Pacific Northwest
NATIONAL LABORATORY

PNNL-36244

Production of 1,3-Butadiene from Renewable Feedstocks Ethanol and 1,3-Butanediol (CRADA 560) Final Report

July 2024

Vanessa Dagle
Robert Dagle
Steven Phillips
Martin Affandy

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99354

Cooperative Research and Development Agreement (CRADA) Final Report

Report Date: July 2024

In accordance with Requirements set forth in the terms of the CRADA, this document is the CRADA Final Report, including a list of Subject Inventions, to be provided to PNNL Information Release who will forward to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research. **PNNL acknowledges that the CRADA parties have been involved in the preparation of the report or reviewed the report.**

Parties to the Agreement:

Battelle

Bridgestone Research, LLC

CRADA number: 560

CRADA Title: Production of 1,3-Butadiene from Renewable Feedstocks Ethanol and 1,3-Butanediol

Responsible Technical Contact at DOE Lab(PNNL): Vanessa Dagle

Name and Email Address of POC at Partner Company(ies):

Terrence Hogan (HoganTerry@BFUSA.com)

Sponsoring DOE Program Office(s): N/A

Joint Work Statement Funding Table showing DOE funding commitment:

	Funding Amounts ($K)			
CRADA Parties	**DOE Funding**	**Funds-In**	***In-kind**	**Total**
Participant(s)	0	362	0	362
DOE Funding to PNNL	0	0	0	0
Total of all Contributions	0	362	0	362

Provide a list of publications, conference papers, or other public releases of results, developed under this CRADA:
No publication, conference papers, or other public releases were generated under this CRADA.

Provide a detailed list of all subject inventions, to include patent applications, copyrights, and trademarks:

A patent application is being filed by PNNL with Terrence Hogan from Bridgestone as co-author. We do not have a number yet.

Executive Summary of CRADA Work

1,3-butadiene is a commodity chemical currently produced from petroleum sources. Producing 1,3-butadiene from renewable resources will contribute to decarbonization, provide new green jobs, and reduce our dependance on oil. Development of multifunctional catalysts that are active, selective, and stable for this reaction has been an area of research and development. This effort reported here builds on our prior work for the 1-step conversion of ethanol to butadiene. The goal of the additional scope performed here was to accelerate the commercial deployment of sustainable butadiene production. We demonstrated that the PNNL Ag-based catalyst is significantly more active than the WWII-era catalyst when operated under the same conditions. A butadiene selectivity of 68% was obtained at 64% conversion for the production of butadiene from ethanol. It was found that ethanol feedstock is preferred over 1,3-butanediol feedstock to produce butadiene due to higher yield resulting in lower butadiene selling price (i.e., $0.4-1.7/ lb). Production of 3.0 Liter of butadiene solution in hexane containing 100 grams of butadiene was achieved and delivered to Bridgestone for producing a butadiene-derived test piece.

Summary of Research Results

This product contains Protected CRADA Information, which was produced on 1/31/24 under CRADA No. 560 and is not to be further disclosed for a period of five (5) years from the date it was produced except as expressly provided for in the CRADA.

Executive summary

1,3-butadiene is a commodity chemical currently produced from petroleum sources. Producing 1,3-butadiene from renewable resources will contribute to decarbonization, provide new green jobs, and reduce our dependance on oil. Development of multifunctional catalysts that are active, selective, and stable for this reaction has been an area of research and development. This effort reported here builds on our prior work for the 1-step conversion of ethanol to butadiene. The goal of the additional scope performed here was to accelerate the commercial deployment of sustainable butadiene production. We demonstrated that the PNNL Ag-based catalyst is significantly more active than the WWII-era catalyst when operated under the same conditions. A butadiene selectivity of 68% was obtained at 64% conversion for the production of butadiene from ethanol. It was found that ethanol feedstock is preferred over 1,3-butanediol feedstock to produce butadiene due to higher yield resulting in lower butadiene selling price (i.e., $0.4-1.7/ lb). Production of 3.0 Liter of butadiene solution in hexane containing 100 grams of butadiene was achieved and delivered to Bridgestone for producing a butadiene-derived test piece.

Summary

Summary of key accomplishments made on the project:

- Catalyst and performance reproducibility was demonstrated for the Ag-based catalyst previously developed by PNNL for direct conversion of ethanol to butadiene.
- The PNNL Ag-based catalyst is 5 times more active than the WWII-era catalyst when operated under the same conditions.
- Addition of alkali metal promoter limits the dehydration activity in favor of the dehydrogenation activity of the Ag-based catalyst for production of butadiene from ethanol.
- Operating conditions were investigated for conversion of ethanol to butadiene. It was found that the formation of butadiene is favored at lower pressure. Butadiene selectivity over 60% was obtained at temperature ≥ 275°C. A selectivity of 68% butadiene was obtained at 64% conversion.

- Preliminary measurements for production of 1,3-butadiene from 1,3-butanediol were conducted. It was found that the selectivity to butadiene decreases rapidly with time on stream (i.e., from 75% for time on stream = 20 hours to 45% for time on stream = 46 hour).

- The preliminary techno-economic analysis projected a minimum 1,3-butadiene selling price of $0.4-1.7/ lb depending on the cost of ethanol. In comparison, using 1,3-butanediol feedstock, the minimum 1,3-butadiene selling price was estimated to be $2.3-6.4/lb depending on the feedstock cost.

- A total of 3.0 Liter of butadiene solution in hexane containing 100 grams of butadiene was produced.

Pacific Northwest National Laboratory

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