



Comparative feedstock analysis for ammonia production via biomass gasification

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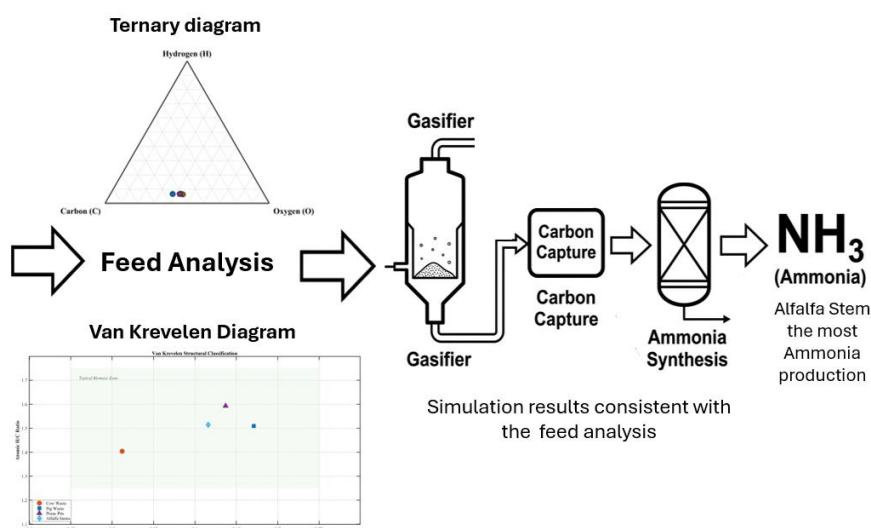
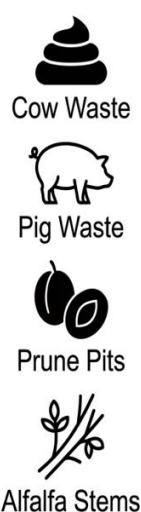
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Abstract

This study simulated ammonia production from biomass gasification using cow waste, pig waste, prune pits, and alfalfa stems. The process included gasification, carbon capture, and ammonia synthesis in Aspen Plus. Feed analysis with the C-H-O ternary and Van Krevelen diagrams showed a consistent composition trend among the four feedstocks. Cow waste was more carbon-rich and less oxygenated, while pig waste was the most oxygen-rich feedstock. Higher O/C ratios increased CO₂ formation and reduced CO production during gasification. Lower O/C ratios favored CO formation and reduced the tendency toward CO₂ generation. Hydrogen production depended on both H/C and O/C₂, not on a single ratio alone. Alfalfa stems produced the highest H₂ fraction because they had the most favorable balance between hydrogen availability and oxygen content. A higher H₂/N₂ ratio in the cleaned gas led to a higher ammonia mass fraction in the synthesis section. On a mass-input basis, the simulated ammonia yields were 0.1089, 0.0915, 0.0919, and 0.0864 kg NH₃ per kg of cow waste, pig waste, prune pits, and alfalfa stems, respectively. Overall, alfalfa stems produced the purest ammonia stream, whereas cow waste delivered the highest overall ammonia yield per unit feedstock mass, indicating that feedstock ranking depends on whether synthesis-gas purity or total mass-based productivity is prioritized.

Graphical Abstract

Biomass Feedstock Selection



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1. Introduction

Recently, ammonia (NH_3) has emerged as an excellent option for carbon-free energy storage and a key component in global electricity supply, large-scale energy storage, eco-friendly transportation sectors. A comprehensive overview of ammonia-fired combustion technologies -including fuel cells, reciprocating engines, and gas turbines- identified critical technical challenges such as elevated NO_x emissions and low flame velocities, while noting that public acceptance remains constrained by ammonia's toxicity and handling hazards [1].

To enhance efficiency, recent techniques aim to eliminate fossil-fuel-dependent steam methane reforming by utilizing renewable, carbon-free hydrogen from water electrolysis. Within this framework, bypassing methane reforming reduces synthesis loop energy consumption by 4.2 GJ per ton of NH_3 , thereby initiating a paradigm shift from centralized facilities toward decentralized production infrastructure [2]. To systematize this transition, a three-generation roadmap has been proposed: Generation 1 (G1) relies on fossil fuels coupled with carbon capture and storage (CCS), Generation 2 (G2) utilizes renewable hydrogen to produce green ammonia, and Generation 3 (G3) achieves direct ammonia synthesis via the electrochemical reduction of nitrogen [3].

From an energy vector perspective, the round-trip conversion efficiencies of these technologies within fuel cell systems have been evaluated [4]. Their data demonstrated that renewable ammonia achieves a 19% round-trip efficiency in PEMFC vehicles, 39% in stationary PEMFC power plants, and exceeds 50% in SOFC systems integrated with waste heat recovery schemes. On a regional scale, the techno-economic and environmental viability of this transition was demonstrated through a roadmap for Qatar [5]. They showed that replacing conventional gray ammonia with blue ammonia could slash national GHG emissions from 7.50 Mt to 4.22 Mt by 2030, using a SWOT analysis to outline strategic implementation policies.

When utilizing carbonaceous and biogenic feedstocks, system integration and carbon management become paramount. In a review of net-zero and negative-emission pathways, integrating chemical looping with the Haber-Bosch process (ICLHB) can reduce coal-to-ammonia emissions to 0.05 tCO_2/tNH_3 . Furthermore, gas switching reforming (GSR) and membrane-assisted autothermal reforming (MA-ATR) can limit natural gas-based emissions to 0.07 and 0.18 tCO_2/tNH_3 , respectively, while biomass-fed ICLHB coupled with BECCS can unlock net-negative emissions as low as -2.9 tCO_2/tNH_3 [6].

This thermochemical conversion relies fundamentally on gasification principles, including reaction kinetics, the Boudouard mechanism, water-gas shift (WGS) dynamics, and CFD modeling criteria [7]. Applying these principles, an equilibrium Aspen Plus model was developed for the steam gasification of food waste, which inherently yields an H_2/CO ratio of approximately 2.13, making it highly favorable for direct Fischer-Tropsch synthesis [8]. In contrast, more complex biomass feedstocks require secondary WGS steps to optimize syngas composition, where performance is heavily dictated by the elemental and organo-inorganic properties of the feed. The co-gasification of high-ash Indian coal blended with press mud and sawdust was investigated, reporting that a 40% biomass blend increased the syngas H_2 concentration from 13.6% to 19.9% and raised the higher heating value (HHV) from 3.42 to 5.59 MJ/Nm^3 [9]. Their mineralogical analysis identified K-feldspar, hematite, CaO, and MgO as critical positive catalysts, whereas kaolinite and phosphate minerals inhibited char reactivity.



2. Materials and Methods

This simulation framework consists of three integrated process zones that are linked to represent a complete ammonia production plant based on biomass gasification. The first zone corresponds to the gasification section, where the selected biomass feedstocks are converted into syngas through thermochemical reactions under defined operating conditions. The raw syngas generated in this stage then enters a gas cleaning and composition-adjustment section. Within this intermediate section, a carbon capture unit is incorporated to separate and remove carbon-containing species, thereby reducing the carbon content of the process stream and improving the suitability of the gas for ammonia synthesis. In the final zone, the conditioned gas is fed into the ammonia production section, where it is processed as the synthesis feed for ammonia generation. Taken together, these three interconnected zones simulate the full plant from biomass conversion to syngas upgrading to ammonia production.

2.1 Process Simulation

2.1.1 Gasification

The gasification section shown in **Fig. 1**, converts the four biogenic feedstocks into raw syngas. Because the entire zone operates at very high temperatures (up to 1000 °C) and near-atmospheric pressure, the ideal-gas behavior is well captured by the IDEAL property method. The wet biomass (21 kg/h as-received) is first dried in a stoichiometric reactor (DRY-REAC) together with 1 kg/h of nitrogen as a sweep gas; a Fortran calculator removes 70 % of the initial moisture. The dried solid then undergoes thermal decomposition in an RYield reactor (DECOMP) that splits the non-conventional biomass into char, tar and elemental gases (C, H₂, O₂, N₂, S).

After separation of char and tar, the light gases enter a Gibbs reactor (PYRO, 700 °C, 1 bar) where the equilibrium composition of the pyrolysis gas is determined by minimization of the free energy.

The main reactions that are automatically considered in this equilibrium step include complete/incomplete combustion (1)–(3), the water-gas shift reaction (4), methanation (5), Boudouard (6), and sulphur Eqs. (7)–(9):



The resulting mixture is partially oxidized in a plug-flow reactor (OXI, 1000 °C) with kinetic parameters taken from Gerun et al. The following kinetic Eqs. [14] (3)–(4), and (10)–(14) are defined:





The stream then enters a second plug-flow reactor for the reduction zone (RED, 800 °C), where the main endothermic reactions (1), (4), (15), and (16) occur with Langmuir-Hinshelwood kinetics:



Steam can optionally be added before the RED reactor to promote char gasification. The raw syngas leaving the RED unit is freed of ash, compressed to 5 bar, cooled to 40 °C, and finally passed through a flash drum (SETELEC) that removes condensed water and switches the property method from IDEAL to ELECNRTL for the downstream carbon-capture section.

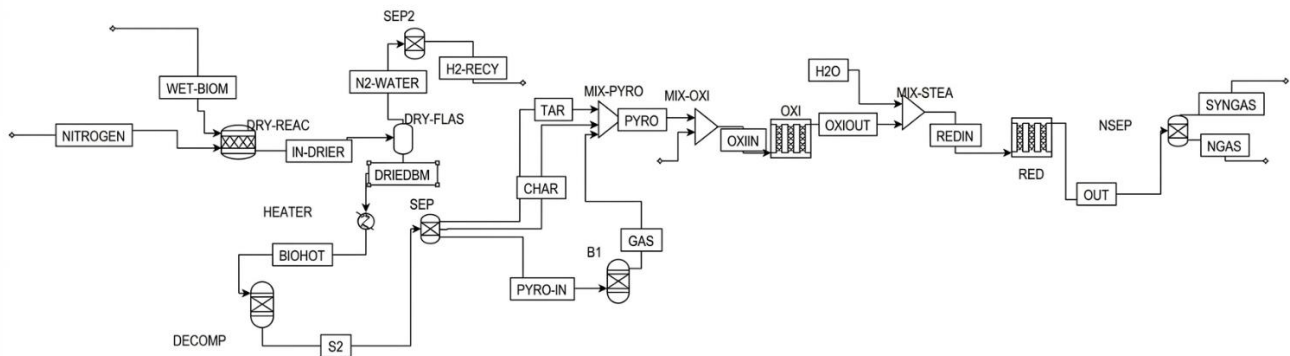


Fig. 1. Gasification process flowsheet.

2.1.2 Carbon Capture

The carbon-capture section removes CO_2 from the syngas using an aqueous MDEA solvent (50 wt%). Because the solvent contains ionic species ($MDEA^+$, HCO_3^- , CO_3^{2-} , H_3O^+ , OH^-) and acid-base equilibria, therefore, the ELECNRTL method is used. The syngas (27 bar, 40 °C) enters the bottom of a 10-stage RadFrac block (ABSORBER), while the lean MDEA solution is fed at the top; a Murphree tray efficiency of 0.4 is used. The following equilibrium (17)–(19) and kinetic (20)–(21) reactions describe the absorption chemistry:





A Design Spec automatically adjusts the solvent flow rate to achieve 95 % CO₂ removal. The rich amine leaving the absorber bottom is pre-heated in a heat-exchanger (HEATX1) and then fed to a 30-stage stripper (STRIPPER) that operates at 2 bar with a kettle reboiler (110–120 °C). In this column, because of the higher temperature and lower pressure, the equilibrium of reactions (17)–(21) is shifted to the left, releasing high-purity CO₂ (≈ 98.5 mol%).

The overhead vapor is cooled to 10 °C and the condensed water is separated in a flash drum (FLASH). The regenerated lean amine is cooled, pumped back to 27 bar, and recycled to the absorber. A small purge can be used to prevent accumulation of non-reactive impurities in the solvent loop. **Fig. 2** shows the entire Carbon capture plant with recycle stream.

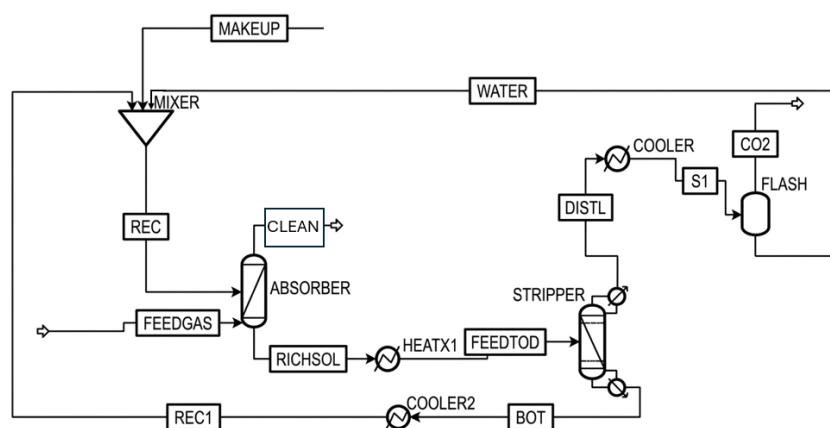


Fig. 2. Carbon capture process flowsheet.

2.1.3 Ammonia Production

As shown in **Fig. 3**, the final section produces liquid ammonia via the Haber-Bosch process. Because the synthesis loop operates at high pressure (200 bar) and contains non-polar gases (H_2 , N_2 , NH_3 , CH_4), the PENG-ROB equation of state is employed.

The gas stream leaving the absorber block from the carbon-capture unit is first sent to a simple separator (SEPARATO) that adjusts the H_2 : N_2 ratio to 3:1 and removes remaining traces of CO , H_2S and water. The conditioned gas is then compressed to 200 bar, pre-heated to 350 °C, and fed into a plug-flow reactor (B1, 6.4 m length, 0.8 m diameter) containing 2200 kg of Fe-based catalyst (bed voidage 0.33). The Haber-Bosch reaction is modelled with a LHHW kinetic expression:



The product stream is then cooled to 0 °C, and the condensed ammonia is separated in a flash drum (B3) as a liquid product (purity >98 mol%). Unreacted H_2 and N_2 are partly purged to avoid build-up of inert impurities (e.g. methane) and partly recycled back to the SEPARATO unit, where they are re-compressed and mixed with fresh feed. This recycle loop is optional and can be activated only when needed to increase overall conversion.

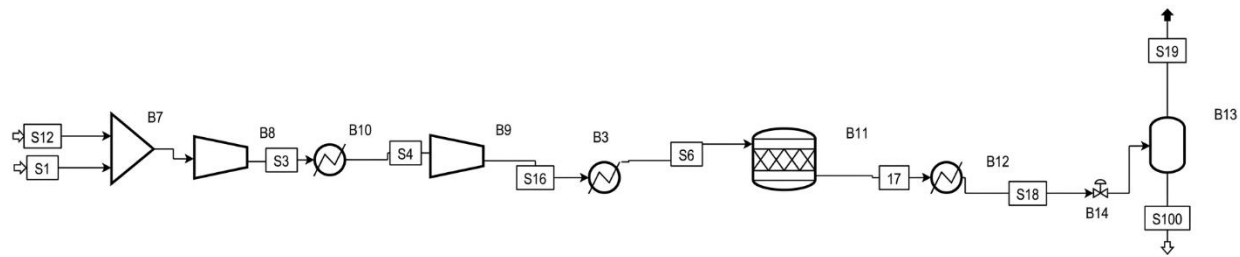


Fig. 3. Ammonia production flowsheet.

2.2 Feed Analysis

2.2.1 Van Krevelen Diagram

To evaluate the inherent thermochemical potential and energy density of our specific case studies, a Van Krevelen diagram (VKD) analysis was performed for the four selected biogenic waste streams: cattle manure, pig manure, prune pits, and alfalfa stems. This empirical mapping was conducted by plotting the ultimate analysis data of each feedstock directly onto the standardized graphical matrix to baseline their solid fuel coordinates.

Because each feedstock composition used in the simulation was taken from a single database record, its representativeness was assessed against other samples of the same feedstock type. Ultimate analyses were compiled from the Phyllis2 database [15]; for pig manure, which had fewer than three suitable records, an additional sample was obtained from the literature [16]. Only untreated materials with complete C, H and O data, converted to a dry, ash-free (daf) basis where necessary, were retained, whereas composted, aged, digested or thermally treated samples and records flagged as unreliable in the database remarks were excluded. Given the scarcity of prune-pit records, prune, peach, cherry and apricot pits were combined into a single stone-fruit pit group, and alfalfa records not specified by plant part were grouped with alfalfa stems. The final dataset comprised 21 samples: cattle manure ($n = 4$), pig manure ($n=3$), stone-fruit pits ($n=6$) and alfalfa ($n=8$) (Fig. 4). Atomic H/C and O/C ratios were calculated on a daf basis ($C=12.011$, $H=1.008$, $O=15.999$ g.mol⁻¹) and expressed as mean $\pm$ standard deviation, which here reflects natural and inter-laboratory variability rather than analytical uncertainty. Differences between feedstock types were evaluated for each ratio by one-way ANOVA with Tukey's HSD post hoc test ($\alpha = 0.05$), after homogeneity of variances was verified with Levene's test; the Kruskal–Wallis test was used to confirm robustness. Statistical analyses were performed in Python (SciPy).

As shown in Fig. 4, the samples used in the simulation were located at $O/C=0.512$ and $H/C=1.405$ for cattle manure, $O/C=0.671$ and $H/C=1.509$ for pig manure, $O/C=0.637$ and $H/C=1.593$ for prune pits, and $O/C=0.617$ and $H/C=1.516$ for alfalfa stems. The corresponding group means of O/C and H/C were 0.520 ± 0.103 and 1.496 ± 0.080 for cattle manure, 0.619 ± 0.048 and 1.367 ± 0.198 for pig manure, 0.608 ± 0.053 and 1.483 ± 0.103 for stone-fruit pits, and 0.597 ± 0.023 and 1.388 ± 0.081 for alfalfa. Considerable variability was observed within each feedstock type, particularly in the O/C ratio of cattle manure (0.39–0.64) and the H/C ratio of pig manure (1.14–1.51). Consequently, the differences between feedstock types were not statistically significant for either H/C ($F(3,17)=1.72$, $p=0.20$) or O/C ($F(3,17)=2.58$, $P=0.09$), and no pairwise comparison reached significance (Tukey's HSD, $p > 0.10$); the Kruskal–Wallis test yielded the same outcome. All simulated samples fell within two standard deviations of their group means and can therefore be regarded as representative of their feedstock types. Notably, the two alfalfa stem samples exhibited higher H/C ratios (1.52) than the other alfalfa records (1.31–1.38). The comparison in the following sections should thus be interpreted

as a comparison of four specific samples with distinct elemental ratios, rather than as a generalized difference between feedstock types.

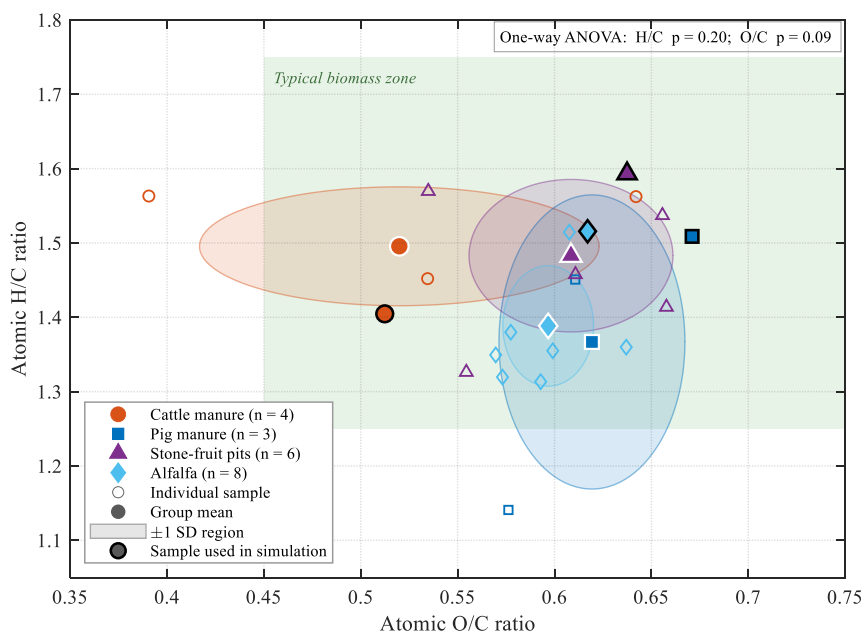


Fig. 4. Van Krevelen diagram of cattle manure, pig manure, stone-fruit pit and alfalfa samples, showing individual samples, group means with ± 1 standard deviation ellipses, and the samples used in the simulation, relative to the typical biomass zone adapted from McKendry (2002) [11].

2.2.2 Ternary Diagram

To visually compare the elemental composition of the four biogenic feedstocks (cow manure, pig manure, prune pits, and alfalfa stems) and to predict their relative tendency toward char formation during gasification, the C-H-O ternary diagram method described by Wang et al. was adopted. The ultimate analysis (mass percentages of C, H, O on a dry, ash-free basis) for each feedstock was retrieved from the Phyllis2 database. These values were normalized to 100%. The ternary coordinates (C, H, O in mass%) were plotted on a triangle.

The C-H-O ternary diagram in **Fig. 5** shows that all four feedstocks are located close to each other near the bottom of the triangle, which means they have fairly similar overall elemental compositions and relatively low hydrogen content. In this diagram, the closer a point is to the carbon vertex, the higher its carbon content, and based on this pattern, cow waste appears to be the most carbon-rich feedstock among the four samples. Pig waste is positioned slightly more toward the oxygen side, suggesting that it is relatively more oxygenated. Prune pits and alfalfa stems fall between these two cases, with alfalfa stems appearing slightly closer to the carbon side than prune pits, which may indicate a somewhat lower oxygen content. Overall, although the feedstocks lie within a narrow compositional range, the diagram still highlights small but important differences in carbon richness and oxygenation that can influence their behavior during thermochemical conversion.

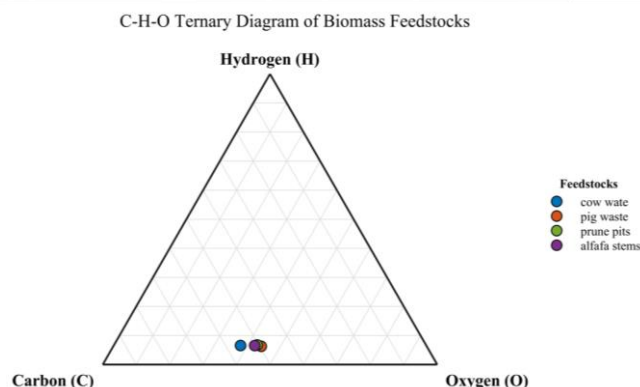


Fig. 5. Ternary diagram for all feedstocks.

Historically, navigating the immense diversity of these biogenic feedstocks required a standardized graphical methodology to screen solid fuels before deploying rigorous chemical kinetic simulations. To address this, the Van Krevelen diagram (VKD) was adopted in bioenergy research as a foundational framework to map different biomass types based on their macro-elemental evolution. It has been highlighted that tracing these solid fuel matrices historically provided a low-cost, preliminary predictive window into how different oxygen-to-carbon profiles affect devolatilization rates and gasification ease [10]. Long before the advent of multi-stage system modeling, placing raw biomass residues within standard fossil-to-biomass conversion corridors served as the primary diagnostic tool to evaluate how chemical structure predetermines syngas quality [11]. Consequently, the integration of the VKD in solid fuel literature represents a critical bridge, demonstrating that the upstream chemical footprint of organic materials inherently dictates their subsequent thermochemical pathways.

The C-H-O ternary diagram is widely employed in the literature to visually compare elemental compositions and predict char formation during the gasification of various biomass feedstocks. A thermodynamic equilibrium model was developed based on minimizing Gibbs free energy on the basis of ternary diagram, identifying three distinct zones within the diagram: carbon deposit, carbon-free, and intermediate zones [12]. This approach has been applied to determine the minimum quantity of gasifying agents (steam, O_2 , CO_2) required to prevent carbon deposition and to compare the effectiveness of gasifying agents for biomass and coal. More recently, this thermodynamic framework employed on ternary diagram was expanded to optimize the addition of co-agents (water and CO_2) for maximizing syngas yield and minimizing char formation [13]. These graphical methods enable rapid assessment of gasification behavior without the need for detailed simulation. Despite these valuable contributions, the existing literature features a noticeable scarcity of comprehensive studies that systematically trace how the complex chemical properties of biomass directly dictate the final efficiency of the synthesis loop. Most available research evaluates either isolated, small-scale gasification of specific residues or focuses on macro-level green hydrogen networks. This leaves a critical gap in multi-stage, feedstock-to-ammonia process integration. For instance, while high-moisture, high-ash feedstocks like cattle manure are known to behave differently from low-moisture, high-carbon agricultural residues like prune pits, no systematic study has yet quantified how these differences cascade through gasification, gas cleaning, and ultimately impact ammonia synthesis efficiency.

Furthermore, although ternary diagrams have been applied individually to describe carbon formation boundaries for single feedstocks, it is not widely mentioned that this graphical tool has been used to systematically compare the characteristics of several biogenic feedstocks (such as high-moisture manure) within an integrated gasification-to-ammonia simulation framework.



To address this limitation, the present study conducts a comprehensive, integrated process simulation in Aspen Plus to comparatively analyze four distinct biogenic feedstocks through a rigorous three-stage framework (comprising gasification, gas cleaning/adjustment, and the final ammonia synthesis loop). Rather than treating the system as a generic conversion process, this work deeply investigates the elemental and physical characteristics of each feedstock. By tracking the cascading thermodynamic impacts across all three operational stages, we generate detailed performance outputs for each material. Ultimately, these simulation results are critically compared against the unique initial properties of the feedstocks to evaluate whether the final energetic and chemical yields align with the chemical footprint of the raw input.

In the following sections, the simulation detailed description and diagram evaluations are expanded, then use of ternary and Van Kerlmen diagrams is interpreted and results are graphed, discussed and validated.

3. Results and Discussion

3.1.1 Feed analysis

after running the simulation on aspen plus, mass fraction of each component in the product of each part is gathered and compared with the expectations from feed analysis diagrams.

Taken together, the C-H-O ternary diagram and the Van Krevelen plot point to the same overall compositional trend and, therefore, support a consistent expectation for the distribution of H_2 , CO , and CO_2 during gasification of the studied feedstocks. In both diagrams, cow waste is positioned in a relatively more carbon-rich and less oxygenated region, whereas pig waste lies in a clearly more oxygen-rich domain, while prune pits and alfalfa stems remain between these two extremes, with alfalfa stems appearing slightly less oxygenated than prune pits. This agreement is especially meaningful because the ternary diagram expresses the relative shares of carbon, hydrogen, and oxygen directly, while the Van Krevelen plot presents the same elemental chemistry through the O/C and H/C atomic ratios, meaning that both figures describe the same structural behavior from two complementary perspectives. On this basis, cow waste would be expected to exhibit the greatest tendency toward CO formation and the lowest tendency toward CO_2 generation, since its lower oxygenation level implies that carbon is less likely to remain in a fully oxidized state during conversion. Pig waste, in contrast, should be more prone to CO_2 formation and less favorable for CO production because its higher O/C character reflects a more oxygenated feed structure and, consequently, a stronger tendency for carbon to appear in more oxidized gaseous products. Prune pits and alfalfa stems should display intermediate behavior, although alfalfa stems are likely to be slightly more favorable for CO and slightly less favorable for CO_2 than prune pits because their position indicates a somewhat lower overall oxygenation condition.

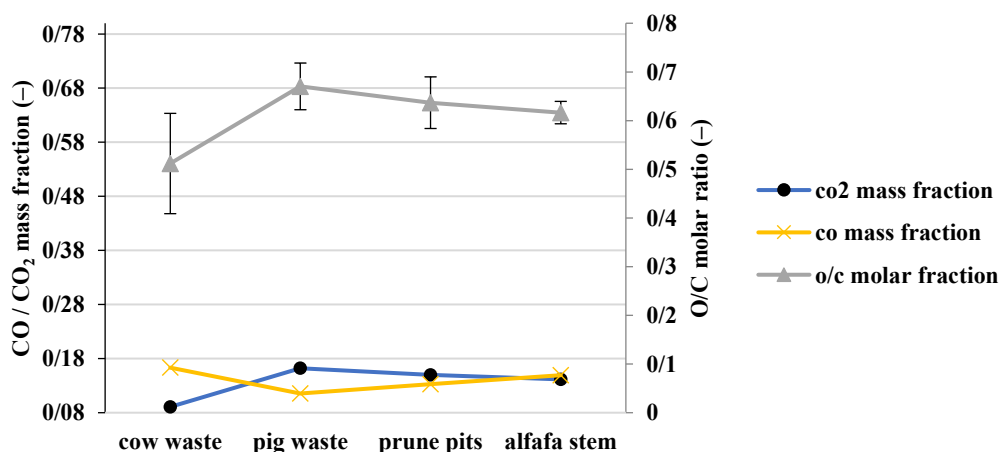


Fig. 6. O/C molar fraction versus CO and CO_2 production.



The gasification simulation results for CO and CO_2 as shown in **Fig. 6** strongly support this interpretation and confirm the role of the O/C molar fraction in governing the final carbon distribution in the product gas. Vertical error bars on the O/C series represent the standard deviation of the O/C atomic ratio calculated from $n = 4, 3, 6,$ and 8 literature-reported ultimate-analysis records for cow waste, pig waste, prune pits, and alfalfa stems, respectively (Phyllis2 database); differences in O/C among the four feedstock groups were not statistically significant (one-way ANOVA, $p = 0.088$). As the CO and CO_2 mass fractions are deterministic outputs of the Aspen Plus gasification model for a fixed feed composition, their uncertainty could not be independently quantified through replicate simulation within the scope of this revision. The increase in O/C from cow waste to pig waste is accompanied by a clear increase in simulated CO_2 and a corresponding decrease in CO , which is exactly the behavior expected for a feedstock with a more oxygenated structure. Pig waste shows this pattern most clearly, exhibiting the highest O/C ratio together with the highest CO_2 fraction and the lowest CO fraction, whereas cow waste shows the reverse behavior, with the lowest O/C ratio, the lowest CO_2 fraction, and the highest CO fraction. Prune pits and alfalfa stems again fall between these two extremes, and the slight reduction in O/C from prune pits to alfalfa stems is accompanied by a modest decrease in CO_2 and a slight increase in CO , in full agreement with the compositional expectations derived from the feed analysis diagrams. Therefore, the simulation results are not only chemically reasonable, but also fully consistent with the trends indicated by both the ternary and Van Krevelen analyses, confirming that the model reproduces the feedstock-dependent gasification behavior in a reliable and physically meaningful way.

To interpret the hydrogen production difference in each feedstock during gasification process, the H/C ratio is examined. **Fig. 7** and **Fig. 8** show the hydrogen mass fraction in the gasification product and the H/C ratio in each feedstock, respectively.

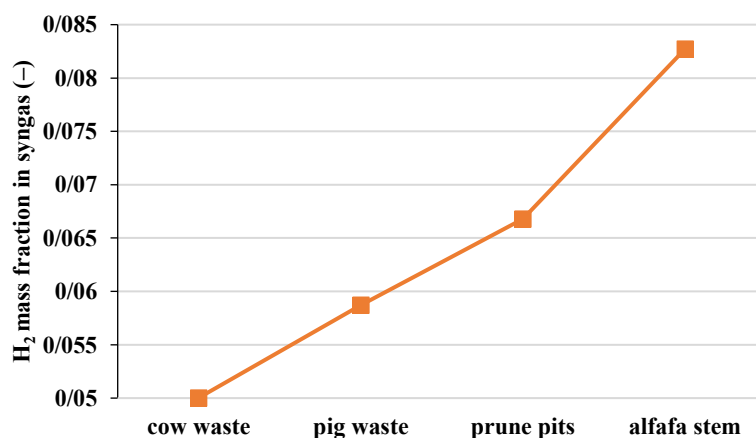


Fig. 7. Hydrogen mass fraction in the gasification product.

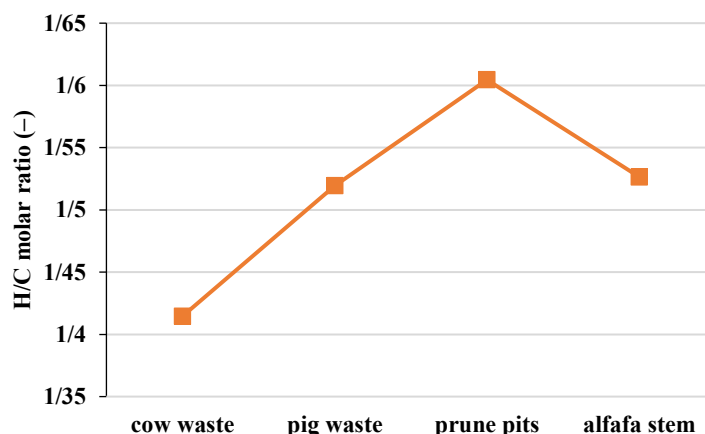


Fig. 8. H/C molar fraction of each feedstock.

The observed rise in hydrogen production across the four feedstocks can be explained by the combined effect of the H/C and O/C molar ratios rather than by only one of them. Although the H/C ratio increases from cow waste to pig waste and reaches its maximum for prune pits, the H_2 fraction in the product gas is more in alfalfa stem, indicating that hydrogen generation is influenced by the balance between hydrogen availability and the degree of inherent oxygenation of the feedstock rather than by H/C alone. In gasification, biomass is converted into CO , H_2 and CO_2 , while subsequent water-gas shift reactions further redistribute CO and steam into additional H_2 and CO_2 ; therefore, the final hydrogen level depends on how the elemental structure of the feed favors these competing pathways. Cow waste shows the lowest H/C ratio and, consistently, the lowest hydrogen yield, which suggests a limited intrinsic capacity for H_2 formation. Pig waste exhibits a higher H/C ratio and thus a moderate increase in hydrogen production, yet its simultaneously highest O/C ratio likely constrains further H_2 enrichment because a more oxygenated feedstock tends to be chemically more oxidized and less favorable for maximizing free hydrogen in the syngas. Prune pits benefit from the highest H/C ratio and therefore outperform pig waste in hydrogen generation, but alfalfa stem ultimately delivers the highest H_2 fraction because it combines a relatively high H/C ratio with a lower O/C ratio than both pig waste and prune pits. This indicates that alfalfa stem provides the most favorable elemental balance among the tested feedstocks, offering sufficient hydrogen potential without the penalty of excessive inherent oxygen, which explains why its gasification product is the richest in hydrogen. The simulation results also indicate a clear positive relationship between the H_2/N_2 ratio of the synthesis feed after the decomposition block and the ammonia mass fraction in the product stream. **Fig. 9** and **Fig. 10** show the ammonia mass fraction in the product stream and H_2/N_2 ratio respectively. As the H_2/N_2 ratio increases from approximately the stoichiometric level for cow waste to substantially higher values for prune pits and alfalfa stem, the NH_3 mass fraction also increases steadily, suggesting that a more hydrogen-rich feed enhances ammonia formation under the simulated operating conditions. This trend is chemically reasonable because ammonia synthesis follows the reaction (22) meaning that hydrogen availability is a fundamental requirement for sustaining nitrogen conversion. Although the stoichiometric ratio is 3:1, a feed containing more hydrogen than this value can still promote higher ammonia production in the practical synthesis however, more that stoichiometric ratios do not perform extreme effect on the ammonia yield but still promoting. Therefore, the higher ammonia production observed for feedstocks such as alfalfa stem is consistent with their higher simulated H_2/N_2 ratio, and the two diagrams together confirm that hydrogen-rich upstream gas conditioning contributes directly to improved downstream ammonia synthesis performance.

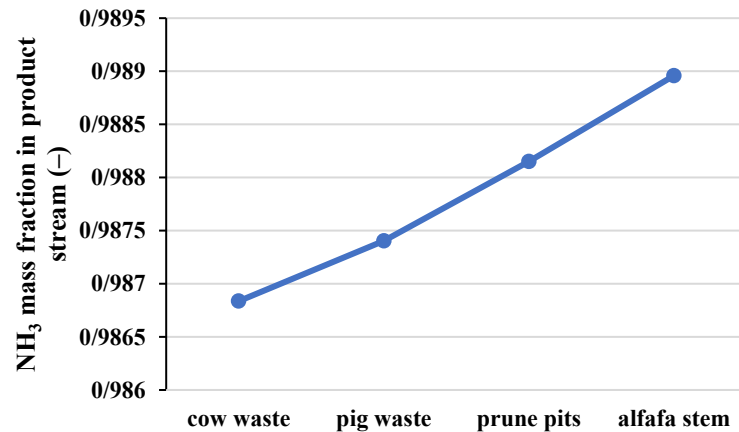


Fig. 9. Ammonia mass fraction in the product stream.

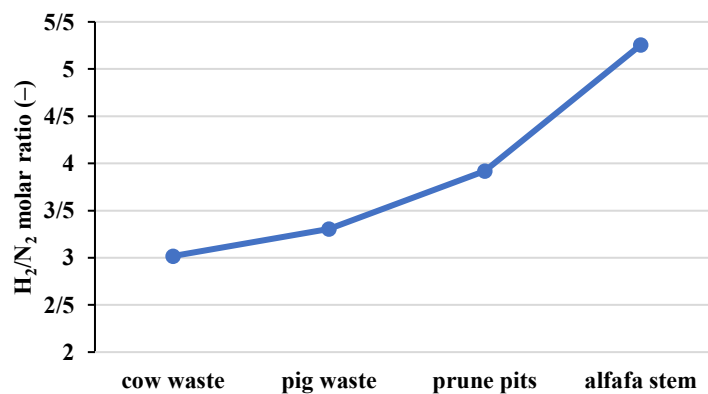


Fig. 10. H₂/N₂ ratio.

Fig. 11 shows the mole fraction of CO₂ in the inlet of Ammonia production plant to the mole fraction of Ammonia in the product stream. The CO₂/ammonia trend shows a clear and meaningful decline from cow waste to alfalfa stem, indicating that the amount of inlet CO₂ required per unit of ammonia produced becomes progressively lower across the feedstocks. This behavior suggests that the downstream ammonia synthesis system operates more efficiently when it is supplied by feedstocks that generate a more favorable synthesis-gas composition, so that a smaller CO₂ burden is associated with each unit of NH₃ formed. In practical terms, the highest ratio observed for cow waste implies a less efficient conversion environment, where more carbon dioxide enters the process relative to the amount of ammonia ultimately produced, while the lowest ratio for alfalfa stem reflects a more advantageous process condition with improved nitrogen hydrogenation performance and lower apparent CO₂ intensity per unit product. This interpretation is fully consistent with the previously observed increase in the H₂/N₂ ratio and ammonia mass fraction from cow waste to alfalfa stem, because a more hydrogen-rich synthesis feed promotes ammonia formation, thereby reducing the relative CO₂ input associated with each unit of NH₃ produced. Accordingly, the monotonic decrease in the feed CO₂/ammonia produced ratio can be taken as further evidence that the alfalfa-stem-derived case provides the most favorable overall integration between upstream gas conditioning and downstream ammonia synthesis, whereas cow waste represents the least favorable case among the studied feedstocks.

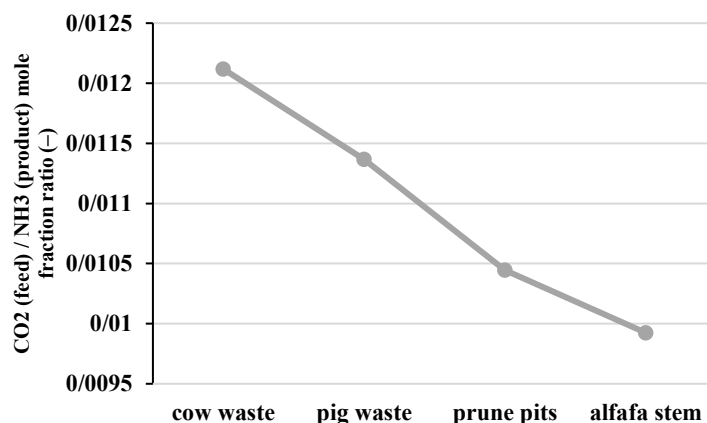


Fig. 11. CO₂ mole fraction in feed/Ammonia mole fraction in the product.

Table 1. Ammonia synthesis loop output for the four feedstocks: total product mass flow, NH₃ mass fraction (purity), and mass-based NH₃ yield per kilogram of feedstock.

Feedstock	Total product mass flow (kg/hr)	NH ₃ mass fraction (%)	NH ₃ yield (kg NH ₃ /kg feed)
Cow waste	2.333	98.18	0.1089
Pig waste	1.958	98.34	0.0915
Prune pits	1.961	98.56	0.0919
Alfalfa stems	1.840	98.81	0.0864

To complement the purity-based comparison shown in **Figs. 9–11**, the ammonia synthesis loop output was also normalized to the feedstock mass basis as summarized in **Table 1**. Cow waste yielded 0.1089 kg NH₃ per kg of feed, followed by prune pits (0.0919 kg/kg) and pig waste (0.0915 kg/kg), while alfalfa stems gave the lowest mass-based yield (0.0864 kg/kg). This ranking is the reverse of the purity trend, in which alfalfa stems achieved the highest NH₃ mass fraction (98.81%) in the product stream and cow waste the lowest (98.18%). This apparent discrepancy is explained by the difference between synthesis-gas quality and total throughput: although cow waste generates a synthesis gas with a comparatively low H₂/N₂ ratio (**Fig. 10**), consistent with its carbon-rich, low-oxygen composition identified from the ternary and Van Krevelen diagrams (**Figs. 4–5**), the total product stream leaving the synthesis section is larger for cow waste (2.333 kg/hr) than for pig waste, prune pits, or alfalfa stems (1.958, 1.961, and 1.840 kg/hr, respectively). Because the absolute ammonia output depends on both stream purity and total mass throughput, the larger throughput associated with cow waste compensates for its lower H₂/N₂ ratio and results in the highest overall mass-based ammonia yield among the four feedstocks. Conversely, alfalfa stems benefit from a more favorable H₂/N₂ ratio that produces a purer ammonia stream, but their smaller total gas throughput limits the absolute ammonia quantity generated per unit of feedstock.

4. Conclusion

The results of this work show that biomass feedstock composition plays a decisive role in determining both gasification behavior and downstream ammonia synthesis performance. The C-H-O ternary and Van Krevelen analyses successfully explained the main product trends, especially the shift between CO and CO₂ with changing oxygen content and the more complex behavior of hydrogen production through the combined influence of H/C and O/C ratios. Feedstocks with higher oxygenation, such as pig waste, were more likely to produce higher CO₂ and lower CO, whereas less oxygenated feedstocks, especially cow waste, showed the opposite tendency. At the same time, alfalfa stems achieved the highest hydrogen production because they offered the best elemental balance, which then translated into a higher H₂/N₂ ratio for ammonia



synthesis and, consequently, a higher ammonia mass fraction in the final product stream. The steady decline in the CO₂/ammonia ratio from cow waste to alfalfa stems further confirmed that better upstream gas quality leads to more efficient downstream ammonia production. In general, the agreement between feed analysis and simulation outputs demonstrates that the model captures the underlying chemistry in a reliable and physically meaningful way. Among the investigated feedstocks, alfalfa stems produced the purest ammonia stream and are therefore preferable when synthesis-gas quality is the primary concern, whereas cow waste achieved the highest overall ammonia yield per unit feedstock mass and would be preferred when maximizing total production from available biomass is the main objective. These findings highlight the importance of careful feedstock selection in biomass-to-ammonia pathways and show that even small differences in elemental composition can significantly affect overall process performance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data is used in this article.

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