Microbial CO_2 Conversion to Acetic Acid: From Laboratory Testing to an Industrial-Scale Model

Growing concerns regarding climate change have heightened interest in utilizing carbon dioxide as a valuable carbon source for chemical production. The acetogen *Thermoanaerobacter kivui* is a thermophilic bacterium that converts CO_2 and H_2 streams into acetic acid. Nevertheless, the limited solubility of the gaseous substrates in the liquid medium has often led to low productivity by the biocatalyst employed. This study aims to enhance the cell-specific acetic acid productivity of *T. kivui* by combining pressure, the composition of the inlet gas mix, and in-flow gas rate. Firstly, the combined effect of pressure and gas composition was assessed through a Design of Experiments approach. Tests were performed in a pressurized bioreactor and indicated that acetic acid cell-specific productivity was achieved at 10 bar, providing a 3:1 H_2:CO_2 blend. Subsequently, supplying this blend at high pressure into the vessel of the reactor, an in-flow gas rate screening was performed to identify completely the parameters that allowed the maximum acetic acid productivity. The optimal flow rate was 60 $mL.min^{-1}$, and the acetic acid cell-specific productivity reached 2.90 $g.g^{-1}.h^{-1}$. Additionally to the experiments in the bioreactor, tests in serum bottles were performed to investigate the influence of the osmotic condition due to different salts and acetic acid inhibition on *T. kivui*.

Optimizing continuous stirred tank bioreactors requires careful consideration of hydrodynamics and bio-dynamics. Based on laboratory data, a 0D model was developed to replicate the system and describe acetic acid production from CO_2 reduction by *T. kivui*. This model addresses the coupling between fluid dynamics and bioreaction dynamics, overcoming gas-liquid mass transfer limitations. Biological kinetic equations were derived from experimental data to model *T. kivui's* growth and metabolic production rates. The model simulates various operational parameters such as pressure, inlet gas composition, flow rate, and impeller speed. It was optimized and validated using experimental data across diverse conditions. The model accurately forecasted the quantities of biomass, acetic acid, and formic acid produced over time. It identified maximum acetic acid productivity at a pressure of 10.20 bar, a gas inlet flow rate of 63.44 $mL.min^{-1}$, and an H_2:CO_2 ratio close to 3:1.

CSTRs are commonly used in laboratory settings for their efficient gas-liquid mixing and uniform substrate distribution to microorganisms. Yet, their significant energy needs for stirring pose economic challenges for large-scale commercial operations. As a result, alternative bioreactor designs like bubble columns, which have lower energy demands, have been studied for scalability. An industrial-scale bubble column 1D model was developed to address the complex interaction between fluid dynamics and bioreaction dynamics. This model pinpointed optimal conditions for pressure, gas and liquid inlet flow rates, and inlet gas composition to maximize acetic acid productivity at steady state. At the biomass concentrations of 5 $g.L^{-1}$ two optimal values of head pressure in the bubble column, have been identified. At a pressure of 10 bar, the productivity of acetic acid and the conversion rates of H_2 and CO_2 are maximized, but the presence of formic acid complicates the purification of the fermentation broth. At a pressure of 2 bar, formic acid production is negligible, and compression costs are lower. However, the specific production rate of acetic acid is 63 % of what is achieved at 10 bar, and the conversion rates of H_2 and CO_2 are approximately 65 % of those at 10 bar. For all tested biomass and pressure values, optimal gas and liquid flow rates were identified to maintain a homogeneous bubbly flow regime in the column and to avoid acetic acid or osmotic

inhibition. Future work should focus on validating the model to evaluate its accuracy, performance, and ensure its robustness.

The target of this work is to provide an analysis of the feasibility of producing acetic acid via gas fermentation on an industrial scale. This analysis accounts for the costs of H_2 and CO_2 required for fermentation, the gas fermentation process itself, and the purification of the resulting culture broth.

A techno-economic analysis was conducted for hydrogen production and carbon dioxide capture processes. H_2 is produced through alkaline electrolysis, while CO_2 capture is achieved through chemical absorption with monoethanolamine. The carbon dioxide is sourced from a concentrated waste stream generated during the upgrading of biogas to biomethane. The water electrolysis plant is designed to produce 1200 $ton.y^{-1}$ of 99 % pure hydrogen. The CO_2 capture process is designed to produce 6790 $ton.y^{-1}$ of 99.5 % pure carbon dioxide. The economic analysis results show a minimum selling price of 5.97 $€.kg^{-1}$ for hydrogen and 0.233 $€.kg^{-1}$ for captured carbon dioxide. The possibility of scaling up both processes to meet increased demand from fermenters was evaluated. The H_2 production plant was scaled up to a productivity of 20 $kton.y^{-1}$, while the CO_2 absorption plant was scaled up to a productivity of 6 $Mton.y^{-1}$. In both cases, increasing the plant size corresponded to a decrease in the minimum selling price. For the larger plant size, the price of hydrogen drops to 3.28 $€.kg^{-1}$, making it competitive in the green hydrogen market. Similarly, the price of carbon dioxide decreases to 0.055 $€.kg^{-1}$, also a competitive value for the process considered.

A techno-economic analysis of fermentation processes for acetic acid production was conducted to estimate the capital and operating costs of gas fermentation, aiming to determine the cost-effectiveness of operating at 2 bar versus 10 bar. Data for fermentation at different pressures were extrapolated from the industrial-scale bubble column 1D model. For a plant with a single fermenter, the minimum fermentation cost for a process with headspace pressures of 2 bar is 0.37 $€.kg^{-1}$, while for a process with headspace pressures of 10 bar, it is 0.45 $€.kg^{-1}$. Furthermore, the production of formic acid at 2 bar is negligible, simplifying downstream operations. Even when scaling to larger capacities of up to 500000 $ton.y^{-1}$ by adding multiple columns in parallel, the minimum fermentation cost remains higher for processes with headspace pressures of 10 bar (0.33 $€.kg^{-1}$) compared to those at 2 bar (0.29 $€.kg^{-1}$). Although fewer fermenters are required in parallel at 10 bar to achieve the same acetic acid output, the higher pressures result in increased capital costs for the fermentation section, leading to a higher minimum fermentation cost.

The fermentation process yields highly diluted acetic acid solutions, making purification essential for commercializing glacial acetic acid. A techno-economic analysis was conducted for the culture broth dehydration process. This involves extracting acetic acid with MTBE, followed by azeotropic distillation to remove the solvent and residual water. The purification costs are 1.01 $€.kg^{-1}$ for a production of 8000 $ton.y^{-1}$ of glacial acetic acid. Scaling up to 500000 $ton.y^{-1}$ reduces the costs to 0.40 $€.kg^{-1}$.

A feasibility analysis of acetic acid production was conducted at a headspace pressure of 2 bar in the fermenter. For a plant with a production capacity of 500000 $ton.y^{-1}$, the minimum acetic acid selling price amount to 1.25 $€.kg_A^{-1}$, exceeding the market price of glacial acetic acid at 0.7 $€.kg^{-1}$. Although less cost-effective than methanol carbonylation, gas fermentation offers reduced fossil fuel dependence and utilizes CO_2 that would otherwise be released into the atmosphere.