ABSTRACT

CATALYST STUDIES ON THE CONVERSION OF BIOBASED INTERMEDIATES TO BIOBASED PRODUCTS

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The goal of this work is to enhance the production of fuels and chemicals from fermentation-derived materials via two routes. Route (a) focuses on Guerbet chemistry, the n-butanol production from ethanol; route (b) studies the production of acrylate esters from 2-acetoxypropanoic acid (APA) esters.

The catalytic condensation of ethanol to n-butanol and higher alcohols, known as the Guerbet reaction, has attracted more attention in recent years due to the commercial availability of ethanol as a bio-renewable feedstock. Among various catalysts considered for this process, none have obtained stable and economically affordable yields; alumina-supported metals have been less explored despite their promising primary results in the lower energy-demanding condensed-phase.

Experiments on the continuous condensed-phase conversion of ethanol to n-butanol using Ni/La₂O₃/γ-Al₂O₃ catalyst present a WHSV of >0.8 h⁻¹ and a temperature range of 210-250 °C as the ideal reaction conditions. Several nickel bimetallic catalysts have been examined to optimize
the reaction performance further; characterization techniques have been employed to understand the behavior of these catalysts more effectively. Copper addition shifts the selectivity of the Guerbet products toward \textit{n}-butanol rather than \textit{C}_6^{+} \text{ alcohols}, which is explained by the copper behavior reducing H\textsubscript{2} adsorption on the catalyst. Furthermore, the number of nickel atoms on the surface of the catalyst correlates directly with the performance of the Guerbet reaction, suggesting that the dehydrogenation of ethanol is the rate-limiting step of the reaction. Among different catalysts and reaction conditions studied, the best results were obtained at the temperature of 250 \degree\text{C} and WHSV of 0.8 h\textsuperscript{-1} using 1.0 wt\% Ni/9.0 wt\% La\textsubscript{2}O\textsubscript{3}/\gamma-Al\textsubscript{2}O\textsubscript{3} with 41\% ethanol conversion and 74\% \textit{C}_4^{+} \text{ alcohols selectivity}. Fusel alcohol Guerbet studies under the same conditions have resulted in 88\% higher alcohols selectivity at 12\% conversion.

Economic analysis for a first-generation facility producing 25 million gallons of \textit{n}-butanol per year has been performed for several scenarios of catalytic performance and process configuration to investigate the viability of the commercial use of this catalyst. Results indicate that the \textit{n}-butanol required selling price at 25\% return on investment (ROI) can vary between $1.30-\text{-}\$1.60 per kg of \textit{n}-butanol, which is reasonably competitive with the current \textit{n}-butanol market price.

The highly selective production of 2-acetoxypropanoic acid (APA) from lactic acid and acetic acid through reactive distillation has motivated the study of the elimination reaction of APA esters to acrylate esters. Among different APA esters studied, the best results are obtained for those with no hydrogen on the \textit{\beta}-carbon of the ester functionality. This hydrogen allows the elimination of the ester group as an alkene, leading to the production of highly reactive materials that can decompose to other side-products and reduce the desired products selectivity. The use of CO\textsubscript{2} as the diluent gas reduces the amount of carbon deposited on the surface of the contact material and maintains the rate of the elimination reaction in extended operation. Highest yields of 35\% for
butyl acrylate and 70% for methyl acrylate and benzyl acrylate at 550 °C and LHSV of 1.9 h⁻¹ have been achieved in this study.

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