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## MASTER THESIS

Subject/Topic:

**IMPACT OF DIGESTATE FORMED DURING BIOGAS  
GENERATION PROCESS ON HYDROGEN PRODUCTION**

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## **DEDICATION**

I give the honor of this work to my dear parents for having fully assumed their duties as parents and for the pains endured for my success in my studies.

Without you, this day of my work presentation would not have taken place.

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## **DECLARATION**

I confirm that I have done all the work in this thesis myself and I only used the sources and materials that I was allowed to use. Any sources I used are properly mentioned. Also, I want to make it clear that I have not submitted this work anywhere else, either in its original form or something similar, for academic purposes.

## ABSTRACT

Hydrogen production from renewable sources has become a key objective in the energy transition to a more sustainable, and low-carbon economy. Among the many potential sources for hydrogen production, ammonia generated from anaerobic digestate presents a promising opportunity. Although digestate has its advantages, the presence of toxic ammonia poses environmental problems. Proper control of ammonia volatilization is essential to minimize risks.

This study highlights the importance of side stream stripping as a viable method of recovering ammonia from digestate to support hydrogen production.

In this study, the ammonium nitrogen ( $\text{NH}_4\text{-N}$ ) data of various substrates used for biogas production and its digestate was collected from a brochure on the results of biogas production measurements in Germany published by the Agency for Renewable Resources (**FNR: Fachagentur Nachwachsende Rohstoffe**). These data were used to estimate the amount of ammonia ( $\text{NH}_3$ ) contained in the digestate of various feedstocks for hydrogen production.

Side-stream stripping has been shown to extract ammonia safely, facilitating handling and reducing gaseous and particulate emissions. In addition, the process reduces transport costs by removing excess water from the digestate, while the stripped digestate is returned to the anaerobic digester, ensuring a closed-loop system. The results of this study showed an increase in ammonia content as a function of the ammonium nitrogen content in the digestate. Digestate with a high ammonium nitrogen content produced more hydrogen respectively.

The hydrogen potential produced depends on the amount of ammonia available in the digestate. This study explores the potential impact of anaerobic digestate on hydrogen production. Regarding the evaluation of catalysts used in ammonia decomposition. Ru-based catalysts are widely regarded as the best choice for highly efficient ammonia ( $\text{NH}_3$ ) decomposition. However, their considerable cost and limited availability are disadvantages for large-scale applications. In contrast, among non-noble metal catalysts, nickel-based catalysts show the highest activity, making nickel a promising alternative material for ammonia ( $\text{NH}_3$ ) decomposition due to its affordability.

At present, challenges remain in improving the efficiency of Ru- and Ni-based catalysts.

**Keywords:** Anaerobic digestate; Side stream stripping; Ammonia decomposition.

## RÉSUMÉ

La production d'hydrogène à partir de sources renouvelables est devenue un objectif clé de la transition énergétique vers une économie plus durable et à faible émission de carbone. Parmi les nombreuses sources potentielles de production d'hydrogène, l'ammoniac généré par les digestats anaérobies représente une opportunité prometteuse. Bien que les digestats présentent des avantages, la présence d'ammoniac toxique pose des problèmes environnementaux. Un contrôle adéquat de la volatilisation de l'ammoniac est essentiel pour minimiser les risques.

Cette étude met en évidence l'importance du stripping du flux latéral comme méthode viable de récupération de l'ammoniac du digestat pour soutenir la production d'hydrogène.

Dans cette étude, la teneur en azote ammoniacal ( $\text{NH}_4\text{-N}$ ) de divers substrats utilisés pour la production de biogaz et de son digestat a été collecté dans une brochure sur les résultats des mesures de production de biogaz en Allemagne publiée par l'Agence des ressources renouvelables (FNR : Fachagentur Nachwachsende Rohstoffe). Ces données ont été utilisées pour estimer la quantité d'ammoniac ( $\text{NH}_3$ ) contenue dans le digestat de différents substrats pour la production d'hydrogène.

Il a été démontré que le stripping à flux latéral permet d'extraire l'ammoniac en toute sécurité, ce qui facilite la manipulation et réduit les émissions de gaz et de particules. En outre, le processus réduit les coûts de transport en éliminant l'excès d'eau du digestat, tandis que le digestat strippé est renvoyé dans le digesteur anaérobie, ce qui garantit un système en boucle fermée. Les résultats de cette étude ont montré une augmentation de la teneur en ammoniac en fonction de la teneur en azote ammoniacal du digestat. Les digestats à forte teneur en azote ammoniacal produisent respectivement plus d'hydrogène. Le potentiel d'hydrogène produit dépend de la quantité d'ammoniac disponible dans le digestat. En ce qui concerne l'évaluation des catalyseurs utilisés dans la décomposition de l'ammoniac. Les catalyseurs à base de Ru sont largement considérés comme le meilleur choix pour une décomposition hautement efficace de l'ammoniac ( $\text{NH}_3$ ). Toutefois, leur coût considérable et leur disponibilité limitée constituent des inconvénients pour les applications à grande échelle. En revanche, parmi les catalyseurs à base de métaux non nobles, ceux à base de nickel ont l'activité la plus élevée, ce qui fait du nickel un matériau alternatif prometteur pour la décomposition de l'ammoniac ( $\text{NH}_3$ ) en raison de son prix abordable. À l'heure actuelle, il reste des défis à relever pour améliorer l'efficacité des catalyseurs à base de Ru et de Ni.

**Mots clés :** Digestat de biogaz ; stripping de flux latéral ; Décomposition de l'ammoniac

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## ACRONYMS AND ABBREVIATIONS

<b>Al<sub>2</sub>O<sub>3</sub></b>	: Aluminium oxide
<b>AD</b>	: Anaerobic Digestion
<b>CNTs</b>	: Carbon Nanotubes
<b>HB</b>	: Haber-Bosch
<b>HHV</b>	: High Heating Value
<b>IDLH</b>	: Immediately Dangerous to Life or Health
<b>H<sub>2</sub>SO<sub>4</sub></b>	: Sulfuric Acid
<b>LPG</b>	: Liquefied Petroleum Gas
<b>LiClO<sub>4</sub></b>	: lithium perchlorate
<b>MCH</b>	: Methyl Cyclohexane
<b>NH<sub>4</sub>-N</b>	: Ammonium Nitrogen
<b>NO<sub>x</sub></b>	: Nitrogen Oxides
<b>NH<sub>4</sub><sup>+</sup></b>	: Ammonium ions
<b>NH<sub>3</sub></b>	: Ammonia
<b>Ni</b>	: Nickel
<b>NTP</b>	: Normal Temperature and Pressure
<b>OH<sup>-</sup></b>	: Hydroxide ions
<b>PSA</b>	: Pressure Swing Adsorption
<b>PEMFCs</b>	: Polymer Electrolyte Membrane Fuel Cells
<b>Ru</b>	: Ruthenium
<b>SiO<sub>2</sub></b>	: Silicon Oxides
<b>Wt%</b>	: Percentage of Weight

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# 1. INTRODUCTION

## Background

Over the past few years, the biogas sector has experienced an important growth in the number of biogas installations all over Europe, and consequently, the quantity of digestate also has had a significant increase. In Europe, biogas production by anaerobic digestion (AD) is a common source of renewable energy and the current number of installations is around 13,000. Together with biogas, digestate is one of the two main by-products resulting from the biogas process. The digested effluent is a liquid product rich in nitrogen (N), phosphorus (P), potassium (K) and micronutrients. Therefore, there is a wide variety of digestate utilization depending on the quality, the origin of the feedstock, the operating conditions of the process as well as the phase of the by-product. The most common end uses are biofertilizer and soil amendment, due to its essential characteristics and when the quality is adequate for agriculture use (Gülzow-Prüzen, 2012).

**The production** of hydrogen from renewable sources has become a key objective in the energy transition toward a more sustainable and low-carbon economy. Among the many potential sources of hydrogen, ammonia from anaerobic digestate presents itself as a promising opportunity. Digestate is a by-product of the degradation of organic waste by anaerobic digestion, and it contains a significant amount of ammonia. The recovery of ammonia contained in the digestate offers a potential route for the production of renewable hydrogen.

Ammonia is a promising hydrogen carrier due to its high gravimetric (17.8 wt% H<sub>2</sub>) and volumetric (121 kg.m<sup>3</sup> in liquid form) H<sub>2</sub> and 1.4 times greater than that of liquid hydrogen (Aziz et al., 2020a; Zhang et al., 2019).

Consequently, transporting and storing ammonia is relatively easy and energy-efficient. By breaking down ammonia for hydrogen production, we can fulfill the demand for nearly carbon-neutral hydrogen, leading to an exceptionally low carbon footprint (Liu et al., 2021).

## Problem statement

Management of digestate involves several topics such as storage, processing, transportation, utilization, economics, and environmental quality. It has many benefits, but also presents several challenges. One of the biggest issues is its ammonia content, which can be toxic to

aquatic life and contribute to air pollution. However, due to its hazards and toxicity, precautions are needed to ensure safety (Lee et al., 2019; Makepeace et al., 2019a; Zhang et al., 2019).

In addition, digestate can be difficult to handle and transport due to its high-water content.

**The main** challenge related to the production of hydrogen from ammonia is the efficiency and cost-effectiveness of converting it into hydrogen.

Therefore, one of the major challenges in the production of hydrogen through ammonia decomposition is the need for efficient catalysts that facilitate the conversion process. Additionally, the safe storage and transportation of the hydrogen produced are also significant concerns. Despite the fact that the catalytic synthesis of ammonia is well-understood, ammonia decomposition remains a process that requires further comprehension and optimization, especially since there is currently no industrial technology available for its efficient implementation (Lamb et al., 2019a)

Ammonia breakdown takes place at high temperatures in the presence or absence of a catalyst.

## **Objectives**

### **Main Objective**

To evaluate the impact of digestate on hydrogen production.

### **Specific Objectives**

- ✓ To estimate the potential of hydrogen production from the digestate of different feedstocks.
- ✓ To determine the energy and power potential content in hydrogen production from the digestate of different feedstocks
- ✓ To compare the values of hydrogen production from the digestate using different catalysts (Ru-based catalysts; Nickel-based catalyst)
- ✓ To develop a model for calculating hydrogen potential from digestate.

## **Structure of a Thesis**

This thesis is structured around the following three parts:

- ✓ **CHAPTER 1: LITERATURE REVIEWS**
- ✓ **CHAPTER 2: METHODOLOGY**
- ✓ **CHAPTER 3: RESULTS AND DISCUSSION**

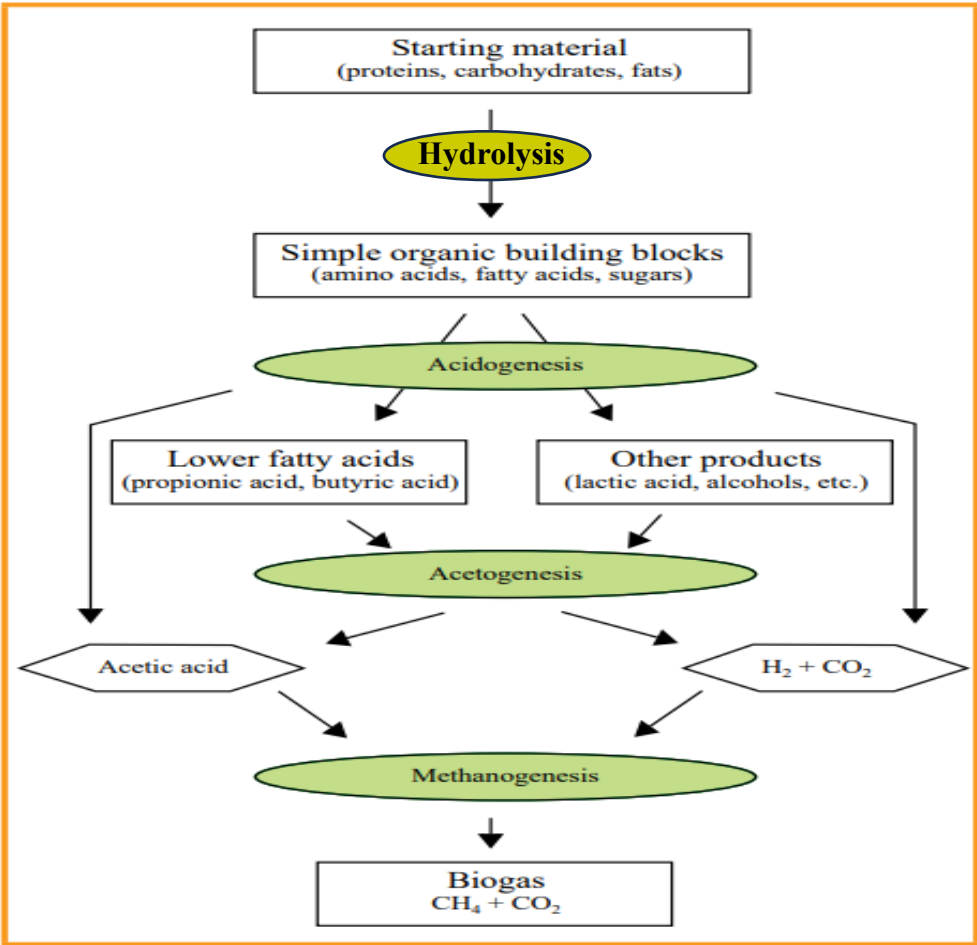
# CHAPTER 1: LITERATURE REVIEWS

## 1.1 General overviews on anaerobic digestate

### 1.1.1 Generation of biogas

Biogas typically refers to a gas mixture produced by the biological breakdown of organic matter in the absence of oxygen. The resulting gas mixture consists primarily of methane (50-75%) and carbon dioxide (25-50%) and smaller amounts of nitrogen (2-8%). Biogas also contains trace levels of hydrogen, hydrogen sulfide, ammonia, and various volatile organic compounds. The composition of the gas is essentially determined by the substrates, the fermentation (digestion) process, and the various technical designs of the plants(Y. Li et al., 2019).

The biogas formation process can be divided into four stages (*Figure 1*). The various stages of decomposition (degradation) must be coordinated and harmonized in the best possible way to ensure the smooth running of the entire process (Gülzow- Prüzen, 2012).



*Figure 1. Schematic representation of anaerobic decomposition*



### 1.1.2 Inhibitors in the anaerobic decomposition process.

In particular, even low concentrations of non-ionic free ammonia ( $\text{NH}_3$ ) can have a harmful impact on the bacteria; this free ammonia is in equilibrium with the ammonium ( $\text{NH}_4^+$ ) ion concentration (ammonia reacts with water to form ammonium and an  $\text{OH}^-$  ion and vice versa). This means that with an increasingly alkaline pH value, in other words as the concentration of  $\text{OH}^-$  ions rise, the equilibrium is shifted, and the ammonia concentration increases. A rise in pH value from 6.5 to 8.0, for example, leads to a 30-fold increase in the concentration of free ammonia. A rise in temperature in the digester also results in the equilibrium being shifted in the direction of ammonia with its inhibition effect. For a digestion system that is not adapted to high nitrogen concentrations, the inhibition threshold is within a range from 80 to 250 mg/L of ammonia ( $\text{NH}_3$ ) (Y. Li et al., 2019). Depending on pH value and digestion temperature, this is equivalent to an ammonium concentration of 1.7-4 g/L. Experience shows that nitrogen inhibition of the biogas process must be expected at a total concentration of ammoniacal nitrogen of 3,000- 3,500 mg/L (Austermann-Haun et al., 1990).

The pH value can increase if ammonia is released during the decomposition of organic nitrogen compounds. Ammonia reacts with water to form ammonium, leading to an increase in pH. This rise in pH can have an inhibitory effect on the process. However, when it comes to process control, it is important to consider that pH measurements have limited effectiveness due to their slow response. Despite this limitation, pH measurement remains crucial due to its significant importance in the overall functioning of the biogas plant. Table 1 below shows inhibitors in anaerobic decomposition processes and the concentrations at which they become damaging (Gülzow-Prüzen, 2012).

**Table 1.** Inhibitors in anaerobic decomposition processes and the concentrations at which they become damaging

Inhibitor	Inhibitory concentration	Comments
Oxygen	> 0.1 mg/l	Inhibition of obligate anaerobic methanogenic archaea
Hydrogen sulphide	> 50 mg/l H <sub>2</sub> S	Inhibitory effect rises with falling pH value
Volatile fatty acids	> 2,000 mg/l HAc (pH = 7.0)	Inhibitory effect rises with falling pH value. High adaptability of bacteria
Ammoniacal nitrogen	> 3,500 mg/l NH <sub>4</sub> <sup>+</sup> (pH = 7.0)	Inhibitory effect rises with rising pH value and rising temperature. High adaptability of bacteria
Heavy metals	Cu > 50 mg/l Zn > 150 mg/l Cr > 100 mg/l	Only dissolved metals have an inhibitory effect. Detoxification by sulphide precipitation
Disinfectants, antibiotics	n.s.	Product-specific inhibitory effect

### 1.1.3 Response against ammonia inhibition

Taking action to reduce ammonia inhibition requires fundamental interventions in the plant. In general, ammonia inhibitions occur when protein-rich input materials are used. If ammonia inhibition has been demonstrably verified, either the temperature must be lowered or the input composition changed. Changing the input composition should result in a reduction in nitrogen load. This can bring about a long-term reduction of the concentration of inhibiting ammonia in the digester. If acidification is already far advanced, it makes sense to swap fermentation residue from a downstream digester in order to reduce acid concentration in the short term.

Whichever method is chosen, it should be done slowly, with close monitoring of the process. Lowering the pH value in order to reduce the proportion of undissociated ammonia is extremely difficult to achieve in the long term and therefore cannot be recommended (Gülzow-Prüzen, 2012).

## 1.2 Digestate

### 1.2.1 Digestate characteristics

Digestate refers to the liquid and solid residue that is generated during the anaerobic digestion (AD) of organic matter. This anaerobic by-product contains essential macronutrients such as nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), sulfur (S), and magnesium (Mg), as well as trace elements including boron (B), chlorine (Cl), manganese (Mn), iron (Fe), zinc (Zn), copper (Cu), molybdenum (Mo), and nickel (Ni) (Weiland, 2010). The specific characteristics of the digestate are typically influenced by the type of input material, the operating conditions of the AD process, and the techniques used for digestate treatment. The nutrient composition of the initial organic matter affects not only the composition of the digestate but also the composition of the biogas produced and the specific yield of methane (Plana & Noche, 2016).

The substrates commonly used in Anaerobic Digestion include agricultural waste, manure, energy crops, waste from food-processing industries, sewage sludge, and organic municipal waste (Appels et al., 2011). Depending on the AD process and the feedstock, the dry solid content can vary in a considerable wide range of about 3.5 to 13% (Wäger-Baumann, 2011).

In general, the anaerobic digestate is rich in nitrogen (N), phosphorous (P), and potassium (K). After solid-liquid separation, the liquid part contains a high percentage of N and the solid part contains high P content. In addition, the presence of heavy metals (Cd, Cr, Pb, Ni, Hg, Cu, and Zn) and organic pollutants can be found (Nilsson et al., 2010). The table below shows some characteristics of digestate (Bernhard et al., 2015)

**Table 2.** Some characteristics of digestate

	ABSOLUTE VALUES	CHANGE <sup>a)</sup>
DM (%)	1.5–13.2	- 1.5 to -5.5
Organic DM (%DM)	63.8–75.0	-5 to -15
Total N (%DM)	3.1–14.0%	b)
Total N (kg Mg <sup>-1</sup> FM)	1.2–9.10	≈0
Total NH <sub>4</sub> <sup>+</sup> (kg Mg <sup>-1</sup> FM)	1.5–6.8	?
NH <sub>4</sub> <sup>+</sup> share on total N (%)	44–81%	+10 to +33
Total C content (%DM)	36.0–45.0	-2 to -3
C: N ratio	3.0–8.5	-3 to -5

Total P content (%DM)	0.6–1.7	b)
Total P (kg Mg -1 FM)	0.4–2.6	≈0
Water soluble P (% of total P)	25–45	-20 to -47
Total K (%DM)	1.9–4.3	b)
Total K (kg Mg-1 FM)	1.2–11.5	≈0
Total Mg (kg Mg-1 FM)	0.3–0.7	≈0
Total Ca (kg Mg-1 FM)	1.0–2.3	≈0
Total S (kg Mg-1 FM)	0.2–0.4	?
pH	7.3–9.0	+0.5 to + 2 units

a) In comparison to undigested liquid animal manures, absolute values. b) Increases with a degree of DM degradation. DM = Dry matter. FM = Fresh matter.? = No data found/no data available.

### 1.2.2 Different types of digestate

Based on its physical properties, digestate can be categorized into three main types: whole digestate, liquid fraction or liquor, and solid fraction or cake. The specific characteristics of these fractions largely depend on the technique used for solid-liquid separation.

Additionally, digestate can also be classified based on the source of the feedstock it originates from. These classifications include agriculture-based digestate, which includes manure and crops as feedstock, digestate derived from food and municipal waste, and digestate obtained from wastewater treatment plants. In table 3 are shown the Substrate parameters influencing digestate composition (Bernhard et al., 2015).

**Table 3.** Substrate parameters influencing digestate composition

SUBSTRATE PARAMETER	IMPACT ON DIGESTATE COMPOSITION
Organic waste	<ul style="list-style-type: none"> <li>• low total solids (TS) content</li> <li>• low percentage of organics in TS</li> </ul>
High amount of abattoir waste	<ul style="list-style-type: none"> <li>• high nitrogen concentration</li> <li>• high percentage of ammonia in total nitrogen</li> </ul>
High amount of manure	<ul style="list-style-type: none"> <li>• low total solids (TS) content</li> <li>• considerable nitrogen concentration</li> </ul>

### 1.2.3 Potential usage of anaerobic digestate

Digestate has a wide range of potential uses, which are determined by the quality and source of the input substrate, as well as the type and characteristics of the digestate itself. The most prevalent application is land utilization, particularly as a fertilizer and soil conditioner. However, this practice is only suitable for digestate that meets the necessary criteria for agricultural purposes, including acceptable levels of heavy metals (cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), mercury (Hg), copper (Cu), and zinc (Zn)) and organic pollutants (Tambone et al., 2009).

The anaerobic digestate can be used as a fertilizer for land-based agriculture and hydroponic cultivation, as well as a bio-product for controlling pests and diseases, and as a substrate in hydroponics. Additionally, the literature suggests that anaerobic digestate can also be beneficial for animal breeding, aquaculture, and algae production (Baştabak & Koçar, 2020).

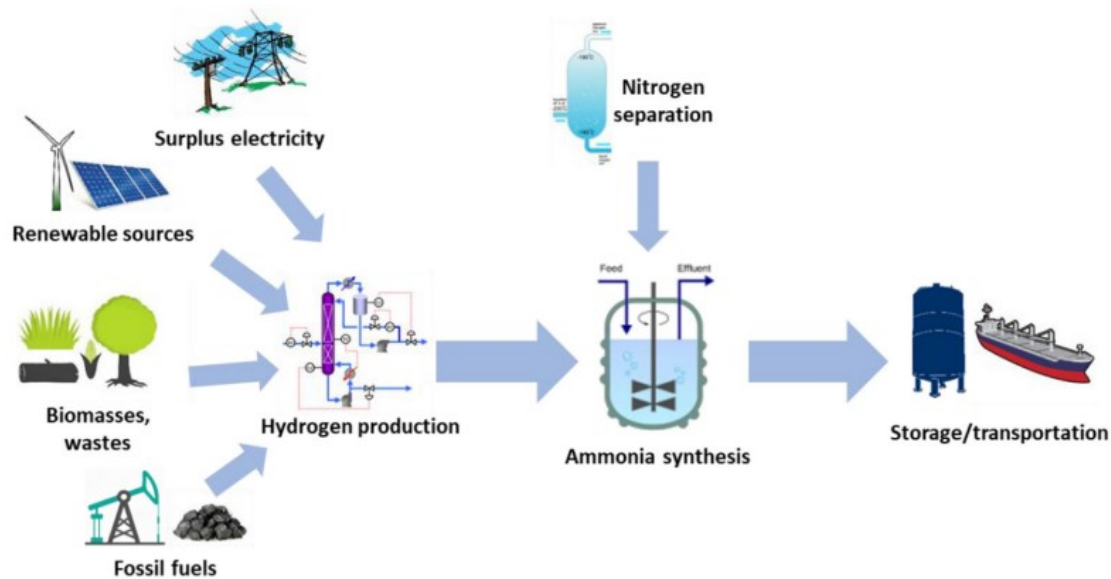
Furthermore, digestate can be transformed into compost (Bustamante et al., 2013), which can be employed as a growing medium for plants and for land regeneration. Additionally, studies have shown that digestate can be utilized as a solid fuel, particularly when dried and pelletized, offering a promising alternative (Kratzeisen et al., 2010). Digestate can also find applications as a building material.

In addition, after the separation of the digestate into its liquid and solid fractions, the liquid phase can be utilized in various ways. It can be directly spread on the land as a nitrogen-rich fertilizer, recirculated back into the anaerobic digestion (AD) process as process water, or undergo further treatment to obtain concentrates or pure water (Fuchs & Drosig, 2013).

Anaerobic digestate provides a potential pathway for the production of renewable hydrogen. Among the various sources of hydrogen, ammonia derived from anaerobic digestate presents itself as a promising opportunity.

### 1.3 Ammonia production methods

Similarly, to hydrogen, ammonia can be produced from different primary energy sources, including (biomass, coal, natural gas, solar, wind, geothermal, hydraulic, and nuclear sources). Ammonia can be produced through different conversion technologies: thermochemical, electrochemical, photochemical, and plasma (C. Li et al., 2020)



**Figure 2:** Conceptual route of ammonia (NH<sub>3</sub>) production from various primary energy sources, including fossil and renewables

When technological practicability and overall energy efficiency are taken into account, there are three main conversion technologies commonly used for ammonia (NH<sub>3</sub>) production. These are the Haber-Bosch process, electrochemical processes, and thermochemical cycles. Each of these methods offers potential technological options for ammonia production (Juangsa et al., 2021).

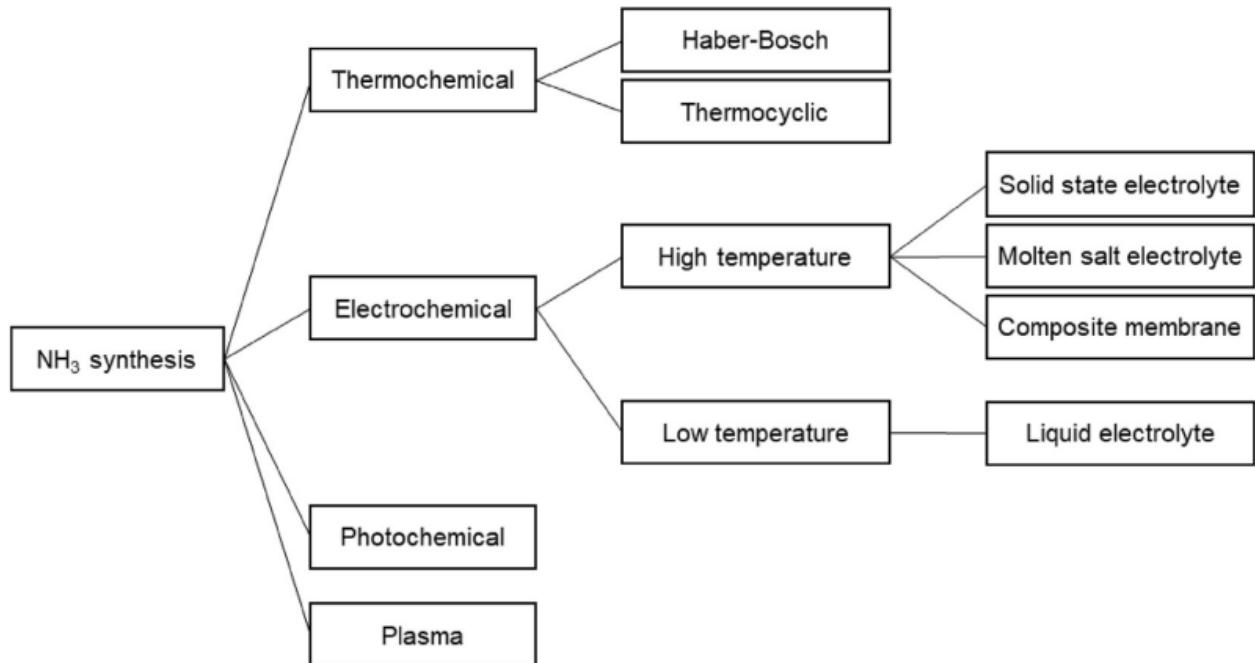
The production of ammonia (NH<sub>3</sub>) by thermochemical processes involves two widely recognized methods: the Haber-Bosch process and the thermocycler. These methods have been widely used and studied.

In addition, ammonia can also be produced by an electrochemical process, which can be carried out at both high and low temperatures, depending on the type of electrolyte used. In general, there are four distinct categories of electrolytes used in the electrochemical production of ammonia:

- **Solid-state electrolyte:** This type of electrolyte operates in a temperature range from room temperature to 700-800°C. It functions as a high-temperature ion conductor to facilitate the electrochemical reactions involved in ammonia production. It functions as a high-temperature ion conductor to facilitate the electrochemical reactions involved in ammonia production.

- **Molten salt electrolyte:** Electrolytes of this type are used at temperatures between 300 and 500°C. They consist of molten salts that enable the movement of ions required for the electrochemical conversion of nitrogen and hydrogen into ammonia.
- **Composite membrane electrolyte:** This type of electrolyte is used at temperatures between 300 and 700°C. It consists of a composite membrane that combines the properties of solid-state electrolytes and molten salts, enabling efficient ammonia production.
- **Liquid electrolytes near room temperature:** Electrolytes in this category operate at or around room temperature. These liquid electrolytes enable ion transport and facilitate the electrochemical reactions required for ammonia production.

These different types of electrolytes offer flexibility in the electrochemical production of ammonia, allowing for different temperature ranges and operating conditions (Giddey et al., 2013a).



*Figure 3. Possible technological options for NH<sub>3</sub> production*

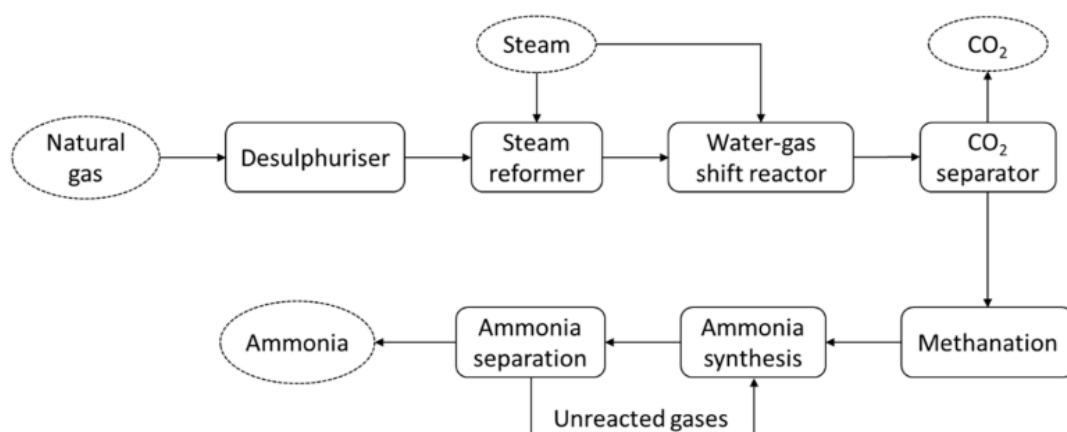
### 1.3.1 Thermochemical ammonia production

#### 1.3.1.1 Haber–Bosch Process

The Haber-Bosch (HB) process governs more than 96% of NH<sub>3</sub> production in this world (Smith et al., 2020). This method relies on natural gas as the main source of hydrogen (H<sub>2</sub>) and involves separating nitrogen (N<sub>2</sub>) from the air. The Haber-Bosch (HB) process is more widely employed compared to other available technologies that involve combining various units for ammonia production using coal or biomass feedstocks. These units include air separation, gasification

(for coal or biomass), sour gas shift, acid gas removal, and NH<sub>3</sub> synthesis. Natural gas is converted to hydrogen, which is then combined with the separated nitrogen, and the resulting mixture undergoes the Haber-Bosch (HB) process with an iron-based catalyst to produce ammonia. While natural gas is the predominant feedstock, alternative feedstocks like coal or biomass require additional units for the production process (Lan et al., 2012; Pattabathula V; Richardson J, 2016)

The ammonia synthesis occurs according to the following reaction:



**Figure 4.** Schematic diagram of ammonia production from natural gas, employing the Haber–Bosch process (HB).

The system is composed of various stages: steam reformation, the water-gas shift reaction, CO<sub>2</sub> removal, syngas purification, and ammonia synthesis and separation. To reduce overall energy consumption, it is crucial to improve the entire process. Ammonia production is known for its high energy intensity, leading to the emission of 289.8 million tons of CO<sub>2</sub> annually during the ammonia synthesis stage (Frattini et al., 2016a). This represents roughly 0.93% of global CO<sub>2</sub> emissions (Gilbert & Thornley, 2010).

Many efforts have been made to minimize the severe conditions of the Haber-Bosch process. They include the addition of an extra component to block catalysis and the modification of the geometry and electronic nature of the reacting components to optimize catalysis energetics (Q. Wang et al., 2019).

Ru-based catalysts may essentially enhance ammonia synthesis under mild circumstances (300–450°C and 4–15 MPa), which are much lower than the conditions required for iron-based

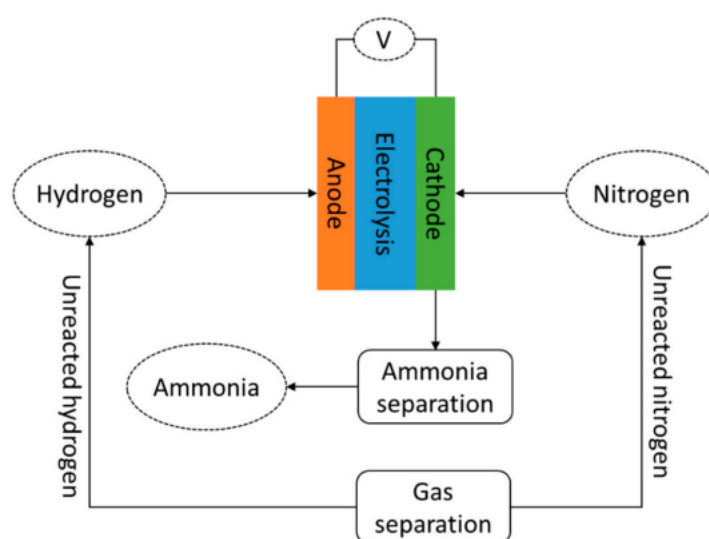


catalysts. However, Ru-based catalysts are costly and prone to hydrogen poisoning (Siporin & Davis, 2004; Smith & Torrente-Murciano, 2021).

### 1.3.1.2 Electrochemical Processing

Although the electrochemical processing method is not as well-established as the Haber-Bosch process, it is expected to offer better energy efficiency. This technique is estimated to consume approximately 20% less energy compared to the Haber-Bosch process (Lipman, 2017).

Due to its perceived simplicity, the electrochemical approach has the potential to reduce system configuration and control complexity. Additionally, the investment costs associated with this method are expected to be lower than those of currently employed ammonia synthesis systems.



**Figure 5.** Schematic diagram of electrochemical ammonia synthesis

The reactions at the cathode and anode of proton-conducting cells are illustrated in reactions (1) and (2), respectively. The cathode and anode reactions are basically reversible.



Four types of electrolytes are currently available: liquid electrolytes, molten salts, composite membranes, and solid electrolytes. Liquid electrolytes can operate at atmospheric temperature and pressure.

There are several potential liquid electrolytes that can be used in the electrochemical production of ammonia (NH<sub>3</sub>). These include LiClO<sub>4</sub> (lithium perchlorate) (0.2 moles) in tetrahydrofuran (Tsuneto et al., 1994), LiClO<sub>4</sub> (lithium perchlorate) in an ionic liquid, LiClO<sub>4</sub> (lithium perchlorate) in H<sub>2</sub>SO<sub>4</sub> and Li<sub>2</sub>SO<sub>4</sub> (lithium sulfate) in sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).

The electrochemical process is considered environmentally friendly and has low energy consumption, as reported by (R. Zhao et al., 2019). In addition, this electrochemical process for  $\text{NH}_3$  production is not dependent on fossil fuels and instead uses water molecules as the source of  $\text{H}_2$ . The electricity required for the reaction is supplied by renewable energy sources such as wind, hydro, geothermal and solar power, integrated with an energy storage system.

However, there are still several challenges associated with this process. One such challenge is the low ammonia ( $\text{NH}_3$ ) yields, as reported by Kordali et al. (2000).

Additionally, the electrolytes used in the process can be expensive, and the operating conditions can be harsh, as mentioned by Lu et al. (2016). These concerns primarily relate to two key factors: **electrolytes and catalysts**.

The presence of electrolytes is crucial in transporting protons from the anode to the cathode, which is necessary for the  $\text{N}_2$  fixation process involved in  $\text{NH}_3$  production. On the other hand, catalysts play a vital role in facilitating the fixation process, thereby enhancing the rate and efficiency of the overall process. Typically, solid-state and molten salt electrolytes are employed in the electrochemical production of  $\text{NH}_3$ , especially at high working temperatures.

## 1.4 General Overviews of hydrogen production from Ammonia

### 1.4.1 Characteristics of ammonia

#### 1.4.1.1 Physical properties

Ammonia has alkaline properties and a relatively strong odor. *Table 4* shows the detailed parameters of the physical properties of ammonia (Aziz et al., 2020b).

**Table 4.** Detail of physical characteristics of ammonia

Properties	Unit	Value
Molar mass	g/mol	<b>17.031</b>
Density at STP	kg/m <sup>3</sup>	<b>0.769</b>
Melting point	°C	<b>-77.73</b>
Boiling point at 100 kPa	°C	<b>-33.4</b>
Vapor pressure at 20 °C	kPa	<b>858</b>
Heat of evaporation	MJ/kg	<b>1.371</b>
Auto ignition temperature	°C	<b>650</b>
Critical temperature	°C	<b>132.4</b>
Critical pressure	MPa	<b>11.28</b>
Viscosity at 25 °C	μPa·s	<b>10.07</b>
Heat capacity at constant pressure (101.325 kPa, 15 °C)	kJ/mol· °C	<b>0.037</b>
Heat capacity at constant volume (101.325 kPa, 15 °C)	kJ/mol· °C	<b>0.028</b>
Heat of combustion	MJ/L	<b>11.2</b>
Thermal conductivity	mW/m· °C	<b>22.19</b>
Critical density	g/mL	<b>0.24</b>
Condensation pressure at 25 °C	MPa	<b>0.99</b>
Flammability limit (equivalence ratio)	-	<b>0.63–1.4</b>
Adiabatic flame temperature	°C	<b>1800</b>
Max. laminar burning velocity	m/s	<b>0.07</b>

From techno-economic analysis, ammonia is considered to be the least expensive fuel compared to other conventional fuels, such as gasoline, natural gas, liquefied petroleum gas (LPG), methanol, and hydrogen (Zamfirescu & Dincer, 2009).

In addition, liquid ammonia has a relatively high volumetric energy density, 12.7 MJ/L, which is higher than liquid hydrogen (8.49 MJ/L) and compressed hydrogen (4.5 MJ/L at a pressure

of 69 MPa and temperature of 25°C). The boiling temperature of ammonia is -33.4°C at atmospheric pressure. Furthermore, ammonia has a significantly higher combustion heat, 11.2 MJ/L, compared to liquid hydrogen (8.58 MJ/L).

Due to its lower density than air (0.769 kg/m<sup>3</sup> compared to 1.225 kg/m<sup>3</sup> at standard temperature and pressure (STP)), gaseous ammonia dissipates fast in the air under atmospheric conditions, reducing the risk of explosion and fire in the event of a leak. Furthermore, because ammonia has a greater auto-ignition temperature (650°C) than hydrogen (520°C), it is less likely to catch fire. The perceived toxicity of liquid ammonia (vapor pressure relative to toxicity at atmospheric temperature) is approximately three orders of magnitude greater than that of gasoline and methanol. This is owing to the fact that liquid ammonia has an IDLH (Immediately Dangerous to Life or Health) concentration of roughly 300 ppm, yet its vapor pressure is rather high; 8.58 10<sup>2</sup> kPa at 20°C (Giddey et al., 2013a).

Ammonia poses certain difficulties due to its restricted flammability range, which spans from 15.15% to 27.35% in dry air and 15.95% to 26.55% in air with 100% relative humidity. Consequently, it is generally considered to be non-flammable when stored or transported. Moreover, as ammonia is predominantly composed of nitrogen, its utilization, particularly at elevated temperatures, has the potential to generate nitrogen oxides (NO<sub>x</sub>). Hence, effective control of ammonia combustion becomes crucial. Additionally, given that ammonia is categorized as a hazardous chemical, appropriate management of associated risks is necessary to mitigate harm to both humans and the environment.

#### **1.4.2 Ammonia as energy carriers**

Ammonia is highly valued as a potential hydrogen storage option. It has high hydrogen density (17.8 wt%), as well as high flexibility in its utilization, including mobile and stationary applications. Due to its stability for long-term storage and transportation, ammonia can fulfill the demand to store energy in time (stationary energy storage) and in space (energy export and import) (Ikäheimo et al., 2018).

Ammonia can be utilized by extracting its stored hydrogen or directly utilized as fuel. Ammonia is currently adopted as an agricultural fertilizer, refrigerant gas, and in the manufacture of explosives, pesticides, and other chemicals. Therefore, the infrastructures to produce, store, transport, and utilize ammonia have been globally established (Fecke et al., 2016), leading to its proven economic performance.

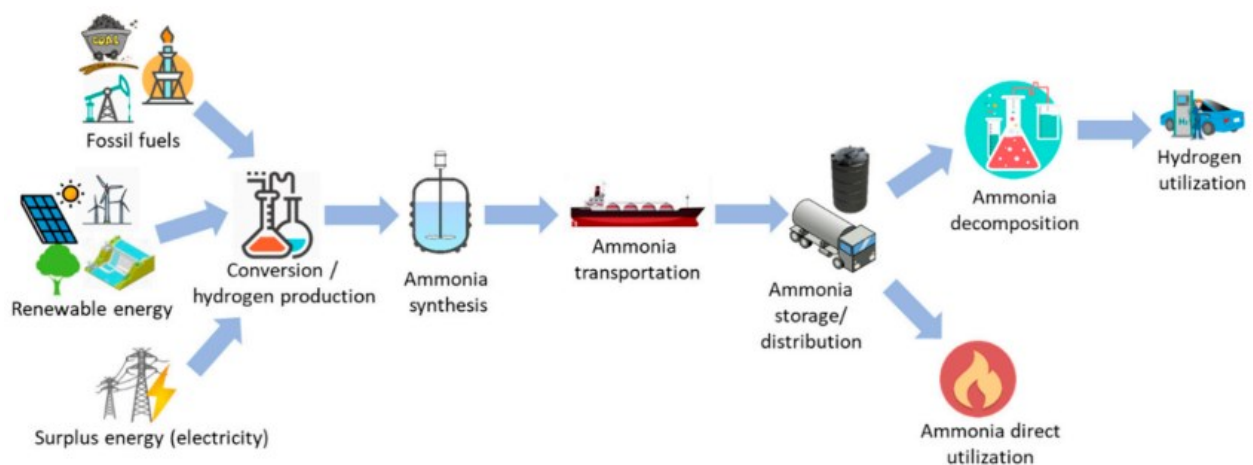
In addition, regulations and procedures for ammonia handling have been established well in the world. The ammonia economy has been investigated in numerous studies, including studies of islanded systems (Frattini et al., 2016b), process modeling, and fertilizer production using renewable energy (Ikäheimo et al., 2018).

However, for applications in the energy sector, ammonia still faces various challenges, including its properties, conversion technologies, and possible environmental problems following its utilization.

**Figure 6** below shows the possible routes for the production and utilization of ammonia.

Ammonia can be produced from both **fossil fuels** and **renewable energy sources**. These primary energy sources are then converted to ammonia through several processes, including: pre-treatment, conversion, and synthesis. In addition, the surplus electricity can also be converted to hydrogen (Ajiwibowo et al., 2019), which is further converted to ammonia, leading to the application of power-to-ammonia.

The produced ammonia is then stored, transported, and distributed to the users for its utilization. Numerous countries in the world have a strong motivation to utilize ammonia as one of the key players in the future energy system. Therefore, these countries have tried to set the future road map, as well as develop the technologies to realize the plan. Japan has clearly decided its plan for ammonia adoption.



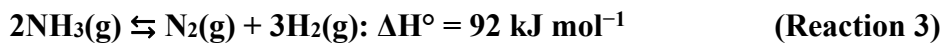
*Figure 6. Production and utilization routes of ammonia in the energy sector*

### 1.4.3 Ammonia as a Source of Hydrogen

The potential use of ammonia as a hydrogen carrier is being examined. In comparison to alternative hydrogen storage substances, ammonia offers several benefits. These include its high hydrogen density, an established technology for synthesis and distribution, and facile catalytic decomposition. Compared to hydrocarbons and alcohols, ammonia holds an advantage in that it does not produce CO<sub>2</sub> emissions at the point of use.

The drawbacks are mainly the toxicity of liquid ammonia and the problems related to trace amounts of ammonia in the hydrogen after decomposition. Storage of ammonia in metal amine salts is discussed, and it is shown that this maintains the high volumetric hydrogen density while alleviating the problems of handling the ammonia. Some of the remaining challenges for research in ammonia as a hydrogen carrier are outlined (Klerke et al., 2008).

The decomposition reaction of ammonia is endothermic (Reaction 3) and reaches 99.99% ammonia conversion at 400 °C and 1 atm according to thermodynamics, considering an inlet flow composed only of ammonia.



This means that a moderately high operating temperature is required to drive the ammonia decomposition reaction to completion and thus produce very high-purity hydrogen. This purity is compulsory if the hydrogen produced is used in fuel cells such as PEMFCs, which are irreparably degraded at very low concentrations of ammonia (ca. 0.1 ppm) (Makepeace et al., 2015)

### 1.4.4 Hydrogen Production from Ammonia

The decomposition of ammonia occurs at high temperatures in the presence or absence of a catalyst. One of the first works about the decomposition of ammonia reaction was carried out in 1904 by Perman and Atkinson (E. P. Perman, (1905).

The effect of temperature and pressure on the decomposition rate was evaluated, as well as the catalytic activity of elements such as mercury (Hg), Ferrous (Fe), and platinum (Pt). Over time, the decomposition of ammonia has proven to be an interesting reaction for different industrial applications; so, in 1934 Tayler proposed the use of the hydrogen produced through the decomposition of ammonia at high pressures (7 to 14 bar) coupled with a residual ammonia scrubber to harden oils (Tayler, 1934).

It is important to mention that the technology of ammonia crackers at ambient pressure was already established in the metallurgical industry to reduce and temper metals. Regarding the effect of pressure, the decomposition of ammonia is favored at low pressures, for this reason, many studies have focused on investigating the reaction rate at low pressures up to ultrahigh vacuum in the presence of platinum (A. J. B. Robertson, 1967), nickel, rhodium, tantalum, tungsten (A. J. B. Robertson, 1967) and iridium catalysts (Choudhary, 2001). More recently, the effect of high pressures on the reaction rate was examined, considering that generally, the hydrogen produced has to be compressed for its supply, for example, to a fuel cell (Sayas, 2020).

In this sense, in order to avoid compressing the hydrogen generated, the decomposition of ammonia has been evaluated directly at high pressures, up to 40 bar, in the presence of ruthenium supported on calcium oxide (**Ru/CaO**) catalyst promoted with K (Sayas, 2020).

DiCarlo et al. (2014) tested ruthenium supported on alumina catalyst (**Ru/Al<sub>2</sub>O<sub>3</sub>**) at pressures between 1 and 10 bar, evaluating the decrease in conversion with increasing pressure.

**Table 5** shows the list of technologies that have been proposed in the literature for ammonia decomposition.

**Table 5.** Technologies Used to Decompose Ammonia for Removal or for the Production of Hydrogen

Technology	Year	Reference
Thermal decomposition	1904, <b>1934</b>	(E. P. Perman, 1905; Tayler, 1934)
Decomposition at pressures other than 1 bar	1967, 1968, 2001, <b>2020</b> , 2014	(A. J. B. Robertson, 1967 ; Di Carlo et al., 2014)
Decomposition with electric current	1997, <b>2000</b> , 2002, 1938, 2013	(Pitselis, 1997 ; Y. Zhao et al., 2013)
Decomposition with an electron beam	1928, 1980, 1970, <b>2013</b>	(McLennan, 1928; Son, 2013)
Decomposition with an ion beam	<b>2016</b>	(Hirabayashi & Ichihashi, 2016)
Microwave decomposition	2017, <b>2017</b> , 1972	(Guler et al., 2017 ; R.Barker, 1972)
Decomposition with plasma technologies	1967, 2013, <b>2019</b> , 2019, 2014, 2017, 2018, 2015	(D. C. Carbaugh, 1967; L.; Y. Y.; Z. Y.; Z. R.; Z. J.; G. H. Wang, 2015)

Decomposition with solar energy	2020, 2019	(Wang, B.; Kong et al., 2019; Hu, 2020)
Decomposition coupled with other reactions	2017, 2018, 2017, 2012, 2011, 2003, 2009, 2013, 2005	(Chen, 2017; Deshmukh & Vlachos, 2005) [Police a changer .....??????]
Electrolysis of liquid NH <sub>3</sub>	2010, 2016	(Hanada, 2010 ; Modisha, 2016)
Photocatalysis in gaseous or aqueous medium	2015, 2018, 1932, 1983, 2012	(Reli et al., 2015; Yuzawa, 2012)
Decomposition with mechanochemical methods	2010	(Paik, 2010)
Reaction of NH <sub>3</sub> with hydrides	2007	(L. Li & Hurley, 2007)
Decomposition in gasification atmospheres	1905, 1996, 1999, 1995, 1997, 2008, 2008, 2004, 1993, 1995, 2002, 2002	(Abashar et al., 2002; White, 1905)
Decomposition in the presence of H <sub>2</sub> S	2008, 2005, 2000, 2002	(Arabczyk & Narkiewicz, 2002 ; Tsubouchi et al., 2008)
Decomposition in the presence of oxygen	2012, 2008, 2015, 2002, 2017	(He, 2012; Nagaoka, 2017)
Decomposition in wastewater	1999	(Goto, 1999)
Decomposition in the presence of water vapor	1977, 2014	(Atsumi, 2014; Friedlander, 1977)

**Source :** (Lucentini et al., 2021a)

Following the initial studies and applications, alternative approaches have emerged to provide the necessary activation energy for thermal decomposition reactions. These methods include utilizing electric current, electron beams, ions, microwaves, plasma, or solar energy. In addition to catalyst-based thermal decomposition, integrated systems have been explored where ammonia decomposition is combined with other exothermic reactions like propane or butane combustion. These techniques can be employed with or without catalysts. Furthermore, research has delved into hydrogen generation through liquid ammonia electrolysis, employing techniques such as photocatalysis, mechanochemical methods, or ammonia decomposition in the presence of other compounds like hydrocarbons, H<sub>2</sub>S, oxygen, or nitrogen.

### **Catalysts for the thermal decomposition**

Among the various technologies, the most technically widespread method for producing hydrogen from ammonia is thermal decomposition or catalytic cracking. It can be carried out with or without a catalyst, as the latter reduces the temperature required for decomposition.



This is why it is important to study the catalysts involved, as well as different reactor configurations, in order to reduce the energy input, in this case in the form of heat, to the system.

## Catalysts

The decomposition of ammonia is the reverse reaction of the Haber-Bosch process, which is commonly used for ammonia synthesis. Initially, the catalysts used for ammonia synthesis, namely Ru and Fe (Makepeace et al., 2019b), were also considered for the thermal decomposition of ammonia based on the principle of micro reversibility in heterogeneous catalysis. However, currently, commercially available catalysts for ammonia decomposition consist of nickel supported on alumina, chosen for its mechanical properties and heat resistance (Klerke et al., 2008b).

In the literature, various catalysts have been investigated for ammonia decomposition, with ruthenium supported on different oxides or structured and unstructured carbon showing the highest catalytic activity (Lamb et al., 2019a). Nonetheless, a major challenge encountered with these catalysts is their tendency to deactivate over time.

However, **ruthenium** is a noble metal, rare in nature, and consequently an expensive element. For this reason, low-cost catalytic compositions with a catalytic activity comparable to that of ruthenium have been actively sought (Mukherjee et al., 2018).

### 1.4.5 Ammonia as Potential Hydrogen Storage

Taking into consideration of energy efficiency and environmental friendliness, ammonia appears to be more interesting as hydrogen-carrying fuel compared to methanol for a wide range of applications (Juangsa et al., 2021).

**Table 6.** Characteristics comparison of compressed hydrogen, liquid hydrogen, methanol, and liquid ammonia (Aziz et al., 2020b).

Properties	Unit	Compressed hydrogen	Liquid hydrogen	Methanol	Liquid Ammonia
Storage method		Compression	Liquefaction	Ambient	Liquefaction
Temperature	°C	25 (room)	-252.9	25 (room)	25 (room)
Storage pressure	MPa	69	0.1	0.1	0.99
Density	kg/m <sup>3</sup>	39	70.8	792	600

The explosive limit in air	%vol	4–75	4–75	6.7–36	15–28
The gravimetric energy density (LHV)	MJ/kg	120	120	20.1	18.6
Volumetric energy density (LHV)	MJ/L	4.5	8.49	15.8	12.7
Gravimetric hydrogen content	wt%	100	100	12.5	17.8
Volumetric hydrogen content	kg-H <sub>2</sub> /m <sup>3</sup>	42.2	70.8	99	121
Hydrogen release	-	Pressure release	Evaporation	Catalytic decomposition at T > 200 °C	Catalytic decomposition at T > 400 °C
Energy to extract hydrogen	kJ/mol-H <sub>2</sub>	-	0.907	16.3	30.6

Liquid ammonia is able to store hydrogen in volumes much higher (121 kg-H<sub>2</sub>/m<sup>3</sup>) than liquid hydrogen (70.8 kg-H<sub>2</sub>/m<sup>3</sup>), which is about 1.7 times as high. Liquid ammonia can be stored at relatively low pressure (0.99 MPa at a temperature of 25°C), which is significantly lower than that of compressed hydrogen. However, in terms of physical density, liquid ammonia has a higher density (600 kg/m<sup>3</sup>) than compressed and liquid hydrogen, leading to heavier storage and transportation.

Methanol is a strong competitor for the storage of hydrogen. It has a higher energy density than ammonia (20.1 MJ/kg compared to 18.6 MJ/kg). However, it has both lower gravimetric and volumetric hydrogen contents than ammonia (12.5 wt% and 99 kg-H<sub>2</sub>/m<sup>3</sup> compared to 17.8 wt% and 121 kg-H<sub>2</sub>/m<sup>3</sup>, respectively) (Andersson & Grönkvist, 2019).

As methanol involves CO<sub>2</sub> in its synthesis, its utilization and decomposition also release CO<sub>2</sub>, leading to environmental concerns. Methanol reformation also leaves the problem of the production of carbon monoxide (CO), which can poison most of the catalysts adopted in fuel cells, and hence shortens the lifetime of the fuel cell (Metkemeijer & Achard, 1994).

To release the hydrogen from ammonia, a relatively huge amount of energy is consumed (30.6 kJ/mol-H<sub>2</sub>).

On the other hand, the regasification of liquid hydrogen only consumes very low energy (0.907 kJ/mol-H<sub>2</sub>). Therefore, ammonia decomposition is a challenging task, especially in terms of total energy efficiency in the utilization of ammonia. The decomposition of ammonia must be followed by hydrogen separation in the case that a high purity of hydrogen is demanded at the utilization site. On the other hand, compressed and liquid hydrogen can deliver highly pure hydrogen.

**Table 7** below-shows the technological levels (for storage conversion, transportation, and H<sub>2</sub> release), advantages, and challenges for compressed hydrogen, liquid hydrogen, methylcyclohexane (MCH), and liquid NH<sub>3</sub> (Juangsa et al., 2021).

**Table 7.** Technological levels (for storage conversion, transportation, and H<sub>2</sub> release), advantages, and challenges for compressed H<sub>2</sub>, liquid H<sub>2</sub>, MCH, and liquid NH<sub>3</sub>

Properties	Compress H <sub>2</sub>	Liquid H <sub>2</sub>	MCH	Liquid Ammonia
Conversion for storage	High	Small: high Large: Mid	Mid	High
Tank storage	Mid	High	High	High
Transportation vessel	Low	Low	High	High
Pipeline	Low	High	High	High
Truck	Mid	High	High	High
Hydrogen release	High	High	Mid	Mid
Distribution	Mid	Mid	Mid	High
Hydrogen release	Expansion	Regasification	Dehydrogenation	Decomposition
Advantages	<ul style="list-style-type: none"> <li>• High purity</li> <li>• Simple hydrogen release</li> </ul>	<ul style="list-style-type: none"> <li>• High purity</li> <li>• Easy regasification</li> </ul>	<ul style="list-style-type: none"> <li>• Stable storage</li> <li>• Existing regulation</li> </ul>	<ul style="list-style-type: none"> <li>• Possible direct use</li> <li>• Establish infrastructure and regulation</li> </ul>
Challenges	<ul style="list-style-type: none"> <li>• Low hydrogen Storage</li> <li>• Leakage risks</li> <li>• Embrittlement</li> </ul>	<ul style="list-style-type: none"> <li>• Insulation technology</li> <li>• Difficult for long term</li> <li>• Boil-off</li> <li>• Leakage risk</li> <li>• Energy-intensive liquefaction</li> </ul>	<ul style="list-style-type: none"> <li>• Low hydrogen storage</li> <li>• Durability</li> <li>• Must be decomposed</li> <li>• Energy intensive</li> <li>• Decomposition</li> </ul>	<ul style="list-style-type: none"> <li>• Low reactivity</li> <li>• Toxic and Strong odor</li> <li>• Energy-intensive decomposition</li> </ul>

Compressed hydrogen H<sub>2</sub>, liquid NH<sub>3</sub>, and small-scale H<sub>2</sub> liquefaction are considered matured technologies that have been massively adopted and are available globally.

However, hydrogenation to produce MCH is still in the demonstration and pilot testing stages, demanding additional research and refinements.

Furthermore, the technology for storing and transporting liquid hydrogen, MCH, and liquid ammonia is well-established; in particular, ammonia has been mass-produced with well-established regulations. H<sub>2</sub> is quickly liberated from compressed and liquid H<sub>2</sub>, whereas MCH and liquid ammonia need dehydrogenation and breakdown, respectively.

Both processes, MCH dehydrogenation, and NH<sub>3</sub> breakdown, require an input of heat to reach the necessary temperatures of 200°C-400°C and 400°C-550°C, respectively. While NH<sub>3</sub> can be utilized directly without undergoing decomposition, MCH cannot be used immediately.

## CHAPTER 2: METHODOLOGY

### 2.1 Raw material and data Collection

The raw material considered in the present work is the digestate from biogas plants. Digestate is a by-product of the degradation of organic waste by anaerobic digestion, and it contains a significant amount of ammonia. The recovery of ammonia contained in the digestate offers a potential route for the production of renewable hydrogen.

In this study, the ammonium nitrogen ( $\text{NH}_4\text{-N}$ ) data of different feedstocks used for biogas production and its digestate was collected from a brochure on the results of biogas production measurements in Germany published by the Agency for Renewable Resources (FNR: Fachagentur Nachwachsende Rohstoffe). These data were used to estimate the amount of ammonia ( $\text{NH}_3$ ) contained in the digestate of different feedstocks for hydrogen production.

All these calculations were carried out using **Excell software** to develop a hydrogen production model.

The table below shows the list of different feedstocks with their ammonium nitrogen content collected for hydrogen production.

**Table 8.** Data collection of ammonium nitrogen ( $\text{NH}_4\text{-N}$ ) from the digestate and its substrates

Feedstocks	$\text{NH}_4\text{-N}$ (Kg/t)	
	(Substrate)s	(Digestate)
<b>A</b> Pig manure (81.7 %), Feed stillage (18.3 %)	2.1	2.6
<b>B</b> Cattle manure (57.5%), Silo corn (20.5 %), Chicken manure (17.1%), rapeseed threshing (4%), lawn clippings (0.6%), horse manure (0.3%)	3.2	4
<b>C</b> Pig manure (86%), Dry chicken droppings (8.8%), Glycerin (2.6%), Coffee residues (1.4%), Sunflower Shell (0.8%), Molasses (0.4%)	4.4	5.2
<b>D</b> Potato peel waste (47.2%), Fat (18.8), Silo maize (15.6), Dry chicken droppings (6.4%), Flour waste (2.3%), Inocilum (2.1%), Apple pomace (2.1%), Whey (1.9%), Cattle manure (1.8%), Grain cleaning (1%), Organic waste (0.5%), Molasses (0.4%)	1.1	2.8
<b>E</b> Silo Maize (50%), Pig manure (23.4%), Grain cleaning (10%), Water (5.2%), Whey (3.6%), Sugar beet leaf (3%), Potatoes (2.4%), Rye (1.2%), Grass Silage (1%) Potato pulp (0.2%)	1.7	3.8

<b>F</b>	Silo Maize (27.4%), Cattle manure (14.1%), Pig manure (13.6%), Leftovers (13.2%), Grass silage (7.9%), Whey (5.8%), Potato pulp (5.2%), Stillage (4.4%), Fat (4%), Dog food (3%), Sun lower (0.8), Apple pomace (0.5%) Grain cleaning (0.1%)	1.5	4
<b>G</b>	Pig manure (56.7%), Corn silage (40.4%), Barley grist (1.5%), Dry chicken droppings (1.5%)	2.2	3.2
<b>H</b>	Pig manure (75%), Corn silage (11.8%), Silage (9.1%), Rye grains (6.1%)	3	4
<b>I</b>	Pig manure (49.9%), Corn silage (44.9%) Wheat grains (5.2%)	1.5	2.4
<b>J</b>	Cattle manure (55.6%), Pig manure (5.7%), Turkey manure (2.1%), Corn silage (34.8%), Rye GPS (1.8%)	1.5	3.1
<b>K</b>	Pig manure (49.3%), Turkey manure (7.4%), Corn silage (30.3%), Grass silage (1.2%), Cereal (11.8%)	2.9	5.7
<b>L</b>	Cattle manure (81.4%), Corn silage (15.9%), Wheat grains (2.7%)	2.3	2.7
<b>M</b>	Cattle manure (81.3%), Dry chicken droppings (9.1%), Corn silage (7%), Barley grains (2.5%)	1.7	3.5
<b>N</b>	Corn silage (85.1%), Chicken manure (5.2%), Cattle manure (5.3%), Grass silage (4.4%)	0.8	3.4
<b>O</b>	Corn silage (69.7%), Rye meal (4.2%), Rye ensilage (Full plant) (2.3%), Grass/summer barley (1.1%), Pig manure (8.2%), Cattle manure (14.1%), Grass silage (0.5%)	0.6	2.6
<b>P</b>	Maize silage/ Grain (29.3%), Pig manure (29.1%), Green rye silage (3.1%), Corn silage (38.5%)	1.2	3.2
<b>Q</b>	Cattle/manure (48%), Corn silage (43.5%), Grass silage (1.2%), Wheat grist (4.1%), Rye ensilage (Full plant) (3.3%)	1.1	2.8
<b>R</b>	Cattle manure (31.8%), corn silage (61.6%) Wheat grist (6.6%)	1.2	3.1
<b>S</b>	Cattle manure (30.7%) Corn silage (38.3%), Rye ensilage (Full plant) (17.5%), Cattle manure (1.3%), Grass silage (8.1%), wheat grains (4.1%)	1.1	2.9
<b>T</b>	Pig manure (23.5%), Corn grain silage (36%), Cattle manure (23.6%), wheat (3.6%), Barley ensilage (Full plant) (3.3%), Corn Silage (10%)	1.1	4.2
<b>U</b>	Cattle manure (42,7%), Corn silage (41.2%), Grass silage (14.1%), Wheat grist (2.1%)	1	2.8
<b>V</b>	Pig manure (50%), Turkey manure (7.5%), Corn silage (8.3%), Grass silage (1.8%), Cereal porridge (20.5%) Corn-Cob-Mix (5.6%), Water (4.3%), Wheat grist (2%)	2.7	5.3

<b>W</b>	Cattle manure (30.3%), Corn silage (14.3%), Grass silage (31.2%), Grain meal (3.9%), Oat/rye ensilage (Full plant) (20.2%)	0.8	2.7
<b>X</b>	Corn silage (49.3%), Pig manure (38.1%), grass silage (10.2%), Wheat grist (2.5%)	1	2.5
<b>Y</b>	Corn silage (81%), Rye ensilage (Full plant) (2.6%), Green rye silage (16.3%)	0.5	3.5
<b>Z</b>	Corn silage (89%), Rye ensilage (Full plant) (9%), Millet/sunflower (2%)	0.7	3.2
<b>AB</b>	Turkey manure (5.4%), Corn silage (83.4%), Rye ensilage (Full plant) (6.2%), Corn-Cob-Mix (2.8%), Wheat grains (1.8%), Potatoes (0.3%)	1.2	2.9
<b>CD</b>	Corn silage (96.9%), Corn-Cob-Mix (2.5%), chicken manure (0.6%)	0.7	2.6
<b>EF</b>	Corn silage (98.3%), Grain meal (1.2%), Sugar Beetz (0.5)	0.5	2.4
<b>GH</b>	Corn silage (81.1%), Grass silage (4.8%), Rye ensilage (Full plant) (12.7%), Wheat grist (0.6%), Cattle manure (0.7%)	0.4	2.6
<b>IJ</b>	Turkey manure (29.9%), Corn silage (50.7%), Rye ensilage (6.5%), Sudan grass (9.5%), Green waste (1%) Grass silage (2.3%)	1.8	2.8
<b>KL</b>	Corn silage (70.2%), rye meal (8.3%), Pig manure (17.9%), Rye ensilage (Full plant) (3.5%)	1	4

**Source:** (Gülzow, 2009)

## 2.2 Applied methods for digestate conversion into ammonia

During anaerobic digestion, the decomposition of organic matter by microorganisms' releases ammonium nitrogen as a by-product. After substrate digestion, the digestate (the residue left after biogas production often contains higher concentrations of ammonium nitrogen than the original substrate).

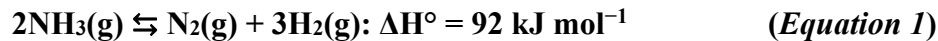
To convert the measured amount of  $\text{NH}_4\text{-N}$  from the digestate into ammonia ( $\text{NH}_3$ ),  $\text{NH}_4\text{-N}$  is multiplied by the conversion factor of **1.2159**. This conversion factor represents the ratio of the molar masses between ammonia ( $\text{NH}_3$ ) and nitrogen (N). This factor converts directly the amount of ammonium nitrogen ( $\text{NH}_4\text{-N}$ ) into the corresponding amount of ammonia ( $\text{NH}_3$ ). The *formula 1* below is used to estimate the amount of ammonia ( $\text{NH}_3$ ) produced in the digestate based on the measured amount of ammonium nitrogen ( $\text{NH}_4\text{-N}$ ) present.

$$\text{Amount ammonia (NH}_3\text{)} = 1.2159 \times \text{amount NH}_4\text{-N} \quad (\text{Formula 1})$$

Knowing that the molar mass of ammonia (NH<sub>3</sub>), equal to **17.03 g/mole** and the molar mass of nitrogen (N), equal to **14.01 g/mole**.

### 2.3 Processes for ammonia conversion into hydrogen

Ammonia can be dissociated to produce hydrogen gas and nitrogen gas. Therefore, this reaction can be written as below (Equation 1).



The decomposition reaction of ammonia is endothermic and reaches 99.99% ammonia conversion at 400°C and 1 atm according to thermodynamics, considering an inlet flow composed only of ammonia. In practice, the rate of conversion depends on both temperature and the types of catalysts used.

Based on the stoichiometry of the reaction, which states that for every 2 moles of ammonia, 3 moles of hydrogen gas and 1 mole of nitrogen are produced means for every 100% of ammonia 75% of hydrogen gas and 25% of nitrogen is produced. The proportion of ammonia NH<sub>3</sub> and H<sub>2</sub> is in the ratio of 2 volumes of ammonia NH<sub>3</sub> to 3 volumes of hydrogen (the molar ratio is 2: 3). The fraction of ammonia that is converted to hydrogen. For this specific equation, the conversion factor is 3/2 which corresponds to 1.5.

The *formula 2* below can be used to calculate the hydrogen potential from ammonia:

$$Q(\text{H}_2) = \alpha \times Q(\text{NH}_3) \quad (\text{Formula 2})$$

Where:

- **H<sub>2</sub>**; is the quantity of hydrogen produced in **(moles)**;
- **NH<sub>3</sub>**; is the quantity of ammonia in **(moles)**;
- **α**; is the conversion factor.

In experimental conditions, various factors can affect the conversion factors in a chemical reaction.

Some of these factors include temperature, pressure, the presence of catalysts, and activation energy. Therefore, determining the appropriate value of alpha requires considering these factors and conducting experimental or theoretical studies to establish the conversion factor specific to the given conditions.



The value of alpha can vary depending on the specific reaction system and the particular circumstances under which ammonia is being converted to hydrogen.

#### ✓ **Temperature**

The rate of a chemical reaction is often temperature-dependent. As temperature increases, the kinetic energy of the reactant molecules increases, leading to more frequent and energetic collisions. Consequently, the conversion factor may change as the reaction rate and equilibrium position can be influenced by temperature.

#### ✓ **Pressure**

For reactions involving gases, changes in pressure can impact the conversion factor according to "*Le Chatelier's principle*".

Altering the pressure can affect the equilibrium position and the partial pressures of the reactants and products, thereby influencing the conversion factors.

#### ✓ **Catalysts**

The presence of a catalyst accelerates a chemical reaction by providing an alternative reaction pathway with lower activation energy. By reducing the activation energy, a catalyst can affect the rate of reaction, potentially leading to different conversion factors.

#### ✓ **Activation energy**

Activation energy represents the energy barrier that reactant molecules must overcome to form the products. By changing the activation energy through factors like temperature or catalyst, the reaction rate and, consequently the conversion factor can be affected.

**Thermal decomposition** or catalytic cracking is the most common technique used for the generation of hydrogen from ammonia. It can be carried out with or without the presence of a catalyst, as the presence of a catalyst allows the decrease of the temperature necessary for the decomposition. For this reason, it is important to study the catalysts involved as well as different reactor configurations in order to decrease the supply of energy, in this case in the form of heat, to the system.

The thermal decomposition of ammonia ( $\text{NH}_3$ ) is an endothermic reaction, which means that it requires the input of heat. Without the presence of catalysts, the temperature range for the

thermal decomposition of ammonia is generally between **700°C** and **1,100°C** (Ristig et al., 2022).

Due to the endothermicity of the reaction, ammonia decomposition is favored by an increase in temperature. Consequently, high efficiency, or even total conversion, in ammonia decomposition requires high temperatures and low pressures for a technical process. Both temperature and pressure must be low for a technical process.

In this work, especially the conversion factor depends on temperature, pressure, catalysts used (Ruthenium-based catalyst and Nickel-based catalyst), activation energy, and conversion rate.

**Table 9.** Catalysts based on Ru, and Ni used to decompose Ammonia and their catalytic performance at 1 atmosphere

Active phase	Support	WHSV (ml/g/h)	%NH <sub>3</sub> inlet flow	Temperature (°C)	Conversion rate (%)	AE (KJ/mole)	Ref.
Ru	SiO <sub>2</sub>	30000	100	500	96	41	(Yao et al., 2011)
Ru	CNTs	30000	100	500	88	69	(Yin et al., 2004)
Ni	Al <sub>2</sub> O <sub>3</sub>	36000	100	600	93	123	(Gu et al., 2015)

Based on the conditions given in **Table 9** above the conversion factors of different catalysts are presented in **Table 10** below.

**Table 10.** Conversion factors of different catalysts

Catalysts	Conversion factor( $\alpha$ )
Ru/SiO <sub>2</sub>	<b>0.72</b>
Ru/CNTs	<b>0.66</b>
Ni/ Al <sub>2</sub> O <sub>3</sub>	<b>0.69</b>

## 2.4 Determination of the energy content from hydrogen

The calculation of the energy content from hydrogen is made according to the **formula 3** below.

First of all, for the calculation of hydrogen potential, the values gotten are in (**moles**), which should be converted into liter knowing that:

At standard temperature and pressure conditions (STP): **1 mole** is equal to **22.4 l**

The following step is to convert the values of hydrogen in liter into volume (**m<sup>3</sup>**) at standard temperature and pressure conditions (STP): **1 liter** is equal to **0.001 m<sup>3</sup>**.

$$\text{Energy content (MJ)} = \text{Mass(kg)} \times \text{HHV of hydrogen} \quad (\text{Formula 3})$$

Where: **Mass (Kg) = Volume of hydrogen × density of hydrogen** (at NTP).

The density of hydrogen at normal temperature and pressure (NTP) is equal to **0.08375 (kg/m<sup>3</sup>)**;

**The High heating value (HHV)** of hydrogen at normal temperature (NTP) is equal to **120 (MJ/kg)**

## **2.5 Determination of Power potential based on the energy content of hydrogen**

To Calculate the power content in kilowatt-hours (kWh) from the energy content of hydrogen. The *formula 4* below converts the energy content of hydrogen from megajoules (MJ) to kilowatt-hours (kWh) by multiplying by the conversion factor of 0.2778 kWh/MJ. This conversion is useful for evaluating the power output or consumption associated with a given hydrogen energy content. After calculating the energy content, the power potential is calculated through this equation:

$$\text{Power content} = 0.2778 \times \text{Energy content (MJ)} \quad (\text{Formula 4})$$

Knowing that the conversion factor between **MJ** and **kilowatt-hour** is: **1MJ** is equal to **0.27 (kW/h)**.

The overall Excel calculation can be seen in **APPENDIX 3**.

## CHAPTER 3: RESULTS AND DISCUSSION

### 3.1 Development of ammonia recovery methodology from the anaerobic digestion process for hydrogen production

The development of ammonia recovery from the anaerobic digestion is accordingly illustrated by the *Figure 7* below.

First of all, Various techniques have been studied to recover ammonia from the digestate streams including (Gas-liquid stripping, ion exchange, electrolysis, membrane separation, adsorption, and struvite)

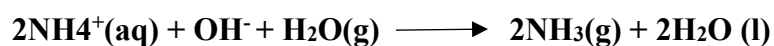
Gas-liquid stripping is a widely established technology used to recover ammonia directly from anaerobic digestate (Palakodeti et al., 2021; Serna-Maza et al., 2015). The process is defined as the mass transfer of ammonia from the liquid phase (digestate) to the gas phase (stripping gas). It is a particularly attractive technology since it is insensitive to solids in the liquid phase and only requires a relatively limited energy input (Srinath & Loehr, 1974).

This technology requires a relatively low energy input compared to other physiochemical separation methods (e.g., ion exchange resins, membrane separation, etc.). Furthermore, it is not adversely affected by solids in the liquid phase, which makes it an attractive separation technology (Georgiou et al., 2019).

The volatilization of ammonia is the primary environmental impact that needs to be effectively controlled and mitigated to minimize the risks of volatilization. In addition, digestate can be difficult to handle and transport due to its high-water content. To address these challenges, side stream stripping can be used to recover ammonia from the digestate, making it safer to handle and reducing its emission impact. This process can also help reduce transportation costs by removing excess water from the digestate.

Side stream stripping is a process that uses steam to separate ammonia from liquid waste. When the digestate moves from the digester to the stripping column the waste is heated and then passes through a distillation column, where the ammonia is separated from the liquid.

During stream stripping, high-temperature steam is passed through digestate and the ammonium ions ( $\text{NH}_4^+$ ) and hydroxide ions ( $\text{OH}^-$ ) present in the digestate react with the steam  $\text{H}_2\text{O}(\text{g})$  to form gaseous ammonia and liquid water  $\text{H}_2\text{O}(\text{l})$ .

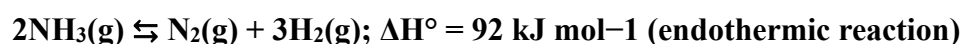


This process is particularly effective for the recovery of ammonia from anaerobic digestate, as it can remove up to 99 % of the ammonia present in the waste and it is also energy efficient, as it uses the heat generated during the digestion process to power the distillation column.

After this step stripped digestate goes back into the digester and the ammonia can then be condensed and collected for use in other applications.

Thermal decomposition or catalytic cracking is the most common means of hydrogen generation from ammonia.

Ammonia gas is stored in the tank and flows from the tank into the ammonia cracker the ammonia molecules each of which contains one nitrogen and three hydrogen atoms travel into the cracker and flow upwards through the cracker Chambers as the ammonia comes into contact with the catalyst. The catalyst separates the nitrogen from the hydrogen atoms.



After this process the mix of 75% hydrogen and 25% nitrogen pass through the adsorbent materials pressure swing adsorption (PSA) which is commonly used to purify hydrogen. The adsorbent material selectively adsorbs the impurities allowing hydrogen to pass through and separate complete nitrogen from hydrogen to produce electricity.

Nitrogen gas is a byproduct of the purification process which can be used for fire suppression; In electronics manufacturing processes, nitrogen gas is used for cooling cleaning, and as a protective atmosphere during soldering and other operations. It helps prevent oxidation and ensures high-quality production of electronic components; Nitrogen gas is sometimes used to inflate vehicle tires. It offers benefits such as maintaining tire pressure for longer periods, reducing tire wear, and improving fuel efficiency; Nitrogen gas is frequently used to create an inert atmosphere in industrial processes. It displaces oxygen and other reactive gases, preventing oxidation, combustion, or undesirable reactions. This is crucial in industries such as food packaging, pharmaceuticals, electronics manufacturing, and chemical production. (“Industrial Uses of Nitrogen Gas,” 2021).

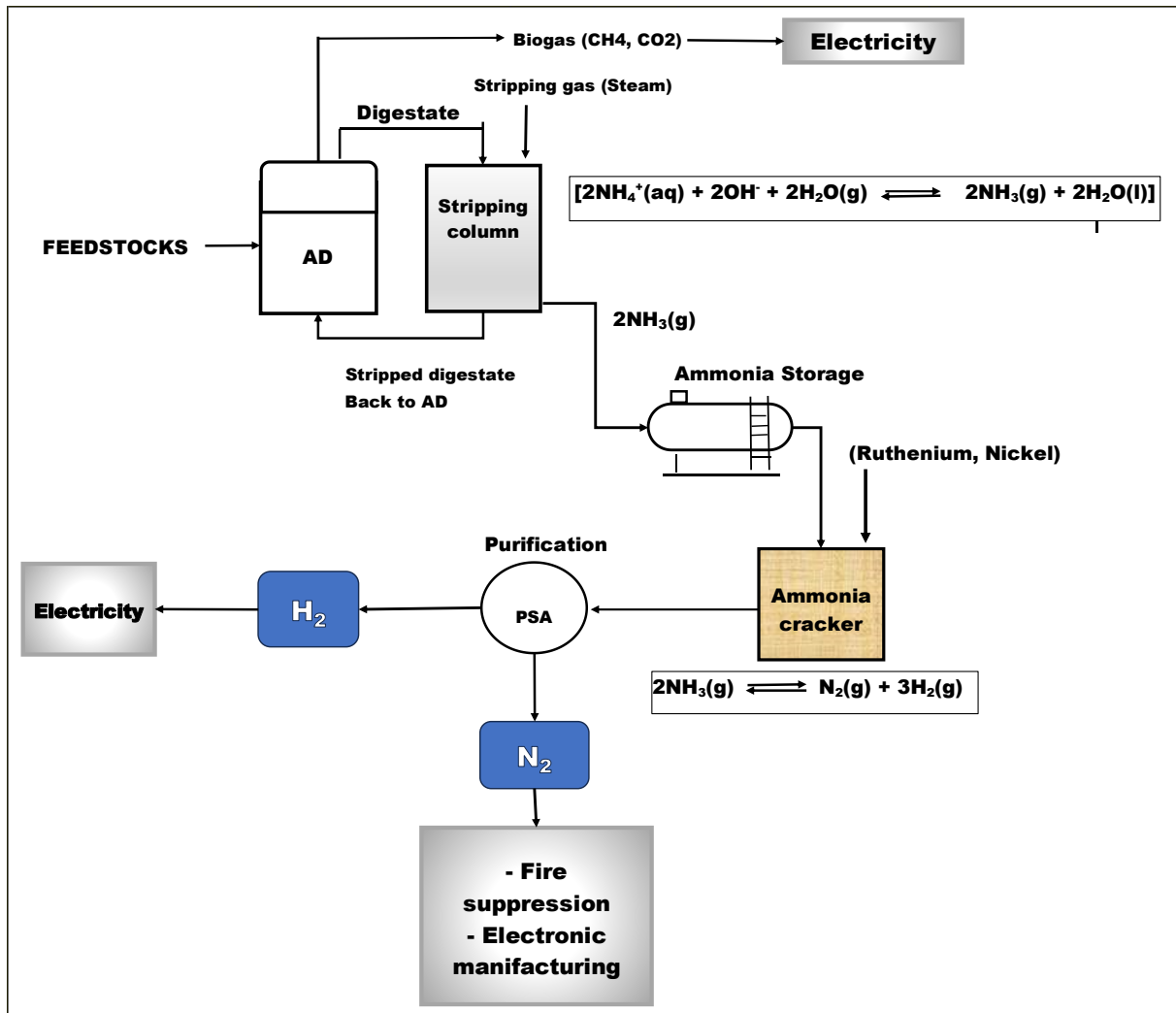


Figure 7. Overall flow sheets

### 3.2 The level of the concentration of ammonium nitrogen content from the digestate and its different substrates

During anaerobic digestion, the decomposition of organic matter by microorganisms' releases ammonium nitrogen as a by-product. After substrate digestion, the digestate (the residue left after biogas production often contains higher concentrations of ammonium nitrogen than the original substrate). This is due to the digestion process, which converts organic nitrogen compounds into ammonium.

Figure 8 below shows the variation in ammonium nitrogen concentration in kg/t in digestate and its various substrates.

It can be seen from the result of this figure that there is generally an increase in ammonium nitrogen content when comparing the substrate to its digestate.

This can be attributed to several factors, such as organic nitrogen conversion, bound nitrogen release, microbial activity, and ammonium retention.

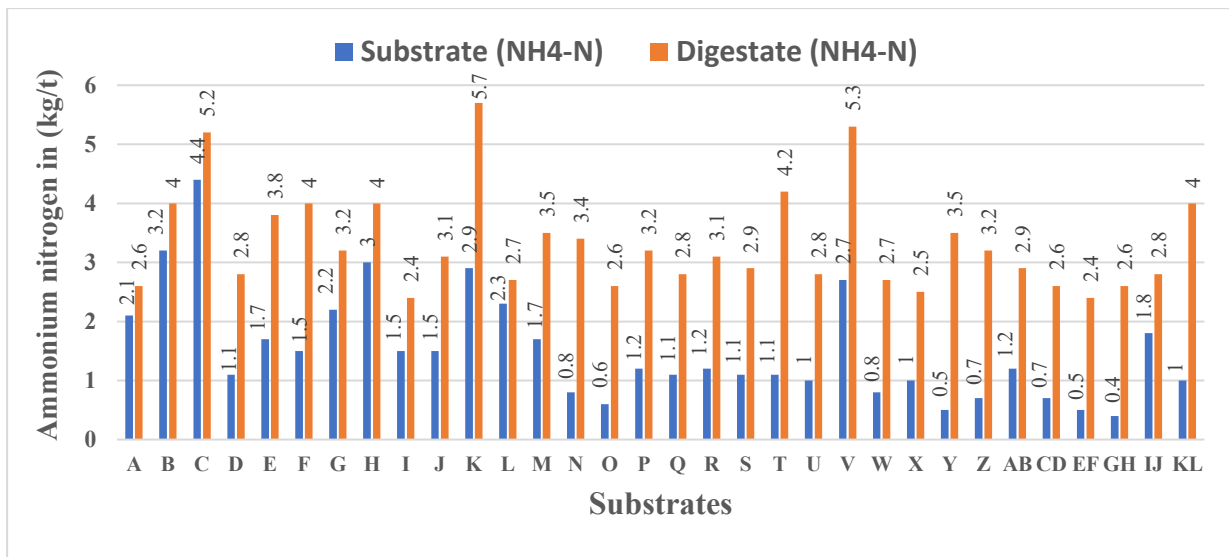
Looking at the result from the figure, among all the feedstocks, substrate K with a concentration of (2.9) kg/t has recorded the highest concentration of ammonium nitrogen from the digestate at about (5.7) kg/t, followed by substrate V with a concentration of (2.7) kg/t has recorded a concentration at about (5.3) kg/t in ammonium nitrogen from the digestate and substrate C with a concentration of (4.4) kg/t has recorded a concentration at about (5.2) kg/t in ammonium nitrogen from the digestate respectively. On the other hand, the lowest concentration of ammonium nitrogen was obtained from substrate I with a concentration of (1.5) kg/t recorded a concentration at about (2.4) kg/t in ammonium nitrogen from the digestate, and substrate EF with a concentration of (0.5) kg/t has recorded a concentration at about (2.4) kg/t in ammonium nitrogen from the digestate respectively.

Therefore, the ammonium nitrogen content in the digestate may not always increase compared to the substrate.

The ammonium nitrogen content in the digestate can be influenced by various factors, including the composition of the substrate, the efficiency of the anaerobic digestion process, and the management practices employed (Peng & Pivato, 2019).

In some cases, the ammonium nitrogen content in the digestate may be lower than that in the substrate due to processes such as microbial assimilation, volatilization, or denitrification. Microorganisms involved in anaerobic digestion can utilize ammonium nitrogen for their own growth and energy needs, resulting in a reduction in its concentration in the digestate. Additionally, under certain conditions, ammonium nitrogen can be transformed into other forms of nitrogen or lost as gaseous ammonia.

It is essential to take into account the specific conditions and characteristics of the anaerobic **digestion** process, including feedstock composition, operating parameters, and management practices, to accurately understand the variations in ammoniacal nitrogen content between substrate and digestate.



**Figure 8.** The level of the concentration of Ammonium nitrogen content in digestate and its different substrates

### 3.3 The level of ammonia content from the digestate of different feedstocks

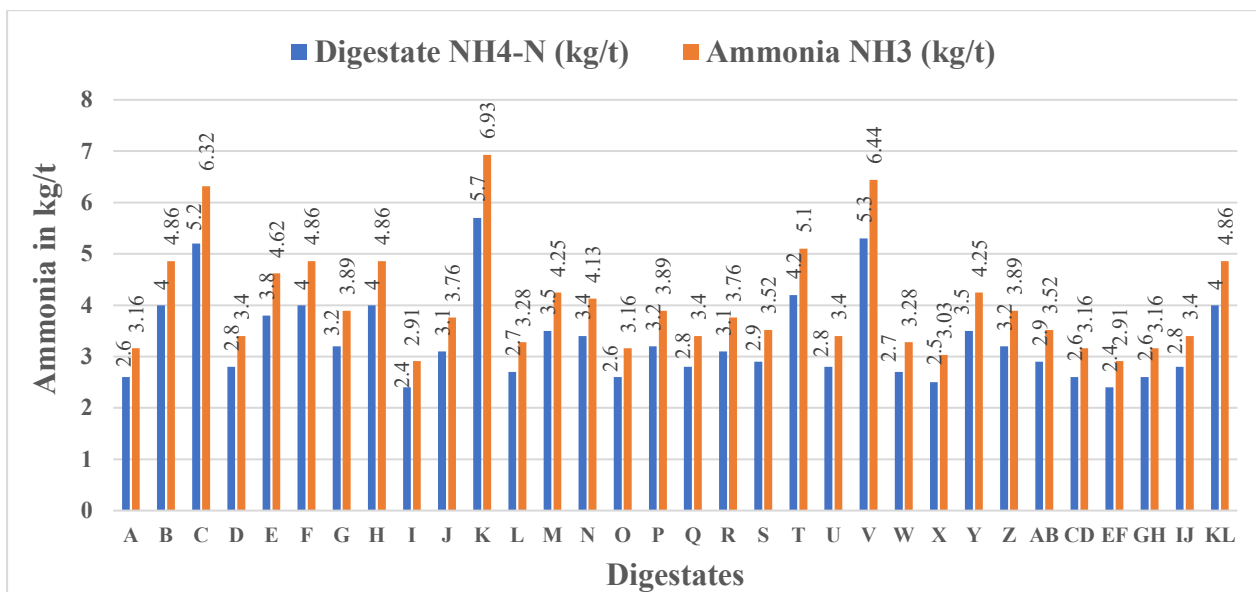
The **Figure 9** below shows ammonia concentration in kg/t as a function of ammonium nitrogen content in digestate from different substrates.

The results in this figure show that there is an increase in ammonia content as a function of the ammonium nitrogen content in the digestate.

The amount of ammonia depends directly on the amount of NH<sub>4</sub>-N (ammonium nitrogen) present in the digestate. As the concentration of ammonium nitrogen in the digestate increases, the quantity of ammonia increases.

Looking at the result from the figure, substrate **K** continues to record the highest concentration of ammonia at about (6.93) kg/t due to its high content of ammonium nitrogen from the digestate at about (5.7) kg/t, followed by substrate **V** with a concentration of (5.3) kg/t ammonium nitrogen has recorded a concentration at about (6.44) kg/t in ammonia content and substrate **C** with a concentration of (5.2) kg/t has recorded a concentration at about (6.32) kg/t respectively. The lowest concentration of ammonia was obtained from substrate **I** with a concentration value of (2.4) kg/t given at about (2.91) kg/t in ammonia and similar to substrate **EF** with a concentration of (2.4) kg/t recorded (2.91) kg/t respectively.





**Figure 9.** Variation of ammonia content as a function of the ammonium nitrogen content from the digestate of different feedstocks

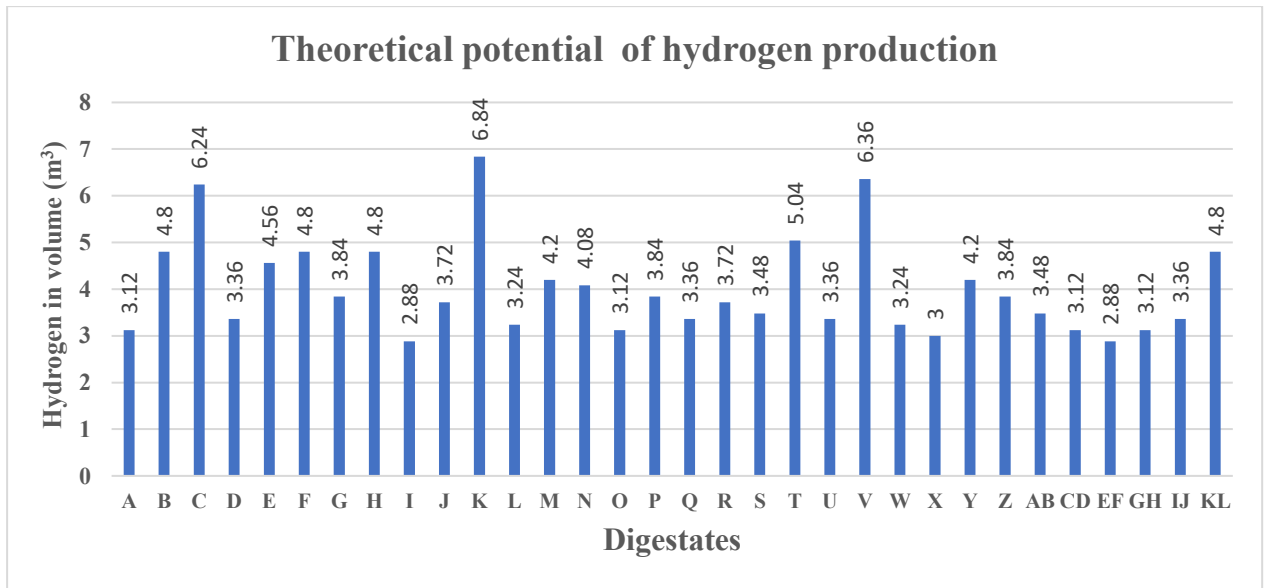
### 3.4 The potential of hydrogen production from the digestate of different feedstocks.

The **Figure 10** below illustrates the result of the theoretical potential of hydrogen production from the digestate of different feedstocks.

According to the results, of all the digestate, substrate K gave the highest hydrogen potential by volume with approx. (6.84 m<sup>3</sup>), followed by digestate from substrate V with approx. (6.36 m<sup>3</sup>) and digestate from substrate C with a value of (6.24 m<sup>3</sup>) respectively. The lowest hydrogen potential was observed in the digestate from substrates I (approx. 2.88 m<sup>3</sup>) and EF (approx. 2.88 m<sup>3</sup>) respectively.

Digestate with a high ammonium nitrogen content produced a lot of hydrogen.

The hydrogen potential produced depends on the amount of ammonia available in the digestate. As the amount of ammonia increases, more hydrogen is produced, which means that for every 100% of ammonia, 25% of nitrogen and 75% of hydrogen are theoretically produced, based on the stoichiometry of the reaction (2 moles of ammonia give 1 mole of nitrogen and 3 moles of hydrogen). For this specific equation, the conversion factor is 75%, which relates the quantity of ammonia to the quantity of hydrogen gas.



*Figure 10. The theoretical potential of hydrogen production from the digestate of different feedstocks*

### 3.5 Energy potential calculation based on the energy content of hydrogen produced

The *Table 11* below shows the result of the power output in kilowatt-hours (kWh) based on the energy content of hydrogen produced.

**Table 11.** Estimated energy potentials for the samples studied

Substrates	Digestate (NH <sub>4</sub> -N)	Hydrogen (m <sup>3</sup> )	Energy content (MJ)	Power output (kWh)
A	2.6	3.12	31.39	8.47
B	4.0	4.8	48.30	13.04
C	5.2	6.24	62.79	16.95
D	2.8	3.36	33.81	9.12
E	3.8	4.56	45.88	12.39
F	4	4.8	48.30	13.04
G	3.2	3.84	38.64	10.43
H	4	4.8	48.30	13.04
I	2.4	2.88	28.98	7.82
G	3.1	3.72	37.43	10.10
K	<b>5.7</b>	<b>6.84</b>	<b>68.83</b>	<b>18.58</b>
L	2.7	3.24	32.60	8.80
M	3.5	4.2	42.26	11.41
N	3.4	4.08	41.05	11.08
O	2.6	3.12	31.39	8.47
P	3.2	3.84	38.64	10.43
Q	2.8	3.36	33.81	9.12

<b>R</b>	3.1	3.72	37.43	10.10
<b>S</b>	2.9	3.48	35.02	9.45
<b>T</b>	4.2	5.04	50.71	13.69
<b>U</b>	2.8	3.36	33.81	9.12
<b>V</b>	5.3	6.36	64.00	17.28
<b>W</b>	2.7	3.24	32.60	8.80
<b>X</b>	2.5	3	30.19	8.15
<b>Y</b>	3.5	4.2	42.26	11.41
<b>Z</b>	3.2	3.84	38.64	10.43
<b>AB</b>	2.9	3.48	35.02	9.45
<b>CD</b>	2.6	3.12	31.39	8.47
<b>EF</b>	2.4	2.88	28.98	7.82
<b>GH</b>	2.6	3.12	31.39	8.47
<b>IJ</b>	2.8	3.36	33.81	9.12
<b>KL</b>	4	4.8	48.30	13.04

This is calculated by multiplying the energy content of hydrogen produced in MJ by the conversion factor of 0.2778 kWh/MJ. This conversion is beneficial for evaluating the power output with a specific energy content of hydrogen.

It can be seen from the previous *Figure 10* that the digestate that has high ammonium nitrogen content has produced more hydrogen means the potential of hydrogen produced depends on the quantity of ammonia available in the digestate.

The quantity of the power output produced depends on the available hydrogen produced.

It can be seen from the table the digestate that has high ammonium nitrogen content has produced more hydrogen and more power respectively.

### **3.6 Evaluation of hydrogen production from the digestate using different catalysts**

In the literature review, numerous catalysts have been investigated for the conversion of ammonia to hydrogen in the catalytic cracking process. Two notable catalyst types that have been extensively studied based on the economic factor, on availability, and found to be scientifically acceptable are ruthenium-based catalysts (Ru/SiO<sub>2</sub>; Ru/CNTs) and nickel-based catalysts (Ni/Al<sub>2</sub>O<sub>3</sub>). These catalysts show promise in facilitating the conversion of ammonia into hydrogen and have been the subject of scientific research and exploration.

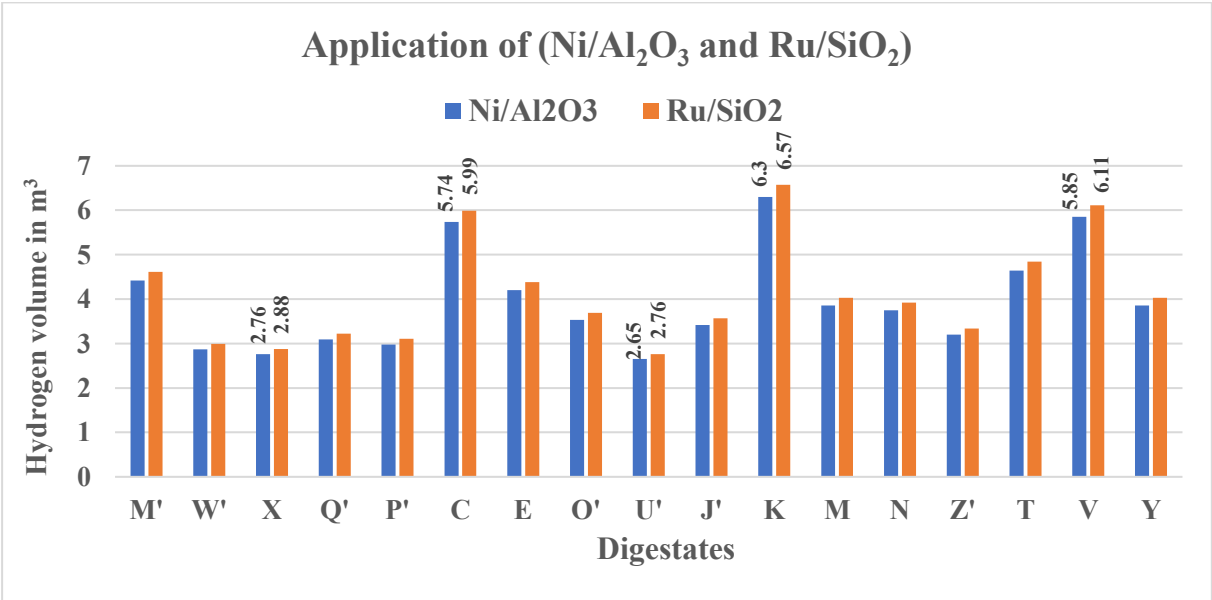
The performance of the catalysts can be quantified using the rate of hydrogen production, conversion fraction of ammonia (fraction of ammonia that is converted to hydrogen), and activation energy (Cheddie, 2012).

The **Figure 11** illustrates a comparison between the applications of Ruthenium supported on silicon dioxide ( $\text{SiO}_2$ ) and Nickel supported on alumina ( $\text{Al}_2\text{O}_3$ ) for the conversion of ammonia to hydrogen. With the application of ruthenium supported on silicon dioxide ( $\text{SiO}_2$ ), according to the results, of all the digestates, substrate K gave the highest hydrogen potential by volume with approx. ( $6.57 \text{ m}^3$ ), followed by digestate from substrate V with approx. ( $6.11 \text{ m}^3$ ) and digestate from substrate C with a value of ( $5.99 \text{ m}^3$ ) respectively. The lowest hydrogen potential was observed in the digestate from substrates U' (I, EF) (approx.  $2.76 \text{ m}^3$ ) and digestate x approximately about ( $2.88 \text{ m}^3$ ).

With regard to the application of nickel on alumina, according to the results, of all the digestates, substrate K gave the highest hydrogen potential by volume with approx. ( $6.3 \text{ m}^3$ ), followed by digestate from substrate V with approx. ( $5.85 \text{ m}^3$ ) and digestate from substrate C with a value of ( $5.74 \text{ m}^3$ ) respectively. The lowest hydrogen potential was observed in the digestate from substrates U' (I, EF) (approx.  $2.65 \text{ m}^3$ ) and digestate x approximately about ( $2.76 \text{ m}^3$ ).

When comparing the application of Ruthenium supported on silicon dioxide ( $\text{SiO}_2$ ) and Ni/ $\text{Al}_2\text{O}_3$  in terms of hydrogen by volume, With the application of ruthenium gave the best yield of hydrogen in volume compared to Nickel supported on alumina ( $\text{Al}_2\text{O}_3$ ).

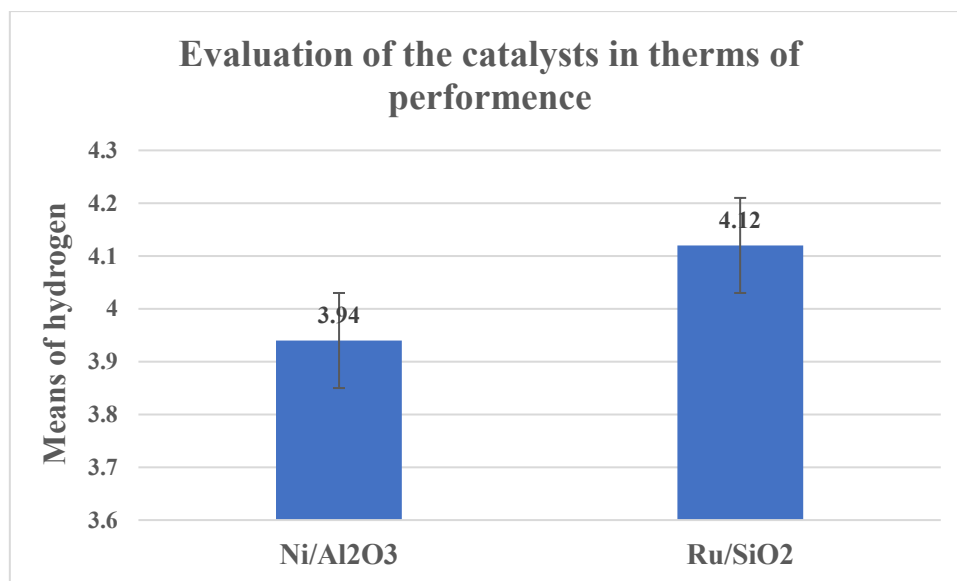
It can be seen from the figure an increment with the application of ruthenium supported on ( $\text{SiO}_2$ ) compared to the application of Nickel supported on alumina ( $\text{Al}_2\text{O}_3$ ).



M' = (B, F, H, KL); J' = (J, R); W' = (A, O, CD, GH); Z' = (AB, S); Q' = (D, Q, U, IJ); O' = (G, P, Z); U' = (I, EF); P' (W, L).

**Figure 11.** Evaluation of hydrogen production from the digestate using different catalysts ( $\text{Ru/SiO}_2$ ;  $\text{Ni/Al}_2\text{O}_3$ )

With the regards of the evaluation of catalysts in terms of performance, by doing statistical analysis. The result of statistical analysis showed that there is no significant difference between the means of the two catalysts (P-value > 5%).



**Figure 12.** Evaluation of the catalysts (*Ru/SiO<sub>2</sub>* and *Ni/ Al<sub>2</sub>O<sub>3</sub>*) in terms of performance

Ru-based catalysts have been documented to exhibit the highest rates of ammonia decomposition, along with the highest conversion rates. It has been reported as the most effective catalyst for low-temperature ammonia decomposition based on its electronic promotion possessing an optimum nitrogen binding energy. The utilization of this catalyst enables a reduction in both temperature and reaction pressure necessary for the decomposition process (Le et al., 2021a).

Nowadays, the commercially used catalyst for the decomposition of ammonia is nickel supported on alumina. This choice is due to its mechanical properties and heat resistance.

Although the activity of the Ni-based catalysts is not as high as that of noble metal catalysts, they have been reported as the best-performing catalysts for NH<sub>3</sub> decomposition among the non-noble metal-based catalysts (Kurtoğlu et al., 2018; Lucentini et al., 2019). The use of Ni catalysts makes them economically viable compared to noble metal catalysts. However, single-component Ni catalysts are unable to meet the activity and stability requirements for catalytic ammonia (NH<sub>3</sub>) decomposition. The dispersion of Ni, the textural morphology, the acidity-basicity properties, and the interaction between the active metal species and the support are crucial factors that have a significant impact on the overall performance of Ni-based catalysts.

In general, supports that possess a high surface area, strong alkalinity, high thermal stability, and great electron transfer capacity are preferable for the  $\text{NH}_3$  decomposition reaction.

In the literature review, numerous developed substrates have been investigated to support Nickel catalysts on various metal oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ). Among these catalysts,  $\text{Ni}/\text{Al}_2\text{O}_3$  was reported with the highest  $\text{NH}_3$  conversion mainly because of the remarkable surface area of  $\text{Al}_2\text{O}_3$  support ( $200 \text{ m}^2/\text{g}$ ) (Le et al., 2021b).

Among the catalysts examined in the available literature, the highest catalytic activity for ammonia decomposition has been observed with ruthenium supported on various oxides or structured and unstructured carbon (Schüth et al., 2012). However, the main issue with ruthenium catalysts is their deactivation over time (Lamb et al., 2019b). Additionally, ruthenium is a noble metal that is rare in nature, making it an expensive element. Consequently, researchers have been actively searching for low-cost catalytic compositions that can exhibit catalytic activity comparable to that of ruthenium.

Aside from the Ruthenium supported on silicon oxide ( $\text{SiO}_2$ ), Ruthenium supported on carbon nanotubes (CNTs) has been demonstrated to be the most suitable support for Ru in  $\text{NH}_3$  decomposition, primarily because of their high electronic conductivity and the greater dispersion on the CNTs surface (S. J. Wang et al., 2004).

This high conductivity enables a more efficient transfer of electrons, ultimately facilitating the desorption of nitrogen ( $\text{N}_2$ ) from the catalyst.

However, the high-cost limitation of commercial CNTs interferes with using Ru/CNTs catalysts on an industrial scale (Le et al., 2021b)

Another important aspect to take into account is the Ru particle size. By varying the size of the Ru particles, the ammonia conversion has been optimized, obtaining the best results with a Ru particle size of about 2 nm (Duan et al., 2010)

The activation energy value for different catalysts used in ammonia conversion depends on the metal used and the support. In general, it is possible to conclude that the lowest apparent activation energy values are found for iron, ruthenium, and nickel catalysts, which are also the most studied catalysts (Lucentini et al., 2021b) in the literature.

It can be concluded that the catalytic activity has a strong dependence on the type of support and promoters.

From the discussion, it can be concluded that noble Ru-based catalysts are widely regarded as the optimal choice for achieving highly efficient ammonia ( $\text{NH}_3$ ) decomposition. However, their considerable cost and restricted availability pose disadvantages when it comes to large-scale applications. On the other hand, among catalysts based on non-noble metals, Ni-based catalysts exhibit the highest activity, making nickel a promising alternative material for ( $\text{NH}_3$ ) decomposition due to its affordability. Currently, there are still challenges that need to be addressed in order to enhance the efficiency of both Ru- and Ni-based catalysts.

### 3.7 CONCLUSION AND PERSPECTIVES

This study highlights the importance of side stream stripping as a viable method of recovering ammonia from digestate to support hydrogen production. Although digestate has its advantages, the presence of toxic ammonia poses environmental problems. Proper control of ammonia volatilization is essential to minimize risks. Side-stream stripping has proved effective in safely extracting ammonia, facilitating handling, and reducing emissions. In addition, this process reduces transport costs by removing excess water from the digestate, while the stripped digestate is returned to the anaerobic digester, ensuring a closed-loop system.

The analysis of data on the concentration of ammonium nitrogen from the digestate and its various substrates has led to the following conclusions:

With regard to the level of ammonium nitrogen concentration in the digestate and its various substrates, the results showed that the ammonium nitrogen content is generally higher in the digestate than in the substrate, which can be attributed to several factors, such as organic nitrogen conversion, the release of bound nitrogen, microbial activity, and ammonium retention.

Regarding the level of ammonia content of the digestate from the different feedstocks, the results showed an increase in ammonia content as a function of the ammonium nitrogen content in the digestate. Of all the feedstocks, substrate K had the highest ammonia concentration (approx. 6.93 kg/t) due to its high ammonium nitrogen content (approx. 5.7 kg/t), while the lowest ammonia concentration was observed in substrates I and EF (approx. 2.91 kg/t).

For the potential of hydrogen production from the digestate of different feedstocks, the result indicated that the digestate that has high ammonium nitrogen content has produced high hydrogen respectively. The potential of hydrogen produced depends on the quantity of ammonia available in the digestate. The digestate from substrate K has demonstrated the greatest hydrogen potential, yielding approximately 6.84 m<sup>3</sup> of hydrogen in volume. This is attributed to its high ammonium nitrogen content from the digestate. On the other hand, the lowest hydrogen potential was observed in substrates I and EF, producing approximately 2.88 m<sup>3</sup> of hydrogen.

Regarding to the calculation of the power potential based on the energy content of hydrogen produced, the results showed that the quantity of the power output produced depends on the available hydrogen produced. The digestate that has high ammonium nitrogen content has produced more hydrogen and more power respectively. The high-power output is obtained from



the digestate of substrate K (approximately 18.58 kWh). On the other hand, the lowest power output was obtained from the digestate of substrates I and EF approximately at about 7.82 kWh

Finally, the evaluation of hydrogen production using different catalysts highlights the superiority of Ruthenium supported on silicon dioxide ( $\text{SiO}_2$ ) over Nickel supported on alumina ( $\text{Al}_2\text{O}_3$ ) in terms of hydrogen yield due to its highest catalytic activity and performance for ammonia decomposition.

## **PERSPECTIVES**

To date, there has been no in-depth research into how the composition, origin, or type of digestate affects ammonia recovery. Therefore, further research and studies are needed to elucidate the critical factor influencing ammonia recovery processes from digestate.

It is essential to understand the impact of different properties of digestate, such as nutrient content, Ph levels, and organic matter composition, on ammonia recovery efficiency, in order to optimize and develop sustainable technologies.

Based on the discussion stated above regarding the evaluation of catalysts, it can be concluded that noble Ru-based catalysts are widely regarded as the optimal choice for achieving highly efficient ammonia ( $\text{NH}_3$ ) decomposition. However, their considerable cost and restricted availability pose disadvantages when it comes to large-scale applications. On the other hand, among catalysts based on non-noble metals, Ni-based catalysts exhibit the highest activity, making nickel a promising alternative material for ( $\text{NH}_3$ ) decomposition due to its affordability. Currently, there are still challenges that need to be addressed in order to enhance the efficiency of both Ru- and Ni-based catalysts.

Further research is needed for low-cost catalytic compositions that can exhibit catalytic activity comparable to that of ruthenium which facilitates the conversion process.

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## APPENDIXES

APPENDIX 1. Evaluation of hydrogen production from the digestate using different catalysts (Ru/SiO<sub>3</sub>; Ni/Al<sub>2</sub>O<sub>3</sub>).

<b>Feedstocks</b>	<b>Ni/Al<sub>2</sub>O<sub>3</sub></b>	<b>Ru/SiO<sub>2</sub></b>
<b>M'</b> (B, F, H, KL)	<b>4.42</b>	<b>4.61</b>
<b>W'</b> (A, O, CD, GH)	<b>2.87</b>	<b>2.99</b>
<b>X</b>	<b>2.76</b>	<b>2.88</b>
<b>Q'</b> (D, Q, U, IJ)	<b>3.09</b>	<b>3.22</b>
<b>P'</b> (W, L)	<b>2.98</b>	<b>3.11</b>
<b>C</b>	<b>5.74</b>	<b>5.99</b>
<b>E</b>	<b>4.2</b>	<b>4.38</b>
<b>O'</b> (G, P, Z)	<b>3.53</b>	<b>3.69</b>
<b>U'</b> (I, EF)	<b>2.65</b>	<b>2.76</b>
<b>J'</b> (J, R)	<b>3.42</b>	<b>3.57</b>
<b>K</b>	<b>6.3</b>	<b>6.57</b>
<b>M</b>	<b>3.86</b>	<b>4.03</b>
<b>N</b>	<b>3.75</b>	<b>3.92</b>
<b>Z'</b> (AB, S)	<b>3.2</b>	<b>3.34</b>
<b>T</b>	<b>4.64</b>	<b>4.84</b>
<b>V</b>	<b>5.85</b>	<b>6.11</b>
<b>Y</b>	<b>3.86</b>	<b>4.03</b>

APPENDIX 2. Evaluation of the catalysts (Ru/SiO<sub>2</sub> and Ni/ Al<sub>2</sub>O<sub>3</sub>) in terms of performance

<b>Parameters</b>	<b>Ni/ Al<sub>2</sub>O<sub>3</sub></b>	<b>Ru/SiO<sub>2</sub></b>
<b>Mean</b>	<b>3.94</b>	<b>4.12</b>
<b>Standard deviation</b>	<b>1.12</b>	<b>1.17</b>
<b>T-test</b>	<b>P-value &gt; 0.66</b>	
	<b>Significant level of 5%</b>	





Corn silage			70,2				0	0	0	0	0	0	0	0	0	0	0	0	0
rye meal	KL	1	8,3	8,1	AD	4	4,8636	4863,6	286,094	214,571	4806,38	4,80638	0,40253	48,3041308	13,04211532				
Pig manure			17,9				0	0	0	0	0	0	0	0	0	0	0	0	0
Rye GPS			3,5				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
cattle/pig manure			48				0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage	Q	1,1	43,5	48,8	AD	2,8	3,40452	3404,52	200,266	150,199	3364,47	3,36447	0,28177	33,8128916	9,129480726				
Grass silage			1,2				0	0	0	0	0	0	0	0	0	0	0	0	0
Wheat grist			4,1				0	0	0	0	0	0	0	0	0	0	0	0	0
Rye GPS			3,3				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Cattle manure			31,8				0	0	0	0	0	0	0	0	0	0	0	0	0
corn silage	R	1,2	61,6	31,2	AD	3,1	3,76929	3769,29	221,723	166,292	3724,95	3,72495	0,31196	37,4357014	10,10763937				
Wheat grist			6,6				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Cattle manure			30,7				0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage			38,3				0	0	0	0	0	0	0	0	0	0	0	0	0
Rye GPS	S	1,1	17,5	65,6	AD	2,9	3,52611	3526,11	207,418	155,564	3484,63	3,48463	0,29184	35,0204948	9,455533609				
Cattle manure			1,3				0	0	0	0	0	0	0	0	0	0	0	0	0
Grass silage			8,1				0	0	0	0	0	0	0	0	0	0	0	0	0
wheat grains			4,1				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Pig manure			23,5				0	0	0	0	0	0	0	0	0	0	0	0	0
Corn grain silage			36				0	0	0	0	0	0	0	0	0	0	0	0	0
Cattle manure	T	1,1	23,6	9,1	AD	4,2	5,10678	5106,78	300,399	225,299	5046,7	5,0467	0,42266	50,7193374	13,69422109				
wheat			3,6				0	0	0	0	0	0	0	0	0	0	0	0	0
Barley GPS			3,3				0	0	0	0	0	0	0	0	0	0	0	0	0
Corn Sillage			10				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Cattle manure			42,7				0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage	U	1	41,2	13,1	AD	2,8	3,40452	3404,52	200,266	150,199	3364,47	3,36447	0,28177	33,8128916	9,129480726				
Grass silage			14,1				0	0	0	0	0	0	0	0	0	0	0	0	0
Wheat grist			2,1				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Grass silage			1,5				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Pig manure	V	2,7	50	18,2	AD	5,3	6,44427	6444,27	379,075	284,306	6368,46	6,36846	0,53336	64,0029733	17,2808028				
Turkey manure			7,5				0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage			8,3				0	0	0	0	0	0	0	0	0	0	0	0	0
Grass silage			1,8				0	0	0	0	0	0	0	0	0	0	0	0	0
Cereal porridge			20,5				0	0	0	0	0	0	0	0	0	0	0	0	0
CCM			5,6				0	0	0	0	0	0	0	0	0	0	0	0	0
Water			4,3				0	0	0	0	0	0	0	0	0	0	0	0	0
Wheat grist			2				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Cattle manure			30,3				0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage	W	0,8	14,3	11,5	AD	2,7	3,28293	3282,93	193,114	144,835	3244,31	3,24431	0,27171	32,6052883	8,803427843				
Grass silage			31,2				0	0	0	0	0	0	0	0	0	0	0	0	0
Grain meal			3,9				0	0	0	0	0	0	0	0	0	0	0	0	0
Oat/rye GPS			20,2				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage	X	1	49,3	18,6	AD	2,5	3,03975	3039,75	178,809	134,107	3003,99	3,00399	0,25158	30,1900818	8,151322076				
Pig manure			38,1				0	0	0	0	0	0	0	0	0	0	0	0	0
Grass silage			10,2				0	0	0	0	0	0	0	0	0	0	0	0	0
Wheat grist			2,5				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage			81				0	0	0	0	0	0	0	0	0	0	0	0	0
Rye GPS	Y	0,5	0,4	23,9	AD	3,5	4,25565	4255,65	250,332	187,749	4205,58	4,20558	0,35222	42,2661145	11,41185091				
Green rye silage			16,3				0	0	0	0	0	0	0	0	0	0	0	0	0
Rye GPS			2,2				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage			89	9,8		3,2	3,89088	3890,88	228,875	171,656	3845,1	3,8451	0,32203	38,6433047	10,43369226				
Rye GPS	Z	0,7	9				0	0	0	0	0	0	0	0	0	0	0	0	0
Millet/sunflower			2				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Turkey manure			5,4				0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage	AB	1,2	83,4	27,2	AD	2,9	3,52611	3526,11	207,418	155,564	3484,63	3,48463	0,29184	35,0204948	9,455533609				
Rye GPS			6,2				0	0	0	0	0	0	0	0	0	0	0	0	0
LKS			2,8				0	0	0	0	0	0	0	0	0	0	0	0	0
Wheat grains			1,8				0	0	0	0	0	0	0	0	0	0	0	0	0
potatoes			0,3				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage			96,9				0	0	0	0	0	0	0	0	0	0	0	0	0
CCM	CD	0,7	2,5	17,5	AD	2,6	3,16134	3161,34	185,961	139,471	3124,15	3,12415	0,26165	31,397685	8,47737496				
chicken manure			0,6				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage			98,3				0	0	0	0	0	0	0	0	0	0	0	0	0
Grain meal	EF	0,5	1,2	19,9	AD	2,4	2,91816	2918,16	171,656	128,742	2883,83	2,88383	0,24152	28,9824785	7,825269193				
Sugar beet/z			0,5				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage			81,1				0	0	0	0	0	0	0	0	0	0	0	0	0
Grass silage	GH	0,4	4,8	44,3		2,6	3,16134	3161,34	185,961	139,471	3124,15	3,12415	0,26165	31,397685	8,47737496				
Rye GPS			12,7				0	0	0	0	0	0	0	0	0	0	0	0	0
Wheat grist			0,6				0	0	0	0	0	0	0	0	0	0	0	0	0
Cattle manure			0,7				0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
							0	0	0	0	0	0	0	0	0	0	0	0	0
Turkey manure			29,9				0	0	0	0	0	0	0	0	0	0	0	0	0
Corn silage			50,7				0	0	0	0	0	0	0	0	0	0	0	0	0
Rye GPS	IJ	1,8	6,5		AD	2,8	3,40452	3404,52	200,266	150,199	3364,47	3,36447	0,28177	33,8128916	9,129480726				
Sudan grass			9,5				0	0	0	0									