# INFLUENCE OF Cu AND Ni CATALYSTS ON ETHANOL GASIFICATION UNDER SUPERCRITICAL WATER CONDITIONS

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**ABSTRACT**

This study aimed to synthesize and evaluate metal catalysts supported on $Al_2O_3$ applied to the supercritical water gasification of ethanol. Monometallic catalysts based on Cu and Ni at 5% by mass and bimetallic catalysts with Mg addition were prepared to achieve this. The catalysts were produced via aqueous impregnation of metal nitrates with excess solvent, followed by calcination and characterization (SEM, XRD, $N_2$ adsorption/desorption, XRF, and TG/DTA). Catalytic tests were performed in a continuous-flow reactor with a feed flow rate of 5 ml/min, ethanol:$H_2O$ molar ratio of 1:10, and 5 g of catalyst, with a temperature range from 450 to 600 ºC. Results revealed that the best ethanol conversions were achieved with Mg in the active phase (58% for Cu-Mg/$Al_2O_3$). However, higher ethanol conversion with bimetallic catalysts did not significantly increase $H_2$ production, with the maximum gas flow achieved at 600 ºC using the Ni/$Al_2O_3$ catalyst.

**Keywords:** heterogeneous catalysis; hydrogen; supercritical water; biomass; renewable energy.

## INTRODUCTION

In the last two decades, global energy consumption increased significantly due to population growth and higher living standards. As energy demand is expected to continue rising, expanding energy generation capacity is important [1]. Currently, fossil fuels dominate the energy mix, accounting for 86% of primary energy demand (36% oil, 27% coal, and 23% natural gas), while nuclear energy contributes 6%, and renewables—such as solar, wind, geothermal, biomass, and hydroelectric—make up about 8%[2]. Fossil fuels, however, are finite resources, with known oil reserves

projected to be depleted within 50 years at current consumption rates [3]. Thus, concerns over oil price volatility, environmental impacts from greenhouse gas emissions, and health and safety issues have intensified the search for new energy sources.

In this context, a sustainable energy system must be both environmentally friendly and economically viable. Countries like Germany, Japan, and France have set ambitious energy transition goals, aiming to significantly reduce greenhouse gas emissions until 2030 [4]. However, fossil fuel use is likely to persist until cost-competitive alternatives are available, decreasing prices of alternative energies. In this way, the drive to diversify the energy mix has spurred research into new technologies to replace oil and coal. Promising alternatives include biofuels, solar, wind, geothermal energy, and hydrogen. In order to achieve this,

Hydrogen, especially, is regarded as the energy carrier of the future, reducing greenhouse gas emissions. Some of the hydrogen production processes include reforming fossil resources and using renewable sources like biomass and water, via electrolysis or photocatalysis [5]. In the search for alternative methods for hydrogen production from renewable sources, supercritical water gasification (ScWG) stands out, due to the benefits from specific water conditions above its critical point (temperature ≥ 374 ºC and pressure ≥ 22.1 MPa) to produce $H_2$-rich syngas. While numerous studies have focused on hydrogen production from ethanol reforming, a fully developed technology has yet to emerge [6,7].

To address the challenge of developing an environmental and cost-effective method for hydrogen production, biomass gasification, including ethanol reforming, has emerged as a promising avenue. In Brazil, ethanol derived from sugarcane is particularly appealing due to its renewability, low cost, and well-established logistics [8]. Furthermore, supercritical water gasification offers advantages such as high reaction rates, improved heat transfer, and reduced process equipment due to the high pressures involved. However, despite these advantages, research on ethanol gasification under supercritical water conditions remains limited.

Therefore, this study aimed to synthesize catalysts based on copper, nickel, and magnesium supported on alumina ($Al_2O_3$) and evaluate their performance in a

heterogeneous reactor system for hydrogen production under supercritical water conditions. The study assessed the effects of feed flow rate, temperature on conversion, product selectivity, and yield. The catalysts were synthesized using wet impregnation and characterized by various analytical techniques, including X-ray fluorescence, scanning electron microscopy, thermogravimetric analysis etc. Thus, the catalyst characterization and testing provided insights into the catalyst's unique properties and improved the process performance.

## MATERIALS AND METHODS

### Preparation of catalysts

The catalysts were synthesized using the excess solvent impregnation method. For this purpose, a solution containing the precursor metal salt to a previously moistened. The metal nitrate salt, which serves as a precursor for the active phase, was dissolved in deionized water to achieve a 5% nominal mass percentage of the metal content (Cu, Ni, and Mg). The mixture is stirred and maintained under controlled time and temperature to allow the salt to diffuse into the pores of the support ($Al_2O_3$). After this, the excess solvent was removed by pre-drying in a rotary evaporator at temperature of 50 °C and stirring of 25 rpm. Then, catalysts were dried in an oven (100 °C) and calcinated in a muffle furnace at temperature of 600 °C for 8 h.

### Characterization

The produced catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetry and differential thermal analysis (TG/DTA), textural analysis of $N_2$ adsorption/desorption isotherms, and X-ray fluorescence (XRF).

### Catalytic tests

To evaluate the catalysts performance, experimental tests were carried out in a continuous flow reactor system under a constant pressure of 25 MPa. The experimental setup comprised a feedstock solution reservoir, a high-pressure isocratic pump (operational range: 1 to 100 mL/min), a helical preheater (set to 350 ºC), and a plug-flow reactor (Inconel 625, ID: 1.1 cm; L: 30 cm; V: 28.5 mL), both

heated by split furnaces equipped with concave infrared resistances. Additionally, the system included a helical heat exchanger, a back-pressure regulator, and a phase separator for collecting both liquid and gaseous phase products. The liquid flow rate was determined by fluid accumulation over time, while the gas flow rate was measured using a glass bubble meter. The experimental apparatus is described in detail by Ribeiro et al. [9].

Catalytic tests were conducted with all prepared materials. A 5 g catalyst sample was packed in the center of the tubular continuous flow reactor. The reaction system was fed with a water/ethanol solution at a molar ratio of 10:1, with a feed flow rate of 5 mL/min. The effect of reaction temperature was evaluated by conducting tests at 450, 500, 550 and 600 °C. Samples of the gas phase generated were analyzed in a gas chromatograph equipped with a thermal conductivity detector (TCD), a 10-way valve system with a Porapak N column in series with a 13X Molecular Sieve.

## RESULTS AND DISCUSSION

To assess the potential application of metallic catalysts in hydrogen production through ethanol gasification under supercritical water conditions, catalysts based on copper, nickel, and magnesium supported on alumina ($Al_2O_3$) were synthesized. The results will be discussed in two phases: first, the characterization of the catalysts, and second, their performance in ethanol gasification, specifically focusing on ethanol conversion to hydrogen.

Firstly, the isotherms adsorption/desorption revealed that all analyzed materials exhibited type IV isotherms, characteristic of mesoporous solids (2 to 50 nm), indicating capillary condensation with H1 hysteresis and a narrow distribution of uniform mesopores. Textural analysis conducted using $N_2$ adsorption/desorption isotherms can be seen in **Table 1**. In can be noted that calcination reduced the surface area of the support to 40% of its initial value, accompanied by a threefold increase in average pore diameter. The addition of metals generally decreased the specific surface area of the alumina, except for the $Mg/Al_2O_3$ catalyst. The XRD of the catalysts showed no identifiable diffraction peaks,

indicating that the metal impregnation process for the active phase did not induce significant structural changes in the support. Images from SEM revealed that the catalyst synthesis process produces a rougher external surface, likely due to the deposition of metal oxides on the pre-existing alumina surface. The XRF analysis demonstrated that the impregnation method using excess solvent was effective, achieving the nominal metal content of approximately 5%.

**Table 1** Textural properties of catalysts

| | BET specific surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Average pore diameter (nm) |
|---|---|---|---|
| $Al_2O_3$ | 299,822 | 0,319 | 4,330 |
| $Al_2O_3$ alcinated | 128,281 | 0,415 | 12,846 |
| $Cu/Al_2O_3$ | 120,615 | 0,382 | 12,594 |
| $Ni/Al_2O_3$ | 125,638 | 0,292 | 12,435 |
| $CuO\text{-}MgO/Al_2O_3$ | 114,568 | 0,237 | 11,940 |
| $NiO\text{-}MgO/Al_2O_3$ | 107,333 | 0,243 | 12,863 |

Secondly, reactions employing catalysts in the gasification of ethanol were performed. Results are shown in **Figure 1**. The catalysts exhibited low ethanol conversion at temperatures up to 500 °C. At 550 °C, only the $Cu/Al_2O_3$ catalyst achieved significant ethanol conversion. A trend was observed indicating that ethanol conversion increased with rising temperature, reaching a maximum of 50% at the highest temperature tested, 600 °C. In terms of molar fraction, all catalysts exhibited low activity up to 550 °C. An enhancement in activity was observed at 550 °C, characterized by an increase in the molar flow rate of the products. The highest molar flow rate of hydrogen, 8.46 mmol/min, was achieved at 600 °C using $Ni/Al_2O_3$, representing the maximum molar flow rate observed among all the tests conducted. The maximum yield of hydrogen achieved was 0.41 mol per mol of ethanol processed.

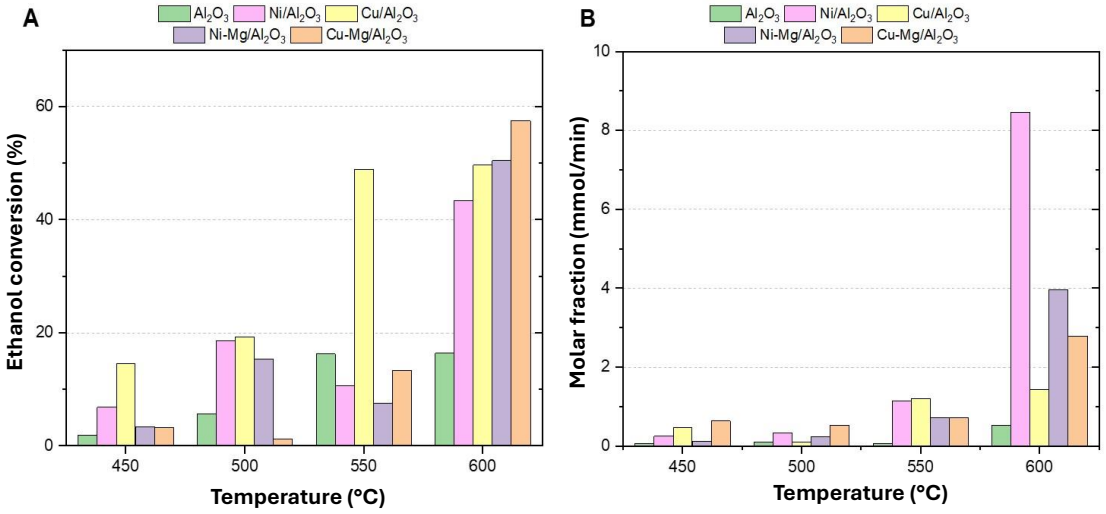


**Figure 1.** Results of ethanol catalytic gasification tests for (A) ethanol conversion and (B) $H_2$ molar flow rate generated.

In general, the selectivity obtained for the $NiO/Al_2O_3$ catalyst revealed that ethene was produced throughout the temperature range of the catalytic tests, indicating the occurrence of the ethanol dehydration reaction ($C_2H_5OH \rightarrow C_2H_4 + H_2O$). At 500 °C, ethanol is also dehydrated to ethyl ether ($(C_2H_5OH)_2 \rightarrow (C_2H_5)_2O + H_2O$). The molar distribution of hydrogen remains between 35% and 40% at temperatures of 500, 550, and 600 °C.

## CONCLUSION

The characterization and catalytic test results reveal several key findings. The XRF analysis confirms the reliability of the catalyst synthesis method. No significant leaching of the active phase occurred, as indicated by XRF, likely due to low solubility in supercritical water. XRD and SEM show that the metals (Cu, Ni, and Mg) are either amorphous or in fine particles dispersed on the support. Textural analysis reveals that calcination reduced the specific surface area of alumina and increased average pore diameter due to vaporization. TG-DTA confirm effective removal of water and decomposition of metal nitrates. The $NiO/Al_2O_3$ catalyst achieved the highest hydrogen selectivity (≅ 50%) and flow rate (8.5 mmol/min) at 600 °C, with the best yield of 0.41 mol $H_2$/mol ethanol. The ethanol gasification process in

supercritical water revealed potential to produce hydrogen. Despite this, further studies are still needed.

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