

Assessment of Energy Efficiency of Green Hydrogen Produced from Biomass and Green Ammonia

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The development of alternative technologies is crucial to mitigate emissions of greenhouse gasses, especially in the transport sector, which is largely dependent on fossil fuels. Considering this, biorefineries are playing a pivotal role in the generation of value-added products, such as biofuels, green hydrogen (H₂) and green ammonia (NH₃). These compounds have potential to be applied in the industrial supply chain or across different sectors, particularly in mobility. Hydrogen stands out for its impressive gravimetric energy density, being a strong candidate for the future of mobility. However, H₂ compression requires a high energy demand and pressure over 700 bar, which is challenging for safety reasons. To circumvent this issue, the use of hydrogen carriers, such as green ammonia, is proposed as a solution. In this scenario, NH₃ is reformed in a reactor to produce H₂ onboard, which is sent to a fuel cell to convert H₂ into electricity. Even so, it has been unclear which process is more efficient: either green H₂ production and compression or green NH₃ production and its reforming for on-site H₂ generation. Therefore, this paper presents the theoretical evaluation of the energy efficiency of both systems, using Aspen Plus® Software. Considering that both processes start from sugarcane bagasse gasification, the system of H₂ compression required less energy and showed a slightly higher H₂ output than onboard production. Through a sensitivity analysis, it was seen that NH₃ reforming is maximised at 1 bar and high temperatures. In the future, it is possible to improve the green NH₃ system to become more competitive.

1. Introduction

Currently, over 80% of the global primary energy comes from fossil fuels, with a great participation of the transport sector, which represents almost a third of the total greenhouse gasses emission, according to the International Energy Agency (IEA, 2023). Based on that, there is a growing concern about climate change, which encourages important scientific and technological advances in mobility with the adoption of alternative energy sources. In this regard, bioenergy, from biomass, is increasing its participation in the global energy mix, helping society to move towards a greener economy. Also, the optimization of industrial processes and their integration with biorefineries contribute to reducing the carbon footprint (Liu et al., 2022).

In biorefineries, biomass can be converted into value-added biofuels and chemicals, such as green hydrogen (H₂) and green ammonia (NH₃). These products that could expand their commercialization beyond industry and agriculture, being promising for transportation. In the case of H₂, it has a great gravimetric energy density of 120 MJ/kg, with potential for energy use, and conversion (Lucentini et al., 2021). However, the current sources for H₂ generation are mostly based on fossil fuels, particularly from steam methane reforming (SMR), which is responsible for one billion tons of CO₂ emissions annually, as stated by the American Chemical Society (ACS, 2020). As for NH₃, it is one of the most commercialised chemicals in the world, but it is traditionally synthesised via the Haber-Bosch reaction, using hydrogen from SMR and nitrogen (N₂) separated from air. Both molecules, H₂ and NH₃, do not generate CO₂ while consumed, but their conventional method of production does (Cha et al., 2021). In this sense, biorefineries could be a viable and clean solution for both molecules, especially considering that biomass from different types of organic matter can be used in the production chain.

Although combustion engine vehicles totally fuelled with biofuels are already available in the market, they cannot surpass the autonomy of hydrogen-powered vehicles. On the other hand, there are some technological and economical challenges that should be overcome to make green hydrogen and hydrogen carriers more feasible. Despite the great amount of energy that H_2 offers, this molecule is very small and can cause the weakening and deterioration of the materials used for its storage and transportation, raising safety concerns. Besides, a high demand of energy is necessary to store hydrogen in gaseous form, at pressures over 700 bar, or in liquid form, through cryogenic conditions at temperatures below $-253\text{ }^\circ\text{C}$ (Lucentini et al., 2021).

Alternatively, green ammonia could be used as a hydrogen source for its generation onboard and on-demand inside the vehicle. In this case, a reactor is used for cracking the NH_3 into H_2 and N_2 , in a process called reforming; then, H_2 is fed to a fuel cell (FC) to produce the electricity necessary to power the car (Chiuta and Bessarabov, 2018). Still, ammonia needs hydrogen to be produced, so more steps and higher investment in machinery would be necessary to obtain NH_3 . Even so, if this process is well integrated in terms of energy utilization, it is possible to make the ammonia production very advantageous.

The use of chemical and process engineering simulation tools is an interesting way to evaluate which industrial process is more energy efficient, either green H_2 production and storage for stationary use or green NH_3 production then reforming for onboard H_2 applications. Through these tools, it is possible to establish the industrial equipment and operational conditions for each case, and to calculate the energy demand and efficiency of the processes (Tavares et al., 2020). In this study, it is proposed the application of the Aspen Plus® software to determine the energy efficiency of both cases, considering that H_2 and NH_3 derive from biomass of sugarcane bagasse. Starting from the biomass gasification, the energy consumption and efficiency of these systems were evaluated. Both processes presented similar results, but the H_2 storage was a little more energetically advantageous in this evaluation. Sensitivity analysis was performed to maximise the onboard hydrogen production from green ammonia, and it was observed that the reaction is favoured at low pressure and high temperatures. Overall, the simulation results are promising, and it is indicated the steps of green NH_3 production and reforming with potential for improvement to make it more energetically competitive.

2. Methodology

2.1 Process Description

This study was performed in the software Aspen Plus® V10 and aims to evaluate the energy efficiency of the green hydrogen production from biomass (P1) versus onboard hydrogen generation from green ammonia (P2). Since NH_3 needs H_2 to be produced, both processes are very similar, differing, above all, by the addition of more steps to produce ammonia. Furthermore, as green ammonia will be used to generate hydrogen onboard, in a vehicle, for example, additional steps are considered to reform NH_3 into H_2 . For a more detailed study, the thermodynamic analyses of processes P1 and P2 started from the gasification of sugarcane bagasse, followed by the water-gas shift reaction (WGSR) on different temperatures, and hydrogen purification via pressure swing adsorption (PSA). In the process P1, after the PSA step, the hydrogen was compressed for future transport and commercialization. As for the process P2, nitrogen separated from air was reacted with purified hydrogen in the Haber-Bosch (HB) process to produce green ammonia, which was then recovered. After that, the NH_3 reforming into H_2 was evaluated. Processes P1 and P2 are detailed respectively in Figure 1a and 1b.

2.2 Simulation Approach

The entire system was assumed to be under steady-state conditions. The thermodynamic model used for the simulations was the cubic equation of state Redlich-Kwong-Soave with the Boston-Mathias alpha function modification (RKS-BM), which is adequate for the temperature conditions of the gasification (Muslim et al., 2017). Since biomass and ash are non-conventional components, their enthalpy and density were calculated by the models HCOALGEN and DCOALIGT (Tavares et al., 2020). Besides, the distribution and particle size of biomass were not considered, and the ash was assumed as an inert material. Conversion was calculated using the *RGibbs* model, and the residence time was enough to reach equilibrium (Kombe et al., 2022).

2.3 Procedure for Aspen Plus Simulation

The steps for the gasification unit are the biomass drying, pyrolysis, and combustion to generate syngas. The biomass used for the simulations was sugarcane bagasse, whose composition on a dry basis is indicated in Table 1 and was based on the work of Kombe et al. (2022). A biomass feed of 100 Kg/h with 10% moisture was considered, which was dried at $150\text{ }^\circ\text{C}$ and 1 bar in a *RStoic* model. The biomass molecular weight was assumed to be 1 g/mol, so the water had a coefficient of 1/18 ($0.05556\text{ }H_2O$). For a 90% water removal, the dried biomass was separated from the water vapor by the separator using the model Sep1. The dried biomass was sent to a *RYield* model, to conduct the pyrolysis reaction at $700\text{ }^\circ\text{C}$ and 1 bar, converting the biomass into carbon, oxygen, nitrogen, hydrogen, and ash.

Table 1: Proximate composition of sugarcane bagasse biomass on dry basis (Kombe et al., 2022).

Compound	(wt. %, dry)	Comp. Attrib.	(wt. %, dry)
Ash	3.30	Fixed Carbon	16.20
C	48.10	Volatile Matter	80.50
H	5.90	Ash	3.30
N	0.15		
Cl	0		
S	0		
O	42.55		

The heat generated in the pyrolysis section is supplied to the COMBUST block to perform the combustion reactions for the syngas production. The combustion step was carried out in a *RGibbs* model, which minimizes the Gibbs free energy to calculate the product composition under chemical and thermodynamic equilibrium. Oxygen was separated from air in an air separation unit (ASU) (170 Kg/h fed to block AIRSEP) and supplied to the reactor, while the nitrogen produced by the ASU was used only in process P2 (ammonia from biomass gasification) for the ammonia synthesis step. The chemical reactions and heat involved in the combustion are shown from equations Eq(1) to Eq(11), under standard conditions. After combustion, the product was sent to block SEP2 to separate the syngas from the solid co-products (ash and carbon).



The produced syngas followed to the water gas shift reaction section (WGSRS) to increase the H₂ yield and to convert CO into CO₂, as indicated in Eq(8). Initially, the syngas and a water stream of 80 kg/h were heated to 300 °C and fed to the high temperature WGS (HTWGS) reactor. Then, the product was cooled down to 200 °C, then sent to the low temperature WGS (LTWGS) reactor. Both reactors operate adiabatically. For these processes, the *RStoic* model was chosen and fractional conversions of 80% and 75% were assumed for HTWGS and LTWGS, respectively. Thereafter, the CO mass fraction was below 2%. The next section was the hydrogen purification, so the product was sent to separator SEP3, to eliminate the water from the process, while the gaseous phase went to the pressure swing adsorption (PSA) block to obtain H₂ with purity of 99.97%, which is a requirement for fuel cell applications (ISO 14687-2:2012). For the process P1 (Figure 1a), the pure hydrogen was sent to a multistage compression system, with seven stages, while in process P2 (Figure 1b) the purified hydrogen was used in additional steps to produce green ammonia.

In the P2 system, the H₂ was used in the ammonia synthesis. The H₂ from the purification section and the N₂ from the AIRSEP unit were supplied to a multistage compressor to reach 150 bar and then sent to an exchanger to heat up to 300 °C. Next, N₂ and H₂ enter the *RGibbs* model to perform the Haber-Bosch reaction for NH₃ production, as shown in Eq(11). Then, the product was sent to a cooler to reduce its temperature to 30 °C and followed to an absorber. The outlet gas (R-GAS-01) was composed of H₂, N₂, and NH₃, so 95% of the stream

was recycled back to the HB process, and the remaining gas was expanded on a turbine and used in combustion for energy generation. As for the aqueous ammonia, it was sent to a distillation column to recover liquid NH_3 at 32 °C and 15 bar. The liquid NH_3 is easier to transport and to be used in onboard H_2 generation systems. After that, the ammonia reforming was also simulated to evaluate the system efficiency and its viability. In that aspect, sensitivity analyses for different temperatures and pressures were tested in a *RGibbs* model, and a membrane was added to purify the H_2 for final use in a fuel cell. The energy spent in processes P1 and P2 with product transportation, storage, and use in a fuel cell were not considered in this study.

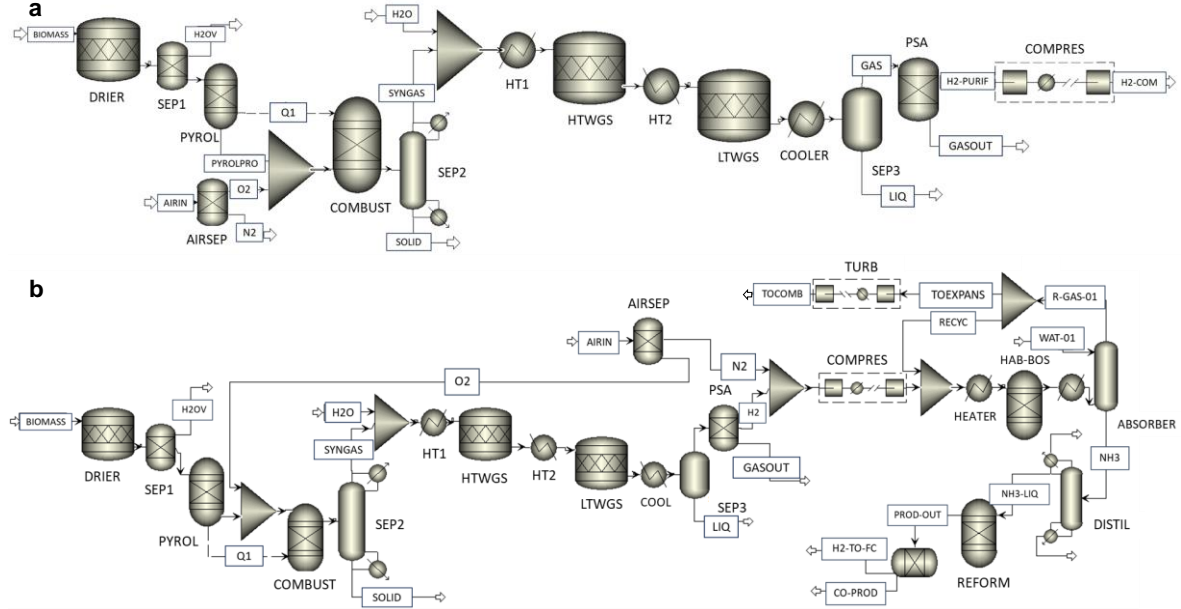


Figure 1: a) Process simulation of biomass gasification for green hydrogen production and compression. b) Process simulation of green ammonia production and reforming for onboard hydrogen generation.

2.4 Sensitivity Analysis

Sensitivity analyses were performed to maximise the onboard hydrogen production from ammonia reforming. In that respect, a temperature range of 400 to 700 °C, with 50 °C increment, and pressures from 1 to 20 bar were evaluated for the block REFORM. The percentage of ammonia conversion (X_{NH_3}) was calculated in mass basis through Eq(12) and used to identify the best operating parameters. Here, $\dot{m}_{\text{NH}_3,in}$ is the inlet mass flow of NH_3 and $\dot{m}_{\text{NH}_3,out}$ is the outlet mass flow.

$$X_{\text{NH}_3} = \frac{\dot{m}_{\text{NH}_3,in} - \dot{m}_{\text{NH}_3,out}}{\dot{m}_{\text{NH}_3,in}} \cdot 100\% \quad (12)$$

2.5 Energy Analysis

To estimate the energy demand of systems P1 and P2, utilities were assigned to the blocks of the process. For the compressors, electricity was the specified utility, while data from literature was used to calculate the energy demand of the ASU (Wu et al., 2020) and PSA (Liemberger et al., 2017). Thereafter, it was possible to calculate the overall energy efficiency (η_{H_2}) of both processes. Using Eq(13), in which LHV is the lower heating value for hydrogen (120 MJ/kg) and biomass (17.36 MJ/kg in dry basis), \dot{m} is the mass flow rate, \dot{Q}_{out} is the heat transfer rate, and \dot{W}_{net} is the net work rate.

$$\eta_{\text{H}_2} = \frac{\dot{m}_{\text{H}_2} \text{LHV}_{\text{H}_2} + \dot{Q}_{out} + \dot{W}_{net}}{\dot{m}_{\text{biomass}} \text{LHV}_{\text{biomass}}} \quad (13)$$

3. Results

To enhance the onboard hydrogen production from green ammonia, a sensitivity analysis was performed at the end of process P2, to maximize the NH_3 cracking into hydrogen. The results are shown in Figure 3a for different temperatures and pressures. As it can be observed, the reaction is favoured by high temperature and low pressure. The effect of temperature is more discreet at 1 bar since the conversions surpass 99% from 400 °C

onwards. On the other hand, at higher pressures, a drop in the ammonia conversion is observed for lower temperatures. Even so, conversions over 98% are seen for temperatures over 550 °C and 600 °C for operating pressures of 10 bar and 20 bar, respectively. These results agree with what is expected, because the ammonia cracking reaction is the inverse of the HB process, being slightly endothermic (46 kJ/mol) and, therefore, facilitated by increasing the temperature. It is interesting to note that these simulations were performed using a *RGibbs* model of Aspen Plus®, which minimizes the Gibbs free energy to reach the thermodynamic equilibrium, disregarding some limitations of the real system, such as the reaction kinetics. Based on the results of the sensitivity analyses, it was decided to operate the reformer at 1 bar and 600 °C.

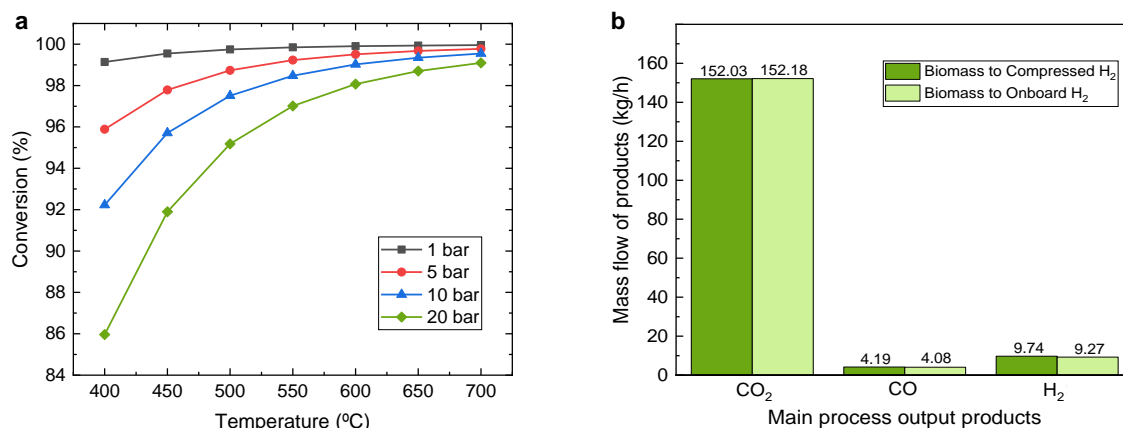


Figure 3 a) Conversion of NH₃ for onboard H₂ production at varying pressures and temperatures. b) Mass flow of output compounds generated from processes of biomass to compressed H₂ (P1) and to onboard H₂ (P2).

The main compounds generated in the outlet streams of systems P1 and P2 are shown in Figure 3b. It is observed that the amount of CO and CO₂ generated in both systems is very close, which can be justified by the similar processes of biomass gasification, WGSR and H₂ purification. Even so, process P2 has a slightly higher output of CO₂, because the nitrogen from the air separation unit (AIRSEP) had remaining oxygen that took part in the WGSR, which is responsible for generating this component. The formation of CH₄ as co-product is negligible for both processes, and only 0.13 kg/h of NH₃ leaves the reformer as non-converted reactant. Additionally, it can be noted that the H₂ content from the onboard production was lower than the H₂ output in system P1. Since the HB reaction has a conversion close to 80% for a Gibbs reactor operating at 300 °C and 150 bar, part of the hydrogen in process P2 is not converted to ammonia. Even with a 95% recycle of the unreacted H₂ (R-GAS-01) to the process, the onboard H₂ generation would be limited to 9.28 Kg/h for NH₃ cracking at 700 °C and 1 bar, but a higher energy demand in the reformer would be necessary to get a hydrogen gain of only 0.01 Kg/h. Although the hydrogen output content for both systems is different, the energy efficiency needs to be calculated to indicate which process is the most efficient.

Table 2: Energy efficiency calculated for processes P1 and P2.

	P1	P2
\dot{m}_{H_2} (kg/h)	9.74	9.27
Electricity (MJ/h)	-37.91	-88.11
ASU (MJ/h)	-155.55	-155.55
PSA (MJ/h)	-13.88	-13.88
Turbine (MJ/h)		27.15
Combustion (MJ/h)		54.77
η_{H_2} (%)	61.56	59.92

The data used for the calculations of energy efficiency are presented in Table 2. The negative values are related to the steps that needed expenses with energy in the processes, such as electricity for the compressors, the air separating unit, and pressure swing adsorption. ASU and PSA require high energy demand, so they were calculated based on data provided in literature, while the duty with electricity was calculated by the software. Although ammonia needs more equipment to be produced and purified, the system can be integrated to also generate energy for the plant. In simulation P2, a positive duty is observed from gas expansion in a turbine. Also, a small fraction of non-recycled H₂ and NH₃ are used to generate energy through combustion. For this

energetic analysis, process P1 was slightly more efficient than process P2, 61.56% versus 59.92%, respectively. Even so, it is possible to carry out an energy integration to improve efficiency in NH₃ production, such as seizing the heat produced by the HB reaction to provide energy for other stages of the process, and/or producing other components in addition to ammonia. Furthermore, considering that the green ammonia is commercialized as a liquid, it is easy to transport and is an already scalable compound, it is very promising for onboard hydrogen applications, being much safer than compressing and transporting hydrogen in system P1.

4. Conclusions

The production of hydrogen was evaluated in two different systems: green hydrogen generation from biomass and its compression (P1) versus green ammonia production from biomass and its reforming for onboard hydrogen generation (P2). Through a sensitivity analysis, it was observed in process P2 that the hydrogen production from ammonia is favoured by high temperatures and 1 bar pressure. According to simulations, it was produced 9.74 kg/h and 9.27 kg/h of H₂ in systems P1 and P2 from a feed of 100 kg/h of biomass, with energy efficiencies of 61.56% and 59.92%, respectively. Despite the lower H₂ output and efficiency in system P2, the use of NH₃ as a hydrogen carrier is very desirable, because NH₃ is easier to transport at scale than compressed H₂ and eliminates the safety issues regarding the high pressures necessary for H₂ storage. Besides, it is possible to perform a heat integration in system P2 to make the NH₃ production process more energy-efficient and competitive.

Nomenclature

LHV_i - lower heating value of a fuel, MJ/h
 \dot{m}_{biomass} - mass flow rate of biomass, kg/h
 \dot{m}_{H_2} - mass flow rate of H₂, kg/h
 $\dot{m}_{\text{NH}_3, \text{in}}$ - inlet mass flow of NH₃, kg/h
 $\dot{m}_{\text{NH}_3, \text{out}}$ - outlet mass flow of NH₃, kg/h

\dot{Q}_{out} - heat transfer rate, MJ/h
 \dot{W}_{net} - net work rate, MJ/h
 X_{NH_3} - reactant conversion, %
 η_{H_2} - energy efficiency, %

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