Antioxidants are commonly used as gasoline additives in order to improve fuel efficiency and minimize the deterioration of the automotive parts. With the support from the ACS PRF, my lab proposed to 1) establish a structure-function relationship of antioxidants based on the butylated phenol core toward identifying key features of “super-antioxidants”, 2) determine antioxidant activity of butylated phenols, and 3) characterize butylated phenol additives in gasoline samples.

During the third year of ACS PRF support which started in Sep 2017, my group has been working on objectives #2 and #3 above.

Objective #2: We have evaluated 4 analogues of tert-butyl-phenol (2,6-di-tert-butyl-4-methylphenol (BHT)) in terms of antioxidant activity. First, we evaluated antioxidants with superoxide anion by electrochemical methods and data indicate that all bulky phenols react with superoxide anion to similar extent. Second, all antioxidants were tested as oxidation substrate in a reaction with hydrogen peroxide and horse radish peroxidase using spectroscopy. We discovered that one bulky phenol reacted selectively with oxidized DAB intermediate to produce a new compound which has been purified by HPLC and identified by mass spectrometry as the major coupling product. We are currently working on characterizing the product by NMR. Third, we evaluated antioxidant capacity by measuring reactivity of bulky phenols with 2,2-diphenyl-1-picrylhydrazyl (DPPH•) radical. UV-vis spectroscopy and electrochemistry was used to monitor reduction in radical level as a function of antioxidant present. We found that antioxidant capacity was highly dependent on the number and site of tert-butyl substituents as illustrated in Fig. 1.

The results of the superoxide anion radical electrochemical assay were submitted for publication in the electrochemical journal and is currently under review. We also plan to submit results and characterization of the new coupling product with DAB intermediate to organic chemistry journal.

**Fig. 1.** Relative effectiveness of various bulky phenols as a function of substrate: DPPH radical, superoxide anion radical (SAR), and horse-radish peroxidase catalyzed reaction with DAB.
Objective #3: As a part of this funding, the third project is aimed at characterizing commercial gasoline samples using the electrochemical methods. This will allow for electrochemical screening of fuel content as well as determination of electrochemical parameters, such as capacitance and resistance of the gasoline. In year 3, we have purchased three types of fuel: regular, ethanol enriched (E85) and diesel at local gas stations in Michigan. We used these samples neat to characterize their electrochemical properties using gold and glassy carbon electrodes. Bulk analysis has revealed that diesel and regular fuels are largely non-conductive with significant resistance on both electrode surfaces. By contrast, ethanol enriched fuel did exhibit some charging current in cyclic voltammetry when gold or glassy carbon electrodes were.

In addition to bulk fuel measurements, the absorption profiles of such fuels on gold and glassy carbon surface was also tested as a function of adsorption time (5 min – 12 h). The rapid adsorption occurred within 30 min in neat fuels. The electrochemical impedance spectroscopy was used to characterize electrode surfaces post adsorption. The most adsorbing fuel, which produced greatest resistance to charge transfer, was E85 on the gold surface, while diesel was the most adsorbing fuel on glassy carbon surface.

Three undergraduate students and one graduate student participated in the ACS PRF funded project (Year 3: Sep 2017-July 2018). One undergraduate student was a full-time paid research assistant during the Summer 2018 in the Oakland University Summer Undergraduate Research Program. The second undergraduate student was full-time paid research assistant during the Summer 2018, as well. The third undergraduate student was a research volunteer in the lab. One graduate student was also contributing to the project. Currently, one undergraduate student is further characterizing fuel samples and their absorption profiles by electrochemical methods on other surface beyond gold or carbon.

During Year 3, two students presented a poster presentation titled: “Evaluation of bulk properties and surface adsorption of fuels by electrochemistry” at the institutional student symposia for the Summer Undergraduate Research Program (Oakland University). The student (3 undergraduates and 1 graduate student authors) also presented poster titled: “Learning new tricks from old bulky phenols using a multimodal approach” at the Pittcon meeting in Orlando in Feb 2018. Other poster presentation titled “Structure-reactivity relationship of bulky phenols in radical reactions” was presented at the regional ACS meeting (Glass Chemistry) in Toledo in June 2018 by student as well (3 undergrad and 1 graduate authors).

The research data acquired during the 3rd year of funding were included in the manuscript under review in the electrochemical journal. The synthetic and characterization data of novel coupling intermediate will be included in the manuscript for submission to organic chemistry journal. The electrochemical gasoline data will become an integral part of the manuscript for submission to the Energy & Fuels journal (ACS).

PRF funding has provided undergraduate and graduate students with research opportunities that are critical for their professional development and future careers. Students involved in the project have acquired research skills in analytical chemistry, electrochemistry and spectroscopy. PRF has certainly increased research productivity in my laboratory, and allowed me to expand my research scope and interests.