NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Catalysis for Mixed Alcohol Synthesis from Biomass Derived Syngas

Cooperative Research and Development Final Report

CRADA Number: CRD-08-292

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Cooperative Research and Development Final Report

In accordance with Requirements set forth in Article XI.A(3) of the CRADA document, this document is the final CRADA report, including a list of Subject Inventions, to be forwarded to the Office of Science and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

CRADA Number: CRD-08-292

CRADA Title: Catalysis for Mixed Alcohol Synthesis from Biomass Derived Syngas

Parties to the Agreement: The Dow Chemical Company

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources
Year 1	$ 650,000.00
Year 2	$ 330,000.00
Year 3	$ 520,000.00
TOTALS	$ 1,500,000.00

Abstract of CRADA work:

The Dow Chemical Company (Dow) developed and tested catalysts for production of mixed alcohols from synthesis gas (syngas), under research and development (R&D) projects that were discontinued a number of years ago. Dow possesses detailed laboratory notebooks, catalyst samples, and technical expertise related to this past work. The National Renewable Energy Laboratory (NREL) is conducting R&D in support of the United States Department of Energy (DOE) to develop methods for economically producing ethanol from gasified biomass. NREL is currently conducting biomass gasification research at an existing 1/2 ton/day thermochemical test platform. Both Dow and NREL believe that the ability to economically produce ethanol from biomass-derived syngas can be enhanced through collaborative testing, refinement, and development of Dow's mixed-alcohol catalysts at NREL's and/or Dow's bench- and pilot-scale facilities. Dow and NREL further agree that collaboration on improvements in catalysts as well as gasifier operating conditions (e.g., time, temperature, upstream gas treatment) will be necessary to achieve technical and economic goals for production of ethanol and other alcohols.

Summary of Research Results:

In brief, the following activities were anticipated:

1. Knowledge transfer: from Dow to NREL on mixed alcohol catalyst development and from NREL to Dow on biomass gasification development;
2. Determination of practical limits to syngas (a mixture of hydrogen, carbon monoxide, and other non-condensable gases) composition for mixed alcohol synthesis from gasified biomass;
3. Bench-scale catalyst performance validation;
4. Formulation of an improved catalyst material at NREL;

5. Testing of Dow's mixed alcohol catalyst in a pilot reactor; and
6. Technoeconomic analysis of a biomass to ethanol process via gasification and mixed alcohol synthesis.

All listed activities were completed to the satisfaction of both Dow and NREL.

Knowledge transfer occurred throughout the CRADA period of performance (POP), but was most active in the first 6 months of work. During this period, technical representatives from Dow visited NREL to provide detailed background on the decades-long development of their mixed alcohol catalyst technology and to inspect NREL's biomass gasification and catalyst testing facilities. NREL provided feedback on Dow's catalyst development as well as ideas for catalyst improvement. NREL visited Dow to detail potential process designs for stand-alone thermochemical biomass to ethanol refineries and to see Dow's catalyst development facilities. Dow provided expert advice on process configurations, model assumptions, and economics. Throughout the POP, experts at both institutions provided prompt feedback on technology development. In sum, these knowledge-transfer activities were extremely useful to both parties and accelerated the refinement of process designs and experimental validations of those designs.

Biomass is significantly different in composition than fossil fuels, and therefore, it was important to understand the limitations a biomass-derived syngas might place on a mixed alcohol catalyst that was originally developed for use with petroleum-derived gases. To this end NREL tested Dow's catalysts with syngas and varying levels of typical biomass syngas contaminants like hydrogen sulfide, carbon dioxide, methane, and steam. It was determined that Dow's catalyst was tolerant to all of these contaminants. Hydrogen sulfide was beneficial to the catalyst, methane a simple non-reactive diluent, and carbon dioxide and steam damaging above certain concentrations. Results of these studies were captured in a publicly-accessible report (National Bioenergy Center report #10772) and presented at the American Institute of Chemical Engineers annual conference in November 2010. Additional literature background was included with experimental data from NREL and Dow in a deliverable report: "Limits to Syngas Composition for Mixed Alcohol Synthesis," prepared in September 2011, available to certain entities per CRADA regulations.

Technoeconomic models require predictions of catalyst performance and therefore, it was important to validate assumptions of mixed alcohol catalyst performance at both NREL and Dow. Performance validation began in the first year of the POP and continued through the end of the POP. NREL initially tested Dow's catalysts in their bench-scale reactors and found the performance to be worse than expected. Feedback from both NREL and Dow led to additional testing that proved the importance of careful catalyst handling and activation; aspects that had previously been considered unimportant for this catalyst. Later into the POP, Dow played a critical role in validating catalyst improvements made by NREL (explained next), demonstrating results at Dow that matched those measured at NREL. Many validation activities were used for technoeconomic justification, sanity checks, and uncertainty estimation, and were not captured in specific reports. However, at least two were documented in publically-accessible reports. The first considered bench-scale catalyst performance of Dow and other industrial mixed alcohol catalysts using bottled syngas (National Bioenergy Center progress report Q2-2011) and the second considered the same using biomass-derived syngas (National Bioenergy Center report #11050).

Through parallel program activities, it became clear in FY 2010 that the performance of Dow's mixed alcohol catalyst was good, but not good enough to meet a DOE cost target for thermochemical ethanol production. Dow did not wish to engage in joint catalyst development activities, so NREL conducted research to improve catalyst productivity (ethanol produced per mass of catalyst per time) and selectivity (ethanol produced relative to byproducts) in a separate non-CRADA project. The catalysts developed in that project were used within this CRADA for validation and for improvement of kinetic models at Dow (explained below). These catalyst improvements are documented in a publicly-accessible report (National

Bioenergy Center report #11109). Catalyst improvements were validated in Dow's bench scale reactors, which showed performance equal to if not greater than that measured at NREL. Extensive data sets were collected with improved materials at NREL, and this data was shared with Dow. Dow incorporated this data into their predictive models, and then shared these updated models with NREL for technoeconomic modeling of a commercial process. As a result, DOE cost targets were met via model prediction and validated at bench-scale at both NREL and Dow facilities.

A critical milestone for this CRADA was testing of Dow's catalyst in a pilot-scale integrated system, whereby biomass was gasified, conditioned, compressed, and converted to mixed alcohols in a concerted process. This was achieved near the end of the POP (summer 2012) with a demonstration run consisting of more than 500 h operation. In this demonstration, Dow's catalyst was proven compatible with biomass-derived syngas, and produced about 5 gallons of crystal-clear mixed alcohol product. Used catalyst material was returned to Dow, who reported no adverse catalyst deactivation. Details of this test were made publicly available (National Bioenergy Center report #11080).

The most valuable synergy within this CRADA was the coupling of Dow's kinetic model for mixed alcohol synthesis and NREL's predictive model for biomass syngas generation. The former model is the result of decades of work at Dow and allows one to rigorously predict ethanol and byproduct formation on both Dow- and NREL-developed mixed alcohol catalysts. The latter model is the result of more than a decade of work at NREL and allows one to predict the quantity and composition of syngas derived from various biomass feedstocks. The combination of models was extremely important because i) predictions are needed at commercial scale despite an inability to validate at commercial scale, ii) process changes upstream or downstream will impact ethanol synthesis in ways that must be quantified, iii) advanced heat integration requires excellent predictive capabilities, and iv) NREL does not have the resources in-house to produce a mixed alcohol kinetic tool with the level of sophistication in Dow's model. Throughout the POP, NREL and Dow worked closely to improve the biomass to ethanol predictive models, and both parties provided feedback and data that improved both upstream and downstream predictive capability. The end result was a full process model that employed innovation from both CRADA partners to meet DOE cost targets for cellulosic ethanol. Details are available in a publicly accessible report (National Bioenergy Center report #11113) and will be published soon in a peer-reviewed journal article.

A significant amount of research was completed during the POP. The costs of this CRADA are explained as follows:

1. Significant improvements to bench- and pilot-plant systems were required to appropriately test Dow catalysts. Specifically, operation at high pressures (up to 2000 psi), use of hydrogen sulfide (a highly toxic gas), and advanced analytical tools to completely quantify reaction products were required. It is estimated that these improvements along with day-to-day consumables represented about 1/3 the CRADA budget.
2. Labor for catalyst testing, equipment modification, calibrations, data analysis, report writing, process modeling, and economic modeling represented the remaining CRADA budget.

As with any project, there were a number of wish list items not spelled out explicitly in the CRADA that Dow and NREL would have liked to explore, given additional time and funds. Major items include:

1. Longer-term catalyst testing at the pilot scale using lower hydrogen to carbon monoxide ratios, packed bed reactors, and recycle of unreacted gases;
2. Analysis of sulfur speciation in crude product and quality of finished ethanol product;
3. Impact of other trace syngas contaminants like phosphorous, chlorine, sodium, etc., especially during long-term operation; and

4. Improved validation of TEA models through the use of recycled gas to other parts of the pilot plant (gasifier, reformer, etc.)

In summary, this CRADA between The Dow Chemical Company and the National Renewable Energy Laboratory was extremely productive and mutually beneficial for both parties. Dow gained important insights into biomass gasification and resultant gas processing, NREL gained critical assistance in modeling and executing mixed alcohol synthesis, and both gained unique perspectives and experience in process design.

Subject Inventions Listing:

None

Report Date:

March 19, 2013

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