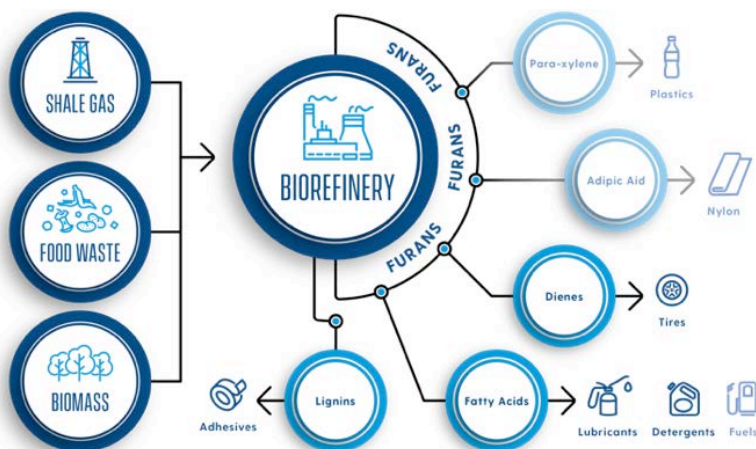


Catalysis Center for Energy Innovation (CCEI)
EFRC Director: Dionisios G. Vlachos
Lead Institution: University of Delaware
Class: 2009 – 2022

Mission Statement: To advance the catalysis science of complex systems with a focus on thermocatalytic transformation of lignocellulosic (non-food-based) biomass into chemicals and transportation fuels.

CCEI has established itself as a transformative catalysis center with a mission to advance fundamental catalysis science in complex systems. We envision innovations toward feedstock diversification for co-processing of biomass with C₄-C₆ shale gas derivatives. We have established three downstream research thrusts for the synthesis of (1) *dienes* via dehydra-decyclization of oxacyclopentanes (saturated furans); (2) *surfactants* via acylation and aldol condensation of furan with fatty or shorter acids; and (3) *lubricants* via hydroxyalkylation/alkylation



CCEI's research portfolio.

chemistry of furans with (di)aldehydes and subsequent decyclization-hydrodeoxygenation of the intermediates. Major chemistry threads that emerge are (1) C-C coupling chemistry to enable coupling of lignocellulose building blocks—among themselves or with shale gas derivatives; and (2) tandem furan ring opening and oxygen removal—as well as possible hydrogenation—to enable the design and synthesis of targeted functional molecules. Furthermore, we attempt feedstock diversification and utilization of renewable or inexpensive carbon sources, such as lignocellulose, food waste, fatty acids and/or shale gas.

For the synthesis of dienes (e.g., butadiene)—important high-volume feedstock for polymers—we envision dehydra-decyclization of sugar-derived, oxacyclopentanes. To that end, we are extending the use of *P-zeosils*, a new class of catalysts discovered by CCEI that consist of phosphoric acid supported on inert, all-silica zeolites. *P-zeosils* are Brønsted acids distinct from typical aluminosilicate zeolites with dynamically evolving P-speciation. Our goal is to improve catalytic activity and selectivity for dienes through fundamental understanding of the structure, dynamics and catalytic properties of *P-zeosils* and through development of new, dynamically confined acids in zeosils and metal organic frameworks.

The synthesis of bio-renewable oleo-furan-sulfonate surfactants with unique properties requires development of a selective route for *direct* α -site acylation of a sugar-derived furan with carboxylic acids (derived from shale gas, sugars, fatty acids or triglycerides) to produce a 2-furyl alkyl-ketone. Fundamental understanding of catalyst design to promote *direct* acylation by fatty acids or triglycerides can provide significant molecular efficiency over the *indirect* route that uses fatty acid anhydrides, the production of which is a multi-step, waste-generating process. Use of bulky acylating agents in porous solid acids introduces new challenges and questions regarding their distribution in porous materials, reaction mechanisms and active site catalyst design in order to accelerate the dehydration of acylating acids and prevent through water management side reactions on strongly acidic sites. Pore design for the control of

the distribution, orientation and diffusion of bulky amphiphiles within porous materials adds one more layer of complexity that we are addressing.

The design and synthesis of macromolecules require the synthesis of multi-functional catalysts for the conversion of furfural derivatives to alkylfurans via hydrogenolysis (surfactants) and for the decyclization-hydrodeoxygenation of the backbone furans to poly-alpha-olefin lubricants. To that end, we are pursuing fundamental research in numerous directions: (1) We are leveraging inverse metal/metal-oxide catalysts as they can possess various sites that cooperate in complex ways. (2) We are exploring selective C-O bond activation and hydrodeoxygenation (HDO) catalysis. Success lies in balancing the C-O bond scission and vacancy formation rates in the presence of H₂. (3) We are exploring use of olefins and dienes from shale gas to produce functionalized substrates, such as aldehydes and acids, for hydroxyalkylation/alkylation chemistry and acylation chemistries.

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