PRF #: 57207-ND2
PRINCIPAL INVESTIGATOR: Dr. William C. Hockaday, Baylor University, Department of Geosciences
CO-INVESTIGATOR: Dr. Touradj Solouki, Baylor University, Department of Chemistry & Biochemistry
PROJECT TITLE: Structure-Catagenesis Relationships: Molecular Controls on Kerogen Thermal Evolution and Hydrocarbon Formation

RESEARCH OBJECTIVES

This project has 3 main objectives. The first objective was to construct a series of hydrous pyrolysis reactor cells in which crude oils could be produced in the laboratory under controlled temperature-pressure conditions from geological source (sedimentary) rocks of terrestrial, lacustrine, and marine origins. The second task was spectroscopic characterization of the kerogens, oils, and bitumens following incremental increases in the temperature-pressure regime. The third task involves the application of a petroleomics approach to the 'matrix' of synthetic crude oils and oil precursors (bitumens). The novel outcome of these activities will be a multivariate database including temperature- and pressure- dependent molecular formulas and molecular structure information for each rock type. This database will serve as the numerical environment in which we develop structure-catagenesis relationships.

RESEARCH PROGRESS

The first objective (reactor construction) is has been completed. We now have eight separate temperature-programable hydrous pyrolysis reactors that has allowed us to efficiently create a matrix synthetic crude oils. This work was the led by Baylor graduate student Owen Craven and constituted approximately half of his M.S. Thesis research (M.S. Geology, 2018). The work of testing and running the hydrous pyrolysis reactors was aided by a Baylor undergraduate research assistant, Emily Blackaby (B.S. Geology, 2018). Owen Craven and Emily Blackaby have prepared a working draft of a manuscript for the journal *Organic Geochemistry* describing the construction of cost-efficient hydrous pyrolysis reactors (shown in Figure 1) and furnaces to be used for simulating natural oil forming (catagenesis) processes. This paper also demonstrates the use of these reactors in the maturation of Eocene lake sediment (Green River formation) and compares and contrast the thermochemical changes to those of modern lacustrine samples from Lake Waco, Texas, USA. For the purpose of quantitative comparison of chemical structure, the oil, bitumen, and kerogen fractions were each analyzed by quantitative solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy.

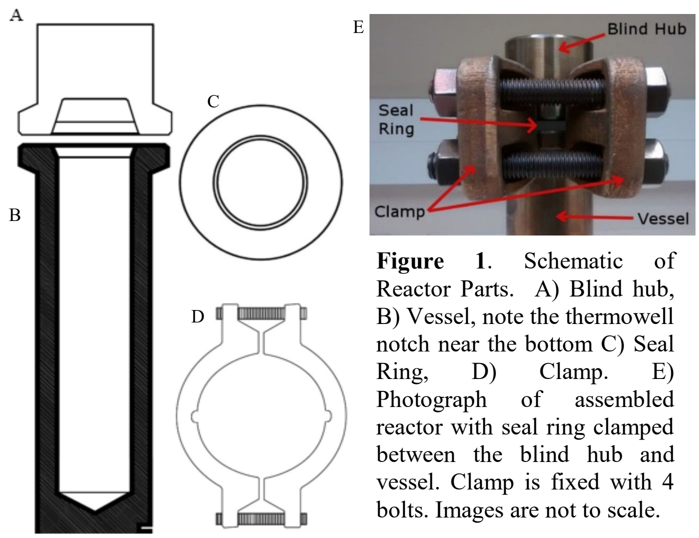

Figure 1. Schematic of Reactor Parts. A) Blind hub, B) Vessel, note the thermowell notch near the bottom C) Seal Ring, D) Clamp. E) Photograph of assembled reactor with seal ring clamped between the blind hub and vessel. Clamp is fixed with 4 bolts. Images are not to scale.

The working draft of a second paper based upon hydrous pyrolysis experiments is nearing completion. This paper is being led by former Baylor PhD student, Dr. Todd Longbottom (now a postdoc at Texas Christian University, TCU) in collaboration with Owen Craven (MS student). The focus of this paper is a comparative thermal evolution of two economic oil source rocks—the Eagleford shale and the Green River shale. The paper demonstrates an apparent thermal disequilibrium between organic matter in the bitumen and kerogen phases. Maturity is assessed in the bitumen phase using hopane and sterane biomarkers, while maturity of the kerogen indexed based upon the carbon aromaticity measured by NMR and the calculated vitrinite reflectance method known as Easy R_o

The second objective (NMR spectroscopy) of characterizing the oil, bitumen, and kerogen fractions before and after hydrous pyrolysis has been completed. Sediment and biofuel feedstocks included marine and lacustrine black shales, coal, algae, and municipal biosolids. This work resulted in methods for predicting maximum oil yield generation from parent kerogen. The data clearly demonstrate that a multitude of chemical parameters of the sediment exert influence on catagenesis reactions. Data analysis and interpretation is ongoing.

Objective 3 (Petroleomics) is the primary task for the second year of the project.

IMPACT ON THE CAREER OF THE PRINCIPAL INVESTIGATOR

Collaborations

1. ***Dr. Xi Fu, University of Houston*** – sent M.S. degree student, Christopher Xiao, to spend several weeks working in Hockaday's lab at Baylor University using the hyrodous pyrolysis reactors. Dr. Xi Fu oversaw the modification of Hockaday's reactor hub for the collection of gases for molecular and isotopic analysis by GC-IRMS. The experiments were designed to evaluate *Carbon isotope fractionation in methane, ethane, and propane during the hydrothermal evolution of kerogen in petroleum source rocks*. The data have been published in Chris Xiao's M.S. thesis.
2. ***Dr. Omar Harvey, Texas Christian University*** – hired Ph.D. graduate Todd Longbottom from Hockaday's lab as a postdoctoral fellow. Longbottom has since fostered a collaboration between Dr. Hockaday and Dr. Harvey. This work combines the chemical structure data from NMR with the thermodynamic data from differential scanning calorimetry (DSC) to understand the effects of catagenesis upon kerogens that have been matured in the laboratory using hydrous pyrolysis.
3. ***Dr. Zhanfei Liu, University of Texas, Marine Science Institute*** – initiated collaboration on NMR characterization of crude oil photochemical decomposition in seawater.

Publications

<u>Thesis</u>

1. Owen Craven, Organic matter structure changes during catagenesis: Implications of kerogen chemical structure on petroleum yield and composition. M.S. Thesis, Baylor University, Department of Geosciences, Waco, TX, USA, May 2018.

<u>PI-directed Manuscripts in preparation</u>

2. Development of economic hydrous pyrolysis reactors applied in a comparative ^{13}C NMR analysis of catagenetic effects on fresh versus fossil lacustrine algae (in preparation for *Organic Geochemistry)*
3. Longbottom, T.L., Craven, O., Harvey, O., Hockaday, W.C., Comparative analysis of molecular thermometry methods through hydrous pyrolysis of ancient sedimentary organic matter (in preparation for *Energy and Fuels*)

<u>Collaborator-led Manuscripts in preparation</u>

4. Wang, Qing; Evans, Meredith; Breecker, Daniel; Hockaday, William; Adegboyega, Nathaniel; Liu, Zhanfei**;** The fate of aromatic hydrocarbons in light Louisiana sweet crude oil after exposure to natural sunlight in Gulf of Mexico, *Environmental Science and Technology*, es-2018-061594 (rejected, under revision).

IMPACT ON STUDENT CAREERS

<u>ACS-PRF supported M.S. Graduate Student Owen Craven</u>

The project funding supported 1 M.S. student (Owen Craven) in the Department of Geosciences at Baylor University. Funding from ACS was used to cover summer stipend, as well as the research supplies and materials costs for the majority of his thesis research. Craven generated most of the data mentioned in this report. His presentation of the data during on-campus interviews with industry recruiters earned him a summer internship with Pioneer Natural Resources, in Fort Worth Texas. This was an invaluable industry work experience, although it did not result in a full-time position with the company. Nevertheless, Owen Craven is now gainfully employed full-time with APTIM, a natural resources engineering firm serving the military, oil, gas, chemical, and power industries.

<u>ACS-PRF supported Postdoc</u>

In year 1, the project provided 9 months support for Post-doc Dr. Nathaniel Adegboyega who shared responsibility for hydrous pyrolysis reactor construction and testing, as well as development of ^{13}C NMR methods for analyzing oil and bitumen samples in the solid-state. The NMR method development led to a collaboration and manuscript submission with Dr Zhanfei Liu at University of Texas, on the characterization of asphaltenes and photodegraded asphaltenes (publication #4 listed above). Dr. Adegboyega is *now a full-time, tenure track, assistant professor of Environmental Chemistry at the University of Southern Illinois*, Edwardsville campus.