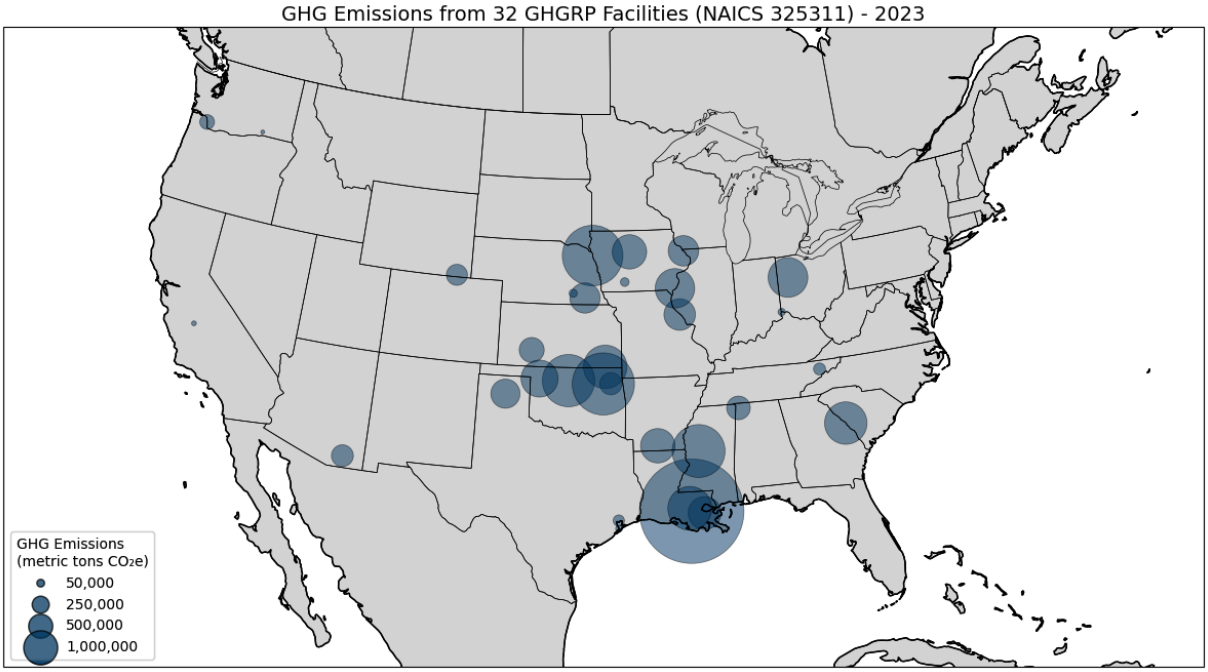
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NAICS Code: Nitrogenous Fertilizer Manufacturing (325311)
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Link to archetype code:
Archetype Name: Nitrogenous Fertilizer Manufacturing

SUMMARY INFO: The U.S. is the third-largest consumer of fertilizer in the world, accounting for 11% of global consumption.[1] Nitrogenous fertilizer manufacturing is a growing industry that uses natural gas to synthesize ammonia, producing final fertilizer products for agricultural and horticultural use. Nitrogenous fertilizer production is expected to reach $20.6 billion in annual revenue by 2032, due to increased demand for high-yield crops.[2] Nitrogenous fertilizer production is highly carbon-intense, releasing high levels of carbon dioxide, nitrous oxide, and methane.[3] The industry is also highly consolidated, with four firms controlling 75% of domestic production.[4]

Emissions and facility overview: According to the United States Census Bureau, there are 194 establishments associated with NAICS 325311 in the United States, 30 of which report annual GHG emissions in the GHGRP.[5] Reported emissions from GHGRP amounted to 10.1 MMT of CO_2e in 2023. The majority of these plants in the US are concentrated in the southeastern states, as summarized in the map below.



[1] The Fertilizer Institute. TFI Study Highlights Fertilizer Industry's $140 Billion Impact and Global Trade Ties. December 2024.
[2] Fortune Business Insights. Nitrogenous Fertilizer Market Size, Share & Industry Analysis, By Type (Urea, Calcium Ammonium Nitrate, UAN, Ammonium Sulphate, and Other Nitrogenous Fertilizers), By Crop Type (Cereals, Pulses & Oilseeds, Fruits & Vegetables, and Turf & Ornamentals), and Regional Forecast, 2019-2032. January 2026.
[3] Josie Heimsoth. Nitrogen Fertilizer Releases Greenhouse Gases Throughout Its Life Cycle. May 2023.
[4] Noah Zahn. Fertilizer companies cash in while farmers struggle. June 2023.
[5] U.S. Census Bureau. 325311: Nitrogenous Fertilizer Manufacturing. In 2023 Economic Surveys Business Patterns. 2023; U.S. Environmental Protection Agency. Greenhouse Gas Reporting Program (GHGRP). 2025.

Sector outputs: The nitrogenous fertilizer manufacturing sector produces both nitrogenous fertilizer materials and nitrogenous materials for mixing into fertilizers. It also manufactures fertilizers from sewage and animal waste.[6]

Process pathways: Ammonia, which is largely used for producing nitrogenous fertilizer, can be produced by three process pathways: steam methane reforming, electrolysis, and coal gasification. Countries such as China use coal gasification due to their abundance of coal, whereas steam methane reforming tends to be used in the United States due to stricter environmental protection laws. Electrolysis is not typically used nowadays.[7] Hence, the archetype for this sector models a steam methane reforming process for producing the ammonia used in nitrogenous fertilizer manufacturing.

Process Overview: A 99% pure methane stream at 25-30°C and 3-25 bar enters an adiabatic compressor that increases its temperature to 100 °C and its pressure to 32.5 bar, using 0.07 MJ of electricity/kg initial methane stream.[8] This compressor is assumed to have 85% efficiency. The stream then enters a preheater that uses 0.006 kg natural gas/kg initial methane stream, assuming 85% efficient fuel usage.[9] Moreover, a stream of air at twice the mass flow rate of the initial methane stream enters the preheater at 25 °C and exits at 340°C. Meanwhile, the methane stream is heated to 215 °C.[10]

The stream then enters a desulfurization unit, in which a stream of added ZnO reacts chemically to form ZnS. The chemical reactions are R-SH + H_2 -> H_2S + RH and H_2S + ZnO -> ZnS + H_2O. Just a small amount of ZnO is added, since only 17 ppm of ZnS forms/100 SCF of natural gas entering the preceding preheater.[11]

Next, the methane stream enters a primary reformer that operates at 815°C. In this chemical reactor, an endothermic catalytic reaction occurs at an enthalpy of 206 kJ/mol methane: CH_4 + H_2O -> CO + $3H_2$. A conversion of 60% is typically achieved. Water enters this reactor as 2.5-5 kg 250°C steam/kg initial methane stream into SMR. To reach the required temperatures, 0.21 kg natural gas/kg initial methane stream into SMR is required.[12] Moreover, 10% of methane in mass is required as compressed air and 0.53 MJ electricity/kg of initial methane stream into SMR is used to power the compressor. This assumes 85% efficient electricity usage. The air exits at 80 °C and 35 bar and enters the primary reformer.[13]

As a result, if 24.3 kg/s methane entering the SMR process is assumed, the main outlet stream emerging from this reformer is composed of 0.6 kmol/s methane, 3.6 kmol/s steam, 0.9 kmol/s CO and 2.9 kmol/s H_2. Meanwhile, the air that enters this reformer from the compressor also exits this reformer at

[6] Executive Office of the President Office of Management and Budget. North American Industry Classification System. 2022.
[7] Banafsheh Jabarivelisdeh et al. Model-Based Analysis of Ammonia Production Processes for Quantifying Energy Use, Emissions, and Reduction Potentials. November 2022.
[8] Harry L. Brown et al. Energy analysis of 108 industrial processes. 1996.
[9] International Energy Agency. Ammonia Technology Roadmap. October 2021.
[10] Harry L. Brown et al. Energy analysis of 108 industrial processes. 1996.
[11] Pacific Gas and Electric Company. Sulfur Information.
[12] Megan Strait et al. Synthesis Gas Reformers.
[13] Harry L. Brown et al. Energy analysis of 108 industrial processes. 1996.

550°C and 35 bar.[14] Finally, an exhaust stream is also emitted from this reformer, consisting of CO_2 and NO_x. This exhaust stream is subject to ongoing research on how to reduce its mass flow rate.[15]

The main outlet stream from the primary reformer now enters a secondary reformer. This secondary reformer is composed of two parts. The first part involves a combustion reaction at adiabatic condition and 35 bar. Assuming 24.3 kg/s methane entering the SMR process, 2.4 kmol/s air enters the first part of secondary reformer at 550 °C. The combustion reaction equation is $CH_4 + 3/2O_2 \rightarrow CO + 2H_2O$ at -520 kJ/mol methane, followed by $H_2 + 1/2O_2 \rightarrow H_2O$ at -242 kJ/mol water formed. A conversion of around 100% is achievable, resulting in a 1200 °C product stream consisting of 0.43 kmol/s methane, 4.44 kmol/s steam, 1.07 kmol/s CO, 2.4 kmol/s H_2, and 1.9 kmol/s N_2.[16] This product stream then enters the second part of the secondary reformer, in which another endothermic catalytic reaction takes place at 35 bar: $CH_4 + H_2O \rightarrow CO + 3H_2$ and $CO + H_2O \rightarrow CO_2 + H_2$ at 206 kJ/mol methane. A conversion of around 100% is also achievable here, resulting in a 990 °C product stream consisting of 3.51 kmol/s steam, 1.0 kmol/s CO, 0.5 kmol/s CO_2, 4.7 kmol/s H_2, and 1.9 kmol/s N_2.[17]

This product stream enters a heat recovery unit that cools it to 330-380 °C. Multiple options exist for the configuration of this heat recovery unit. One option, operating at 500°C and 32.5 bar, injects 0.0288 kg steam/kg initial methane stream into SMR at 180 °C, which then exits this unit at 315 °C.[18] The main product stream that exits this heat recovery unit then enters a shift converter that removes carbon monoxide using the exothermic water-gas shift reaction $CO + H_2O \rightarrow CO_2 + H_2$ at -41 kJ/mol CO removed. This reaction first takes place at 400 °C and then at 250 °C. A 180 °C stream of steam is injected at 0.00864 kg steam/kg initial methane stream into SMR, emerging at 315 °C. This amounts to 0.4 MMBtu steam/ton ammonia formed.[19] Furthermore, a conversion of around 100% is achievable in this reaction. As a result, assuming 24.3 kg/s methane entering the SMR process, the main product stream emerges at 30 – 35°C, consisting of 1.5 kmol/s CO2, 5.7 kmol/s H2, and 1.9 kmol/s N2. A 2.51 kmol/s water stream also exits this shift converter, albeit as a separate outlet stream.[20]

To remove CO_2 from this main product stream, the stream enters a CO_2 absorption unit that uses an adsorbent such as activated carbon, zeolite 5A, and monoethanolamine (MEA),[21] along with (0.1-0.3 MJ electricity/kg CO_2). This CO_2 removal unit often takes place in a pressure swing adsorption at 30 °C and 2-32.5 bar. As a result, we can assume that the CO_2 removal efficiency is around 100%.[22]

[14] Megan Strait et al. Synthesis Gas Reformers.
[15] James Clarke et al. U.S. Average Nitrogen Fertilizer Production Baseline Documentation for 45Q Life Cycle Analysis. June 2024.
[16] Sukmanto Dibyo et al. Analysis on Operating Parameter Design to Steam Methane Reforming in Heat Application RDE. 2018.
[17] Ali Ashour Al-Dhfeery and Ala'a Abdulrazaq Jassem. Modeling and Simulation of an Industrial Secondary Reformer Reactor in the Fertilizer Plants. July 2012.
[18] Harry L. Brown et al. Energy analysis of 108 industrial processes. 1996.
[19] ScienceDirect. High-Temperature Shift Reactor: An Overview.
[20] Seyed Reza Janbarari and Ali Tajeri Najafabadi. Simulation and Optimization of Water Gas Shift Process in Ammonia Plant: Maximizing CO Conversion and Controlling Methanol Byproduct. July 2023.
[21] Banafsheh Jabarivelisdeh et al. Model-Based Analysis of Ammonia Production Processes for Quantifying Energy Use, Emissions, and Reduction Potentials. November 2022.
[22] Harry L. Brown et al. Energy analysis of 108 industrial processes. 1996.

In case some CO and CO_2 do remain in the main product stream at this point, the stream enters a methanation unit to complete their removal process. Two chemical reactions take place: $CO + 3H_2$ -> $CH_4 + H_2O$ at -206 kJ/mol CO and $CO_2 + 4H_2$ -> $CH_4 + 2H_2O$ at -165 kJ/mol CO_2.[23] These reactions take place at 200-550 °C. Moreover, water from the two chemical reactions exits as a separate outlet stream relative to the main outlet stream emerging from this methanation unit.[24]

Prior to entering the synthesis chemical reactor that produces the desired ammonia, the main product stream from methanation first undergoes adiabatic compression to ensure that the stream is at 100 – 200 bar. This compressor is powered by 0.25 MJ electricity/kg initial methane stream into SMR, corresponding to 85% efficiency. To prevent the temperature of the main compressor outlet from exceeding 270 °C, 4.67 kg cooling water/kg initial methane stream into SMR is injected into the compressor at 30 °C, which increases to 90 °C upon emerging from the compressor.[25] The main compressor outlet then enters an indirect-fired heater that increases its temperature to 450 °C. This is done using 0.050 kg natural gas/kg initial methane stream into SMR, corresponding to 85% heating efficiency.[26] The process stream of interest now enters the synthesis reactor.

Ammonia is formed in the synthesis reactor via $N_2 + 3H_2$ -> $2NH_3$ at -46 kJ/mol ammonia formed, resulting in a conversion of 20 – 30%. This occurs at 350-550 °C and 100-250 bar. A stream of cooling water at a rate of 3.1l of cooling water per kg of methane going into the SMR is injected into the reactor to cool the product stream to 210 °C prior to entering a low-pressure steam generation and boiler feed water preheat unit. The cooling water emerges from the reactor as high-pressure steam.[27] In the low-pressure steam generation and boiler feed water preheat unit where the main ammonia product enters, a stream of 1.2 kg water at 100 °C/kg initial methane stream into SMR and a stream of 6.8 kg water at 30°C/kg initial methane stream into SMR are also injected. Aside from the main ammonia stream emerging from the unit at 35 °C, the low-pressure steam generation and boiler feed water preheat unit also produces low-pressure steam and a stream of water at 100 °C. Assuming 24.3 kg/s methane entering the SMR process, the main ammonia stream from this unit contains 13.3 kmol/s H_2, 4.433 kmol/s N_2, and 3.8 kmol/s ammonia.[28]

The main ammonia stream is now cooled using 6.4 kg water at 10 °C/kg initial methane stream into SMR, so that the ammonia stream condenses at 26.9 °C. This water stream emerges from the cooler at 20°C. Aside from the stream that contains mainly ammonia at 25 °C, the cooler produces a purge gas stream,[29] along with a stream containing H_2 and N_2 from the initial ammonia stream that emerged from the synthesis reactor. This H_2 and N_2 stream is heated at 85% efficiency using 0.19 kg natural gas/kg

[23] Richard M. Felder and Ronald W. Rousseau. Elementary Principles of Chemical Processes. 2005.
[24] Harry L. Brown et al. Energy analysis of 108 industrial processes. 1996.
[25] International Energy Agency. Ammonia Technology Roadmap. October 2021.
[26] James Clarke et al. U.S. Average Nitrogen Fertilizer Production Baseline Documentation for 45Q Life Cycle Analysis. June 2024.
[27] Ahmet K. Avci and Z. Ilsen Önsan. Catalysts. 2018.
[28] International Energy Agency. Ammonia Technology Roadmap. October 2021.
[29] Brian P. Flannery, and Jan W. Mares. Greenhouse Gas Index for Products in 39 Industrial Sectors: Nitrogenous Fertilizer Manufacturing. RFF. September 2022.

initial methane stream into SMR and is then recycled to the synthesis reactor.[30] Meanwhile, the cooled ammonia enters an ammonia splitter at 25 °C that, aside from some ammonia itself, returns three other products: urea, ammonium sulfate, and a mixture of nitric acid and ammonium nitrate.[31]

From the ammonia that enters the splitter, 15.2% of it is used to form urea, 1.8% is used to form ammonium sulfate, and 29% is used to form the nitric acid and ammonium nitrate mixture. The rest of the ammonia exits the SMR process to be used for nitrogenous fertilizer production.[32] For the ammonia used to form urea, urea is produced at a rate of 1.77 kg/kg ammonia. For the ammonia used to form ammonium sulfate, ammonium sulfate is produced at a rate of 7.8 kg/kg ammonia. Finally, for the ammonia used to form nitric acid and ammonium nitrate, the mixture is produced at a rate of 2.8 kg/kg ammonia. Half of the mixture mass is composed of nitric acid and the other half is ammonium nitrate.[33] These split and production rates are typical industry standard.

For the ammonia used to form urea, the ammonia is first preheated to 160°C using 0.11 kg saturated steam/kg urea produced. This steam is injected at 180 °C and 10 bar. In addition, a stream of 0.52 kg CO_2/kg initial methane stream into SMR enters a compressor powered by 0.23 MJ electricity/kg urea produced, which corresponds to 85 % energy efficiency. This CO_2 is compressed to 200 bar and also enters the preheater. The steam that enters the preheater emerges from it as hot water. Moreover, both the CO_2 and the ammonia streams that leave the preheater enter a urea process unit.[34] The chemical reaction $2NH3 + CO_2 \rightarrow CO(NH_2)_2 + H_2O$ occurs in this process unit at -117 kJ/mol urea formed. A conversion of 80-100% is typically achievable at 160-200 °C and 150 – 300 bar.[35] Assuming 24.3 kg/s methane entering the SMR process, 0.289 kmol/s urea and 0.289 kmol/s water are produced by the urea process unit in a single outlet stream. To ensure that the urea product temperature is 190°C, 5.1 kg cooling water/kg initial methane stream into SMR enters the process unit at 30°C, which then emerges at 90°C.[36] Finally, while some of the urea produced is used to form urea ammonium nitrate, others enters a process unit that uses deionized water to form a 32.5% urea solution in deionized water at eutectic point.[37]

For the ammonia used to form nitric acid and ammonium nitrate, 70% of it first undergoes a series of chemical reactions known as the *Ostwald process*. It is first preheated at 85% efficiency using 0.11 kg natural gas/kg nitric acid produced. Moreover, 9.3 kg air/kg initial methane stream into SMR at 1 bar enters a compressor powered at 85% efficiency by 0.076 MJ electricity/kg nitric acid produced. Aside from this preheated ammonia split, 12.4 kg air/kg initial methane stream into SMR exits the preheater at 4 bar, and both streams then enter the Ostwald process unit. Four adiabatic and isothermal chemical reactions occur at 800-900 °C and 4-10 bar on a platinum catalyst in this process unit: $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ at -907 kJ/4 mol NH3, $4NO + 2O_2 \rightarrow 4NO_2$ at -147 kJ/2 mol NO, $3NO_2 + H_2O \rightarrow 2HNO_3$

[30] Harry L. Brown et al. Energy analysis of 108 industrial processes. 1996.
[31] Casale SA. N-ELEVA™ — SMR-Based Ammonia Process for Traditional Plants. 2024.
[32] Banafsheh Jabarivelisdeh et al. Model-Based Analysis of Ammonia Production Processes for Quantifying Energy Use, Emissions, and Reduction Potentials. November 2022.
[33] International Finance Corporation. Nitrogenous Fertilizer Plants. 2005.
[34] Kevin Rouwenhorst. Decarbonizing Urea Production in India via Renewable Ammonia. December 2024.
[35] Prem Baboo. Fundamentals of Ammonia Plants. 2020.
[36] Mosaic. Urea Ammonium Nitrate.
[37] Kevin Rouwenhorst. Decarbonizing Urea Production in India via Renewable Ammonia. December 2024.

+ NO at 19 kJ/3 mol NO_2, and $4NO_2 + 1.33H_2O$ -> $2.67HNO_3 + 1.33NO$ at 8.6-11.3 MMBtu/ton HNO_3. A conversion of 100% is typically achievable under this process condition. Assuming 24.3 kg/s methane entering the SMR process, 0.75 kmol/s HNO_3, 0.75 kmol/s NO, 0.8 kmol/s H_2O, 0.11 kmol/s O2, and 5.86 kmol/s N_2 emerge from the Ostwald unit.[38] Furthermore, the unit can emit 5 – 8 kg N_2O/ton HNO_3 produced, which can act as a greenhouse gas.[39]

Both the nitric acid formed in the Ostwald process unit and the 30% of ammonia used for nitric acid and ammonium nitrate production are cooled to 180 °C using 4.1 kg water at 30 °C/kg initial methane stream into SMR, which itself emerges from the cooler at 90 °C. The cooled ammonia and nitric acid now enter the ammonium nitrate process unit to undergo the chemical reaction $HNO_3 + NH_3$ -> NH_4NO_3 at -365 kJ/mol ammonium nitrate produced. This reaction, for which 100% conversion is achievable, occurs at 170 – 185°C and 4 – 6 bar, resulting in an adiabatic temperature rise of 5 °C. Assuming 24.3 kg/s methane entering the SMR process, 0.33 kmol/s ammonium nitrate and 0.42 kmol/s nitric acid emerge as a mixture at 185 °C.[40] Finally, recall that some of the urea produced by the urea process unit is used to form urea ammonium nitrate. A roughly equal mass flow rate of urea as this mixture of ammonium nitrate and nitric acid enters a urea ammonium nitrate process unit as two distinct streams to form urea ammonium nitrate.[41] Urea ammonium nitrate can also be used as fertilizer in liquid form. At the same time, the production of urea ammonium nitrate typically produces neither harmful emissions nor any waste product.[42]

For the ammonia used to produce ammonium sulfate, it first enters a preheater, along with a stream of H_2SO_4 at 0.27 kg/kg initial methane stream into SMR, both at 25 °C. This preheater uses 0.016 kg saturated steam/kg ammonium sulfate produced at 100°C and 1 bar. As a result, the H_2SO_4 and ammonia streams exit the preheater at 60 °C prior to entering an ammonium sulfate process unit. In this process unit, the chemical reaction $2NH_3 + H_2SO_4$ -> $(NH_4)_2SO_4$ occurs at -116 kJ/mol ammonium sulfate produced. The reaction takes place at 30°C – 80°C and 1 – 2 bar and does so under both adiabatic and isothermal conditions. As a result, assuming 24.3 kg/s methane entering the SMR process, 0.134 kmol/s ammonium sulfate is produced.[43]

[38] ChemEurope. Ostwald process.
[39] Endress+Hauser. Emission Monitoring Solutions.
[40] International Energy Agency. Ammonia Technology Roadmap. October 2021.
[41] Mosaic. Urea Ammonium Nitrate.
[42] James Clarke et al. U.S. Average Nitrogen Fertilizer Production Baseline Documentation for 45Q Life Cycle Analysis. June 2024.
[43] Pacific Gas and Electric Company. Sulfur Information.

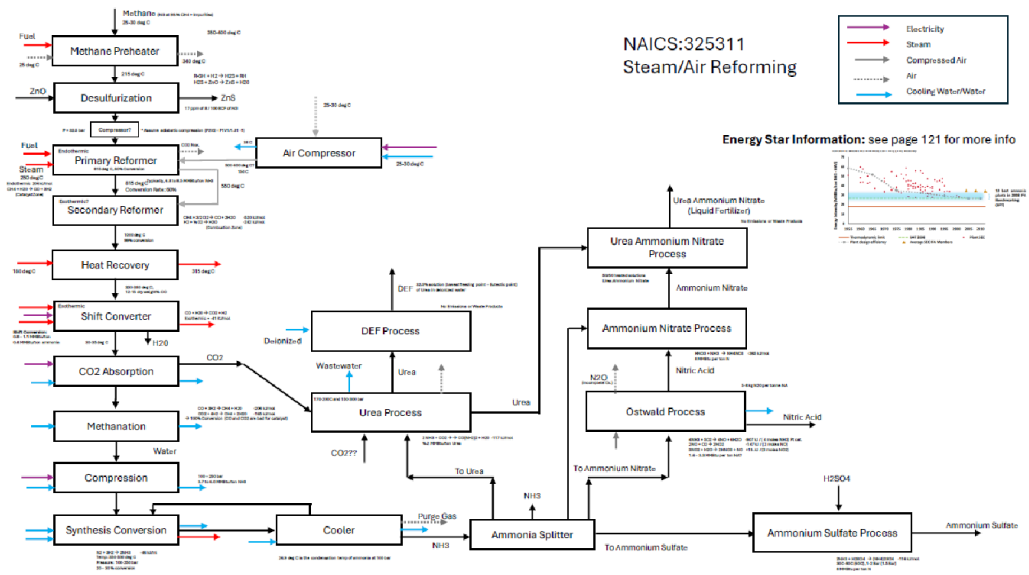


Figure 1: Process Flow Diagram for Nitrogenous Fertilizer Manufacturing

Archetype Unit Process Assumptions: Figure 1 depicts the unit processes, mass flows, and energy flows modeled in our process system archetype. Assumptions taken have been included in text.

Limitations and future work: The sources consulted and our archetype for this sector have discrepancies in energy demand between them. Moreover, we explored only the SMR process for making ammonia, whereas ammonia can be formed also via electrolysis and coal gasification. Future work should also investigate the two latter approaches for ammonia production to identify the key differences in process units and energy demands involved in nitrogenous fertilizer manufacturing.