



Electrified Ammonia Synthesis with Methanol Production as Carbon Capture and Utilization System

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Ammonia production is a process critical to modern-day society. It is a main ingredient of the fertilizers that allow the amount of food necessary for the world's population. The Haber-Bosch process is the primary process used for ammonia synthesis, but it is energy intensive. An example of an electrified plant is designed which only uses renewable energy to drive the reaction through induction heating and capturing any generated carbon by co-producing methanol.

Keywords: Ammonia Synthesis, Carbon Neutral, Electrification.

1 Introduction

Ammonia is a key ingredient in many processes such as fertilizer production or even explosives manufacturing. Ammonia also holds the potential to be used as a hydrogen fuel storage because of its relatively large mass fraction (17.75%) compared to other sources, as well as the potential to exploit existing liquid fuel infrastructures [1]. Despite its importance, a large-scale production method was not known until the beginning of the twentieth century [2]. This method, the Haber-Bosch process, opened the door to modern-day living as the production of fertilizer could be massively scaled up. Today, large amounts are produced and ammonia production accounts for almost 1.8% of global energy usage, primarily through the Haber-Bosch process [1].

Unfortunately, its production has some drawbacks. First, the process requires a large amount of hydrogen. If the hydrogen were green, this would not be a problem. However, the main method of hydrogen production for ammonia synthesis is steam methane reformation, which generates CO₂ as a side product [3]. The other drawback is that the rest of the reaction is energy intensive due to the required reaction conditions of high temperatures and pressures. The energy is normally supplied using fossil fuels, creating even more greenhouse gases.

This paper describes a process which is completely carbon neutral with the assumption that the provided electricity comes from renewable resources. First, the reaction will be described. Then, optional process routes will be explored. The electrification of the design is detailed. The final process is then chosen, and a case study system is described.

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J. Gorimbo et al. (eds.), *Proceedings of the 1st international symposium on African Sustainable Energy Solutions (AfrSusEnS 2024)*, Advances in Engineering Research 271, https://doi.org/10.2991/978-94-6463-797-7_16

2 Reaction

The Haber-Bosch process is simple in concept— using gaseous nitrogen and a hydrogen source to make ammonia. The reaction itself follows the formula in Equation 1. The reaction is reversible. In order to favor the forward products, certain reaction conditions are commonly used. High pressures, typically around 150 bars are used to help drive the gaseous reactants to a liquid product [4]. The reaction is carried out at approximately 400°C [4]. These reaction conditions are necessary for a successful and efficient reaction.

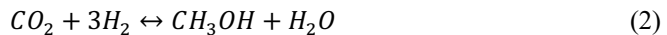


3 Carbon Dioxide Handling

Steam methane reformation with water-gas shift is often used for hydrogen production [5]. This process generates carbon dioxide that must be handled. Venting CO₂ to the atmosphere is an option but is irresponsible towards the environment. Capturing and storing CO₂ is a viable option though economically challenging. Instead, the CO₂ byproduct can be further reacted to form valuable products which can be sold. Two such routes are considered.

3.1 Methanol Synthesis

The first potential byproduct is methanol. Equation 2 shows the potential reaction pathway for methanol from CO₂. This process is exothermic, with an ΔH_{298}° of -49.5 kilojoules per mole of CO₂. All of this is done in the presence of a copper-based catalyst at 250-300 °C and 5-10 MPa [6].



Azhari et al. [6] warn that initial conversion is only 15-25%. They also warn that CO₂ may also convert back into CO via the reverse water gas shift reaction. Another warning was that the water produced from the reaction may inactivate the catalyst.

Careful design of the reactor must be employed in order to account for these weaknesses. First, the effluent stream must be separated then recycled to improve conversion. If recycling is not desired, multiple reactors in series could also be chosen to increase selectivity. Next, the reactor must be cooled [6]. Because the reverse WGS is endothermic, cooling the reactor prevents the excess heat from the forward reaction from causing the reverse WGS to occur.

Finally, care must be taken to ensure the water does not deactivate the catalyst. Choosing a different catalyst than the conventional copper can result in entirely better outcome. If a gold indium oxide catalyst is used, then methanol is produced at around 100% selectivity at temperatures below 225°C, and there is no risk of water inactivation [6].

3.2 Dimethyl Ether Synthesis

The other option for carbon capture is dimethyl ether (DME) production. DME production differs from methanol production in that the synthesis is usually not a single step process. DME synthesis requires three separate steps [7]. Mondal and Yadav [7] explain this process. First, methanol is synthesized from CO_2 and H_2 . Then the methanol is dehydrated. Finally, the reverse WGS reaction is carried out.

These reactions usually take place at moderate temperatures and pressures. The usual temperatures are 200-300 °C and the usual pressures are 4-10 MPa [8]. Zhou et al. [8] state that the selectivity was only 30-50% with a 10-30% conversion overall. They further state that the DME formation is limited by the methanol synthesis step.

4 Reactor Design

The SMR/WGS reaction is of great interest. This reaction is where the majority of the heating in the plant is needed. The reaction must take place at high temperatures (900°C) and high pressure. The reaction is endothermic, absorbing 206 kilojoules per mole of methane feed. The reactor is to use tubes and operates packed with nickel catalyst as a packed bed reactor at 900°C and an initial pressure of 20 bar. A molar steam to carbon ratio of 3:1 is used in the feed, in keeping with literature recommendations [9, 10]. Because the Haber-Bosch process immediately follows this step at a lower temperature (400°C), cooling, not heating, is required prior to entering the next reactor. It is important, therefore, to heat the SMR/WGS reactor in a way that does not use fossil fuels.

The solution to this problem is via induction heating [11]. For this technique, a conductor is wound around the target, which must also be conductive. Once alternating current is applied to the conductor, an alternating current is induced in the target. This induced current is considered an eddy current, as it circulates wholly within the target metal [12]. The alternating eddy current generates heat within the targeted metal itself. If the target material is magnetic, then hysteretic heating also occurs as a result of the inductive heating, causing the inductive heating to be even more efficient [12]. This effect is present until the target reaches its Curie temperature and is no longer magnetic. Then only the eddy currents generate heat [12]. The conductor is not immune to these effects. Because the conductor is subject to AC current, it also heats up, and can reach dangerous temperatures. This side effect is usually negated in practical uses by using conductive tubing as the inductor. This tubing can be cooled by running water or some other coolant through it [12, 13]

This heating technique has many advantages aside from being carbon-free. Perhaps the largest advantage is the lack of losses. Unlike fired heating, or even resistive heating, all of the energy provided to the heater goes directly to target. Flames and resistive heating techniques heat their environments as much as the targeted equipment. Inductive heaters only heat the target and the inductor itself, greatly reducing the mass and material that need be heated to reach a desired temperature.

Determining sizes for such a reactor is more complicated than conventional reactors. The volume throughput binds together the flow velocity and the radius of the packed

bed reactor. As the velocity changes, so does the length of the overall reactor. The reactor must be long enough for sufficient interaction of the reactants with the catalysts. Therefore, a balance is needed to be found from a practicality standpoint between the length of the reactor, its cross section, and the velocity of the gas. Too high a velocity and work would be lost in accelerating the gas. Too low a velocity and the reactor would be incredibly short to maintain certain residence times. It is unrealistic to ensure sufficient heating in short reactors. This is especially the case for induction heating. As discussed previously, induction heating requires that a conductor be wrapped around the target, reactor tubing in this case. Only the tubing walls are heated as a result. A short, large-diameter cylinder has significantly less wall area than a long, narrower cylinder. Also, the reactant gases inside would have significantly less contact to absorb the heat from the walls in such a scenario. These factors must all be considered when choosing the tube length.

To gain the advantages of narrow cylinders while maintaining high throughput, the reactor can take the form of many small tubes bundled together. The summation of all of the smaller tubes' cross-sectional areas would result in the same effective area as a large, single tube design. As the number of smaller tubes increases, the total mass of the tubing will also increase. This mass increase relates directly to the amount of energy required to heat the system to temperature at startup. As the radius of the tubing decreases, the pressure loss across the system increases, which corresponds to extra work being lost. However, because the pressure is already increasing as a result of the reaction, these effects are of lesser concern. Finally, for every tube an entire induction system must be created, increasing the complexity of the build.

With these factors in mind, the optimization problem can be formulated. The radius should be altered to maximize the surface area, minimize the total mass of the tube walls with a constant wall thickness, minimize the pressure drop across the tube, and maximize the total number of tubes used. This optimization problem is defined in Equation 3. In the given equation, L is tube length, f is the friction factor using the Haaland equation, v is the velocity, D is the hydraulic diameter, and w_x is the weighting for each factor.

$$\begin{aligned} \min_r w_1 \text{mass}(r) + w_2 \Delta P(r) - w_3 n(r) - w_4 \text{area}(r) \\ \text{mass} = \pi((r + 0.00635)^2 - r^2)L \\ \Delta P = \frac{f\rho v^2}{2D} \\ n = \frac{r_{tot}^2}{r^2} \\ \text{area} = 2\pi vL \end{aligned} \quad (3)$$

Each reactor tube must be made of half-inch carbon steel. This steel has a high melting point ($> 1400^\circ\text{C}$) [14] and would be able to handle the pressure. Because it is steel, it can be heated inductively, which is a necessary quality of the tubing. Unfortunately, the required material's heat capacity causes each tube to require significant heating to raise to temperature on startup.

5 Process Design

Fig. 1 shows the chosen route. Methanol production was chosen as the process to capture the carbon dioxide. Methanol production was selected over DME production because of the hydrogen requirements. DME requires four H_2 molecules for every carbon. The SMR with WGS only produces four H_2 molecules. This would mean that in order to completely have carbon neutral hydrogen production, all of the produced hydrogen would be used by the carbon capture. there would not be any left over for the ammonia production. Because ammonia production is the goal of this process, it must be produced. Methanol, on the other hand, does not require all of the produced hydrogen and therefore is a feasible method of carbon capture to lead to a neutral process.

5.1 Case Study

A case study is explored with the following specifications to illustrate the design shown in Fig. 1. The plant should produce 500 kilotonnes of anhydrous ammonia per working year. The working year is defined as 8160 hours. This equates to about 61.3 tonnes per hour. The ammonia should be liquefied and exit at ambient temperature and 15 bar. The ammonia and SMG reactors are selected to have a residence time of one second.

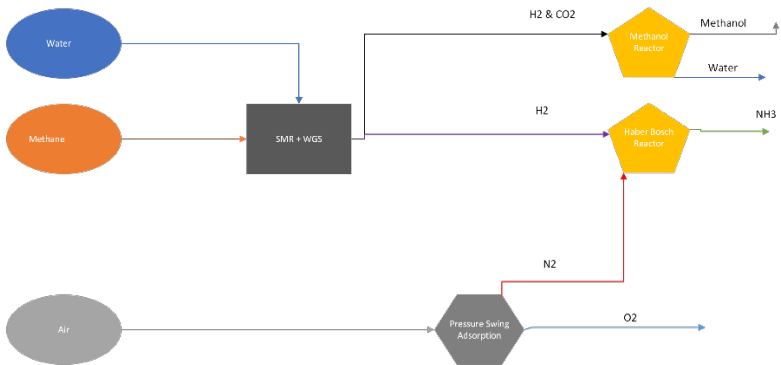


Fig. 1. The chosen process flow diagram.

Water and Methane are fed into an electrified reactor following the description given in Section 4. By solving the optimization problem and adjusting continuous sizes to common tube sizes, the optimal tube inner diameter can be found to be 80 cm. 625 tubes of this size would be needed, 17.8 meters in length to maintain the targeted residence time. With these dimensions the feed gases will be highly turbulent, aiding heat transfer. Each tube will require 525 kilowatts to maintain the reaction with $25^{\circ}C$ gases entering. At steady state, this is a combined heating duty of 328.125 megawatts.

The effluent is then separated into a CO_2 & H_2 stream and an H_2 stream. This can be done using pressure swing adsorption (PSA) to high purity [9]. It is assumed that the

H₂ purity is 100%, since PSA can hit 99.999% [9]. Air is also fed into a PSA designed to purify nitrogen. The effluent nitrogen is assumed to be 100% pure, as it can also obtain high quality [15]. The oxygen is sent back to the atmosphere. The nitrogen and pure hydrogen are cooled and sent to the Haber Bosch reactor to form ammonia. The carbon dioxide and remaining hydrogen are combined in a methanol reactor to produce methanol. The excess water can either be recycled or handled by the plant for any purpose other than food product.

6 Conclusion

In many ways, the proposed production scheme is similar to current Haber-Bosch processes. It uses SMR, WGS, and it effectively produces ammonia. What is uncommon about this process is its carbon footprint, or lack thereof. Provided that all electricity is obtained from renewable resources, this process has no waste carbon. All of the carbon generated from the SMR process is transformed into methanol pure enough to be sold. Another key difference is that the SMR reactor is heated via inductive heaters. This actually provided the required heat for the remainder of the process. Electrified, carbon-neutral processes are feasible using current technology, provided the required electricity is obtainable through renewable sources.

Disclosure of Interests. The authors have no competing interests to declare relevant to the article.

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