

# Cyan Hydrogen: Advancing Sustainable Hydrogen Production from Bio-Alcohols and Metaborate Waste

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## Highlights

- Development of an innovative hydrogen production process from bio-alcohols and waste metaborate.
- Mild process operating condition (300 °C).
- Carbon valorization in polymeric side products and liquid organic compounds.

## 1. Introduction

One of the most significant contemporary challenges is the escalating worldwide energy demand due to population growth and increasing prosperity. Coal, oil, and natural gas, classified as fossil fuels, are presently the primary energy sources. However, the usage of these fuels poses a dilemma due to their CO<sub>2</sub> and other greenhouse gases (GHG) emissions, which have been established as a principal cause of global warming.[1]

Hydrogen is widely recognised as a promising and sustainable energy carrier, due to its high energy density and efficient energy conversion. Nevertheless, most hydrogen is presently produced from pathways with low efficiency and high cost.[2] These pathways include grey hydrogen produced via steam reforming of natural gas, blue hydrogen produced by coupling grey hydrogen with CO<sub>2</sub> capture technologies, and green hydrogen generated through water electrolysis.[3]

Presented herein is a novel hydrogen production process, called *cyan* hydrogen, which involves the processing of bio-alcohols, low-cost waste metaborate, and water at mild conditions based on Patent WO2023105545A1.[4]

## 2. Methods

The process consists of consecutive steps exercised under batch conditions and 300 °C, involving the alternating addition of bio-alcohol and water to an alkali metal salt of metaborate ( $YBO_2 \cdot xH_2O$ , Y=alkali metal), a by-product of hydrogen storage process, as shown in Figure 1.

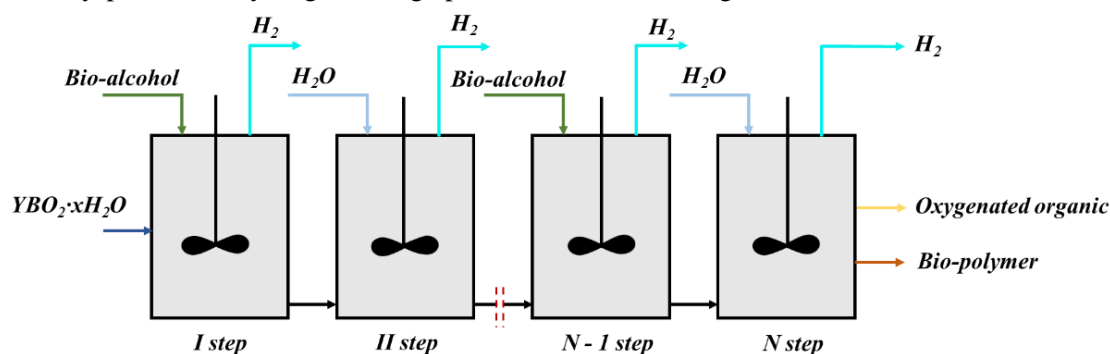


Figure 1. Block diagram of Cyan Hydrogen production process.

Experimental tests were carried out in a batch reactor (Parr 4567) with a 450 mL volume. Different bio-alcohol were tested, such as ethanol, glycerol, and ethylene glycol for 4 process steps. The organic alcohol reagent (85.60 mmol) was added in the first and third stages to sodium metaborate  $NaBO_2 \cdot 4H_2O$  (14.5 mmol), while water (555.0 mmol) was employed in the second and fourth stages. At each stage,

gaseous products were sampled and analyzed by micro-GC, while, at the end of process, liquid and solid products were separated by centrifugation and analyzed separately. Particularly, the solid products were analyzed by FT-IR, TGA.

### 3. Results and discussion

By utilizing ethanol as the bio-alcohol feedstock and sodium metaborate as the borate salt, a simultaneous production of a 95% v/v hydrogen stream, a polymeric by-product featuring a repetitive carbon pattern (-CH<sub>2</sub>-CH<sub>2</sub>-), analogous to the polyethylene repetitive unit, and a liquid phase rich in oxygenated chemicals is achievable at temperatures lower than conventional hydrogen production processes.[5] Glycerol, on the other hand, has lower H<sub>2</sub> volumetric composition (around 50% v/v in the process steps) and higher CO<sub>2</sub> production. In addition, it was found that the ethylene glycol was an intermediate in terms of hydrogen production, which is around 70% v/v with lower CO<sub>2</sub> production than glycerol. In Table 1, the gas analysis results by microGC are reported.

<i>Process step</i>	<b>H<sub>2</sub> (%)</b>	<b>CO<sub>2</sub> (%)</b>	<b>CO (%)</b>	<b>Other (%)</b>
	<i>Ethanol</i>			
I step	94.83	1.67	/	3.5
II step	93.49	5.71	/	0.8
III step	98.56	1.9	/	0.35
IV step	95.21	2.55	/	2.24
	<i>Glycerol</i>			
I step	52.63	35.33	4.58	7.46
II step	44.76	42.75	2.52	9.97
III step	52.34	41.47	3.60	2.59
IV step	39.23	42.90	2.44	15.43
	<i>Ethylene Glycol</i>			
I step	59.98	21.177	14.019	4.82
II step	58.06	33.671	3.794	4.47
III step	65.13	28.365	5.357	1.14
IV step	74.45	22.096	2.821	0.64

**Table 1.** Volumetric composition of process steps for ethanol, glycerol and ethylene glycol.

### 4. Conclusions

In conclusion, our research on the Cyan Hydrogen process, utilizing bio-alcohols and metaborate by-products, presents a promising avenue for hydrogen production. Operating at 300 °C, the process demonstrates the simultaneous generation of a hydrogen-rich stream, polymeric by-products, and oxygenated chemicals. With varying bio-alcohol feedstocks, the method exhibits adaptability in hydrogen compositions and CO<sub>2</sub> production rates. The integrated carbon valorization and fine chemical production underscore the environmental potential of this approach. This study represents a step towards a more sustainable energy landscape, leveraging cost-effective biomass-derived materials for hydrogen production.

### References

- [1] International Energy Agency. Global Hydrogen Review 2022. Available from: [www.iea.org/t&c/](http://www.iea.org/t&c/)
- [2] Di Nardo A, Portarapillo M, Russo D, Di Benedetto A. Hydrogen production via steam reforming of different fuels: thermodynamic comparison. *International Journal of Hydrogen Energy* 55 (2024) 1143–1160.
- [3] Arcos JMM, Santos DMF. The Hydrogen Color Spectrum: Techno-Economic Analysis of the Available Technologies for Hydrogen Production. *Gases*. 3 (2016) 25–46.
- [4] Di Benedetto A, Portarapillo M, Landi G, Luciani G. Process for green hydrogen production. WO2023105545A1. 2023.
- [5] Di Nardo A, Portarapillo M, Russo D, Luciani G, Landi G, Ruoppolo G, Pezzella A, Di Benedetto A. Cyan Hydrogen Process: a new route for simultaneous hydrogen production and carbon valorisation. *ACS Omega* In press. 2023.

### Keywords

Hydrogen, bio alcohols, process, polymer.