**ABSTRACT**

Greenhouse gas emissions (GHGs) and sustainability are incredibly important topics affecting the chemical industry today. While significant efforts are underway to reduce GHGs by addressing feedstocks, manufacturing, and products, maintaining viable process economics requires careful tailoring of solutions. For example, process intensification (PI) may be implemented because it improves efficiency and profitability in many cases. On the other hand, process electrification addresses GHGs from manufacturing more directly, but is not as readily adopted due to the expenses of industrial electricity exceeding the cost of fossil fuels. A new class of electrification technologies such as microwaves (MWs) can be used to enable PI in ways conventional heating cannot. These MW “co-benefits” include direct, volumetric, and selective heating, and may be used to enhance process performance. Currently, understanding of reported MW-enhancements of various processes is lacking and design and implementation principles for MW reactors need to be developed. This thesis aims to build understanding of MWs as a co-beneficial electrification technology for chemical manufacturing, targeting the production of HMF from bio-derived sugars for enhancement via PI.

The first focus of this dissertation is the expansion of sensing methodologies for and in MW-heated environments. We detail the design and implementation of a simple benchtop approach for quantifying complex dielectric permittivity – a critical property for predicting MW heating behavior – for liquids at variable temperatures. We report temperature-dependent datasets for water, alcohols, organic solvents, and hydrochloric acid solutions. To effectively
measure temperature, a new methodology was implemented for submergible optical fibers to directly measure temperature in pressurized, MW-heated flows for the first time. New thermometry approaches paint a vivid portrait: in MW-heated systems, temperature varies tremendously in both time and space.

The second focus of this dissertation is building understanding of MW effects on chemical processes and implementing effective MW processes. A modular MW flow reactor is demonstrated. A joint computational fluid dynamic (CFD) and machine learning (ML) framework is implemented for quick optimization of the reactor geometry for optimal heating efficiency. A modular MW-assisted continuous flow system for high flowrate HMF production from fructose is then showcased, representing a 36-times scale up. With the implementation of heat recirculation, more than 200 mL/min is heated to produce HMF at 0.1 kg/hr – an 8-times increase upon conventionally heated approaches.

We demonstrate temperature gradients in MW-heated liquid-liquid systems for the first time. Because MWs selectively heat the aqueous phase, a $\Delta T$ develops which is affected by process variables such as input power, dielectric properties, and surface area between solvents. A simple analytical model is shown to be predictive of $\Delta T$, enabling the design of systems with large temperature gradients. The effect of $\Delta T$ on the extraction of HMF and reactive extractions is explored. By introducing a cooler organic phase via MW-induced temperature gradients, the partitioning of HMF ($K_{HMF}$) shifts toward the organic phase. The temperature of the liquid-liquid interface is found to set the partitioning performance. COSMO-RS is used to estimate the effect of MWs on >500 solvents, and several candidates are predicted to exhibit superior performance (>50% $K_{HMF}$ boosts). CFD and experiments are both used to show that MWs increase the extraction efficiency and the volumetric mass transfer coefficient $k_La$ because of a Rayleigh instability caused by the density difference due to the temperature difference. The combined partitioning and mass transfer enhancement are predicted to grant significant advantages to HMF yield in reactive extractions.