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

Introduction. The premise of our work is that relationships between the molecular structural properties of kerogen, bitumen, and oil are discoverable through molecular spectroscopy and mass spectrometry and that these relationships provide insight to chemical processes of petroleum formation. By studying the formation of petroleum in the laboratory, under controlled conditions of hydrous pyrolysis, we aimed to develop empirical expressions to describe specific structure-catagenesis relationships. If successful, the resulting system of equations could be applied in the emerging field of petroleomics; providing a quantitative molecular framework for assessing the kerogen source and thermal history of petroleum crudes.

Completed Tasks. The first objective was to construct a series of hydrous pyrolysis reactor cells in which bitumen and crude oils could be produced in the laboratory under selected temperature-pressure conditions from sedimentary rocks of terrestrial, lacustrine, and marine origins. The second objective was the quantitative characterization of kerogens, bitumens, and oils by ^{13}C NMR spectroscopy as a means of quantitatively relating differences in bulk molecular structure to the experimental increases in the temperature-pressure regime.

Ongoing tasks. The third objective involves the application of a petroleomics approach to studying the elemental and molecular composition synthetic crude oils and oil precursors (bitumens), followed by graphical and numerical treatments to describe the molecular composition changes resulting from the experimental changes in the temperature-pressure regime. Two approaches, utilizing high resolution mass spectrometry (MS) and inductively couple plasma (ICP) MS, were employed to determine the concentration and molecular speciation of organic sulfur. Due to mass resolving power limitations of the available instrument (Thermo Fisher orbitrap Discovery with the APCI/APPI ion source), characterization of the sulfur containing compounds based on isotopic separation of $^{34}S_1$ and $^{13}C_2$ isotopomers was challenging. This work is ongoing, and we plan to use the in-house (FTICR-MS) instrument to provide the needed resolution. For the ICP-MS work, an Agilent 7900 ICP-MS instrument was used. This instrument uses a single quadrupole with unit mass resolution and generally allows for quantitative analysis of elemental composition. Metals in the crude oils including V, Cr, Mn, Fe, Co, and Ni were successfully quantified. However, analysis was not reliable for Cu, Mo and Zn. Additionally, ^{32}S is difficult to differentiate from $^{16}O^{16}O$ and other polyatomic interferences that make it challenging to determine sulfur concentration with low resolution instruments. We employed various intense digestion methods, but improvements were modest. To overcome this, we prepared several calibration curves, using both internal and external standards, for accurate determination of sulfur content. We are currently addressing the background interferences and the observed variations from multiplicate runs so that we can publish the acquired data in a peer-reviewed journal.

Conference Presentations in 2019:

1. Kyle L. Wilhelm; Drew Stolpman; Zhao Wang; Bill Hockaday; Touradj Solouki, "Development of Predictive Methods of Sulfur Content in Hydrous pyrolysis Oil Products by Elemental Sulfur Analysis of Crude Oil Feedstocks", Proceedings of the 67th ASMS Conference on Mass Spectrometry and Allied Topics 2019, Atlanta, GA June 2 - 6, 2019. (Poster)
2. Craven, Owen; Longbottom, Todd; Hockaday, William, Insights to catagenesis reactions from molecular mass balance in experimental hydrous pyrolysis. *American Chemical Society National Meeting*, Orlando, FL. March 31 - April 4, 2019. (Talk)

IMPACT ON THE CAREER OF THE PRINCIPAL INVESTIGATORS

Collaborations resulting from the project

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. Fu oversaw the modification of Hockaday's reactor to collect gases for molecular and isotopic analysis. The work is described in Christopher Xiao's M.S. thesis, *Carbon isotope fractionation in methane, ethane, and propane during the hydrothermal evolution of kerogen in petroleum source rocks*
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 the Hockaday and Harvey labs. This work combines the chemical structure data from NMR with the thermodynamic data from differential scanning calorimetry (DSC) to understand relationships between kerogen kerogen molecular structure, maturity, and activation energy.
3. ***Dr. Zhanfei Liu, University of Texas, Marine Science Institute*** – the quantitative ^{13}C NMR methods developed by the ACS-funded postdoc (Adegboyega) are being used by Baylor doctoral student (Burke Leonce) to the characterize the changes in the molecular composition of crude oil in seawater caused by abiotic photochemical oxidation.

Publications resulting from the project

Thesis

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.

PI-directed Manuscripts in preparation

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*)

Collaborator-led Manuscripts in preparation

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, being revised for resubmission).
5. Qing Wang, Burke Leonce, Meredith Evans Seeley, Nathaniel F. Adegboyega, Kaijun Lu, Daniel O. Breecker, William C. Hockaday, and Zhanfei Liu, Elucidating the chemical structure of photogenerated asphaltenes from light Louisiana sweet crude oil exposure to natural sunlight in Gulf of Mexico, *Environmental Science and Technology* (in preparation).

IMPACT ON STUDENT CAREERS

Owen Craven - M.S. in Geology, Baylor University

Support from ACS PRF covered summer stipend, research supplies and materials costs for Craven's thesis research. Craven generated most of the data mentioned in this report. His presentation of the data during on-campus interviews with industry recruiters led to an industry internship after graduation. Craven is now gainfully employed full-time with APTIM, a natural resources engineering firm.

Nathaniel Adegboyega – Postdoc, Baylor University

The project provided 9 months support for Postdoc 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. The NMR method development led to collaboration and manuscript submission with Dr Zhanfei Liu at University of Texas, on asphaltene photooxidation (papers # 4 and 5 listed above). Dr. Adegboyega is *now a full-time, tenure track, assistant professor of Environmental Chemistry at the University of Southern Illinois*, Edwardsville campus.