A Superstructure Based Optimization for the Development of Green Fertilizers

Justin Galin, Dr. Juan Manuel Restrepo-Flórez

Abstract

Ammonia is currently produced via the Haber-Bosch Process at high temperatures and pressures and uses hydrogen which is typically produced from natural gas. These factors lead to ammonia production's noticeable contribution towards global carbon emissions. However, this is not the only method of producing fertilizer and this paper will aim to explore cleaner ways of producing fertilizers using gasification, electrolysis, electrocatalysis, and urea production. First, a superstructure was developed to map the methods of producing ammonia and urea fertilizer. Then, these processes were modeled in Aspen Plus to obtain costing and flow parameters. Finally, a mathematical model was developed and programmed in GAMS to represent the superstructure. The objective function maximizes net present value (NPV) when producing ammonia and/or urea. Results indicate that the biomass gasification to Haber-Bosch route is the optimal pathway to produce profitable fertilizer. This paper provides a starting point for future exploration of green ammonia production and how CO2 incentives may allow for more profitable urea production.

Introduction

Fertilizers have been of vital importance for humans since the advent of farming and have only become more important over time. Fertilizers are used to provide critical macro and micronutrients to plants. The focus of this work is in nitrogen. Most nitrogen exists as inert gas in the atmosphere that is difficult to use or transform due to the strong triple bonds that hold together nitrogen atoms. Before synthetic fertilizers were commercialized the primary pathway to transform atmospheric nitrogen into ammonia (a molecule that can be readily used by plants) was via nitrifying bacteria.[6,12] Fertilizers were so scarce that in previous centuries bird guano with high nitrogen content, was a major commodity and a source of international conflict.[28] These methods alone could not sustain the rapid pace of population growth and so Fritz Haber and Carl Bosch developed a method to synthesize the fertilizer ammonia, NH_3, using nitrogen and hydrogen gas as feedstocks with an iron catalyst at extreme temperatures and pressures.[5] The Haber-Bosch Process has remained the dominant means of fertilizer production into the present and has brought its problems with it. The main problem with the process is that due to its operation at extreme temperature and pressures, as well as its reliance on hydrogen gas as a feedstock it has become a sizeable contributor towards global carbon emissions.[9] As the world moves towards becoming a more sustainable place, alternatives for this century old process need to be explored to reduce global carbon emissions.

Ammonia is worthwhile studying because it is a valuable product with a cost of around US \$500/t with a worldwide market value of \$250 billion.[5] Each year about 400 million metric tons of ammonia fertilizer are produced along with 12 giga tons of CO_2 equivalents which accounts for around 1.5% of carbon emissions world-wide.[5] Currently more than 80% of ammonia produced is used directly as a fertilizer, the remaining 20% is used to produce urea and ammonium nitrate.[1] Urea production is performed using the Bazarov reaction $NH_3 + CO_2 \rightarrow NH_2CONH_2 + H_2O$ which is notable as the process produces a valuable fertilizer while consuming CO_2.[10] While most of the ammonia consumption is in fertilizer-based products, ammonia also presents potential as an energy

carrier due to its high hydrogen content. Hydrogen gas is an exciting fuel alternative but presents problems due to its low energy density and limited methods of storage and transport.[7] Ammonia has a much higher boiling point compared to hydrogen and can be feasibly transported and stored as a liquid and later converted to hydrogen when ready to be used as fuel.[1]

While a useful product, ammonia production is plagued with a large carbon footprint due to the energy usage needed to attain the high temperatures and pressures needed in the Haber-Bosch process ($2N_2 + 3H_2 \rightarrow 2NH_3$). These extreme conditions are required to push equilibrium towards the products while having a high rate of reaction. In addition to the high utility usage required of the Haber-Bosch Process, ammonia production necessitates hydrogen gas which itself has a sizeable carbon footprint resulting from the cryogenic separation process and required to achieve the required level of purity.[8] The most economically viable hydrogen production method is steam methane reforming (SMR) $CH_4(g) + H_2O(g) \leftrightharpoons CO(g) + 3H_2(g)$ coupled with the water gas shift reaction $CO(g) + H_2O(g) \leftrightharpoons CO_2(g) + H_2(g)$ but due to its use of methane from fossil sources (although biological derived methane is a possibility) and high temperature and pressure is also carbon intensive. Greener alternatives to the Haber-Bosch Process as a whole or just to hydrogen production from SMR represent a large potential for reduction in global carbon emissions due to ammonia's large scale of production and high carbon emissions.

Exploring every possible combination of processes to determine the optimal pathway to produce ammonia is possible but cumbersome as each simulation requires significant effort. An alternative to this exhaustive approach is to develop a network of possible combinations of processes called a superstructure and use it to formulate an optimization problem that will determine the best pathway.[28] This greatly reduces the time needed to configure combinations of flowsheets and is especially useful when considering a large number of processes.[11] Furthermore, considering all alternatives simultaneously allows to identify synergies and trade-offs that otherwise are difficult to spot.

Many studies exist that have explored alternatives and potential solutions to the problems presented thus far. Technologies such as electrocatalytic pathways towards directly producing ammonia without the Haber-Bosch process as well as technologies like electrolysis and biomass gasification which present alternatives to hydrogen production represent especially promising possibilities.[6] While these and many more technologies have been explored individually there has been little research done on considering all these technologies at once with an optimization approach. A superstructure-based optimization presents additional complexity due to the necessity to develop and program a mathematical model but in return provides not only a result that shows the most promising alternatives but also a tool that allows for robust sensitivity analysis and the exploration of multiple objectives.

This study aims to develop a superstructure encompassing promising methods of ammonia production, using Aspen Plus® as a tool to identify relevant cost parameters associated with each superstructure element; finally, a mathematical model that can be solved as an optimization problem in GAMS is developed. There are plentiful innovative methods of producing ammonia, especially in regard to electrochemistry; for both the electrochemical production of hydrogen gas from water as well as the electrocatalytic conversion of water and nitrogen gas to ammonia there are many routes that were not considered for the purposes of this paper. Instead, the focus of this paper is to identify the most promising areas to focus future developments on and compare them to the industry standard.

Methodology

Developing the Superstructure

Research started by conducting a literature review on the potential methods to produce ammonia and hydrogen gas. From the literature it was concluded that by far the most common method for ammonia production is the Haber-Bosch Process; however, new processes involving electrocatalysis and biochemistry are being developed and may show promise as cleaner alternatives in the future. Greener methods of producing hydrogen gas were also researched as hydrogen is a key reagent in the production of ammonia and is most commonly produced through SMR which has a significant carbon footprint. The most promising alternative technologies to SMR were found to be biomass gasification and water electrolysis. Biomass gasification is a process similar to SMR but with the key difference that it only requires biomass as a reactant as opposed to SMR which requires natural gas (most commonly of fossil origin). In contrast, water electrolysis forgoes the aforementioned gasification methods and harnesses the power of electricity to split water into hydrogen and oxygen. There are three main types of electrolysis that are currently being explored for uses in hydrogen production, Alkaline Water Electrolysis (AWE), Polymer Electrolyte Membrane Water Electrolysis (PEM), and Solid Oxide Water Electrolysis (SOE).[2] AWE is the most prevalent technology in current electrolytic hydrogen production due to its general simplicity that results in lower capital and catalyst costs. Both PEM and SOE have advantages, PEM being well suited as a candidate for electrolysis from solar electricity due to its flexible operation and SOE having high potential for large scale systems due to high thermal and kinetic efficiency, however for the purposes of this study we will only consider AWE as it is the most mature technology.[2] Another promising technology that aims to replace the Haber-Bosch Process is electrochemical ammonia production. This process takes in water and nitrogen gas as feedstocks and converts them directly to ammonia. The process works by first producing H^+ ions through water electrolysis in the anode and then after migrating through a proton exchange membrane and reacting the ions with nitrogen gas ammonia is produced.[14] Additionally, methods of producing urea as an alternative fertilizer were explored. The important process for the purpose of this study regarding the production of urea was found to be the Bazarov reaction $2NH_3 + CO_2 \rightarrow (NH_2)_2CO + H_2O$ which consumes ammonia and carbon dioxide to produce urea (after going through an ammonium carbamate intermediate). This process is of significant interest as it consumes CO_2 and yields urea, a valuable fertilizer, with a global demand of 187.8 million metric tons and expected growth of 2% by 2026.[4] the processes explored were used to formulate the superstructure associated with this process (Figure 1).
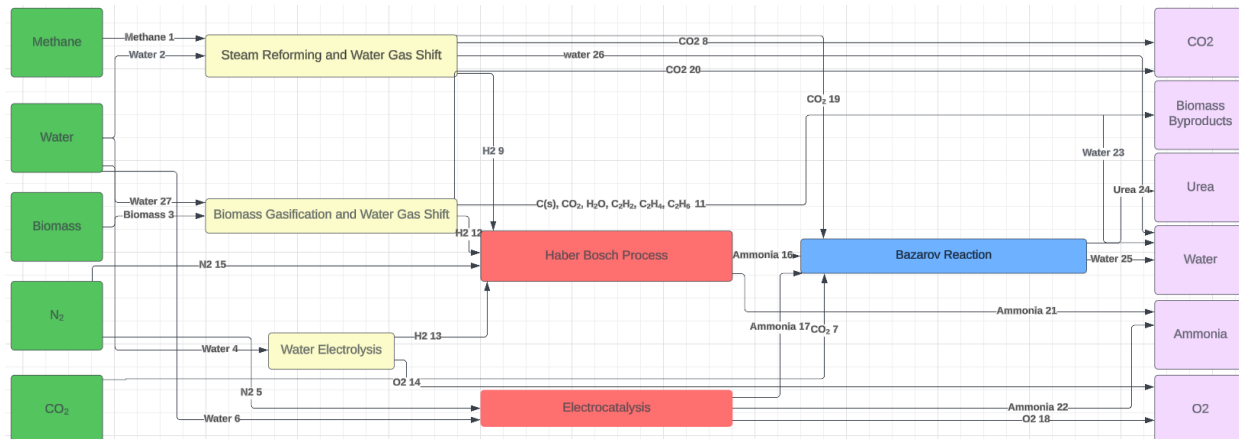
Figure 1. Sustainable ammonia production superstructure. Green blocks are feedstocks, yellow are hydrogen production, red are ammonia production, blue are urea production, and purple are products/wastes. Streams are labeled according to their components followed by their stream number.

Modeling and Costing in Aspen Plus

Now that a superstructure has been formulated, it is important to develop process simulations for each of the six blocks, we will use these simulations to identify cost related parameters and utility consumption for each process. Importantly, in the electrolysis process we use literature reports instead of detailed simulations.[13] Aspen Plus® simulations include included modeling of the reactor, the separation network following the reactor, and any recycle loops. Heat exchanger networks for each process were also developed through Aspen Energy Analyzer (AEA). This design information was then used to obtain capital (CAPEX) and operating costs (OPEX). Any equipment that could not be costed in Aspen was costed by using a similar reference in the literature. Catalysts, if present, were costed according to literature values for their cost, the weight hour space velocity (WHSV) was used to obtain the required mass of catalyst, a shelf life of one year was assumed. OPEX were calculated using the energy usage values obtained from the AEA heat exchanger networks. These values were then converted to USD/year using prices from Aspen Plus® along with price of feedstock and catalyst, cost of wastewater treatment, and fixed costs. Finally, estimates for the carbon production associated with the utility use, feedstock use, and CO_2 as products were calculated using CO_2 emission factor literature values.

Table 1. Reference Flow, CAPEX, OPEX, and Carbon Emissions from Utilities of each process

Process	Reference Flow (kg/s)	CAPEX (M$/year)	OPEX (M$/year)	GHG emissions from utilities (M kg CO_2/year)
SMR	1.6	15	27	110
BiomassGasification	1.4	51	12	27
AWE	0.027	0.74	0.36	88
Haber-Bosch	0.078	45	4.3	17
Electrocatalysis	0.56	50	7.6	18
Urea Production	4.7	86	130	56

Mathematical Model

After finishing the cost and emission estimation the mathematical model that will be used to optimize the superstructure is developed. The model defines the set of elements in the superstructure as any block in the diagram and represents them with the index $i \in I$. Streams are represented as connections between these blocks and are represented with the index $j \in J$. Finally, a set of components is defined with the index $k \in K$. Our goal is to develop a multi-objective model in which we pursue maximization of net present value NPV [Eq. 1][4] and minimization of GHG emissions [Eq. 2]. NPV was chosen as it is a robust economic metric that allows the model to take into account the time value of money, which a simpler metric like profit would not. (parameters are in red). NPV is summed over all chosen processes to obtain the objective function.

$$NPV = \sum_{m=1}^{n} \frac{(R-X)_m(1-t)}{(1+r)^m} + \sum_{m=1}^{n} \frac{D_m t}{(1+r)^m} + \frac{C_S + C_W}{(1+r)^n} - (C_I + C_W) \quad (1)$$

Where C_I = fixed capital investment, C_S = salvage value, C_W = working capital, r = after tax rate of return (0.1), n = useful plant life (set to 10), R = sales/year, X = manufacturing costs, D = depreciation/year, t = tax rate (set as 0.21), profit/year = $(R-X)$, taxes = $(R-X-D)*t$, and after tax profit = $(R-X)(1-t)+Dt$.

$$\sum_{i=1}^{n} [FCE_i + UCE_i + PCE_i - CCE_i] = GHG \quad (2)$$

Where FCE_i is the carbon emissions associated with the feedstocks used in process i, UCE_i is carbon emissions associated with the utility usage in process i, PCE_i is the carbon emissions, produced by the reaction chemistry of process i, and CCE_i is the carbon consumed by the reaction chemistry of process i, all four variables are in units of $\frac{millions\ of\ kg\ CO_2}{year-molN\ in\ produc}$.

Table 2 Useful Parameters

Parameter	Value	Unit
Tax Rate (t)	0.21	
Discount Rate (r)	0.1	
Operating Hours	8410	hours/year
Big M Parameter (M)	50000	
Price of Urea	0.62	$/kg
Price of Ammonia	0.51	$/kg

Superstructure based optimization makes decisions on which pathways to follow and these choices are modeled with a binary variable Y_i representing a process block, i, either being chosen, $Y_i = 1$ and $Y_i = 0$ meaning the block is not chosen. The addition of binary variables to the model causes it to become a mixed integer non-linear problem (MINLP) and adds significant complexity towards solving it. To understand why this complexity is added it is important to understand the common method towards finding optimal solutions to functions. Gradient descent, an algorithm that checks the slope of the current position and then takes a step towards the optimal based on that slope and repeats until a maximum or minimum is found is a common method for finding the optimum of a convex function, or a function that only has one maximum/minimum. By adding the binary constraint to our model, we are ensuring that the objective function will be non-convex and discontinuous, thus will not be able to be solved with standard gradient descent methods. Gradient

descent doesn't work for non-convex functions because by definition it stops when it encounters a point where the first derivative of the objective function is 0, which in a convex function will be the optimum, however in a non-convex function there are more than one points with first derivative equal to zero, and such gradient descent has no way of knowing if it stops at a local optimum or the global optimum. Furthermore, since the function is discontinuous, and the algorithm relies on the derivative it will have problems in handling the existence of binary variables in the model. A promising way to alleviate these limitations is to use a deterministic global optimization algorithm. The solver BARON used in this work belongs to this category, in this type of algorithm a combination of combinatorial optimization principles and convex optimization are used such that instead of finding a local optimum, one converges to the global optimum of the function.

In our models, we introduce the binary variables used to model the selection of optimal pathways by means of a big M constraint,

$$F_{j,k} < M * Y_i \quad (2)$$

where $F_{j,k}$ is the flow of component k in stream j, Y_i is the binary variable with respect to the process i, and M is a large number that serves to bound the flow of streams, set to 50,000 for this study. A capacity constraint is also placed on the model to specify how much product needs to be produced.

$$F_{21,ammonia} + F_{22,ammonia} + F_{24,urea} = c$$

where c is plant capacity, set as 15 kg/s or 450,000,000 kg/year. Next, a mass balance is implemented to constrain the flow through each process block.

$$F_{j,k}^{in} + x^i F_{in}^r = F_{j,k}^{out} \quad (3)$$

Where $F_{j,k}^{in}$ is the flow of component k in stream j onto the reactor, x^k is the yield of component k, F_{in}^r is the flow of the limiting reactant into the reactor, and $F_{j,k}^{out}$ is the flow of component k in stream j out of the reactor.

Table 3. Reaction Yields

	H$_2$	CO$_2$	CH$_4$	H$_2$O	Bio	Biomass Byproducts	O$_2$	N$_2$	NH$_3$	Urea
SMR	0.91	2.09	-1	-2						
Biomass Gasification	0.19	1.03		-0.45	-1	0.23				
AWE	0.1			-1			0.9			
Haber-Bosch	-0.12							-1	1.12	
Electrocatalysis	-1						1.01	-0.54	0.53	
Urea Production		-1.45		1.01					-1	1.44

The last constraint added to the model is the epsilon constraint, which is used to model the multi-objective nature of the problem,

$$\sum_{i=1}^{n} [FCE_i + UCE_i + PCE_i - CCE_i] \leq \varepsilon \quad (4)$$

ε is chosen so as to restrict how much CO$_2$ the chosen path is allowed to produce. By varying this constraint, we can identify how the optimal path changes as allowable carbon emissions change.

Lastly, the model calculates some important equations for costing the processes as follows, capital cost

$$CC_i = C_i^{ref} * \left(\frac{F_i}{F_i^{ref}}\right)^{0.6} \quad (5)$$

where CC_i is the process capital cost, C_i^{ref} is the capital cost of the reference value, F_i is the total process flow of all components entering process i, and F_i^{ref} is the reference flow of process i process, working capital is defined as twenty percent of the capital cost, the depreciation for a process is defined as

$$D_m = \sum_{m=3}^{n} CC_i * depreciationRate(m) \quad (6)$$

Where *depreciationRate* is a set of values associated with each year of the plant such that $depreciationRate = \{0,0,0,0.1429,0.2449,0.1749,0.1249,0.0893,0.0892,0.0893\}$.
Lastly, salvage value for a process is defined as
$$C_s = 0.35 * CC_i \quad (7)$$

Table 4. *Feedstock Emission Factors[35]*

Component	Emissions Factor [kg CO_2 / kg of feedstock]
Water	0.03
Methane	0.53
N_2	0.43
Biomass	0.11
CO_2	1

Results and Discussion

Table 5. Comparisons of 1-2 process path results

Path	NPV	Carbon Emissions [MM kg Co2/year]
Biomass Gasification +Haber	41	340
SMR + Haber	18	210
Electrocatalysis	-230	77
Electrolysis + Haber	-370	91

Biomass gasification represents both more profitability and more carbon emissions associated with it when compared to SMR, both surprising. Currently SMR is significantly more widespread in industry than biomass gasification so it was expected that biomass gasification would represent a reduction in carbon emissions at the expense of profitability. While surprising, these results can be understood due to the low hydrogen yield of biomass gasification (0.19) when compared to SMR (0.91). Due to the lower yield for biomass gasification, it requires more feedstock and may consume more utilities to produce the same amount of hydrogen as SMR, resulting in more carbon emissions. Additionally, it is important to talk about the biogenic nature of using biomass. This means that the carbon emissions produced due to biomass gasification will be consumed by the

growth of new biomass to feed the process in the future.[29] Since our model does not consider the biogenic nature of biomass it makes sense that biomass gasification appears to have higher carbon emissions. With future improvements to energy efficiency and yield, biomass gasification will represent an extremely viable option for cleaner hydrogen production. It should also be noted that biomass is significantly less energy dense than natural gas, about 19 MJ/kg compared to 54 MJ/kg and as such is much more expensive to transport.[6, 30] Since the model does not consider variable transport costs, this process may be less profitable than it appears.

Results show that electrocatalysis is significantly less profitable than either SMR or Biomass Gasification but also producing the least carbon emissions. This is expected, electrocatalysis is still new technology when compared to the century old Haber-Bosch Process. However, due to the mild conditions of electrocatalysis, significantly less utilities are needed to support this process than the Haber-Bosch Process, making the carbon emissions associated with this process significantly lower than any other path. Additionally, this technology works with easier feedstocks to handle and can be operated on fully renewable sources; as the grid transitions towards renewable forms of electricity in the coming decades will continue to reduce the carbon emissions associated with this process.

Electrolysis represents a large reduction in carbon emissions when compared to SMR and Biomass Gasification technologies, however, this comes at a significant price as this process is also the least profitable ammonia production method by a significant margin. This lack of profitability likely comes from the high electricity requirements as well as the exceptionally low yield associated with the process. One advantage water electrolysis has over a technology like biomass gasification is that water electrolysis can be profitable when looking at smaller plants that don't rely on economies of scale to become profitable as biomass does. This is primarily because the transportation and general infrastructure around transporting water electrolysis is vastly less expensive than the transportation associated with biomass. Additionally, water electrolysis is an extremely active and developing field and while it is not profitable currently, new advances and process improvements will greatly improve efficiency and profitability, making electrolysis an appealing means of hydrogen production.
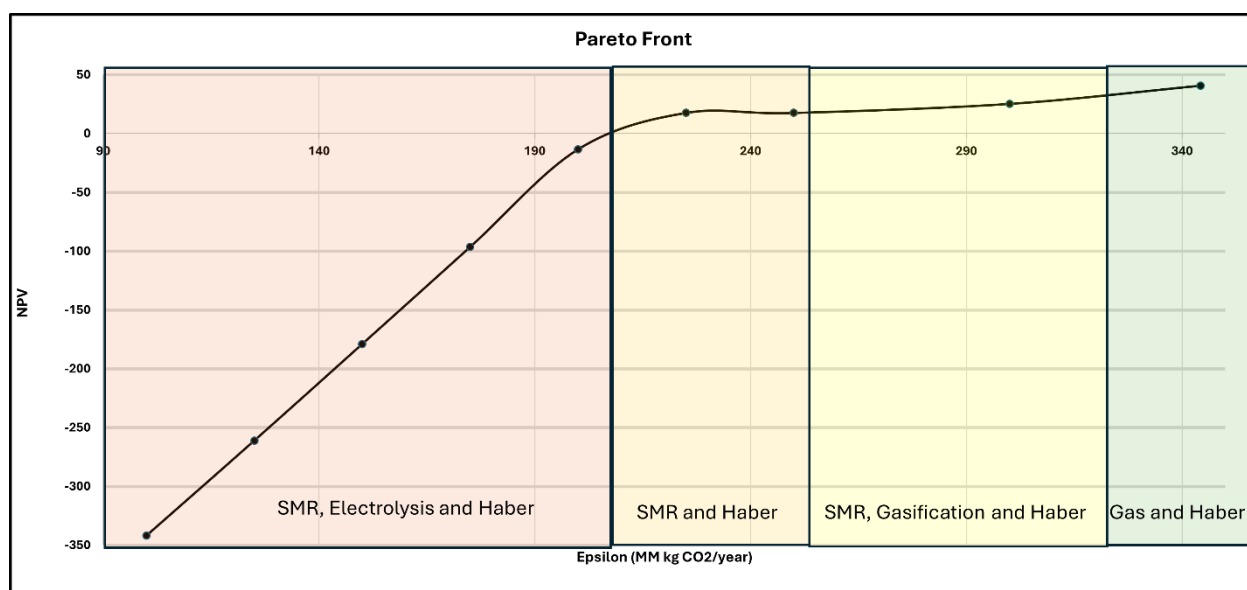

Figure 2. Pareto front optimizing NPV and Carbon Emissions

Figure 2 shows the pareto front for the two objectives of interest (NPV and GHG emissions). The most interesting information to take away from this graph are the points where transitions between technologies occur as objectives are given different levels of importance. Looking at Figure 2, the most profitable but also highest carbon emission path involves biomass gasification and the Haber-Bosch Process, which then transitions to a mix of SMR, biomass gasification, and the Haber-Bosch Process which produces slightly less emissions for a slightly lower NPV, to only SMR and Haber-Bosh, until the last section where hydrogen production from electrolysis supplements SMR. Clearly, electrolysis is the most promising technology in regard to reducing the carbon footprint associated with ammonia production, but it comes at the cost of profitability as the technology is currently under development. Electrocatalysis is not present in the optimal set of solutions for this model, this is surprising since electrocatalysis was determined to be a more profitable process that produces less carbon emissions when compared to the electrolysis and Haber-Bosch Process path. This can be understood since solutions that incorporate electrolysis also involve SMR and thus the Haber-Bosch Process is involved in the solution, since the Haber-Bosch process is already selected by the model, electrolysis presents a better solution than electrocatalysis.

It is important to mention once again that the biogenic nature of biomass is not accounted for in the model, and accounting for this by ignoring the carbon emissions associated with the stoichiometry of biomass gasification results in the same NPV of 41 but with carbon emissions of 60 MM kg Co2/year. This makes biomass gasification coupled with the Haber-Bosch Process the optimal way to produce ammonia profitably while reducing carbon emissions for a large plant with accessible biomass.

Finally, it is apparent that the production of urea from ammonia was not present in any of the optimal solutions. This was expected as the selling price of urea is only slightly higher than the price of ammonia and the production of urea involves high temperatures and pressures with expensive equipment and high utility consumption. These factors combine to result in the best path involving the production of urea having a NPV of -2200 and carbon emissions of 300 M kg Co2/year. It is quite apparent that the advantages urea production presents by producing valuable fertilizer while consuming carbon dioxide do not currently offset the cost of the process and the emissions released due to the high degree of utilities consumed. Further optimization or process alternatives to reduce utility consumption and operate under more mild conditions would make this process considerably more appealing.

Conclusions

In this study, we implemented a superstructure-based optimization to analyze the most promising fertilizer production processes simultaneously in a MINLP model. Using the epsilon constraint method, a pareto front was generated by using solutions to the model and varying the acceptable amount of carbon emissions produced by the path chosen by the model. It was found that biomass gasification and the Haber-Bosch Process is the most profitable pathway through the superstructure, and when the biogenic nature of biomass gasification is taken into account this pathway also produces the least carbon emissions for a large plant that can take advantage of economies of scale and has easily accessible biomass that doesn't cost a significant amount to transport to the plant. Superstructure-based optimizations are at their most powerful when analyzing large amounts of alternatives, and while the scope of this study was limited, it lays a foundation for future exploration in the space of carbon neutral fertilizer production and helps to identify some of the limiting factors towards current alternatives.

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35. *Category 1 Category 2 Category 3 Title Unit Emission factor (kg CO2eq per unit)*. (n.d.).

Reactions

- Steam Reforming
  - $CH_4(g) + H_2O(g) \leftrightharpoons CO(g) + 3H_2(g)$
- Water Gas Shift
  - $CO(g) + H_2O(g) \leftrightharpoons CO_2(g) + H_2(g)$
- Gasification
  - $C_1H_{1.569}O_{0.541} \rightarrow 0.3074C_{(s)} + 0.2163CO + 0.1190CO_2 + 0.187H_2 + 0.0867H_2O + 0.1674CH_4 + 0.0219C_2H_2 + 0.0650C_2H_4 + 0.0080C_2H_5$
- Water Electrolysis
  - $H_2O(l) \rightarrow H_2(g) + O_2(g)$
- Haber Bosch Process
  - $N_2 + 3H_2 \rightarrow 2NH_3$
- Electrocatalysis
  - $3H_2O + N_2 \rightarrow 2NH_3 + 1.5O_2$
- Bazarov Reaction
  - $2NH_3 + CO_2 \rightarrow NH_2CO_2$
  - $NH_2CO_2 \rightarrow H_2O + CO(NH_2)_2$