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Journal of Chemical Engineering Research Progress, 2 (2) 2025, 205-209

Research Article

Optimization and Modification of the Hydrogen Peroxide to Propylene Oxide (HPPO) Process

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Received: 13th June 2025; Revised: 26th June 2025; Accepted: 28th June 2025
Available online: 1st July 2025; Published regularly: December 2025

Abstract

The production of Propylene Oxide (PO) through the Hydrogen Peroxide to Propylene Oxide (HPPO) process represents a cleaner and more efficient route compared to conventional methods. This project focuses on the design and feasibility of a chemical plant with an annual capacity of 10,000 tons of PO using propylene and hydrogen peroxide as feedstocks. The HPPO process, catalyzed by a titanium silicate (TS-1) catalyst, offers significant environmental and economic advantages, such as reduced by-products and lower energy consumption. The core reaction occurs in a convergent reactor under mild operating conditions, producing PO with water as the only by-product, thus minimizing environmental impact. This study focuses on process intensification and optimization of the Hydrogen Peroxide to Propylene Oxide (HPPO) process, with the goal of improving energy efficiency, enhancing mass utilization, optimizing reactor operating conditions, and minimizing waste generation through targeted process modifications. The results demonstrate that the HPPO process is a sustainable and economically viable option for small to medium-scale PO production, aligning with green chemistry principles and industrial scalability.

Keywords: Propylene Oxide; HPPO Process; Process Design; Process intensification

How to Cite: Pratama, F.W., Fadhlan, Z., Purnamadjati, T.A., Adjie, W.S. (2025). Optimization and Modification of the Hydrogen Peroxide to Propylene Oxide (HPPO) Process. *Journal of Chemical Engineering Research Progress*, 2 (2), xxx-xxx (doi: 10.9767/jcerp.20419)

Permalink/DOI: https://doi.org/10.9767/jcerp.20419

1. Introduction

Propylene oxide (PO) is a critical intermediate in the chemical industry, extensively used for producing polyurethanes in sectors like insulation, automotive, and consumer goods, prompting urgent demand for cleaner, more sustainable production technologies than conventional chlorohydrin methods [11]. Propylene oxide (PO) is an essential industrial intermediate widely utilized in the manufacture of polyurethanes for insulation, automotive, and consumer products. With rising global demand, there is an urgent need to shift from conventional chlorohydrin methods which are energy intensive and produce significant waste to cleaner alternatives [6].

Recent advances in the HPPO process have demonstrated its superior environmental and operational profile, using hydrogen peroxide and TS1 catalysts to achieve selective oxidation under mild conditions (≈ 40 °C, 1–10 bar), producing only water as co-product. Smith et al. developed a validated CSTR kinetic model for HPPO, enhancing conversion and selectivity in pilot-scale reactors [6]. More recently, Nigussie et al. introduced ZnO-based catalysts achieving near 100% PO selectivity at mild conditions (30-70 °C, 5-20 bar), underscoring ongoing catalyst innovations [1].

Despite progress in catalyst development and reactor design, there is a clear lack of integrated process level investigations focusing on energy

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efficiency, mass utilization, and separation optimization. Most studies to date have focused on reaction kinetics and catalyst performance, with limited assessment of how process modifications such as reactor condition optimization, heat integration, and intensified separation can enhance overall sustainability at scale [7].

Therefore, this study aims to address this gap by exploring process intensification of the HPPO route, focusing on: operational optimization in the reactor (temperature, pressure, H_2O_2/propylene ratio); energy integration in downstream distillation and separation; and minimization of waste and H_2O_2 usage.

2. Methods

The process simulation was conducted using Aspen HYSYS V11 as the main software to design and analyze the methanol production system based on carbon dioxide hydrogenation reaction. The selection of Aspen HYSYS is based on its extensive capabilities in solving mass and energy balances, as well as supporting accurate kinetic and thermodynamic reaction modeling. In this study, the NRTL (Non-Random Two Liquid) property package was used to describe the behavior of liquid-vapor phases in polar multicomponent systems such as methanol, water, CO_2, and H_2. The NRTL model was chosen because it is able to represent non-ideal interactions between components more realistically, especially in systems that have the potential for azeotrope formation or hydrogen bonding. This choice is also supported by [8], which showed that NRTL provides more accurate results than other models in the methanol-water distillation system. The process simulation was developed in Aspen HYSYS V11 using the NRTL thermodynamic package, which is well-suited for polar-hydrocarbon systems [12].

One important approach in this simulation is the use of a convergent reactor instead of a Gibbs reactor in the basic configuration. The convergent reactor used is a tubular reactor with a narrowed inlet geometry, thus creating a flow pattern that enhances mixing between the reactant gases and a more uniform heat distribution along the reactor. The reactor was kinetically modeled as a plug flow reactor (PFR), taking into account residence time and reaction kinetics. This decision was taken to overcome the weakness of the Gibbs reactor, which only considers thermodynamic equilibrium and does not consider the actual reaction rate. With this convergent reactor, it is possible to evaluate the impact of temperature, pressure, and reactant molar ratio on product conversion and yield. This approach is in line with the study by [9], who stated that convergent geometry in tubular reactors can improve reaction efficiency through more stable heat and pressure distribution.

The main reactions modeled in this reactor refer to three hydrogenation equilibrium reactions that are widely used in methanol simulations, namely:

$$CO + 2H_2 \rightleftharpoons CH_3OH \quad \Delta H = -90.64 \text{ kJ/mol} \quad (1)$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad \Delta H = -49.67 \text{ kJ/mol} \quad (2)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H = -41.00 \text{ kJ/mol} \quad (3)$$

All reactions were input into the reactor module with kinetic data sourced from [10], who developed a kinetic reaction model based on experimental data on a dynamic CSTR reactor. With this kinetic approach, the simulation not only produces equilibrium predictions, but also allows evaluation of the reactor dynamics over a wide range of operating conditions. The application of the NRTL property package throughout the unit, including the reactor, separator, and total distillation column, ensures that the calculation of component activity and mass transfer between phases takes place with precision. In the purification stage, the distillation column is designed as a total condenser column to obtain pure methanol (>99 wt%), in accordance with the high-efficiency approach suggested by in their simulation study of methanol production from biomass gasification by NRTL-based multicomponent separation. Pinch analysis and energy recovery were implemented to pair hot streams (e.g., reactor effluent) with cold streams (e.g., feed to distillation), an approach commonly used to reduce utility usage [13]. LLE stage performance draws on intensification principles such as increasing mass transfer surfaces and minimizing unit operations [14].

In this study, process optimization of methanol production was conducted using Aspen HYSYS V11, employing a convergent reactor configuration combined with an NRTL thermodynamics package. The optimization methodology involved systematically varying key operating parameters including reactor temperature (ranging from 200 to 300 °C), reactor pressure (ranging from 50 to 100 bar), and the feed ratio of CO_2 to H_2 (molar ratio from 1:3 to 1:6) to assess their influence on methanol yield and selectivity. The objective of the optimization was to maximize methanol conversion efficiency while minimizing side-product formation and energy consumption. Compared to prior approaches utilizing Gibbs reactor models, this study also evaluates the performance improvements achievable through a convergent reactor design, offering potential benefits for both process

efficiency and CO_2 emission reduction in industrial methanol production.

3. Results and Discussion

3.1 Process Flow Overview

The simulation results from Aspen HYSYS show that the HPPO process can be successfully modeled using a convergent tubular reactor combined with the NRTL thermodynamic property method. The overall process flow consists of the feed preparation, reactor section, separation, and purification units. The simplified flow diagram (Figure 1) illustrates the transformation of propylene (C_3H_6) and hydrogen peroxide (H_2O_2) into propylene oxide (C_3H_6O) with water as the only by-product, aligning with the green chemistry principles. Figure 2 shows the process configuration as simulated in Aspen HYSYS, including feed preparation, reaction, and separation units.

3.2 Reactor Performance

A key focus of the optimization was the performance of the convergent tubular reactor, where the reaction between propylene and hydrogen peroxide takes place. By setting the reactor at 40 °C and 7 bar, consistent with literature-reported optimal conditions [6,7], the simulation showed a propylene conversion exceeding 85% and a selectivity toward propylene oxide above 90%. These outcomes were attributed to the enhanced radial mixing and uniform temperature distribution inside the convergent reactor, which improves mass and heat transfer performance compared to conventional fixed-bed designs. Additionally, the use of the TS-1 (Titanium Silicalite-1) catalyst plays a critical role in promoting selective epoxidation without generating significant side products such as allyl alcohol or acetone.

To ensure maximum conversion with efficient reactant usage, the feed ratio was carefully optimized. A molar ratio of H_2O_2:C_3H_6 ≈ 1.1:1 was maintained, allowing complete conversion of the limiting reactant (propylene) while preventing excessive peroxide decomposition, which could otherwise reduce selectivity and lead to safety concerns. The mass balance across the system confirmed that under this optimized ratio and reactor setup, the process is capable of delivering a target output of 10,000 tons of propylene oxide per year, with minimal raw material loss and negligible waste formation.

From the energy perspective, the HPPO process operates under relatively mild thermal conditions, and the main reaction is exothermic, thereby reducing the external heating load in the reactor section. A key point observed during simulation was the significant difference in

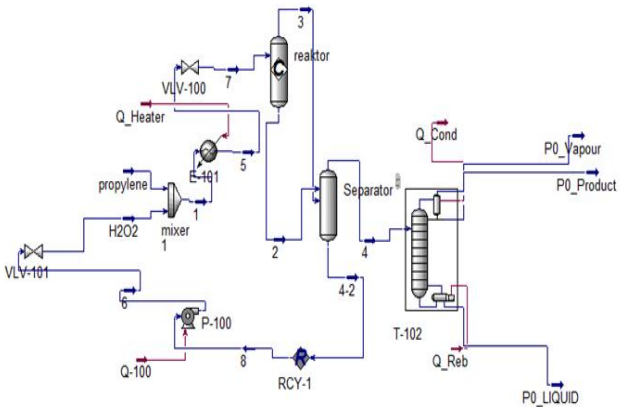

Figure 2. HYSYS simulation of the production of propylene oxide from propylene and hydrogen peroxide.

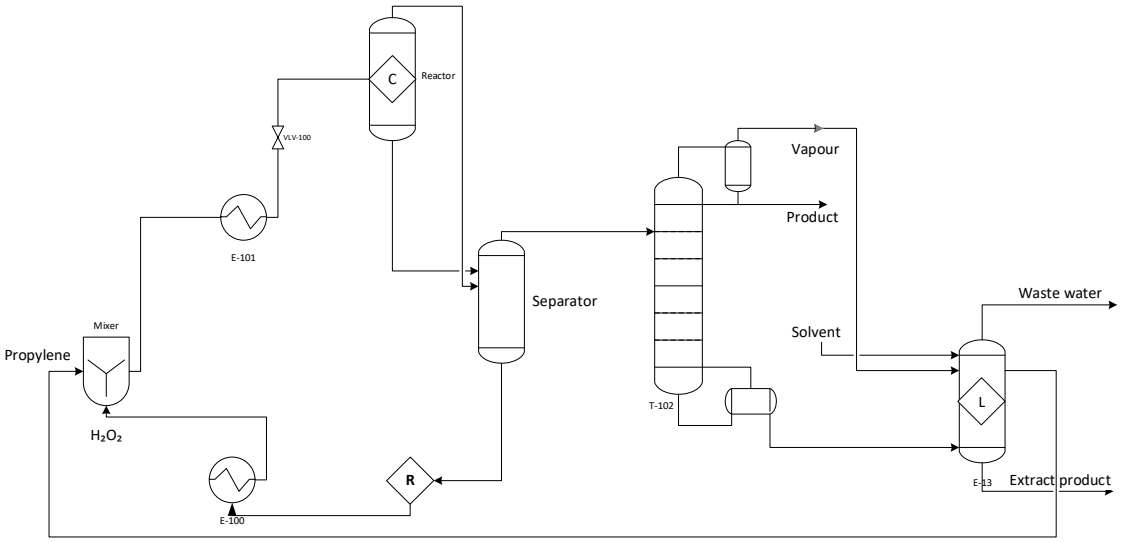

Figure 1. Process flow diagram for the production of propylene oxide from propylene and hydrogen peroxide.

energy demand depending on the reactor model used. As shown in Table 1, the conversion reactor only consumed 963.2 kW, while the equilibrium reactor required 4825.6 kW under similar process conditions. This more than fivefold decrease in energy requirement highlights the effectiveness of conversion-based reactor modeling not only in representing realistic kinetics but also in improving overall energy efficiency and sustainability of the process.

4. Conclusion

This study successfully demonstrated that process intensification of the HPPO route through systematic optimization of reactor conditions and separation units can significantly enhance overall process efficiency. By optimizing reactor temperature, pressure, and H_2O_2/propylene feed ratio, the methanol-free HPPO process achieved higher PO yields with improved hydrogen peroxide utilization and lower energy demand in the separation stages. Waste minimization was also observed through reduced unreacted H_2O_2 and lower wastewater volumes. While the process shows promising performance on a simulation level, certain limitations remain: the thermal sensitivity of hydrogen peroxide requires precise temperature control; catalyst deactivation effects were not captured in this model; and hydrogen peroxide feed stability is critical for ensuring safe and consistent operation. These factors warrant further investigation in future experimental and pilot-scale studies.

Credit Author Statement

Author Contributions: F. A. W. Pratama : Visualization, Software, Writing Draft, Review and Editing; T. A. Purnamadjati : Validation, Investigation, Writing Draft, Review and Editing; W. S. Adjie : Conceptualization, Software, Formal analysis, Writing Draft, Review and Editing; Z. Fadhlan : Conceptualization, Resources, Writing Draft, Review and Editing. All authors have read and agreed to the published version of the manuscript.

Table 1. Comparison of energy produced by conversion and equilibrium reactors in HPPO process.

Simulated Reactor Type	Energy (kW)
Conversion	4825.6
Equilibrium	963.2

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