TO: Texas Hazardous Waste Research Center

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SUBJECT: Annual Progress Report

PROJECT NUMBER: 513LUB0022H

PROJECT TITLE: Heterogeneous Catalyst Development for the Conversion of Phospholipid-Containing Feedstocks to Renewable Transportation Fuels

PROJECT PERIOD: 1 Sept 2013 – 31 Aug 2015

DATE: **29 Jan 2016**

Project Description

To eliminate concerns with using food type oils for fuel, researchers have identified several potential feedstocks that are noncompetitive with the food industry. These oils are microbial derived oils (MDOs) and contain not only acylglycerides, but also vast amounts of free fatty acids and phospholipids, which are not amenable to biodiesel processing. The plant-derived oils (PDOs) currently used in biodiesel manufacturing contain ≤2% of phospholipids, which can be cheaply removed *via* a degumming pretreatment before converting the triglyceride oils to biodiesel. Phospholipids are the major component of cellular membranes; their function is to regulate nutrients into and wastes out of the cell. The oleaginous yeast R. Glutinous contains 17 wt% phospholipids and microalgae up to 40 wt%. Studies by Revellame and co-workers, which Dr. Benson is a co-author, suggest that wastewater sludges offer a viable feedstock solution for the displacement of petroleum-derived fuels. In fact, 25 – 65% of operating expenses of wastewater treatment facilities are associated with excess sludge removal. Therefore, conversion of microbially activated sludges into salable fuels and chemicals offers profit potentials for these facilities.

Furthermore, the U.S. Department of Energy (DOE) has invested significant resources over the past decade to develop the biorefinery concept. Rather than removing and discarding phospholipids in a pretreatment step, using phospholipids (and their acylglyceride counterparts) as a biofuel would be most beneficial. This research would allow for the recycling of phosphorus, which can then be used for biochemical processes, as flame-retardants, fertilizers, and pesticides.

The process developed in Dr. Benson's laboratory (Fig. 1) requires no wash water, and thus, is an environmentally friendlier, sustainable process.

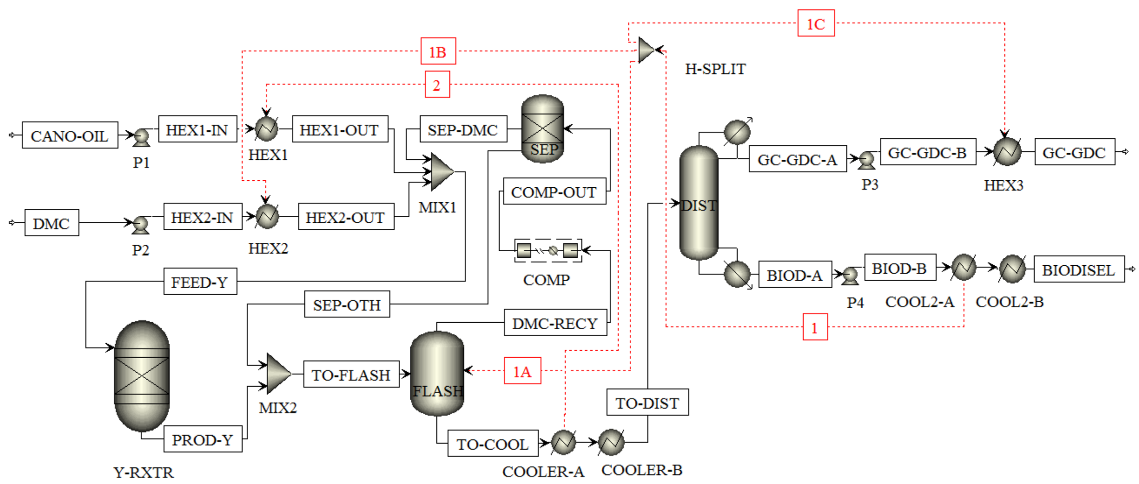


Fig. 1. Process flow diagram using Aspen Plus simulation for a glycerol-free biofuel production facility. The red dotted lines indicate heat integration techniques that reduce overall energy input. This process is 15% more energy efficient than current biodiesel production facilities. . http://dx.doi.org/10.1016/j.fuproc.2013.03.030

Objectives

The overall goal of this project was to develop a heterogeneous catalyst for the conversion of crude lipid oils to green fuels. Previous work by the Benson Research Group has shown that refined row-crop oils (i.e. canola oil, soy bean oil, etc.) can be converted to biodiesel but without the unwanted byproduct, glycerol, and without generating process wastewater. Since the lipid feedstocks envisioned by Dr. Benson would be from microbial-based feedstocks and used greases, a research effort was needed to determine the extent of conversion and any deleterious affects that these feedstocks would have on the catalysts developed in Dr. Benson's group. Therefore, the objectives of this project were to use crude oils, containing high free fatty acid concentrations, and phospholipids to test for overall conversions, kinetics, and catalyst robustness.

Methodology

A series of LDH catalysts have been synthesized containing a wide range of ligand/TBD complexes and exposed cationic LDH surfaces to create a bifunctional catalyst. (Fig. 2). The mixture of acid and base sites on the bifunctional catalyst allows for rapid conversion of both triglyceride and FFAs via transesterification and esterification mechanisms, respectively (Fig. 3). In these reactions, methanol and dimethyl carbonate (DMC) were tested as methylating agents.

Although methanol is the current choice in industry, DMC alters the chemistry and avoids the formation of glycerol.

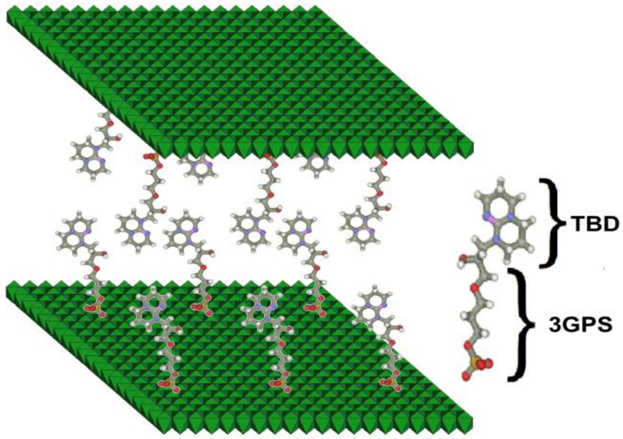
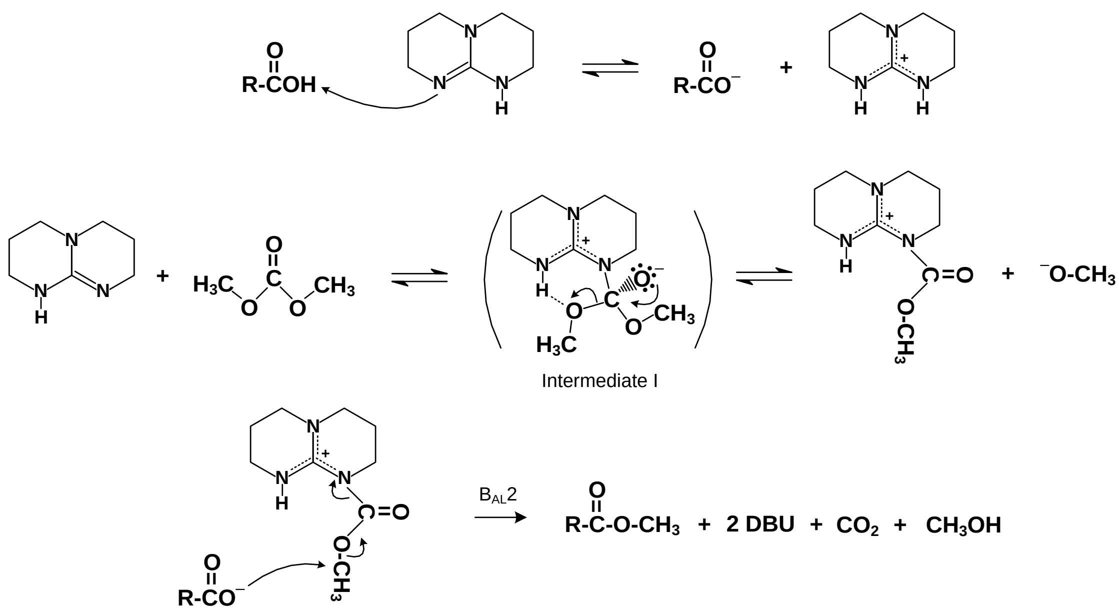


Fig. 2. Schematic illustration of TBD-3GPS arrangement in the interlayer of Mg/Al LDH.



Reaction Scheme 1. Possible mechanism for TBD catalyzed esterification of FFAs.

Another aspect of this project was the development of an online Raman analysis technique to quickly determine the conversion of lipids to biofuel. The current method used for determining conversion uses a high-temperature GC analysis, which requires tedious sample preparation. The Raman method simply uses a fiber optic Raman probe in the reaction vessel for analysis. However, the reaction mixture contained not only the reacts and productions but also the TBD-LDH heterogeneous catalyst, which made for a unique challenge for Raman Spectroscopy (Fig. 3 (left)). A Gaussian deconvolution method (using Excel) was developed to aid in the Raman analysis. The

Raman results compared quite favorably with the samples taken for GC analysis (Fig. 3 (right)). The Gaussian peak fitting program was written for parameter fitting of unconstrained nonlinear optimization using peak height, center of peak, and the full width at half max (FWHM) to calculate the peak area for peaks hidden (or obscured) by spectroscopic signatures

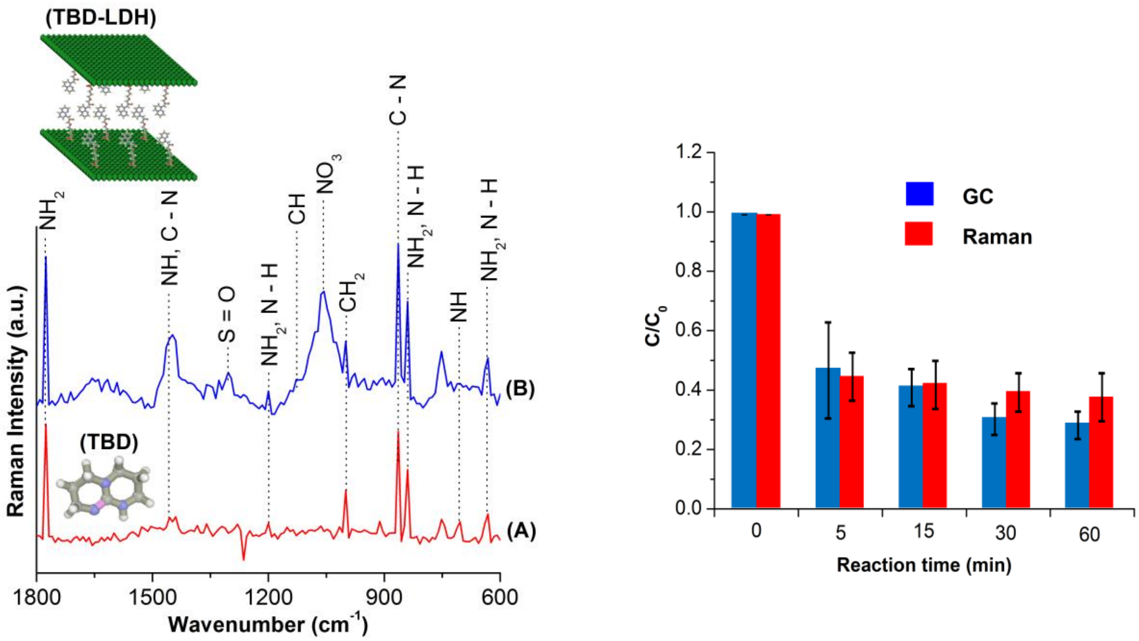


Figure 3 (left) Raman spectra of (A) TBD and (B) TBD-LDH detected with a Perkin Elmer 785 nm Raman spectrometer, and (right) Concentration of triglyceride oil using DMC as methylating agent and T_{rxn} = 70 °C.

Accomplishments/Problems

Dr. Benson has had three graduate students, both Masters level, and one undergraduate student working on this project. Mr. Keyvan Mollaeian, Mr. Josh Borton (both graduated) and Mr. Frank Lopez (graduating May 2016) are the three graduate students, while Ms. Bleinie Dickerson is the undergrate student and has worked closely with Mr. Mollaeian. Mr. Mollaeian has been tasked with developing the *in situ* Raman analysis for this project. Mr. Borton's focus has been on the kinetic evaluation as well as evaluating crude lipids oils, containing 4.5, 14.5, and 45 wt% FFAs, obtained from Renewable Biofuels (Port Neches, TX). Mr. Lopez's work has been developing the robustness of the TBD-LDH catalyst along with the steady state reaction process development (i.e. reactor sizing and operation).

The parametric study used crude lipid oils obtained from Renewable Biofuels, Inc.(Port Neches, TX) to determine reaction conversions depending on the quality of the oil. Using the TBD catalyst, Mr. Borton performed experiments using both methanol and dimethyl carbonate as methylating agents. Methanol was used as a base comparison since it is the industry standard for biodiesel production. Molar ratios of DMC (or methanol):oil (6 – 24) and FFA content (4.5 – 45 wt%) were tested. Samples were analyzed using GC-FID in collaboration with colleagues at University of Louisiana – Lafayette. (Conversions as high as 90% were achieved even with 45 wt % FFA.

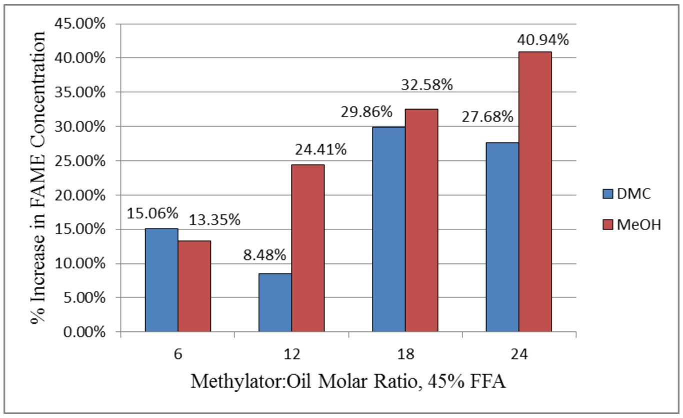


Fig. 4. The effect of FFA content on reaction conversion using TBD catalyst and T_{rxn} = 70 °C

Future Work

Preliminary work has been performed towards the development of the kinetic parameters for the heterogeneous LDH-TBD catalyst (see figure below). However, it was found that LDH-TBD has limited shelf life, unless stored in desiccator to prevent oxidation of the TBD by moisture and air. LDH-TBD takes approximately one week to synthesize from Mg and Al salt solutions and can be stored for ~2 months in dessicator. Currently, we are working to produce larger batches of LDH-TBD catalyst (up to 500 g) before completing the kinetic evaluations. Future work will entail the kinetic evaluations using the *in situ* Raman analysis method developed by this work. In addition, proposals for both NSF and DOE are being developed as well as industry contacts for future implementation of this biofuel technology.

List of Publications and Presentations

25 Sept 2013 – “Catalytic and Process Development for Glycerol-free Biofuel from Lipids” Presented to Renewable Biofuels, Inc. (invited talk)

3 Nov 2013 – “Kinetic Evaluation and Reactor Modeling for Transesterification of Lipids With Dimethyl Carbonate Using the Homogeneous Catalyst Triazabicyclodecene” Presented at annual AIChE conference in San Franscisco, CA

7 Nov 2013 – “Development of a Heterogeneous Guanidine Base Catalyst for the Conversion of Lipids to a Sustainable Biofuel” Presented at annual AIChE conference in San Franscisco, CA.

6 May 2014 – “Overview: What’s Around the Corner for the Glycerol Market?” Presented at the annual AOCS Conference in San Antonio, TX

Mollaeian, K., Wei, S., Islam, M.R., Dickerson, B., Holmes, W.E., Benson, T.J. “Development of an Online Raman Analysis Technique for Monitoring the Production of Biofuels” Energy & Fuels (In Review)

Obakore, A., Borton, J., Mollaeian, K., Benson, T.J. “A Parametric Study for the Conversion of High Free Fatty Acid Lipid Feedstocks to Biofuel Using Triazabicyclodecene Catalyst” Biomass & Bioenergy (In Review)

Keyvan Mollaeian (MS Student) – Thesis Title “Layered Double Hydroxide Catalyst for the Conversion of Crude Vegetable Oils to a Sustainable Biofuel” (Expected Graduation Dec 2014)

Josh Borton (MS Student) – Thesis Title “Parametric Evaluation for the Conversion of Crude Lipid Oils Containing High Free Fatty Acid Content to a Sustainable Biofuel” (Expected Graduation Dec 2014)