Thermodynamic analysis of photocatalytic ammonia synthesis via quantum chemical calculations with process-level considerations

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Bruno Ramos[1,*], Gustavo V. Olivieri[1], Ricardo B. Torres[1]

[1]*Centre for Research and Innovation in Energy Transition for Sustainable Mobility (IGNIS), Centro Universitario FEI, São Bernardo do Campo, Brazil*

[*]*brunoramos@fei.edu.br*

The photocatalytic synthesis of ammonia under ambient conditions has emerged as a viable alternative to the Haber–Bosch process, particularly when driven by solar energy and earth-abundant materials. In this study, following experimental investigations[1], we evaluate the thermodynamic feasibility of nitrogen reduction to ammonia on hematite (α-Fe_2O_3) surfaces, coupling quantum chemical calculations with process-level simulations. Density Functional Theory (DFT) calculations were performed using the ORCA package on a finite Fe_2O_3 cluster model to simulate key steps in the reaction pathway, including N_2 adsorption, protonation sequences, NH_3 formation, and product desorption[2]. Thermodynamic parameters (ΔE, ΔH, ΔG) were obtained at ambient and elevated temperatures via frequency calculations, allowing assessment of the driving forces associated with key steps. The formation of surface-bound intermediates such as $^*NNH$ and $^*NH_2$ was examined, and the overall ΔG for ammonia evolution was computed. Preliminary results indicate that while the initial N_2 activation barrier remains high, subsequent hydrogenation steps are thermodynamically favourable. Calculated equilibrium constants were then incorporated into a simplified Aspen Plus model (Fig. 1) of a solar-driven photocatalytic reactor to evaluate ammonia yields and estimate solar-to-chemical conversion efficiency. This multiscale approach enables the identification of thermodynamic bottlenecks and operational windows for low-temperature ammonia production using semiconductor-based photocatalysts.

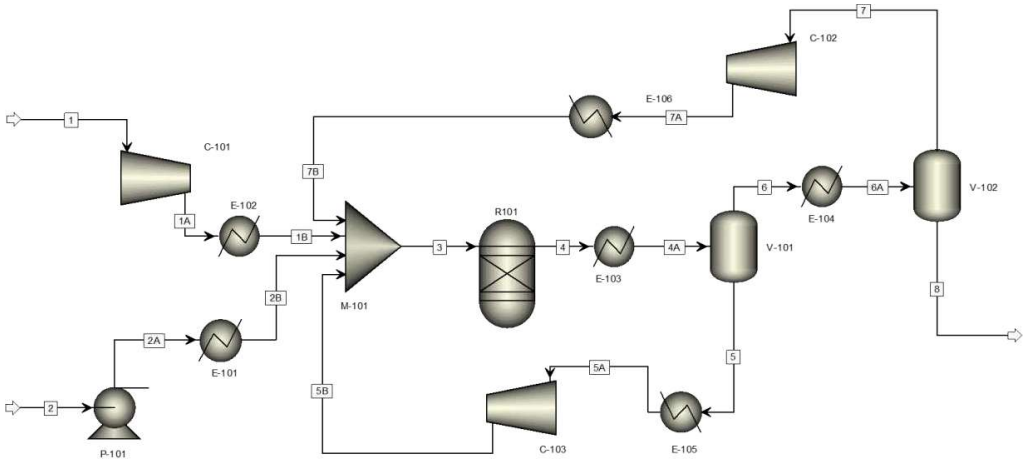

Figure: Solar-driven photocatalytic plant flowsheet

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References

1. C.A.P. Alves, P.H. Palharim, B. Pratto, A.L. da Silva, D. Gouvêa and B. Ramos, *J. Photochem. Photobiol. A: Chem.* 2025, **460**, 116159.
2. T. Žibert, B. Likozar and M. Huš, *ChemSusChem* 2024, **17**, e202301730.