Cyprus University of Technology

Faculty of Geotechnical Sciences and Environmental Management

Doctoral Dissertation

EXPERIMENTAL AND COMPUTATIONAL INVESTIGATION OF CARBON-FREE HYDROGEN CARRIERS FOR GREEN H_2 GENERATION IN BATCH SYSTEMS

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Limassol, February 2026

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Approval Form

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ABSTRACT

The scientific and research community has put great effort to find alternative solutions regarding the global shift from conventional carbon-based fuels to sustainable energy sources to mitigate climate change. A promising solution is the utilisation of hydrogen (H_2) as fuel, which is green and carbon-neutral, however, its production, storage and transportation challenges, hinders its widespread adoption as an energy carrier. Thus carbon-free hydrogen carriers can be used, offering better control and the potential of generating H_2 on-site. Hence, the scope of the present work is the experimental and theoretical investigation, using computational fluid dynamics (CFD) of hydrous hydrazine (HH) and ammonia borane (AB) as carbon-free hydrogen carriers for green H_2 production in batch reactor systems.

Initially, the catalytic decomposition of HH was examined using a commercial catalyst in a lab-scale batch system, evaluating the effect of stirring rate, temperature, catalyst mass, HH concentration and NaOH concentration. The optimum conditions led to a H_2 yield above 90%. A 0-D model was developed, integrating a power law reaction model, which validated well the experimental data and following, 2-D simulations of the reactor system were conducted providing velocity, temperature, HH and catalytic particles profiles distribution within the reactor. A subsequent study on HH catalytic decomposition was carried out using a lab-synthesised catalyst, evaluating the same experimental parameters. After a good validation from the 0-D model, a 2-D model of a different batch reactor geometry was developed to compare its performance with the one studied experimentally. Further CFD studies were conducted evaluating the velocity field distribution from various stirrer shapes, besides the one used experimentally. Finally, a 2-D model of a packed bed microreactor was developed to compare its performance in terms of H_2 yield with the batch system. The CFD simulations, not only validated the experimental outcomes but provided also insightful information regarding the system's uniformity, including velocity and temperature field distributions and dispersion of HH and particles in the batch system.

Afterwards, the catalytic hydrolysis of AB was examined experimentally and theoretically, studying the influence of temperature, stirring rate, AB concentration and catalyst amount. In all cases H_2 yield was over 85%, achieving also high turnover frequency (TOF) values, even at the lowest studied temperature. A 0-D model was developed using Langmuir-Hinshelwood (L-H) kinetics, which validated well the experimental data. To uncover the statistical significance of each parameter to the three response variables (reaction time, TOF and H_2 yield), statistical analysis was conducted using one-factor-at-a-time (OFAT) approach. This was further extended to examine the simultaneous influence of two factors and study their interactions as well. Temperature was ranked as the most important factor to optimise TOF, followed by stirring rate for H_2 yield and substrate to catalyst ratio for reaction time. Then, the catalytic hydrolysis of AB was investigated using a non-noble metal catalyst. After studying experimentally and computationally the effect of temperature, catalyst mass and AB concentration, a Box-Behnken Design (BBD) was implemented to study the complex interactions among the three studied parameters on the three response variables. Nonlinear relationships were revealed between each factor and the mean of reaction time and for all response variables, the substrate to catalyst ratio was a dominant contributor. The multiobjective optimisation analysis which was performed afterwards, identified optimal experimental conditions, with H_2 yields above 74 % and reaction times below 30 minutes. A 0-D modelling study followed which validated these optimised results.

Lastly, the photocatalytic hydrolysis of AB and photocatalytic decomposition of HH were examined through CFD studies. A 3-D modelling study was initially developed for the AB hydrolysis to validate literature-based results. Then, a 3-D study was developed based on our photoreactor to investigate irradiation profiles and catalytic particles distribution. The results showed a higher intensity profile near the lamp, with no effect from the stirrer. Since the particles were distributed everywhere, a pseudo-homogeneous assumption was made. Thus, a 2-D axisymmetric view of the photoreactor was modelled, validating the experimental results obtained by varying the concentration of HH and the catalyst amount.

Keywords: Hydrogen, Hydrous Hydrazine, Ammonia Borane, Reactor Design, CFD, Photocatalysis.