Catalytic Upgrading of C_5 Feedstocks to Ethylene and Propylene Glycols

Previous FY Cost: $ 0K
Estimated FY 1997 Cost: $60K
Proposed FY 1998 Cost: $0K

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Project Description

The objective of this project was to develop capabilities and technologies for the conversion of pentose sugars (C_5) to value-added products. Primary products from the conversion of pentose sugars are ethylene and propylene glycols. In this project, we developed processing methods for the production of commodity chemicals from C_5 feedstocks. The work focused on catalytic hydrogenation and hydrogenolysis for the production of glycols. Chemical analytical methods were developed in order to adequately evaluate the processing experiments. Preliminary economics of the process were also determined for the process.

Technical Accomplishments

Semi-batch reactor tests were performed with different candidate catalysts using both xylitol and arabinotol, C_5 sugar alcohols (monomer pentahydroxypentanes) which are derived from biomass C_5 structures. These results have suggested the uniformity of the processing using either feedstock, i.e. nearly identical product mixtures were formed at essentially the same rates for either feedstock. Therefore, complex feeds derived from biomass containing mixtures of C_5 sugars should not add any significant complexity to the process. We have tested both C_5 sugar alcohols with a commercial nickel metal catalyst and a PNNL-developed, stabilized nickel metal catalyst to develop a baseline activity and then proceeded to promoted nickel metal catalysts and precious metal catalysts.

The results with the alternative catalysts suggest a range of products can be produced from C_5 sugar alcohols under hydrogenolysis conditions (150-250°C temperature, 100 atm pressure hydrogen and 0 to 6 hours residence time). Tests with promoted nickel catalysts showed good activities for polyol production. Total conversion of xylitol was achieved with 77% yield of glycols and less than 1% gas formation. The processing specifics are considered to be important intellectual property. Attempts to reduce the activity of ruthenium catalysts in this environment were unsuccessful in that the major product remained methane with limited production of polyols. Tests with palladium catalysts and copper catalysts showed little activity at these processing conditions.

We have been developing our analytical methods to better quantify feed and products in the aqueous hydrogenolysis of C_5 sugar alcohols. We tested gas chromatography with flame ionization and mass selective detectors and showed that C_5 and lighter products could be quantitatively analyzed by gas chromatography. We demonstrated a new method of ion chromatography with a pulsed amperometric detector for use with the C_5 hydrogenolysis product stream. In addition, ^{13}C nuclear magnetic resonance spectrometry was evaluated for this use. Despite the complexity of the NMR spectra for these mixed products, with the higher frequency instruments now available at PNNL, we are able to quantify the components in the product solutions. All of these methods were developed to a higher level of proficiency than we have been able to demonstrate in previous C_6 polyol processing research. We have also coordinated our analytical needs with the new instrumentation coming on line in the Wiley-EMSL, providing samples for use in start-up and test-out of the equipment and operator training.

The economic model for polyols production developed at International Polyol Chemicals, Inc. (IPCI) was modified from its original C_6 application to address the economics of C_5 processing. Based on this model an Internal Rate of Return of 47% is predicted. This is a preliminary number that only indicates what is possible with further development to prove out the steps for utilization of C_5 sugars. The model assumes the use of crude hemicellulosic feedstocks (corn fiber, wood pulping byproduct, bagasse) with "dirty" hydrogenolysis to directly produce a polyol stream from which the final products can be recovered. This preliminary result suggests that with sufficient process development research to demonstrate the model assumptions, this type of chemical production could be highly profitable.

Publications

We helped author a proposal, "Industrial Oxy-Chemical from Corn Fiber Biomass", submitted to the Department of Commerce Advanced Technologies Program as a subcontractor to IPCI.

An FWP on Aqueous Phase Catalysis was submitted to DOE-EE/OIT for funding in FY1998. New catalyst technology developed in such a project is an important component for development, demonstration and commercialization of C_5 processing.

Presentations

We have participated in several meetings within the laboratory in support of a proposal for a Joint Venture to develop C_5 chemistry with Pentose Chemicals, Inc. (a sister company of IPCI). Presentations included a review by DC Elliott of polyol process development work at PNNL for representatives of the South African Industrial Development Corporation.