Natural Nitrogen Fixation

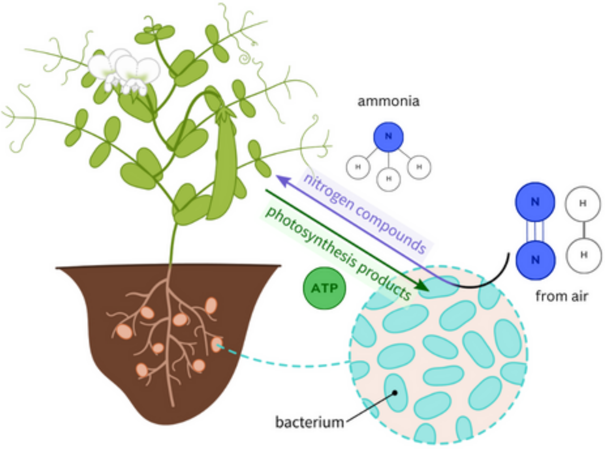
LEGUME RHIZOBIA

Legumes can form a symbiotic relationship with diazotrophic (nitrogen-fixing) soil bacteria called rhizobia [1].

Inoculation initiates in the root hair of the plant, where bacteria are enclosed by plant membrane [2].

Through these nodules the plant provides the bacteria with sugars from photosynthesis, a source of energy for the bacteria to convert atmospheric nitrogen into ammonia.

Source: Australian National University [4]



Source: Modified from Nefronus, Wikipedia [5]

The rhizobia bacteria utilise the enzyme nitrogenase to catalyse the conversion of atmospheric nitrogen (N_2) to ammonia (NH_3).

This reaction is energy intensive, and requires 17,400 kJ of energy supplied by photosynthesis within the plant to convert 1 kg of nitrogen into 12 kg of ammonia [1].

Incompatibility frequently occurs, such that a bacterial strain is unable to nodulate a particular host plant or forms nodules that are incapable of fixing nitrogen. Only a select Rhizobium or Bradyrhizobium bacteria will inoculate a select number of plant genera, and thus it is essential to select the correct bacteria for the specific crop.

The total annual terrestrial inputs of N from biological nitrogen fixation as given by range from 139 million to 175 million tonnes of N [3].

Legumes prefer to fix nitrogen from nitrates and ammonia already present in soil, as the bacterial catalysation of ammonia is very energy intensive for the plant.

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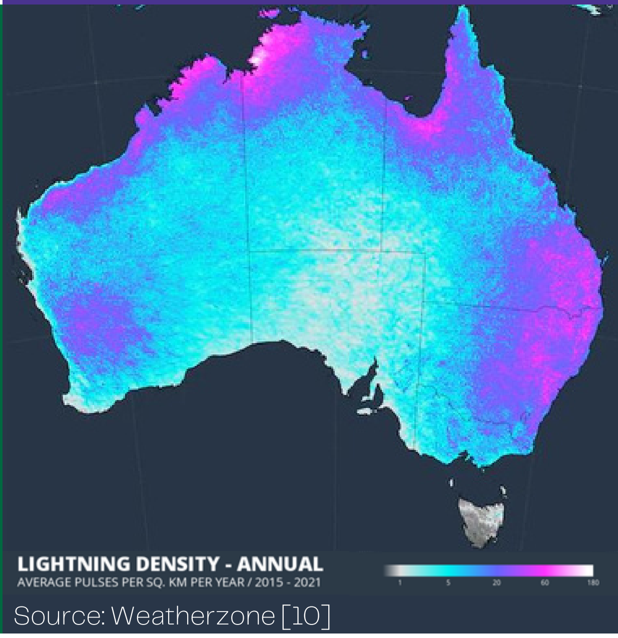
Natural Nitrogen Fixation

LIGHTNING

Lightning is a rapid and powerful electric current that occurs in clouds when two areas of opposite charge develop near each other [6].

Earth's atmosphere experiences up to 3 million lightning striker per day. This amount of lightning can fix up to 13,000 tonnes of nitrates a day [7].

A flash of lightning can heat up the surround air to 30,000°C, and is about 100 million Volts and 30,000 Amps [8].



Source: Weatherzone [10]

To break the triple covalent bond of molecular nitrogen (N_2), 941 kJ/mol are required.

The energy of lightning is enough to break the triple covalent bond formed between two N atoms in molecular nitrogen found in the atmosphere [7].

The nitrogen can then react with water molecules to form nitrates (NO), (NO_2), (NO_3).

The nitrates and ammonia produced stay in the atmosphere until precipitation carries them down to the ground. As most lightning is intracloud, a large portion of these nitrates remain high in the atmosphere [7].

Source: Rahul Viswanath via Unsplash [11]

10 % of Earth' nitrate budget is contributed by lightning.

Each flash of lightning can convert 3.5 kilograms of N_2 into chemically reactive ammonia and nitrate [9].

Scientists estimate that a global 5 million metric tonnes of nitrates are produced by lightning each year [9].

SANTFA
CONSERVATION AGRICULTURE IN ACTION

SAGIT

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Hydrogen Production

STEAM METHANE REFORMING

Feedstock	Natural Gas
Energy Consumption	23.9 kWh per kg of H_2
Net GHG Emissions	9.3 kg of CO_2 per kg of H_2
Availability	★ ★ ★ ★ ★

Natural gas reforming is a process by which high temperature is used to produce hydrogen from a methane source [12].

In 2021, 62% of the world's hydrogen was produced by steam methane reforming (SMR) without carbon capture and utilisation [13].

At an efficiency level of 74-85%, the SMR method requires 2kWh per cubic meter of H_2, or 23.9 kWh per kg of H_2 [14].

Globally, 98% of the hydrogen required for ammonia production is derived from fossil fuels [15]:

72% is derived from steam methane reforming processes
26% is derived from coal

Hydrogen from SMR production has an average cost of 1.3 and 1.5 $/kg H_2, with and without a carbon capture (CC), respectively [16].

Emissions Profile

100% of the carbon in the incoming methane is ultimately converted to CO_2
1 million standard cubic feet of H_2 will produce 13 metric tons of CO_2 by the chemical reactions alone [17].

Additionally, for every 1 million standard cubic feet of H_2 produced, the processes emit:

Steam generation: 2.5 metric tons of CO_2
Combustion for reforming: 3.7 metric tons of CO_2
Power compression & separation: 0.1 metric tons of CO_2

This totals 19.3 metric tons of CO_2 produced per million SCF of H_2, equivalent to 9.3 kg of CO_2 per kg of H_2 production [17].

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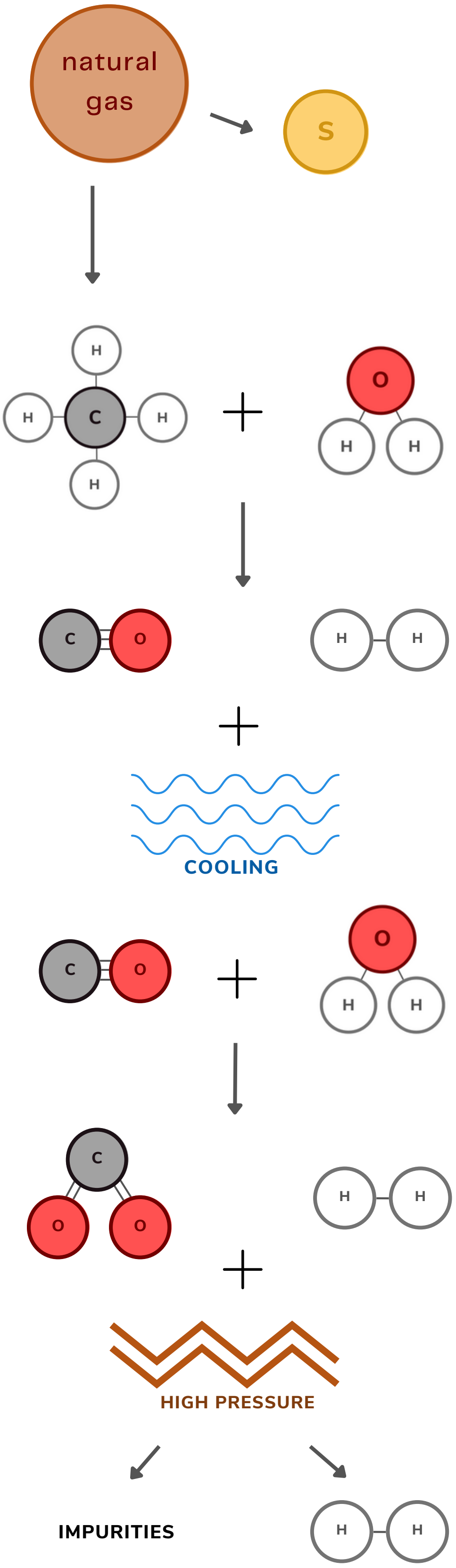
STEAM METHANE REFORMING

How Hydrogen is Produced by SMR



STEP 1: DESULPHURISATION.

The natural gas is passed by a cobalt-based catalyst to remove any sulphur compounds from the feedstock.

This step prevents the corrosion of the processing equipment, and limits sulphur emissions [12].

STEP 2: REFORMING

The natural gas is reacted with high temperature steam (700°C–1,000°C) over a nickel-based catalyst.

This produces hydrogen, carbon monoxide, and a small amount of carbon dioxide [12].

STEP 3: WATER-GAS SHIFT REACTION

The reformed gas is cooled, producing steam. The carbon monoxide is then reacted with said steam to form more hydrogen and carbon dioxide [12].

STEP 4: PRESSURE SWING ADSORPTION

The resulting gasses are pressurised in the presence of an adsorbent. Impurities bind to the absorbent, leaving pure hydrogen behind. The saturated absorbent can be used as fuel gas [12].

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Ammonia Production

HABER-BOSCH PROCESS

Feedstock	Hydrogen, Air
Energy Consumption	10 kWh per kg of NH_3
Net GHG Emissions	5.3 kg of CO_2 per kg of NH_3
Availability	★★★★★

The Haber-Bosch process was developed during WW1, and is the high-pressure reaction between nitrogen and hydrogen to produce ammonia [18].

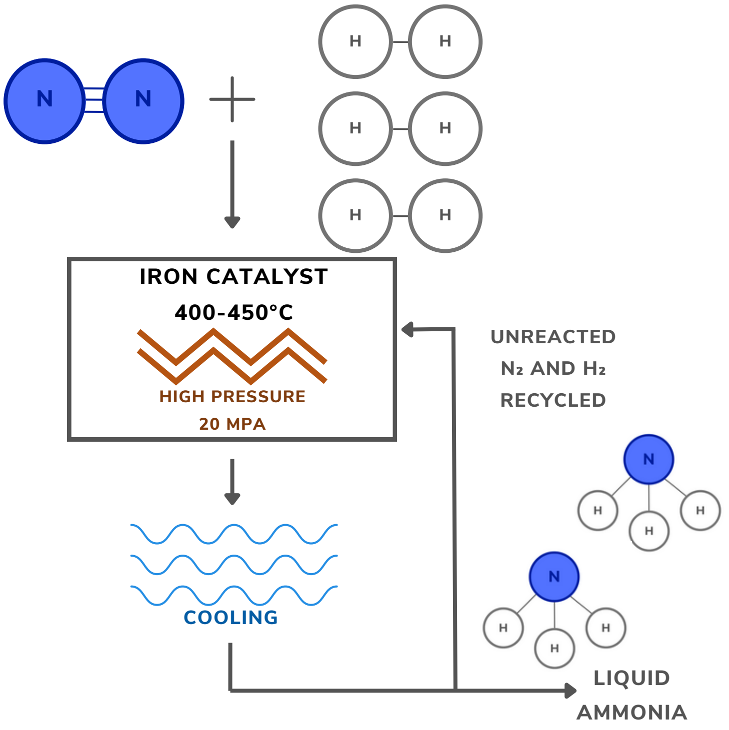
In 2021, 150 million metric tonnes of ammonia were produced worldwide using this process [19].

Pressures of up to 20 MPa are used in order to break the strong double bond between nitrogen atoms [20].

Temperatures between 400-500°C are used for a desired reaction time with a 10-20% yield. All unreacted feedstock is recycled [20].

The conditions of this process require 10 MWh of electricity per metric ton of ammonia produced. The generation of the electricity produces 5.3 kg of CO_2 emissions per kg of ammonia [20][21].

The global production of these high pressures and temperatures for the process account for 1% of the world's total energy production, and 1.4% of global CO_2 emissions [22].



Process

Nitrogen, from the air, and hydrogen, most commonly from methane steam reforming, are compressed and sent to the reactor to form ammonia.

The reaction takes place in the presence of an iron or ruthenium catalyst to increase reaction time.

The gases are cooled, liquefying the ammonia.

The unreacted gases are recycled back to the reactor for future use [22].

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Hydrogen Production

ELECTROLYSIS

Electrolysis is the process of using electricity to split water into hydrogen and oxygen [23].

About four percent of world's hydrogen is produced by electrolysis [23].

Water is an ideal source for hydrogen production as the only by-product released is oxygen.

Around 9L of water are needed to produce 1 kg of H_2, this reaction produces 8kg of oxygen [24].

Feedstock	Water
Energy Consumption	53 kWh per kg of H_2
Net GHG Emissions	up to 28 kg of CO_2 per kg of H_2
Availability	★★★★☆

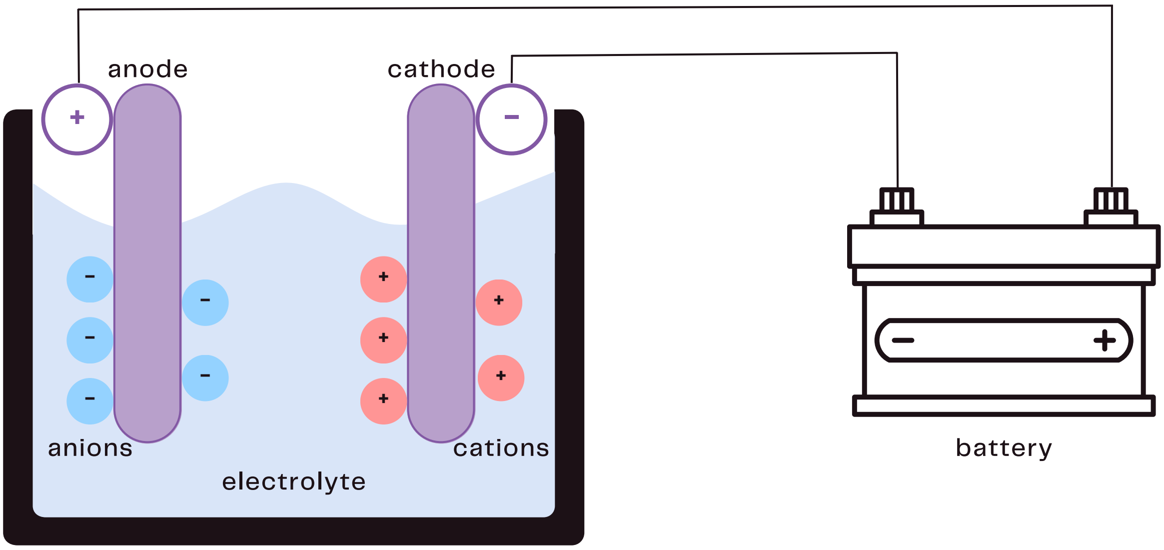
How Electrolysis Works

Electrolysis is a technique that uses direct electric current to drive an otherwise non-spontaneous chemical reaction [25].

An electrolysis reaction takes place in a unit called an electrolyser, which consists of a positively charged anode and a negatively charged cathode, separated by an electrolyte [25].

Commercial electrolysis requires around 53 kWh of electricity to produce 1 kg of hydrogen, which holds 33.6 kWh of energy [26].

If the 53 KWh of electricity is generated from fossil fuel combustion, 28 kg of CO_2 are emitted per kg of hydrogen produced. If the electricity is generated via renewable methods, the process will be emission free [21].



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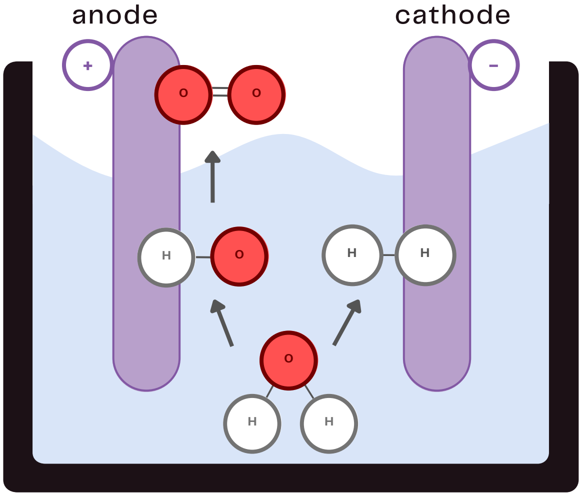
3 Types of Hydrogen Electrolysers

ALKALINE ELECTROLYSER



cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
anode: $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

A well established electrolysis technique that has been used at an industrial scale for 100+ years.

The electrolyte used is a strong base and caustic, most commonly Sodium (NaOH) or Potassium hydroxide (KOH).

At the cathode: water is split to form H_2 and hydroxide ions OH^-

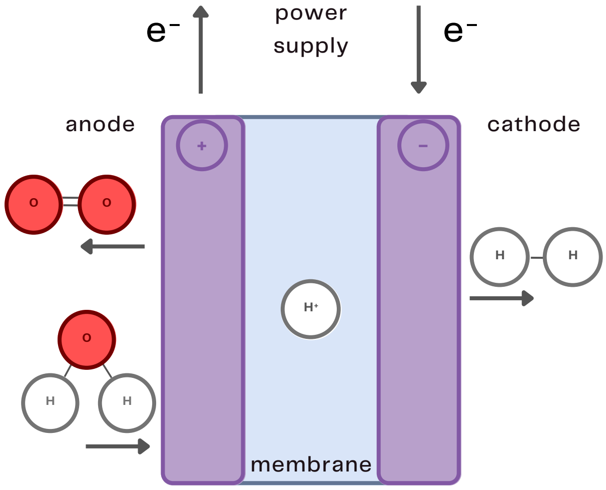
At the anode: Hydroxide ions recombine to form O_2

PROTON EXCHANGE MEMBRANE ELECTROLYSER

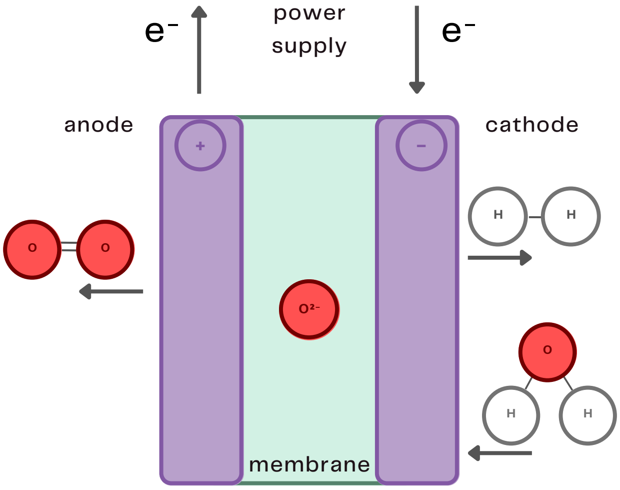
The electrolyte used is a solid thin proton conducting polymer membrane instead of a liquid one.

At the anode: water is split to form oxygen O_2 and hydrogen ions H^+

At the cathode: hydrogen ions H^+ bonds with electrons to form hydrogen gas H_2



cathode: $4H^+ + 4e^- \rightarrow 2H_2$
anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$



cathode: $H_2O + 2e^- \rightarrow H_2 + O^{2-}$
anode: $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$

SOLID OXIDE ELECTROLYSER

The electrolyte used is a solid ceramic material instead of a liquid one.

HTC performs the electrolysis of water vapour at high temperatures, which lead to higher efficiencies (80-90%)

At the cathode: water is combined with electrons to produce hydrogen H_2 and oxygen ions O^{2-}

At the anode: the oxygen ions combine to produce oxygen gas O_2

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Hydrogen Production

HYDGENE BIOCATALYST

Feedstock	Biomass and organic waste
Energy Consumption	65 kWh per kg of H_2
Net GHG Emissions	-9 kg of CO_2 per kg of H_2
Availability	★★★☆☆

HydGene Renewables have engineered a highly robust biocatalyst using synthetic biology, capable of efficiently converting biomass carbohydrates and sugars into hydrogen [27].

The hydrogen producing enzymes found in algae, known as hydrogenases, are utilized to produce high-purity hydrogen biologically from a range of plant-based feedstocks, including straw waste, elephant grass, bamboo, industrial food waste, and hay [28].

At commercial scale the biocatalyst can produce 60kg of H_2 per day per L of biocatalyst, and yields 30kg of hydrogen per tonne of biomass feedstock.

Trials using the biocatalyst to produce hydrogen have exceeded the one year mark of continuous production, with no reduction in performance of the biocatalyst. This trial is ongoing [29].

Emissions Profile

The biocatalyst produces a gas containing ~97% pure H_2 and ~3% biogenic CO_2. For every 1 kg of hydrogen produced from the biocatalyst, 11kg of biogenic carbon dioxide is generated [29]. Only 1kg of this CO_2 is released to the atmosphere (or can be further captured), the remaining 10kg is sequestered as carbonate. This process is therefore carbon negative as biogenic carbon dioxide is not considered a greenhouse gas as the carbon originates from the biomass used for hydrogen production.

There are three mitigation pathways by which CO_2 is prevented from entering the atmosphere [30]:

1. Prevents the release of new carbon. By not using fossil fuel methods to produce H_2, 9.3 kg of new CO_2 per kg of H_2 are prevented from entering the atmosphere.
2. Prevents the release of biogenic carbon by preventing the combustion of biomass
3. Reduces methane emissions by reducing landfill.

The total emissions abatement is over 9 tonnes of CO_2 for every tonne of H_2.

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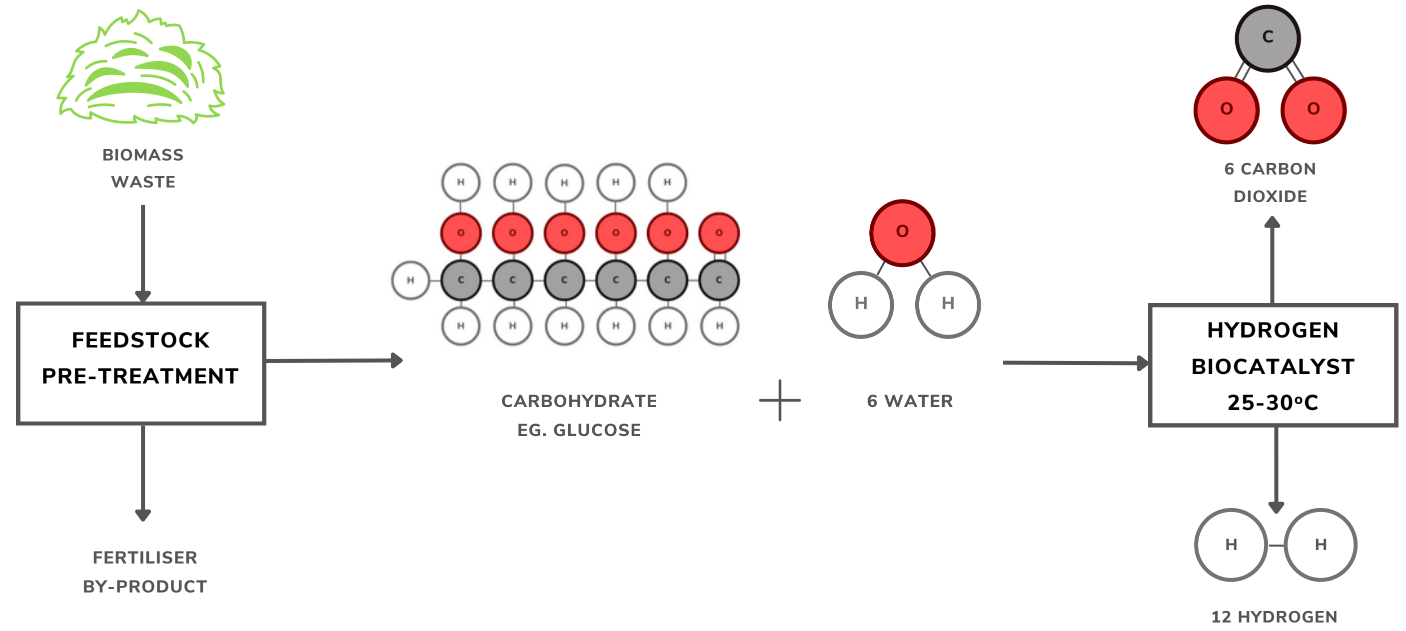
How Hydrogen is Produced with the Biocatalyst



BIOMASS
WASTE

FEEDSTOCK
PRE-TREATMENT

FERTILISER
BY-PRODUCT

CARBOHYDRATE
EG. GLUCOSE

+

6 WATER

HYDROGEN
BIOCATALYST
25-30°C

6 CARBON
DIOXIDE

12 HYDROGEN

The current scale of producing the biocatalyst is at 20L commercial scale. The team at HydGene are currently working to upscale the production capacity to industrial scale (up to 20,000L).

The bacteria cells can be harvested and stored for up to 9 months, for future hydrogen production [31].

To produce 1 kg of hydrogen, the biocatalyst uses 65 kW of energy extracted from the feedstock sugar [29].

The biocatalyst is arranged in a modular cartridge, which can be scaled to meet production requirements.

Minimal infrastructure is required for this production method due to the biocatalyst cartridges and simple reactor vessel design. This also reduces transportation and installation costs.

These factors eliminate the need for large scale storage and transportation as pure hydrogen can be produced on-site and on demand [27].

After the optimisation of the industrial scaled up process, HydGene aim to stabilize the cost of their hydrogen between \$2 and \$4 AUD per kg of H_2 [31].

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Hydrogen Production

METHANE PYROLYSIS

Feedstock	Natural Gas
Energy Consumption	10 kWh per kg of H_2
Net GHG Emissions	up to 5.3 kg of CO_2 per kg of H_2
Availability	★★★☆☆

Methane pyrolysis is a process by which high temperature is used to produce hydrogen and solid carbon from a natural gas source [32].

The natural gas is superheated by electricity, which is a is combustion-free and CO_2 free process.

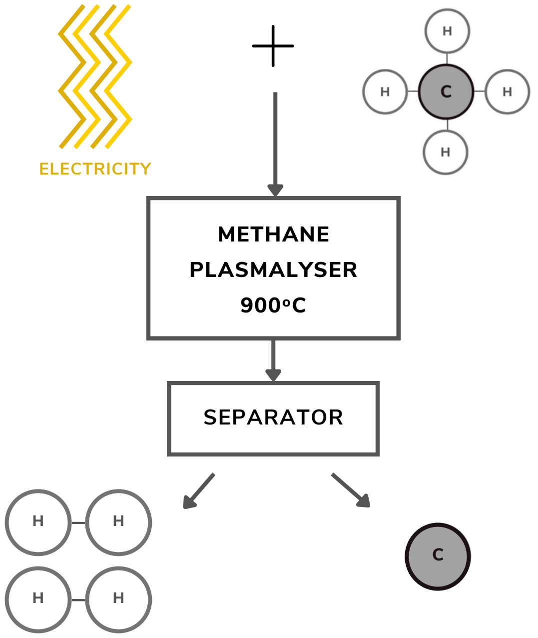
4 kg of methane and 10 kWh of electricity produces 1 kg of hydrogen and 3 kg of elemental carbon [33].

Methane pyrolysis is highly efficient, and can produce high quality hydrogen with a purity of up to 99.999% [32].

If biomethane and renewable electricity is used, methane can be a CO_2 sink (from -10 to -22 kg CO_2 eq/kg H_2) [34].

If the 10 kWh of electricity is generated from fossil fuel combustion, 5.6 kg of CO_2 are emitted per kg of hydrogen produced. If the electricity is generated via renewable methods, the process will be emission free [21].

The carbon produced is an additional source of revenue. It is used in the manufacturing of batteries, electrodes, and rubber goods [35].



Process

Methane is heated to 900°C in the absence of oxygen, using electricity as the power source.

The heat breaks the bonds between the hydrogen and carbon in the natural gas molecule.

The hydrogen and the carbon black are separated and stored onsite, until the product is sold [32].

For more information on available technology visit:
https://plenesys.com/
https://www.graforce.com/en/
https://monolith-corp.com/

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Hydrogen Production

BIOMASS GASIFICATION

Feedstock	Biomass and Organic Waste
Energy Consumption	75.9 kWh per kg of H_2
Net GHG Emissions	7.37 kg of CO_2 per kg of H_2
Availability	★★★★☆

Biomass gasification is the high-temperature conversion of organic residue, into carbon monoxide, hydrogen, and carbon dioxide, without combustion [36].

The feedstock is any locally available organic residue, such as forestry, agriculture, and processing waste (eg. corn stover, citrus pulp, black liquor from paper mills, digestate from anaerobic digestion) [36].

The usage of plant-based feedstock offsets the carbon dioxide produced during the biomass gasification. Carbon dioxide is effectively “recycled”, as the feedstock plants consumed CO_2 during their growth process, making the net greenhouse gasses emitted lower [37].

In high-temperature biomass gasification, tars form within the reactor [38]. A scrubber removes tars from the gas using oil, and a stripper regenerates the washing liquid. The gas cleaning and conditioning can increase investment costs by over 40% [37].

For a plant with an expected hydrogen output of over 100,000 kg/day and cost of biomass in the range of 70–120$ /dry-ton AUD, the hydrogen production cost is expected to be 2.75–3.20 $/kg [38].

Very small biomass gasification systems are not feasibly profitable because the costs of producing one unit is higher the smaller facility.

A biomass gasification plant emits 7.37 kg CO_2 per kg H_2 produced, with the primary energy demand being electricity for manufacturing. Carbon capture, coupled with carbon-neutral feedstock, can lead to negligible or zero net CO_2 emissions [39].

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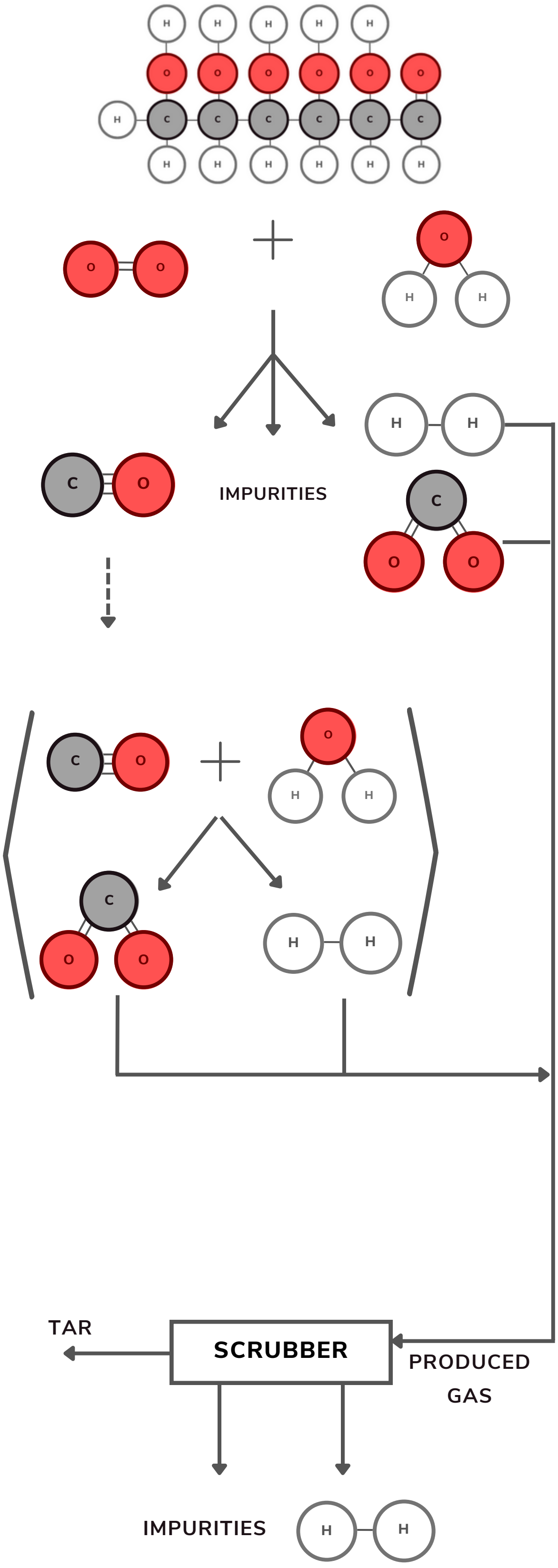
How Hydrogen is Produced by Biomass Gasification



STEP 1: GASIFICATION OF BIOMASS

The biomass is exposed to a gasifying agent, such as air, steam or oxygen, heated to 700°-1200°C. Without combustion, the biomass is converted to carbon monoxide (CO), hydrogen (H_2) and carbon dioxide (CO_2) [38].

The heat can be either added with an external medium or generated internally by the full combustion of some biomass.

*diagram shows steam and oxygen as gasifying agents

*diagram uses glucose as a substitute for the composition of biomass

STEP 2: WATER-GAS SHIFT REACTION

The carbon monoxide in the produced gas is then reacted with more steam to form more hydrogen and carbon dioxide.

STEP 3: CLEANING THE PRODUCT

Once all hydrogen producing reactions have taken place, the produced gas must be refined for better purity.

The gas passes through a scrubber, where H_2O is condensed, and tar is removed from the stream.

Nitrate Production

NON-THERMAL PLASMA

Feedstock	Water, Air
Energy Consumption	64 kWh per kg of NO_x
Net GHG Emissions	up to 33 kg of CO_2 per kg of NO_x
Availability	★☆☆☆☆

Nitrates can be formed by passing air and irrigation water through a high-voltage non-thermal plasma unit. In this process, the strong electric field generates high-energy electrons that break atomic bonds of molecules in the air, while the gas molecules stay at room temperature and pressure. The broken molecules then recombine to create nitrogen oxide species (NO_x) [40].

The environmental impact of fixing nitrogen is reduced by using water and air for the H_2 and N_2 sources respectively, instead of pure hydrogen and nitrogen gas from steam-methane reforming [41].

It takes 64 kWh of electricity for every 1 kg of NO_x species produced in solution [42]. If this electricity is generated from fossil fuel combustion, it emits 33 kg of CO_2 per kg of nitric oxides produced. Using renewable methods for electricity generation makes the process emission-free [21].

ADVANTAGES

- Flexible synthesis, nitrogen solution processing can be conducted closer to the point of consumption [43].
- Eliminates freight emissions and cost.
- The irrigation water doesn't contain nitrate salts, allowing plants to uptake a high percentage of the nitrates.

DISADVANTAGES

- Technology is only available for small scale applications.
- Further research is required to improve efficiency and conversion rates.

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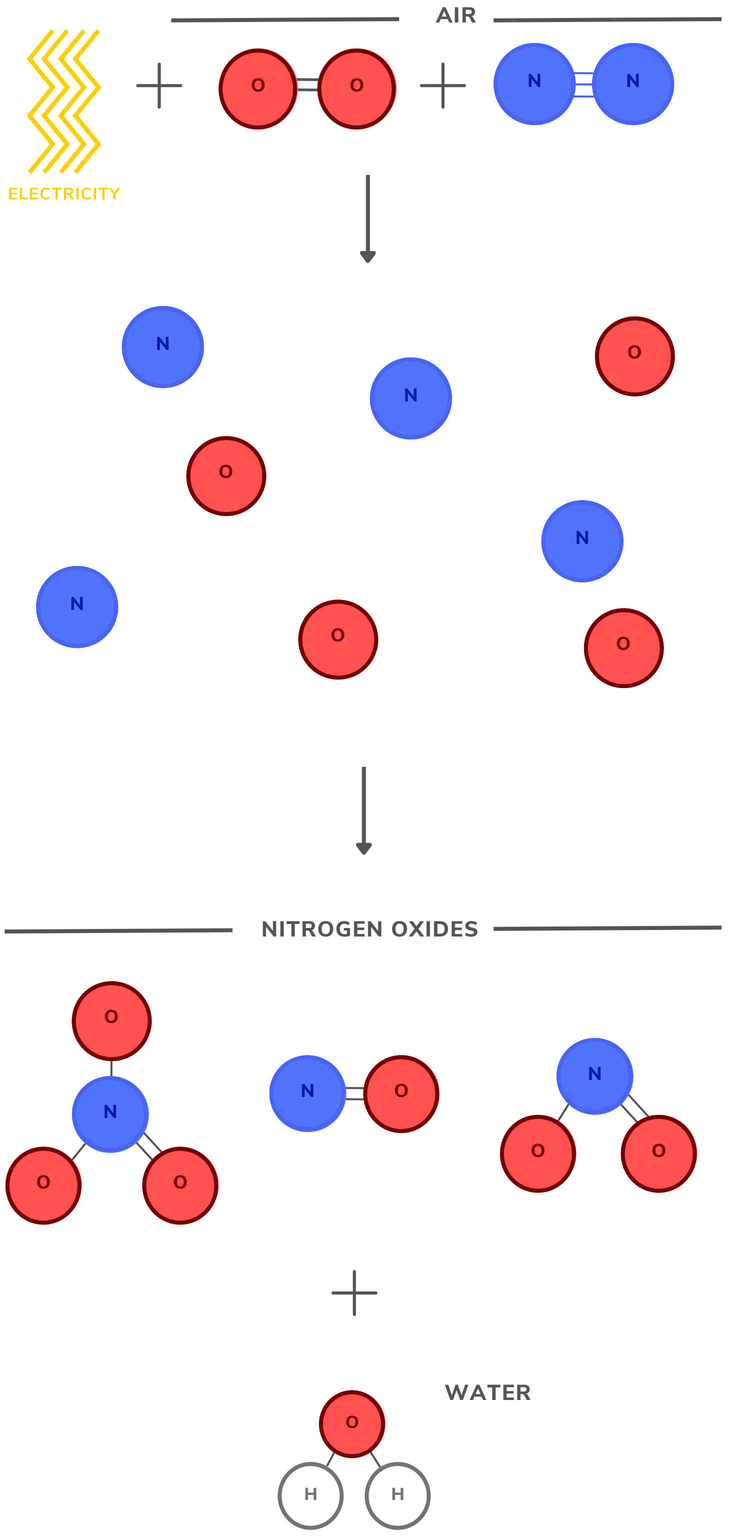
How Non-Thermal Plasma Produces Nitrogen Compounds



STEP 1:

Air is passed through a plasma field. The oxygen and nitrogen molecules split up into individual atoms.

STEP 2:

The oxygen and nitrogen atoms recombine and form the nitrogen oxides: nitric oxide (NO), nitrite (NO_2), nitrate (NO_3) [41].

STEP 3:

Water is added to the plasma, and the nitrogen oxide species react with it to form nitrous acid (HNO_2) and nitric acid (HNO_3).

The final solution of irrigation water provides plants with multiple sources of nitrogen as well as high levels of oxygen.

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