



Catalytic Conditioning and Conversion of Bio-Syngas

Cooperative Research and Development Final Report

CRADA Number: CRD-10-418

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Cooperative Research and Development Final Report

In accordance with Requirements set forth in Article XI. Reports and Abstracts A.(3), of the CRADA agreement, 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.

Parties to the Agreement: Enerkem, Inc.

CRADA Number: CRD-10-418

CRADA Title: Catalytic Conditioning and Conversion of Bio-Syngas

Joint Work Statement Funding Table Showing DOE Commitment:

| Estimated Costs | NREL Shared Resources |
|------------------------|------------------------------|
| Year 1 | \$250,000 .00 |
| Year 2 | \$250,000.00 |
| Year 3 | \$250,000.00 |
| TOTAL | \$750,000.00 |

Abstract of CRADA Work:

There is a critical need to increase the carbon yield of the gasification process. To this end, it has been suggested that tars and chars formed as by-products of gasification be re-injected into the gasifier. In this CRADA work facile and inexpensive methods of modifying chars and tars received from Enerkem are studied with the aim of increasing their gasification rate upon re-injection into the gasifier. Adding iron to the char, both in nitrate form and in clay form, speeds the CO₂ gasification of the char ($\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$). It has been more difficult to speed the gasification of tar mixed with char, likely due to clogging of pores, resulting in a reduced accessible surface area.

Summary of Research Results:

Char and tar-char (AKA sludge after centrifuge) samples were received from Enerkem, characterized and gasified with and without potentially catalytic additives. Proximate analysis was performed using ASTM-D7582-12 in a LECO carousel TGA. Ultimate analysis was performed via high temperature combustion with a LECO TruSpec. Initially, char gasification experiments were performed in a U-tube fixed bed reactor whose schematic diagram is shown in Figure 1. In this reactor the char was heated to the reaction temperature and allowed to temperature equilibrate under an inert gas before the CO₂ was added to gasify. There was concern that the dispersion of any catalyst added to the char might be altered by leaving the sample at a high temperature prior to gasification. To mimic Enerkem's gasification process more closely, prevent agglomeration of metal atoms just prior to gasification and to speed data

collection, subsequent data was collected on a reactor allowing for rapid insertion of the samples into a hot furnace, shown in Figure 2. In both reactors gasification occurs at atmospheric pressure under 35 volume percent CO₂ in inert and the products are monitored with a mass spectrometer.

Char samples have been characterized and studied their gasification in CO₂ with and without low cost additives. The time required for complete gasification of wood-derived char was observed to decrease with three different additives: (1) iron from iron nitrate, (2) clays (bentonite and mica) and (3) an ash-rich char (MSW-derived char).

In the final quarter of this year tar-char samples were received. The moisture content of these samples was found to be about 50%. The tar-char samples were either dried, devolatilized, or extruded with clays and then gasified with CO₂. The devolatilized tar-char gasified faster than the dried while the extruded gasified more slowly than the dried.

CO₂ gasification of the wood-derived char was performed as a function of the mass of char and it was found that mass transfer limitations exist when using a 30 mg sample in the rapid-exchange reactor at 1000°C. This result will influence the design of future experiments. The increase in gasification rate upon the addition of iron is still conclusive, as the total mass of carbon in the sample changed insignificantly when up to 2 wt.% iron was added. These results clearly showed the enhanced gasification of the modified chars and the process will be used at Enkern at their Edmonton , Alberta facility to increase carbon conversion from municipal solid waste gasification.

Subject Inventions Listing:

None

Report Date:

June 30, 2016

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