Catalytic Process Modelling for Hydrogen Production via Ethanol Reforming and Amine Synthesis through Hydrogen Sulfide driven Nitroaromatic Reduction

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Abstract

Ethanol is emerging as a sustainable and efficient renewable feedstock for hydrogen (H_2) production, offering a promising alternative to conventional steam methane reforming, especially amid growing environmental and sustainability concerns. Hydrogen plays a vital role in refinery hydrotreating processes for removing sulfur and nitrogen from crude oil, making its sustainable production. The effective industrial-scale management of by-products such as hydrogen sulfide (H_2S) and ammonia (NH_3) is increasingly important.

This study investigates ethanol reforming for hydrogen production through Aspen Plus simulation, emphasizing challenges caused by carbon formation. To overcome these, oxygen-assisted dry reforming of ethanol (DRE) was introduced to reduce carbon formation and enhance catalyst stability. Thermodynamic analysis revealed that carbon deposition could be significantly suppressed with small oxygen additions (0.25 mol at 775 °C and 0.20 mol at 800 °C) under a CO_2/ethanol ratio of 1. Without oxygen, 0.39 mol of carbon is predicted at 800 °C.

Energy efficiency analysis of both DRE and steam reforming of ethanol (SRE) showed that heat recovery via integration with a heat exchanger reduced energy demand by 35% in the DRE process at 800 °C, and by 24–33% in the SRE process across varying temperatures. Experimental investigations into ethanol steam reforming were conducted using a bimetallic Ni-Co catalyst supported on a CeO_2-Al_2O_3. The bimetallic catalyst with Ni:Co mole ratio of

2:1 exhibited a high hydrogen yield (4.18 kmol H_2/kmol ethanol), excellent resistance to coke formation (9.47 mgC/gcat·h), and stable operation at 600 °C.

Beyond hydrogen production, the study addresses sustainable H_2S management. A novel valorisation approach converts *m*-iodonitrobenzene (*m*-INB) to *m*-iodoaniline (*m*-IA) using H_2S-enriched ammonia and a phase-transfer catalyst (TBAB). Kinetic analysis indicated pseudo-first-order behaviour with an activation energy of 40.0 kJ/mol.

Statistical methods like Design of Experiments offer a more efficient and systematic approach for optimizing multivariable chemical processes. A Box-Behnken design optimized the process, achieving 100% *m*-INB conversion at specific reaction conditions, with the model validated by an R^2 value of 0.9937.

This integrated study provides a pathway for renewable hydrogen generation from ethanol while enabling effective H_2S utilization, improving the overall sustainability and efficiency of hydrogen production and by-product toxic H_2S management in petroleum refining.

Keywords: Hydrogen, Ethanol, Reforming, Thermodynamics, H_2S, *m*-Iodoaniline, Multivariate analysis, Response surface modelling.