaced by different fractions of biogas (BG) in 25, 50, 75, and 100%. However, the natural gas used as fuel in the SMR burner is not replaced in these cases:

<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
Feedstock: 75% NG - 25% BG	Feedstock: 50% NG - 50% BG	Feedstock: 25% NG - 75% BG	Feedstock: 0% NG - 100% BG
SMR Burner fuel: 100% NG	SMR Burner fuel: 100% NG	SMR Burner fuel: 100% NG	SMR Burner fuel: 100% NG

The following table presents the mass flow of natural gas and biogas used in each case:

<i>Feedstock Replacement</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
Mass flow - Inlet streams					
Natural gas (as Feedstock)	<i>kg/hr</i>	20265.75	13514.16	6755.25	0.00
Natural gas (as Fuel)	<i>kg/hr</i>	10631.15	10631.15	10631.15	10631.15
Natural gas total Consumption	<i>kg/hr</i>	30896.90	24145.31	17386.40	10631.15
Biogas (as Feedstock)	<i>kg/hr</i>	15594.85	31198.16	46784.55	62379.41
Biogas (as Fuel)	<i>kg/hr</i>	0.00	0.00	0.00	0.00
Biogas Total Consumption	<i>kg/hr</i>	15594.85	31198.16	46784.55	62379.41
Biomethane (as Feedstock)	<i>kg/hr</i>	0.00	0.00	0.00	0.00
Biomethane (as Fuel)	<i>kg/hr</i>	0.00	0.00	0.00	0.00
Biomethane Total Consumption	<i>kg/hr</i>	0.00	0.00	0.00	0.00
Total Feedstock	<i>kg/hr</i>	35860.60	44712.32	53539.80	62379.41
Total Fuel	<i>kg/hr</i>	10631.15	10631.15	10631.15	10631.15

There is an increase of **130.79%** in the feedstock total mass flow, from the base case of **27028.34 kg/hr** to the complete biogas replacement case of **62379.41 kg/hr**. This increase is expected as biogas' energy content depends mainly on methane. Since biogas is composed of 60 – 70 vol% of methane and the rest being CO₂, more biogas would have to be supplied to replace the energy content removed from natural gas. In terms of feasibility, supplementing large quantities of biogas would have to be first analyzed given an existing ammonia plant with specific equipment designs.

The following table presents the total energy input per inlet stream at the beginning of the process. The lower heating value (LHV) of natural gas and biogas are multiplied by their respective streams entering the ammonia plant.

<i>Feedstock Replacement</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
<i>Total Energy Input</i>					
Natural Gas LHV	<i>MJ/kg</i>	46.50	46.50	46.50	46.50
Biogas LHV	<i>MJ/kg</i>	20.14	20.14	20.14	20.14
Biomethane LHV	<i>MJ/kg</i>	45.67	45.67	45.67	45.67
Natural Gas (Feedstock) Energy input	<i>MJ</i>	942307.14	628374.94	314102.38	0.00
Natural Gas (Fuel) Energy input	<i>MJ</i>	494321.97	494321.97	494321.97	494321.97
Biogas (Feedstock) Energy input	<i>MJ</i>	314102.38	628375.10	942307.13	1256409.51
Biogas (Fuel) Energy input	<i>MJ</i>	0.00	0.00	0.00	0.00
Biomethane (Feedstock) Energy input	<i>MJ</i>	0.00	0.00	0.00	0.00
Biomethane (Fuel) Energy input	<i>MJ</i>	0.00	0.00	0.00	0.00
<i>Total Energy input</i>	<i>MJ</i>	1750731.49	1751072.01	1750731.48	1750731.48
<i>Total Energy input</i>	<i>MW</i>	486.31	486.41	486.31	486.31

The total energy input is equal in all the cases, indicating in this manner that the energy content removed from the natural gas feedstock was correctly supplemented with the necessary amount of biogas in each case.

The outlet streams and products obtained from the different feedstock biogas replacement cases are summarized in the following table:

<i>Feedstock Replacement</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
<i>Outlet Streams</i>					
Ammonia Product to Urea Plant	<i>kg/hr</i>	55975.50	56299.01	56604.12	55905.11
Ammonia Product to Storage	<i>kg/hr</i>	0.00	0.00	0.00	0.00
<i>Total Ammonia</i>	<i>kg/hr</i>	55975.50	56299.01	56604.12	55905.11
CO ₂ stream Product to Urea Plant	<i>kg/hr</i>	73366.70	73772.05	74131.76	73194.35
CO ₂ stream Product to Storage	<i>kg/hr</i>	5404.85	13640.74	21886.07	31330.99
<i>Total CO₂ stream</i>	<i>kg/hr</i>	78771.55	87412.79	96017.83	104525.34
Urea Product	<i>kg/hr</i>	98537.75	99110.36	99646.41	98401.65

The total amount of ammonia produced in all the cases remains almost the same compared to the base case of **56097.51 kg/hr**. The percent errors for the biogas replacement cases of 25, 50, 75 and 100%, were: **0.21**, **0.35**, **0.90**, and **0.34%** respectively. Percent errors being within an acceptable margin of error make the ammonia produced in each case acceptable.

The total amount of CO₂ also increases in each biogas replacement case. As previously mentioned, biogas is composed primarily of methane in a range of 60 to 70 vol%, and the remaining being carbon dioxide. By replacing a major fraction of natural gas with biogas, more CO₂ is also supplied to the process.

The amount of ammonia product to storage in all the cases is zero compared to the base case, where there was an amount destined for storage. The reason for the no utilization of this amount of ammonia in the base case was that there was not enough CO₂ captured for the urea plant. Hence, with the surplus amount of CO₂ captured in each biogas replacement case, it is possible to use this amount of ammonia and produce more urea. This can be seen in the results of urea produced in each case compared to the base case of **94082,40 kg/hr**.

The specific energy consumption per kilogram of urea produced for each biogas replacement case was the following:

<i>Feedstock Replacement</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
<i>Specific Consumptions Per Urea</i>					
Natural Gas (as Feedstock)	<i>MJ/kg Urea</i>	9.56	6.34	3.15	0.00
Natural Gas (as Fuel)	<i>MJ/kg Urea</i>	5.02	4.99	4.96	5.02
Biogas (as Feedstock)	<i>MJ/kg Urea</i>	3.19	6.34	9.46	12.77
Biogas (as Fuel)	<i>MJ/kg Urea</i>	0.00	0.00	0.00	0.00
Biomethane (as Feedstock)	<i>MJ/kg Urea</i>	0.00	0.00	0.00	0.00
Biomethane (as Fuel)	<i>MJ/kg Urea</i>	0.00	0.00	0.00	0.00
<i>Feed + Fuel</i>	<i>MJ/kg Urea</i>	17.77	17.67	17.57	17.79

The total amount of energy consumption per kg of urea in each case is approximately the same since a specific amount of biogas compensates for the amount of energy content removed from the natural gas used as feedstock.

Now the specific emissions for the biogas replacement cases can be addressed. In order to make the respective calculations, the following information is necessary:

- The results regarding the total carbon dioxide captured during the process. In the following table, the *Feedstock* section covers the amount of CO₂ released from the stripper column, the amount sent to the urea plant, and storage. Meanwhile, the *SMR burner fuel* section covers the total amount of CO₂ captured and the amount released through the flue gas to stack. In the feedstock replacement cases with biogas, no capture process was considered for the flue gas.

<i>Feedstock Replacement</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
<i>Specific Emissions</i>					
<i>Feedstock</i>					
Total Only CO ₂ Released from Stripper	<i>kg/hr</i>	77661.72	86201.75	94706.10	103114.93
Captured Only CO ₂ to PLANT	<i>kg/hr</i>	72333.02	72749.99	73119.03	72206.70
Captured Only CO ₂ to STORAGE	<i>kg/hr</i>	5328.70	13451.76	21587.07	30908.22
<i>SMR Burner fuel</i>					
Total Only CO ₂ produced	<i>kg/hr</i>	29712.22	29840.11	30028.29	29731.90
Total Only CO ₂ captured to STORAGE	<i>kg/hr</i>	0.00	0.00	0.00	0.00
<i>Total Only CO₂ in flue gas to stack</i>	<i>kg/hr</i>	29712.22	29840.11	30028.29	29731.90

* ONLY CO₂ refers to the component CO₂ present in the stream only, not counting other components within the complete stream.

- The equivalent molar flow of CO₂ from the natural gas and biogas streams entering and leaving the ammonia fertilizer plant, which is presented in the table below. As previously mentioned in the base case results section, the equivalent molar flow of CO₂ in the inlet varies from the values reported in the outlet streams. This is due to the existence of a small quantity of unconverted CO₂ in the form of methane or carbon monoxide.

<i>Feedstock Replacement</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
<i>Inlet - Equivalent Molar Flow of CO₂</i>					
Natural Gas feedstock	<i>kmol/hr</i>	1219.73	813.37	406.58	0.00
Natural Gas fuel	<i>kmol/hr</i>	639.86	639.86	639.86	639.86
biogas feedstock	<i>kmol/hr</i>	601.83	1203.99	1805.49	2407.32
biogas fuel	<i>kmol/hr</i>	0.00	0.00	0.00	0.00
Biomethane feedstock	<i>kmol/hr</i>	0.00	0.00	0.00	0.00
Biomethane fuel	<i>kmol/hr</i>	0.00	0.00	0.00	0.00
<i>Total Inlet</i>	<i>kmol/hr</i>	2461.42	2657.22	2851.92	3047.18
<i>Outlet - Equivalent Molar Flow of CO₂</i>					
Urea Carbon Content	<i>kmol/hr</i>	1643.57	1653.04	1661.43	1640.70
Total CO ₂ to STORAGE	<i>kmol/hr</i>	121.08	305.65	490.51	702.30
<i>Total not emitted</i>	<i>kmol/hr</i>	1764.65	1958.70	2151.94	2343.00
Flue gas to stack	<i>kmol/hr</i>	675.13	678.03	682.31	675.58
Vents	<i>kmol/hr</i>	0.00	0.00	0.00	0.00
Emission	<i>kmol/hr</i>	675.13	678.03	682.31	675.58
<i>Total Outlet</i>	<i>kmol/hr</i>	2439.78	2636.73	2834.25	3018.58

With the results from the tables above, it is then possible to calculate the emissions for the feedstock replacement cases with biogas.

Thus, with the formulas described in the previous section, the results obtained from the calculations were the following:

<i>Emission Calculations</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
Specific CO ₂ Emission	<i>kg/kg Urea</i>	0.3015	0.3011	0.3013	0.3021
Equivalent CO ₂ in Urea Product	%	66.7733	62.2096	58.2564	53.8432
Captured CO ₂ to Storage	%	4.9191	11.5028	17.1992	23.0477
Overall CO ₂ not emitted	%	71.6924	73.7124	75.4556	76.8909

For the feedstock replacement cases with biogas, only natural gas was considered as SMR burner fuel with no capture process for the flue gas. For that reason, the results obtained are also approximately the same compared to the base case specific CO₂ emission of 0.3168 kg/kg urea.

The equivalent CO₂ present in urea product gradually decreases in each case due to an increase in the equivalent amount of CO₂ entering the ammonia plant and more urea production. Consequently, the amount of captured CO₂ to storage and overall CO₂ not emitted also increases in each case.

Finally, the negative emissions are analyzed for the feedstock replacement cases with biogas. The table below presents the information required to determine the total CO₂ emissions for each case:

CO₂ emissions		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
(A) Biogenic CO ₂ in Feedstock	kg/hr	26486.40	52987.16	79459.20	105945.60
(B) Biogenic CO ₂ in Fuel	kg/hr	0.00	0.00	0.00	0.00
(C) Total CO ₂ in the flue gas emitted	kg/hr	29712.22	29840.11	30028.29	29731.90
(D) Total CO ₂ in Ammonia Stream	kg/hr	710.98	748.52	804.60	728.69
(E) Total CO ₂ to Urea Plant	kg/hr	72356.28	72773.44	73142.66	72230.04
(F) Emissions from NGCC power plant	kg/hr	2673.56	3258.71	4022.06	5244.70
Amount of urea produced	kg/hr	98537.75	99110.36	99646.41	98401.65
Scenario 1: (C+D)-(A+B)	kg/hr	3936.81	-22398.53	-48626.31	-75485.01
Scenario 2: (C+D+F)-(A+B)	kg/hr	6610.37	-19139.82	-44604.25	-70240.31
Scenario 3: (C+D+E+F)-(A+B)	kg/hr	78966.65	53633.62	28538.41	1989.73
Specific CO₂ emissions for Scenario 1	kg CO₂/kg urea	0.0400	-0.2260	-0.4880	-0.7671
Specific CO₂ emissions for Scenario 2	kg CO₂/kg urea	0.0671	-0.1931	-0.4476	-0.7138
Specific CO₂ emissions for Scenario 3	kg CO₂/kg urea	0.8014	0.5412	0.2864	0.0202

As seen in the table, the specific CO₂ emissions are net positive for the third scenario and negative for the first two scenarios (exempting for the 25% replacement case with biogas). Hence, for the first two scenarios, it is possible to achieve negative emissions by replacing natural gas with biogas starting with a 50% fraction, even without a MEA carbon capture system for the flue gases. Nevertheless, in a more comprehensive scenario such as the third one, it would not be achievable.

5.3. Burner fuel replacement cases

For the SMR burner fuel replacement cases, natural gas is replaced in different fractions of 25, 50, 75, and 100% with biogas (BG) and biomethane (BM). The natural gas feedstock destined for the production of ammonia is not replaced in these cases.

<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>
Feedstock: 100% NG	Feedstock: 100% NG	Feedstock: 100% NG	Feedstock: 100% NG
SMR Burner fuel: 75% NG - 25% BG	SMR Burner fuel: 50% NG - 50% BG	SMR Burner fuel: 25% NG - 75% BG	SMR Burner fuel: 0% NG - 100% BG

<i>I</i>	<i>J</i>	<i>K</i>	<i>L</i>
Feedstock: 100% NG	Feedstock: 100% NG	Feedstock: 100% NG	Feedstock: 100% NG
SMR Burner fuel: 75% NG - 25% BM	SMR Burner fuel: 50% NG - 50% BM	SMR Burner fuel: 25% NG - 75% BM	SMR Burner fuel: 0% NG - 100% BM

The following table presents the mass flow of natural gas, biogas, and biomethane used as feedstock or fuel.

SMR burner fuel replacement (BG)		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
Mass flow - Inlet streams					
Natural gas (as Feedstock)	kg/hr	27028,34	27028,34	27028,34	27028,34
Natural gas (as Fuel)	kg/hr	7973,00	5315,00	2658,00	0,00
Natural gas total Consumption	kg/hr	35001,34	32343,34	29686,34	27028,34
Biogas (as Feedstock)	kg/hr	0,00	0,00	0,00	0,00
Biogas (as Fuel)	kg/hr	6135,74	12271,47	18407,21	24542,95
Biogas Total Consumption	kg/hr	6135,74	12271,47	18407,21	24542,95
Biomethane (as Feedstock)	kg/hr	0,00	0,00	0,00	0,00
Biomethane (as Fuel)	kg/hr	0,00	0,00	0,00	0,00
Biomethane Total Consumption	kg/hr	0,00	0,00	0,00	0,00
Total Feedstock	kg/hr	27028,34	27028,34	27028,34	27028,34
Total Fuel	kg/hr	14108,74	17586,47	21065,21	24542,95

SMR burner fuel replacement (BM)		75% NG 25% BM	50% NG 50% BM	25% NG 75% BM	0% NG 100% BM
Mass flow - Inlet streams					
Natural gas (as Feedstock)	kg/hr	27028,34	27028,34	27028,34	27028,34
Natural gas (as Fuel)	kg/hr	7973,36	5315,57	2657,79	0,00
Natural gas total Consumption	kg/hr	35001,70	32343,91	29686,13	27028,34
Biogas (as Feedstock)	kg/hr	0,00	0,00	0,00	0,00
Biogas (as Fuel)	kg/hr	0,00	0,00	0,00	0,00
Biogas Total Consumption	kg/hr	0,00	0,00	0,00	0,00
Biomethane (as Feedstock)	kg/hr	0,00	0,00	0,00	0,00
Biomethane (as Fuel)	kg/hr	2705,79	5411,59	8117,39	10823,19
Biomethane Total Consumption	kg/hr	2705,79	5411,59	8117,39	10823,19
Total Feedstock	kg/hr	27028,34	27028,34	27028,34	27028,34
Total Fuel	kg/hr	10679,15	10727,17	10775,18	10823,19

There is an increase of **130.85%** in the *Total Fuel* mass flow, from the base case of **10631.15 kg/hr** to the complete biogas replacement case of **24542.95 kg/hr**. As explained previously, this increase is expected as biogas' energy content depends mainly on methane. Since biogas is composed of 60 – 70 vol% of methane and the rest being CO₂, more biogas would have to be supplied to replace the energy content removed from natural gas. In the same manner, in terms of feasibility, the supplementation of larger amounts of biogas as fuel to the SMR burner would have to be first analyzed, given an existing ammonia plant with a specific SMR burner design.

In the fuel replacement cases with biomethane, the *Total Fuel* mass flow remains approximately the same. The reason for the slight increase is due to the composition of biomethane. As biogas, the energy content of biomethane depends on its methane content. Biomethane is composed of 96 - 97 vol% of methane, and the rest being N₂, O₂, and CO₂. These minor components accumulate in each case's supplementation process and result in a slight increase in the total fuel mass flow entering the SMR burner. Thus, the possibility of using biomethane as fuel without drastically affecting the design of an existing SMR burner in an ammonia plant is more feasible. Nevertheless, this decision of implementation of biomethane relies on other economic analyses.

The following table presents the total energy input per inlet stream at the beginning of the process. The lower heating value (LHV) of natural gas, biogas, and biomethane is multiplied by their respective streams entering the ammonia plant.

<i>SMR burner fuel replacement (BG)</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
<i>Total Energy Input</i>					
Natural Gas LHV	<i>MJ/kg</i>	46,50	46,50	46,50	46,50
Biogas LHV	<i>MJ/kg</i>	20,14	20,14	20,14	20,14
Biomethane LHV	<i>MJ/kg</i>	45,67	45,67	45,67	45,67
Natural Gas (Feedstock) Energy input	<i>MJ</i>	1256750,78	1256750,78	1256750,78	1256750,78
Natural Gas (Fuel) Energy input	<i>MJ</i>	370724,73	247134,32	123590,41	0,00
Biogas (Feedstock) Energy input	<i>MJ</i>	0,00	0,00	0,00	0,00
Biogas (Fuel) Energy input	<i>MJ</i>	123582,43	247164,87	370747,26	494329,74
Biomethane (Feedstock) Energy input	<i>MJ</i>	0,00	0,00	0,00	0,00
Biomethane (Fuel) Energy input	<i>MJ</i>	0,00	0,00	0,00	0,00
<i>Total Energy input</i>	<i>MJ</i>	1751057,95	1751049,97	1751088,45	1751080,51
<i>Total Energy input</i>	<i>MW</i>	486,40	486,40	486,41	486,41

<i>SMR burner fuel replacement (BM)</i>		75% NG 25% BM	50% NG 50% BM	25% NG 75% BM	0% NG 100% BM
<i>Total Energy Input</i>					
Natural Gas LHV	<i>MJ/kg</i>	46,50	46,50	46,50	46,50
Biogas LHV	<i>MJ/kg</i>	20,14	20,14	20,14	20,14
Biomethane LHV	<i>MJ/kg</i>	45,67	45,67	45,67	45,67
Natural Gas (Feedstock) Energy input	<i>MJ</i>	1256750,78	1256750,78	1256750,78	1256750,78
Natural Gas (Fuel) Energy input	<i>MJ</i>	370741,48	247160,99	123580,49	0,00
Biogas (Feedstock) Energy input	<i>MJ</i>	0,00	0,00	0,00	0,00
Biogas (Fuel) Energy input	<i>MJ</i>	0,00	0,00	0,00	0,00
Biomethane (Feedstock) Energy input	<i>MJ</i>	0,00	0,00	0,00	0,00
Biomethane (Fuel) Energy input	<i>MJ</i>	123586,16	247172,96	370759,40	494345,93
<i>Total Energy input</i>	<i>MJ</i>	1751078,42	1751084,73	1751090,67	1751096,70
<i>Total Energy input</i>	<i>MW</i>	486,41	486,41	486,41	486,42

The total energy input is equal in all the fuel replacement cases with biogas and biomethane, indicating in this manner that the energy content removed from the natural gas fuel was correctly supplemented with the necessary amount of biogas or biomethane in each case.

The outlet streams and products obtained from the different fuel replacement cases with biogas and biomethane are summarized in the following table:

<i>SMR burner fuel replacement (BG)</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
<i>Outlet Streams</i>					
Ammonia Product to Urea Plant	<i>kg/hr</i>	53440,31	53440,31	53440,31	53440,31
Ammonia Product to Storage	<i>kg/hr</i>	2657,20	2657,20	2657,20	2657,20
<i>Total Ammonia</i>	<i>kg/hr</i>	56097,51	56097,51	56097,51	56097,51
CO ₂ stream Product to Urea Plant	<i>kg/hr</i>	70088,00	70088,00	70088,00	70088,00
CO ₂ stream Product to Storage	<i>kg/hr</i>	0,00	0,00	0,00	0,00
<i>Total CO₂ stream</i>	<i>kg/hr</i>	70088,00	70088,00	70088,00	70088,00
Urea Product	<i>kg/hr</i>	94082,40	94082,40	94082,40	94082,40

<i>SMR burner fuel replacement (BM)</i>		75% NG 25% BM	50% NG 50% BM	25% NG 75% BM	0% NG 100% BM
<i>Outlet Streams</i>					
Ammonia Product to Urea Plant	<i>kg/hr</i>	53440,31	53440,31	53440,31	53440,31
Ammonia Product to Storage	<i>kg/hr</i>	2657,20	2657,20	2657,20	2657,20
<i>Total Ammonia</i>	<i>kg/hr</i>	56097,51	56097,51	56097,51	56097,51
CO ₂ stream Product to Urea Plant	<i>kg/hr</i>	70088,00	70088,00	70088,00	70088,00
CO ₂ stream Product to Storage	<i>kg/hr</i>	0,00	0,00	0,00	0,00
<i>Total CO₂ stream</i>	<i>kg/hr</i>	70088,00	70088,00	70088,00	70088,00
Urea Product	<i>kg/hr</i>	94082,40	94082,40	94082,40	94082,40

The natural gas feedstock destined for ammonia production is not replaced in these SMR burner fuel replacement cases. For that reason, the results for the urea product, ammonia produced, and carbon dioxide remain the same.

The specific energy consumption per kilogram of urea produced for each burner fuel replacement case with biogas and biomethane replacement case was the following:

<i>SMR burner fuel replacement (BG)</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
<i>Specific Consumptions Per kg Urea</i>					
Natural Gas (as Feedstock)	<i>MJ/kg Urea</i>	13,36	13,36	13,36	13,36
Natural Gas (as Fuel)	<i>MJ/kg Urea</i>	3,94	2,63	1,31	0,00
Biogas (as Feedstock)	<i>MJ/kg Urea</i>	0,00	0,00	0,00	0,00
Biogas (as Fuel)	<i>MJ/kg Urea</i>	1,31	2,63	3,94	5,25
Biomethane (as Feedstock)	<i>MJ/kg Urea</i>	0,00	0,00	0,00	0,00
Biomethane (as Fuel)	<i>MJ/kg Urea</i>	0,00	0,00	0,00	0,00
<i>Feed + Fuel</i>	<i>MJ/kg Urea</i>	18,61	18,61	18,61	18,61

<i>SMR burner fuel replacement (BM)</i>		75% NG 25% BM	50% NG 50% BM	25% NG 75% BM	0% NG 100%BM
<i>Specific Consumptions Per kg Urea</i>					
Natural Gas (as Feedstock)	<i>MJ/kg Urea</i>	13,36	13,36	13,36	13,36
Natural Gas (as Fuel)	<i>MJ/kg Urea</i>	3,94	2,63	1,31	0,00
Biogas (as Feedstock)	<i>MJ/kg Urea</i>	0,00	0,00	0,00	0,00
Biogas (as Fuel)	<i>MJ/kg Urea</i>	0,00	0,00	0,00	0,00
Biomethane (as Feedstock)	<i>MJ/kg Urea</i>	0,00	0,00	0,00	0,00
Biomethane (as Fuel)	<i>MJ/kg Urea</i>	1,31	2,63	3,94	5,25
<i>Feed + Fuel</i>	<i>MJ/kg Urea</i>	18,61	18,61	18,61	18,61

The total amount of energy consumption per kg of urea in each case is approximately the same since the initial amount of energy removed from the natural gas fuel is compensated by a specific amount of biogas or biomethane.

Now the specific emissions for the burner fuel replacement cases with biogas and biomethane can be addressed. In order to make the respective calculations, the following information is necessary:

- The results regarding the total carbon dioxide captured during the process. In the following tables, the *Feedstock section* covers the amount of CO₂ released from the stripper column, the amount sent to the urea plant, and storage. Meanwhile, the *SMR Burner fuel* section covers the total amount of CO₂ captured and the amount released through the flue gas to stack. For the burner fuel replacement cases with biogas and biomethane, a capture process using MEA with a carbon capture rate of 90% was considered for the flue gas.

<i>SMR burner fuel replacement (BG)</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
<i>Specific Emissions</i>					
<i>Feedstock</i>					
Total Only CO ₂ Released from Stripper	<i>kg/hr</i>	69080,07	69080,07	69080,07	69080,07
Captured Only CO ₂ to PLANT	<i>kg/hr</i>	69080,07	69080,07	69080,07	69080,07
Captured Only CO ₂ to STORAGE	<i>kg/hr</i>	0,00	0,00	0,00	0,00
<i>SMR Burner Flue gas</i>					
Total Only CO ₂ produced	<i>kg/hr</i>	33159,56	36536,69	39915,82	43295,23
Total Only CO ₂ captured to STORAGE	<i>kg/hr</i>	29843,61	32883,02	35924,24	38965,70
<i>Total Only CO₂ in flue gas to stack</i>	<i>kg/hr</i>	3315,96	3653,67	3991,58	4329,52

<i>SMR burner fuel replacement (BM)</i>		75% NG 25% BM	50% NG 50% BM	25% NG 75% BM	0% NG 100%BM
<i>Specific Emissions</i>					
<i>Feedstock</i>					
Total Only CO ₂ Released from Stripper	<i>kg/hr</i>	69080,07	69080,07	69080,07	69080,07
Captured Only CO ₂ to PLANT	<i>kg/hr</i>	69080,07	69080,07	69080,07	69080,07
Captured Only CO ₂ to STORAGE	<i>kg/hr</i>	0,00	0,00	0,00	0,00
<i>Burner Flue gas</i>					
Total Only CO ₂ produced	<i>kg/hr</i>	29587,38	29393,74	29199,95	29006,17
Total Only CO ₂ captured to STORAGE	<i>kg/hr</i>	26628,64	26454,37	26279,96	26105,55
<i>Total Only CO₂ in flue gas to stack</i>	<i>kg/hr</i>	2958,74	2939,37	2920,00	2900,62

* ONLY CO₂ refers to the component CO₂ present in the stream only, not counting other components within the complete stream

- The equivalent molar flow of CO₂ from the natural gas, biogas, and biomethane streams entering and leaving the ammonia fertilizer plant, presented in the table below. As previously mentioned, the equivalent molar flow of CO₂ in the inlet varies from the values reported in the outlet streams. This is due to the existence of a small quantity of unconverted carbon dioxide in the form of methane or carbon monoxide.

SMR burner fuel replacement (BG)		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
Inlet - Equivalent Molar Flow of CO₂					
Natural Gas feedstock	kmol/hr	1626,75	1626,75	1626,75	1626,75
Natural Gas fuel	kmol/hr	479,89	319,93	159,96	0,00
biogas feedstock	kmol/hr	0,00	0,00	0,00	0,00
biogas fuel	kmol/hr	236,79	473,58	710,36	947,15
Biomethane feedstock	kmol/hr	0,00	0,00	0,00	0,00
Biomethane fuel	kmol/hr	0,00	0,00	0,00	0,00
Total Inlet	kmol/hr	2343,43	2420,25	2497,08	2573,90
Outlet - Equivalent Molar Flow of CO₂					
Urea Carbon Content	kmol/hr	1569,66	1569,66	1569,66	1569,66
Total CO ₂ to STORAGE	kmol/hr	678,11	747,18	816,28	885,39
Total not emitted	kmol/hr	2247,77	2316,83	2385,94	2455,04
Flue gas to stack	kmol/hr	75,35	83,02	90,70	98,38
Vents	kmol/hr	0,00	0,00	0,00	0,00
Emission	kmol/hr	75,35	83,02	90,70	98,38
Total Outlet	kmol/hr	2323,12	2399,85	2476,63	2553,42

SMR burner fuel replacement (BM)		75% NG 25% BM	50% NG 50% BM	25% NG 75% BM	0% NG 100% BM
Inlet - Equivalent Molar Flow of CO₂					
Natural Gas feedstock	kmol/hr	1626,75	1626,75	1626,75	1626,75
Natural Gas fuel	kmol/hr	479,89	319,93	159,96	0,00
biogas feedstock	kmol/hr	0,00	0,00	0,00	0,00
biogas fuel	kmol/hr	0,00	0,00	0,00	0,00
Biomethane feedstock	kmol/hr	0,00	0,00	0,00	0,00
Biomethane fuel	kmol/hr	155,56	311,13	466,69	622,25
Total Inlet	kmol/hr	2262,20	2257,80	2253,40	2249,00
Outlet - Equivalent Molar Flow of CO₂					
Urea Carbon Content	kmol/hr	1569,66	1569,66	1569,66	1569,66
Total CO ₂ to STORAGE	kmol/hr	605,06	601,10	597,14	593,18
Total not emitted	kmol/hr	2174,72	2170,76	2166,80	2162,83
Flue gas to stack	kmol/hr	67,23	66,79	66,35	65,91
Vents	kmol/hr	0,00	0,00	0,00	0,00
Emission	kmol/hr	67,23	66,79	66,35	65,91
Total Outlet	kmol/hr	2241,95	2237,55	2233,14	2228,74

With the results from the tables above, it is then possible to calculate the specific emissions for the SMR burner fuel replacement cases with biogas and biomethane.

Thus, with the formulas described in the previous section, the results obtained from the calculations were the following:

<i>SMR burner fuel replacement (BG)</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
<i>Emission Calculations</i>					
Specific CO ₂ Emission	<i>kg/kg Urea</i>	0,0352	0,0388	0,0424	0,0460
Equivalent CO ₂ in Urea Product	%	66,9811	64,8550	62,8597	60,9835
Captured CO ₂ to Storage	%	28,9368	30,8718	32,6894	34,3987
Overall CO ₂ not emitted	%	95,9180	95,7268	95,5491	95,3822

<i>SMR burner fuel replacement (BM)</i>		75% NG 25% BM	50% NG 50% BM	25% NG 75% BM	0% NG 100% BM
<i>Emission Calculations</i>					
Specific CO ₂ Emission	<i>kg/kg Urea</i>	0,0314	0,0312	0,0310	0,0308
Equivalent CO ₂ in Urea Product	%	69,3861	69,5213	69,6571	69,7934
Captured CO ₂ to Storage	%	26,7466	26,6233	26,4995	26,3751
Overall CO ₂ not emitted	%	96,1327	96,1447	96,1565	96,1685

The specific CO₂ emission for the SMR burner fuel replacement cases with biogas and biomethane ranges from ***0.0310 to 0.0460 kg/kg urea***, significantly low compared to the base case. The reason for the specific CO₂ emission values to be significantly low is because a capture process, using MEA with a carbon capture rate of 90%, was considered for the flue gas coming out from the SMR burner.

The equivalent CO₂ present in urea product gradually decreases in the fuel replacement cases with biogas due to an increase in the equivalent amount of CO₂ entering the ammonia plant, produced by the supplementation of biogas. However, this value remains almost the same in the fuel replacement cases with biomethane due to its composition with low CO₂ content. Thus, not significantly affecting the equivalent amount of CO₂ entering the ammonia plant during its supplementation.

Regarding the captured CO₂ going to storage, for the fuel replacement cases with biogas, the gradual increase is due to the increased equivalent amount of CO₂ entering the ammonia plant. Thus, more CO₂ being captured and sent to storage. However, the results are almost the same for the fuel replacement cases with biomethane. The reason as well is due to the low CO₂ content in biomethane. Thus, not significantly affecting the equivalent amount of CO₂ entering the ammonia plant during its supplementation.

Finally, the negative emissions are analyzed for the fuel replacement cases with biogas and biomethane. The table below presents the information required to determine the emissions of CO₂:

SMR burner fuel replacement (BG)					
CO₂ emissions		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
(A) Biogenic CO₂ in Feedstock	kg/hr	0.00	0.00	0.00	0.00
(B) Biogenic CO₂ in Fuel	kg/hr	10420.98	20841.95	31262.93	41683.91
(C) Total CO₂ in the flue gas emitted	kg/hr	3318.71	3656.43	3994.34	4332.28
(D) Total CO₂ in Ammonia Stream	kg/hr	735.18	735.18	735.18	735.18
(E) Total CO₂ to Urea Plant	kg/hr	69062.94	69115.92	69062.94	69062.94
(F) Emissions from NGCC power plant	kg/hr	5668.55	6115.77	6487.09	6921.02
Amount of urea produced	kg/hr	94082.40	94082.40	94082.40	94082.40
Scenario 1: (C+D)-(A+B)	kg/hr	-6367.09	-16450.35	-26533.41	-36616.45
Scenario 2: (C+D+F)-(A+B)	kg/hr	-698.54	-10334.58	-20046.32	-29695.44
Scenario 3: (C+D+E+F)-(A+B)	kg/hr	68364.40	58781.34	49016.62	39367.50
Specific CO₂ emissions for Scenario 1	kg CO ₂ / kg urea	-0.0677	-0.1749	-0.2820	-0.3892
Specific CO₂ emissions for Scenario 2	kg CO ₂ / kg urea	-0.0074	-0.1098	-0.2131	-0.3156
Specific CO₂ emissions for Scenario 3	kg CO ₂ / kg urea	0.7266	0.6248	0.5210	0.4184

As seen in the results for the fuel replacement cases with biogas, the specific CO₂ emissions are net positive for the third scenario and negative in the first two scenarios. Hence, without considering the CO₂ emissions from the urea product in the first two scenarios, negative emissions can be achieved by replacing a 25% fraction of natural gas fuel with biogas along with a MEA carbon capture system for the flue gases. Nevertheless, in a more comprehensive scenario such as the third one, considering the emissions from the flue gas, the methane in the ammonia product, the NGCC power plant, and the urea product, negative emissions would not be possible to achieve even with the MEA carbon capture system or by completely replacing natural gas fuel with biogas.

SMR burner fuel replacement (BM)					
CO₂ emissions		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
<i>(A) Biogenic CO₂ in Feedstock</i>	<i>kg/hr</i>	0.00	0.00	0.00	0.00
<i>(B) Biogenic CO₂ in Fuel</i>	<i>kg/hr</i>	6846.28	13692.60	20538.90	27385.20
<i>(C) Total CO₂ in the flue gas emitted</i>	<i>kg/hr</i>	2961.49	2942.13	2922.75	2903.37
<i>(D) Total CO₂ in Ammonia Stream</i>	<i>kg/hr</i>	735.18	735.18	735.18	735.18
<i>(E) Total CO₂ to Urea Plant</i>	<i>kg/hr</i>	69062.94	69062.94	69062.94	69062.94
<i>(F) Emissions from NGCC power plant</i>	<i>kg/hr</i>	5267.29	5275.00	5251.75	5228.85
<i>Amount of urea produced</i>	<i>kg/hr</i>	94082.40	94082.40	94082.40	94082.40
<i>Scenario 1: (C+D)-(A+B)</i>	<i>kg/hr</i>	-3149.61	-10015.29	-16880.97	-23746.65
<i>Scenario 2: (C+D+F)-(A+B)</i>	<i>kg/hr</i>	2117.68	-4740.30	-11629.22	-18517.80
<i>Scenario 3: (C+D+E+F)-(A+B)</i>	<i>kg/hr</i>	71180.62	64322.64	57433.72	50545.14
<i>Specific CO₂ emissions for Scenario 1</i>	<i>kg CO₂/kg urea</i>	-0.0335	-0.1065	-0.1794	-0.2524
<i>Specific CO₂ emissions for Scenario 2</i>	<i>kg CO₂/kg urea</i>	0.0225	-0.0504	-0.1236	-0.1968
<i>Specific CO₂ emissions for Scenario 3</i>	<i>kg CO₂/kg urea</i>	0.7566	0.6837	0.6105	0.5372

As seen in the results for the fuel replacement cases with biomethane, the specific CO₂ emissions are net positive for the third scenario and negative in the first two scenarios (except for the first case of 25% replacement in the second scenario). Hence, without considering the CO₂ emissions from the urea product in the first two scenarios, negative emissions can be achieved by replacing a 25% fraction of natural gas fuel with biomethane in the first scenario and 50% for the second scenario, both cases considering a MEA carbon capture system for the flue gases. Nevertheless, in a more comprehensive scenario such as the third one, considering the emissions from the flue gas, the methane in the ammonia product, the NGCC power plant, and the urea product, negative emissions would not be possible to achieve even with the MEA carbon capture system or by completely replacing natural gas fuel with biomethane.

In the following section, the respective calculations are performed for the feedstock and fuel combined replacement cases.

5.4. Combination of feedstock and fuel replacement cases

In this section, the combination of both feedstock and fuel replacement cases is performed to evaluate the impact of the combined replacement of natural gas with biogas. The results obtained from the combination cases, such as mass flow, energy input, outlet streams, energy consumption, and others, will be present in the annexes section. For the present section, only the possibility to achieve negative emissions in each combined arrangement will be analyzed.

<i>AE</i>	<i>AF</i>	<i>AG</i>	<i>AH</i>
<i>Feedstock:</i> 75% NG - 25% BG	<i>Feedstock:</i> 75% NG - 25% BG	<i>Feedstock:</i> 75% NG - 25% BG	<i>Feedstock:</i> 75% NG - 25% BG
<i>SMR Burner fuel:</i> 75% NG - 25% BG	<i>SMR Burner fuel:</i> 50% NG - 50% BG	<i>SMR Burner fuel:</i> 25% NG - 75% BG	<i>SMR Burner fuel:</i> 0% NG - 100% BG

<i>BE</i>	<i>BF</i>	<i>BG</i>	<i>BH</i>
<i>Feedstock:</i> 50% NG - 50% BG	<i>Feedstock:</i> 50% NG - 50% BG	<i>Feedstock:</i> 50% NG - 50% BG	<i>Feedstock:</i> 50% NG - 50% BG
<i>SMR Burner fuel:</i> 75% NG - 25% BG	<i>SMR Burner fuel:</i> 50% NG - 50% BG	<i>SMR Burner fuel:</i> 25% NG - 75% BG	<i>SMR Burner fuel:</i> 0% NG - 100% BG

<i>CE</i>	<i>CF</i>	<i>CG</i>	<i>CH</i>
<i>Feedstock:</i> 25% NG - 75% BG	<i>Feedstock:</i> 25% NG - 75% BG	<i>Feedstock:</i> 25% NG - 75% BG	<i>Feedstock:</i> 25% NG - 75% BG
<i>SMR Burner fuel:</i> 75% NG - 25% BG	<i>SMR Burner fuel:</i> 50% NG - 50% BG	<i>SMR Burner fuel:</i> 25% NG - 75% BG	<i>SMR Burner fuel:</i> 0% NG - 100% BG

<i>DE</i>	<i>DF</i>	<i>DG</i>	<i>DH</i>
<i>Feedstock:</i> 0% NG - 100% BG	<i>Feedstock:</i> 0% NG - 100% BG	<i>Feedstock:</i> 0% NG - 100% BG	<i>Feedstock:</i> 0% NG - 100% BG
<i>SMR Burner fuel:</i> 75% NG - 25% BG	<i>SMR Burner fuel:</i> 50% NG - 50% BG	<i>SMR Burner fuel:</i> 25% NG - 75% BG	<i>SMR Burner fuel:</i> 0% NG - 100% BG

The tables below present the CO₂ emissions for the different combined replacement cases are analyzed:

Feedstock and SMR burner fuel replacement (BG)					
CO₂ emissions		AE	AF	AG	AH
		25% BG 25% BG	25% BG 50% BG	25% BG 75% BG	25% BG 100% BG
(A) Biogenic CO₂ in Feedstock	<i>kg/hr</i>	26486.40	26486.40	26486.40	26486.40
(B) Biogenic CO₂ in Fuel	<i>kg/hr</i>	10420.98	20841.95	31262.93	41683.91
(C) Total CO₂ in the flue gas emitted	<i>kg/hr</i>	3309.07	3646.79	3984.70	4322.64
(D) Total CO₂ in Ammonia Stream	<i>kg/hr</i>	710.98	710.98	710.98	710.98
(E) Total CO₂ to Urea Plant	<i>kg/hr</i>	72356.33	72356.33	72356.33	72356.33
(F) Emissions from NGCC power plant	<i>kg/hr</i>	6348.84	6810.42	7203.83	7652.11
Amount of urea produced	<i>kg/hr</i>	98537.7486	98537.7486	98537.7486	98537.7486
Scenario 1: (C+D)-(A+B)	<i>kg/hr</i>	-32887.32	-42970.58	-53053.64	-63136.68
Scenario 2: (C+D+F)-(A+B)	<i>kg/hr</i>	-26538.48	-36160.16	-45849.82	-55484.57
Scenario 3: (C+D+E+F)-(A+B)	<i>kg/hr</i>	45817.85	36196.17	26506.51	16871.76
Specific CO₂ emissions for Scenario 1	kg CO₂/kg urea	-0.3338	-0.4361	-0.5384	-0.6407
Specific CO₂ emissions for Scenario 2	kg CO₂/kg urea	-0.2693	-0.3670	-0.4653	-0.5631
Specific CO₂ emissions for Scenario 3	kg CO₂/kg urea	0.4650	0.3673	0.2690	0.1712

As seen in the results for the first set of combined cases, where a 25% of natural gas feedstock is replaced with biogas and natural gas fuel is replaced in different fractions, the specific CO₂ emissions are net positive for the third scenario and negative in the first two scenarios. Hence, without considering the CO₂ emissions from the urea product in the first two scenarios, negative emissions can be achieved by replacing 25% of natural gas feedstock and fuel with biogas, along with a MEA carbon capture system for the flue gases. Nevertheless, in a more comprehensive scenario such as the third one, considering the emissions from the flue gas, the methane in the ammonia product, the NGCC power plant, and the urea product, negative emissions would not be possible to achieve even with the MEA carbon capture system or even by completely replacing natural gas fuel with biogas.

Feedstock and SMR burner fuel replacement (BG)					
CO₂ emissions		BE	BF	BG	BH
		50% BG 25% BG	50% BG 50% BG	50% BG 75% BG	50% BG 100% BG
(A) Biogenic CO₂ in Feedstock	<i>kg/hr</i>	52987.16	52987.16	52987.16	52987.16
(B) Biogenic CO₂ in Fuel	<i>kg/hr</i>	10420.98	20841.95	31262.93	41683.91
(C) Total CO₂ in the flue gas emitted	<i>kg/hr</i>	3321.86	3659.57	3997.49	4335.43
(D) Total CO₂ in Ammonia Stream	<i>kg/hr</i>	748.52	748.52	748.52	748.52
(E) Total CO₂ to Urea Plant	<i>kg/hr</i>	72774.15	72774.15	72774.15	72774.15
(F) Emissions from NGCC power plant	<i>kg/hr</i>	6952.09	7422.75	7832.62	8293.15
Amount of urea produced	<i>kg/hr</i>	99110.3599	99110.3599	99110.3599	99110.3599
Scenario 1: (C+D)-(A+B)	<i>kg/hr</i>	-59337.75	-69421.02	-79504.08	-89587.12
Scenario 2: (C+D+F)-(A+B)	<i>kg/hr</i>	-52385.66	-61998.27	-71671.46	-81293.97
Scenario 3: (C+D+E+F)-(A+B)	<i>kg/hr</i>	20388.48	10775.88	1102.69	-8519.82

<i>Specific CO₂ emissions for Scenario 1</i>	<i>kg CO₂/kg urea</i>	-0.5987	-0.7004	-0.8022	-0.9039
<i>Specific CO₂ emissions for Scenario 2</i>	<i>kg CO₂/kg urea</i>	-0.5286	-0.6255	-0.7231	-0.8202
<i>Specific CO₂ emissions for Scenario 3</i>	<i>kg CO₂/kg urea</i>	0.2057	0.1087	0.0111	-0.0860

As seen in the results for the second set of combined cases, where a 50% of natural gas feedstock is replaced with biogas and natural gas fuel is replaced in different fractions, the specific CO₂ emissions are net positive for the third scenario (exempting the last case), and negative in the first two scenarios. Thus, without considering the CO₂ emissions from the urea product in the first two scenarios, negative emissions can be achieved by replacing natural gas feedstock in 50% and natural gas fuel in 25% with biogas (along with a MEA carbon capture system for the flue gases). However, as seen in the more comprehensive scenario, considering the emissions from the flue gas, the methane in the ammonia product, the NGCC power plant, and the urea product, negative emissions are possible to achieve with the MEA carbon capture system and by replacing natural gas feedstock in 50% and completely replacing natural gas fuel with biogas.

<i>Feedstock and SMR burner fuel replacement (BG)</i>					
<i>CO₂ emissions</i>		<i>CE</i>	<i>CF</i>	<i>CG</i>	<i>CH</i>
		<i>75% BG 25% BG</i>	<i>75% BG 50% BG</i>	<i>75% BG 75% BG</i>	<i>75% BG 100% BG</i>
<i>(A) Biogenic CO₂ in Feedstock</i>	<i>kg/hr</i>	79459.20	79459.20	79459.20	79459.20
<i>(B) Biogenic CO₂ in Fuel</i>	<i>kg/hr</i>	10420.98	20841.95	31262.93	41683.91
<i>(C) Total CO₂ in the flue gas emitted</i>	<i>kg/hr</i>	3340.68	3678.39	4016.31	4354.25
<i>(D) Total CO₂ in Ammonia Stream</i>	<i>kg/hr</i>	804.60	804.60	804.60	804.60
<i>(E) Total CO₂ to Urea Plant</i>	<i>kg/hr</i>	73143.15	73143.15	73143.15	73143.15
<i>(F) Emissions from NGCC power plant</i>	<i>kg/hr</i>	7700.97	8182.83	8607.42	9075.63
<i>Amount of urea produced</i>	<i>kg/hr</i>	99646.4098	99646.4098	99646.4098	99646.4098
<i>Scenario 1: (C+D)-(A+B)</i>	<i>kg/hr</i>	-85734.90	-95818.16	-105901.22	-115984.26
<i>Scenario 2: (C+D+F)-(A+B)</i>	<i>kg/hr</i>	-78033.93	-87635.33	-97293.80	-106908.63
<i>Scenario 3: (C+D+E+F)-(A+B)</i>	<i>kg/hr</i>	-4890.78	-14492.18	-24150.65	-33765.48
<i>Specific CO₂ emissions for Scenario 1</i>	<i>kg CO₂/kg urea</i>	-0.8604	-0.9616	-1.0628	-1.1640
<i>Specific CO₂ emissions for Scenario 2</i>	<i>kg CO₂/kg urea</i>	-0.7831	-0.8795	-0.9764	-1.0729
<i>Specific CO₂ emissions for Scenario 3</i>	<i>kg CO₂/kg urea</i>	-0.0491	-0.1454	-0.2424	-0.3389

As seen in the results for the third set of combined cases, where a 75% of natural gas feedstock is replaced with biogas and natural gas fuel is replaced in different fractions, the specific CO₂ emissions are negative for all the scenarios. Thus, in the more comprehensive scenario, considering the emissions from the flue gas, the methane in the ammonia product, the NGCC power plant, and the urea product, negative emissions are possible to achieve with the MEA carbon capture system and by replacing natural gas feedstock in 75% and natural gas fuel in 25% with biogas.

Feedstock and SMR burner fuel replacement (BG)					
CO₂ emissions		DE	DF	DG	DH
		100% BG 25% BG	100% BG 50% BG	100% BG 75% BG	100% BG 100% BG
(A) Biogenic CO₂ in Feedstock	<i>kg/hr</i>	105945.60	105945.60	105945.60	105945.60
(B) Biogenic CO₂ in Fuel	<i>kg/hr</i>	10420.98	20841.95	31262.93	41683.91
(C) Total CO₂ in the flue gas emitted	<i>kg/hr</i>	3311.04	3648.75	3986.67	4324.61
(D) Total CO₂ in Ammonia Stream	<i>kg/hr</i>	728.69	728.69	728.69	728.69
(E) Total CO₂ to Urea Plant	<i>kg/hr</i>	72229.98	72229.98	72229.98	72229.98
(F) Emissions from NGCC power plant	<i>kg/hr</i>	8960.13	9456.72	9903.42	10386.04
<i>Amount of urea produced</i>	<i>kg/hr</i>	98401.6535	98401.6535	98401.6535	98401.6535
Scenario 1: (C+D)-(A+B)	<i>kg/hr</i>	-112326.84	-122410.11	-132493.17	-142576.21
Scenario 2: (C+D+F)-(A+B)	<i>kg/hr</i>	-103366.71	-112953.39	-122589.75	-132190.16
Scenario 3: (C+D+E+F)-(A+B)	<i>kg/hr</i>	-31136.73	-40723.41	-50359.77	-59960.18
Specific CO₂ emissions for Scenario 1	kg CO₂/kg urea	-1.1415	-1.2440	-1.3465	-1.4489
Specific CO₂ emissions for Scenario 2	kg CO₂/kg urea	-1.0505	-1.1479	-1.2458	-1.3434
Specific CO₂ emissions for Scenario 3	kg CO₂/kg urea	-0.3164	-0.4138	-0.5118	-0.6093

As seen in the results for the last set of combined cases, where a 100% of natural gas feedstock is replaced with biogas and natural gas fuel is replaced in different fractions, the specific CO₂ emissions are negative for all the scenarios. Thus, in the more comprehensive scenario, considering the emissions from the flue gas, the methane in the ammonia product, the NGCC power plant, and the urea product, negative emissions are possible to achieve with the MEA carbon capture system and by completely replacing natural gas feedstock and natural gas fuel in 25% with biogas.

Finally, in the following section, a plant performance analysis will be done for all the proposed cases in the present study.

5.5. Plant performance

In the present section an analysis is performed for the plant performance and different energy requirements for all the proposed cases in the following order:

<i>n</i>	<i>Case</i>	<i>Feedstock</i>	<i>SMR Burner fuel</i>	<i>Emission type</i>
1	Base Case	100% NG	100% NG	Fossil
2	Base Case (with CCS)	100% NG	100% NG	Fossil
3	BM - Burner fuel replacement	100% NG	75% NG - 25% BM	Fossil + Biogenic
4	BM - Burner fuel replacement	100% NG	50% NG - 50% BM	Fossil + Biogenic
5	BM - Burner fuel replacement	100% NG	25% NG - 75% BM	Fossil + Biogenic
6	BM - Burner fuel replacement	100% NG	0% NG - 100% BM	Fossil + Biogenic
7	BG - Burner fuel replacement	100% NG	75% NG - 25% BG	Fossil + Biogenic
8	BG - Burner fuel replacement	100% NG	50% NG - 50% BG	Fossil + Biogenic
9	BG - Burner fuel replacement	100% NG	25% NG - 75% BG	Fossil + Biogenic
10	BG - Burner fuel replacement	100% NG	0% NG - 100% BG	Fossil + Biogenic
11	BG - Feedstock replacement	75% NG - 25% BG	100% NG	Fossil + Biogenic
12	BG - Feedstock replacement	50% NG - 50% BG	100% NG	Fossil + Biogenic
13	BG - Feedstock replacement	25% NG - 75% BG	100% NG	Fossil + Biogenic
14	BG - Feedstock replacement	0% NG - 100% BG	100% NG	Fossil + Biogenic
15	BG - Feedstock and fuel replacement	75% NG - 25% BG	75% NG - 25% BG	Fossil + Biogenic
16	BG - Feedstock and fuel replacement	75% NG - 25% BG	50% NG - 50% BG	Fossil + Biogenic
17	BG - Feedstock and fuel replacement	75% NG - 25% BG	25% NG - 75% BG	Fossil + Biogenic
18	BG - Feedstock and fuel replacement	75% NG - 25% BG	0% NG - 100% BG	Fossil + Biogenic
19	BG - Feedstock and fuel replacement	50% NG - 50% BG	75% NG - 25% BG	Fossil + Biogenic
20	BG - Feedstock and fuel replacement	50% NG - 50% BG	50% NG - 50% BG	Fossil + Biogenic
21	BG - Feedstock and fuel replacement	50% NG - 50% BG	25% NG - 75% BG	Fossil + Biogenic
22	BG - Feedstock and fuel replacement	50% NG - 50% BG	0% NG - 100% BG	Fossil + Biogenic
23	BG - Feedstock and fuel replacement	25% NG - 75% BG	75% NG - 25% BG	Fossil + Biogenic
24	BG - Feedstock and fuel replacement	25% NG - 75% BG	50% NG - 50% BG	Fossil + Biogenic
25	BG - Feedstock and fuel replacement	25% NG - 75% BG	25% NG - 75% BG	Fossil + Biogenic
26	BG - Feedstock and fuel replacement	25% NG - 75% BG	0% NG - 100% BG	Fossil + Biogenic
27	BG - Feedstock and fuel replacement	0% NG - 100% BG	75% NG - 25% BG	Fossil + Biogenic
28	BG - Feedstock and fuel replacement	0% NG - 100% BG	50% NG - 50% BG	Fossil + Biogenic
29	BG - Feedstock and fuel replacement	0% NG - 100% BG	25% NG - 75% BG	Fossil + Biogenic
30	BG - Feedstock and fuel replacement	0% NG - 100% BG	0% NG - 100% BG	Biogenic

The results presented for the proposed cases are for the following:

- **Total amount of urea produced:**

$$\text{Total Amount of urea produced in each case} = \text{urea produced [kg/hr]} \quad (15)$$

- **Total CO₂ captured and stored per kg of urea:**

$$\text{Total CO}_2 \text{ to storage} = \frac{\text{Total CO}_2 \text{ to Storage (feedstock + fuel) [kg/hr]}}{\text{Total amount of urea produced [kg/hr]}} \quad (16)$$

- ***The specific and equivalent fossil emission intensity:***

Specific fossil emission intensity:

$$\frac{CO_2 \text{ Fossil Emissions (fuel) [kg/hr]}}{\text{Total amount of urea produced [kg/hr]}} \quad (17)$$

Equivalent emission intensity:

$$\text{Specific fossil emission intensity} + \frac{\text{Emissions from NGCC power plant [kg/hr]}}{\text{Total amount of urea produced [kg/hr]}} \quad (18)$$

Emissions from NGCC power plant:

$$\text{Net electrical input [MJ/hr]} * E_{el} [\text{kg CO}_2/\text{MJ}] \quad (19)$$

Where: $E_{el} = 0,0977 [\text{kg CO}_2/\text{MJ}]$
*Refers to the avoided CO₂ intensities of steam
and electricity exports (Nazir et al., 2019)*

- ***The total CO₂ emissions per kg of urea:***

$$\text{Scenario 1: } (C+D) - (A+B) \quad (12)$$

$$\text{Scenario 2: } (C+D+F) - (A+B) \quad (13)$$

$$\text{Scenario 3: } (C+D+F+E) - (A+B) \quad (14)$$

Where: **(A)** Biogenic CO₂ in Feedstock
(B) Biogenic CO₂ in Fuel
(C) Total CO₂ in the flue gas emitted
(D) Total CO₂ in Ammonia Stream
(E) Total CO₂ to Urea Plant
(F) Emissions from NGCC power plant

- **The specific and equivalent energy consumption per kg of urea:**

Specific energy consumption per kg of urea:

$$\frac{\text{Energy input Feedstock [MJ/kg]} + \text{Energy input fuel [MJ/kg]}}{\text{Total amount of urea produced [kg/hr]}} \quad (20)$$

Equivalent energy consumption per kg of urea:

$$\text{Specific energy consumption} + \frac{\text{net electrical input [MJ/hr]}}{\text{Total amount of urea produced [kg/hr]} * nE_{el}} \quad (21)$$

Where: $nE_{el} = 0.583$

Refers to the efficiency associated with using natural gas for steam generation in a combined cycle power plant (NGCC) (Nazir et al., 2019)

- **The specific net electricity energy input per kg of urea:**

Specific energy consumption per kg of urea:

$$\frac{\text{Net electrical input [MJ/hr]}}{\text{Total amount of urea produced [kg/hr]}} \quad (22)$$

- **The specific electricity requirement in different components per kg of urea:**

Specific electricity requirement per kg of urea:

$$\frac{\text{Electricity requiremnet for a specific equipment in plant [MJ/hr]}}{\text{Total amount of urea produced [kg/hr]}} \quad (23)$$

- **Biogas and biomethane specific consumption:**

Biofeedstock specific consumption:

$$\frac{\sum(\text{Biogas or Biomethane used as feedstock or fuel}) [\text{kg/hr}]}{\text{Total amount of urea produced [kg/hr]}} \quad (24)$$

The total amount of urea produced:

As previously stated, the available amount of ammonia to storage was used in the cases where there was a surplus of carbon dioxide. In this manner, making possible to produce more urea as in the base case there was not enough CO₂ to keep the feedstock molar ratio of ammonia and CO₂ at the inlet of the urea plant. Hence, the total amount of urea produced in each case was the following:

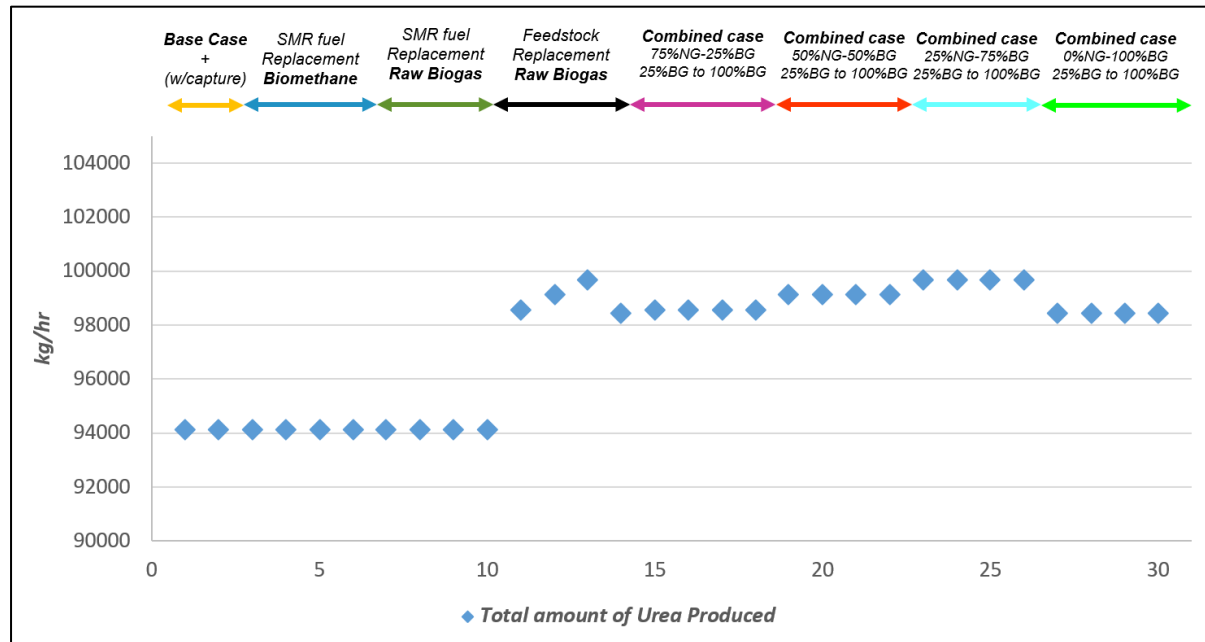


Figure 9. Total amount of urea produced in each case.

The total CO₂ captured and stored per kg of urea:

The amount of CO₂ that was captured and stored increases in each case as the replacement of natural gas feedstock and fuel increases. It is calculated according to equation (16).

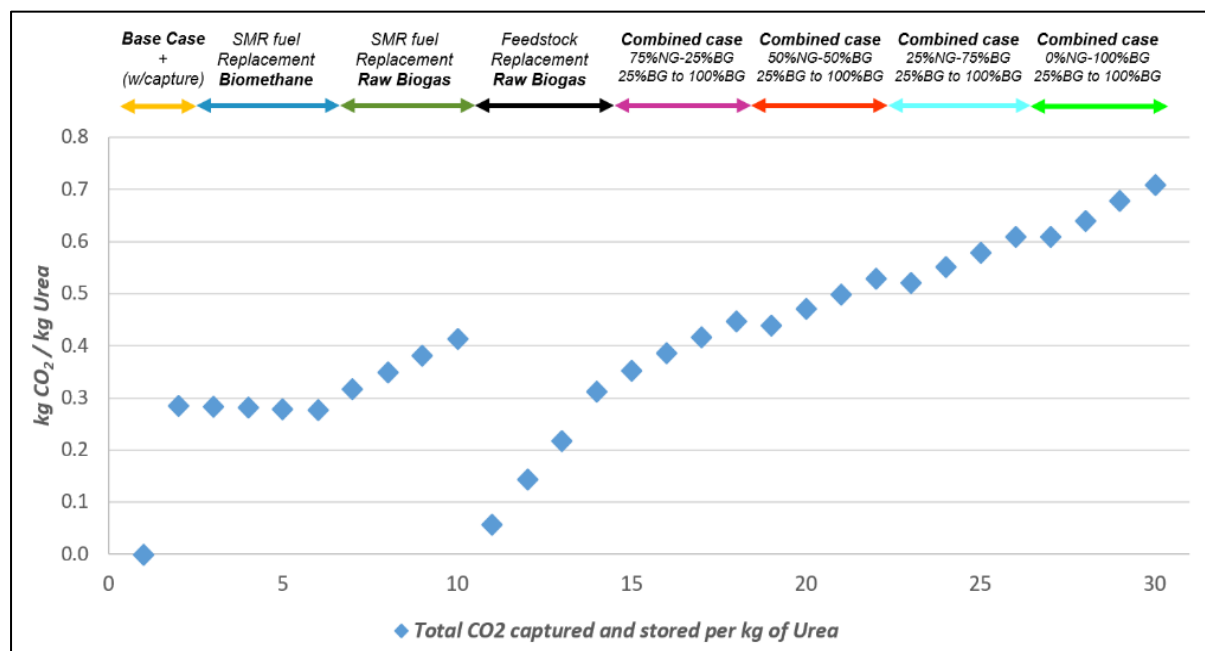


Figure 10. Total CO₂ captured and stored per kg of urea produced in each case.

The Specific and Equivalent fossil emission intensity:

As seen in the results, the fossil emissions are significantly reduced in the cases with the MEA carbon capture system for the flue gases, and in the cases where the natural gas fuel is being replaced in different fractions, compared to the base case and the cases where natural gas feedstock was being replaced in different fractions with biogas, but without considering any natural gas fuel replacement nor the MEA carbon capture system for the flue gas. It is calculated according to equations (17), (18) and (19).

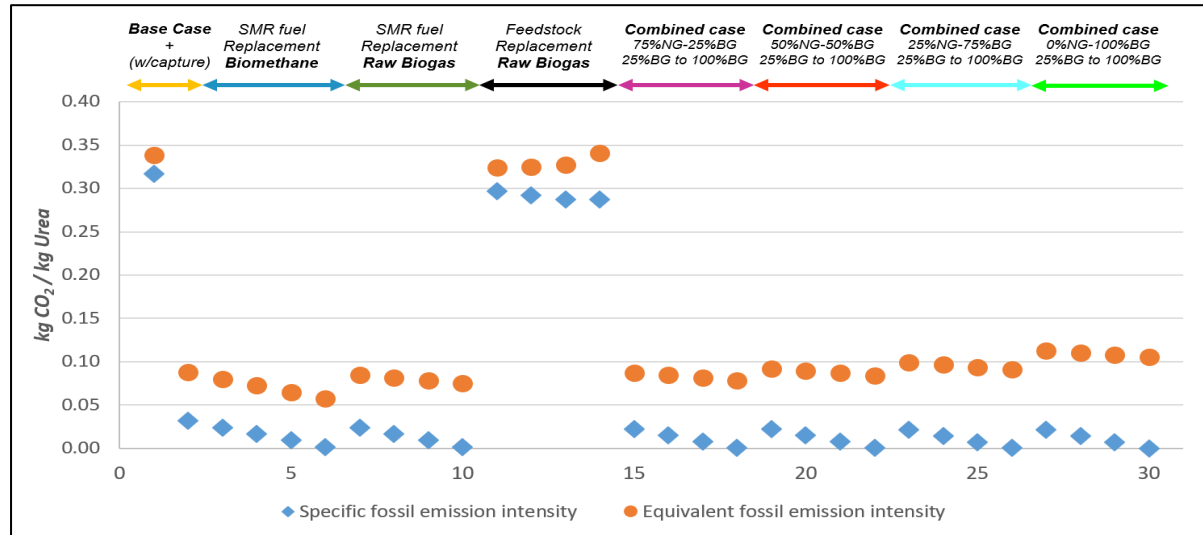


Figure 11. Specific and Equivalent fossil emissions per kg of urea produced in each case.

The total CO₂ emissions per kg of urea:

As seen in the negative emission calculations for each case in the previous section, the more comprehensive scenario, considering the emissions from the flue gas, the methane in the ammonia product, the NGCC power plant, and the urea product, negative emissions are possible to be achieved first in the case with the MEA carbon capture system and by replacing natural gas feedstock in 50% and completely replacing natural gas fuel with biogas. It is calculated according to equations (12), (13), and (14).

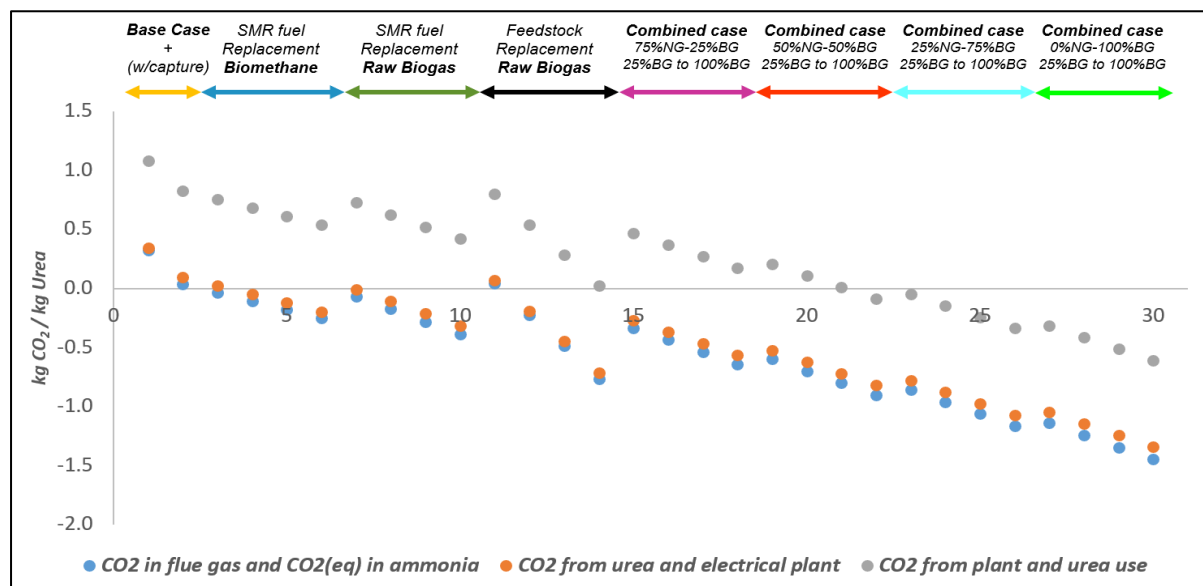


Figure 12. Total CO₂ emissions per kg of urea produced in each case and according to each scenario.

The Specific and Equivalent energy consumption per kg of urea:

As seen in the graph below, the equivalent energy consumption does not significantly increase from the specific energy consumption for the cases where no MEA carbon capture system is considered. However, it significantly increases in the cases where the flue gas is captured. Thus, we can notice a growing trend in the increase as a major fraction of natural gas feedstock and fuel is being replaced with biogas. It is calculated according to equations (20) and (21).

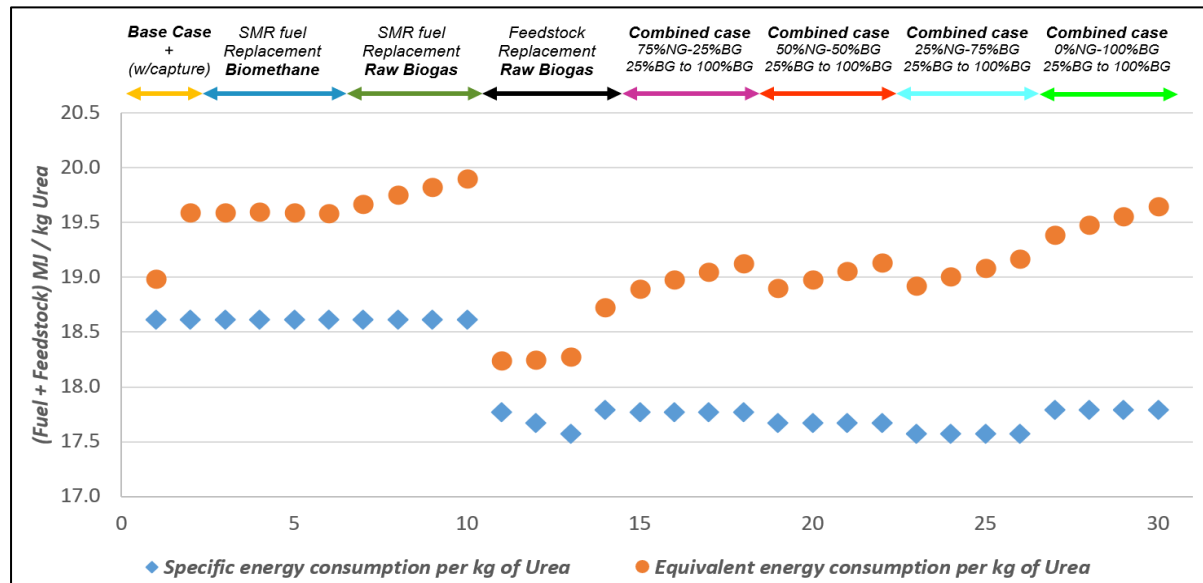


Figure 13. Specific and equivalent consumption of energy per kg of urea produced in each case.

The Specific net electrical energy input per kg of urea:

The amount of specific net electrical energy that has to be provided to the plant, increases in **394.65%** from **0.2184 MJ/kg urea** for the base case to **1.0803 MJ/kg urea** for the complete replacement of natural gas feedstock and fuel with biogas. The reason behind this significant increase is due to the energy required to capture the surplus of CO₂ (and consequently the energy requirements for the different components involved in the process) in each case as a major fraction of natural gas feedstock and fuel is being replaced with biogas. It is calculated according to equation (22)

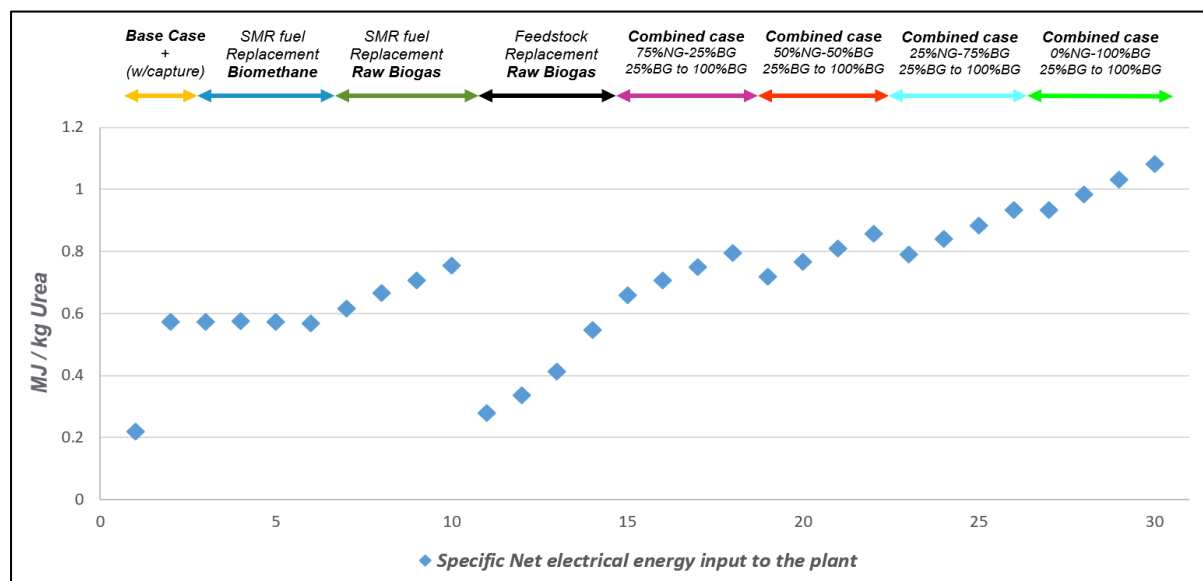


Figure 14. Specific net electrical energy input per kg of urea produced required in each case.

The specific electricity requirement in different components per kg of urea:

As mentioned in the last point, the energy requirements for the different components in the plant increase as a major fraction of natural gas feedstock and fuel is replaced with biogas. This is reflected in the following figure where we can notice that the cases with a major replacement of natural gas require more electricity from the different components involved in the process to capture the surplus amount of CO₂, such as the compressors to storage for the surplus CO₂ emitted from the biogas feedstock used, the compressor to storage for the CO₂ emitted from the fluegas, and the compressor of CO₂ to urea plant. It is calculated according to equation (23).

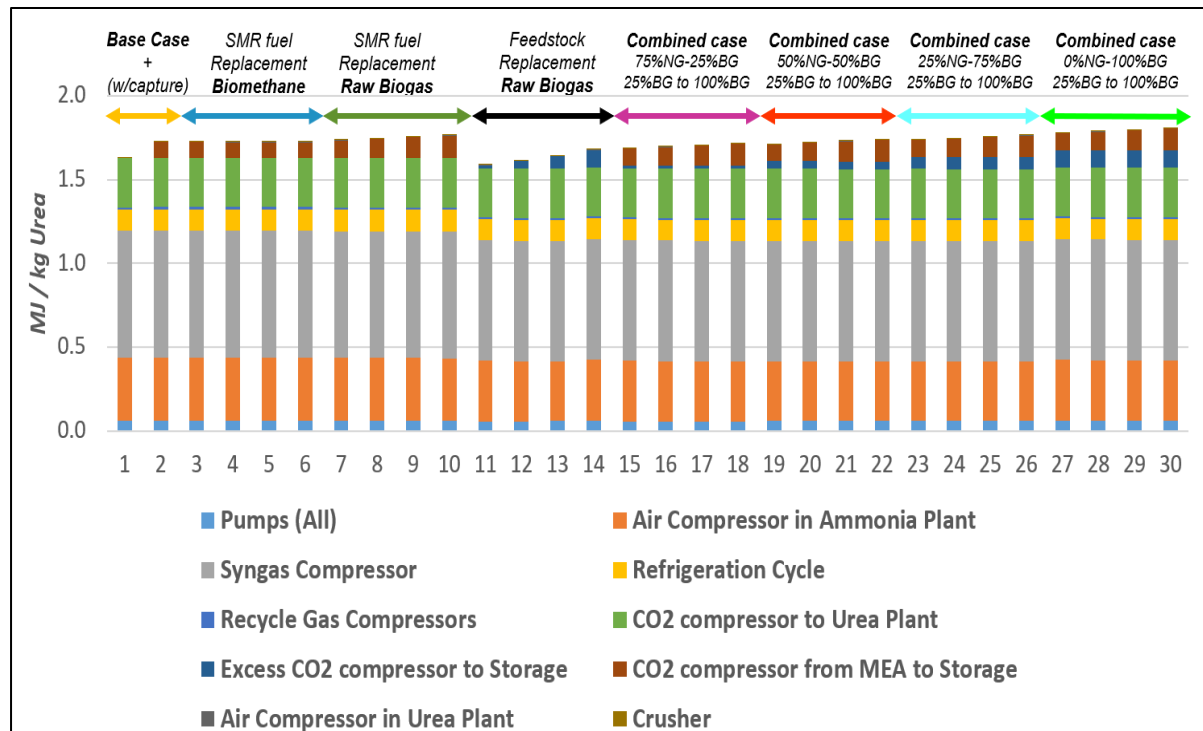


Figure 15. Specific electricity requirement for different equipments in plant per kg of urea produced.

Biogas and biomethane specific consumption:

Finally, from the results obtained for the biofuel specific consumption that is required in each case, we can notice that by introducing more biofuels to the process, we would have a surplus of CO₂ that can be used along with the ammonia that was initially sent to storage and thus produce more urea. Hence, we would be able to produce approximately **6%** more urea by replacing natural gas with biogas. Furthermore, the graph can help us determine what amount of biofeedstock we would require to achieve negative emissions and a specific amount of urea product, for example if we consider the more comprehensive scenario that considers urea production and utilization, we would require approximately 0.5311 kg bio-feedstock/kg Urea (by replacing Natural gas feedstock and fuel with biogas and including CCS), meanwhile by replacing only Natural gas fuel with Biomethane and Biogas, and including CCS, we would require 0.0575 kg BM/kg Urea, and 0.1304 kg BG/ kg Urea respectively. It is calculated according to equation (24).

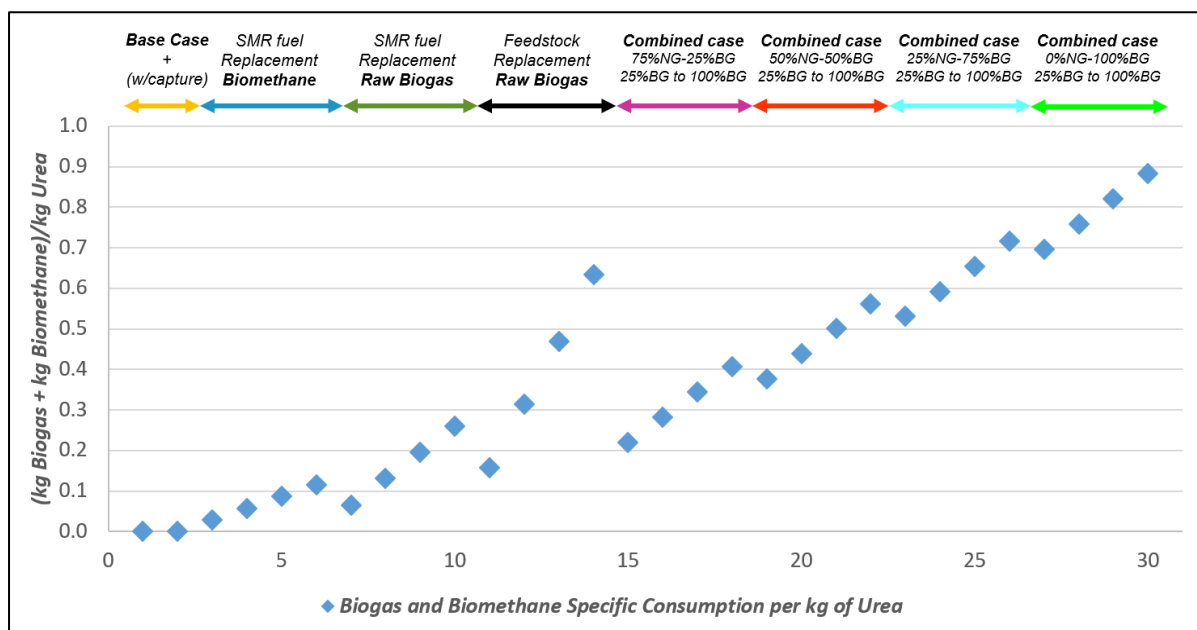


Figure 16. Specific biofeedstock consumption per kg of urea produced in each case.

6. Conclusions

According to the results obtained from the different proposed cases for the present study, it is possible now to have a clear and more comprehensive answer to the research questions set at the beginning of the study, hence:

- **Can ammonia fertilizer (urea) plant be a negative emission plant?**

Yes, without considering the CO₂ emissions from the urea product and considering a 90% carbon capture from the flue gas, it is possible to achieve a negative emission plant by introducing 25% of biofuels (biogas or biomethane) in the SMR burner fuel (alongside NG). More specifically, the amount of biomethane needed would be approximately 0.03 kg BM/kg of urea, and the amount of biogas needed would be approximately 0.07 kg BG/kg urea.

- **Can ammonia fertilizer (urea) plant be a negative emission plant if CO₂ from Urea is also released to the atmosphere after its application?**

Yes, considering the CO₂ emissions from the urea product from its production and application, and with a 90% carbon capture from the flue gas, it is possible to achieve a negative emission plant by introducing 50% of biogas in the feedstock (alongside natural gas), and 75% of biogas in the SMR burner fuel (alongside natural gas). More specifically, the amount of biogas required in this case would be approximately 0.5 kg BG/kg urea.

- **What will be the energy intensity of negative emission urea plant compared to a fossil fuel-based urea plant with/without capture?**

The equivalent energy intensity for a negative emission urea plant, considering the urea production and use, would be 0.32% and 3.37% lower compared to the fossil fuel-based case without/with carbon capture and storage. Meanwhile, the equivalent energy intensity for a negative emission urea plant, considering urea production and the electrical plant (NGCC) only, would be:

- 3.53% and 0.05% higher by replacing natural gas fuel with 50% BM and CCS
- 4.00% and 0.81% higher by replacing NG fuel with 50% BG and CCS
- 3.89% and 6.84% lower by replacing NG feedstock with 50% BG without CCS.

- **How much bio-feedstock we need to achieve negative emissions in urea production and use?**

we would require 0.5311 kg bio-feedstock/ kg Urea by replacing NG feedstock and fuel with BG and including CCS. Meanwhile, by replacing NG fuel with BM and BG and including CCS, we would require 0.0575 kg BM/kg Urea, and 0.1304 kg BG/ kg Urea respectively.

- **Can we produce more urea by using bio-feedstocks?**

Yes, we can produce approximately 6% more urea by replacing a fraction of NG with biogas. This is because there is a surplus of carbon dioxide that can be used with the ammonia product that was going to storage.

7. Proposed future work

As for some recommendations and proposed future work, with the results obtained from the different proposed cases for the present study, it is possible now to perform an economic analysis and study the application viability of the most relevant and interesting cases. Economic analysis will give a more comprehensive view about the potential of implementing biofuels and capture the CO₂ emissions in existing ammonia fertilizer plants.

Furthermore, a study performed by “*Stockholm Trafikförvaltningen*” proposed the possibility to gradually “*electrify*” the buses operating in a specific region in the following years (Stockholm Trafikförvaltningen, 2019). The study highlights that the strategy proposed will allow the continued exploitation of existing investments in biogas, thus thus strengthening the sector, and contributing to better air quality, reduced noise in the region, and moreover an increased energy efficiency of the use of the current resources. All of these benefits in the long term will lead to an attractive and climate neutral Stockholm region. Most importantly from a climate perspective, the strategy to switch from biofuel buses to electric ones in the following years will free up limited amounts of sustainable biofuels to be used in other sectors that cannot be easily electrified. Hence, the environmental benefits obtained from this transition to electric drive trains in the following years will free up biofuels that were initially used in buses today, and will be available for other industrial sectors such as the fertilizer industry. Indeed this is an interesting possibility to be analyzed in the near future.

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9. Annexes

FEEDSTOCK REPLACEMENT CASES

<i>Feedstock Replacement</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
INLET STREAMS					
Natural gas (as Feedstock)	kg/hr	20265.75	13514.16	6755.25	0.00
Natural gas (as Fuel)	kg/hr	10631.15	10631.15	10631.15	10631.15
Natural gas total Consumption	kg/hr	30896.90	24145.31	17386.40	10631.15
Biogas (as Feedstock)	kg/hr	15594.85	31198.16	46784.55	62379.41
Biogas (as Fuel)	kg/hr	0.00	0.00	0.00	0.00
Biogas Total Consumption	kg/hr	15594.85	31198.16	46784.55	62379.41
Biomethane (as Feedstock)	kg/hr	0.00	0.00	0.00	0.00
Biomethane (as Fuel)	kg/hr	0.00	0.00	0.00	0.00
Biomethane Total Consumption	kg/hr	0.00	0.00	0.00	0.00
TOTAL ENERGY INPUT					
Natural Gas LHV	MJ/kg	46.50	46.50	46.50	46.50
Biogas LHV	MJ/kg	20.14	20.14	20.14	20.14
Biomethane LHV	MJ/kg	45.67	45.67	45.67	45.67
Natural Gas (Feedstock) Energy input	MJ	942307.14	628374.94	314102.38	0.00
Natural Gas (Fuel) Energy input	MJ	494321.97	494321.97	494321.97	494321.97
Biogas (Feedstock) Energy input	MJ	314102.38	628375.10	942307.13	1256409.51
Biogas (Fuel) Energy input	MJ	0.00	0.00	0.00	0.00
Biomethane (Feedstock) Energy input	MJ	0.00	0.00	0.00	0.00
Biomethane (Fuel) Energy input	MJ	0.00	0.00	0.00	0.00
Total Energy input	MJ	1750731.49	1751072.01	1750731.48	1750731.48
Total Energy input	MW	486.31	486.41	486.31	486.31
OUTLET STREAMS					
Ammonia Product to Urea Plant	kg/hr	55975.50	56299.01	56604.12	55905.11
Ammonia Product to Storage	kg/hr	0.00	0.00	0.00	0.00
Total Ammonia	kg/hr	55975.50	56299.01	56604.12	55905.11
CO2 stream Product to Urea Plant	kg/hr	73366.70	73772.05	74131.76	73194.35
CO2 stream Product to Storage	kg/hr	5404.85	13640.74	21886.07	31330.99
Total CO2 stream	kg/hr	78771.55	87412.79	96017.83	104525.34
Urea Product	kg/hr	98537.75	99110.36	99646.41	98401.65
Urea energy content	MJ/kg	32.70	32.70	32.70	32.70
Total Energy of Urea	MJ	3222184.38	3240908.77	3258437.60	3217734.07
Total Energy in Product	MW	895.05	900.25	905.12	893.82

<i>Feedstock Replacement</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
SPECIFIC CONSUMPTIONS PER UREA					
Natural Gas (as Feedstock)	<i>MJ/kg Urea</i>	9.56	6.34	3.15	0.00
Natural Gas (as Fuel)	<i>MJ/kg Urea</i>	5.02	4.99	4.96	5.02
Biogas (as Feedstock)	<i>MJ/kg Urea</i>	3.19	6.34	9.46	12.77
Biogas (as Fuel)	<i>MJ/kg Urea</i>	0.00	0.00	0.00	0.00
Biomethane (as Feedstock)	<i>MJ/kg Urea</i>	0.00	0.00	0.00	0.00
Biomethane (as Fuel)	<i>MJ/kg Urea</i>	0.00	0.00	0.00	0.00
Feed + Fuel	<i>MJ/kg Urea</i>	17.77	17.67	17.57	17.79
SPECIFIC EMISSIONS					
FEEDSTOCK					
Total Only CO ₂ Released from Stripper	<i>kg/hr</i>	77661.72	86201.75	94706.10	103114.93
Captured Only CO ₂ to PLANT	<i>kg/hr</i>	72333.02	72749.99	73119.03	72206.70
Captured Only CO ₂ to STORAGE	<i>kg/hr</i>	5328.70	13451.76	21587.07	30908.22
BURNER FLUEGAS					
Total Only CO ₂ produced	<i>kg/hr</i>	29712.22	29840.11	30028.29	29731.90
Total Only CO ₂ captured to STORAGE	<i>kg/hr</i>	0.00	0.00	0.00	0.00
Total Only CO₂ in fluegas to stack	<i>kg/hr</i>	29712.22	29840.11	30028.29	29731.90
Required Only CO ₂ Stream for Ammonia in Urea Plant	<i>kg/hr</i>	72333.02	72749.99	73119.03	72206.70
STORAGE - Total Available captured CO ₂	<i>kg/hr</i>	5328.70	13451.76	21587.07	30908.22
EMISSION CALCULATIONS					
Specific CO ₂ Emission	<i>kg/kg Urea</i>	0.3015	0.3011	0.3013	0.3021
Equivalent CO ₂ in Urea Product	%	66.7733	62.2096	58.2564	53.8432
Captured CO ₂ to Storage	%	4.9191	11.5028	17.1992	23.0477
Overall CO ₂ not emitted	%	71.6924	73.7124	75.4556	76.8909

* ONLY CO₂ refers to the component CO₂ present in stream only, not counting the entire stream.

<i>Feedstock Replacement</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
INLET - EQUIVALENT MOLAR FLOW OF CO ₂					
Natural Gas feedstock	<i>kmol/hr</i>	1219.73	813.37	406.58	0.00
Natural Gas fuel	<i>kmol/hr</i>	639.86	639.86	639.86	639.86
Biogas feedstock	<i>kmol/hr</i>	601.83	1203.99	1805.49	2407.32
Biogas fuel	<i>kmol/hr</i>	0.00	0.00	0.00	0.00
Biomethane feedstock	<i>kmol/hr</i>	0.00	0.00	0.00	0.00
Biomethane fuel	<i>kmol/hr</i>	0.00	0.00	0.00	0.00
Total Inlet	<i>kmol/hr</i>	2461.42	2657.22	2851.92	3047.18
OUTLET - EQUIVALENT MOLAR FLOW OF CO ₂					
Urea Carbon Content	<i>kmol/hr</i>	1643.57	1653.04	1661.43	1640.70
Total CO ₂ to STORAGE	<i>kmol/hr</i>	121.08	305.65	490.51	702.30
Total not emitted	<i>kmol/hr</i>	1764.65	1958.70	2151.94	2343.00
Flue gas to stack	<i>kmol/hr</i>	675.13	678.03	682.31	675.58
Vents	<i>kmol/hr</i>	0.00	0.00	0.00	0.00
Emission	<i>kmol/hr</i>	675.13	678.03	682.31	675.58
Total Outlet	<i>kmol/hr</i>	2439.78	2636.73	2834.25	3018.58
Equivalent CO ₂ in Urea Product %	%	66.77	62.21	58.26	53.84
Captured CO ₂ to STORAGE %	%	4.92	11.50	17.20	23.05
Amount of Carbon not Emitted	%	71.69	73.71	75.46	76.89

<i>Feedstock Replacement</i>		75% NG 25% BG	50% NG 50% BG	25% NG 75% BG	0% NG 100% BG
EQUIVALENT MASS FLOW OF CO₂ IN STREAMS					
Natural gas (as Feedstock)	<i>kg/hr</i>	53680.00	35796.36	17893.33	0.00
Natural gas (as Fuel)	<i>kg/hr</i>	28159.82	28159.82	28159.82	28159.82
Total CO₂ from Natural Gas	<i>kg/hr</i>	81839.83	63956.19	46053.16	28159.82
Biogas (as Feedstock)	<i>kg/hr</i>	26486.39	52987.16	79459.19	105945.59
Biogas (as Fuel)	<i>kg/hr</i>	0.00	0.00	0.00	0.00
Total CO₂ from Biogas	<i>kg/hr</i>	26486.39	52987.16	79459.19	105945.59
Biomethane (as Feedstock)	<i>kg/hr</i>	0.00	0.00	0.00	0.00
Biomethane (as Fuel)	<i>kg/hr</i>	0.00	0.00	0.00	0.00
Total CO₂ from Biomethane	<i>kg/hr</i>	0.00	0.00	0.00	0.00
Total equivalent mass flow of CO₂	<i>kg/hr</i>	108326.23	116943.35	125512.35	134105.42
CO₂ EMITTED FROM - FEEDSTOCK					
<i>Biogenic CO₂</i>	<i>kg/hr</i>	26486.40	52987.16	79459.20	105945.60
<i>Fossil CO₂</i>	<i>kg/hr</i>	53680.01	35796.36	17893.34	0.00
Total Equivalent CO₂ from Feedstock	<i>kg/hr</i>	80166.40	88783.53	97352.53	105945.60
% <i>Biogenic CO₂</i> in Feedstock	%	33.04	59.68	81.62	100.00
% <i>Fossil CO₂</i> in Feedstock	%	66.96	40.32	18.38	0.00
% Total	%	100.00	100.00	100.00	100.00
Actual ONLY CO₂ Present in Syngas before MDEA capture	<i>kg/hr</i>	78825.20	87504.65	96096.64	104683.39
Actual ONLY CO ₂ Present in Syngas after capture	<i>kg/hr</i>	1156.26	1267.79	1378.96	1558.49
Actual ONLY CO₂ Released from Stripper	<i>kg/hr</i>	77661.54	86201.55	94705.88	103114.69
Actual ONLY CO ₂ to Plant	<i>kg/hr</i>	72333.01	72749.98	73119.02	72206.70
Actual ONLY CO ₂ to Storage	<i>kg/hr</i>	5328.70	13451.75	21587.07	30908.22
% CO₂ going to Storage from Total	%	6.86	15.61	22.79	29.97
<i>Mass flow of Biogenic CO₂ going to STORAGE</i>	%	1760.56	8028.18	17619.38	30908.22
CO₂ EMITTED FROM - FLUEGAS					
<i>Biogenic CO₂</i>	<i>kg/hr</i>	0.00	0.00	0.00	0.00
<i>Fossil CO₂</i>	<i>kg/hr</i>	28159.83	28159.83	28159.83	28159.83
Total CO₂	<i>kg/hr</i>	28159.83	28159.83	28159.83	28159.83
Captured CO ₂ from Biogas - Fluegas (90%)	<i>kg/hr</i>	0.00	0.00	0.00	0.00
Total CO ₂ present in Fluegas before Capture	<i>kg/hr</i>	29781.05	29781.05	29781.05	29781.05

Biogas: Feedstock and fuel replacement cases

<i>AE</i>	<i>AF</i>	<i>AG</i>	<i>AH</i>
Feedstock: 75% NG - 25% BG	Feedstock: 75% NG - 25% BG	Feedstock: 75% NG - 25% BG	Feedstock: 75% NG - 25% BG
SMR Burner fuel: 75% NG - 25% BG	SMR Burner fuel: 50% NG - 50% BG	SMR Burner fuel: 25% NG - 75% BG	SMR Burner fuel: 0% NG - 100% BG

<i>Combination (AE – AH)</i>		<i>AE</i>	<i>AF</i>	<i>AG</i>	<i>AH</i>
<i>CO₂ Emitted from – Feedstock</i>					
<i>Biogenic CO₂</i>	<i>kg/hr</i>	26486.40	26486.40	26486.40	26486.40
<i>Fossil CO₂</i>	<i>kg/hr</i>	53680.01	53680.01	53680.01	53680.01
<i>Total Equivalent CO₂ from Feedstock</i>	<i>kg/hr</i>	80166.40	80166.40	80166.40	80166.40
<i>% Biogenic CO₂ in Feedstock</i>	<i>%</i>	33.04	33.04	33.04	33.04
<i>% Fossil CO₂ in Feedstock</i>	<i>%</i>	66.96	66.96	66.96	66.96
<i>% Total</i>	<i>%</i>	100.00	100.00	100.00	100.00
<i>Actual Only CO₂ present in syngas before MDEA capture</i>	<i>kg/hr</i>	78825.2001	78825.2001	78825.2001	78825.2001
<i>Actual Only CO₂ Present in syngas after capture</i>	<i>kg/hr</i>	1156.268395	1156.268395	1156.268395	1156.268395
<i>Actual Only CO₂ released from the stripper column</i>	<i>kg/hr</i>	77661.54212	77661.54212	77661.54212	77661.54212
<i>Actual Only CO₂ to Plant</i>	<i>kg/hr</i>	72333.0154	72333.0154	72333.0154	72333.0154
<i>Actual Only CO₂ to Storage</i>	<i>kg/hr</i>	5328.701816	5328.701816	5328.701816	5328.701816
<i>% of CO₂ going to Storage from the total CO₂ released</i>	<i>%</i>	6.86	6.86	6.86	6.86
<i>Mass flow of Biogenic CO₂ going to Storage</i>	<i>kg/hr</i>	1760.5645	1760.5645	1760.5645	1760.5645

<i>Combination (AE – AH)</i>		<i>AE</i>	<i>AF</i>	<i>AG</i>	<i>AH</i>
<i>CO₂ Emitted from – Flue gas</i>					
<i>Biogenic CO₂</i>	<i>kg/hr</i>	10420.98	20841.95	31262.93	41683.91
<i>Fossil CO₂</i>	<i>kg/hr</i>	21119.87	14079.91	7039.96	0.00
<i>Total CO₂</i>	<i>kg/hr</i>	31540.85	34921.87	38302.88	41683.91
<i>Captured biogenic CO₂ from biogas - Flue gas (90%)</i>	<i>kg/hr</i>	9378.88	18757.76	28136.64	37515.52
<i>Total CO₂ present in Flue gas before Capture</i>	<i>kg/hr</i>	33159.56	36536.69	39915.82	43295.23

BE	BF	BG	BH
Feedstock: 50% NG - 50% BG	Feedstock: 50% NG - 50% BG	Feedstock: 50% NG - 50% BG	Feedstock: 50% NG - 50% BG
SMR Burner fuel: 75% NG - 25% BG	SMR Burner fuel: 50% NG - 50% BG	SMR Burner fuel: 25% NG - 75% BG	SMR Burner fuel: 0% NG - 100% BG

<i>Combination (BE – BH)</i>		<i>BE</i>	<i>BF</i>	<i>BG</i>	<i>BH</i>
<i>CO₂ Emitted from – Feedstock</i>					
<i>Biogenic CO₂</i>	<i>kg/hr</i>	52987.16	52987.16	52987.16	52987.16
<i>Fossil CO₂</i>	<i>kg/hr</i>	35796.36	35796.36	35796.36	35796.36
<i>Total Equivalent CO₂ from Feedstock</i>	<i>kg/hr</i>	88783.53	88783.53	88783.53	88783.53
<i>% Biogenic CO₂ in Feedstock</i>	<i>%</i>	59.68	59.68	59.68	59.68
<i>% Fossil CO₂ in Feedstock</i>	<i>%</i>	40.32	40.32	40.32	40.32
<i>% Total</i>	<i>%</i>	100.00	100.00	100.00	100.00
<i>Actual Only CO₂ present in syngas before MDEA capture</i>	<i>kg/hr</i>	87504.6562	87504.6562	87504.6562	87504.6562
<i>Actual Only CO₂ Present in syngas after capture</i>	<i>kg/hr</i>	1267.796327	1267.796327	1267.796327	1267.796327
<i>Actual Only CO₂ released from the stripper column</i>	<i>kg/hr</i>	86201.55139	86201.55139	86201.55139	86201.55139
<i>Actual Only CO₂ to Plant</i>	<i>kg/hr</i>	72749.9885	72749.9885	72749.9885	72749.9885
<i>Actual Only CO₂ to Storage</i>	<i>kg/hr</i>	13451.75724	13451.75724	13451.75724	13451.75724
<i>% of CO₂ going to Storage from the total CO₂ released</i>	<i>%</i>	15.61	15.61	15.61	15.61
<i>Mass flow of Biogenic CO₂ going to Storage</i>	<i>kg/hr</i>	8028.1835	8028.1835	8028.1835	8028.1835

<i>Combination (BE – BH)</i>		<i>BE</i>	<i>BF</i>	<i>BG</i>	<i>BH</i>
<i>CO₂ Emitted from – Flue gas</i>					
<i>Biogenic CO₂</i>	<i>kg/hr</i>	10420.98	20841.95	31262.93	41683.91
<i>Fossil CO₂</i>	<i>kg/hr</i>	21119.87	14079.91	7039.96	0.00
<i>Total CO₂</i>	<i>kg/hr</i>	31540.85	34921.87	38302.88	41683.91
Captured biogenic CO ₂ from biogas - Flue gas (90%)	<i>kg/hr</i>	9378.88	18757.76	28136.64	37515.52
Total CO ₂ present in Flue gas before Capture	<i>kg/hr</i>	33159.56	36536.69	39915.82	43295.23

<i>CE</i>	<i>CF</i>	<i>CG</i>	<i>CH</i>
Feedstock: 25% NG - 75% BG	Feedstock: 25% NG - 75% BG	Feedstock: 25% NG - 75% BG	Feedstock: 25% NG - 75% BG
SMR Burner fuel: 75% NG - 25% BG	SMR Burner fuel: 50% NG - 50% BG	SMR Burner fuel: 25% NG - 75% BG	SMR Burner fuel: 0% NG - 100% BG

<i>Combination (CE – CH)</i>		<i>CE</i>	<i>CF</i>	<i>CG</i>	<i>CH</i>
<i>CO₂ Emitted from – Feedstock</i>					
<i>Biogenic CO₂</i>	<i>kg/hr</i>	79459.20	79459.20	79459.20	79459.20
<i>Fossil CO₂</i>	<i>kg/hr</i>	17893.34	17893.34	17893.34	17893.34
<i>Total Equivalent CO₂ from Feedstock</i>	<i>kg/hr</i>	97352.53	97352.53	97352.53	97352.53
<i>% Biogenic CO₂ in Feedstock</i>	<i>%</i>	81.62	81.62	81.62	81.62
<i>% Fossil CO₂ in Feedstock</i>	<i>%</i>	18.38	18.38	18.38	18.38
<i>% Total</i>	<i>%</i>	100.00	100.00	100.00	100.00
<i>Actual Only CO₂ present in syngas before MDEA capture</i>	<i>kg/hr</i>	96096.6457	96096.6457	96096.6457	96096.6457
<i>Actual Only CO₂ Present in syngas after capture</i>	<i>kg/hr</i>	1378.963648	1378.963648	1378.963648	1378.963648
<i>Actual Only CO₂ released from the stripper column</i>	<i>kg/hr</i>	94705.88563	94705.88563	94705.88563	94705.88563
<i>Actual Only CO₂ to Plant</i>	<i>kg/hr</i>	73119.02517	73119.02517	73119.02517	73119.02517
<i>Actual Only CO₂ to Storage</i>	<i>kg/hr</i>	21587.07398	21587.07398	21587.07398	21587.07398
<i>% of CO₂ going to Storage from the total CO₂ released</i>	<i>%</i>	22.79	22.79	22.79	22.79
<i>Mass flow of Biogenic CO₂ going to Storage</i>	<i>kg/hr</i>	17619.3832	17619.3832	17619.3832	17619.3832

<i>Combination (CE – CH)</i>		<i>CE</i>	<i>CF</i>	<i>CG</i>	<i>CH</i>
<i>CO₂ Emitted from – Flue gas</i>					
<i>Biogenic CO₂</i>	<i>kg/hr</i>	10420.98	20841.95	31262.93	41683.91
<i>Fossil CO₂</i>	<i>kg/hr</i>	21119.87	14079.91	7039.96	0.00
<i>Total CO₂</i>	<i>kg/hr</i>	31540.85	34921.87	38302.88	41683.91
Captured biogenic CO ₂ from biogas - Flue gas (90%)	<i>kg/hr</i>	9378.88	18757.76	28136.64	37515.52
Total CO ₂ present in Flue gas before Capture	<i>kg/hr</i>	33159.56	36536.69	39915.82	43295.23

DE	DF	DG	DH
Feedstock: 0% NG - 100% BG	Feedstock: 0% NG - 100% BG	Feedstock: 0% NG - 100% BG	Feedstock: 0% NG - 100% BG
SMR Burner fuel: 75% NG - 25% BG	SMR Burner fuel: 50% NG - 50% BG	SMR Burner fuel: 25% NG - 75% BG	SMR Burner fuel: 0% NG - 100% BG

<i>Combination (DE – DH)</i>		<i>DE</i>	<i>DF</i>	<i>DG</i>	<i>DH</i>
<i>CO₂ Emitted from – Feedstock</i>					
<i>Biogenic CO₂</i>	<i>kg/hr</i>	105945.60	105945.60	105945.60	105945.60
<i>Fossil CO₂</i>	<i>kg/hr</i>	0.00	0.00	0.00	0.00
<i>Total Equivalent CO₂ from Feedstock</i>	<i>kg/hr</i>	105945.60	105945.60	105945.60	105945.60
<i>% Biogenic CO₂ in Feedstock</i>	<i>%</i>	100.00	100.00	100.00	100.00
<i>% Fossil CO₂ in Feedstock</i>	<i>%</i>	0.00	0.00	0.00	0.00
<i>% Total</i>	<i>%</i>	100.00	100.00	100.00	100.00
<i>Actual Only CO₂ present in syngas before MDEA capture</i>	<i>kg/hr</i>	104683.3982	104683.3982	104683.3982	104683.3982
<i>Actual Only CO₂ Present in syngas after capture</i>	<i>kg/hr</i>	1558.497794	1558.497794	1558.497794	1558.497794
<i>Actual Only CO₂ released from the stripper column</i>	<i>kg/hr</i>	103114.6928	103114.6928	103114.6928	103114.6928
<i>Actual Only CO₂ to Plant</i>	<i>kg/hr</i>	72206.70303	72206.70303	72206.70303	72206.70303
<i>Actual Only CO₂ to Storage</i>	<i>kg/hr</i>	30908.22222	30908.22222	30908.22222	30908.22222
<i>% of CO₂ going to Storage from the total CO₂ released</i>	<i>%</i>	29.97	29.97	29.97	29.97
<i>Mass flow of Biogenic CO₂ going to Storage</i>	<i>kg/hr</i>	30908.2222	30908.2222	30908.2222	30908.2222

<i>Combination (DE – DH)</i>		<i>DE</i>	<i>DF</i>	<i>DG</i>	<i>DH</i>
<i>CO₂ Emitted from – Flue gas</i>					
<i>Biogenic CO₂</i>	<i>kg/hr</i>	10420.98	20841.95	31262.93	41683.91
<i>Fossil CO₂</i>	<i>kg/hr</i>	21119.87	14079.91	7039.96	0.00
<i>Total CO₂</i>	<i>kg/hr</i>	31540.85	34921.87	38302.88	41683.91
Captured biogenic CO ₂ from biogas - Flue gas (90%)	<i>kg/hr</i>	9378.88	18757.76	28136.64	37515.52
Total CO ₂ present in Flue gas before Capture	<i>kg/hr</i>	33159.56	36536.69	39915.82	43295.23

INLET - Equivalent MOLAR FLOW of CO₂

		HYCO Plant	Base Case	Feedstock Replacement 75% NG 25% BG	Feedstock Replacement 50% NG 50% BG	Feedstock Replacement 25% NG 75% BG	Feedstock Replacement 0% NG 100% BG
Natural Gas feedstock	kmol/hr	1626,75	1626,75	1219,73	813,37	406,58	0,00
Natural Gas fuel	kmol/hr	639,86	639,86	639,86	639,86	639,86	639,86
biogas feedstock	kmol/hr	0,00	0,00	601,83	1203,99	1805,49	2407,32
biogas fuel	kmol/hr	0,00	0,00	0,00	0,00	0,00	0,00
Biomethane feedstock	kmol/hr	0,00	0,00	0,00	0,00	0,00	0,00
Biomethane fuel	kmol/hr	0,00	0,00	0,00	0,00	0,00	0,00
Total Inlet	kmol/hr	2266,61	2266,61	2461,42	2657,22	2851,92	3047,18

OUTLET – Equivalent MOLAR FLOW of CO₂

Urea Carbon Content	kmol/hr	1567,57	1569,66	1643,57	1653,04	1661,43	1640,70
TOTAL CO2 to storage	kmol/hr	0,00	0,00	121,08	305,65	490,51	702,30
Total not emitted	kmol/hr	1567,57	1569,66	1764,65	1958,70	2151,94	2343,00
Flue gas to stack	kmol/hr	693,31	677,32	675,13	678,03	682,31	675,58
Vents	kmol/hr	0,00	0,00	0,00	0,00	0,00	0,00
Emission	kmol/hr	693,31	677,32	675,13	678,03	682,31	675,58
Total Outlet	kmol/hr	2260,88	2246,97	2439,78	2636,73	2834,25	3018,58
Equivalent CO2 in Urea Product %	%	69,16	69,25	66,77	62,21	58,26	53,84
Captured CO2 to Storage %	%	0,00	0,00	4,92	11,50	17,20	23,05
Amount of Carbon not Emitted	%	69,16	69,25	71,69	73,71	75,46	76,89

INLET - Equivalent MOLAR FLOW of CO ₂									
		RW Burner Fuel Replacement 75% NG 25% BG	RW Burner Fuel Replacement 50% NG 50% BG	RW Burner Fuel Replacement 25% NG 75% BG	RW Burner Fuel Replacement 0% NG 100% BG	BM Burner Fuel Replacement 75% NG 25% BM	BM Burner Fuel Replacement 50% NG 50% BM	BM Burner Fuel Replacement 25% NG 75% BM	BM Burner Fuel Replacement 0% NG 100% BM
Natural Gas feedstock	kmol/hr	1626,75	1626,75	1626,75	1626,75	1626,75	1626,75	1626,75	1626,75
Natural Gas fuel	kmol/hr	479,89	319,93	159,96	0,00	479,89	319,93	159,96	0,00
biogas feedstock	kmol/hr	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
biogas fuel	kmol/hr	236,79	473,58	710,36	947,15	0,00	0,00	0,00	0,00
Biomethane feedstock	kmol/hr	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Biomethane fuel	kmol/hr	0,00	0,00	0,00	0,00	155,56	311,13	466,69	622,25
Total Inlet	kmol/hr	2343,43	2420,25	2497,08	2573,90	2262,20	2257,80	2253,40	2249,00
OUTLET – Equivalent MOLAR FLOW of CO ₂									
Urea Carbon Content	kmol/hr	1569,66	1569,66	1569,66	1569,66	1569,66	1569,66	1569,66	1569,66
TOTAL CO2 to storage	kmol/hr	678,11	747,18	816,28	885,39	605,06	601,10	597,14	593,18
Total not emitted	kmol/hr	2247,77	2316,83	2385,94	2455,04	2174,72	2170,76	2166,80	2162,83
Flue gas to stack	kmol/hr	75,35	83,02	90,70	98,38	67,23	66,79	66,35	65,91
Vents	kmol/hr	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Emission	kmol/hr	75,35	83,02	90,70	98,38	67,23	66,79	66,35	65,91
Total Outlet	kmol/hr	2323,12	2399,85	2476,63	2553,42	2241,95	2237,55	2233,14	2228,74
Equivalent CO2 in Urea Product %	%	66,98	64,85	62,86	60,98	69,39	69,52	69,66	69,79
Captured CO2 to Storage %	%	28,94	30,87	32,69	34,40	26,75	26,62	26,50	26,38
Amount of Carbon not Emitted	%	95,92	95,73	95,55	95,38	96,13	96,14	96,16	96,17

INLET – Equivalent MOLAR FLOW of CO ₂									
<i>COMBINATION</i> Feedstock replacement Fuel replacement	%	Feedstock: 75% NG - 25% BG Burner Fuel: 75% NG - 25% BG	Feedstock: 75% NG - 25% BG Burner Fuel: 50% NG - 50% BG	Feedstock: 75% NG - 25% BG Burner Fuel: 25% NG - 75% BG	Feedstock: 75% NG - 25% BG Burner Fuel: 0% NG - 100% BG	Feedstock: 50% NG - 50% BG Burner Fuel: 75% NG - 25% BG	Feedstock: 50% NG - 50% BG Burner Fuel: 50% NG - 50% BG	Feedstock: 50% NG - 50% BG Burner Fuel: 25% NG - 75% BG	Feedstock: 50% NG - 50% BG Burner Fuel: 0% NG - 100% BG
Natural Gas feedstock	kmol/hr	1219,73	1219,73	1219,73	1219,73	813,37	813,37	813,37	813,37
Natural Gas fuel	kmol/hr	479,89	319,93	159,96	0,00	479,89	319,93	159,96	0,00
biogas feedstock	kmol/hr	601,83	601,83	601,83	601,83	1203,99	1203,99	1203,99	1203,99
biogas fuel	kmol/hr	236,79	473,58	710,36	947,15	236,79	473,58	710,36	947,15
Biomethane feedstock	kmol/hr	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Biomethane fuel	kmol/hr	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Total Inlet	kmol/hr	2538,24	2615,07	2691,89	2768,71	2734,04	2810,87	2887,69	2964,52
OUTLET – Equivalent MOLAR FLOW of CO ₂									
Urea Carbon Content	kmol/hr	1643,57	1643,57	1643,57	1643,57	1653,04	1653,04	1653,04	1653,04
TOTAL CO2 to storage	kmol/hr	799,19	868,26	937,36	1006,47	983,77	1052,83	1121,93	1191,04
Total not emitted	kmol/hr	2442,76	2511,83	2580,93	2650,04	2636,81	2705,88	2774,98	2844,09
Flue gas to stack	kmol/hr	75,35	83,02	90,70	98,38	75,35	83,02	90,70	98,38
Vents	kmol/hr	0,00	1,00	2,00	3,00	4,00	5,00	6,00	7,00
Emission	kmol/hr	75,35	84,02	92,70	101,38	79,35	88,02	96,70	105,38
Total Outlet	kmol/hr	2518,11	2595,85	2673,63	2751,42	2716,16	2793,89	2871,68	2949,46
Equivalent CO2 in Urea Product %	%	64,75	62,85	61,06	59,36	60,46	58,81	57,24	55,76
Captured CO2 to Storage %	%	31,49	33,20	34,82	36,35	35,98	37,46	38,85	40,18
Amount of Carbon not Emitted	%	96,24	96,05	95,88	95,71	96,44	96,26	96,10	95,94

INLET – Equivalent MOLAR FLOW of CO ₂									
<i>COMBINATION</i>	%	Feedstock: 25% NG - 75% BG Burner Fuel: 75% NG - 25% BG	Feedstock: 25% NG - 75% BG Burner Fuel: 50% NG - 50% BG	Feedstock: 25% NG - 75% BG Burner Fuel: 25% NG - 75% BG	Feedstock: 25% NG - 75% BG Burner Fuel: 0% NG - 100% BG	Feedstock: 0% NG - 100% BG Burner Fuel: 75% NG - 25% BG	Feedstock: 0% NG - 100% BG Burner Fuel: 50% NG - 50% BG	Feedstock: 0% NG - 100% BG Burner Fuel: 25% NG - 75% BG	Feedstock: 0% NG - 100% BG Burner Fuel: 0% NG - 100% BG
Natural Gas feedstock	kmol/hr	406,58	406,58	406,58	406,58	0,00	0,00	0,00	0,00
Natural Gas fuel	kmol/hr	479,89	319,93	159,96	0,00	479,89	319,93	159,96	0,00
biogas feedstock	kmol/hr	1805,49	1805,49	1805,49	1805,49	2407,32	2407,32	2407,32	2407,32
biogas fuel	kmol/hr	236,79	473,58	710,36	947,15	236,79	473,58	710,36	947,15
Biomethane feedstock	kmol/hr	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Biomethane fuel	kmol/hr	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Total Inlet	kmol/hr	2928,75	3005,57	3082,40	3159,22	3124,00	3200,83	3277,65	3354,48
OUTLET – Equivalent MOLAR FLOW of CO ₂									
Urea Carbon Content	kmol/hr	1661,43	1661,43	1661,43	1661,43	1640,70	1640,70	1640,70	1640,70
TOTAL CO ₂ to storage	kmol/hr	1168,62	1237,68	1306,79	1375,90	1380,42	1449,48	1518,58	1587,69
Total not emitted	kmol/hr	2830,05	2899,11	2968,22	3037,33	3021,12	3090,18	3159,28	3228,39
Flue gas to stack	kmol/hr	75,35	83,02	90,70	98,38	75,35	83,02	90,70	98,38
Vents	kmol/hr	8,00	9,00	10,00	11,00	12,00	13,00	14,00	15,00
Emission	kmol/hr	83,35	92,02	100,70	109,38	87,35	96,02	104,70	113,38
Total Outlet	kmol/hr	2913,40	2991,13	3068,91	3146,70	3108,46	3186,20	3263,98	3341,77
Equivalent CO ₂ in Urea Product %	%	56,73	55,28	53,90	52,59	52,52	51,26	50,06	48,91
Captured CO ₂ to Storage %	%	39,90	41,18	42,40	43,55	44,19	45,28	46,33	47,33
Amount of Carbon not Emitted	%	96,63	96,46	96,30	96,14	96,71	96,54	96,39	96,24

Equivalent CO ₂ MASS FLOW in Streams (kg/hr)							
		HYCO Plant	Base Case	Feedstock Replacement 75% NG 25% BG	Feedstock Replacement 50% NG 50% BG	Feedstock Replacement 25% NG 75% BG	Feedstock Replacement 0% NG 100% BG
Natural gas (as Feedstock)	kg/hr	71592.7807	71592.7807	53680.0051	35796.3647	17893.3350	0.0000
Natural gas (as Fuel)	kg/hr	28159.8271	28159.8271	28159.8271	28159.8271	28159.8271	28159.8271
TOTAL CO₂ from Natural Gas	kg/hr	99752.6078	99752.6078	81839.8322	63956.1918	46053.1621	28159.8271
Biogas (as Feedstock)	kg/hr	0.0000	0.0000	26486.3993	52987.1627	79459.1977	105945.5972
Biogas (as Fuel)	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL CO₂ from Biogas	kg/hr	0.0000	0.0000	26486.3993	52987.1627	79459.1977	105945.5972
Biomethane (as Feedstock)	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Biomethane (as Fuel)	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL CO₂ from Biomethane	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL equivalent mass flow of CO₂	kg/hr	99752.6078	99752.6078	108326.2315	116943.3545	125512.3598	134105.4243
Equivalent CO ₂ MASS FLOW Emitted from <i>FEEDSTOCK</i>							
Biogenic CO ₂	kg/hr	0.00	0.00	26486.40	52987.16	79459.20	105945.60
Fossil CO ₂	kg/hr	71592.78	71592.78	53680.01	35796.36	17893.34	0.00
TOTAL Equivalent CO₂ from Feedstock	kg/hr	71592.78	71592.78	80166.40	88783.53	97352.53	105945.60
% Biogenic CO ₂ in Feedstock	%	0.00	0.00	33.04	59.68	81.62	100.00
% Fossil CO ₂ in Feedstock	%	100.00	100.00	66.96	40.32	18.38	0.00

% TOTAL	%	100.00	100.00	100.00	100.00	100.00	100.00
<i>Actual ONLY CO₂ Present in Syngas before MDEA capture</i>	<i>kg/hr</i>	-	70127.8749	78825.2001	87504.6562	96096.6457	104683.3982
Actual ONLY CO ₂ Present in Syngas after capture	<i>kg/hr</i>	-	1030.6160	1156.2684	1267.7963	1378.9636	1558.4978
<i>Actual ONLY CO₂ Released from Stripper</i>	<i>kg/hr</i>	-	69079.9100	77661.5421	86201.5514	94705.8856	103114.6928
Actual ONLY CO ₂ to PLANT	<i>kg/hr</i>	68988.48	69080.0658	72333.0154	72749.9885	73119.0252	72206.7030
Actual ONLY CO ₂ to STORAGE	<i>kg/hr</i>	0.00	0.0000	5328.7018	13451.7572	21587.0740	30908.2222
% of CO₂ going to Storage From TOTAL	%	0.00	0.00	6.86	15.61	22.79	29.97
<i>Mass flow of Biogenic CO₂ going to Storage</i>	%	0.0000	0.0000	1760.5645	8028.1835	17619.3832	30908.2222
Negative Emission Achieved from FEEDSTOCK (REVIEW)	<i>kg/hr</i>	0.00	0.00	2.20	9.04	18.10	29.17
Equivalent CO₂ MASS FLOW Emitted from <i>FLUEGAS</i>							
Biogenic CO ₂	<i>kg/hr</i>	0.00	0.00	0.00	0.00	0.00	0.00
Fossil CO ₂	<i>kg/hr</i>	28159.83	28159.83	28159.83	28159.83	28159.83	28159.83
TOTAL CO₂	<i>kg/hr</i>	28159.83	28159.83	28159.83	28159.83	28159.83	28159.83
Captured CO ₂ from BIOGAS Fluegas (90%)	<i>kg/hr</i>	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL CO ₂ present in Fluegas before Capture	<i>kg/hr</i>	-	29781.05	29781.05	29781.05	29781.05	29781.05
Negative Emission Achieved	%		0.00	0.00	0.00	0.00	0.00

% TOTAL	%	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
<i>Actual ONLY CO₂ Present in Syngas before MDEA capture</i>	<i>kg/hr</i>	70127.8749	70127.8749	70127.8749	70127.8749	70127.8749	70127.8749	70127.8749	70127.8749
Actual ONLY CO ₂ Present in Syngas after capture	<i>kg/hr</i>	1030.6160	1030.6160	1030.6160	1030.6160	1030.6160	1030.6160	1030.6160	1030.6160
<i>Actual ONLY CO₂ Released from Stripper</i>	<i>kg/hr</i>	69079.9100	69079.9100	69079.9100	69079.9100	69079.9100	69079.9100	69079.9100	69079.9100
Actual ONLY CO ₂ to PLANT	<i>kg/hr</i>	69080.0658	69080.0658	69080.0658	69080.0658	69080.0658	69080.0658	69080.0658	69080.0658
Actual ONLY CO ₂ to STORAGE	<i>kg/hr</i>	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
% of CO₂ going to Storage From TOTAL	%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>Mass flow of Biogenic CO₂ going to Storage</i>	%	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Negative Emission Achieved from FEEDSTOCK (REVIEW)	<i>kg/hr</i>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Equivalent CO₂ MASS FLOW Emitted from <i>FLUEGAS</i>									
Biogenic CO ₂	<i>kg/hr</i>	10420.98	20841.95	31262.93	41683.91	6846.28	13692.60	20538.90	27385.20
Fossil CO ₂	<i>kg/hr</i>	21119.87	14079.91	7039.96	0.00	21119.87	14079.91	7039.96	0.00
TOTAL CO₂	<i>kg/hr</i>	31540.85	34921.87	38302.88	41683.91	27966.15	27772.52	27578.86	27385.20
Captured CO ₂ from BIOGAS Fluegas (90%)	<i>kg/hr</i>	9378.88	18757.76	28136.64	37515.52	6161.66	12323.34	18485.01	24646.68
TOTAL CO ₂ present in Fluegas before Capture	<i>kg/hr</i>	33159.56	36536.69	39915.82	43295.23	29587.38	29393.74	29199.95	29006.17
Negative Emission Achieved	%	28.28	51.34	70.49	86.65	20.83	41.93	63.30	84.97

Equivalent CO ₂ MASS FLOW in Streams (kg/hr)									
		Feedstock: 75% NG - 25% BG Burner Fuel: 75% NG - 25% BG	Feedstock: 75% NG - 25% BG Burner Fuel: 50% NG - 50% BG	Feedstock: 75% NG - 25% BG Burner Fuel: 25% NG - 75% BG	Feedstock: 75% NG - 25% RB Burner Fuel: 0% NG - 100% RB	Feedstock: 50% NG - 50% RB Burner Fuel: 75% NG - 25% RB	Feedstock: 50% NG - 50% RB Burner Fuel: 50% NG - 50% RB	Feedstock: 50% NG - 50% RB Burner Fuel: 25% NG - 75% RB	Feedstock: 50% NG - 50% RB Burner Fuel: 0% NG - 100% RB
Natural gas (as Feedstock)	kg/hr	53680.0051	53680.0051	53680.0051	53680.0051	35796.3647	35796.3647	35796.3647	35796.3647
Natural gas (as Fuel)	kg/hr	21119.8703	14079.9135	7039.9568	0.0000	21119.8703	14079.9135	7039.9568	0.0000
TOTAL CO₂ from Natural Gas	kg/hr	74799.8754	67759.9186	60719.9618	53680.0051	56916.2350	49876.2782	42836.3214	35796.3647
Biogas (as Feedstock)	kg/hr	26486.3993	26486.3993	26486.3993	26486.3993	52987.1627	52987.1627	52987.1627	52987.1627
Biogas (as Fuel)	kg/hr	10420.9771	20841.9542	31262.9280	41683.9085	10420.9771	20841.9542	31262.9280	41683.9085
TOTAL CO₂ from Biogas	kg/hr	36907.3764	47328.3535	57749.3273	68170.3078	63408.1398	73829.1169	84250.0907	94671.0712
Biomethane (as Feedstock)	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Biomethane (as Fuel)	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL CO₂ from Biomethane	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL equivalent mass flow of CO₂	kg/hr	111707.2518	115088.2721	118469.2892	121850.3129	120324.3748	123705.3951	127086.4122	130467.4359
Equivalent CO ₂ MASS FLOW Emitted from <i>FEEDSTOCK</i>									
Biogenic CO₂	kg/hr	26486.40	26486.40	26486.40	26486.40	52987.16	52987.16	52987.16	52987.16
Fossil CO₂	kg/hr	53680.01	53680.01	53680.01	53680.01	35796.36	35796.36	35796.36	35796.36
TOTAL Equivalent CO₂ from Feedstock	kg/hr	80166.40	80166.40	80166.40	80166.40	88783.53	88783.53	88783.53	88783.53
% Biogenic CO₂ in Feedstock	%	33.04	33.04	33.04	33.04	59.68	59.68	59.68	59.68
% Fossil CO₂ in Feedstock	%	66.96	66.96	66.96	66.96	40.32	40.32	40.32	40.32

% TOTAL	%	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
<i>Actual ONLY CO₂ Present in Syngas before MDEA capture</i>	<i>kg/hr</i>	78825.2001	78825.2001	78825.2001	78825.2001	87504.6562	87504.6562	87504.6562	87504.6562
Actual ONLY CO ₂ Present in Syngas after capture	<i>kg/hr</i>	1156.268395	1156.268395	1156.268395	1156.268395	1267.796327	1267.796327	1267.796327	1267.796327
<i>Actual ONLY CO₂ Released from Stripper</i>	<i>kg/hr</i>	77661.54212	77661.54212	77661.54212	77661.54212	86201.55139	86201.55139	86201.55139	86201.55139
Actual ONLY CO ₂ to PLANT	<i>kg/hr</i>	72333.0154	72333.0154	72333.0154	72333.0154	72749.9885	72749.9885	72749.9885	72749.9885
Actual ONLY CO ₂ to STORAGE	<i>kg/hr</i>	5328.701816	5328.701816	5328.701816	5328.701816	13451.75724	13451.75724	13451.75724	13451.75724
% of CO₂ going to Storage From TOTAL	%	6.86	6.86	6.86	6.86	15.61	15.61	15.61	15.61
<i>Mass flow of Biogenic CO₂ going to Storage</i>	%	1760.5645	1760.5645	1760.5645	1760.5645	8028.1835	8028.1835	8028.1835	8028.1835
Negative Emission Achieved from FEEDSTOCK (REVIEW)	<i>kg/hr</i>	2.20	2.20	2.20	2.20	9.04	9.04	9.04	9.04
Equivalent CO₂ MASS FLOW Emitted from <i>FLUEGAS</i>									
Biogenic CO ₂	<i>kg/hr</i>	10420.98	20841.95	31262.93	41683.91	10420.98	20841.95	31262.93	41683.91
Fossil CO ₂	<i>kg/hr</i>	21119.87	14079.91	7039.96	0.00	21119.87	14079.91	7039.96	0.00
TOTAL CO₂	<i>kg/hr</i>	31540.85	34921.87	38302.88	41683.91	31540.85	34921.87	38302.88	41683.91
Captured CO ₂ from BIOGAS Fluegas (90%)	<i>kg/hr</i>	9378.88	18757.76	28136.64	37515.52	9378.88	18757.76	28136.64	37515.52
TOTAL CO ₂ present in Fluegas before Capture	<i>kg/hr</i>	33159.56	36536.69	39915.82	43295.23	33159.56	36536.69	39915.82	43295.23
Negative Emission Achieved	%	28.28	51.34	70.49	86.65	28.28	51.34	70.49	86.65

Equivalent CO ₂ MASS FLOW in Streams (kg/hr)									
		Feedstock: 25% NG - 75% RB Burner Fuel: 75% NG - 25% RB	Feedstock: 25% NG - 75% RB Burner Fuel: 50% NG - 50% RB	Feedstock: 25% NG - 75% RB Burner Fuel: 25% NG - 75% RB	Feedstock: 25% NG - 75% RB Burner Fuel: 0% NG - 100% RB	Feedstock: 0% NG - 100% RB Burner Fuel: 75% NG - 25% RB	Feedstock: 0% NG - 100% RB Burner Fuel: 50% NG - 50% RB	Feedstock: 0% NG - 100% RB Burner Fuel: 25% NG - 75% RB	Feedstock: 0% NG - 100% RB Burner Fuel: 0% NG - 100% RB
Natural gas (as Feedstock)	kg/hr	17893.3350	17893.3350	17893.3350	17893.3350	0.0000	0.0000	0.0000	0.0000
Natural gas (as Fuel)	kg/hr	21119.8703	14079.9135	7039.9568	0.0000	21119.8703	14079.9135	7039.9568	0.0000
TOTAL CO₂ from Natural Gas	kg/hr	39013.2053	31973.2486	24933.2918	17893.3350	21119.8703	14079.9135	7039.9568	0.0000
Biogas (as Feedstock)	kg/hr	79459.1977	79459.1977	79459.1977	79459.1977	105945.5972	105945.5972	105945.5972	105945.5972
Biogas (as Fuel)	kg/hr	10420.9771	20841.9542	31262.9280	41683.9085	10420.9771	20841.9542	31262.9280	41683.9085
TOTAL CO₂ from Biogas	kg/hr	89880.1748	100301.1519	110722.1258	121143.1063	116366.5743	126787.5513	137208.5252	147629.5057
Biomethane (as Feedstock)	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Biomethane (as Fuel)	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL CO₂ from Biomethane	kg/hr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL equivalent mass flow of CO₂	kg/hr	128893.3802	132274.4005	135655.4176	139036.4413	137486.4446	140867.4649	144248.4820	147629.5057
Equivalent CO ₂ MASS FLOW Emitted from <i>FEEDSTOCK</i>									
Biogenic CO₂	kg/hr	79459.20	79459.20	79459.20	79459.20	105945.60	105945.60	105945.60	105945.60
Fossil CO₂	kg/hr	17893.34	17893.34	17893.34	17893.34	0.00	0.00	0.00	0.00
TOTAL Equivalent CO₂ from Feedstock	kg/hr	97352.53	97352.53	97352.53	97352.53	105945.60	105945.60	105945.60	105945.60
% Biogenic CO₂ in Feedstock	%	81.62	81.62	81.62	81.62	100.00	100.00	100.00	100.00
% Fossil CO₂ in Feedstock	%	18.38	18.38	18.38	18.38	0.00	0.00	0.00	0.00

% TOTAL	%	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
<i>Actual ONLY CO₂ Present in Syngas before MDEA capture</i>	<i>kg/hr</i>	96096.6457	96096.6457	96096.6457	96096.6457	104683.3982	104683.3982	104683.3982	104683.3982
Actual ONLY CO ₂ Present in Syngas after capture	<i>kg/hr</i>	1378.963648	1378.963648	1378.963648	1378.963648	1558.497794	1558.497794	1558.497794	1558.497794
<i>Actual ONLY CO₂ Released from Stripper</i>	<i>kg/hr</i>	94705.88563	94705.88563	94705.88563	94705.88563	103114.6928	103114.6928	103114.6928	103114.6928
Actual ONLY CO ₂ to PLANT	<i>kg/hr</i>	73119.02517	73119.02517	73119.02517	73119.02517	72206.70303	72206.70303	72206.70303	72206.70303
Actual ONLY CO ₂ to STORAGE	<i>kg/hr</i>	21587.07398	21587.07398	21587.07398	21587.07398	30908.22222	30908.22222	30908.22222	30908.22222
% of CO₂ going to Storage From TOTAL	%	22.79	22.79	22.79	22.79	29.97	29.97	29.97	29.97
<i>Mass flow of Biogenic CO₂ going to Storage</i>	%	17619.3832	17619.3832	17619.3832	17619.3832	30908.2222	30908.2222	30908.2222	30908.2222
Negative Emission Achieved from FEEDSTOCK (REVIEW)	<i>kg/hr</i>	18.10	18.10	18.10	18.10	29.17	29.17	29.17	29.17
Equivalent CO₂ MASS FLOW Emitted from <i>FLUEGAS</i>									
Biogenic CO ₂	<i>kg/hr</i>	10420.98	20841.95	31262.93	41683.91	10420.98	20841.95	31262.93	41683.91
Fossil CO ₂	<i>kg/hr</i>	21119.87	14079.91	7039.96	0.00	21119.87	14079.91	7039.96	0.00
TOTAL CO₂	<i>kg/hr</i>	31540.85	34921.87	38302.88	41683.91	31540.85	34921.87	38302.88	41683.91
Captured CO ₂ from BIOGAS Fluegas (90%)	<i>kg/hr</i>	9378.88	18757.76	28136.64	37515.52	9378.88	18757.76	28136.64	37515.52
TOTAL CO ₂ present in Fluegas before Capture	<i>kg/hr</i>	33159.56	36536.69	39915.82	43295.23	33159.56	36536.69	39915.82	43295.23
Negative Emission Achieved	%	28.28	51.34	70.49	86.65	28.28	51.34	70.49	86.65

