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Research Article

Optimizing Operating Conditions to Increase the Effective Hydrogen Partial Pressure and Reduce Fresh Hydrogen in Vapor-Phase Cyclohexanol Production

Aisyah Hanunaida Yusriyyah*, Rivan Pradipta Wibisono, Yulianazhwa Tiarawati

Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro, Semarang, Indonesia.

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Abstract

Cyclohexanol is a vital intermediate in nylon precursor production, making its efficient synthesis highly relevant for large-scale chemical industries. Conventional processes often face inefficiencies such as excessive hydrogen consumption and poor energy utilization, which hinder economic viability. This study aims to optimize cyclohexanol production by improving hydrogen recovery and heat integration. Thermodynamic analysis confirmed the reaction is highly exothermic and favorable across the operating temperature range, emphasizing the need for strict thermal control. Process simulation was then employed to evaluate the baseline flowsheet and identify inefficiencies. A revised configuration was developed incorporating effluent cooling, vapor–liquid separation, and hydrogen recycling. The improved system significantly enhanced hydrogen efficiency, reactor performance, and energy utilization, leading to higher conversion rates and more stable operation. In conclusion, the optimized process demonstrates the importance of integrating reaction engineering with process-level design. The simulation framework also provides a foundation for future studies on intensified reactor–separator systems and advanced energy-saving strategies.

Keywords: Phenol Hydrogenation; Vapor-Phase Reactor; Process Optimization; Hydrogen Recycle

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1. Introduction

Cyclohexanol is a pivotal intermediate in the manufacture of adipic acid and caprolactam, which together account for more than 90% of global nylon production capacity [1]. As demand for high-performance polymer materials continues to rise, enhancing the efficiency of cyclohexanol production routes has become a critical priority for modern chemical processing industries [2]. Among the available industrial pathways, vapor-phase hydrogenation of phenol is widely regarded as particularly advantageous, offering operational simplicity, reduced oxidation losses, and higher selectivity compared with liquid-phase hydrogenation or conventional cyclohexane oxidation routes [3].

* Corresponding Author.
Email: aisyahnaida@students.undip.ac.id (A.H. Yusriyyah)

From a process-engineering perspective, the vapor-phase hydrogenation route is highly sensitive to reactor operating conditions such as temperature, pressure, hydrogen-to-phenol molar ratio, and gas hourly space velocity (GHSV), all of which directly influence conversion, selectivity, and catalyst stability [4]. Suboptimal operation can result in excessive hydrogen consumption, increased by-product formation, inefficient heat removal, and elevated net energy usage, ultimately diminishing the profitability of large-scale production. In high-capacity plants (>30,000 TPA), heat-integration limitations and non-isothermal reactor behavior further exacerbate energy demand, underscoring the need for accurate process modeling and optimization [1].

Recent research on phenol hydrogenation has predominantly emphasized catalyst development such as Ni-based MOF-derived structures, carbon-

encapsulated Ni–Co alloys, and Pd-supported zeolites to enhance activity and selectivity [2]. Beyond catalyst formulation, mechanistic studies have shown that product selectivity in phenol hydrogenation whether toward cyclohexanone or cyclohexanol is fundamentally governed by the characteristics of the active catalytic sites. Coordinatively unsaturated edge and step sites preferentially facilitate complete hydrogenation to cyclohexanol, whereas higher coordinated terrace sites favor partial hydrogenation, yielding cyclohexanone. This site-specific reactivity provides a compelling mechanistic explanation for the parallel product distribution commonly observed in vapor-phase phenol hydrogenation systems [5]. While these advances have improved catalytic performance, they often overlook the broader process level considerations essential for industrial implementation, including dynamic temperature profiles, reactor pressure drop, energy recovery strategies, and recycle-stream optimization. Catalyst improvements alone are insufficient unless integrated with optimized reactor design and separation system operation [1].

A significant research gap persists in the integration of phenol hydrogenation reaction engineering, process simulation, and energy-minimization strategies, particularly for continuous vapor-phase processes with capacities exceeding 10,000 TPA. Comprehensive studies that evaluate the combined effects of temperature, pressure, and reactant stoichiometry on both process yield and overall net-energy consumption remain limited, even though these parameters critically determine the efficiency and sustainability of industrial cyclohexanol production [2]. Moreover, the lack of systematic process level optimization especially through advanced simulation platforms such as Aspen HYSYS continues to hinder the translation of catalytic research into practical, implementable industrial designs.

Given these limitations, the development of a structured optimization framework for vapor-phase phenol hydrogenation is essential to bridge laboratory-scale advances with industrial implementation. In a 40,000 TPA plant, the economic impact of reactor optimization is substantial, as even marginal improvements in conversion or selectivity can yield significant reductions in energy consumption and raw material usage. Accordingly, the objective of this study is to optimize the key operating parameters of the vapor-phase hydrogenation reactor to maximize phenol conversion, enhance cyclohexanol selectivity, and minimize overall net-energy demand. This research integrates recent catalytic insights with process simulation, sensitivity analysis, and mass energy performance evaluation to establish a more efficient and industrially relevant flowsheet for cyclohexanol production.

2. Methods

The vapor-phase hydrogenation of phenol to cyclohexanol was simulated using Aspen HYSYS V11 to assess reaction behavior and thermal performance under representative industrial operating conditions [6]. Phenol was designated as the primary feedstock and hydrogen as the reductant, following the well-established sequential pathway phenol → cyclohexanone → cyclohexanol, widely reported in aromatic hydrogenation studies [7]. Phase equilibrium and thermophysical properties were modeled using the Peng–Robinson equation of state (PR-EOS), a widely adopted approach for high-pressure hydrogenation systems due to its ability to accurately represent non-ideal gas behavior and vapor–liquid equilibrium [8].

The simulated process comprised four subsystems: feed conditioning, reactant mixing, plug-flow reaction, and vapor–liquid separation. The liquid phenol feed was preheated and vaporized prior to mixing to ensure uniform gas-phase contact and prevent catalyst wetting, in accordance with industrial practice [1]. Hydrogen was compressed to the designated operating pressure before entering the mixer, as its partial pressure strongly influences phenol conversion and cyclohexanol selectivity [4]. The two vapor streams were then combined and introduced into a plug-flow reactor (PFR), selected for its ability to capture axial concentration gradients and represent the temperature-dependent kinetics characteristic of vapor-phase hydrogenation processes [9,10].

To ensure reproducibility and complete convergence of the recycle loop, all components relevant to the hydrogenation pathway phenol, cyclohexanone, cyclohexanol, and hydrogen were explicitly included in the HYSYS component list. The Peng–Robinson equation of state (PR-EOS) was verified for thermodynamic consistency by confirming critical properties, acentric factors, and mixing-rule parameters for each species [9]. The reaction network was implemented as a two-step stoichiometric set corresponding to the established phenol → cyclohexanone → cyclohexanol mechanism [7], with full stoichiometric specification to prevent "reaction not complete" errors encountered during preliminary setup.

For convergence checks and initial sensitivity analysis, the hydrogenation pathway was represented using a stoichiometric reactor model (RStoic). Final kinetic evaluation employed a plug-flow reactor (PFR) to capture temperature-

dependent behavior consistent with literature reactor configurations [10]. In cases where detailed kinetic data were unavailable, a pseudo-first-order approximation under hydrogen-excess conditions was applied, following commonly accepted modeling assumptions in industrial hydrogenation simulations [4]. Reaction enthalpies were sourced from standard-state thermodynamic data to maintain internal consistency with the global energy balance.

The vapor–liquid separation system incorporated a cooler and flash separator, with the vapor outlet connected to a hydrogen recycle loop. A tear stream and initial recycle-flow guess were specified, and the HYSYS recycle solver with under-relaxation was applied until full numerical convergence was achieved. Stream data including temperature, pressure, molar flow, composition, phase fraction, and enthalpy were extracted only after the recycle block reached a steady solution. This ensured that all reported results reflect a properly converged and thermodynamically consistent simulation, in accordance with best practices in process modeling [6,11].

Given the highly exothermic nature of phenol hydrogenation, the reactor effluent was cooled before entering a flash separator. In the flash unit, unreacted hydrogen was separated from the condensed organic product phase. The hydrogen-rich vapor stream was then recycled to the reactor inlet to enhance the effective hydrogen partial pressure and reduce fresh hydrogen consumption, a strategy widely employed in industrial phenol hydrogenation systems [1,3]. Model validation included verifying mass and energy balance closure and ensuring that simulated conversion trends aligned with literature-reported behavior under varying temperature, pressure, and hydrogen-to-phenol feed ratios [2,6].

3. Results and Discussion

3.1 Reaction Stoichiometry and Standard Thermochemical Data

The main reaction considered in all HYSYS simulations is:

$$C_6H_5OH_{(s)} + 3H_{2(g)} \longrightarrow C_6H_{11}OH_{(l)} \quad (1)$$

Table 1. Standard thermochemical properties (298.15 K).

Component	$\Delta H^o_{f,298K}$ (kJ.mol⁻¹)	S° (J.mol⁻¹.K⁻¹)
Phenol (C_6H_5OH)	−165.0	144.01
Cyclohexanol ($C_6H_{11}OH$)	−349.2	199.6
Hydrogen (H_2)	0.0	130.68

The standard thermochemical properties at 298.15 K used as reference values are listed in Table 1. Standard enthalpy change (ΔH°_{rxn}) of reaction can be calculated:

$$\Delta H^\circ_{rxn} = \Delta H^\circ_{(\text{cyclohexanol}))} - \Delta H^\circ_{(\text{phenol})} - 3 \cdot \Delta H^\circ_{(\text{hydrogen})} = -184.2 \text{ kJ.mol}^{-1} \quad (2)$$

This strongly negative value confirms that phenol hydrogenation is highly exothermic. Reaction entropy changes and Gibbs free energy change at 298 K:

$$\Delta S^\circ_{rxn} = S^\circ_{(\text{cyclohexanol})} - S^\circ_{(\text{phenol})} - 3 \cdot S^\circ_{(\text{hydrogen})} \quad (3)$$

$$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn} \quad (4)$$

$$\Delta G^\circ_{rxn} = -83.8874 \text{ kJ.mol}^{-1}$$

This confirms the reaction is highly favorable at standard conditions. Equilibrium constant (K) at 298 K:

$$\Delta G^\circ = -RT \ln K \quad (5)$$

$$K = e^{33.84} \approx 4.97 \times 10^{14}$$

Thus, equilibrium overwhelmingly favors cyclohexanol formation at ambient temperature.

3.2. Thermodynamics at Industrial Reactor Conditions (200 °C)

For the reactor design, the nominal operating temperature is 200 °C (473.15 K). Assuming ΔH and ΔS vary weakly with temperature:

$$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn} \quad (4)$$

$$\Delta G^\circ_{(473.15)} = -25.01 \text{ kJmol}^{-1}$$

Therefore, equilibrium constant (K) at 200 °C:

$$K = e^{6,36} \approx 5.78 \times 10^2$$

3.3. Process Modification

In the basic process flow diagram and process simulation (Figures 1 and 2), the phenol feed entered the process as a liquid at 25 °C and 1 bar with a flowrate of 100 kmol/h and was preheated to 200 °C before entering the reactor. Hydrogen was also introduced at 25 °C and 1 bar. However, in the initial simulation, hydrogen had not yet been included in the component list. Consequently, HYSYS temporarily treated the feed as a single-component phenol stream. This issue was later corrected by explicitly adding hydrogen to ensure accurate representation of the mixed-feed composition and thermodynamic behavior.

The combined feed entered the reactor at 200 °C, and the reactor effluent exited at

approximately 220 °C due to the exothermic heat release from the hydrogenation reaction. After leaving the reactor, the stream was cooled to 25 °C prior to entering the separation unit. In this unmodified configuration, no hydrogen recovery or recycle was implemented; therefore, any unreacted hydrogen was vented from the system, leading to unnecessarily high fresh hydrogen consumption. Additionally, the significant heating and cooling duties observed in this configuration were not utilized for heat integration, resulting in poor overall energy efficiency. Overall, the base-case flowsheet lacked hydrogen recycle, heat recovery, and effective utilization of reaction heat.

After modification, the reactor effluent at approximately 220 °C was no longer directed immediately to the separation unit (Figures 3 and 4). Instead, it was cooled to 25 °C to induce controlled vapor–liquid phase separation. This cooling step stabilized the thermal profile of the process and ensured that the mixture entered the flash drum under conditions suitable for effective phase splitting. Within the flash unit, the liquid phase containing cyclohexanol and unreacted phenol was separated from the hydrogen-rich vapor phase. The vapor fraction was recycled to the reactor inlet through RCY-1, significantly reducing fresh hydrogen demand and increasing the effective hydrogen partial pressure in the reactor. These changes improved reaction performance and enhanced hydrogen utilization efficiency. Beyond gas recovery, the modified flowsheet enabled better thermal management. The substantial heat released during the exothermic hydrogenation reaction and from the high-temperature reactor effluent can now be leveraged through heat-integration strategies, such as preheating incoming feeds. This marks a major improvement over the base-case configuration, where heat was simply removed and wasted without contributing to internal energy savings. Overall, the modified setup delivers improved hydrogen efficiency, enhanced energy recovery, and greater operational stability compared to the original design.

3.4 Operational and Safety Considerations

Hydrogen presents significant safety challenges due to its wide flammability range and extremely low ignition energy, meaning that even small leaks can lead to fires or explosions if not promptly detected. Safety reviews highlight that hydrogen disperses rapidly and can form flammable mixtures at very low concentrations, making continuous gas detection, adequate ventilation, and automatic shutdown systems essential for preventing hazardous accumulation [13,14].

The hydrogenation reaction is also highly exothermic, requiring strict temperature control to avoid thermal runaway. Loss of cooling capacity or the formation of localized hotspots can cause

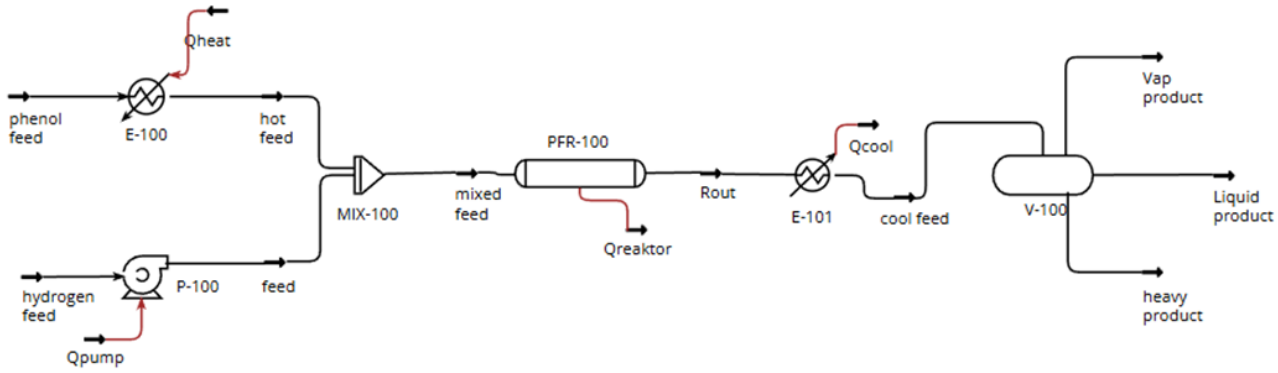

Figure 1. The basic (unmodified) process flow diagram (PFD) for cyclohexanol production.

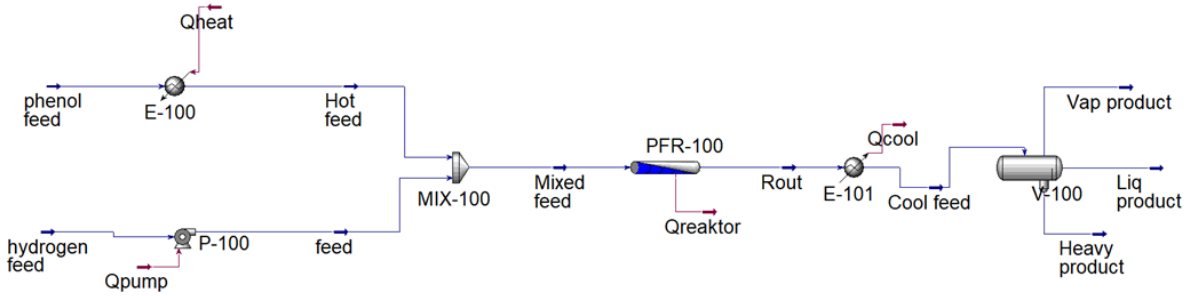

Figure 2. The basic (unmodified) Aspen HYSYS process simulation for cyclohexanol production.

rapid pressure increases and threaten process stability. Studies emphasize that effective heat removal, properly designed venting systems, and pressure-relief protection are key elements in ensuring safe operation of units handling hydrogen [15]. Therefore, the implementation of hydrogen detectors, relief valves, temperature-control loops, and reliable vent systems is crucial for maintaining safe and stable reactor performance.

4. Conclusion

This study successfully achieved its objective of optimizing operating parameters for vapor-phase phenol hydrogenation, enabling efficient and sustainable cyclohexanol production at industrial scale. The integration of hydrogen recovery, effluent cooling, and heat-integration strategies markedly enhanced hydrogen utilization, energy efficiency, and reactor stability relative to the base-case configuration. By uniting reaction engineering with process-level optimization, this work advances the current state of knowledge through a validated simulation framework that connects laboratory-scale catalytic innovation with industrial-scale application. The framework provides a solid foundation for future exploration of intensified reactor–separator designs and energy-minimization strategies, thereby contributing to the continued development of sustainable technologies for large-scale cyclohexanol production.

CRedit Author Statement

Author Contributions: A.H. Yusriyyah contributed to the conceptualization, methodology, investigation, resource provision, data curation, writing, review and editing, as well as supervision. Y. Tiarawati participated in conceptualization, methodology, formal analysis, data curation, draft preparation, visualization, software processing, and project administration. R.P. Wibisono was responsible for validation, draft writing, review and editing, and data curation. All authors have read and agreed to the published version of the manuscript.

References

[1] Chen, C., Hu, Y., Wei, Z., Dai, Y., Wang, X., Xiao, J. (2020). Selective hydrogenation of phenol to cyclohexanol over Ni/CNT in the absence of external hydrogen. *Energies*, *13*(4), 846. DOI: 10.3390/en13040846

[2] Xia, H., Liu, Z., Chen, L., Wang, A. (2021). Tunable selectivity of phenol hydrogenation to cyclohexane or cyclohexanol by solvent-driven effect over Pd/NaY catalyst. *Catalysis Science & Technology*. 11, 1881-1887. DOI: 10.1039/D0CY02188A

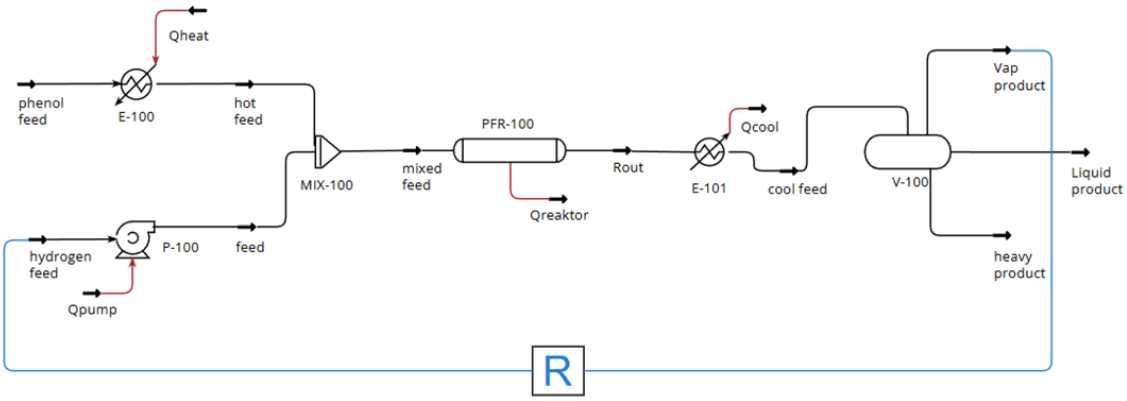

Figure 3. The modified process flow diagram (PFD) for cyclohexanol production.

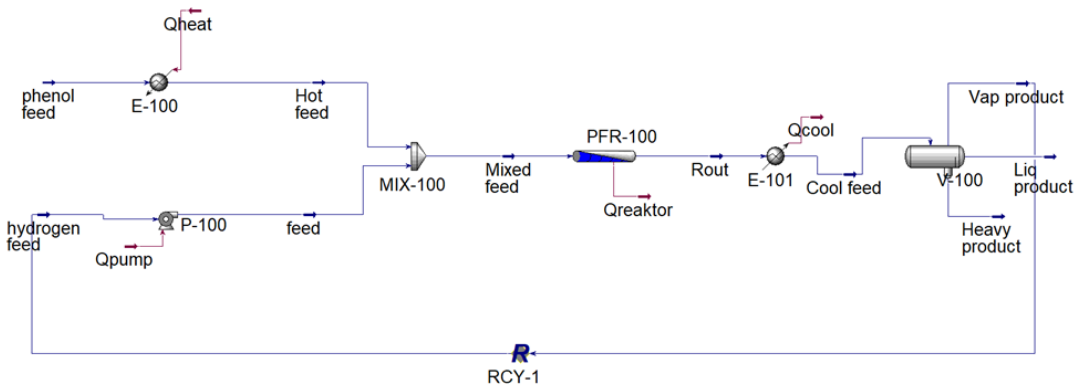

Figure 4. The modified Aspen HYSYS process simulation for cyclohexanol production.

[3] Wang, S., Zhang, J., Hu, R., Liu, Y. (2022). Hydrogenation of phenol to cyclohexanol using carbon-encapsulated Ni–Co alloy nanoparticles. *Reaction Chemistry & Engineering*. 7, 429-441. DOI: 10.1039/D1RE00457C

[4] Zhang, H., Han, A., Okumura, K., Zhong, L., Li, S., Jaenicke, S., Chuah, G.K. (2018). Selective hydrogenation of phenol to cyclohexanone by SiO2-supported rhodium nanoparticles under mild conditions. *Journal of Catalysis*, *364*, 354–365. DOI: 10.1016/j.jcat.2018.06.002

[5] Wang, S., Zhang, J., Chen, G., Liu, Y. (2022). Highly efficient hydrogenation of phenol to cyclohexanol over Ni-based catalysts derived from Ni-MOF-74. *Reaction Chemistry & Engineering*. 7, 170-180. DOI: 10.1039/D1RE00302J.

[6] Chen, H., Sun, J. (2021). Selective hydrogenation of phenol for cyclohexanone: A review. *Journal of Industrial and Engineering Chemistry*, *94*, 78–91. DOI: 10.1016/j.jiec.2020.11.022.

[7] Foppa, L., Dupont, J. (2015). Benzene partial hydrogenation: Advances and perspectives. *Chemical Society Reviews*, *44*(7), 1886–1897. DOI: 10.1039/C4CS00324A.

[8] Radzuan, M.R.A., Nursyahirah, S., Syihabuddin, M.A., Alikasturi, A.S., Faizal, T. A. (2019). Comparative analysis of cyclohexane production from benzene and hydrogen: Via simulation and sustainability evaluator approach. *Materials Today: Proceedings*, *19*, 1693–1702. DOI: 10.1016/j.matpr.2019.11.199

[9] Giarracca, L., Isufaj, F., Lizardo-Huerta, J.C., Fournet, R., Glaude, P.-A., Sirjean, B. (2021). Experimental and kinetic modeling of the ignition delays of cyclohexane, cyclohexene and cyclohexadienes: Effect of unsaturation. *Proceedings of the Combustion Institute*, *38*(1), 1017–1024. DOI: 10.1016/j.proci.2020.07.151

[10] Joseph, W. (2016). Three-phase catalytic reactors for hydrogenation and oxidation reactions. *Physical Sciences Reviews*, *1*(1). DOI: 10.1515/psr-2015-0019

[11] Zhu, W., Ye, H., Yang, Y., Zou, X., Dong, H. (2022). Simulation-Based Optimization of a Multiple Gas Feed Sweetening Process. *ACS Omega*, *7*(3), 2690–2705. DOI: 10.1021/acsomega.1c05193

[12] National Institute of Standards and Technology. (n.d.). NIST Chemistry WebBook: Phenol thermochemical data. Retrieved from https://webbook.nist.gov/cgi/cbook.cgi?ID=C108952&Mask=1E9F

[13] Calabrese, M., Portarapillo, M., Di Nardo, Benedetto, A. (2024). Hydrogen Safety Challenges: A Comprehensive Review on Production, Storage, Transport, Utilization, and CFD-Based Consequence and Risk Assessment. *Energies*, *17*(6). DOI: 10.3390/en17061350

[14] Qanbar, M.W., Hong, Z. (2024). A Review of Hydrogen Leak Detection Regulations and Technologies. *Energies*, *17*(16). DOI: 10.3390/en17164059

[15] Cekerevac, Z., Cekerevac, D. (2025). Hydrogen Hazards, Risks, and Protection: an in-Depth Review. *MEST Journal*, *13*(SP), 23–48. DOI: 10.12709/mest.13.13.sp.02