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Elizabeth G Rasmussen

Continuous Flow of Supercritical Phase Fluids for Nanomaterial Synthesis

Elizabeth G. Rasmussen

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Reading Committee:

John Kramlich, Co-Chair

Igor Novosselov, Co-Chair

Michael Martin

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Abstract

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Elizabeth G. Rasmussen

Co-Chairs of the Supervisory Committee:
Professor John Kramlich
Research Associate Professor Igor Novosselov
Department of Mechanical Engineering

For fluids in the supercritical phase, slight variations in temperature or pressure can lead to large changes in thermophysical properties. This tunability of these fluid properties provides a unique opportunity to enhance the heat transfer and mixing environment for nanomaterial synthesis. Optimizing the synthesis environment is critical to the eventual scale-up of processes that are currently performed only at laboratory scale. A core challenge in the use of supercritical fluids as reaction media arises from these large variations in thermodynamic and transport properties with small changes in temperature and pressure. Direct measurement of these properties under these conditions is difficult with the property values holding a high uncertainty. Because of this, the design and scale-up of synthesis reactors has relied on modeling. Fortunately, the improved availability of computer resources provides an important tool to aid accurate design decisions. The work presented here focuses on two aspects of the use of modeling in the supercritical reactor design problem. The first aspect involves the selection of appropriate equations of state to characterize the challenging behavior near the critical point. The second involves the use of this information to design and operate a continuous flow supercritical reactor for the synthesis of nanoparticle metal organic framework materials. An important goal of the latter is the demonstration of scale-up methodologies and performance.

This dissertation begins with a theoretical investigation on the impact of equation of state (EoS) selection on computational cost and accuracy for modeling the behavior of supercritical carbon dioxide (scCO₂). Four EoS's of varying accuracy ranging from the simple Ideal Gas Law to the multiparameter Helmholtz-energy EoS were studied in a robust 99-case simulation matrix for scCO₂. This theoretical EoS study developed a set of guidelines for producing simulations that accurately capture heat and mass transfer.

In the second part of this dissertation, these guidelines are used to design a custom counter-current mixer, leading to the first report in the literature of a continuous flow scCO₂ synthesis reactor. This novel continuous flow scCO₂ reactor synthesized the zirconium-based MOF UiO-66 at a production rate ten times higher than previous state-of-the-art methods. Expanding on the continuous flow scCO₂ reactor work, a 25-experiment mechanistic study was completed that examined the effect of varying scCO₂ temperature, reactor temperature, reactor pressure, and mole fraction of CO₂ on the properties of the copper-based MOF, HKUST-1. The robustness of the simulation, design, and execution methodology was then repeated with similar success for the tunable synthesis of vanadium (IV) oxide nanoparticles in a continuous flow supercritical water (H₂O) reactor. All of these approaches demonstrated the synthesis of high surface area nanoparticles in short reactor residence times.

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Dedication

For the Lord my Rock (Psalm 144)

I know this dissertation was inspired and guided by a power greater than myself, so I dedicate it now to that power. May the research described here bring glory and honor to God by providing some inkling of wisdom to those flipping through the pages (Proverbs 8).

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Chapter 1. INTRODUCTION

Scientific advances have led to both the discovery and application of novel nanomaterials. The applications of these nanomaterials include enabling next-generation technologies such as thermochromic smart windows, catalysts, and targeted drug delivery. A challenge to realizing the benefits of nanomaterials is the difficulty in scaling up production rates from the small values typical of the laboratory to the much larger industrial scale. Continuous flow reactors offer a promising solution to scalability, as do supercritical phase fluids. Computer simulations are commonly used to design and optimize engineered systems operating with supercritical phase fluids, but a lack of certainty in the underlying physical models can lead to poor designs. This dissertation presents research focused on (1) understanding the tunable thermophysical properties of supercritical phase fluids and (2) using this information on supercritical phase fluids to develop continuous flow reactors for scalable nanomaterial synthesis. The dissertation covers these research topics from both the computational and experimental approaches. This chapter contains a background on the science and technology relevant to the supercritical fluid synthesis of these materials. Additionally, this chapter includes a discussion the gaps in literature that motivated this research and the scope of the research directions. The chapter concludes with an outline of the dissertation.

1.1 SUPERCRITICAL PHASE FLUIDS

The supercritical (sc) phase is reached when temperature, T , and pressure, P , are above a material's critical (cr) point. Near the critical point slight variations in temperature or pressure lead to large changes in a material's thermophysical properties.¹ For example, **Figure 1-1** highlights the property changes for carbon dioxide (CO_2) near its critical point of $T_{\text{cr}}=304\text{K}$ and $P_{\text{cr}}=7.38\text{MPa}$.

Property changes within the supercritical phase are most extreme around the pseudocritical (pc) point. The pseudocritical point occurs for a particular pressure ($P > P_{cr}$) at the temperature ($T > T_{cr}$) corresponding to the maximum value of the specific heat, c_p . The pseudocritical point is generally closer to the critical temperature at pressures near the critical pressure and further away from the critical temperature at higher pressures. As shown in Figure 1-1, the property variations are most extreme close to the critical point. In the context of this dissertation, this region of large property variations above the critical point is the “near-critical” region. While there are no set criteria for this region, for scCO₂, we are considering the region between 304 K and 330 K, and 7.38 MPa and 10 MPa, as the “near-critical” region, with the most extreme variations encountered at pressures between the critical pressure and 8 MPa.

These extreme material property changes can be harnessed to the advantage of a wide range of applications.² For example, Brayton cycles using scCO₂ with concentrated solar power have been proposed as a high-efficiency alternative for fossil and nuclear thermal energy plants.^{3,4} The high density and heat capacity of supercritical fluids make it a promising cooling fluid for applications such as high-heat flux electronics and emergency cooling for nuclear reactor systems.⁵⁻⁷ Finally, employing supercritical fluids in material synthesis reactors has enabled green chemistry, rapid synthesis, and improved energy efficiency over other methods.⁸⁻¹⁰

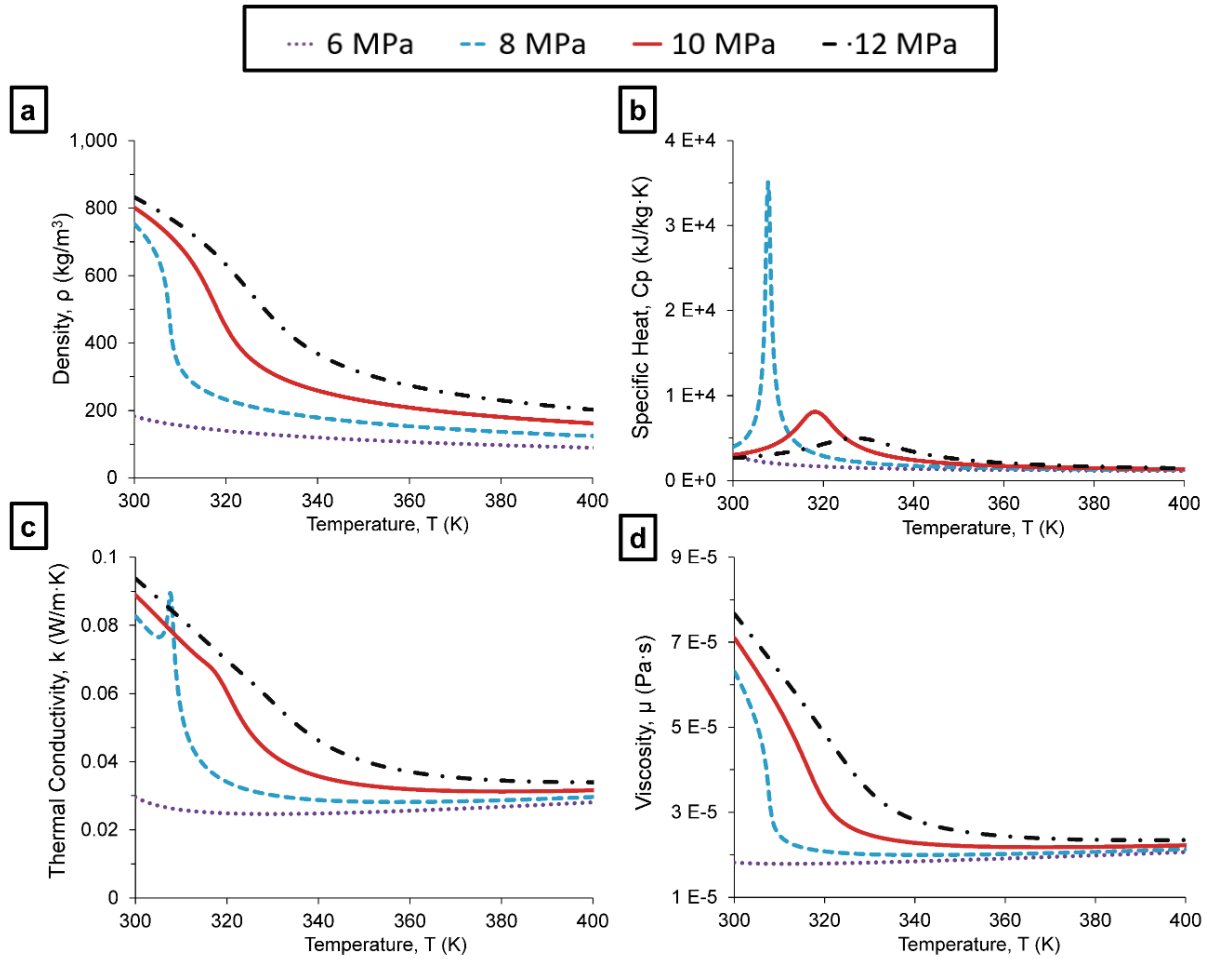


Figure 1-1. Plots of carbon dioxide (CO₂) thermophysical properties as a function of temperature at pressures of 6 MPa, 8 MPa, 10 MPa, and 12 MPa (a) Density (b) Specific heat (c) Thermal Conductivity and (d) Viscosity. The critical point for CO₂ is 304K and 7.37 MPa.

1.2 EQUATIONS OF STATE (EOS)

While there is a diverse and growing number of applications for supercritical phase fluids, the sensitivity near the critical point makes experimental measurements for properties challenging to obtain.¹¹ Beyond sensitivity in this region, other difficulties facing experimental testing include procurement of materials that will not corrode at high temperatures and can withstand the high P_{cr} of many supercritical fluids.¹²⁻¹⁴ Finally, because of elevated temperature and pressure conditions, experimental set-up shortcomings, such as flow through a heated pipe, have led to insufficient

comprehension of heat transfer properties or no experiments being carried out at all for flow-field velocity and temperature measurements.^{15, 16}

Given the challenges of applying experimental methods, the increasing ease and availability of computer resources have led to more reliance on simulations to aid the design of supercritical phase systems. An essential first step in setting up a simulation is selecting an appropriate approach for modeling the relationship between pressure, temperature, and volume. The algebraic relationship between pressure, temperature, and volume are called an Equation of State (EoS). While the advantages of simulations are well established, a disadvantage is that the selection of an inappropriate physics model, like an improper EoS, leads to inaccurate results.^{17,}

¹⁸

Inaccuracies caused by EoS selection in computer simulations may be compounded by extreme variation in transport properties near the critical point¹⁹. For example, thermal conductivity, k , spikes near the carbon dioxide critical point²⁰, see Figure 1c. The variation in k can lead to phenomena such as non-linear particle-fluid heat transfer²¹. Viscosity, μ , also undergoes a rapid change near the critical point, see Figure 1-1d.²²

Accurately calculating density, ρ , and specific heat, c_p , near a material's critical point requires replacing the rudimentary ideal gas law (IGL), $P/\rho = Pv = RT$, with an EoS that considers real gas behavior. The Virial EoS's are polynomial series in P or inverse v whose coefficients are functions only of temperature. While more accurate than the IGL, Virial EoS are only appropriately applied at low pressure and only for pure fluid calculations.²³

Analytical real gas EoS approaches provide more accuracy than a Virial EoS in estimating properties. Analytical EoS's allows for the straightforward derivation of thermodynamic properties and direct analytical or numerical solutions. A cubic EoS (cEoS) is an analytical EoS

that is at least cubic in v . There are many cEoS models, but two commonly applied are the Soave-Redlich-Kwong (SRK) ²⁴ and the Peng-Robinson (PR). ²⁵ The SRK cEoS extends the Redlich-Kwong (RK) cEoS²⁶, which itself is an extension of the van der Waals cEoS. ²⁷ The PR cEoS was developed to provide reasonable accuracy near a material's critical point for polar and associated substances. While analytical real gas cEoS's estimate properties more accurately than a Virial EOS, cEoS still has over 50% error near a material's critical point. ²⁸

For increased accuracy beyond the ability of a cEoS model approach, a nonanalytic EoS should be selected. Nonanalytic EoS is the most accurate approach for estimating the complex property behavior near a material's critical point. The experimentally centered ultra-high accurate nonanalytic EoS are thus used by researchers seeking the highest degree of precision, such as the US National Institute of Standards and Technology's (NIST) Reference Fluid Thermodynamic and Transport Properties (REFPROP) software. ²⁹ Nonanalytic EoS that can be derived from the Helmholtz energy formulation are called Wagner models. ³⁰ A full Wagner EoS can contain over 40 parameters whose values are obtained by regression on experimental data for many material properties over a wide range of conditions. ³¹⁻³³ The numerous parameters in a Wagner EoS lead to material properties having <0.1% error near the critical point. ²⁸ Regarding EoS of solid substances covering a different set of thermodynamic modes of excitations than supercritical phase fluids, Latimer *et al.* recently completed an evaluation of using density functional theory (DFT) derived EoS as a part of The Materials Project, concluding that Birch (Eulerian), Tait, and Vinet EoS gave the best overall quality of fit. Further details on EoS are detailed by Poling, Prausnitz, and O'Connell, but this brief background to EoS models is sufficient to recognize the role EoS plays in a simulation's accuracy. ^{23, 34, 35} **Figure 1-2** highlights the different results EoS will have for density as a function of temperature for CO₂ at 8MPa.

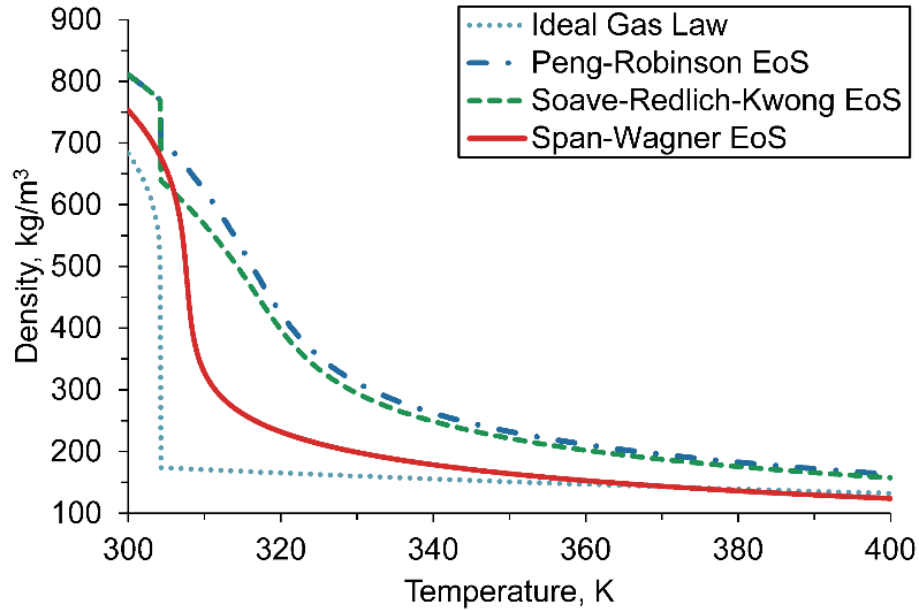


Figure 1-2. Plot of density as a function of temperature for carbon dioxide at 8MPa using four Equation of State (EoS) approaches to highlight the different density values each EoS calculates near the critical point. The critical point for CO₂ is 304K and 7.37MPa.

Lack of recognition EoS selection's role has on accurate simulations leads cEoS to commonly be selected as cEoS's balance computational complexity with reasonable accuracy.³⁶ For example, PR cEoS has been applied for simulations of turbulent flows.³⁷⁻⁴⁰ SRK cEoS has been applied for simulations with turbulent and reacting flows.⁴¹⁻⁴³ PR and SRK cEoS have been applied for simulations with turbulent, reacting, and multiphase flows.^{36, 44-46} High-fidelity simulations using a nonanalytic EoS, like the Helmholtz energy-based Wagner EoS, have rarely been completed. Two sectors that have utilized nonanalytic EoS are turbomachinery design and geothermal systems.⁴⁷⁻⁵⁰ None of these studies examined the sensitivity of their results as a function of EoS models, so it is unknown how EoS selection altered the accuracy, and in turn safety, of these real-world systems.

Research that highlights the role EoS selection has on supercritical phase simulations is insufficient, as noted in a recent review by Vega.⁵¹ Petit *et al.* reported on the effect between PR and SRK cEoS selection accuracy in multiphase and turbulent supercritical nitrogen jet simulation.

⁵² Basha *et al.* studied the effects of EoS choice (Virial, Redlich–Kwong, Soave-Redlich-Kwong, and Peng-Robinson) on the prediction of heat transfer in supercritical nitrogen flow over a horizontal cylinder. Notably, this study did not include a nonanalytic EoS or a near-critical point analysis. ⁵³ The most detailed EoS comparison found was conducted by Zhao *et al.*, who compared the accuracy of IGL, PR, SRK, Wagner, and other EoS models for scCO₂'s material properties near the critical point, concluding that the Helmholtz energy-based Wagner EoS was most accurate. ¹⁷ Furthermore, previous experimental ^{54, 55}, and numerical ^{40, 56-58} literature has established that mixed forced and free convection heat transfer occurs in supercritical phase systems, but decoupling these effects for the pure forced convective case has not been completed. ⁵⁹ To better understand how EoS selection impacts a simulation's accuracy analysis should be conducted for a standard geometry stripped away from layers of complexity that could convolute results. The lack of literature investigating EoS selection's effect on accuracy for near critical point simulations is what motivated the research presented in Chapter 2 of this dissertation.

1.3 CONTINUOUS FLOW SYNTHESIS OF NANOMATERIALS IN SUPERCRITICAL PHASE FLUIDS

Traditionally, the synthesis of nanomaterials is conducted in batch reactors using an autoclave, but the process can take from 12-90 hours. Continuous flow methods can decrease the synthesis time to a matter of seconds, thus making it an attractive alternative for scaling nanoparticle synthesis and motivating the research direction presented in this dissertation of continuous flow reactors for synthesizing nanomaterials. The two classes of materials studied in this dissertation for synthesis in continuous flow reactors using supercritical phase fluids are metal-organic framework (MOF) and metal-oxide materials. Chapter 3 and Chapter 4 study the synthesis of the zirconium-based MOF UiO-66 and the copper-based MOF HKUST-1, respectively.

Focusing efforts on the UiO-66 and HKUST-1 MOFs was motivated by their wide range of applications, heightening their need for scalable synthesis. Synthesis of MOFs other than UiO-66 and HKUST-1 is beyond the scope of this dissertation. Chapter 5 studies the synthesis of the metal-oxide Vanadium (IV) oxide (VO_2) nanoparticles in a continuous flow reactor using supercritical water as a heating and mixing medium. The motivation for studying VO_2 was its applications in thermochromic smart windows and to test if the first principal models developed in Chapter 3 and Chapter 4 would prove helpful in a different fluid, namely water versus carbon dioxide. In turn, this section provides background on the materials studied in Chapters 3-5 and presents relevant literature about previous efforts done for scaling these materials.

1.3.1 *Metal-Organic Frameworks (MOFs)*

Metal-Organic Frameworks (MOFs) are porous coordination polymers with high surface areas and tunable structures.⁶⁰ Hoskins and Robson reported on the potential of porous coordination polymers in the early 1990s, with the term MOF being popularized by Yagi.⁶¹⁻⁶⁴ In the past 30 years, over 90,000 MOF materials have been synthesized, and over 500,000 structures have been hypothesized⁶⁵. These material characteristics are desirable for a wide range of applications, such as catalysis, gas storage, and drug delivery.⁶⁶⁻⁶⁹ Even with such exciting opportunities, current MOF synthesis methods are time-consuming, costly, and produce toxic waste – resulting in unscalable production.^{70, 71}

MOFs are commonly synthesized in solvothermal batch processes.⁷² To promote widespread adoption, MOF synthesis must move towards large-scale manufacturing methods that are fast, environmentally friendly⁷³, and economically favorable.⁷⁴ Continuous-flow methods are desirable for industrial production compared to batch reactors⁷⁵. Many continuous technologies have been explored for MOF synthesis in the past decade, including mechanochemical^{76, 77},

microwave-assisted ⁷⁸⁻⁸⁰, spray drying ^{81, 82}, hydrothermal ^{83, 84}, supercritical water ⁸⁵, and microfluidic ⁸⁶⁻⁸⁸, each with its own set of advantages and disadvantages ^{89, 90}. Rubio-Martinez *et al.* recently reviewed the various synthesis methods, including a discussion of the advantages and disadvantages of each of the approaches. ⁸³

The reaction medium plays a critical role in the synthesis of MOFs; it affects the properties of the MOF (such as specific surface area), the equipment design. Supercritical (sc) fluids can offer several advantages; these fluids have tunable thermophysical properties such as density, viscosity, and specific heat with minor changes to pressure or temperature near the critical point. This tunability of supercritical fluid properties can affect nanoparticle nucleation. ⁹¹ In turn, MOF synthesis in a supercritical environment shows great promise as a scalable manufacturing approach. Production rates are over ten times higher than other continuous-flow methods, and synthesis occurs in seconds instead of tens of hours. ^{85, 92, 93} To our knowledge, before the research presented in this dissertation, there was only one account in the literature of a continuous flow reactor using supercritical phase fluids to synthesize MOFs. The singular report was by Lester and coworkers in 2015 who synthesized the ZIF-8 MOF via a continuous hydrothermal flow synthesis reactor at 24 MPa and 400 °C (critical point for water is $T_{c,H_2O} = 373\text{ °C}$, $P_{c,H_2O} = 22.06\text{ MPa}$). ^{85, 94}

1.3.2 Vanadium (IV) oxide (VO_2)

Vanadium (IV) oxide (VO_2) has garnered attention for its use in energy-efficient thermochromic smart window films and building materials. ^{95, 96} VO_2 has a reversible transformation from a monoclinic insulating phase (M-phase) to a metallic rutile phase (R-phase) above a critical transition temperature of 68°C. This reversible transformation from M-phase to R-phase makes VO_2 an ideal material for window films that can passively allow in or reflect specific wavelengths of light. ⁹⁷ Previous studies have shown that VO_2 's structural reversibility can be used

to let in near-infrared (NIR) wavelengths felt as heat during cold, winter months (as VO₂ in M-phase is present), and block this NIR heat during hot, summer months (as VO₂ in R-phase is present).⁹⁸ However, despite the extensive historical work done on the material, few affordable commercialized products for VO₂ exist on the market today. It is thought that due to the challenge of working with multivalent vanadium, which exhibits various stable oxidation states (V²⁺, V³⁺, V⁴⁺, V⁵⁺) in addition to its many polymorphs phases (B-, A-, M-, D-, and P-phase), the processing techniques are too complicated, requiring multiple steps that consume both time and energy.⁹⁹⁻¹⁰²

Traditionally, the synthesis of M-phase VO₂ nanoparticles is achieved via a batch method using an autoclave. The batch-method synthesis of the reactants and additives takes extended periods of time, from 12-48 hours, and yields nanoparticles in various sizes and shapes from rods, nanowires, and nano-belts, to snowflakes and spheres, all requiring an additional annealing step to convert the material fully from B-phase to A-phase, and then finally M-phase.^{99, 100, 103} In comparison, continuous flow reactors can be a technology disruptor in the inorganic nanoparticle synthesis industry. Beyond being a scalable synthesis method, continuous flow reactors also provide precise control over operating conditions like flow rate, temperature, and pressure—tunable parameters that can precisely lead to the emergence of desirable material characteristics, like size and shape.^{104, 105} In addition to a continuous flow method, raising water above the critical temperature of 373 °C¹⁰⁶ and critical pressure of 22.06 MPa¹⁰⁷ could allow for the scalability of M-phase VO₂ nanoparticles. Supercritical phase water has the distinct properties of allowing optimum supersaturation to occur, maximizing nucleation rates by more than 10³.¹⁰⁸ Additionally, supercritical phase fluids have much lower viscosity, density, and dielectric constants, allowing formerly soluble polar inorganic salts to become insoluble due to the highly hydrolyzing environment; this allows precipitation at much higher rates than in otherwise ambient

conditions.¹⁰⁹⁻¹¹¹ Finally, using water as a solvent instead of highly acidic or highly alkaline media used in many batch syntheses can lead to economic savings and is also a much safer material to work.¹¹²

1.4 DISSERTATION OUTLINE

This dissertation is organized into six chapters. Chapter 1 presents the dissertation research motivation, background, and organization. Chapter 2 examines how the equation of state selection impacts accurate results in near critical point supercritical phase fluids simulations. Chapter 3 models supercritical phase carbon dioxide to design a counter current mixing section embedded in a continuous flow supercritical carbon dioxide reactor to synthesize the zirconium-based MOF UiO-66. Chapter 4 expands upon the continuous flow supercritical carbon dioxide MOF synthesis reactor method to synthesize the copper-based MOF HKUST-1 across a matrix of 25 experiments, proving the method's robustness. Chapter 5 shows how the design principles and analysis can apply to a continuous flow reactor using supercritical water to synthesize vanadium (IV) oxide nanoparticles. Chapter 6 closes the dissertation by summarizing the research contributions, highlighting possible future research directions, and outlining recommendations for the scalable and sustainable synthesis of nanoparticles in continuous flow reactors using supercritical phase fluids.

Chapter 2. HOW EQUATION OF STATE SELECTION IMPACTS ACCURACY NEAR THE CRITICAL POINT: FORCED CONVECTION SUPERCRITICAL CO₂ FLOW OVER A CYLINDER

2.1 INTRODUCTION

The objective of the work reported in this chapter is to understand how the equation of state (EoS) selection affects forced convective heat transfer numerical simulation results near the critical point. The chapter's objective is met by studying a canonical problem: single-phase supercritical CO₂ two-dimensional laminar flow around a heated or cooled circular cylinder. The research described in this chapter has been published in the Journal of Supercritical Fluids. Copyright permissions for the inclusion of the published research in this dissertation are outlined in Appendix E.¹¹³ This research has also been presented at the 72nd Annual Meeting of the American Physical Society Division of Fluid Dynamics.¹¹⁴

CO₂ was selected as a representative fluid for simulations because of its use in a wide, and growing, number of applications. Due to the diffused interface typically observed in supercritical flows, approaching the critical point from above allows for a single-phase flow system, thus reducing the possible convolution with multiphase flow systems.¹¹⁵ Limiting the study to forced convective heat transfer decouples the two modes of convective heat transfer, allowing for clear recognition of EoS selection implications. Studying external flow over a bluff body allows for analysis to be conducted on how flow structure changes as the cylinder is heated and cooled and how EoS selection impacts the ability of simulations to predict these changes. Four different models with varying levels of complexity and accuracy were employed using identical boundary conditions: Ideal Gas Law, Soave-Redlich-Kwong (SRK) cubic EoS, Peng-Robinson cubic EoS,

or the Helmholtz energy-based Span-Wagner EoS. As mentioned previously, the ultra-accurate Helmholtz energy based EoS model for CO₂ was developed by Span and Wagner, thus it is referred to as Span-Wagner (SW) EoS. The results obtained by different EoS are then presented, allowing for the selection of an appropriate EoS to balance accuracy with computational cost. An extended set of simulations using the SW EoS, underscores how temperature variations near the critical point create non-linear behavior. Validation of IGL and isothermal simulation results against experimental measurements, as well as comparison of the computational cost related to EoS complexity, are included. Thus, a total of 99 single-phase cases were simulated above CO₂'s critical point at the isobaric condition of 8MPa, both with and without heat transfer near CO₂'s critical point (304K, 7.38MPa). Developing a new EoS is beyond the scope of the current work.

2.2 NUMERICAL MODEL

2.2.1 *Formulation and derivation of Equation of State (EoS) models*

The simplest method to estimate thermophysical properties is by the Ideal Gas Law (IGL): $PV=nRT$ where R is the gas constant for a substance, and n is the number of moles. The IGL was used in simulations to highlight its inaccuracies and, in turn, discourage IGL use in simulations computed in the supercritical phase. Two cEOS models, the SRK and PR were chosen because of their frequent use in past and current numerical simulations. Equation (1) shows the general form of a cEoS. The five parameters, Θ , b , η , δ , and ε vary depending upon the specific cEoS model chosen. Parameters may be constants or vary with T , composition, or both.

$$P = \frac{RT}{v - b} - \frac{\Theta(v - \eta)}{(v - b)(v^2 + \delta v + \varepsilon)} \quad (1)$$

To obtain parameter values, the compressibility factor, Z , can be applied. Where $Z \equiv \frac{PV}{RT}$. and if

$Z = f_V(T, V)$ Equation (1) turns into Equation (2).

$$Z = \frac{v}{v-b} - \frac{(\Theta/RT)v(v-\eta)}{(v-b)(v^2 + \delta v + \varepsilon)} \quad (2)$$

In turn, outlined in Equation (3) is the cubic root of Z for cEoS found analytically.

$$Z^3 + (\delta' - B' - 1)Z^2 + [\Theta' + \varepsilon' - \delta'(B' + 1)]Z - [\varepsilon'(B' + 1) + \Theta'\eta'] = 0 \quad (3)$$

The dimensionless parameters of Equation (3) are outlined in Equation (4), where V must always

be greater than b , Z is found from a given T , P and parameter values.

$$B' \equiv \frac{bP}{RT} \quad \delta' \equiv \frac{\delta P}{RT} \quad \Theta' \equiv \frac{\Theta P}{(RT)^2} \quad \varepsilon' \equiv \varepsilon \left(\frac{P}{RT} \right)^2 \quad \eta' \equiv \frac{\eta P}{RT} \quad (4)$$

Following, using the corresponding states principle¹¹⁶ the critical constants can be found using

Equation (5) where $\eta = b$.

$$Z_{cr} = \frac{1}{1 - b/v_{cr}} - \frac{(\Theta/BRT_c)(b/v_{cr})}{(1 + \delta/b)(b/v_{cr}) + (\varepsilon/b^2)(b/v_{cr})^2}$$

$$\lim_{V \rightarrow V_{cr}} \left(\frac{\partial P}{\partial v} \right)_{T=T_{cr}} = 0$$

$$\lim_{V \rightarrow V_{cr}} \left(\frac{\partial^2 P}{\partial v^2} \right)_{T=T_{cr}} = 0 \quad (5)$$

Table 2-1 outlines the parameters for SRK and PR cEoS as well as the number (#) of parameters and if the cEoS can be generalized. The reduced temperature, T_r , was defined as $T_r = \frac{T}{T_{cr}}$. The acentric factor, ω , is a commonly used pure component constant for property estimation that is dependent on T_{cr} , P_{cr} vapor pressure and boiling temperature¹¹⁷. For CO₂ the ω equals 0.22394²⁹.

Table 2-1. Parameters for Cubic Equations of State (cEoS)

cEoS	δ	ε	Θ	# of Parameters [†]	Generalized? [‡]
Soave-Redlich-Kwong (SRK)	b	0	$a\alpha(T_r)$	3: $a, b, \alpha(1)$	Y(T_{cr}, P_{cr}, ω)
Peng and Robinson (PR)	$2b$	$-b^2$	$a\alpha(T_r)$	3-4: $a, b, \alpha(1-2)$	N (1-2)

[†]Total number of constant substance-specific parameters including those explicit in $\alpha(T)$. Additional parameters may be included in any temperature dependence of parameters.

[‡]Y means that the corresponding state principal relation exist to connect all parameters to $T_{cr}, P_{cr}, Z_{cr}, \omega$. N means that at least one parameter values are found by data regression of liquid densities and/or vapor pressures while others are critical properties or ω .

Differences in the δ and ε parameters adjust the cubic EoS's density dependence while $\alpha(T)$ adjust temperature dependence. The expression of $\alpha(T)$ for the SRK EoS is: $1 + (2.756m - 0.7)(1 - T_r^{1/2})^2 + m(1 - T_r)$ where $m = 0.484 + 1.515\omega - 0.44\omega^2$. The expression of $\alpha(T)$ for the PR EoS is: $[1 + (0.37464 + 1.54226\omega + 0.2699\omega^2)(1 - T_r^{1/2})]^2$.

The general form of the nonanalytical EoS Wagner model based on the residuals of the Helmholtz energy, Equation (6), is

$A^r/RT = [A(T, v) - A^o(T, v)]/RT$ (6)

where $A^o(T, V)$ is the ideal gas Helmholtz energy at T and V ³⁰. The thermodynamic partial derivative that defines the compressibility factor for Equation (6) is shown in Equation (7)

$$Z = 1 - v \left. \frac{\partial \left(\frac{A^r}{RT} \right)}{\partial v} \right|_{\tau} = 1 + \delta \left\{ \sum_i \sum_j n_{ij} d_i \delta^{d_i-1} \tau^{t_j} + \sum_i \sum_j \sum_k n_{ijk} \delta^{d_i-1} \tau^{t_j} [\exp(-\delta^{c_k})][d_i - c_k \delta^{c_k}] \right\} \quad (7)$$

where n_{ijk} is a fitted coefficient, $\delta = V/V_{cr}$, $\tau = T_{cr}/T$, and d_i, t_j, c_k are integers with various ranges. In total, there can be 393 terms and associated parameters in a Wagner model EoS, but optimization leads to 30-50 terms and associated parameters¹¹⁸.

2.2.2 Governing Equations

If the length of the boundary to the diameter of the cylinder L/d is greater than 10 the cylinder ends can be neglected, simplifying the problem to two dimensions¹¹⁵. The two-

dimensional (2D) study was performed under steady-state conditions as no shedding vortices are present when $Re < 40$ ¹¹⁹. The continuity equation was expressed as

$$\frac{\partial(\rho U_j)}{\partial x_j} = 0 \quad (8)$$

and the conservation of momentum equation was described as

$$\frac{\partial}{\partial x_j}(\rho U_i U_j) = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j} \left[\mu \left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right) \right] \quad (9)$$

and the energy equation was described as

$$\frac{\partial}{\partial x_j} (\rho U_j c_p T) = \frac{\partial}{\partial x_j} \left(k \frac{\partial T}{\partial x_j} \right) \quad (10)$$

where k is the thermal conductivity of the fluid evaluated at the film temperature T_f , which was the average of T_w and T_o . Thermophysical properties were evaluated according to the defined simulation EoS. To focus on the effect EoS selection has on forced convective heat transfer results, the effects of radiative heat transfer and buoyancy forces were not included. The convective heat transfer coefficient h over the cylinder was calculated by Equation (11)

$$h = \frac{q'}{\pi \cdot d \cdot (T_w - T_o)} \quad (11)$$

where q' is the heat flux along the cylinder wall. Nondimensional Reynolds, Re , Prandtl, Pr , and Nusselt number, Nu , were defined, Equation (12), with lengths non-dimensionalized by the cylinder diameter, d .

$$Re = \frac{U \cdot \rho \cdot d}{\mu}, Pr = \frac{\mu \cdot C_p}{k}, Nu = \frac{h \cdot d}{k} \quad (12)$$

The drag coefficient C_D , Equation (13), was defined as

$$C_D = \frac{2F_D}{\rho d U^2} \quad (13)$$

where F_D is drag force on the cylinder. The F_D was computed by integrating the pressure and shear stress over the cylinder.

An incompressible flow assumes ρ is constant, whereas a compressible flow accurately allows for ρ variations. Near a material's critical point, significant ρ variations occur with slight changes in pressure, temperature, or volume. **Table 2-2** quantifies the significant ρ variations that occur with small pressure and temperature changes under conditions used in the current study. A +1% change in pressure results in a 33% change in ρ , furthermore, even a $\pm 0.5\%$ change in pressure results in over at 2.5% change in ρ from the initial condition of $P=8\text{MPa}$. For low-speed flow, and in turn, a low Mach number, M , the impact of an incompressible flow assumption is usually minimal. Although generally minimal in the current laminar conditions, to achieve the objective of understanding how relationships between P , T , and V are handled based on EoS selection in the most accurate way possible, a numerical method that solves for compressible flow was applied.

Table 2-2. Overview of how small pressure, P , changes result in large density changes for conditions used in the current study of near critical point supercritical fluids.

Change in P	Temperature (K)	Density ($\text{kg}\cdot\text{m}^{-3}$)	Percent Change of Density [†]
0% - Initial condition	305	656.77	-
($P_0=8\text{MPa}$)	310	327.71	-
1% increase	305	688.54	4.84
($P=8.08\text{MPa}$)	310	437.76	33.58
1% decrease	305	577.58	12.08
($P=7.92\text{MPa}$)	310	264.45	19.30
0.5% increase	305	660.78	0.61
($P=8.04\text{MPa}$)	310	336.95	2.82
0.5% decrease	305	652.48	0.65
($P=7.96\text{MPa}$)	310	319.24	2.58

[†]From initial pressure condition of 8MPa at that temperature

The applicability of compressible flow ρ variation is further realized in the buoyancy force approximations present in free convection heat transfer calculations. Free convection heat transfer

is a result of buoyancy forces driving the relative motion between the fluid and surface as opposed to an external force driving the motion. Buoyancy forces are a result of a body force, in this case, gravity, g , and a density variation, $\Delta\rho/\rho$, in the fluid. The ratio of buoyancy and viscous forces is modeled by the dimensionless Grashof number, Gr , in Equation (14).

$$Gr = \frac{g(\Delta\rho/\rho)d^3}{\mu^2} = \frac{g(\rho - \rho_o)d^3}{\rho_o\mu^2} \quad (14)$$

The relation of Gr to the relative importance of each mode of convective heat transfer can be described by the nondimensional Richardson number, Ri , where $Ri = Gr/Re^2$ ¹²⁰. The Ri criteria commonly defines which convective heat transfer mode dominates: if $Ri \gg 1$ inertia forces are negligible and natural convection effects dominate, if $Ri \approx 1$ both forced and free convection effects need to be considered, and if $Ri \ll 1$ buoyancy forces are negligible and forced convection effects dominate¹²¹⁻¹²³. This buoyancy criteria, as well as others, was recently reviewed by Huang and Li for supercritical phase fluids⁵⁹. Huang and Li concluded that (1) buoyancy criteria accuracy to experimental results depends on many factors such as characteristic length and flow direction, (2) a buoyancy criterion that works for one fluid cannot be directly applied to another fluid, and (3) discrepancies in criteria to experimental data require new correlations to be defined.

Beyond uncertainty in the criteria to identify which model of convective heat transfer dominates, on a more fundamental level, there is uncertainty about methods to compute Gr . A common assumption made is that density variation is only a function of temperature. This assumption leads to the thermodynamic property of a material's volumetric thermal expansion coefficient, β shown in Equation (15) to be used.

$$\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (15)$$

Then, β is further simplified through the Oberbeck-Boussinesq approximation ¹²⁴ where $\beta \approx -\Delta\rho/\rho\Delta T$ reducing to $\Delta\rho \approx \rho\beta(T - T_o)$. Recently, the validity of Oberbeck-Boussinesq approximation has been questioned for pressure dependent properties ¹²⁵. Beyond pressure dependent property errors, the thermodynamic property β is also subject to error from EoS accuracy. Furthermore, error in β can cascade from Gr calculations into other correlations such as the Rayleigh number, Ra which quantifies the strength of a buoyancy induced flow ¹²⁶.

In summary, the decoupling of free and forced convective heat transfer results is key given the uncertainty of criteria to guide the impact of forced versus free convection effects on heat transfer - even at the low Re used in the current study. Additionally, uncertainty in the accuracy of the terms used in such criteria increases the relevance of decoupling convective heat transfer. Conclusively, it is appropriate and reasonable for the current study to focus on forced convective heat transfer of single-phase supercritical CO_2 so that EoS selection effects can be fully recognized.

2.2.4 *Studied geometry and mesh*

The following geometric specifications were used for numerical simulations. The cylinder diameter d was defined as 1cm to avoid surface roughness effects. To eliminate any blockage affects the simulation domain inlet was $10 \cdot d$ upstream, and the outlet was $20 \cdot d$ downstream of the cylinder, for a total length, L , of $31 \cdot d$. Similarly, the simulation domain extended $15 \cdot d$ above and below the cylinder for a height, H , equal to $31 \cdot d$. The domain dimensions meet or exceed those previously used to study flow around a circular cylinder ^{127, 128}. **Figure 2-1a** presents a schematic of the simulation domain.

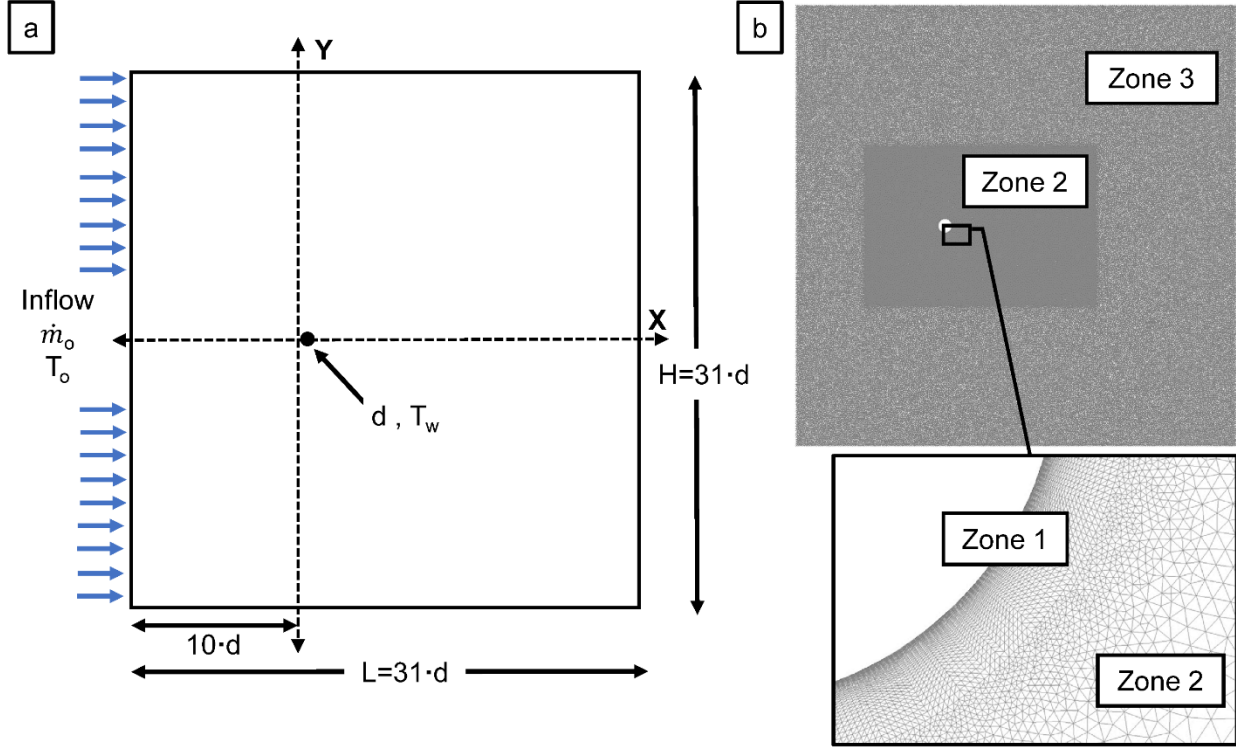


Figure 2-1. (a) Schematic of the simulation geometry including dimensions of the computational domain (b) Mesh of the computational domain with the three mesh structure zones identified

A no-slip, no-throughflow constant temperature boundary condition was set at the cylinder surface. The cylinder wall temperature, T_w , was set at 305 K, 310 K, 350 K, or 390 K. All cases were performed at isobaric pressure, P_o , of 8 MPa for $T_{ps}=307.8$ K. The inlet boundary condition was an inlet temperature, T_o , and an inlet mass flow rate, $\dot{m}_o$, calculated by Equation (16)

$$\int \rho \vec{U} \cdot d\vec{A} = \sum_{i=1}^n \rho_i \vec{U}_i \cdot \vec{A}_i \quad (16)$$

where A is the facet area. The two T_o were defined (1) above T_{cr} and below T_{ps} at 305K ($T_{cr} < T_o < T_{ps}$) and (2) above T_{cr} below T_{ps} and 310K ($T_{cr} < T_{ps} < T_o$). As mentioned earlier in this manuscript, these temperatures were selected to allow evaluation of the effects in the supercritical phase, without the convolutions introduced by multi-phase flow modeling.

The cylinder wall temperature, T_w , was set at 305 K, 310 K, 350 K, or 390 K. The 305 K and 310 K T_w conditions were computed for two reasons (1) to provide isothermal conditions useful in model validation and creating a baseline for comparison (2) to provide insight into how small temperature changes near the critical point effects simulation results. The 350 K and 390 K T_w conditions were computed to present insight to how relatively medium and large temperature differences between a flow and heated cylinder would impact results. Furthermore, the 350 K and 390 K conditions includes applications like in turbomachinery where operations near 390 K are still considered near the critical point ¹²⁹.

As EoS dictates the value of ρ_o at T_o , constancy between cases was created by using the same $\dot{m}$ based on the ρ_o from the SW EoS that resulted in Re=1, 2.5, 5, 7.5, 10, 15, 20, 25, 30, or 35. Using the same $\dot{m}$ resulted in simulations having a <0.2% difference between desired Re and actual Re. If the inlet velocity, U_o , based on ρ_o from the SW EoS had been used to maintain consistency between different EoS models simulations, would have had over 35% difference between desired Re and actual Re. The outlet boundary condition was a pressure-based outlet.

A tetrahedral mesh consisting of 404,790 elements was created using Pointwise v.14 and is shown in Figure 3b ¹³⁰. The number of mesh elements was arrived at from a grid convergence index test performed at the most extreme temperature gradient and flow conditions simulated -SW EoS, $T_o=305$ K, $T_w=390$ K, and Re=35. Under the discribed boundary conditions three meshes were created with 202,000 elements, 404,790 elements, and 808,900 elements respectively. The Nusselt number values did not change between the 404,790 element mesh and 808,900 element mesh, so to reduce computational cost the 404,790 element mesh was used for simulations. The mesh was based on the cylinder's diameter and split into three zones to ensure all physics would be captured and the dimensionless wall distance $y^+ < 1$ ¹³¹. Due to only the laminar regime being

considered in this study, concerns about mesh independence are minimal, nevertheless, near-wall mesh was designed to adequately resolve both the momentum and thermal boundary layers ¹³². The first zone had cells with an average area of 10^{-6}m^2 that surround the cylinder wall with 50 hexahedral layers of cells at a growth rate of 1.1. This growth rate minimized the element size transition to zone two, the next coarser mesh zone. Zone two consisted of cells with an average mesh size of 10^{-5}m^2 and formed a rectangle around the cylinder five diameters in front, above and below the cylinder and ten diameters behind the cylinder. The third zone consisted of cells with an average area of 10^{-4}m^2 and extended five diameters in front, ten diameters behind, above, and below zone two.

2.2.5 *Solver Algorithm*

Governing equations with the imposed boundary conditions were solved with Ansys Fluent v19.1 ¹³³. The Semi-Implicit Method for Pressure Linked Equations, SIMPLE, scheme was used to couple pressure and velocity in the momentum equation. Spatial discretization for pressure was calculated using a second-order scheme and continuity, energy, and momentum equations were calculated by the second-order upwind scheme. For simulations using the Span-Wagner EoS calculations were carried out by the NIST REFPROP API without modifications. For simulations using the Ideal Gas Law, Soave-Redlich-Kwong, and Peng-Robinson EoS transport properties were curve fit using a user defined function (UDF) with an average absolute deviation (AAD) under 1% to literature data ^{134, 135}. The code for the UDF used are available open access on GitHub (<https://github.com/erasmuss/EquationsofStateData>). The convergence criterion of root mean square residuals for continuity, x-velocity and y-velocity variables was set to less than 10^{-5} and less than 10^{-8} for energy. Given the low Re used in this study a laminar model was applied.

2.3 RESULTS AND DISCUSSION OF EOS SELECTION ON SIMULATION ACCURACY

In this section, the results from the simulation matrix consisting of 99 cases outlined in **Table 2-3** are presented. The validation of the numerical model is presented in 2.3.1. Section 2.3.2 reports on the impact EoS selection has on momentum and thermal field variables. Then, in 2.3.3, results on how the variation of T near the critical point impacts momentum and thermal field variables the high-fidelity Helmholtz energy-based SW EoS. Finally, in 2.3.4 insight is provided regarding the computational cost related to the complexity of EoS selected.

Table 2-3. Summary of the 99-cases (C) of supercritical carbon dioxide at 8MPa simulated at inlet flow temperature (T_o), cylinder wall temperature (T_w), and Reynolds number. The simulation matrix is sectioned by Equation of State (EoS) – Ideal Gas Law (IGL), Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), and Span-Wagner (SW).

EoS	T_o	T_w	Reynolds Number								
			1	2.5	5	7.5	10	15	20	30	35
IGL	305	305	C1		C2		C3				
		310	C4		C5		C6				
		350	C7		C8		C9				
		390	C10		C11		C12				
	310	305	C13		C14		C15				
		310	C16		C17		C18				
		350	C19	C20	C21	C22	C23	C24	C25	C26	C27
		390	C28		C29		C30				
PR	305	305	C31		C32		C33				
	310	350	C34	C35	C36	C37	C38	C39	C40	C41	C42
		390	C43		C44		C45				
SRK	305	305	C46		C47		C48				
	310	350	C49	C50	C51	C52	C53	C54	C55	C56	C57
		390	C58		C59		C60				
SW	305	305	C61		C62		C63				C64
		310	C65		C66		C67	C68			C69
		350	C70		C71		C72	C73			C74
		390	C75		C76		C77				C78
	310	305	C79		C80		C81				C82
		310	C83		C84		C85				C86
		350	C87	C88	C89	C90	C91	C92	C93	C94	C95
		390	C96		C97		C98				C99

Properties were nondimensionalized to the inlet conditions, Equation (17) shows the nondimensionalized temperature, T^* .

$$T^* = \frac{T - T_o}{T_w - T_o} \quad (17)$$

The nondimensional x-velocity, u^* , density, ρ^* , viscosity, μ^* , and thermal conductivity, λ^* , values are the ratio of u , ρ , μ , and λ to the free-stream inlet values u_o , ρ_o , μ_o , and λ_o respectively. As simulations were carried out at 8MPa the $T_{pc}=307.8K$.

2.3.1

Validation of Numerical Model

Because there are relatively few reliable experimental results near the critical point, the model will be validated by direct comparison with existing correlations for flow over an unheated cylinder. As previously mentioned in the introduction, there are currently no experimental results covering all of the boundary conditions of our supercritical phase external flow numerical simulations. Nevertheless, using isothermal cases the simulations can be validated in two ways. First, the simulation is validated with respect to the two inlet temperatures and for the different Reynolds numbers. A comparison between the drag coefficient, C_D found for isothermal simulated cases at $Re=1, 5, 10$, and 35 along with the correlation based on experimental values¹³⁶ is shown in **Figure 2-2** for the Helmholtz energy-based Span-Wagner (SW) EoS. The results show good agreement with experimental results, validating the simulation method.

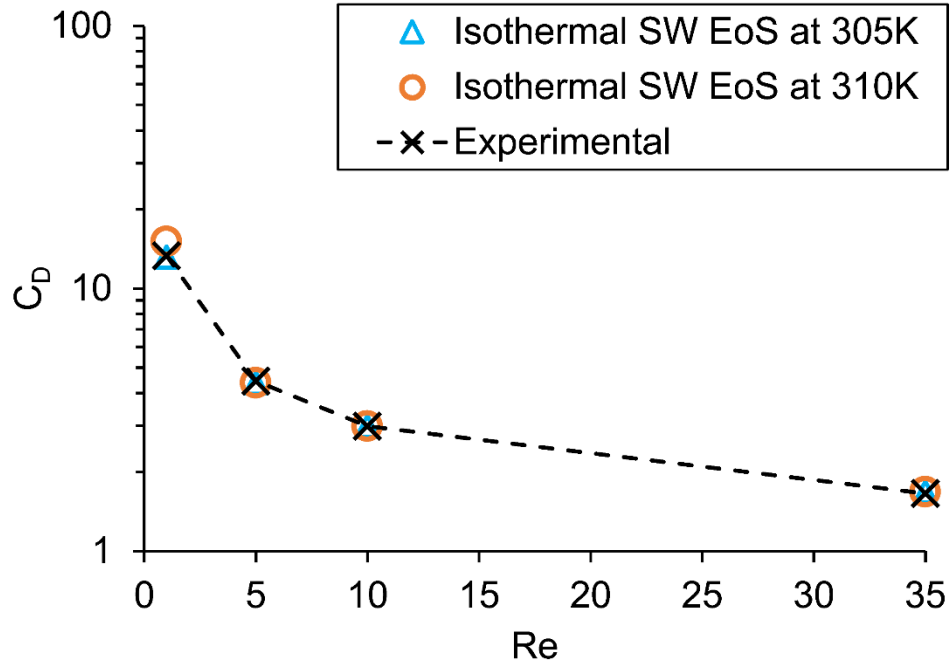


Figure 2-2. Plot of the Reynold Number, Re , and Drag Coefficient, C_D , of supercritical carbon dioxide at 8MPa for the isothermal case of inflow temperature, T_o , equal to cylinder wall temperature, T_w , $T_o=T_w=305K$ and $T_o=T_w=310K$ and experimental correlation ¹³⁶.

Second, the same approach can be used for all four EoS models for isothermal flows at low Mach numbers, simulations with different EoSs should show slight variation in the drag coefficient, since they will have constant properties. **Table 2-4** shows C_D obtained using the different EoS methods agree well with each other and the experimental literature for unheated cylinder cases. The drag coefficients for the unheated cylinder cases are within 0.5% of previously reported values of C_D at the simulated Reynolds numbers, validating the simulation method. In turn, for isothermal flows EoS selection is not expected to impact results.

Table 2-4. Drag Coefficient, C_D , for unheated cylinder case, $T_o=T_w=310K$ at Reynolds number, Re , of 10 obtained from different Equation of State (EoS) and experimental methods.

Method:	Experimental ¹³⁶	SW	PR	SRK	IGL
C_D :	2.99	2.99	2.97	2.97	2.98

This section will present the results from applying four different EoS to simulations with otherwise identical boundary conditions. First, the results for momentum and wake structure will be presented, followed by thermal variables. **Figure 2-3** shows a comparison of the wake structure from simulations with different EoS for the simulation conditions of $T_w=350\text{K}$, $T_o=310\text{K}$ at $Re=35$. As the results show, simulations with IGL predict velocity recovery point downstream of the simulations with non-ideal EOS. Simulations with cubic EoS compared to ultra-accurate Span-Wagner E-S predict similar wake recovery, but the wake structure differs extensively.

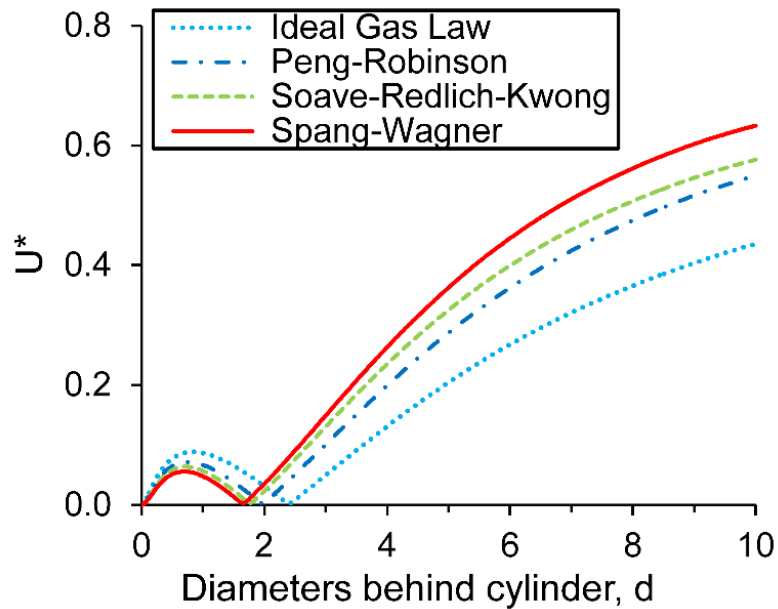


Figure 2-3. Nondimensional x-velocity, u^* of supercritical carbon dioxide at 8MPa and inflow temperature $T_o=310\text{K}$, behind a horizontal circular cylinder at wall temperature, $T_w=350\text{K}$, for Reynolds number, $Re=35$.

The effect of EoS selection can be further realized in **Figure 2-4** where the cases of $T_o=310\text{K}$ and cylinder temperature $T_w=350\text{K}$ is examined. At $Re<10$ IGL and cEoS's SRK and PR underestimate C_D values. When $Re>20$, the cubic EoS begins to overestimate C_D values. The cubic EoS overestimated C_D values by over 18% when $Re=30$, and overestimated C_D values by

over 25% when $Re=35$. Furthermore, increasing ΔT so that $T_w=390K$ resulted in cEoS PR and SRK underestimating C_D by 42% when $Re=5$ and 28% when $Re=10$.

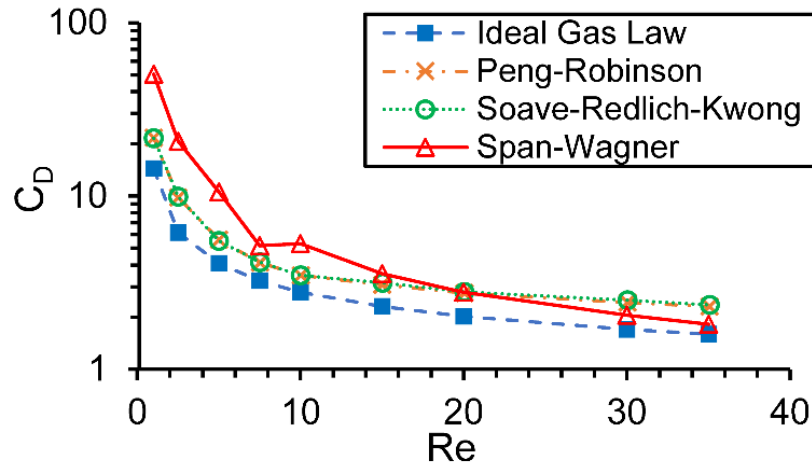


Figure 2-4. Plot of drag coefficient, C_D , and Reynolds number, Re , for supercritical carbon dioxide at 8MPa and inflow temperature $T_o=310K$, for a horizontal circular cylinder at wall temperature, $T_w=350K$. Demonstrates how different Equation of State (EoS) selection will impact dimensionless results.

Next, the effect of EoS selection has on heat transfer will be presented. The first case to be reviewed is for $T_o=310K$ and $T_w=350K$. For this case, the EoS selection resulted in major thermal wake structure differences, **Figure 2-5**. cEoS reported the highest T^* values far from the cylinder wall at both lower Re , $Re=1$, and higher Re , $Re=35$ cases. Compared to the SW EoS cEoS reported a T^* at $10 \cdot d$ behind the cylinder wall at $Re=1$ cEoS reported a 118% increase, and for $Re=35$ cEoS reported 305% increase in T^* value. While the IGL reported, on average, a T^* value 65-82% greater than SW EoS computed values.

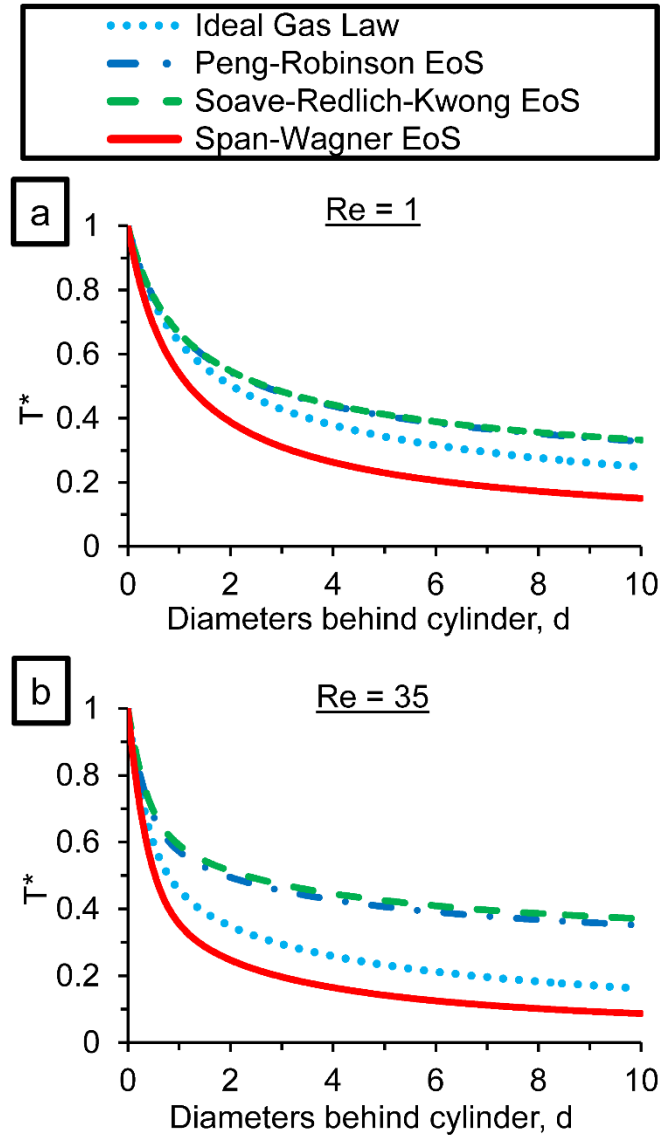


Figure 2-5. Plot of nondimensional temperature, T^* , for supercritical carbon dioxide at 8MPa and inflow temperature $T_o=310K$, behind a horizontal circular cylinder at wall temperature, $T_w=350K$ at Reynolds number, Re (a) $Re=1$ (b) $Re=35$. Demonstrates how different Equation of State (EoS) selection will impact thermal wake structure results.

To visualize the effect that EoS selection has on temperature wake, **Figure 2-6** presents pseudocolor plots of T^* for IGL, PR, and SW EoS.

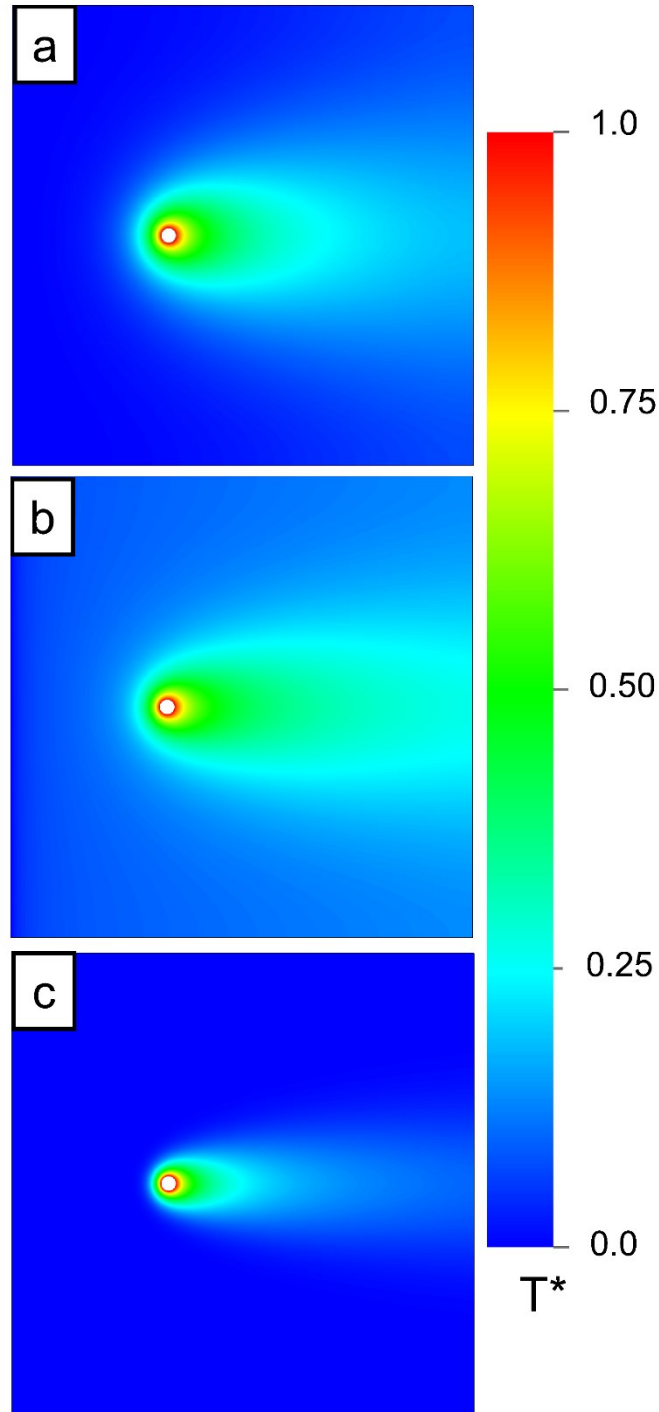


Figure 2-6. Pseudocolor plot of nondimensional temperature, T^* , for supercritical carbon dioxide at 8MPa, Reynold number, $Re=35$ and inflow temperature $T_o=310K$ for a horizontal circular cylinder at wall temperature, $T_w=350K$ using three different Equation of State (EoS) methods (a) Ideal Gas Law (b) Peng-Robinson EoS (c) Span-Wagner EoS

When comparing EoS results for the nondimensional Nu value, **Figure 2-7**, the SW EoS calculated Nu on average of 38% higher compared to IGL, SRK, and PR EoS studied. This significant difference between Nu shows how varied simulation results can be from EoS selection for conductive to forced convective heat transfer. These results demonstrate the importance of decoupling forced and free convective heat transfer to highlight the difference one mode of convective heat transfer has on EoS selection and resulting heat transfer correlations.

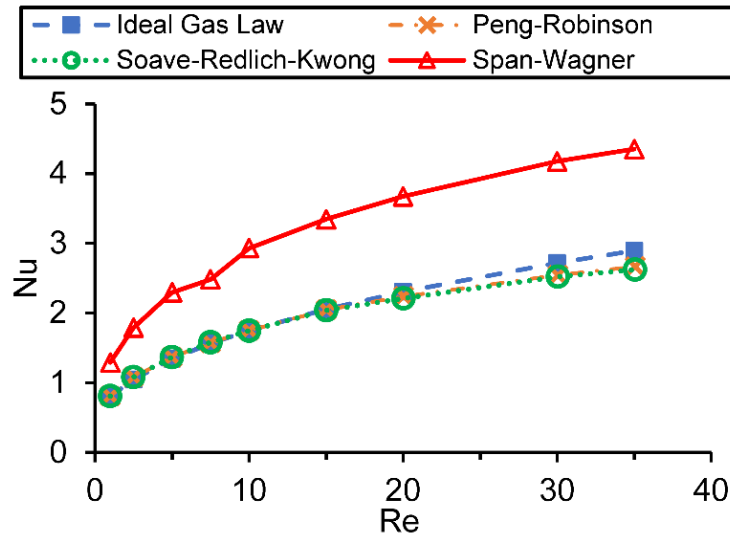


Figure 2-7. Plot of Nusselt number, Nu, and Reynolds number, Re, for supercritical carbon dioxide at 8MPa and inflow temperature $T_o=310\text{K}$, for a horizontal circular cylinder at wall temperature, $T_w=350\text{K}$. Demonstrates how different Equation of State (EoS) selection will impact nondimensional results.

When the cylinder temperature was increased to $T_w=390\text{K}$ for $\text{Re}=1, 5$, and 10 , Figure 2-8 the SW EoS calculated Nu on average 33% higher than IGL and on average 27% higher than the SRK and PR EoS.

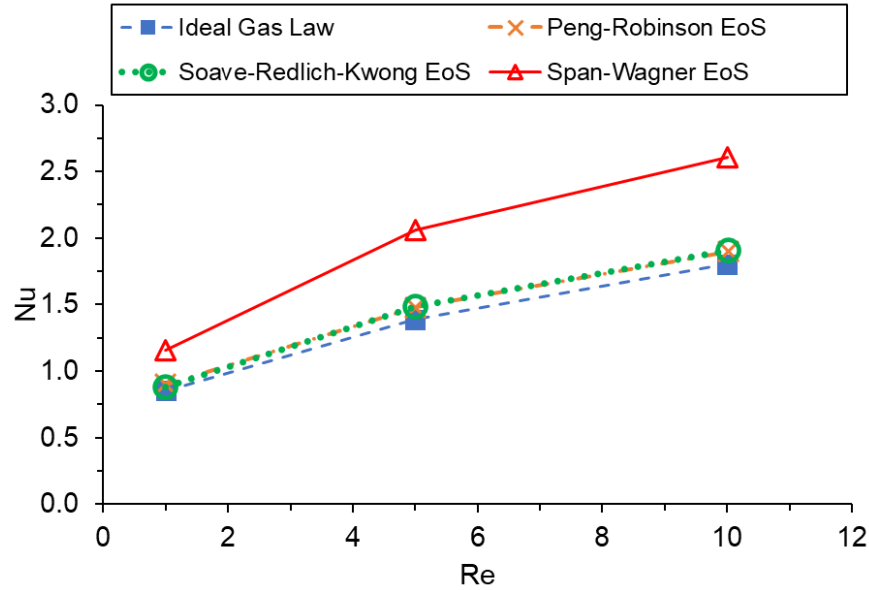


Figure 2-8. Plot of Nusselt number, Nu , and Reynolds number, Re , for supercritical carbon dioxide at 8MPa and inflow temperature $T_o=310K$, behind a horizontal circular cylinder at wall temperature, $T_w=390K$. Demonstrates how different Equation of State (EoS) selection will impact nondimensional results.

2.3.3 *Effects of temperature change near the critical point using Span-Wagner EoS*

With the confidence of the SW EoS accuracy, additional cases were computed to study the effect of temperature changes near the critical point, specifically the effect of a fluid crossing the pseudocritical temperature. **Figure 2-9** shows the magnitude of density variations seen in cases for $Re=1$ and 10. In all the heated cylinder cases considered, the fluid ρ near the cylinder was up to 50 percent the initial inflow ρ value. In extreme cases, the density of the fluid near the cylinder wall was only 20% of the initial inflow flow ρ value. These ρ changes are enough to cause large changes in the overall flow structure. They also suggest that any drag or heat transfer correlation developed using a constant- ρ fluid model is unlikely to provide accurate predictions of flow quantities such as drag force or heat transfer.

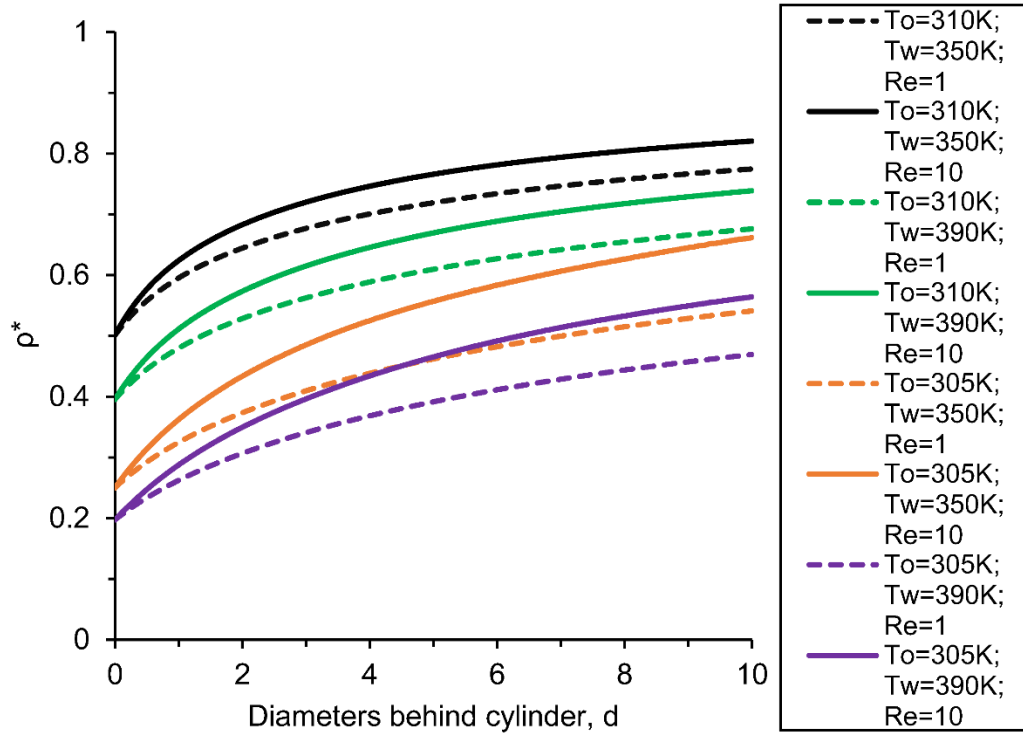


Figure 2-9. Plot of nondimensional density, ρ^* , for supercritical carbon dioxide at 8MPa and inflow temperature T_o , for a horizontal circular cylinder at wall temperature, T_w Re=1 and Re=10. Shows how crossing pseudocritical point (307.8K)

Momentum Variables and Wake Structure

The nondimensional velocity magnitude U^* was defined as the velocity magnitude divided by the free-stream velocity U_o . Pseudocolor plots of U^* for Re=35 and $T_o=305K$ in **Figure 2-10**, highlight the wake structure changes when $T_w=305K$, 310K, and 390K. When a small ΔT is present ($T_w=310K$), the wake structure contracts and the downstream velocity decreases. When ΔT is large ($T_w=390K$), the wake expands, and the downstream velocity increases. However, in both heated cylinder cases, the wake is smaller than for the unheated cylinder case.

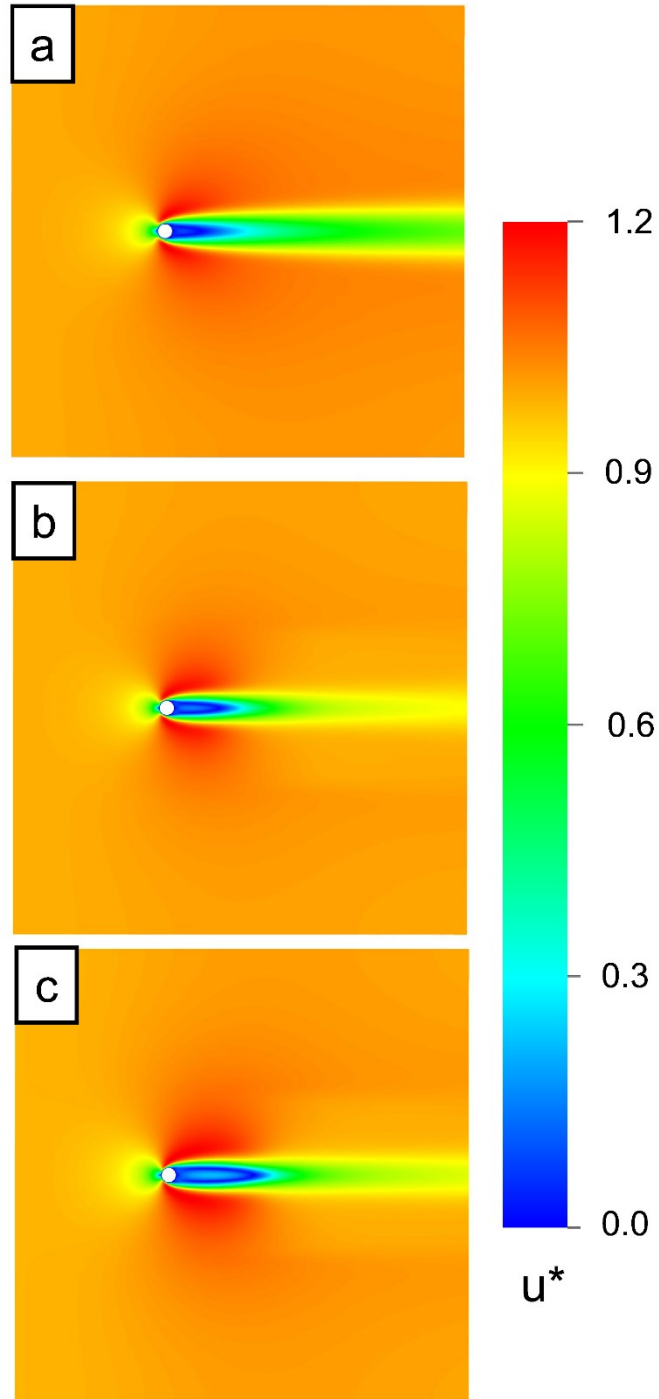


Figure 2-10. Pseudocolor plot of nondimensional x-velocity, u^* , for supercritical carbon dioxide at 8MPa, $Re=35$ and inflow temperature $T_o=305K$ for a horizontal circular cylinder at wall temperature, T_w (a) $T_w=305K$ (b) $T_w=310K$ and (c) $T_w=390K$.

Figure 2-11 shows U^* through the centerline behind the cylinder for $Re=1, 10$, and 35 and a range T_o and T_w . There are three trends visible from these U^* SW EoS results. First, crossing the pseudocritical point by slight cooling, $\Delta T=-5K$, or heating, $\Delta T=5K$ changes the near cylinder wall behavior of external flow, especially if $Re>1$. If the flow crosses the pseudocritical point by heating, recirculation occurred farther from the cylinder wall than if the flow was cooled. In the case of $Re=10$ and $\Delta T=5K$, recirculation was observed at $0.25 \cdot d$ behind the cylinder, while no recirculation occurred when $\Delta T=-5K$. This trend was also observed when $Re=35$, for $\Delta T=5K$ recirculation occurred $2.5 \cdot d$ behind the cylinder versus when $\Delta T=-5K$ recirculation occurred at $1.5 \cdot d$, 40% closer to the cylinder wall. The second trend was if $\Delta T \geq 40K$ and the pseudocritical point is not crossed (T_w and $T_o > T_{ps}$) doubling ΔT will have $<10\%$ effect on U^* , and will not affect flow structure. The lack of sensitivity to changing temperature as long as the pseudocritical point is not crossed is an important observation. It informs that if less sensitive temperature control is available, experiments should be conducted above the pseudocritical point versus operating above the critical temperature. The third trend was that if an external flow ($T_o < T_{ps}$) crosses pseudocritical point ($T_w > T_{ps}$), the Re affects the amount that ΔT will impact far-field U^* and near-field flow structure.

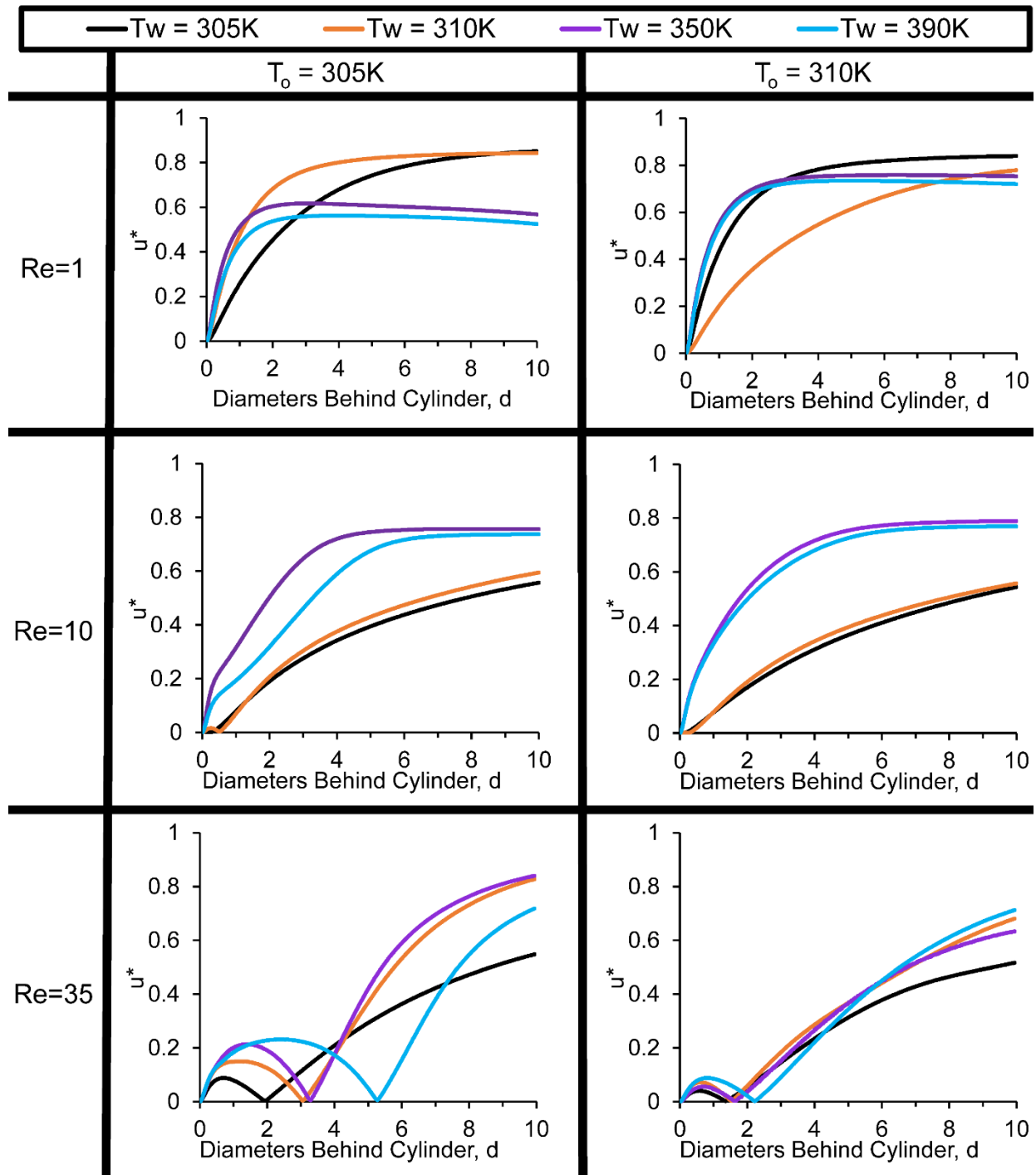


Figure 2-11. Nondimensional x-velocity, u^* of supercritical carbon dioxide at 8MPa and inflow temperature T_o , behind a circular cylinder at wall temperature, T_w , for different Reynolds number, Re . Demonstrates how ΔT between T_o and T_w and crossing the pseudocritical temperature ($T_{pc}=307.8K$) effect wake structure.

A related observation is that drag force on a cylinder for $T_o=305\text{K}$ fluid and $T_w=310\text{K}$ differs significantly from the drag on a cylinder in a 310K fluid with a surface temperature of 305K , suggesting that using average properties to describe the system will not accurately capture all of the physics of the system. The resulting C_D results show heating and cooling of the cylinder has a dramatic effect on the drag coefficient of the cylinder, especially at Reynolds numbers less than 10. Heating increases the C_D value. The case simulated where the cylinder is cooled, $T_o=310\text{K}$ and $T_w=305\text{K}$, shows a decrease in C_D . As expected, the heat transfer was sensitive to fluid velocity, T_o , and T_w .

The large variations in drag and heat transfer seen in the flow of scCO_2 suggest that the overall flow structure changes due to the highly temperature-dependent properties. Inspecting the velocity, temperature, and density fields, as well as the variations in transport properties in the wake, will allow these changes to be characterized in more detail. **Figure 2-12** shows a plot of the Nu versus Re . When $T_w=305\text{K}$, Nu is consistently higher than when $T_w=310\text{K}$. This reflects the effect of the pseudocritical spike in thermal conductivity in this region. As ΔT increases, the impact decreases. These results suggest that the conventional definition of film temperature used in convective heat transfer correlations will be less reliable for scaling results, including supercritical fluids near the critical point.

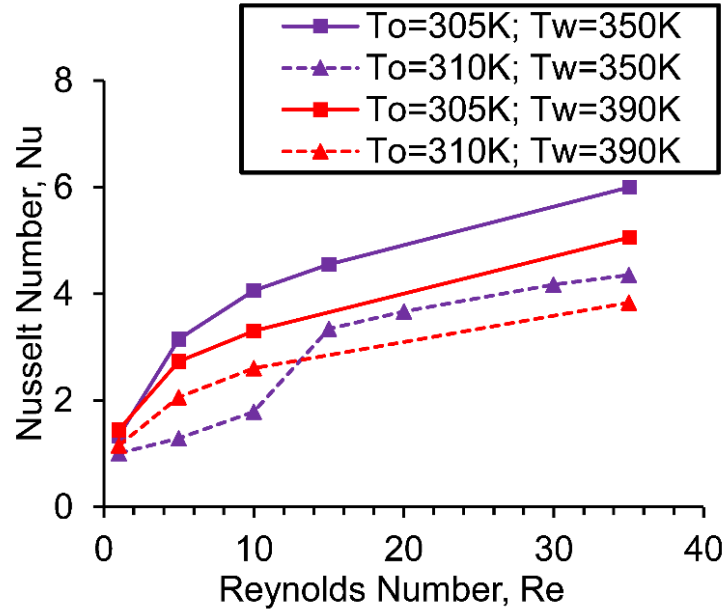


Figure 2-12. Nu versus Re at inflow temperature $T_o=305\text{K}$ and 310K for supercritical carbon dioxide at 8MPa and horizontal circular cylinder at wall temperature, $T_w=305$ and 390K . Note the larger Nu difference observed when a medium ($40\text{--}45\text{K}$) temperature difference is present between a flow and blunt body versus when there is a large ($80\text{--}85\text{K}$) temperature difference.

The most commonly used correlation for estimating Nu based on Re has the form of Equation (18)

$$Nu = C Re_d^m Pr^{1/3} \quad (18)$$

where C and m are fitting coefficients, and Pr is the Prandtl number based on the film temperature.

For Re considered in this work, two different sets of fitting coefficients were applied. At $Re < 4$, a value of $C = 0.989$ and $m = 0.330$ was applied and when $Re > 4$ a value of $C = 0.911$ and $m = 0.385$ was applied. The ability of this relationship, or similar correlations, to predict heat transfer in a sCO_2 near the critical point can be evaluated by computing $Nu \cdot Pr^{-\frac{1}{3}}$ and plotting against Re, as shown in **Figure 2-13**. Instead of reducing onto a single curve, the results clustered in two separate groupings that are more than an order of magnitude difference when the pseudocritical point is crossed.

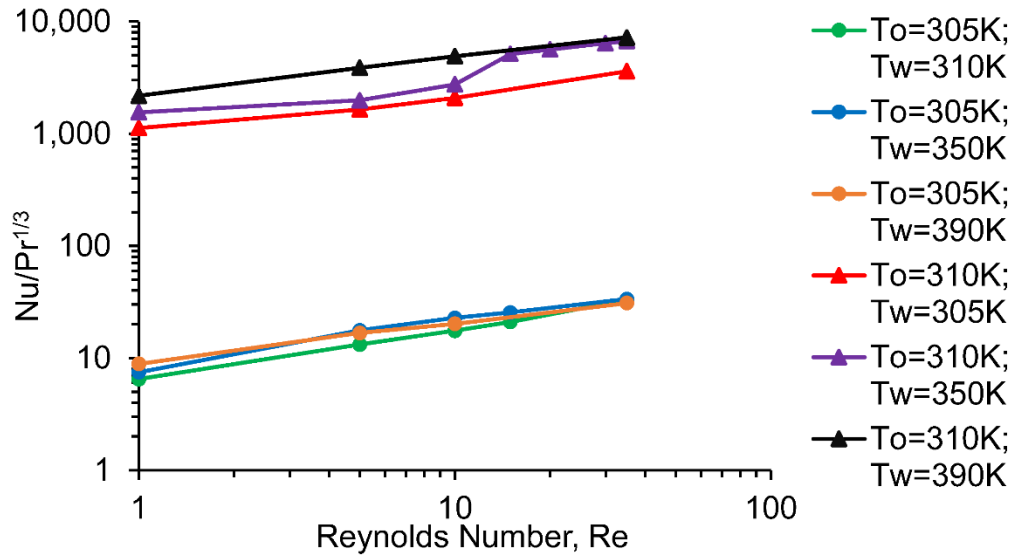


Figure 2-13. Plot of heat transfer correlation, $Nu \cdot Pr^{-\frac{1}{3}}$ and Reynold number, Re for supercritical carbon dioxide at 8MPa and inflow temperature T_o , behind a horizontal circular cylinder at wall temperature, T_w , and Reynold number, $Re=1-35$. If an external flow is below the pseudocritical temperature and crosses the pseudocritical point the heat transfer is over 100 times greater than if the external flow temperature is already above the pseudocritical temperature. This difference in heat transfer is noticed regardless of a small (5K) or large (80K) temperature difference between the external flow and heated cylinder body.

The discrepancy between common correlations and our results can be understood by examining the c_p , k , μ , and Pr as a function of temperature. Pr varies by more than an order of magnitude in the pressure and temperature range studied, as shown in **Figure 2-14**.

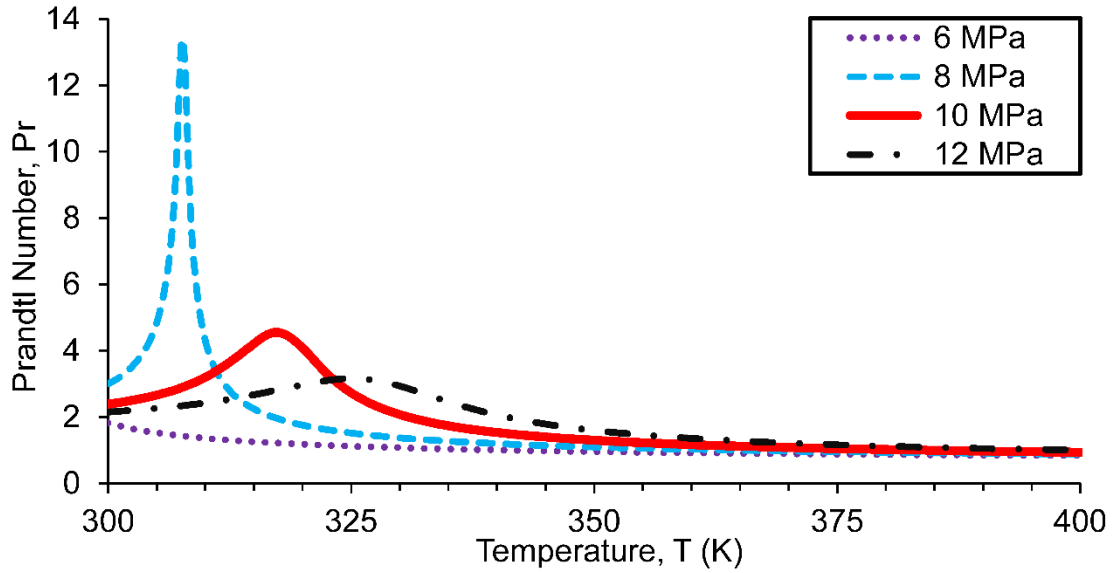


Figure 2-14. Prandtl Number, Pr , as a function of Temperature, T , at different pressures for carbon dioxide (critical point 304K, 7.31MPa).

Figure 2-15 shows the centerline temperatures in the wake for $Re=1$ and $Re=35$ for a range of wall temperatures. This analysis demonstrates that for a heated cylinder the wake is much more persistent when crossing the pseudocritical point. The effects of crossing the pseudocritical point affects the wake structure even at large values of ΔT . The profiles are not self-similar for these cases but appear to approach self-similarity for cases that do not cross the pseudocritical point. For example, at $Re=35$, an abrupt change in the temperature profile behind the cylinder occurs as the T_w increases to 350K and 390K for both $T_o=305K$ and 310K. Finally, a comparison between the heating and cooling cases shows that they maintain similar temperature profiles at a $Re=1$, but have different profiles as Re increases.

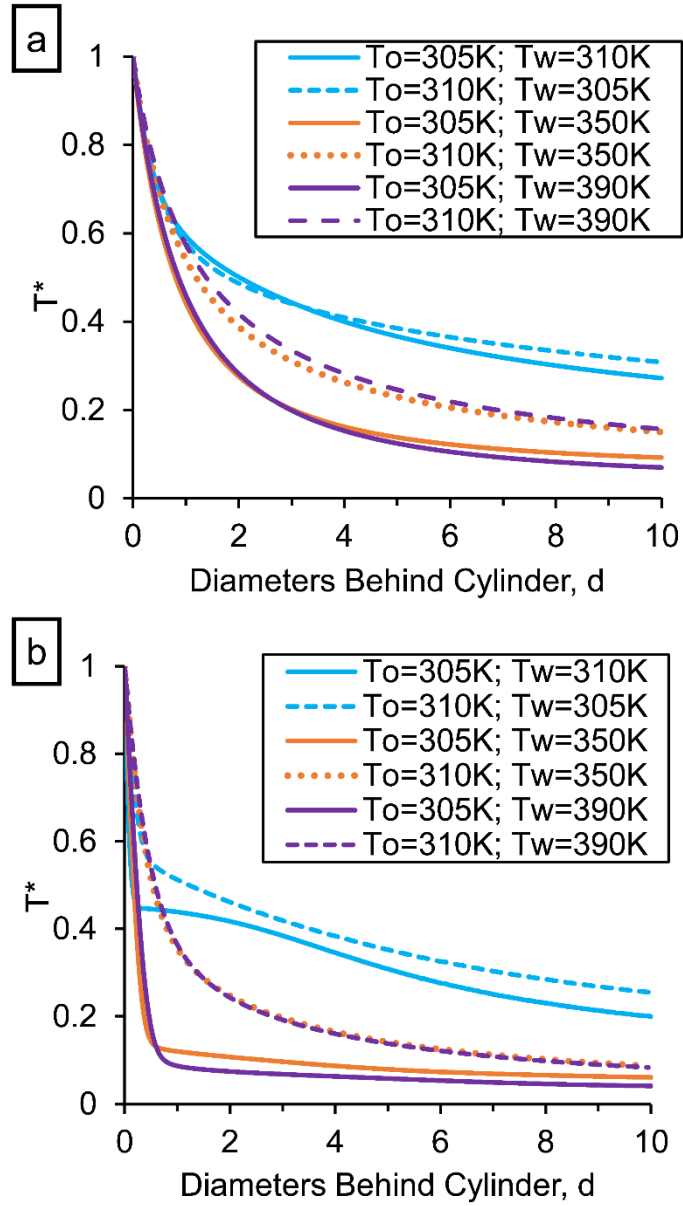


Figure 2-15. Plot of non-dimensional temperature T^* values along the centerline of the cylinder wake at (a) $Re=1$ and (b) $Re=35$ showing that crossing the pseudocritical point has a greater effect on wake structure than Re or temperature difference between the external flow and cylinder.

To visualize the effect that EoS selection has on temperature wake, Figure 2-16 presents pseudocolor plots of T^* for $To=305K$ at $Re=35$ with wall temperature $T_w=310K$ and $T_w=390K$.

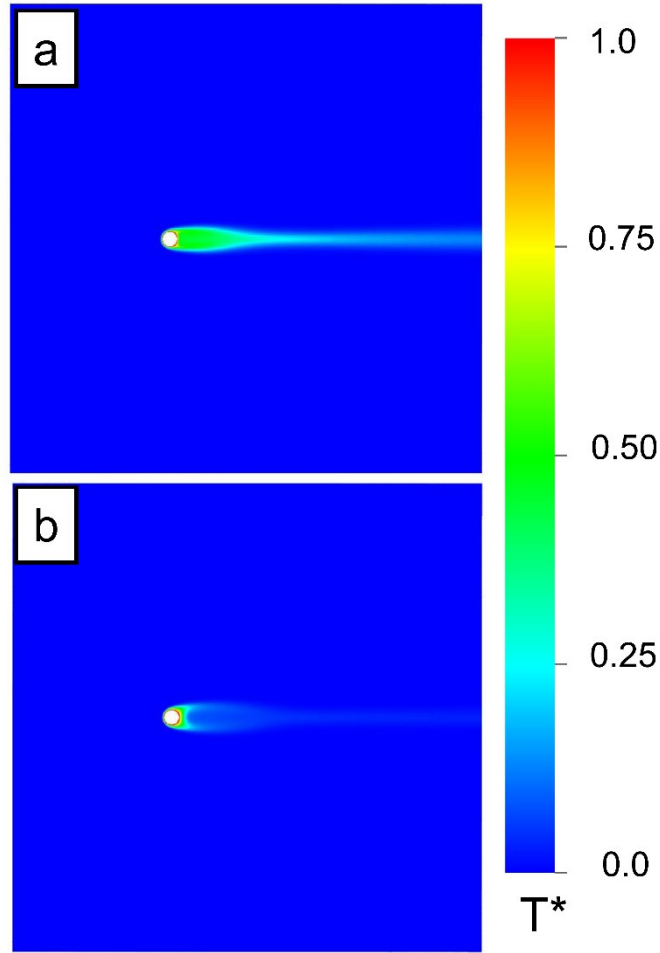


Figure 2-16. Contour plot of nondimensional temperature, T^* , of supercritical carbon dioxide at 8MPa for inlet flow temperature $T_o=305\text{K}$ at $Re=35$ for a horizontal heated circular cylinder with wall temperature of (a) $T_w=310\text{K}$ and (b) $T_w= 390\text{K}$

2.3.4

Computational cost and EoS selection

It is valuable to identify the relationship between simulation accuracy and computation cost to appropriately and optimally apply limited computing resources^{137, 138}. To study the accuracy-to-computation cost relationship across EoS selection, the case of $Re=10$, $T_o=310\text{ K}$, $T_w=390\text{ K}$, was simulated using IGL, SRK, PR, and SW EoS. For IGL, a case where the transport properties are defined as a single constant value was completed to see the effect on computation time. All simulations were performed on the Peregrine supercomputer located at the U.S. Department of

Energy National Renewable Energy Laboratory (NREL). Cases were computed in parallel across 16 cores on a single node containing the Intel(R) Xeon(R) E5-2670 v3 processor. Presented in Table 2-5 is the number of iterations, wall time, and time per iteration.

Table 2-5. Comparison of the computational cost required for different Equations of State

Equation of State	Number of Iterations*	Time to Compute (h:min:s)	Time/Iteration (s)
Ideal Gas Law [†]	8233	2:58:16	1.30
Ideal Gas Law [‡]	8862	6:42:59	2.72
Soave-Redlich-Kwong	4087	4:16:09	3.75
Peng-Robinson	4079	4:14:57	3.74
Span-Wagner	1703	5:00:51	10.60

* Needed for root mean square residuals of continuity, x-velocity and y-velocity variables to be less than 10^{-5} and less than 10^{-8} for energy

[†] Constant value for transport properties

[‡] User defined function for transport properties

Results showed more complex EoS's did require more time to compute, but surprisingly also required fewer iterations for the solution to converge. The SRK and PR cEoS models required about half the iterations compared to an IGL model, but 43% more wall-time. The increased computational time could be because of the increased complexity of the cEoS calculation of properties at each iteration compared to IGL. This reasoning is proven with the number of iterations between the two IGL simulations being relatively equal, but a 125% increase in the wall-time occurred when the model allowed for the transport properties to vary with temperature. The increased wall-time for IGL with variable transport properties lead to the method having a 35% greater wall-time than the high-fidelity SW EoS method wall-time. Compared to the SRK cEoS, the SW EoS required less than half the number of iterations and only 17% more wall-time.

2.4 CONCLUSIONS AND FUTURE WORK

This chapter comprehensively investigates the effect EoS selection has on numerical simulations through a 99-case simulation matrix. The simulation matrix consists of single-phase scCO_2 2D laminar isobaric external flow at 8MPa with $\text{Re}=1\text{-}35$ and two T_o , both above T_{cr} , one below T_{ps} ($T_o=305\text{ K}$) and the other above T_{ps} ($T_o=310\text{ K}$). The external flow travels over a horizontal circular cylinder at four different wall temperatures ($T_w=305\text{ K}$, 310 K , 350 K , and 390 K). Large variations in properties lead to thermal and momentum behavior far more complicated than found in fluids of other phases. Furthermore, crossing the pseudo-critical point from above or below results in major differences in recirculation. At low Reynolds numbers recirculation was not observed when crossing the pseudocritical point from above (heated cylinder), but recirculation was observed when crossing from below (cooled cylinder). At high Reynolds numbers, the size of the recirculation region differed by 40% depending on if the pseudocritical point was crossed from above or below. These effects lead to EoS of lower accuracy like the Ideal Gas Law and including the commonly used cubic EoS PR and SRK -to be inaccurate. Thus, it is not recommended to use the Ideal Gas Law for numerical simulations near the critical point. With regard to the use of cubic EoS we reiterate their shortcomings as a warning. Compared to the high-fidelity SW EoS, cEoS's underestimated Nu values by up to 38% and cEoS underestimated C_D values by 18-42%. With regards to the computational cost of EoS selection, high accuracy SW EoS required half the number of iterations of medium accuracy cEoS SRK, while adding only 17% wall-time to simulations. Thus, the computational cost should not be a significant deterrent to applying this higher accuracy EoS to future numerical simulations. These findings pave the way for robust and scalable simulation solutions in the supercritical phase.

Chapter 3. SCALEABLE CONTINUOUS FLOW METAL-ORGANIC FRAMEWORK (MOF) SYNTHESIS USING SUPERCRITICAL CO₂

3.1 INTRODUCTION

The principal objective of this chapter is to develop an environmentally friendly system that uses supercritical carbon dioxide (scCO₂) as rapid heating and mixing medium for metal-organic framework (MOF) nanomaterial synthesis in a scalable continuous-flow reactor. A US patent application and a WO patent application have been submitted based on the work described in this chapter. Appendix D presents the intellectual property details. Additionally, this research has been published in the journal ACS Sustainable Chemistry and Engineering.¹³⁹ Appendix E outlines the copyright permissions for the inclusion of the published research in this dissertation. Presented here is (1) the evaluation of the rate of the transport processes within the reactor's mixer section (Goal: maximize the mixing and heating rate in the mixing section) and (2) the demonstration of MOF synthesis within the reactor via material characterization. The research in this chapter is the first report of MOF synthesis in a continuous flow reactor using scCO₂ as a heating and mixing medium.

Thus far, water (H₂O) has been the supercritical fluid of choice for nanomaterial synthesis, including MOFs.^{92, 140, 141} A disadvantage of supercritical water (scH₂O) is its high critical temperature and pressure values (620K, 22.1MPa)¹⁴², which results in large process energy consumption and expensive materials of construction¹⁴³⁻¹⁴⁵. The high critical temperature of scH₂O also causes the thermal degradation of some MOF precursor materials. For example, N, N-Dimethylformamide (DMF) is frequently used in MOF synthesis because of practical acid-base chemistry and high boiling point¹⁴⁶, decomposes at about 623K, causing ligand defects in MOFs.

¹⁴⁷ Additionally, in scH₂O, precursor materials are subject to hydrolysis degradation. ¹⁴⁸ This thermal and hydrolysis precursor degradation limits the potential of scH₂O based continuous-flow reactors to synthesize a wide range of MOFs. Recently Chen *et al.* studied alternative zirconium MOF generation processes that are designed to avoid thermal degradation during synthesis. Still, the method was completed in a batch process taking 48 hours leading to a production rate of 0.417g·h⁻¹, and many common MOF recipes remain disadvantaged by precursor degradation¹⁴⁹.

In comparison to scH₂O, supercritical carbon dioxide (scCO₂) has a lower critical point (304K, 7.31 MPa) ¹⁵⁰. Thus, a scCO₂ based MOF synthesis method consumes less energy, has a lower reactor construction cost, and avoids the precursor degradation disadvantages of scH₂O. Another advantage of scCO₂ systems is the natural separation of the MOF from the effluent, allowing easy recycling of solvents, thus decreasing waste stream flow ^{151, 152}. In the current work, we use scCO₂ for scalable continuous-flow MOF synthesis to overcome the disadvantages of scH₂O.

Historically, continuous-flow scCO₂ processes focused on applications involving botanical extraction ¹⁵³, coal gasification ¹⁵⁴, and turbomachinery power cycles ¹⁵⁵⁻¹⁵⁷— not on the synthesis of complex materials such as MOFs. Recently in a batch process, scCO₂ was used to synthesize MOFs ¹⁵⁸, but in addition to being non-continuous, the method also had long reaction times, between 3-90 hours. ¹⁵⁹ In contrast to the batch method, a continuous-flow process requires managing phase changes occurring in the reactor. ^{160, 161} Additionally, because thermodynamic properties vary significantly near the critical point, design decisions must consider these nonlinearities. Not fully realizing the complex physics occurring near the critical point could lead to inaccurate, unsafe, and unsuccessful reactor operation. ^{21, 114}

To rapidly create an environment favorable for MOF synthesis, the thermal and mass transfer between the scCO₂ and MOF precursor materials must be optimized. Thus, the design of the mixer is critical. Very broadly, the issues involved in this design include (1) equilibrium solubility to define the maximum amount of scCO₂ that can be dissolved into the MOF precursors, (2) mass transfer to define the rate at which the scCO₂ dissolves into the precursors, and (3) heat transfer to define the rate at which the scCO₂ heats the precursors. We chose a counter-current mixing (CCM) configuration due to its simplicity and previous use in scH₂O reactors^{72, 84, 85, 162, 163}. Tighe et al.¹⁶⁴ performed experimental temperature measurements and computational fluid dynamics (CFD) within a CCM, identifying geometric configurations affecting mixing¹⁶⁵. **Figure 3-1** presents a CCM schematic. For a given a CCM geometry, six key variables influence whether the effluent will be completely mixed before reaching the reactor section (i) the temperature of scCO₂; (ii) the reactor pressure; (iii) the flow rates of scCO₂ and MOF precursor materials; (iv) the inner inlet pipe's inner diameter, d_1 ; (v) the outer inlet pipe's inner diameter, d_2 ; and (vi) the length of the mixing section, ℓ . Here, the mixing section length is defined as the distance from the end of the inner inlet pipe to the reactor section pipe's centreline. These six variables determine the effluent's mass transfer time, heat transfer time, and convective time. The heat and mass transfer processes should be completed within the mixing section before the effluent enters the reactor section¹⁶⁶.

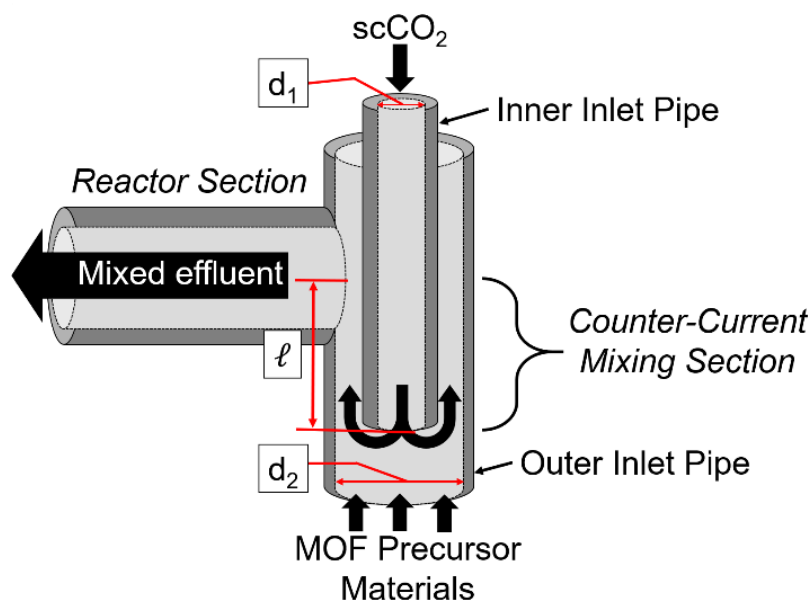


Figure 3-1. Schematic of the counter-current mixing section with design variables identified

3.2 THERMODYNAMIC ANALYSIS FOR CONTROLLING PHASES WITHIN REACTOR

To create an environment friendly for MOF synthesis, and safe for operation, a theoretical thermodynamic analysis was completed for the reactor. **Table 3-1** outlines the states that the CO₂ undergoes during the reactor operation.

Table 3-1. Breakdown of the seven primary states that carbon-dioxide undergoes within the continuous-flow MOF synthesis reactor including different temperature conditions explored for states 2 and 7

	State	Temperature (°C / K)		Pressure (MPa)	Entropy (kJ/kg·K)	Enthalpy (kJ/kg)	Internal Energy (kJ/kg)	Volume (m ³ /kg)	Phase
In CO ₂ tank	1	25	298	3.45	1.9783	468.36	4.23E+02	1.31E-02	vapor
In Cold Bath at 5°C	2*	5	278	3.45	1.881	440.35	4.02E+02	1.10E-02	vapor
In Cold Bath at -5°C	2*	-5	268	3.45	0.95487	187.75	1.84E+02	1.04E-03	liquid
In Cold Bath at -10°C	2	-10	263	3.45	0.91114	176.13	1.73E+02	1.01E-03	liquid
Pumped into reactor	3	25	298	10	1.1713	256.38	2.44E+02	1.22E-03	liquid
Exit Preheater	4	120	393	10	2.0052	532.86	4.73E+02	5.98E-03	supercritical
Exit Mixing Section	5	78	351	10	1.8277	467.08	4.23E+02	4.42E-03	supercritical

Post cooling	6	25	298	10	1.1713	256.38	2.44E+02	1.22E-03	liquid
BPR heated, 110°C	7	110	383	0.101	2.9651	583.37	5.11E+02	7.19E-04	vapor
BPR unheated, 25°C	7*	25	298	0.101	2.7374	505.84	4.50E+02	5.55E-01	vapor

*The state under these conditions was not used for reasons explained in the text

Figure 3-2 presents a temperature-entropy (T-s) graph of these seven states. In turn, two areas of the reactor were identified for analysis. First, the phase changes of CO₂ from the gas cylinder to the reactor. Second, the phase change of the effluent in the reactor throttled through the BPR. This section presents the theoretical methods and resulting calculations used to address these complex areas in the reactor, which defined design and experimental boundary conditions. While complex and worthy of analysis, the mixing section of the reactor will be separately explored in Section 4. The kinetics of MOF synthesis and chemical interaction between scCO₂ and precursor materials is beyond the scope of the current analysis.

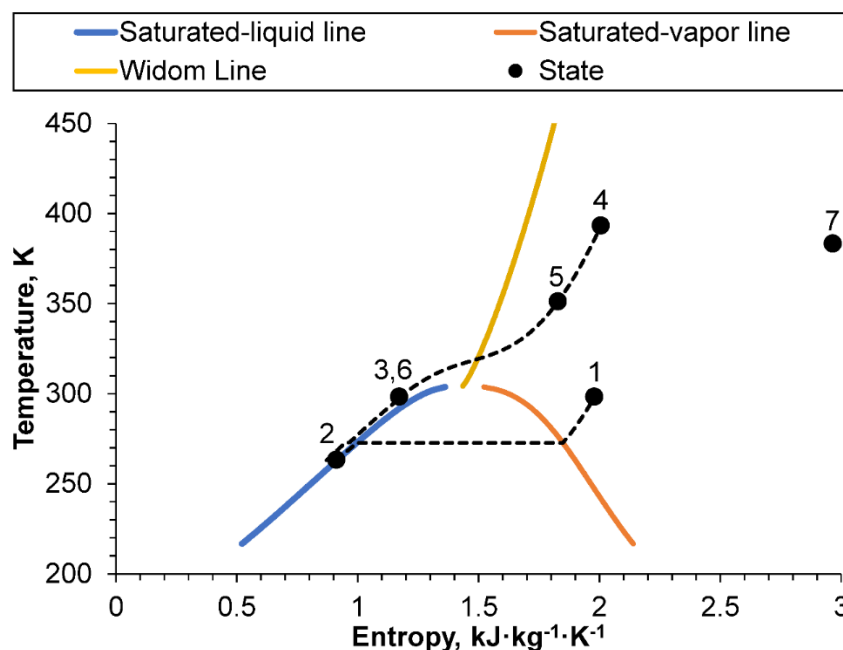


Figure 3-2. Temperature- Entropy plot of the seven states that CO₂ undergoes in the continuous flow MOF synthesis reactor

A commercial supply of CO₂, like the one used for the presented reactor, at ambient room 298 K, and an exiting pressure of 3.45 MPa is in the vapor phase, *State 1*. The pump to be used

was designed for pumping liquid, so the CO₂ would have to be in a liquid phase before entering the pump. As the exiting pressure of a commercial gas cylinder can not be easily increased compared to the temperature being decreased, a cold bath can be employed. A water/ice mixture cold bath can commonly only maintain a temperature of 273 K, but a cold bath mixture to decrease the CO₂ temperature below 273 K is required for liquid phase CO₂ into the pump. Given ambient air heating between the exit of the cold bath and the pump's inlet, a cold bath temperature between 263-268K is suggested, *State 2*. Figure 3-2 shows a temperature-entropy (T-s) plot of the phase change and different cold bath conditions. This single-component phase change analysis and defined conditions of a cold bath complete the first analysis area of the reactor. Once the liquid CO₂ reaches the pump, it will be pressurized to the reactor operating pressure of 10 MPa, and reach ambient room temperature, *State 3*. Then CO₂ will need to be heated above the critical temperature of 311.0 K, *State 4*, before entering the mixing section, *State 5*, followed by cooling from the heat exchanger, *State 6*. After the heat exchanger, the now liquid CO₂ exits the reactor through the BPR. As the BPR acts like a throttle, if left unheated, there will be a large volumetric expansion that could lead to clogs or ice formation. Given this, a heat source is advised to be used to decrease these adverse effects, *State 7*.

3.3 EXPERIMENTAL METHODS

All chemical materials were obtained from the indicated suppliers without additional purification and stored under recommended conditions. The UiO-66 MOF precursor materials are prepared following previously reported methods¹⁶⁷ utilizing the less toxic zirconyl chloride octahydrate, ZrOCl₂·8H₂O, (Sigma Alrich, 98%) metal base compared to the more commonly used ZrCl₄⁷³. The metal precursor reactant 0.1mol (35.40g) ZrOCl₂·8H₂O was dissolved in 200mL (2.58mol) of N, N – dimethylformamide (DMF) anhydrous (Sigma Aldrich, 99.8%) and 1mL of

acetic acid (Sigma Aldrich, 99%) by stirring and ultrasonic treating for five minutes. The organic precursors 0.1mol (18.24g) H₂BDC and 200mL (2.58mol) of DMF were combined and stirred in a second flask and were also ultrasonic treated for five minutes.

The continuous-flow MOF synthesis reactor, shown in **Figure 3-3**, can operate between 298-873K (25-600°C) and 0.101-30MPa. Thermocouples (type K, Omega) connect to a data acquisition module (TC-08, Omega). The data acquisition module was connected to a computer equipped with recording software (PicoLog v.6.1, Pico Technology). All piping and connections were high pressure rated 316 stainless steel (High-Pressure Equipment, Inc). Two High-Performance Liquid Chromatography (HPLC) pumps (model 515, Waters Corp.) initially filled the reactor with DI water, and the reactor is pressurized to 10MPa. The reactor was pressurized using a back-pressure regulator (BPR) (Tescom 26-1700, Branom Instrument Co), and measured using a vibration-resistant gauge (McMaster-Carr).

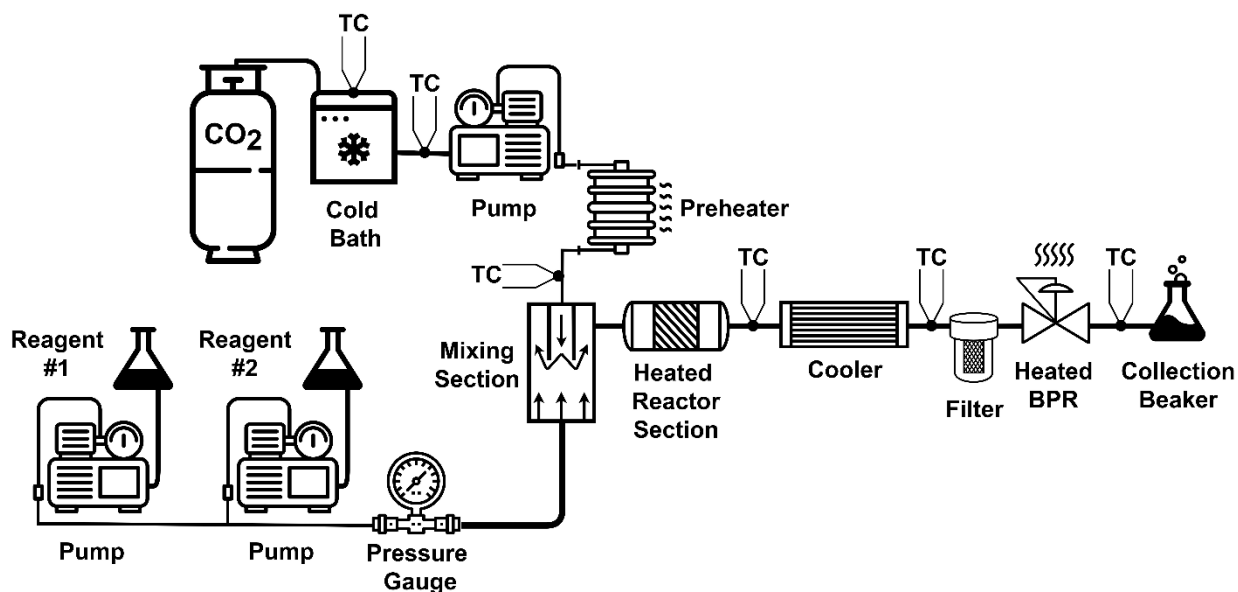


Figure 3-3. Continuous-flow MOF synthesis reactor using supercritical CO₂ to synthesize the zirconium-based MOF UiO-66 with the reactor with components including thermocouple (TC) and back pressure regulator (BPR) identified.

Once the reactor was pressurized, CO₂ was supplied from a gas cylinder (99.99% purity, Praxair). At ambient temperature, the CO₂ was in the vapor phase at 298K and 3.45MPa. The CO₂ HPLC pump (model 305, Gilson) is usually used for pumping liquid, so the CO₂ had to be condensed to the liquid phase before entering the pump. A calcium chloride cold bath (83-87%/technical grade, McMaster-Carr) was used to provide sufficient cooling (263-268K) to ensure that liquid CO₂ entered the pump¹⁶⁸. Following the CO₂ pump, the liquid CO₂ was heated above the critical temperature by a cartridge heater (800W-240V, Tempco) and power control console (Tempco). After the scCO₂ had reached 393K in steady-state conditions, the HPLC pumps are switched to MOF precursor materials and ran at 10ml·min⁻¹. To isolate the role of scCO₂ as a heating mechanism, the MOF precursors were not pre-heated. The ambient temperature MOF precursors were combined in a T-coupling before entering the mixing section, where they were then mixed with scCO₂. The mixture is then passed through the reactor section. Heat loss from the reactor section is minimized by wrapping the section with a heating cable set at 351K with a programmable temperature controller and a layer of ceramic insulation (McMaster-Carr). A heat exchanger (model 2000W Modular Liquid Cooling System, Koolance) cools the effluent to ambient temperature. A tee-type filter with 0.5μm sintered 316 stainless steel element (Swagelok) collected MOFs. The effluent exited the reactor through the BPR. Since the throttling action of the BPR can lead to dry ice formation, a wrap heater was used to avoid this problem. Downstream of the BPR, a flask collected effluent and gaseous CO₂ separated naturally. A photograph of the laboratory setup for the reactor is shown in **Figure 3-4**.

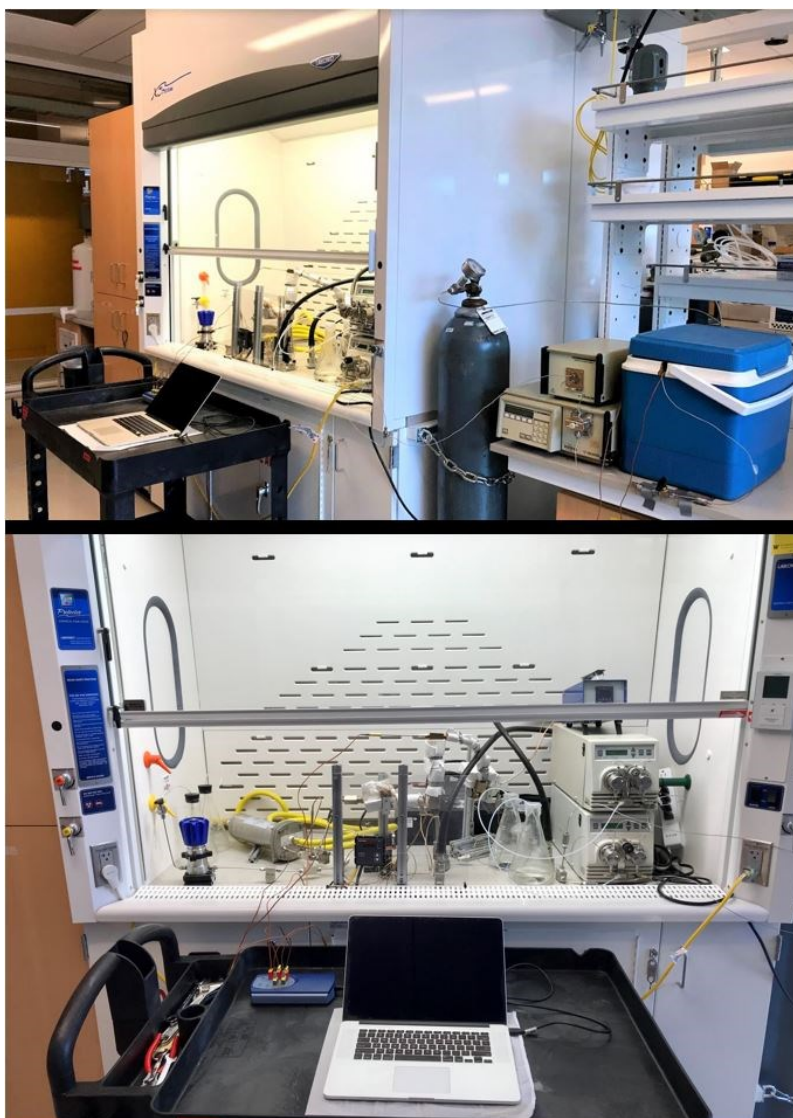


Figure 3-4. Photographs of continuous supercritical CO₂ flow MOF synthesis reactor (top) showing CO₂ cylinder, cold bath, and HPLC pump to the side of the reactor, computer, and thermocouple data logger (bottom) centered showing the reactor, computer, and thermocouple data logger

After collection, the material was activated by following standard procedures¹⁶⁹. Particles were washed with DMF three times to remove any unreacted precursors. The particles are then washed three times with ethanol and centrifuged (Eppendorf, 5910 R) at 10,000 rpm for 3 minutes. The UiO-66 product was vacuum dried at 393K overnight. Final product yield was measured using an analytical balance (Mettler Toledo, ME54TE).

A 15mg homogenous layer of the activated sample was dispersed on a glass slide for powder X-ray diffraction (PXRD) crystallinity characterization. PXRD spectra were collected using a Bruker D8 Discover with I μ S 2-D detector at 50kV, 1000 μ A for CuK α ($\lambda=1.5418\text{\AA}$) radiation at room temperature over the angular range from 5°-60° at a scanning rate of 2deg·min⁻¹. For physisorption analysis, 150mg of the activated sample was further evacuated in a vacuum oven at 383K for 8 hours, then transferred to a pre-weighed sample tube and degassed on a micrometrics Smart VacPrep 067 degassing station at 383K until the outgassing rate was <5 μ mHg. The sample tube was then reweighed to obtain a consistent mass for the degassed sample. N₂ isotherms were obtained using a micrometrics 3Flex machine at 77K using a liquid nitrogen bath. Ultra-high-purity grade, 99.999% N₂ gas was used throughout the experiment (Praxair). Morphology analysis was performed on an FEI Sirion XL30 scanning electron microscope (SEM) at 5kV. For the SEM study, 15mg of the activated sample was dispersed in ethanol and pipetted onto an oxygen plasma cleaned silicon wafer to form a film. The wafer was then placed under a vacuum at room temperature overnight.

3.4 RESULTS AND DISCUSSION

As outlined above, the research objective reported here is to develop a system for the continuous production of MOFs using scCO₂. We initially discuss the attributes of the mixer that are critical for achieving the rapid mixing and heating needed for short residence time operation (Section 3.1). We then report on the characterization of the MOF material produced by this system (Section 3.2). Both sections conclude with discussions of the sustainability of the presented method.

For the heat and mass transfer analysis, the MOF precursors are assumed to consist solely of DMF, as the influent DMF ratio to other precursor materials ranges from a 20:1¹⁷⁰ up to a 133:1 ratio¹⁷¹. Values used in the analysis, presented in **Table 3-2**, were taken as close to the reactor's operating conditions as possible, though the DMF properties are frequently not defined above atmospheric pressure. As DMF remains in the liquid phase, it can be considered an incompressible fluid, and thus thermodynamic properties such as specific heat, density, and thermal conductivity will experience less than a 1% change between atmospheric pressure of 0.1MPa and the 10MPa pressure used in this study. In addition, values for the mass diffusivity, $\mathcal{D}$, were not found for DMF-CO₂ mixtures, so mass diffusivity information for DMF-H₂O mixtures was used as a substitute.

Table 3-2. Properties used for designing the scCO₂ continuous-flow MOF synthesis reactor

Property	Value (unit)	Reference
Mass fraction equilibrium solubility of liquid CO ₂ in CO ₂ -DMF Mixture at 393K, 10MPa	0.29715 (kg)	172
Mass diffusivity at 313K, 0.101MPa (99.92%DMF, 0.08%H ₂ O)	1.63±0.02 (m ² ·s ⁻¹)	173
Density of DMF at 351K, 10MPa*	894.28 (kg·m ⁻³)	174
Density of DMF at 298K, 10MPa*	950.41 (kg·m ⁻³)	174
Dynamic Viscosity of DMF at 351K, 0.101MPa*	4.581E-04 (kg·m ⁻¹ ·s ⁻¹)	175
Specific heat capacity of DMF at 351K, 0.101MPa*	2171.0 (J·kg ⁻¹ ·K ⁻¹)	176
Thermal Conductivity of DMF at 351K, 0.101MPa*	0.1735 (W·m ⁻¹ ·K ⁻¹)	176
Thermal Diffusivity of DMF at 351K, 0.101MPa*	8.916 (m ² ·s ⁻¹)	176
Density of CO ₂ at 351K, 10MPa	226.08 (kg·m ⁻³)	142
Density of CO ₂ at 273K, 10MPa	974.05 (kg·m ⁻³)	142

*Temperature was interpolated from experimental data provided in reference

The inlet temperature of CO₂ (T=393K) and reactor pressure (P=10MPa) were chosen for three reasons. First, these conditions keep the CO₂ in the supercritical phase. Second, at 10MPa scCO₂ properties can be manipulated, but are not so sensitive as to require high-precision controls. Third, 393K provides sufficient temperature to enable the MOF formation reaction without causing thermal degradation of the precursors. At this pressure and temperature, scCO₂ is to the right of

the Widom line and thus behaves similarly to superheated vapor. The precursor materials enter as a compressed liquid; they are not pre-heated and are at $P=10\text{MPa}$. Thus, the system essentially consists of bubbles of scCO_2 vapor rising through liquid DMF [71].

To ensure the DMF liquid is fully saturated with scCO_2 vapor-liquid equilibrium (VLE) data were used to select the flow rates of scCO_2 and DMF. Few VLE solubility studies of DMF- CO_2 mixtures are reported in the literature. Most recently, Shokouhi et al.¹⁷⁷ reported DMF- CO_2 VLE data at $T=305\text{-}353\text{K}$, $P=0.101\text{-}2\text{MPa}$. At this low pressure, CO_2 never reaches the supercritical phase. Byun *et al.* examined DMF- CO_2 VLE to study the mixture's critical properties¹⁷⁸. Jödecke *et al.* also reported DMF- CO_2 VLE solubility data within their investigation of DMF+ H_2O - CO_2 solubility, but their pure DMF- CO_2 experiments covered a lower mole fraction and pressure used in this current study¹⁷⁹. Duran-Valencia et al. reported DMF- CO_2 VLE for temperatures between $293\text{-}338\text{K}$ and $0.101\text{-}12\text{MPa}$ ¹⁷². This research spans the critical point of CO_2 , and within the pressure range of our study, providing a helpful comparison. At equilibrium, Duran-Valencia reported the vapor phase contained almost no DMF ($>0.01\%$); thus, it was assumed the VLE vapor phase consisted solely of CO_2 . To extrapolate Duran-Valencia's three isothermal VLE experiments at 293K , 313K , and 338K , and the Lewis Randall rule was applied to calculate the fugacity of the CO_2 in the liquid phase, see Appendix B¹⁸⁰. Then the Clapeyron-Clausius relationship was used to extrapolate the liquid phase fugacity to 393K . Finally, the Lewis Randall rule was used to estimate the liquid phase fraction of CO_2 at 10MPa and 393K . This resulted in an equilibrium mass fraction of 0.2408g of CO_2 in the liquid DMF. The volumetric flow rates, V , for the CO_2 and DMF are set to of $20\text{mL}\cdot\text{min}^{-1}$, which resulted in mass flow rates, $\dot{m}$, of $0.316\text{g}\cdot\text{s}^{-1}$ for DMF, and $0.324\text{g}\cdot\text{s}^{-1}$ for CO_2 . Given the almost equal mass flow rates, but lower mass fraction solubility, the DMF will be incapable of dissolving all the scCO_2 . This results

in excess scCO_2 , resulting in a two-phase effluent. **Figure 3-5** shows a schematic of the CCM section reaching the vapor-liquid equilibrium.

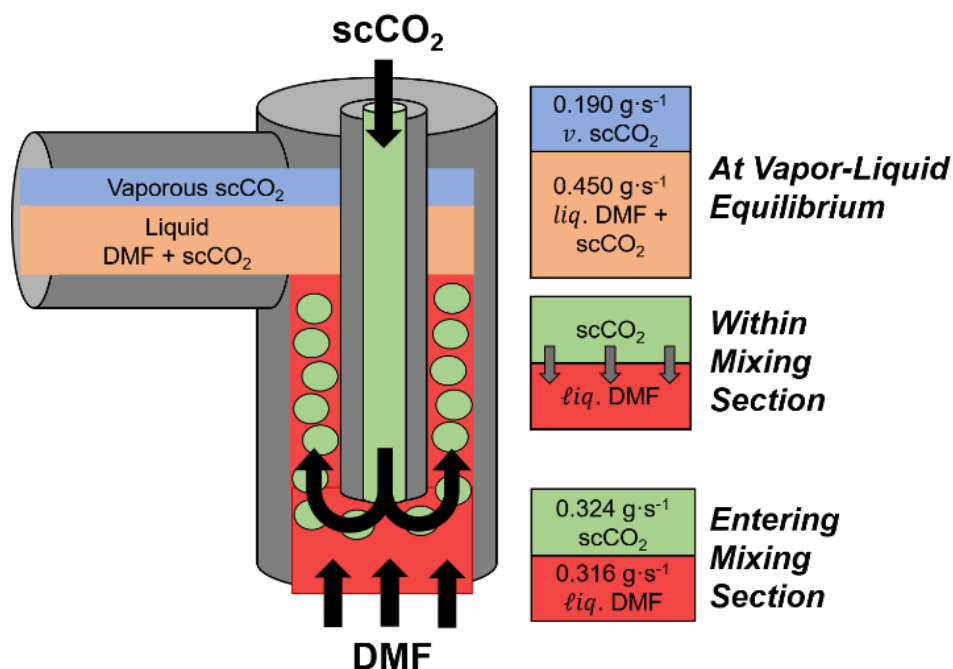


Figure 3-5. Schematic of the continuous supercritical CO₂ flow counter-current mixing section with vapor-liquid equilibrium phases outlined

The mass-transfer rate of scCO_2 into the DMF liquid determines the rate of approach to DMF-CO₂ VLE. The mixture average temperature leaving the CCM is determined using specific heats and mass flow rates at the average temperature of 351K (77.85°C). Property values used from this point are calculated based on this average temperature unless otherwise noted. The scCO_2 bubble diameter, d_b , is defined as the inner inlet pipe's inner diameter, d_1 , 1.52×10^{-3} m (1/8in outer diameter). This size pipe was selected because it balanced the need for a small pipe diameter leading to faster diffusion, with rigidity to keep the tube concentric within the larger mixing section inlet pipe. The bubble terminal velocity, $v_{o,b}$, was found using Equation 1 from the method outlined by Welty et al.¹⁸¹ with the use of drag coefficient, C_D , equation defined by Morrison¹⁸².

$$v_{o,b} = \sqrt{\frac{4 \cdot d_b \cdot (\rho_{CO_2} - \rho_{DMF}) \cdot g}{3 \cdot C_D \cdot \rho_{DMF}}} \quad (19)$$

The scCO₂ bubble's terminal velocity was found to be $v_{o,b}=0.168\text{m}\cdot\text{s}^{-1}$. With a defined DMF dynamic viscosity, μ_{DMF} , the Reynolds number, Re , was calculated as 497, according to Equation (20) ¹⁸³.

$$Re = \frac{d_b \cdot v_{o,b} \cdot \rho_{DMF}}{\mu_{DMF}} \quad (20)$$

Next, using Equation (21) and Equation (22), the Schmidt number, Sc , and Grashof number, Gr , were calculated as 316 and 1.15×10^5 , respectively ¹⁸¹.

$$Sc = \frac{\mu_{DMF}}{\rho_{DMF} \cdot \mathcal{D}_{CO_2,DMF}} \quad (21)$$

and

$$Gr = \frac{d_b^3 \cdot \rho_{DMF} \cdot g \cdot (\rho_{CO_2,inlet} - \rho_{DMF,inlet})}{\mu_{DMF}^2} \quad (22)$$

With these results, the mass-transfer was within the forced convection regime with negligible free convection contribution, $Re \geq 0.4 \cdot Gr^{\frac{1}{2}} \cdot Sc^{-\frac{1}{6}}$. The Peclet number, Pe , was calculated, $Pe = Re \cdot Sc$, as 1.57×10^5 . The relationship by Brian and Halls ¹⁸⁴ shown in Equation (23) for Sherwood number, Sh , was used

$$Sh = \frac{h \cdot d_b}{\mathcal{D}_{CO_2,DMF}} = (4 + 1.21 \cdot Pe^{2/3})^{1/2} \quad (23)$$

resulting in $Sh=85.85$. This yields a convective mass transfer coefficient of a single $scCO_2$ bubble in DMF, h , of $0.0821 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. Thus, the characteristic time for the mass of a bubble of $scCO_2$ to transfer in DMF was 2.15 seconds.

Next, the time it would take for the heat transfer from the $scCO_2$ to DMF was determined. The Prandtl number, Pr , defined according to Equation (24)

$$Pr = \frac{\mu_{DMF} \cdot c_{p,DMF}}{k} \quad (24)$$

where $c_{p,DMF}$ is the specific heat in $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ of DMF, k is the thermal conductivity in $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ resulting in $Pr=5.76$. The Lewis number, Le , in terms of Pr and Sc , $Le = \frac{Sc}{Pr}$ was found to be 54.7. This result shows that heat transport will occur over fifty times faster than mass-transport within the mixing section. The characteristic time it would take the heat of a $scCO_2$ bubble to transfer into the DMF at the defined conditions is 0.0393 seconds.

Based on the calculated characteristic times, the two remaining CCM geometric parameters were set. The outer pipe's inner diameter, d_2 , was set as $5.159 \times 10^{-3} \text{ m}$ (3/8in outer diameter), and mixing section length, ℓ , to $3.81 \times 10^{-2} \text{ m}$ (1.5in). These dimensions created a sufficiently long convective time for both heat and mass transfer to be completed before exiting the mixing section. The convective time for the mixture to flow through the mixing section was 2.39 seconds.

Table 3-3 summarizes the CCM section variables and characteristic times; these deemed sufficient to provide the rapid heating and mass transfer desired before the mixture entered the reactor section.

Table 3-3. Resulting terms, including time scales, for the continuous-flow MOF synthesis reactor using $scCO_2$ mixing section

Calculated Term		Result (unit)
	Temperature of $scCO_2$	393 (K)

<i>Mixing Section Variables</i>	Reactor pressure	10 (MPa)
	Flow rate of scCO ₂ and MOF precursor materials, V	20 (mL·min ⁻¹)
	Inner diameter of the inner pipe, d_1	1.52×10 ⁻³ (m)
	Inner diameter of the outer pipe, d_2	5.16×10 ⁻³ (m)
	Length of mixing section, ℓ	3.81×10 ⁻² (m) or 1.5 (in)
<i>Mass Transfer</i>	Effluent equilibrium temperature	351.1 (K)
	Supercritical CO ₂ bubble terminal velocity, $v_{o,b}$	0.168 (m·s ⁻¹)
	Reynolds number, Re	497.6
	Schmidt number, Sc	315.7
	Grashof number, Gr	1.15×10 ⁵
	Peclet number, Pe	1.57×10 ⁵
	Sherwood number, Sh	85.85
	Convective mass transfer coefficient, h	0.0821 (kg·m ⁻² ·s ⁻¹)
<i>Heat Transfer</i>	Prandtl number, Pr	5.76
	Lewis number, Le	54.7
<i>Characteristic Times</i>	Time for equilibrium <i>mass</i> transfer of CO ₂ into DMF	2.15 (s)
	Time for equilibrium <i>heat</i> transfer of CO ₂ into DMF	0.0393 (s)
	Mixture residence time in the mixing section	2.39 (s)

As mentioned earlier, a drawback of continuous flow scH₂O MOF synthesis is the high energy consumption due to a high critical temperature (647K). The energy, E , consumption required to increase the temperature of H₂O can be easily realized in a simple first law analysis where $E = q = m \cdot c_p \cdot \Delta T$. Starting with room temperature and atmospheric pressure H₂O (298K, 0.101MPa) being pumped into a reactor at a flow rate of 20mL·min⁻¹ for one hour leads to mass of the H₂O being 1209g. Using c_p values from NIST REFPROP at the commonly used⁸⁵ operating pressure of 24MPa, the energy required to increase the temperature of the H₂O above the critical point to an operating temperature of 673K (400°C) is 3037kJ. Using the same method (details provided in Appendix B) for scCO₂ reactor results in an energy consumption of 393kJ, or 13% of the energy required for a scH₂O reactor. Additionally, a hydrothermal reactor with a target operating temperature of 418K results in an energy consumption of about 603kJ. Thus, our scCO₂ reactor consumes only 65% of the energy requirement compared to a hydrothermal reactor. This

first-order analysis demonstrates that the continuous flow scCO₂ reactor has the potential to be more energy-efficient than a comparable continuous flow scH₂O or hydrothermal reactor.

3.4.2 *UiO-66 MOF Synthesis*

Under the described experimental and post-processing conditions, the UiO-66 synthesis yield was measured as 8.71g in 5 minutes, for a production rate of 104g·h⁻¹. To our knowledge, this production rate of UiO-66 is higher than any other values reported in the literature ⁷⁵. **Table 3-4** outlines the methods used to synthesize the UiO-66 MOF as well as the reaction time, production rate, temperature constraints, and solvents recycling capability.

Table 3-4. Comparison between methods to synthesize zirconium-based UiO-66 MOF and reaction time, production rate, synthesis temperature, and option to recycle solvents.

Synthesis Method	Reaction time	Production rate (g·h ⁻¹)	Synthesis temperature ≤120°C	Option to recycle solvents	Reference
Solvothermal batch	24 h	Unreported, estimated <0.1	Yes	No	185
Mechanochemical	75 min	2.28	Yes	N/A – solvent-free conditions	77
Continuous flow – Microwave	7 min	14.40	Yes	No	80
Continuous flow - Microfluidics	15 min	Unreported, estimated <0.1	No	No	88
Continuous flow – solvothermal	10 min	1.68	Yes	No	75
Continuous flow - Supercritical H ₂ O*	< 5 s	250	No	No	85
Continuous flow – Supercritical CO ₂	< 3 s	104	Yes	Yes	this work

*UiO-66 MOF synthesis has not been reported using this method, values are provided for zinc-based MOF ZIF-8

The synthesized UiO-66 properties were found to be consistent with those reported in the literature. Morphology was examined using scanning electron microscopy (SEM) imaging shown

in **Figure 3-6**. Using the commercial Bruker Eva software estimation from the Scherrer formula applied to the PXRD spectra showed the average particle size to be 211nm, which agrees with SEM images taken, Figure 3-6a. SEM image Figure 3-6b highlights larger particles up to 1000nm in size, which agrees with previous reports of continuous flow methods for UiO-66 MOF synthesis¹⁸⁶. UiO-66 has cubic symmetry that frequently appears as cubic crystals, as indicated in Figure 3-6.

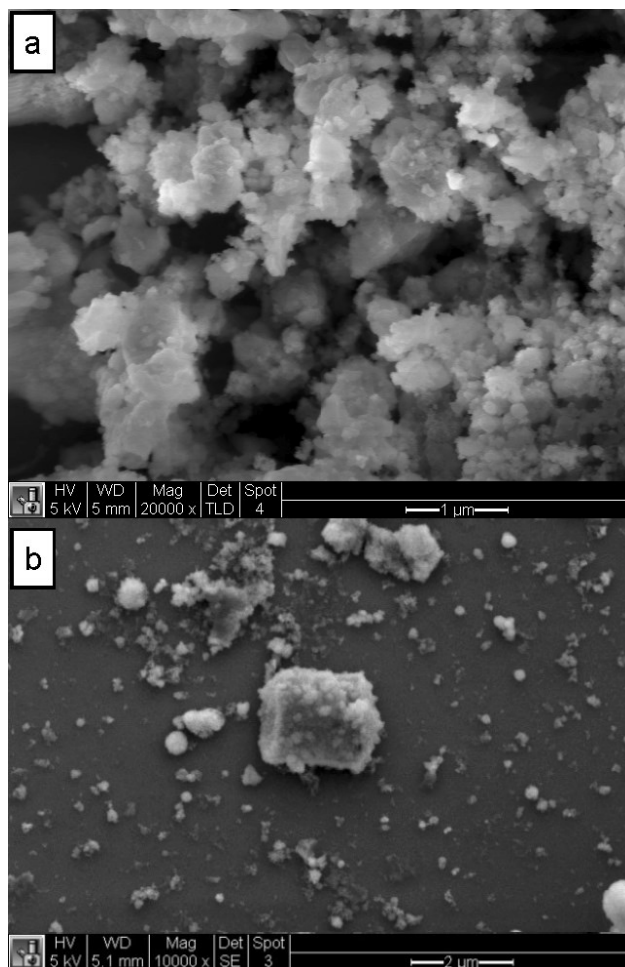


Figure 3-6. SEM images of synthesized UiO-66 nanoparticles (a) smaller UiO-66 particles (b) more dispersed UiO-66 particles highlighting particles of a larger size

Physisorption analysis via N₂ gas isotherms generated the results shown in **Figure 3-7a**. Using the Brunauer-Emmett-Teller (BET) equation the surface area was calculated as 1109.6m²·g⁻¹

¹. Using the Horvath-Kawazoe method the pore size distribution was determined, Figure 3-7b, and the total pore volume was found to be $0.381\text{ cm}^3\cdot\text{g}^{-1}$. The pore size distribution was consistent with prior UiO-66 reports¹⁸⁷⁻¹⁸⁹ with centric octahedral pore occurring at $\sim 12\text{Å}$, corner tetrahedral pores occurring at 8Å that are connected through triangular pores occurring at 6Å . The broad distribution of pores from $8\text{-}10\text{Å}$ is larger than in a batch synthesis method, but it is consistent with other continuous-flow synthesis methods⁷⁵.

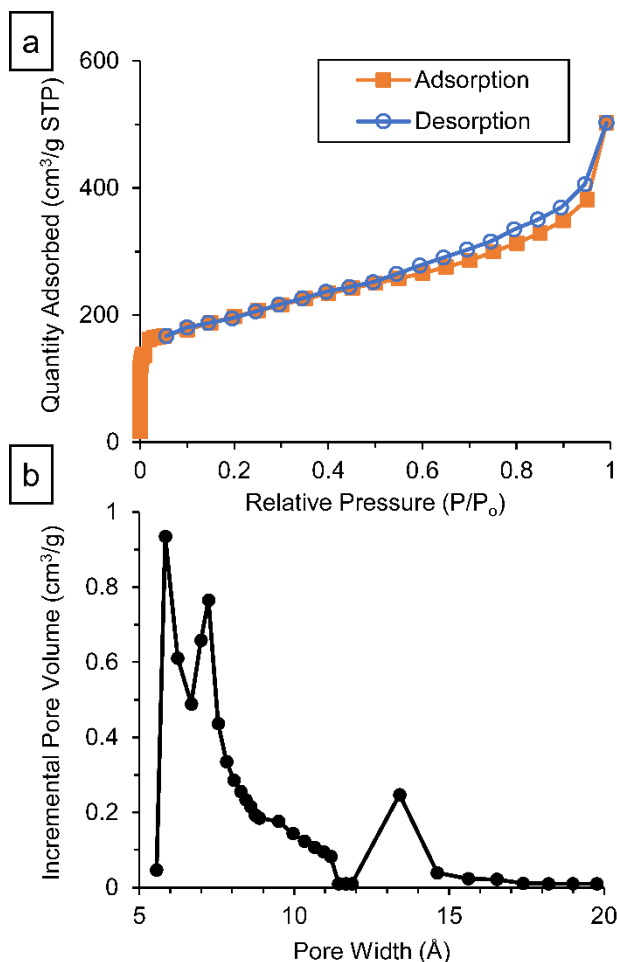


Figure 3-7. Physisorption characteristics of UiO-66 MOF prepared in continuous-flow synthesis reactor with scCO_2 injection at 393K and 10MPa (a) N_2 adsorption and desorption isotherms (b) Pore size distribution based on Horvath-Kawazoe method

Figure 3-8 shows that the powder X-ray diffraction (PXRD) spectra of our sample matches the International Centre for Diffraction Data (ICDD) UiO-66 reference¹⁹⁰.

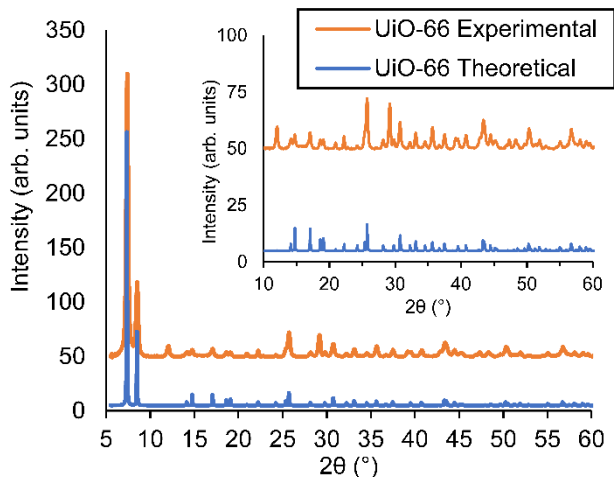


Figure 3-8. Experimental and theoretical PXRD patterns of UiO-66 MOF

In achieving the industrially viable production of MOFs, synthesis is only one of the challenges; the activation of the synthesized frameworks is crucial to obtain maximum use of the material's porosity. Material activation is a time-consuming process that involves a solvent exchange via washing and centrifugation, followed by 2-12 hours of degassing performed in a vacuum chamber ¹⁶⁸. Previous work has used scCO₂ as a MOF activation medium ¹⁶⁹. This suggests that the scCO₂ could also act as an activation medium to reduce the ordinarily twelve-hour degassing time. In our experiments, ten minutes of degassing at 393K in a vacuum oven provided the same surface area and crystallinity as a sample degassed at the same temperature for 12 hours. A sample dried at room temperature for 6 hours, Figure 3-9, shows PXRD spectra characteristic peaks at $2\theta = 7.34^\circ$ and 8.48° but generally showing a more amorphous structure, possibly due to guest inclusion inside the MOF pores. Given these findings, the ongoing investigation within this reactor design includes the activation of synthesized MOFs using scCO₂.

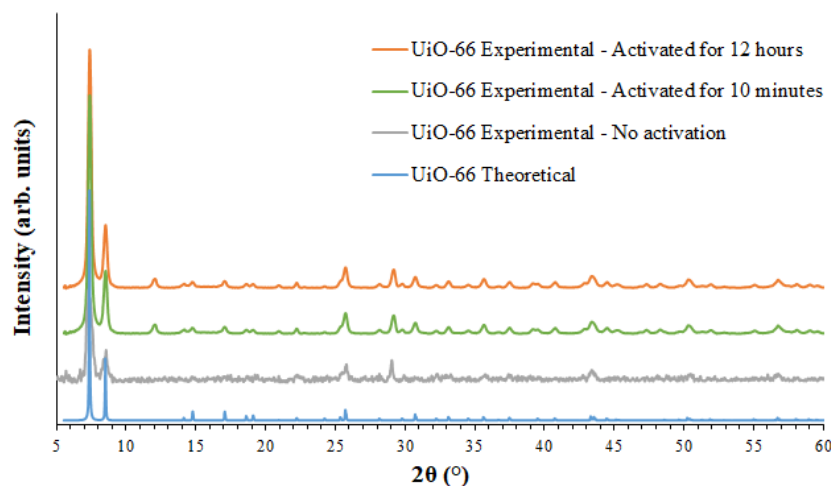


Figure 3-9. Comparison of PXRD patterns for theoretical (blue), experimental with no activation time (grey), experimental with 10 minutes activation time (green), and experimental with 12 hours of activation time (orange) for synthesized UiO-66

Two issues related to the sustainability of a process are (1) the toxic hazard associated with the raw materials used, and (2) the amount and toxicity of waste generated. The present process uses a less toxic Zr-metal precursor. One measure of toxicity is the mean lethal dose (LD50) metric.¹⁹¹ The Zr-metal precursor used for this study, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, has an LD50 of $3500\text{mg} \cdot \text{kg}^{-1}$ ^{192, 193}, while the commonly used Zr-metal precursor for UiO-66 MOF synthesis, ZrCl_4 , has an LD50 of $1688\text{mg} \cdot \text{kg}^{-1}$.^{194, 195} While the LD50 value is only one measure going into a complete life cycle analysis, selecting raw materials is an important consideration for sustainable MOF synthesis.¹⁹⁶
¹⁹⁷ Concerning waste, the CO_2 naturally flashes into the vapor phase as the pressure is relieved. The separation of CO_2 and DMF is clean as the VLE solubility of CO_2 in DMF at 0.1MPa is below 0.01%¹⁷². This separation opens the opportunity to recycle the DMF. Recycling unused reagents is not typical in solvothermal methods. Overall, it was calculated (details in Appendix B) that compared to our scCO_2 method, a continuous flow microwave method⁸⁰ creates two times more DMF waste while a continuous flow solvothermal method⁷⁵ creates six times more DMF waste.

3.5 CONCLUSIONS

In conclusion, this chapter demonstrates an innovative approach for rapidly producing MOFs in an environmentally friendly and scalable continuous scCO₂ flow reactor. The approach successfully synthesized the zirconium-based UiO-66 MOF at a production rate of 104 g·h⁻¹ with a reaction time of under three seconds. A methodology for designing a system for rapid mixing and heating of the reagents with scCO₂ was demonstrated. This methodology can be used to design scaled up systems. Accordingly, it is proposed to use a continuous scCO₂ flow reactor as a means for large-scale MOF manufacturing. Scalable synthesis methods can enable the widespread integration of MOFs into commercial applications like energy storage devices, targeted drug delivery, and gas capture.

For the continued advancement of this technology, the method should be investigated with other materials, such as zinc or copper-based MOFs. More in-depth investigation through high-fidelity numerical simulations could provide further insight into mixing, reaction kinetics, and opportunities for further process optimization. For accurate simulations and improve the reactor operation, the material properties of MOF precursors need to be defined at the relevant temperatures and pressures.

Chapter 4. CONTINUOUS FLOW SYNTHESIS OF HIGH-QUALITY HKUST-1 MOF IN SUPERCRITICAL CARBON DIOXIDE

4.1 INTRODUCTION

Identification of the influence of the thermodynamic and kinetic parameters involved in synthesizing high-quality metal-organic framework (MOF) materials is vital for scale-up, optimization, and application efforts. Few experimental studies report such information to date. As Chapter 3 of this dissertation discusses, continuous flow reactors using supercritical carbon dioxide (scCO₂) as a heating and mixing medium are highly appealing for sustainable and scalable MOF synthesis. This chapter expands upon the work completed in Chapter 3 of this dissertation by presenting the first report of the copper-based MOF HKUST-1 synthesis in a continuous scCO₂ flow reactor. Of the thousands of MOF materials reported, the copper-based MOF HKUST-1 (also called Cu₃(BTC)₂) discovered in 1999 by Chui *et al.* remains one of the most studied due to its stability, tunability, and low-cost precursors.¹⁹⁸⁻²⁰² HKUST-1 has demonstrated potential for a wide range of applications, including wound healing²⁰³, hydrogen storage²⁰⁴, carbon dioxide storage²⁰⁵, and methane hydrate growth.²⁰⁶ Additionally, 25 experiments investigate the effect pressure, scCO₂ temperature, reactor section temperature, residence time, and mole fraction CO₂ have on HKUST-1 properties such as specific surface area, particle size and particle morphology. The research described in this chapter is currently being prepared for submission to a journal for publication.

A significant challenge to the practical application of MOFs is that the laboratory synthesis techniques used to discover MOFs generally are not amenable to being scaled up^{70, 207, 208} To address this issue, efforts have recently begun that focus on developing and implementing scalable

MOF synthesis methods.²⁰⁹ Shifting from the batch reactors that dominate laboratory-scale synthesis to continuous flow reactors have been identified as one of the more promising paths towards scaling up MOF synthesis.⁷² A recent review by Teo *et al.* outlines advancements in the scalable synthesis of MOFs. We briefly outline here the principal continuous flow methods, supercritical fluid methods, and carbon dioxide (CO₂) methods to synthesize HKUST-1.²¹⁰

Early studies of scalable MOFs synthesis focused on reducing the 90 hour solvothermal batch synthesis time. The first scalable synthesis reported for industry use was in 2005 by BASF researchers Muller *et al.* for electrochemical synthesis of MOFs, including HKUST-1.^{211, 212} In 2012, Lester and coworkers reported "instant" (under 1 s) synthesis of CPO-27(Ni) and HKUST-1 MOFs using a hydrothermal continuous flow reactor.⁸⁴ The study found that when the reaction temperature exceeded 300 °C, the HKUST-1 MOF collapsed to Cu₂O, indicating an upper limit to the reaction temperature. In 2013 Faustini *et al.* reported using a microfluidic system to synthesize HKUST-1, which offered a high surface area to volume ratio and fast synthesis time.²¹³ Still, the scalability of the method has been identified as an issue. Also, in 2013, Carné-Sánchez *et al.* report the first use of continuous flow spray synthesis for HKUST-1, where the temperature was reduced, and more favorable production rates were reached compared to hydrothermal or microfluidic approaches.²¹⁴ In 2021, Kubo *et al.* improved the continuous flow spray synthesis, identifying key variables to increase production efficiency.²¹⁵ Using a flow-chemistry approach in 2014, Rubio-Martinez *et al.* synthesized three MOFs, HKUST-1, UiO-66, and NOTT-400, in a solvothermal reactor.⁷⁵ The use of solvent-free synthesis of MOFs via the mechanochemistry route, including HKUST-1, was introduced by Crawford *et al.* in 2015.²¹⁶ In 2017, McKinstry *et al.* synthesized HKUST-1 in a continuous flow stirred tank reactor and a continuous flow microwave reactor, making a case for space-time yield (STY) and surface area space-time yield

(SSTY) metric for comparison of MOF synthesis methods.²¹⁷ Continuous flow microwave reactor yielded the highest SSTY for HKUST-1, but the MOF surface area was reduced to only $600 \text{ m}^2 \cdot \text{g}^{-1}$, well a typical $1600\text{-}1900 \text{ m}^2 \cdot \text{g}^{-1}$ values.

The reaction medium plays a critical role in the synthesis of MOFs; it affects the properties of the MOF (such as specific surface area), the equipment design. Supercritical (sc) fluids can offer several advantages; these fluids have tunable thermophysical properties such as density, viscosity, and specific heat with minor changes to pressure or temperature near the critical point. This tunability allows for achieving unique mass transfer and synthesis conditions.²¹⁸ As the CO_2 critical temperature is lower than that of H_2O ($T_{\text{c,H}_2\text{O}} = 373^\circ\text{C}$ versus $T_{\text{c,CO}_2} = 37^\circ\text{C}$) and the critical pressure is also lower ($P_{\text{c,H}_2\text{O}} = 22.06 \text{ MPa}$, $P_{\text{c,CO}_2} = 7.38 \text{ MPa}$), CO_2 can be more energy-efficient, economical, and offer safer operation compared to supercritical water. A lower critical temperature is especially helpful in avoiding the thermal degradation of MOF precursors. In 2014, Peng *et al.* used expanded liquid CO_2 in a batch process to synthesize HKUST-1.²¹⁹ The reactor operated at 30°C and varied pressure in $2.0\text{-}6.6 \text{ MPa}$ range, which is below the critical temperature and critical pressure of CO_2 ; nevertheless, the study reported increased porosity of HKUST-1 as mesoporous structures ($13\text{-}23 \text{ nm}$) were obtained. Only one study reported HKUST-1 synthesis using scCO_2 ; in 2016 Lopez-Periango *et al.* synthesized HKUST-1, ZIF-8 and MIL-100(Fe) in a batch reactor with scCO_2 at 65°C and 20 MPa for a residence time of ~ 10 hours.²²⁰ Continuous flow sc-fluid systems have the potential to be more efficient and economical²²¹; however, to our knowledge, there are only two reports where sc-fluid continuous flow systems were used for MOF synthesis. In 2015 Lester and coworkers synthesized the ZIF-8 MOF via a continuous hydrothermal flow synthesis reactor at 24 MPa and 400°C .^{85, 94} The second -- is our earlier work, Chapter 3,

describing the use of scCO₂ for the production of MOF UiO-66.¹³⁹ To date, the continuous scCO₂ synthesis of HKUST-1 has not been reported.

This chapter presents the first use of scCO₂ in a continuous flow reactor to synthesize high-quality copper-based MOF HKUST-1. Throughout 25 experiments, the effects of pressure (8, 9, and 10 MPa), scCO₂ mixing section injection temperature (80-180°C), and mole fraction of CO₂ (0.392 – 0.720) on MOF morphology, crystallinity, and porosity are investigated. The MOF synthesis environment is characterized from a fundamental perspective in calculations focused on the heat and mass transfer occurring in the mixing section and calculations focused on the fluid mechanics in the reactor section.

4.2 MATERIALS AND METHODS

The continuous-flow scCO₂ synthesis reactor, **Figure 4-1** was designed to operate in the range T=25-600 °C and P=0.101-30 MPa. The reactor configuration and operation have been described in our previous work, therefore only a brief description and updates are provided here.¹³⁹ The reactor system incorporates two reagent feeds: a metal precursor and an organic precursor. Neither precursors are heated. The third stream is the scCO₂, which is heated. The mixing section combines these three streams with the goal of maximizing the mixing rate to provide rapid heating of the reagent by the scCO₂. The mixture enters the heated reactor section in which the temperature is controlled by PID. Following the reactor section, the effluent is cooled to room temperature and passed through a back pressure regulator. The reaction products, including the MOFs, are collected in the liquid phase while the CO₂ is exhausted to the fume hood.

Several modifications were made to our earlier system.³⁶ A thermocouple (T5) was added to the mixing section and another thermocouple (T6) was added to monitor the fluid temperature before entering the reaction section. To enable experiments with longer residence times, the reactor

section length was increased from approximately 25 cm to 305 cm. To eliminate dry ice formation due to throttling and improve pressure stability, the spring-loaded BPR was replaced with a dome loaded BPR (Equilibar B6R, Equilibar Precision Fluid Control). The dome-loaded BPR allowed the removal of the particle filter so that the nanoparticles could be collected in a flask downstream of the BPR.

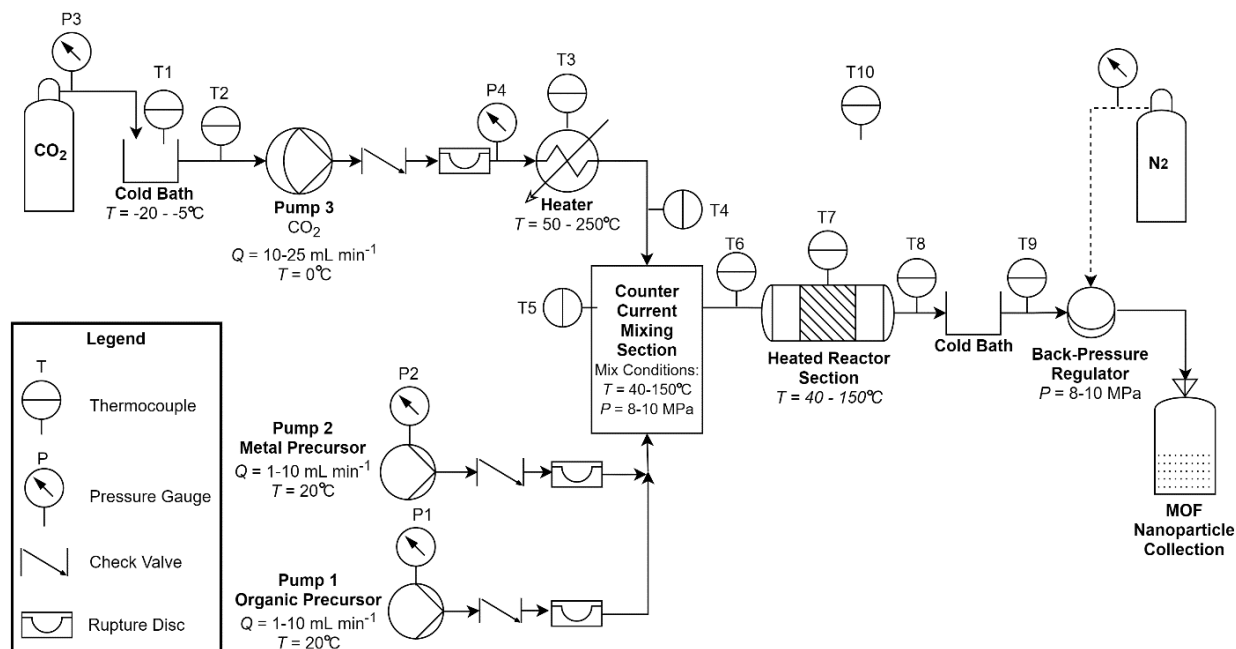


Figure 4-1. Continuous-flow MOF synthesis reactor using supercritical CO₂ with the reactor with components, including thermocouples and dome loaded back pressure regulator (BPR), identified.

At the start of each experiment, the reactor was tested for leaks by pumping DI water (Pump 1 and Pump 2) at the operational pressure of 10 MPa. A gas cylinder supplied CO₂ (99.99% purity, Praxair). This was condensed to the liquid phase via a cold bath (T1 and T2), pumped into the reactor (Pump 3), and heated by a cartridge heater before entering the mixing section (T4).¹⁶⁸ When the experimental temperature and pressure were reached, precursor pumps were started to introduce the reagents. The precursors were combined in a T-coupling before entering the counter-current mixing section (T5). Following the mixing section, the fluid flowed through the reactor,

which was a stainless steel tube coiled around a cartridge heater (T7). The fluid temperature in the reactor section (T8) was controlled within $\pm 2^{\circ}\text{C}$ of the mixing temperature (T5 and T6), creating an isothermal environment. The fluid temperature was lowered to below 40°C in a cold bath before entering the BPR (T9) to avoid damaging the BPR diaphragm. After exiting the BPR, the effluent was collected in a flask while gaseous CO_2 separated naturally. To evaluate repeatability, duplicate experiments were performed. Cross-contamination between experiments completed on the same day was avoided by flushing the reactor with ethanol for 15 minutes before each experiment.

All chemical materials were obtained from Sigma-Aldrich without additional purification and stored under recommended conditions unless otherwise noted. The precursor material preparation followed previously reported methods utilizing only ethanol as the solvent.⁷⁵ In a typical experiment, solutions of 0.1 M Copper(II) nitrate trihydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and 0.24 M benzene-1,3,5-tricarboxylic acid (BTC) solutions were dissolved in pure ethanol (EtOH). The precursor concentration was kept constant for all experiments. After collection, the particles were isolated by centrifugation (9,000 rpm for 10 minutes, Allegra X-30, Beckman Coulter) and washed with ethanol twice. The blue product was then placed in glass vials and dried at 393K overnight. The final product yield was measured using an analytical balance (ME54TE, Mettler Toledo).

X-ray diffraction (XRD) spectra were collected (D8 Advance, Bruker) using an $\text{I}\mu\text{S}$ 1-D detector (operating conditions: 40 kV, 40 mA for $\text{CuK}\alpha$ ($\lambda=1.5418\text{\AA}$) radiation at room temperature over the angular range of $2\theta = 5^{\circ}$ - 50° at a scanning rate of $2\text{deg}\cdot\text{min}^{-1}$). Physisorption analysis was completed by transferring 150 mg of activated sample to a pre-weighed sample tube and further degassed (Smart VacPrep 067, Micrometrics) at 383K until the outgassing rate was $<5\ \mu\text{m Hg}$. The sample tube was then reweighed to obtain a consistent mass for the degassed sample. N_2 isotherms were obtained (3Flex, Micrometrics) at 77 K using a liquid nitrogen bath. Ultra-high-

purity grade, 99.999%, N₂ gas was used throughout the experiment (Praxair). Morphology analysis was performed on an FEI Sirion XL30 scanning electron microscope (SEM) at 15 kV. For the SEM study, 15mg of the activated sample was dispersed on carbon tape and sputter-coated with gold (108 Manual Sputter Coater, Ted Pella) to decrease charging effects. Particle size was determined by measuring the length of over 100 nanoparticles for three SEM images taken at different locations and at least two different magnifications, usually 40,000X and 20,000X.²²²⁻²²⁴ Attempts to define the nanoparticle size using the Dynamic Light Scattering (DLS) technique (Litesizer 500, Anton-Paar) proved inaccurate. DLS consistently reported nanoparticle sizes three to ten times larger than SEM imaging observations. A discrepancy between DLS and SEM particle size is well known, so the SEM imaging method is preferable for accurate reporting.^{225, 226}

4.3 RESULTS AND DISCUSSION

4.3.1 *Reactor Synthesis Conditions*

This section outlines the synthesis conditions within the continuous flow reactor using scCO₂ to synthesize the copper-based MOF HKUST-1. The goal is to evaluate the environment experienced by reagents as they undergo mixing, heating, and reaction. For simplicity, and in the absence of reference data, the precursors' properties were assumed to be the same as pure ethanol. The values used in the analysis are obtained from the NIST ThermoLit database based on the NIST SOURCE Data Archive and NIST REFPROP as presented in **Table 4-1**^{227, 228} The value for mass diffusivity, $\mathcal{D}$, is at a lower temperature, 313 K (40 °C) than the mix temperatures measured in experiments because it is the only mass diffusivity report in literature for scCO₂ and EtOH.²²⁹

Table 4-1. Properties used for the scCO₂ continuous-flow MOF synthesis reactor

Property	Value (unit)	Reference
Mass diffusivity CO ₂ into EtOH at 313 K, 10 MPa	2.198±0.02E-8 (m ² ·s ⁻¹)	229
Thermal Diffusivity of EtOH at 338 K, 10 MPa	7.65E-7 (m ² ·s ⁻¹)	229
Density of EtOH at 338 K, 10MPa	760.13 (kg·m ⁻³)	230
Density of EtOH at 298 K, 10MPa	793.81 (kg·m ⁻³)	230
Dynamic Viscosity of EtOH at 338 K, 10 MPa	5.81E-04 (kg·m ⁻¹ ·s ⁻¹)	230
Specific heat capacity of EtOH at 338 K, 10 MPa	2763.6 (J·kg ⁻¹ ·K ⁻¹)	230
Thermal Conductivity of EtOH at 338 K, 10 MPa	0.1617 (W·m ⁻¹ ·K ⁻¹)	231
Density of CO ₂ at 338 K, 10MPa	226.08 (kg·m ⁻³)	30
Density of CO ₂ at 273 K, 10MPa	974.05 (kg·m ⁻³)	30

To create an optimal environment for rapid MOF synthesis, heat and mass transfer between the scCO₂ and MOF precursor materials should occur rapidly within the mixing section, ideally on a short time scale relative to the characteristic reaction time. Our previous work outlines the methodology used to obtain the characteristic heat and mass transfer rates in the counter-current mixing section.¹³⁹ The residence time in the mixing section was calculated to be 650 ms. The characteristic time for mass transfer between scCO₂ into EtOH was calculated as 270 ms. The characteristic time for heat transfer between scCO₂ and EtOH occurs almost instantly, at 8 ms. The characteristic times reported here are based on experimental conditions of 10 MPa, T₈=65 °C, precursor volumetric flow rates, Q_{Pump 1} and Q_{Pump 2}, of 10 ml·min⁻¹, and scCO₂ volumetric flow rate, Q_{Pump 3}, of 20 ml·min⁻¹. Calculations were completed for all experiment settings with the same result, mass and heat transfer occurred between the MOF precursors and scCO₂ were completed within the mixing section.

Depending on the mixture composition, temperature, and pressure, the reactor fluid can exist as either a two-component (EtOH/CO₂) single-phase fluid or a two-component two-phase fluid. There are only two reports in literature for EtOH/CO₂ vapor-liquid equilibrium applicable to the pressure and temperatures studied in this paper, nevertheless, it is clear that for high molar concentrations of CO₂, at or above 0.807, the mixture will be single-phase.^{232, 233} At lower molar concentrations of CO₂, depending on the temperature, the fluid in the reactor section could exist as a two-phase fluid. Only a very limited number of our conditions had lower molar concentrations of CO₂, and even so, Sima *et al.* noted that the general cubic equation of state (GEOS) equation used to define the fluid phase boundary could be predicting a higher bubble-point pressure for the CO₂-EtOH mixture.²³³ Given this, the fluid in the reactor section was assumed to be single-phase for all the experiments.

An important issue associated with the reactor is the residence time distribution. This is influenced by (1) the velocity profile in the reactor and (2) the influence of the helical coil shape of the reactor. To predict the fluid flow pattern within the reactor section, Reynolds number, Re , was calculated using equation (25)

$$Re = \frac{\rho u D}{\mu} \quad (25)$$

where u is the flow rate, D is the diameter of the reactor section tube, and ρ is the fluid's density.

^{183, 233} The μ term is dynamic viscosity, with a value defined by Zhu *et al.* of 6.1 E-5 Pa·s.²³⁴ The Re was calculated for each experiment and found to be between 0.23-0.51, associated with a laminar flow regime, and as $Re < 1$ the fluid specifically represents the subset referred to as creeping flow.

The reactor was coiled as a helix around the cartridge heater. The Dean's number (De) was calculated to determine if the curved pathway would cause flow perturbations or secondary flow structures. A value of $De < 40$ indicates unidirectional flow that is not influenced by the curved trajectory of the tube. To calculate De (26) was used

$$De = Re \sqrt{\frac{D}{2 \cdot R_c}} \quad (26)$$

where D is the diameter of the reactor section tube and R_c is the radius of curvature of the path of the reactor section pipe helically coiled around the cartridge heater. To calculate R_c Equation (27) was used

$$R_c = r \left[1 + \left(\frac{h}{2 \cdot \pi \cdot r} \right)^2 \right] = \frac{r^2 + \left(\frac{h}{2 \cdot \pi} \right)^2}{r} \quad (27)$$

where r is the radius from the center of the coil to the center of the flow and h is the height of the coil resulting in $R_c = 20.75$ mm.²³⁵

Residence time distribution (RTD) provided useful tools to analyze the continuous flow reactor and its possible effects on the HKUST-1 MOF nanoparticle nucleation and growth. The first moment of the RTD is the mean residence time, defined here using plug-flow residence time, $\tau = \frac{V_{reactor}}{Q_{reactor}}$, where τ is the residence time, $V_{reactor}$ is the reactor volume calculated to be 73.9 mL, and $Q_{reactor}$ is volumetric flow rate. The residence time was found to be between 70-166 s, depending on experimental conditions. The second moment of the RTD is the variance. Variance calculations showed that over 75% of the reactor section volume passed through the reactor within the calculated plug-flow residence time. There is no variance for plug-flow reactors, so the

variance was calculated using the laminar-flow RTD function.²³⁶ Refer to a review by Nauman for information on RTD theory and Foger for a calculation walkthrough.^{237, 238}

It should be noted that there is currently no high-fidelity Equation of State (EoS) for the binary mixture of CO₂-Ethanol, and deriving such an EoS is beyond the scope of this work. Thus, an accurate computational fluid dynamics (CFD) simulation is not attempted here. It is recognized that the high-fidelity EoS and CFD analysis could provide insight into the mixing process and the reactor environment. Nevertheless, the reactor mass transfer, heat transfer, phase equilibrium, and fluid mechanic calculations outlined in this section provide a useful information of the synthesis environment.

4.3.2 *HKUST-1 Synthesis Analysis*

SEM analysis was used to evaluate the morphology of MOF nanoparticles from scCO₂ synthesis and compare them with literature reports.^{213, 239, 240} Both spheroid and octahedral HKUST-1 particles were observed. The nanoparticles with diameters (d_{np}) < 100 nm had spheroidal shapes, the particles in the d_{np} ~ 100-250 nm range were mostly octahedral and occasionally truncated octahedra. Particles with d_{np} > 250 nm had octahedral shapes. There was an observed monomodal distribution of particle size, which agrees with previous reports.^{241, 242}

The XRD spectra were compared with the ICDD database indexed file for HKUST-1, PDF 00-065-1028, confirming that pure HKUST-1 is synthesized in all experiments. There are reports in the literature indicating that by-products can be present in the synthesis of HKUST-1 in addition to the unreacted precursors. First, Cu₂O marked by a peak at $2\theta = 36.4^\circ$ can be present, which is distinct from the HKUST-1 peaks at $2\theta = 35.20^\circ$, 35.37° , and 37.83° .^{204, 240} Second, Stolar *et al.* noted their synthesis method produced an intermediate phase marked by a peak at $2\theta = 6.1^\circ$, which is distinct from the HKUST-1 peaks at $2\theta = 5.80^\circ$ and 6.70° .²⁴³ Our MOFs did not show any

peaks associated with precursor materials, metal oxide, or intermediate phases. In summary, the XRD results show that the synthesis method of scCO₂ continuous flow produces pure HKUST-1 MOFs across a wide range of experimental conditions.

The following subsections discuss the effect of reactor operating parameters on MOFs properties. Statistical analysis was performed to identify correlations and determine if these correlations are statistically significant.

Influence of CO₂ Injection Temperature on HKUST-1

A total of ten experiments, A1-A10, were completed varying the scCO₂ injection temperature of 80 °C, 90 °C, 100 °C, 110 °C, and 120 °C to evaluate the effect on HKUST-1 crystallinity, physisorption, or morphology, **Figure 4-2a**. Specifically, an aim was to understand the limits of temperature in the reactor as too low of temperature could not form MOFs and too high of temperature could collapse the HKUST-1 MOF into Cu₂O.⁸⁴ For experiments A1 – A10, the reactor operated at constant 10 MPa, the flow rate of the precursor pumps, Pump 1 and Pump 2, as well as the flow rate of the scCO₂, Pump 3, were constant at 10 mL·min⁻¹, 10 mL·min⁻¹, and 20 mL·min⁻¹, respectively. The reactor section was kept at isothermal conditions, i.e., at the temperature of the outlet of the mixing section (T6). Figure 4-2b, shows the XRD spectra indicating that pure HKUST-1 is synthesized for all reaction conditions. SEM images, Figure 4-2c, shows primarily spherical morphology, and Figure 4-2d shows a plot of the particle size for experiments. Figure 4-2e shows the BET surface area for experiments ranges from 1467 to 2268 m²·g⁻¹. Performing multivariable linear analysis showed no statistically significant parameters. Analysis showed a positive correlation between particle size and post reactor temperature (T8) with a Pearson r-value = 0.61. The associated correlation p-value = 0.060 between particle size and post reactor temperature, indicating a possibly statistically significant relationship.

Additionally, in repeated experiments, like A1 and A2, the resulting BET surface area and particle size were nearly identical, showing good repeatability of the method.

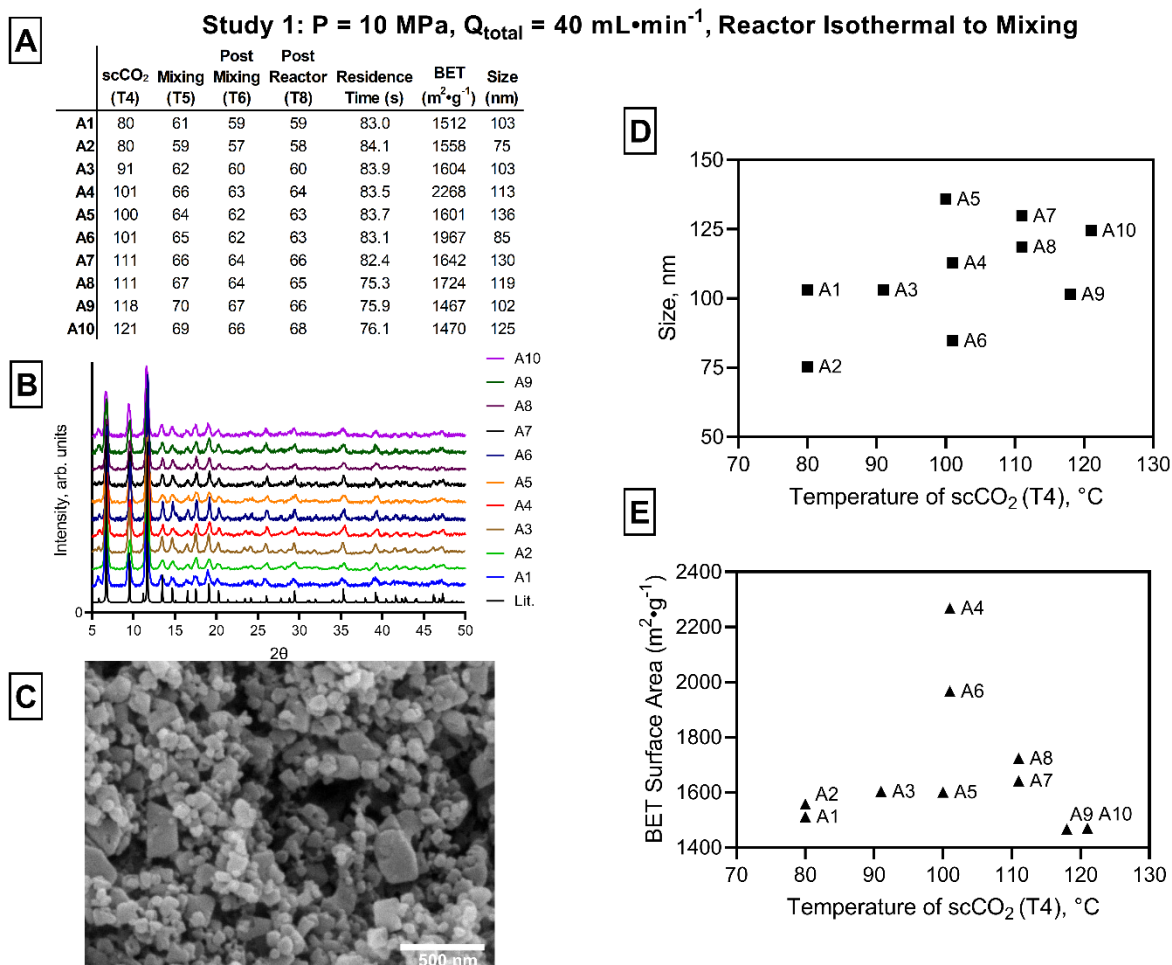


Figure 4-2. Study evaluating changing scCO₂ temperature (T4) within the continuous flow reactor for HKUST-1 MOF synthesis given a reactor pressure of 10 MPa, a reactor section temperature kept isothermal with the mixing temperature, and constant total volumetric flow rate, Q_{total} of 40 mL·min⁻¹. A) Table outlining parameters and results B) XRD spectra for experiments in study and literature reference spectra. C) SEM image of synthesized HKUST-1 nanoparticles from experiment A1, D) Plot of HKUST-1 size to injection temperature of scCO₂, E) Plot of HKUST-1 BET surface area and injection temperature of scCO₂.

Motivated by the slight correlation between injection temperature of scCO₂ and particle size suggested by experiments A1 – A10, a second study consisting of five experiments, B1-B5,

was performed where the reactor section was kept at a temperature independent of the mixing section temperature. Experiments B1-B3 maintained a constant volumetric flow rate for Pump 1, Pump 2, and Pump 3 at $10 \text{ mL} \cdot \text{min}^{-1}$, $10 \text{ mL} \cdot \text{min}^{-1}$, and $20 \text{ mL} \cdot \text{min}^{-1}$ for a mole fraction of CO_2 in the system of 0.563. To test the effect changing the reactor temperature would have on the HKUST-1 synthesis, experiment B4 was identical to experiment B2, except for increasing the reactor temperature, T8, from 68°C to 95°C . Experiment B5 was identical to experiment B4, except for decreasing the volumetric flow rate for the precursor pumps by half to $5 \text{ mL} \cdot \text{min}^{-1}$ each resulting in a mole fraction of CO_2 of 0.720. **Figure 4-3** provides experimental results for B1 – B5. The XRD spectra, **Figure 4-3b**, confirmed that all experiments produced pure HKUST-1 MOFs. SEM images, **Figure 4-3c** showed particle sizes ranging from 60 – 210 nm, with the particles being primarily spherical. Correlation analysis and accompanying p-value calculations showed particle size had a statistically significant negative correlation to the post mixing temperature (T6) with a Pearson r-value = -0.83 and p-value = 0.04, **Figure 4-3d**. There was no correlation between reactor section temperature and BET surface area, **Figure 4-3e**.

Study 2: $P = 10 \text{ MPa}$, $Q_{\text{total}} = 40 \text{ mL} \cdot \text{min}^{-1}$, Reactor Not Isothermal to Mixing

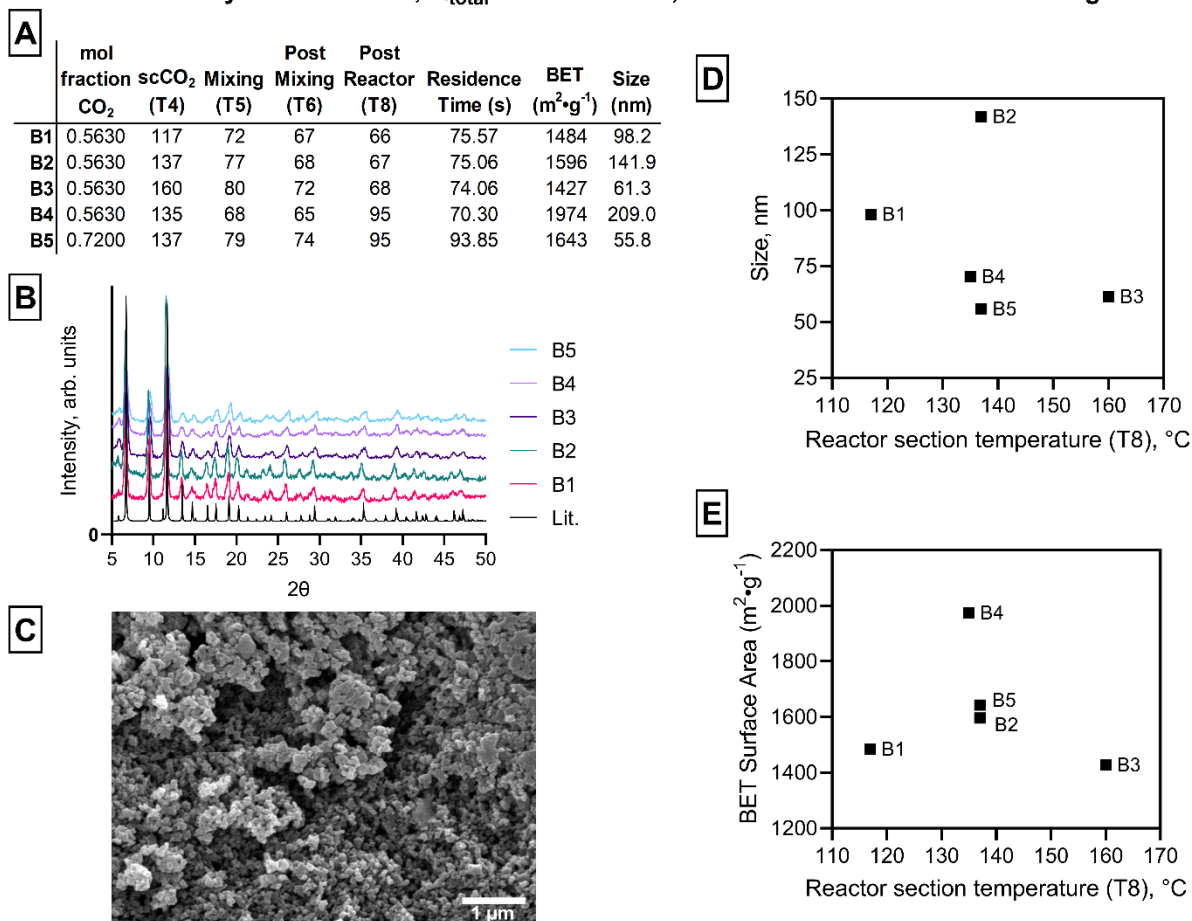


Figure 4-3. Results from evaluating reactor section temperature (T_8) independent of mixing section temperature within the continuous flow reactor A) Table outlining parameters and results, B) XRD spectra for experiments and literature reference spectra confirming HKUST-1 MOF synthesis, C) SEM image from experiment B1 D) Plot of HKUST-1 size and reactor section temperature, E) Plot of HKUST-1 BET surface area and reactor section temperature.

In summary, it was found that varying the scCO_2 from 80°C to 120°C , but keeping all else constant, produced repeatable and pure HKUST-1 MOFs with a positive, but not a statistically significant, correlation of increasing temperature to increasing particle size. Additionally, it was found that setting the reactor section temperature independent of the mixing section temperature had a statistically significant negative correlation to HKUST-1 particle size. These fifteen studies, A1 – A10 and B1 – B5, thus provide a detailed mechanistic exploration into temperature parameters influence on HKUST-1 MOF synthesis.

Influence of mole fraction CO₂ on HKUST-1

The mole fraction of the CO₂ was adjusted across five experiments, C1-C5, to see if it would influence the HKUST-1 crystallinity, physisorption, or morphology. For experiments C1-C5 the reactor pressure was constant at 10 MPa, the temperature of the scCO₂, T4, was constant at 120 °C, and the reactor section was kept isothermal to the mixing section. Figure 4-4 shows a table of key experimental variables along with XRD spectra and SEM images.

Study 3: P = 10 MPa, scCO₂ temperature (T4) = 120 °C, Reactor Isothermal to Mixing

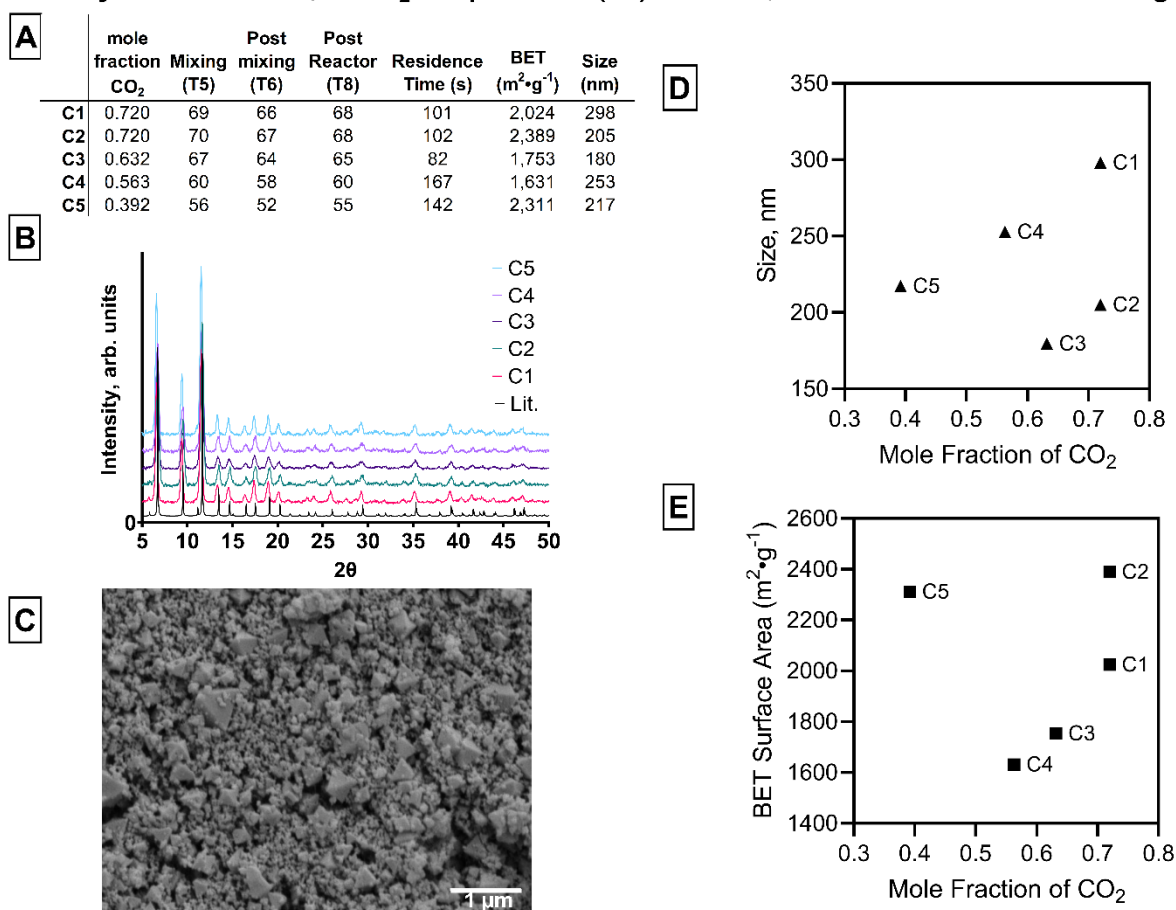


Figure 4-4. Study evaluating changing flow rate of the continuous flow reactor using supercritical CO₂ for HKUST-1 MOF synthesis A) Table outlining parameters and results, B) XRD spectra for experiments and literature reference spectra confirming HKUST-1 MOF synthesis, C) SEM image from experiment C3 D) Plot of HKUST-1 size and reactor section temperature, E) Plot of HKUST-1 BET surface area and reactor section temperature.

The experimental conditions, including mole fraction of CO₂, for experiment C4 was equal to that of experiment A10, but the overall flow rate through the system, Q_{total} , was halved. The halving Q_{total} led to a ~220% increase in the residence time, 167 s versus. 76 s, an increase in BET surface area, 1631 m²·g⁻¹ versus 1470 m²·g⁻¹, and increase in particle size, 253 nm versus 125 nm. Multiple linear analysis showed no statistically significant relationship in changing the mole fraction of CO₂ and BET surface area or particle size. Correlation analysis using Person's r-value showed a positive correlation between residence time and particle size, $r = 0.64$, and p-value approaching significance, $p\text{-value} = 0.065$. Another experiment, C6, was attempted at the same mole fraction of experiments C1 and C2 but at an elevated scCO₂ temperature, T4, of 140 °C. The collected XRD spectra for experiment C6 showed that pure HKUST-1 was synthesized. Additionally, the BET surface area for experiment C6 was measured as 1,474 m²·g⁻¹ and SEM images revealed experiment C6 had an average particle size of 267 nm. It should be noted that reactor operation for experiment C6 was challenging. From analyzing the vapor-liquid equilibrium data of Sima *et al.*, the difficulty in maintaining reactor pressure could have been caused by the mixture fluid in the reactor section operating as a two-phase fluid.²³³ In summary, varying the mole fraction of CO₂ from 0.720 to 0.392 did not affect HKUST-1 particle characteristics, but by varying the mole fraction of CO₂ or Q_{total} a correlation of that residence time impact on particle size was observed. It is also advised that two-phase fluid operation be avoided to increase ease of continuous flow operation.

Influence of reactor pressure on HKUST-1

Knowing if the continuous scCO₂ flow reactor pressure will influence HKUST-1 synthesis can be valuable in scale-up efforts such as operator guidance and precision control reactor modifications. A positive correlation in BET surface area and synthesis pressure for the batch

synthesis of HKUST-1 in CO₂ was reported by Peng *et al.* Still, the investigation was limited to pressures of 2, 4.5, and 6.6 MPa, below CO₂'s critical pressure ($P_{c,CO_2} = 7.38$ MPa) and at a reaction temperature of 30 °C ($T_{c,CO_2} = 37$ °C).²¹⁹ Here, the influence pressure has on HKUST-1 synthesis above P_{c,CO_2} is presented in experiments D1-D3 for reactor pressures of 8 MPa, 9 MPa, and 10 MPa. During experiments scCO₂ temperature, T4, was 120 °C, and the reactor section temperature, T8, was isothermal to the mixing section. Additionally, for experiments D1-D3, the volumetric flow rate was constant at 10 ml·min⁻¹ for the precursor pumps, Pump 1 and Pump 2, and at 20 ml·min⁻¹ for scCO₂ pump, Pump 3. A constant flow rate led to a residence time of 75 s ± 1 s. Figure 4-5 shows an overview of the resulting experiment parameters. The mixing and post mixing temperatures increased slightly with increasing pressure, which could be due to the specific heat of the scCO₂ increasing with increasing temperature (1.24 J·g⁻¹·K⁻¹ at 8 MPa versus 1.37 J·g⁻¹·K⁻¹ at 10 MPa). The collected XRD spectra confirmed the synthesis of HKUST-1 at all three reactor pressures. SEM images revealed nearly identical particle morphology across experiments with an average particle size of 98, 113, and 102 nm and particles of primarily spherical shape, although larger particles appeared with octahedral shape. The BET surface area for experiments D1 – D3 were 1374±26 m²·g⁻¹, 1492±24 m²·g⁻¹, 1467±49 m²·g⁻¹, corresponding to reactor pressure of 8 MPa, 9 MPa, and 10 MPa. The synthesized HKUST-1 BET surface area's reported here in supercritical CO₂ are two times higher than in sub-critical CO₂ reported by Peng *et al.*²¹⁹ Similar to the morphology results, change in pressure did not affect the HKUST-1 porosity in a statistically significant way; the Pearson r-value showed a positive correlation, r-value = 0.75, but p-value = 0.254. Experiment D3 conditions were the same as experiment A10 and yielded nearly identical BET surface areas (1467 and 1470 m²·g⁻¹) and similar particle sizes (102 and 124 nm). In closing, experiments of HKUST-1 synthesis in supercritical CO₂ where the reactor pressure was adjusted

from 8-10 MPa did not present a mechanistic conclusion but compared to literature reports of HKUST-1 synthesis in sub-critical CO₂ a clear increase in porosity was observed.

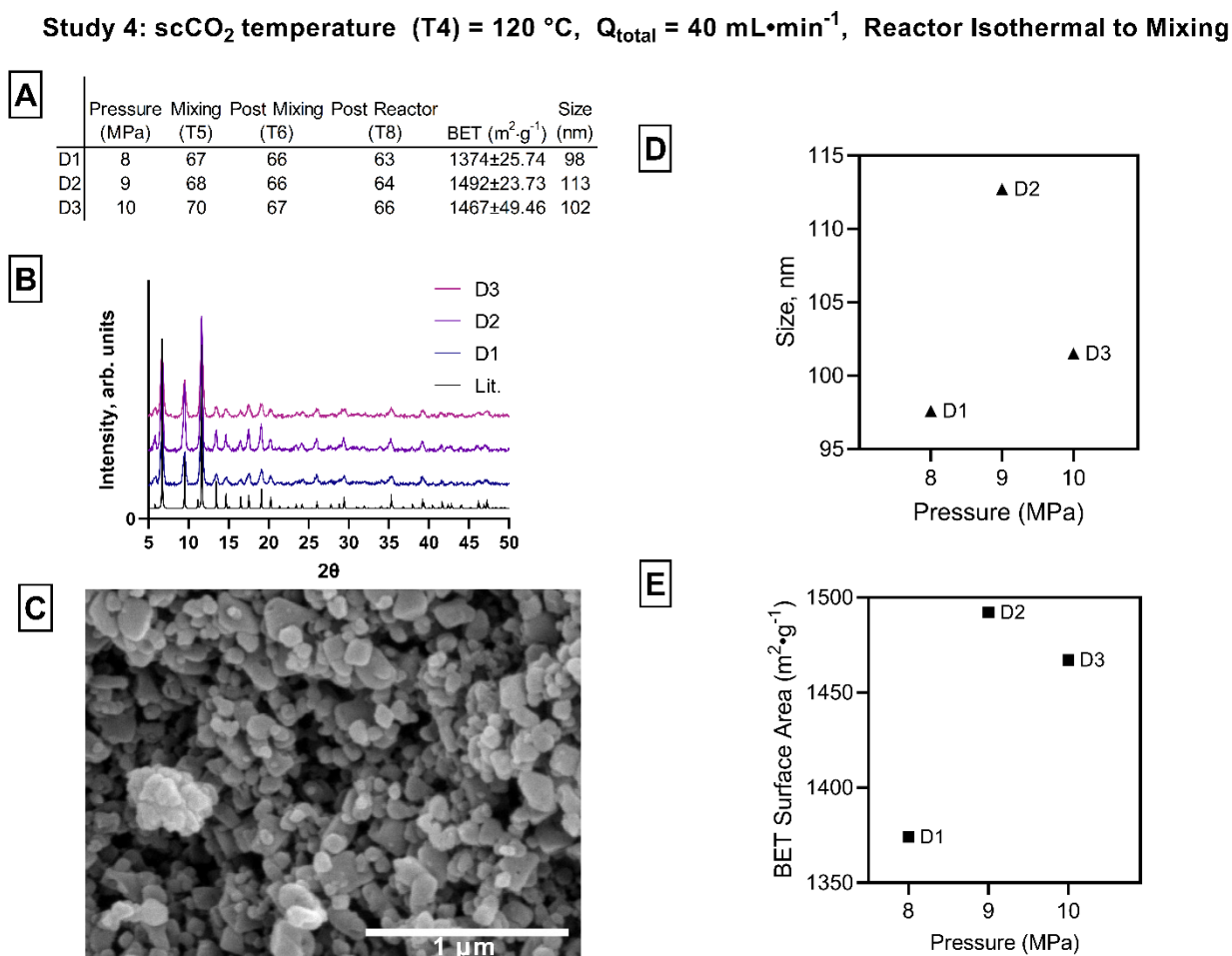


Figure 4-5. Results of analyzing the effect of changing the pressure of the continuous flow reactor using supercritical CO₂ for HKUST-1 MOF synthesis, A) Table outlining parameters and results, B) XRD spectra for experiments and literature reference spectra confirming HKUST-1 MOF synthesis, C) SEM image from experiment D2 D) Plot of HKUST-1 size and reactor section temperature, E) Plot of HKUST-1 BET surface area and reactor section temperature.

It can be valuable to compare synthesis methods using similar metrics. For scalability of synthesis analysis, several synthesis metrics have historically been used, such as: reaction time, space-time yield (STY), and, more recently, surface area production rate (SAPR).²¹⁷ These metrics aim to compare reactors of different sizes in STY and compare production rate with the quality of materials output in SAPR. **outlines both** batch and continuous flow methods currently reported for the synthesis of the MOF HKUST-1.

Table 4-2 outlines both batch and continuous flow methods currently reported for the synthesis of the MOF HKUST-1.

Table 4-2. Methods to synthesize copper-based HKUST-1 MOF with reaction time, space time yield (STY), surface area (SA), and surface area production rate (SAPR) included.

Synthesis Method	Reaction time	STY ^a ($\text{kg} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$)	SA ($\text{m}^2 \cdot \text{g}^{-1}$)	SAPR ^a ($\text{m}^2 \cdot \text{m}^{-3} \cdot \text{d}^{-1}$)	Reference
Solvothermal batch	24 h	Unreported, estimated <0.1	BET 692.2	N/A	198
Microwave batch	300 s	3,550	Langmuir 1,664±595	$5.9 \cdot 10^9$	217
Continuous flow – Stirred Tank	15 s	1,479	Langmuir 910±250	$1.3 \cdot 10^9$	217
Continuous flow – Microwave	13 s	400,000	Langmuir 600±100	$2.4 \cdot 10^{11}$	217
Continuous flow - Microfluidics	6 min	5.79	BET 1,958	$1.1 \cdot 10^7$	213
Continuous flow – solvothermal	1.2 min	13,600	1,805	$2.5 \cdot 10^{10}$	75
Continuous flow - Hydrothermal	<1 s	N/A	BET 1,950 Langmuir 1,998	N/A	84
Electrochemical (Commercial, BASF)	150 min	307.8*	Langmuir 1,820	$5.6 \cdot 10^8$	211, 212

Continuous flow – Supercritical CO ₂	2.1 min	2,685	BET 2,389	6.4·10 ⁹	this work
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^aDay defined by 24 hours; *calculated from reference data

The highest reported SAPR is via the continuous flow microwave method at $2.4 \cdot 10^{11} \text{ m}^2 \cdot \text{m}^{-3} \cdot \text{d}^{-1}$. However, a trade-off was made using the continuous flow microwave method in the form of a significantly reduced surface area to $600 \text{ m}^2 \cdot \text{g}^{-1}$ to achieve the high STY. The continuous flow solvothermal method produces the highest SAPR for HKUST-1 with a surface area above $1,000 \text{ m}^2 \cdot \text{g}^{-1}$ at $2.5 \cdot 10^{10} \text{ m}^2 \cdot \text{m}^{-3} \cdot \text{d}^{-1}$. Figure 4-6 shows a graph outlining the SA and SAPR for the continuous flow methods to synthesize HKUST-1 MOF.

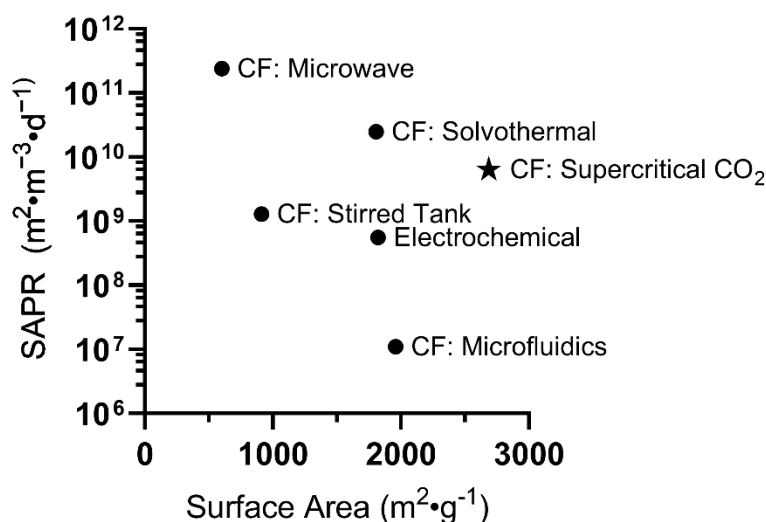


Figure 4-6. A plot of HKUST-1 MOF surface area versus surface area production rate (SAPR) using continuous flow, CF, synthesis methods (●) previously reported (★) presented in this research.

A comprehensive comparison between MOF synthesis methods is difficult for many reasons including different precursor compositions and different molar ratios of precursors used across methods. Additionally, defining morphology characteristics such as particle size, uniformity, and surface area can vary based on measurement techniques. This suggests that more metrics beyond just STY or SAPR may be valuable. Finally, green chemistry methods and the environmental

impact of a method should be considered before any significant investment. There is currently no life cycle analysis literature for different MOF synthesis methods, which would be helpful when considering scale-up efforts.

The method of continuous flow scCO₂ for HKUST-1 MOF synthesis outlined in this paper has three advantages. First, the method produces high-quality HKUST-1 MOFs as defined by surface area with a BET surface area of over 2,000 m²·g⁻¹ produced four times, in experiments A4, C1, C2, and C5. The HKUST-1 material produced in experiment C2 presented the highest BET surface area at 2,389 m²·g⁻¹. Second, the quality of the material synthesized was essentially independent of the experimental conditions, suggesting a potentially robust process for scale-up. Particle size was the only property that was influenced by the experimental conditions. Third, as this method uses CO₂, which naturally separates from effluent in the collection beaker, an option to reuse any unreacted precursors is present.

4.4 CONCLUSIONS

This chapter presents the first report of the synthesis of the copper-based MOF HKUST-1 in a continuous flow reactor using supercritical carbon dioxide as a rapid heating and mixing medium. The method resulted in no unreacted precursors or unwanted by-products in the final material for all 25 experimental conditions analyzed, proving process robustness. Pressure variation from 8 to 10 MPa did not impact HKUST-1 particle morphology or surface area, but overall presented surface areas double that of HKUST-1 synthesized in sub-critical CO₂. Adjusting the scCO₂ temperature from 80 – 120 °C did present correlations to changing particle size, but this was a weak variation. Increasing the reactor section temperature independently of the mixing section temperature led to a statistically significant negative correlation between reactor section temperature and particle size. Four sets of experiments showed excellent repeatability for both

particle size and porosity. Finally, this synthesis method proved to repeatably result in high-quality HKUST-1 MOF materials with a maximum BET surface area of over $2,389 \text{ m}^2\cdot\text{g}^{-1}$. As the synthesis conditions were carefully characterized, scaling up the method to increase the SAPR is readily feasible. Future work should include experiments at an increased range of temperatures and pressures as this study only tested 8-10 MPa pressures and kept temperatures below 120°C , well below the HKUST-1 MOF material decomposition limit that has been recorded to occur at about 300°C . Research that defines the thermodynamic properties of CO_2 -Ethanol binary mixtures would also be valuable towards enabling computational simulations of reactor systems and providing increased precision concerning mechanistic analysis.

Chapter 5. HIGH THROUGHPUT ANALYSIS OF VANADIUM (IV) OXIDE NANOPARTICLE SYNTHESIS USING SUPERCRITICAL WATER IN A CONTINUOUS FLOW REACTOR

5.1 INTRODUCTION

This chapter presents further exploration of supercritical phase fluids in continuous flow reactors for synthesizing nanoparticles. Deviating from earlier chapters of synthesizing a metal-organic framework nanomaterial, this chapter focuses on synthesizing a metal-oxide nanomaterial. Additionally, instead of using supercritical carbon dioxide (scCO₂) as a heating and mixing medium, this chapter uses supercritical water. The research in this chapter was undertaken given the success of applying first-principal analysis of supercritical carbon dioxide as a heating and mixing medium in continuous flow reactor described in Chapter 3 and tunability of supercritical phase fluids for altering particle size described in Chapter 4. Specifically, this chapter demonstrates that harnessing the tunable thermophysical properties of supercritical water in a continuous flow reactor can enable the manufacturing of ultra-small, uniform M-phase Vanadium (IV) oxide (VO₂) nanoparticles. Research described in this chapter has been prepared as a manuscript that is currently under review, but an open source version has been published on ChemRxiv.²⁴⁴ This research was also presented at the 73rd Annual Meeting of the Applied Physical Society Division of Fluid Dynamics.²⁴⁵

Background on VO₂ was presented earlier in this dissertation in section 1.3.2. Restated here briefly, vanadium (IV) oxide (VO₂) has garnered attention for its use in energy-efficient thermochromic smart window films and building materials.^{95, 96} VO₂'s reversible transformation from an insulating monoclinic phase (M-phase) to a metallic rutile phase (R-phase) above a critical

transition temperature of 68°C makes it an ideal window film material that can passively allow in or reflect certain wavelengths of light.⁹⁷ However, despite the extensive historical work done on the material, few affordable commercialized products for VO₂ exist on the market today. In the case of VO₂ nanoparticles for smart window applications, it is desirable to manufacture large quantities of homogeneous M-phase VO₂ nanoparticles under 50 nm to minimize the light scattering reduction.^{95, 246} This chapter demonstrates that continuous flow reactor with supercritical water can be used to manufacture scalable amounts of ultra-small, uniform M-phase VO₂ nanoparticles that are of a high interest for applications such as smart window films' applications.

5.2 MATERIALS AND METHODS

5.2.1 *Precursor Preparation*

All chemicals used in the experiments were purchased from Sigma-Aldrich and used as received without further purification, unless otherwise stated. Following procedures previously outlined in literature, the starting reagent for experiments was a 0.0356 M [V⁴⁺] precursor solution made using 1 mol vanadium pentoxide (V₂O₅, 1.29 g) to 3 mol oxalic acid dihydrate (C₂H₂O₄·2H₂O, 2.69 g), measured using an analytical balance (Mettler Toledo, ME54TE).²⁴⁷ The solid powders were mixed with 400 mL of deionized water (DI), **Figure 5-1**.

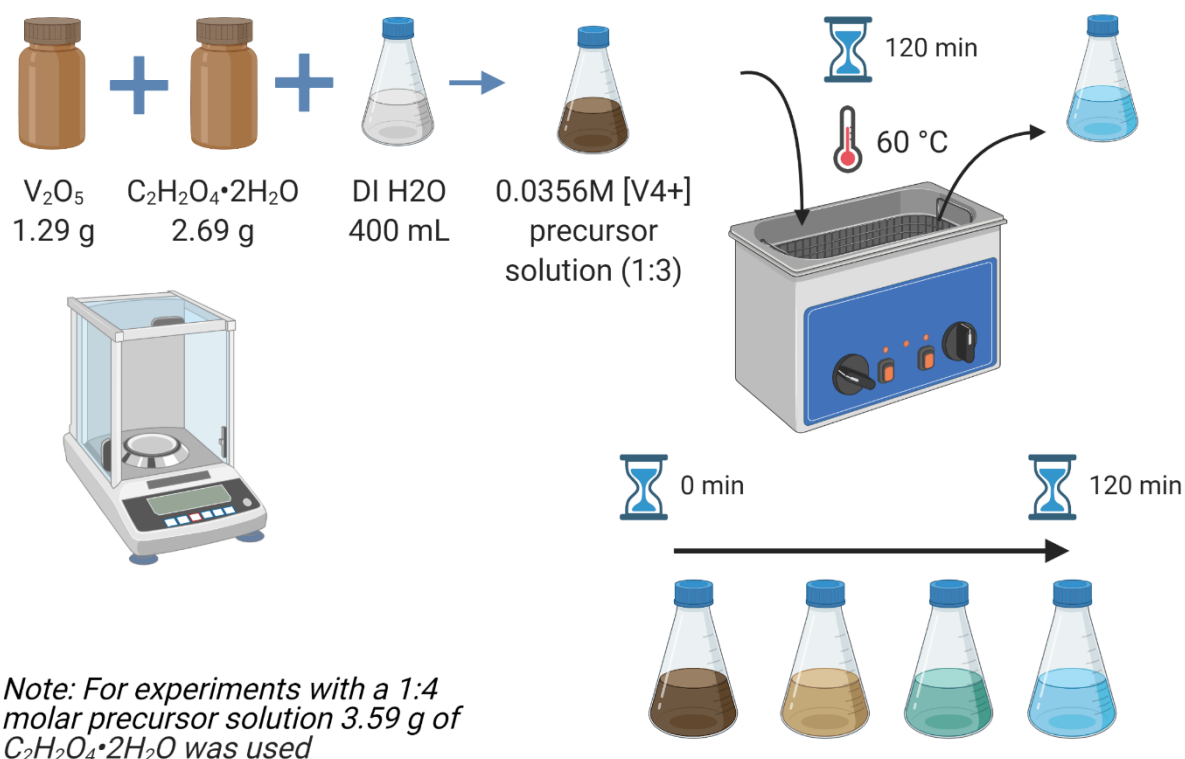


Figure 5-1. Schematic of the Vanadium (IV) oxide (VO_2) precursor preparation procedure.

The resulting opaque, brown solution was then placed in an ultrasonication bath (Branson, 8510) at 60°C for 3 hours or until the mixture turned a clear, aqua blue, **Figure 5-2**. For the final optimized experiments, a precursor solution of 1 mol V_2O_5 (1.29 g) to 4 mol $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (3.59 g), was used. This 1:4 ratio precursor mixture formed a clear, but deeper blue color following an ultrasonication bath at 60°C for 3 hours, .

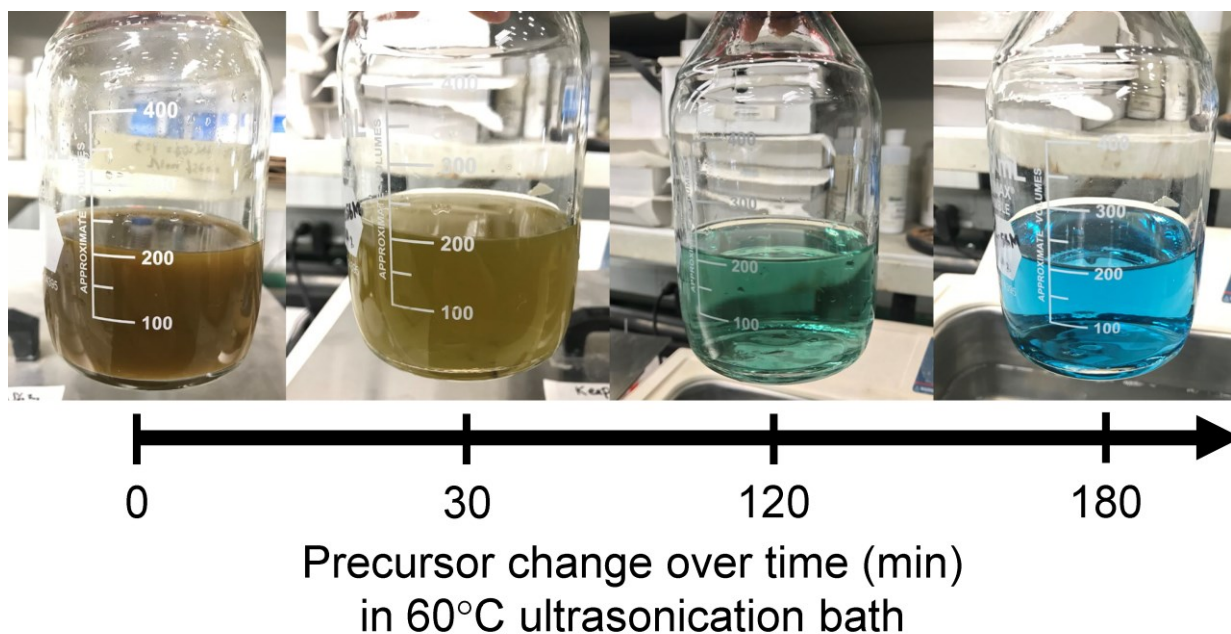
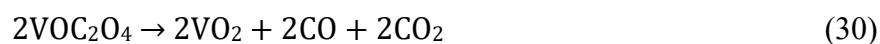
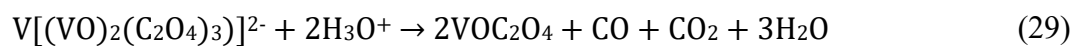
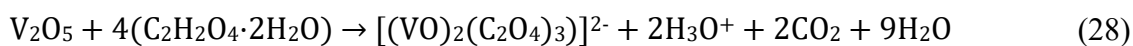


Figure 5-2. Photographs of the [V4+] precursor material (0.01187 molarity) along different stages of preparation in a heated ultrasonic water bath at 60°C.

The synthesis of VO₂ nanoparticles is based on the reaction between vanadium pentoxide and oxalic acid dihydrate (C₂H₂O₄·2H₂O) that results in the formation of VOC₂O₄ that later decomposes. Decomposition of VOC₂O₄ is accompanied by release of gases such as CO and CO₂, Equ (28), than was directly observed in collection beaker. Depending on the experimental conditions the color of the resulting colloidal solution varied from black-gray to blue-gray in color. The turbidity of the solution depended on the given experiment's flow rate and precursor concentrations. The hydrolysis and dehydration pathway for this reaction is shown in Equation (28) - (30).



A continuous hydrothermal flow synthesis (CHFS) reactor was custom-built within a walk-in chemical fume hood, as shown in **Figure 5-3**. The reactor includes 1) precursor and deionized (DI) water high pressure pumps (Teledyne SSI HF300, Pulsafeeder HL 55) to deliver precursor mixture and heating water; 2) a cast-in brown water heater (Tempco, Model CHX-20138, 6 kW at 208VAC) to heat the water to the temperature exceeding supercritical point of 374°C; 3) 0.5 inch outer diameter (OD) counter-flow tubing reactor with wall thickness of 0.083 inch where cold precursor and hot water mix and reaction occurs; and 4) a coil heat exchanger (Sentry Inc., Model#: TSR4225) to cool the colloidal effluent down. The system pressure is controlled by using two TESCO back pressure regulators (Model#: BPR 26-1763-24-688) in series to elongate the lifetime. The temperature, pressure, and flow rate can be tuned independently. The system also featured several safety measures including 1) check valves to prevent back-flow; 2) seven thermocouples connected to a data acquisition system for real-time temperature control and monitoring back-pressure regulators, 3) proportional pressure relief valves to discharge if over-pressurized; and 4) an American Society of Mechanical Engineers (ASME)-stamped and certified rupture disc that would immediately burst in an overpressure situation,²⁴⁸ All pipes were constructed of either 0.5 inch OD (0.083 in wall thickness) high pressure 316 stainless steel material or 0.25 inch OD (0.049 wall thickness). Before any experiments were conducted, the reactor was pressure tested with deionized water (DI) water for any leaks to ensure safe operation. After experiments, the reactor was flushed with DI water for 30 minutes and finally a valve was opened after the heat exchanger that allowed a vacuum pump to clean any residual products from within the reactor. These residual products were collected in a backflush collection beaker.

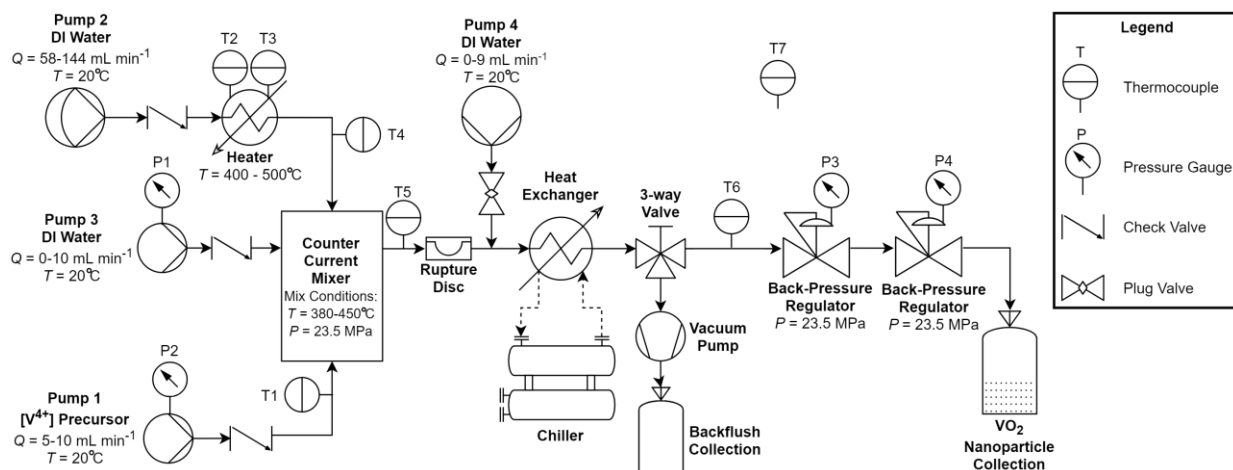


Figure 5-3. A schematic of the continuous hydrothermal flow synthesis (CHFS) reactor.

A photograph of the reactor with key components outlined can be seen in **Figure 5-3**.

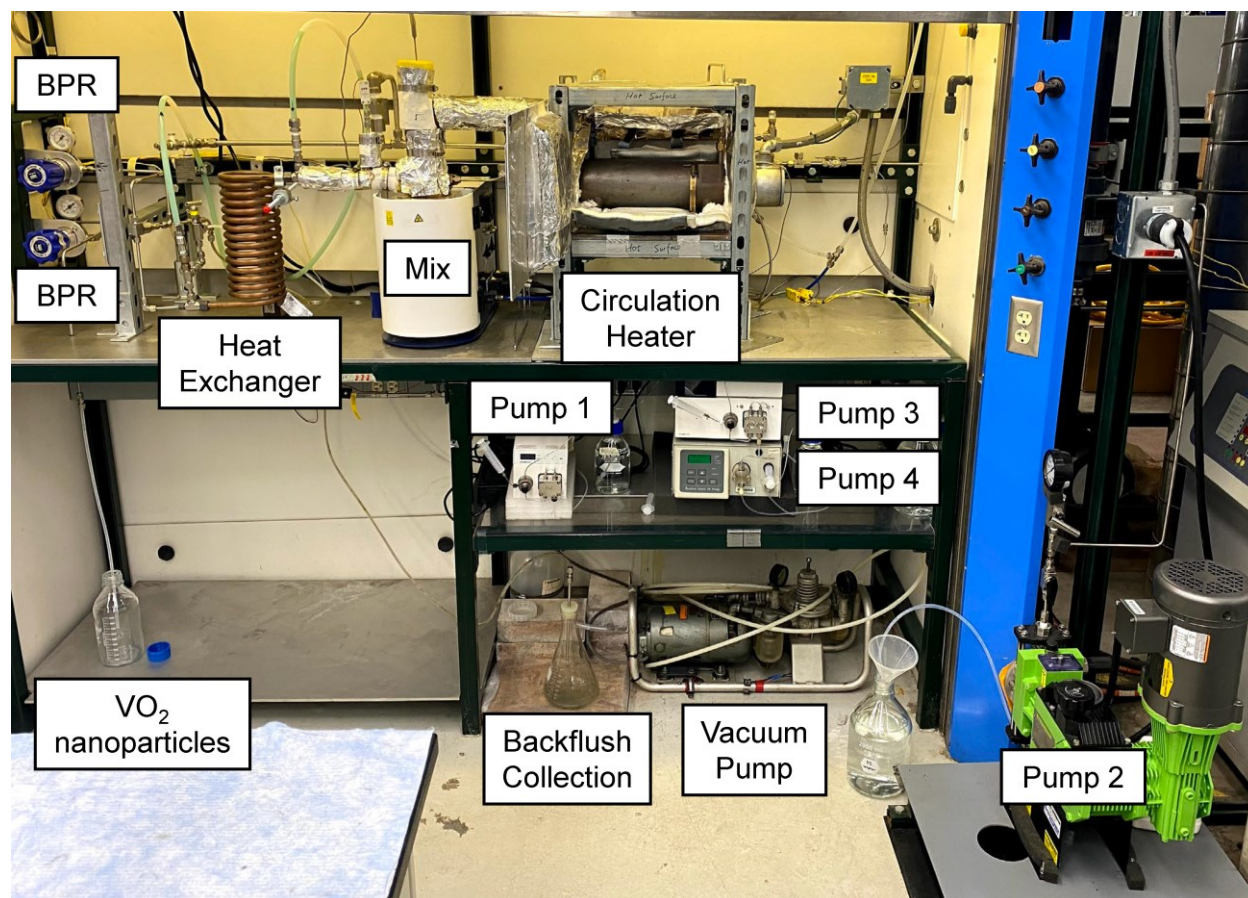


Figure 5-4. Photograph of the continuous flow hydrothermal reactor set up with key components identified including the two back pressure regulators (BPR).

In a typical experiment, a recirculation chiller (MTI Corporation, KJ6200) was the first to be initiated. The chiller is connected to a circulation heat exchanger (Sentry, DTC-SSA/CUA-4-1-1) to lower the temperature of hot fluid effluent that passes right after the reaction zone. Next, Pump 1 (Teledyne SSI, HF-300), Pump 2 (Pulsafeeder, 55HL), Pump 3 (Knauer, LS40P), and Pump 4 (Teledyne SSI, Accuflow Series 3), all were initially connected to DI water, set to the desired flow rate, and turned on. The reactor pressure was gradually increased above the critical pressure of water (22.06 MPa) and stabilized to 23.5 ± 0.5 MPa using two back pressure regulators in series (Tescom, 26-1700). Internal pressure was monitored using vibration and corrosion resistant pressure gauges (McMaster-Carr). After reaching a stable operating pressure, a cast-in circulation heater (Tempco, CHX20138) was then turned on to raise the DI water temperature from Pump 2 above water's critical temperature of 374°C. To prevent heat loss from the system to the surroundings, an insulation blanket (Tempco) surrounded the cast-in heater. A modified flow reactor (ThalesNano, Phoenix) with built in two-stage heaters and insulation was used to maintain a constant temperature throughout the mixing section of the reactor. High-heat ceramic insulation (Owens Corning) was wrapped around all pipes and fittings. Once the temperature within the reactor reached steady state, the vanadium precursor solution was connected to Pump 1 to officially start nanoparticle synthesis. The precursor solution from Pump 1 entered the mixing section and mixed with the heated supercritical phase water from Pump 2 in a counter-current geometry, and the VO₂ nanoparticle product is formed. At the end of the inner inlet tube where the supercritical phase water exited, a 316 stainless steel filter with 20 µm averaged pore size (Mott Corporation) was attached to aid in uniform dispersion of the supercritical water into the precursor liquid. The hot solution then exited the mixing section of the reactor. At the exit of mixing section Pump 3

and Pump 4 allowed for an option to add either an organic capping agent or room temperature DI water to the colloidal solution. Following the mixing section, the colloidal solution was immediately mixed with a stream of room temperature DI water from Pump 3 and Pump 4 and then passed through the heat exchanger and back-pressure regulators. When Pump 3 or Pump 4 were not used for an experiment, possible back flow or dead zones were eliminated by using a valve in the case of Pump 3, and a cap in the case of Pump 4 at the connection locations. A schematic of the counter-current mixing section and reactor section, including the inlet locations for Pump 3 and Pump 4, is shown in **Figure 5-5**. Finally, the end product of VO₂ nanoparticles dispersed in water, hereby known as the resulting colloidal solution, was collected at the end of the system.

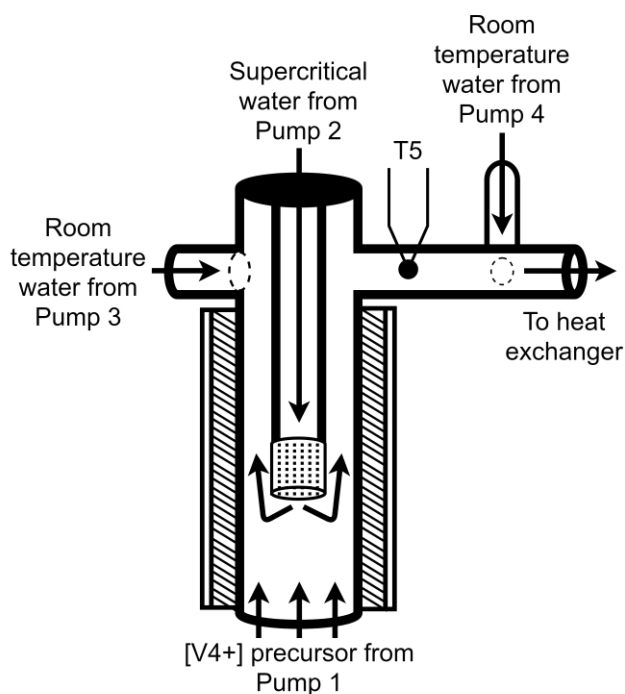


Figure 5-5. A schematic of the CHFS reactor's mixing section.

During a typical experiment, the fluid temperature at different points of the reactor was measured using six high temperature Inconel type K thermocouples (Omega, TJ36) with accuracy

of $\pm 2.2^{\circ}\text{C}$. The first thermocouple (T1) was placed in the fluid line after Pump 1, which was expected to maintain room temperature conditions. Two more thermocouples were placed within and just outside the circulation heater as a control (T2) and limit measurement (T3) as a safety measure. The fourth thermocouple (T4) was placed in the fluid line right before the mixing section to measure the supercritical phase water temperature upon entering the mixing section. The fifth thermocouple was placed in the fluid line right after the mixing section (T5) to measure the reaction temperature at which the nanoparticles formed. The sixth thermocouple (T6) was placed in the fluid line after the heat exchanger to ensure the colloidal solution had cooled sufficiently before running through the back-pressure regulator. A seventh type K thermocouple (T7) with a probe for air (McMaster-Carr) was placed inside the fume hood above the reactor system to monitor the ambient air temperature.

5.3 EXPERIMENTAL OUTLINE

Throughout this chapter, the seven studies explored the effect of: Study 1) supercritical phase water (scH_2O) flow rate from Pump 2, experiments labeled “A”; Study 2) precursor concentration, experiments labeled “B”; Study 3) varying scH_2O flow rate at elevated temperatures using diluted precursor defined in study 2, experiments labeled “C” and “D”; Study 4) changing the V_2O_5 to $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ precursor molar ratio from 1:3 to 1:4, experiments labeled “E”; Study 5) additional reactor section flow rate from Pump 4, experiments labeled “F”; Study 6) precursor flow rate from Pump 1, experiments labeled “G”; and Study 7) additional mixing section flow rate from Pump 3, which refer to the experiments labeled “H”. **Table 5-1** outlines the experimental conditions studied in this chapter across the seven studies.

Table 5-1. Experiential Conditions Employed for Seven Parametric Studies Synthesizing VO₂ Nanoparticles in a Continuous Hydrothermal Flow Synthesis (CHFS) Reactor with scH₂O.

Experiment	[V ⁴⁺] (M)	Volumetric Flow Rate (mL·min ⁻¹)			
		Pump 1	Pump 2	Pump 3	Pump 4
Study 1: scH ₂ O Flow Rate (Pump 2)					
A1	0.0356	10	58	10	9
A2	0.0356	10	86	10	9
A3	0.0356	10	115	10	9
A4	0.0356	10	144	10	9
A5	0.0356	10	172	10	9
Study 2: Precursor Concentration					
B1	0.0356	10	144	10	9
B2	0.0178	10	144	10	9
B3	0.01187	10	144	10	9
B4	0.00712	10	144	10	9
B5	0.00356	10	144	10	9
Study 3: scH ₂ O Flow Rate (Pump 2) at Elevated Temperature					
C1	0.01187	10	58	10	9
C2	0.01187	10	86	10	9
C3	0.01187	10	115	10	9
C4	0.01187	10	172	10	9
D1	0.01187	10	58	10	9
D2	0.01187	10	86	10	9
D3	0.01187	10	115	10	9
D4	0.01187	10	144	10	9
D5	0.01187	10	172	10	9
Study 4: Molar Ratio– Precursor changed from 1:3 to a 1:4 ratio of V ₂ O ₅ to C ₂ H ₂ O ₄ ·2H ₂ O					
E1	0.01187	10	144	10	9
E2	0.01187	10	115	10	9
Study 5: Additional Reactor Section Flow Rate (Pump 4)					
F1	0.01187	10	115	10	9
F2	0.01187	10	115	10	0
F3	0.01187	10	115	10	0
F4	0.01187	10	115	10	0
Study 6: Precursor Flow Rate (Pump 1)					
G1	0.01187	5	115	10	0
G2	0.01187	5	115	10	0
G3	0.01187	10	115	10	0
G4	0.01187	15	115	10	0
Study 7: Additional Mixing Section Flow Rate (Pump 3)					
H1	0.01187	10	115	10	9
H2	0.01187	10	115	10	0
H3	0.01187	10	115	0	0
H4	0.01187	10	115	0	0

Immediately following an experiment, a 15 mL sample was extracted from the experiment's colloidal solution, allowed to cool to room temperature, and probed by a Dynamic Light Scattering (DLS) particle analyzer (MicroTrac, NanoTrack Flex). Using an intensity distribution calculated over three runs with a run time of 60 s each and assuming spherically shaped particles, the intensity average and number average particle sizes were recorded. The intensity average (M_I), also known as the Z-average or the intensity based harmonic mean, gives an indication of a particle distribution weighted by the scattered intensity from the particle, so the presence of larger particles will cause this average to also be large. The number average (M_N) on the other hand, can give a better indication of the average based on the sizes from a total quantity of particles, i.e. larger particles' higher scattering intensity will not overshadow the measurement of the smaller particles.²⁴⁹ Both methods were used to gain insight into the VO₂ particle distribution of the experiments.

The remaining colloidal solution from an experiment was then centrifuged (Beckman Coulter, Optima L-100 XP) three times at 40,000 relative centrifugal force (rcf) for 10 min each. After pouring the supernatant off the first run, the second and third repetitions of centrifugation were rinsed with DI water and ethanol, respectively. The nanoparticles were left to dry overnight at room temperature and atmospheric pressure. X-ray diffraction (XRD) analysis was used to determine the phase composition of the resulting nanoparticles. XRD samples were prepared by dispersing 10 mg of nanoparticles onto a silicon wafer, then analysis was performed (Bruker, AXS D8 Advance) with CuK α ($\lambda=1.5418\text{\AA}$) radiation at room temperature over the angular range from 10° to 80° 2 θ at a scanning rate of 0.5 deg·min⁻¹. Scanning electron microscopy (SEM) was used to reveal particle morphology and confirm nanoparticle size from DLS characterization. For SEM

characterization, about 10 mg of nanoparticles were adhered to carbon tape attached to a silicon wafer, then analysis (Jeol, JSM-7500F) was conducted using a 20keV electron beam.

5.3.2

Flow Characterization

Flow characteristics in the CHFS reactor system are performed by calculation of the Reynolds number (Re), which characterizes the degree of mixing and residence time; parameters that can thus describe how heat is distributed among nanoparticles and allow conversion to M-phase for each experiment. The temperature is defined at the location where the colloidal solution exits the mixing section, T5 (Figure 5-5). The internal pressure of the CHFS system is defined at P3, being 23.5 MPa. The equation for the Reynolds Number (Re) was calculated using equation (31)

$$Re = \frac{\rho u D}{\mu} \quad (31)$$

where ρ is the density of the fluid in $\text{kg}\cdot\text{m}^{-3}$, u is the flow rate in $\text{m}\cdot\text{s}^{-1}$, D is the diameter of the reactor section tube in m, and μ is the dynamic viscosity of the fluid measured in $\text{Pa}\cdot\text{s}$.¹⁸³ The values of flow rate and diameter were physical dimensions obtained from the experimental setup in the reaction zone of the reactor, while the density and viscosity values were obtained from the National Institute of Standards and Technology (NIST) RefProp.²⁵⁰ A Re value greater than 4000 indicates turbulent flow, while a Re value less than 2100 is classified as laminar flow, and any flow falling in between 2100-4000 is considered transitional.²⁵¹

Residence time in the mixing section and the reactor section of the CHFS system was calculated for each experiment. Calculations were completed by first converting volumetric flow rate, Q , to mass flow rate, $\dot{m}$, for each of the four pumps, given the density from of liquid's temperature and pressure being pumped (20 °C, 23.5 MPa). Then the $\dot{m}$ for the mixing and reactor

section were defined. The $\dot{m}$ for the mixing section was then defined as the sum of $\dot{m}$ for Pump 1 and Pump 2 whereas the $\dot{m}$ for the reactor section was defined as the sum of the $\dot{m}$ for all the pumps, Pump 1-4. The volume in the mixing section was defined as the area of the inner inlet pipe minus the area of the outer pipe multiplied by the length of the mixing section. Here, the mixing section length is defined as the distance from the end of the inner inlet pipe to the reactor section pipe's centerline as commonly done in counter current mixing sections.¹³⁹ The volume for the flow in the reactor section was defined by the inner diameter of the reactor section pipe and the length of the reactor section. The density of the fluid in the mixing and reactor sections was defined from NIST RefProp at the isobaric pressure of 23.5 MPa and using the thermocouple data, T5, for the temperature of the colloidal solution exiting the mixing section. From the density and $\dot{m}$, the velocity and consequently residence time of the colloidal solution was derived.

5.4 RESULTS AND DISCUSSION

*Note: Experiments in Sections 5.4.1 – 5.4.4 were led by Mai Kim Tran, but are included here for completeness. Experiments in Sections 5.4.5 – 5.4.7 were led by Elizabeth Rasmussen. Split experiment leads were required due to limited on-site laboratory access imposed because of the COVID-19 global pandemic.

VO₂ nanoparticles were synthesized in a continuous hydrothermal flow synthesis (CHFS) reactor using supercritical water (scH₂O) as the solvent. Over the course of seven studies different effects on the VO₂ nanoparticle size, morphology, and phase were observed. The Phoenix two-stage heater surrounding the mixing section ensured that the nanoparticles on the wall are also evenly heated during the mixing. The upper-stage heater is maintained at 330 °C and the lower-stage heater is maintained at 270 °C for Study 1, 2, and 3-C. For Study 3-D, the upper and lower heaters are maintained at 450 °C and 360 °C respectively. Study 4 had upper and lower heater temperatures of 450 °C and 400 °C respectively. The differences in the Phoenix heating

temperatures were adjusted to ensure that the temperature of the colloidal solution exiting the mixing section (T5) was maintained above the critical temperature of water (374 °C) and to ensure particles are able to achieve full M-phase conversion. Upon centrifugation, the colloidal solutions yielded yellow-tinted supernatants when a 1:3 ratio of vanadium pentoxide to oxalic acid is used. However, when the ratio is changed to 1:4, the supernatant solution is clear indicating the complete conversion of the vanadium precursor.

Different flow rates for synthesis were explored and it was found that scH₂O flow rates between 60 mL·min⁻¹ and 150 mL·min⁻¹ allowed the most consistence in maintaining constant temperatures for experiments. As the non-linear heat transfer effects near the critical point have been presented near the critical point in previous work, the flow rate below 60 mL·min⁻¹ and above 150 mL·min⁻¹ are to be avoided in future work.²¹ The size of synthesized nanoparticles was routinely analyzed using a DLS particle analyzer. In turn, morphology and crystallinity are studied by SEM imaging and XRD. The role of thermodynamics in the system was also studied by analysis of residence time calculated from the temperature of the scH₂O (T4) and colloidal solution (T5). Seven parametric studies explore the parametric space available in CHFS reactor systems. The following section presents the results and discussions for the seven different studies. Each study was based on the optimization of the parameters in the previous set of the experiments.

5.4.1 *Effect of Supercritical Water (scH₂O) Flow Rate*

In this set of experiments, called “Study 1” in Table 5-1, the scH₂O volumetric flow rate, Pump 2, for was varied between 58 mL·min⁻¹ and 172 mL·min⁻¹, leading to a total system flow rate between 87 mL·min⁻¹ and 201 mL·min⁻¹. **Table 5-2** presents the flow rate, key temperatures T4 (scH₂O entering the mixing section) and T5 (colloidal solution exiting the mixing section), residence times, DLS, XRD, and SEM material characterization results for experiments A1-A5.

Table 5-2. Experiments in Study 1: scH₂O Flow Rate (Pump 2) Effect on VO₂ nanoparticles synthesized in a CHFS reactor- Experimental Parameters, Residence Time, Re, and DLS, XRD, SEM Material Characterization

Exp.	Total/ Pump 2 Flow Rate (mL·min ⁻¹)	Average Temperature (°C)		Residence Time (s)			Re	DLS		XRD Phase	SEM [†]
		T4	T5	Mixing Section	Reactor Section	Total		M _I	M _N		
A1	87/ 58	520.8	383.5	0.51	2.01	2.51	7,177	370.0	145.1	A, M	FP, S
A2	115/ 86	394.8	380.6	0.48	2.04	2.52	8,146	383.0	108.9	A, M	FP, R, S
A3	144/ 115	391.1	382.2	0.30	1.34	1.64	11,367	276.7	101.5	A	FP, R, S
A4	173/ 144	387.9	381.3	0.27	1.20	1.47	13,143	162.5	88.5	A, M	-
A5	201/ 172	387.5	379.0	0.37	1.67	2.04	10,934	136.5	70.7	A, M	R, S

†Abbreviations used for SEM morphology: FP for Flaky Plates, R for Rods, and S for Spheres

The DLS particle analyzer showed the intensity average particle size decreased from 370.0 nm to 136.5 nm, and the number average decreased from 145 nm to 70.7 nm, at increasing flow rates, Figure 5-6a. At higher flow rates, the reaction mixture spends less time in the hot reaction zone. As a result, shorter reaction time leads to smaller nanoparticles. Additionally, it is observed that more turbulent mixing conditions, as indicated by the Re number, generally led to smaller particle sizes. Experiment A5 did not follow these observed trends, which could be due to temperature fluctuations occurring in the cast heater and in turn the scH₂O entering the mixing section during the experiment as the flow rate for scH₂O was 172 ml/min, above the mentioned 160 ml/min. The corresponding SEM images revealed the structures with elongated, Figure 5-6b, c, and rounded, **Figure 5-6d**, particle morphology. The formation of elongated structures is previously explained as a result of the shear forces from the mixing of the precursor and supercritical water in the reaction zone that affects the growth kinetics.¹⁰ Almost all experimental conditioned tested in this set of experiments resulted in the formation of VO₂ nanoparticles with A-phase peaks (Figure 5-6e). VO₂ (A), as referenced by JCPDS card No. 42-0876 have peaks corresponding to X-ray diffraction at (110), (102), (220), and (330) planes.^{252, 253} However, in contrast to other studies which often exhibit B-phase when using additive-free techniques, this

CHFS reactor has shown the co-existence of A- and M-phase VO₂. Moreover, the samples synthesized at the highest flow rate had only M-phase. The VO₂ M-phase peaks observed for the samples synthesized under the lowest flow rate likely had more chance to undergo a phase transition as a result of a longer residence time since the nanoparticles are in the reaction zone longer. It is thought also that the Phoenix two-stage heater set at 330 °C and 270 °C are not sufficiently high enough to convert the nanoparticles at the wall of the reactor during the mixing. The appearance of M-phase as evidenced by the (011) peak at $2\theta = 29.0^\circ$ under the highest flow rate (201 mL·min⁻¹, experiment A5 in Table 5-2), is hypothesized to be directly connected with the increase of the residence time in the reactor section by 38% as compared to experiment A4. The increase in residence time was due to a temperature (T5) decrease by 2 °C for experiment A5. Such a small decrease in temperature is usually not impactful, but as experiments were conducted near the critical point (373°C for water) and specifically near the pseudo-critical point (379°C at 23.5 MPa), large changes in the thermophysical properties of scH₂O occur. Thus, the 2 °C temperature decrease resulted in a 48.5% increase in density, from 235 kg·m⁻³ to 349 kg·m⁻³.

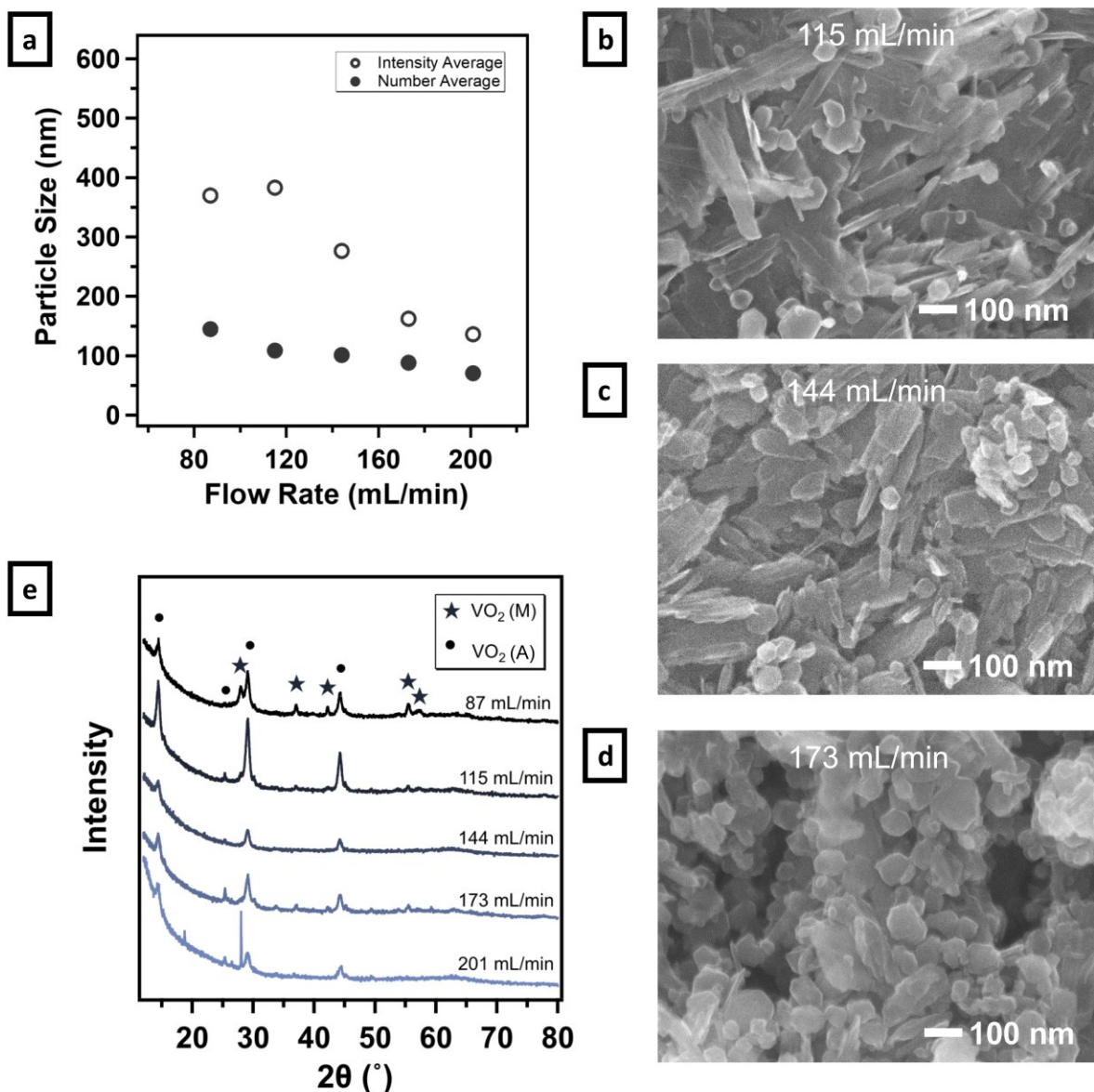


Figure 5-6. VO₂ material characterization results from experiment set A: scH₂O flow rate effect on VO₂ nanoparticle (a) size using DLS, (b-d) morphology using SEM, and (e) crystallinity and phase using XRD.

5.4.2 Effect of Precursor Concentration

In this parametric study the total system flow rate was kept constant at 173 mL·min⁻¹ while the vanadium precursor concentration was varied from 0.0356 M (no dilution) to 0.0178 M (2x diluted), 0.01187 M (3x diluted), 0.00712 M (5x diluted), and 0.00356M (10x diluted). **Table 5-3**

presents the key temperatures, residence time, and material characterization results for experiments B1-B5 in this study.

Table 5-3. Experiments in Study 2: Precursor Concentration Effect on VO₂ nanoparticles synthesized in a CHFS reactor - Experimental Parameters, Residence Time, Re, DLS and XRD Material Characterization

Exp.	[V ⁴⁺] (M)	Average Temperature (°C)		Residence Time (s)			Re	DLS		XRD Phase	SEM [†]
		T4	T5	Mixing Section	Reactor Section	Total		M _I	M _N		
B1	0.0356	388.0	381.3	0.27	1.20	1.47	13,143	162.5	88.5	A	-
B2	0.0178	387.0	381.3	0.27	1.20	1.47	13,143	132.8	42.1	A	FP, S
B3	0.01187	386.5	381.2	0.27	1.20	1.47	13,143	127.2	21.93	A, M	S
B4	0.00712	386.2	381.4	0.27	1.20	1.47	13,143	88.6	34	-	S
B5	0.00356	386.0	380.1	0.30	1.35	1.65	12,254	97.7	43.2	-	S

[†]Abbreviations used for SEM morphology: FP for Flaky Plates and S for Spheres

Figure 5-7a shows the DLS particle size where the intensity average particle size decreased from a diameter of 162.5 nm with no dilution to a diameter of 88.6 nm with a 5x dilution factor before increasing in size again at the lowest (10x) dilution. The number average likewise exhibited a general decreasing trend from 88.5 nm with no dilution down to 21.9 nm with a 3x dilution before slightly increasing in size with further dilution (5x and 10x). From the perspective of residence time, the increase in particle size in experiment B5 follows the trend that longer residence time yields larger nanoparticles. Although temperature was typically consistent during all experiments, during experiment B5, a 1 °C temperature decrease was exhibited, leading to a 12.4% increase in the colloidal solution density, and in turn a 12.2% increase in residence time. The observed increasing number average particle size trend may also be an indication of a plateau, as lower concentrations of nanoparticles tend to hit the limits of the DLS instrumentation and produce noisier data due to the weak signal produced in the sample. While SEM images in **Figure 5-7b** and **Figure 5-7c** show the formation of spheres and some flaky plates, the SEM image in **Figure 5-7d** corresponding to the 0.0119 M [V⁴⁺] (3x diluted) sample shows a relatively spherical

morphology throughout, indicating that the dilution of the precursor likely aided in reducing the aggregation after nanoparticles nucleated, but due to the high solubility and surface energy of the particles at the scH₂O conditions, smaller particles may be re-dissolving and some degree of Ostwald ripening may still be occurring, therefore contributing to some of the variation in the particle size distribution.²⁵⁴ As for the precursor concentration's effect on the VO₂, the presence of M-phase is the most pronounced at 0.01187 M [V⁴⁺] as it is evidenced by appearance of peaks corresponding to (011) VO₂ M-phase peak, **Figure 5-7e**. Similar to the case of the higher flow rate, experiment A5, at 201 mL·min⁻¹, it may be possible that the more diluted precursor samples were able to mix their components more efficiently at high temperature and therefore convert more nanoparticles into VO₂ of M-phase.¹⁰³

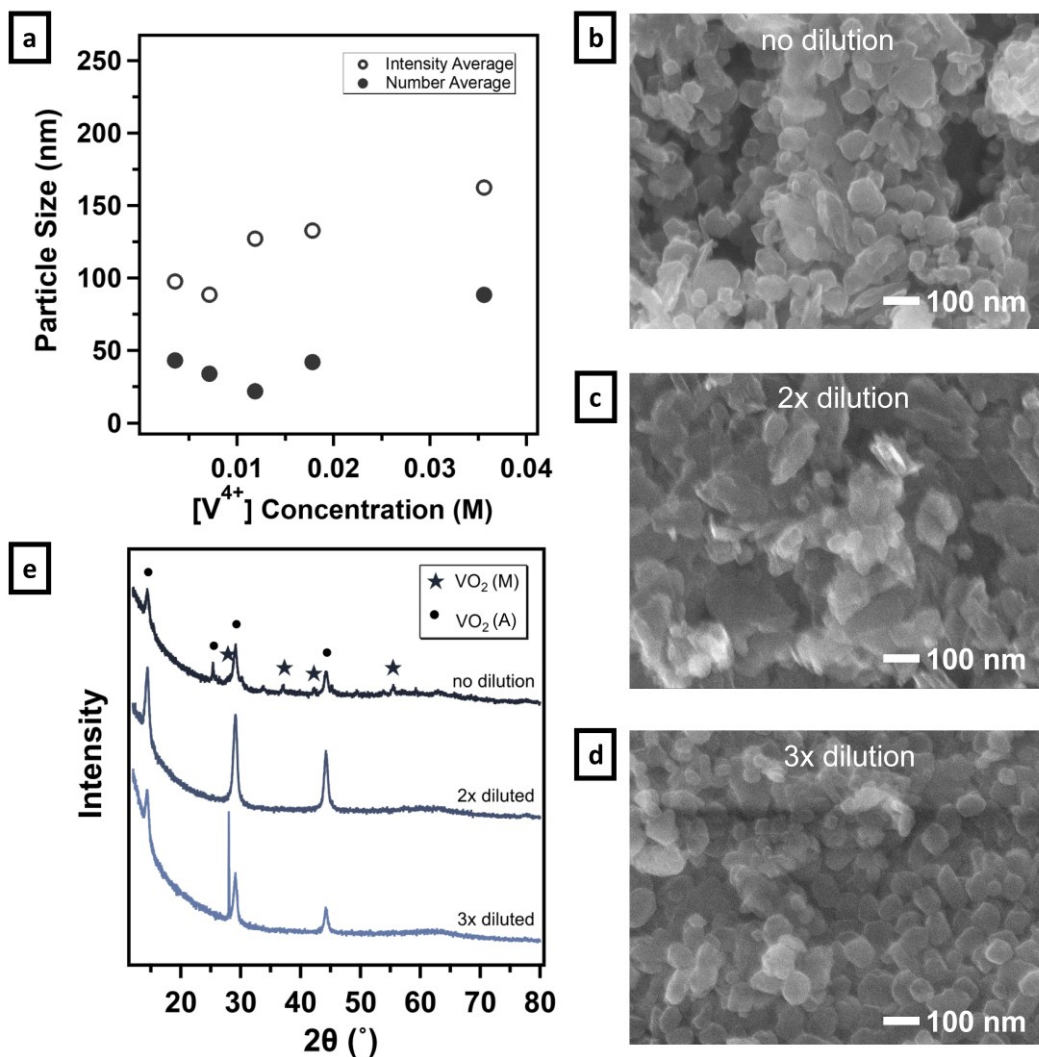


Figure 5-7. VO₂ material characterization results from experiment set B: vanadium precursor concentration's effect on VO₂ nanoparticle (a) size using DLS, (b-d) morphology using SEM, and (e) crystallinity phase via XRD.

5.4.3 Effect of Supercritical Water Flow Rate at Elevated Temperature

The third parametric study is focused on the precursor dilution effect. The concentration of the vanadium precursor is selected to maintain the small nanoparticle size, while also keeping the overall nanoparticle yield at a higher end, the latter factor which would be greatly affected by diluting the precursor too much. Thus, for this study the precursor concentration was held constant at 0.01187 M (3x diluted) while varying the system flow rate once again between 87 mL·min⁻¹ and

201 mL·min⁻¹. For the first set of experiments, set C, the mixing section's outlet temperature (T5) was similar to previous experiments. In the second set of experiments, set D, the temperature in T5 is increased by 5.5 °C . **Table 5-4** presents the flow rate, key temperatures, residence times, DLS, XRD, and SEM material characterization results for experiments in this third study.

Table 5-4. Experiments in Study 3: scH₂O Flow Rate (Pump 2) and Elevated Temperature Effect on VO₂ nanoparticles synthesized in a CHFS reactor - Experimental Parameters, Residence Time, Re, DLS and XRD Material Characterization

Exp.	Total/ Pump 2 Flow Rate (mL·min ⁻¹)	Average Temperature (°C)		Residence Time (s)			DLS			XRD Phase	SEM [†]
		T4	T5	Mixing Section	Reactor Section	Total	Re	M _I	M _N		
C1	87/ 58	397.9	379.4	0.85	3.34	4.19	5,292	179.6	83.6	-	FP, S
C2	115/ 86	398.7	382.0	0.40	1.67	2.07	9,078	150.6	87.7	-	FP, R, S
C3	144/ 115	391.9	382.8	0.29	1.27	1.55	11,660	143.8	56.7	-	FP, S
C4	201/ 172	385.1	378.6	0.37	1.67	2.04	10,934	93.1	52	-	S
D1	87/ 58	464.6	383.6	0.51	2.01	2.51	7,177	199	92.7	A	FP, R, S
D2	115/ 86	479.1	387.1	0.31	1.31	1.63	9,980	152.2	53.1	A, M	FP, R, S
D3	144/ 115	457.2	393.1	0.21	0.93	1.14	12,870	145.4	64.3	-	FP, S
D4	173/ 144	406.7	387.2	0.19	0.87	1.07	15,013	140.6	30.5	A	S
D5	201/ 172	386.1	381.3	0.23	1.03	1.26	15,271	103.7	45.8	A	S

†Abbreviations used for SEM morphology: FP for Flaky Plates, R for Rods, and S for Spheres

Given the new precursor concentration, the purpose of the first set of experiments in this Study 3, set C, was to confirm previously observed particle morphology characteristics. Similar to the previous experiments with increasing system flow rates, a decrease in both intensity average and number average particle size is observed. However unlike in the first parametric study, for this Study 3, the lower concentration precursor seemed to add robustness in the downward trend, even when a temperature decreased in C4 resulted in an increased residence time closer to that of experiment C2. Through SEM imaging, particle morphology transitioned from a mixture of flaky plates, rods, and spheres to a homogeneous distribution of spherical particles. Unfortunately, predominantly A-phase nanoparticles are observed in the XRD.

Hence, for the second set of experiments within Study 3, set D, the temperature of the colloidal solution exiting the mixing section (T5) was increased to see if the phase composition of the smaller nanoparticles could be fully converted to M-phase. The Phoenix two-stage heater was also adjusted to an upper heater temperature of 450°C and a lower heater temperature of 360°C to facilitate a higher overall temperature of the mixing section's reactor walls. **Figure 5-8a** shows the DLS particle sizes decreased from an intensity average of 199.0 nm at 87 mL·min⁻¹ flow rates down to 103.7 nm at the highest flow rate of 200 mL·min⁻¹, but no full conversion to M-phase is seen in the XRD. With particular attention to experiment D4, the number average particle size decreased from 92.7 nm at the lowest flow rate, down to 30.5 nm at a higher flow rate and consequently lowest residence time. D5, while the highest flow rate, exhibited a number average of 45.7 nm which is thought to increase again in size relative to D3 because of a slightly longer residence time in the reactor. **Figure 5-8b** and **Figure 5-8c** show large flaky plates with a few rods and spheres at these lower flow rates. This mixed morphology indicated some evidence of coalescence and occasional nano-rods that formed, perhaps due to the high surface energy of the particles coupled with an inducing effect from the high pressure and shearing forces.^{100, 255} However, for the SEM image corresponding with the sample at 144 mL·min⁻¹ (**Figure 5-8d**), the particles appeared to show uniform spheres with sizes appearing to be much smaller than the smallest particles from the earlier parametric studies. However, while the majority of particles were spherical, there was some evidence of coalescence and occasional nano-rods that formed, perhaps due to the high surface energy of the particles coupled with an inducing effect from the high pressure and shearing forces.^{100, 255} The slight increase in temperature, as a result of the higher heated scH₂O and Phoenix heater, did not appear to have a significant effect on the conversion to M-phase of a 0.01187 M (3x diluted) sample. As shown in **Figure 5-8e**, the sample at the lowest

flow rate tested, $87 \text{ mL} \cdot \text{min}^{-1}$, showed strong A-phase peaks with a slight peak broadening at $2\theta \cong 29^\circ$ which indicated very limited conversion to M-phase. However, the sample at $115 \text{ mL} \cdot \text{min}^{-1}$ had a strong M-phase peak at $2\theta = 28.0^\circ$, suggesting that the theory of increased mixing may be the reason for the conversion. When the flow rate was increased to $144 \text{ mL} \cdot \text{min}^{-1}$ there seemed to be a trend back towards VO_2 (A) perhaps due to the presence of unreacted reactants; a strong oxalic acid dihydrate peak emerged at $2\theta = 31.7^\circ$.

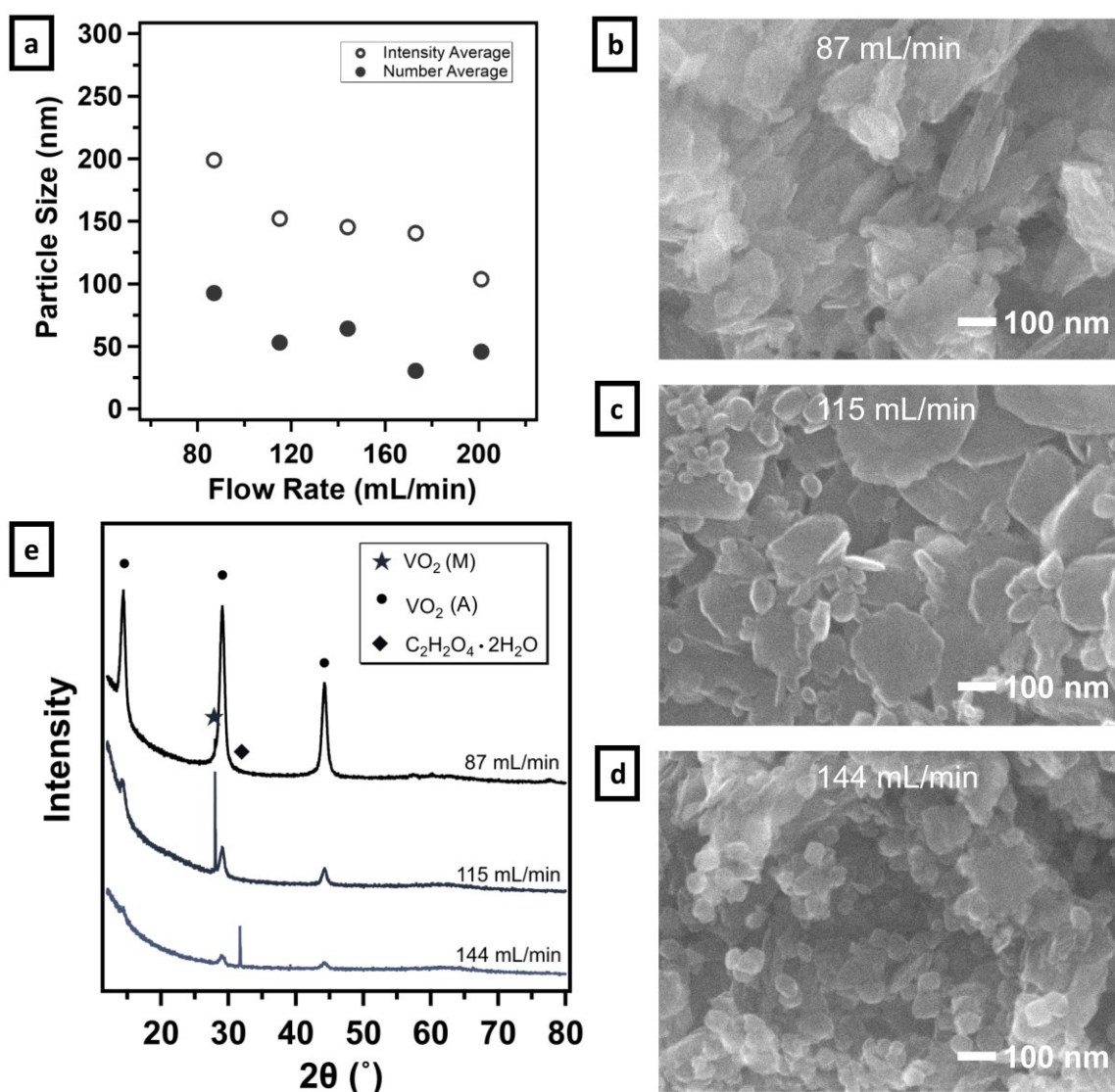


Figure 5-8. VO_2 material characterization results from experiment set D: effect of elevated temperature of the supercritical water (Pump 2) and flow rate on VO_2 nanoparticle (a) size using DLS, (b-d) morphology using SEM, and (e) crystallinity phase using XRD.

5.4.4 Effect of the Molar Ratio

Since previous parametric studies allowed us to achieve conditions that lead to the synthesis of ~50 nm spherical particles, this next fourth study was conducted with the objective to additionally convert these nanoparticles to single, pure M-phase VO₂. Combining many of the optimal parameters ascertained from the previous experiments, the study used a 0.01187 M (3x diluted) vanadium precursor concentration at 144 and 173 mL·min⁻¹ system flow rates and elevated temperature. Additionally, the molar ratio of the V₂O₅ and C₂H₂O₄·2H₂O precursor was changed from a 1:3 to 1:4 ratio. It was observed that experiments D2-D5 had a yellow supernatant after centrifuging, an indication of V⁵⁺ present in the solution, it was thus hypothesized that by using a greater amount of reducing agent, the product yield would increase.¹⁸

Figure 5-9a shows the particle size distribution of the two experiments, E1 and E2. The particle size intensity averages were 94.6 nm and 88.8 nm, with number averages at 57.3 nm and 51.4 nm, which represent system flow rates of 144 and 173 mL·min⁻¹ respectively. The corresponding SEM images, **Figure 5-9b** and **Figure 5-9c** confirm the particle sizes were around or below 50 nm in diameter with uniform, spherical morphology. The addition of extra oxalic acid dihydrate appeared to promote the nucleation and hence higher number of smaller sized of synthesized nanoparticles.^{103, 256} **Figure 5-9d** showed that pure M-phase was achieved at the 173 mL/min⁻¹ system flow rate, but at 144 mL·min⁻¹, there remained two VO₂(A) peaks. The peaks at $2\theta = 28.0^\circ, 37.0^\circ, 42.4^\circ, 55.5^\circ, \text{ and } 56.4^\circ$ which correspond to the (011), (200), (-212), (220), and (022) planes in monoclinic VO₂ however suggest that this phase dominates. This study indicated that a higher amount of a reductant agent along with a higher reactor outlet temperature are key parameters toward achieving a higher yield of nanoparticles, a result that is also similar to observations reported by Bruyère *et al.*¹⁸ The presence of A-phase is observed to vanish at higher

flow rates. This observation could be due to the increased availability of water, but as the Re decreased from 12,496 to 12,254 for E1 and E2 respectively, it is not evident that turbulence played a role in full conversion of the reaction precursors. Another explanation for the residual oxalic acid dihydrate disappearance could be that for experiment E2, $173 \text{ mL} \cdot \text{min}^{-1}$ system flow rate, the colloidal solution had about a 28% longer residence time which allowed for full synthesis to occur while still decreasing the particle size compared to experiment E1 at the lower, $144 \text{ mL} \cdot \text{min}^{-1}$, system flow rate.

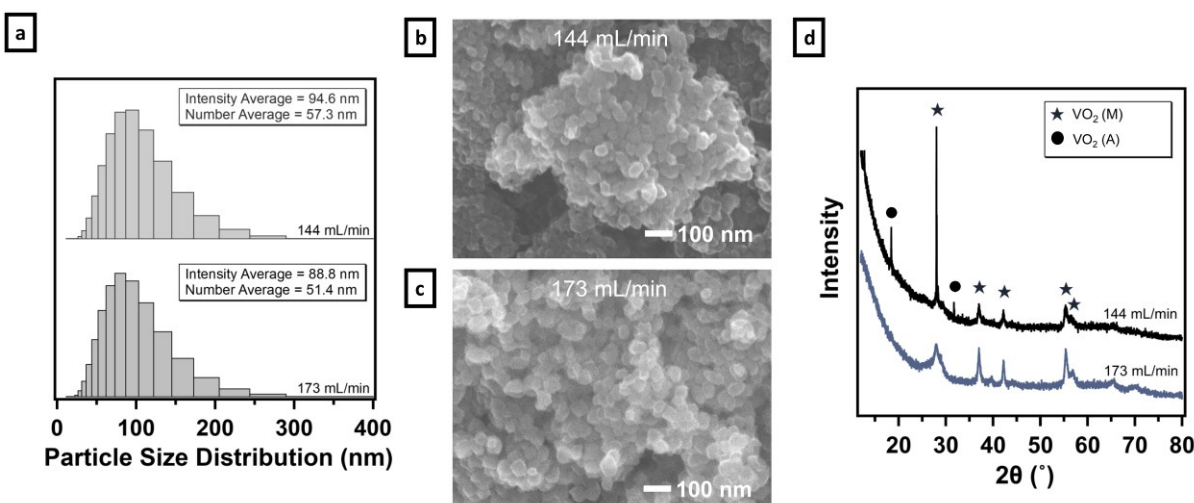


Figure 5-9. VO_2 material characterization results of experiments E1 and E2, resulting in fully M-phase converted, spherical nanoparticles under 50nm in diameter. (a) VO_2 nanoparticle size results from DLS, (b-c) nanoparticle morphology results from SEM, and (d) crystallinity phase results from XRD.

5.4.5 Effect of Reactor Section Flow Rate

The fifth parametric study was completed to confirm results and repeatability of the reactor settings identified in the fourth parametric study as well as test to see the effect that the reactor section flow rate, given from Pump 4, had on the VO_2 nanoparticles size and phase. The effect of increasing the flow rate of the colloidal solution at the beginning of the reactor section was studied computationally, showing non-existent effects of Pump 4 at flow rate of $9 \text{ mL} \cdot \text{min}^{-1}$, and experiments were desired to confirm this calculation.²⁴⁵ In turn, experiments were carried out over

the course of four days with experiment F1 replicating the settings of experiment E2, and experiments F2-F4, eliminating the flow rate from Pump 4; this is achieved by turning the pump off and placing a cap over the inlet location to prevent any backflow. The precursor concentration was held constant at 0.01187 M using a 1:4 molar ratio, and Pump 1, 2, and 3 flow rates were kept constant at 10, 115, and 10 mL·min⁻¹ respectively. Building from the third parametric study and following experiment E2 from the fourth parametric study, higher colloidal solution temperatures, around 387 ± 2 °C, were observed for this study. Achieving this precision across experiment days shows the stability of the reactor to reach and maintain desired operating conditions near the critical point. Results from experiments are outlined in **Table 5-5**.

Table 5-5. Experiments in Study 5: Reactor Section (Pump 4) Flow Rate Effect on VO₂ nanoparticles synthesized in a CHFS reactor - Experimental Parameters, Residence Time, Re, DLS and XRD Material Characterization

Exp.	Total/ Pump 4 Flow Rate (mL·min ⁻¹)	Average Temperature (°C)		Residence Time (s)			Re	DLS		XRD Phase
		T4	T5	Mixing Section	Reactor Section	Total		M _I	M _N	
F1	144/ 9	438.2	387.7	0.24	1.05	1.29	12,496	94.6	57.3	M
F2	135/ 0	427.1	387.5	0.24	1.12	1.36	11,715	94.4	44.5	M
F3	135/ 0	427.5	386.9	0.24	1.15	1.39	11,635	94.6	57.9	M
F4	135/ 0	422.1	385.3	0.26	1.21	1.47	11,431	90.0	41.6	M

Regarding the residence time across this study, all experiments had about 0.24 s in the mixing section, with F4 having a longer time in the mixing section because the temperature of the scH₂O was about 5°C lower than for other experiments, leading to a lower temperature of the colloidal solution exiting the mixing section (T5). The residence time for the colloidal solution in the reactor section was the lowest at 1.05 s for experiment F1; this was due to the use of Pump 4 leading to a higher velocity of the solution. Experiment F1 also had the highest Re of 12,496. For experiments F2-F4 the total residence time was within 11 ms and the resulting Re was smaller than F1, but still within the turbulence zone: 11,573 ± 142, ±2% between experiments. Experiment F1 produced nearly identical DLS results to E2, with an intensity average particle size of 94 nm and

a number average particle size of 57 nm, thereby concluding the repeatability of the experimental results and the reliability of the system parameters. The DLS results showed intensity average particle sizes between 90.0-94.6 nm, which was equal to or smaller than the 94.6 nm that was found when there was additional flow rate provided by Pump 4 in experiment F1. Similarly, the number average particle size range of 41.6-57.9 nm for experiments without the use of Pump 4 shows smaller sizes than when Pump 4 is used. Accordingly, the experimental results are repeatable and the flow rate induced by Pump 4 has a limited effect on the particle properties in the test range. Interestingly, it was seen that at the lower flow rates, and in turn lower Reynolds number the particle size slightly decreased. As all experiments, F1-F4, had about equal residence time in the mixing section, this observation could be due to Pump 4 actually acting to add turbulence and mixing in the reactor section led to particles to experience increased aggregation or growth Ostwald ripening that did not occur in more laminar conditions. For all experiments in this study the XRD analysis confirmed VO₂ products were of a single M-phase, and no residual precursors were observed.

5.4.6 *Effect of Precursor Flow Rate*

The sixth parametric study was conducted over two days to investigate if the amount of precursor introduced into the CHFS reactor system would have a noticeable effect on VO₂ nanoparticles. Experiments were conducted, varying the flow rate of Pump 1 to 5, 10, 15 and 19 mL·min⁻¹. Pump 4 was not used in any of the experiments in this study as the fifth parametric study showed that the 9 mL·min⁻¹ flow rate added by Pump 4 to the reactor section did not have a noticeable effect on the final VO₂ nanoparticle size, and no effect on the phase. Not employing Pump 4 can be advantageous as the amount of water in the colloidal solution was decreased, easing the post processing steps of filtering out the nanoparticles and decreasing waste. The precursor

concentration was held constant at 0.01187 M using a 1:4 molar ratio, and the flow rate of Pump 2, and 3 was kept constant at 115, and 10 mL·min⁻¹ respectively. Results from experiments are outlined in **Table 5-6**.

Table 5-6. Experiments in Study 6: Precursor Flow Rate (Pump 1) Effect on VO₂ nanoparticles synthesized in a CHFS reactor - Experimental Parameters, Residence Time, Re, DLS and XRD Material Characterization

Exp.	Total/ Pump 1 Flow Rate (mL·min ⁻¹)	Average Temperature (°C)		Residence Time (s)			Re	DLS		XRD Phase
		T4	T5	Mixing Section	Reactor Section	Total		M _I	M _N	
G1	130/ 5	432.6	393.7	0.22	1.02	1.23	11,648	116.2	58.6	M
G2	130/ 5	427.7	390.7	0.23	1.08	1.31	11,508	114	62.3	M
G3	135/ 10	427.5	386.9	0.24	1.15	1.39	11,635	94.6	57.9	M
G4	140/ 15	401.1	383.3	0.27	1.25	1.51	11,549	95.4	45.8	M

For the first two experiments, G1 and G2, the precursor flow rate was decreased from the standard 10 mL·min⁻¹ to 5 mL·min⁻¹. DLS results for experiment G1 was about the same as to experiment G2 for intensity average at 114.0nm and 116.2nm respectively, but G1 had a larger number average particle size then G2 at 62.3nm and 58.6nm. The smaller particle sizes observed in experiment G1 is thought to be due to the higher temperature of the scH₂O (T4) and in turn of the colloidal solution exiting the mixing section (T5) being higher than for experiment G2. The higher temperatures resulted in experiment G1 having a lower total residence time of 1.23 s versus 1.31s for G2. Experiment G1 also had a higher Reynolds number, Re, at 11,648 compared to experiment G2 at 11,508 which highlights that although in general a system with a higher Re yields smaller particles, it is not a perfect predictor, and further studies relating this metric to particle growth would be beneficial. Experiment G3 was conducted at identical conditions as experiment F3 in the fifth parametric study with the precursor flow rate at the standard 10 mL·min⁻¹, and the DLS and XRD results agreed with the VO₂ characteristics in F3. Although the temperature of the scH₂O (T4) between G2 and G3 were nearly identical, the resulting colloidal solution temperature (T5) was about 4°C lower for G3. This suggests that it was the increased amount of precursors

converting to products in an endothermic reaction that led to the observed decrease in colloidal solution temperature. From the lower temperature in G3, the total residence time was longer at 1.39s, but this did not seem to affect the particle size in the experimental conditions as the intensity average was determined to be 94.6 nm, while the number average was 57.9 nm, smaller and about equal to that of G2, respectively. For experiment G4, the DLS number average reported smaller particles at 45.8 nm compared to G3. For G4 the total residence time was the longest in the study due to the lower temperature in the mixing and reactor section which also decreased the Re. Overall, it was observed that the increase of precursor flow rate leads to the smaller VO₂ nanoparticles. The crystalline phase of the VO₂ nanoparticles for all four experiments, G1-G4, was confirmed as pure M-phase. This study successfully showed that under the scH₂O and the top of mixing section, Pump 2 and 3, and the precursor flow rate (Pump 1) could be increased to produce M-phase VO₂ particles sized around 50 nm $\pm$ 10 nm as long as the heat transfer and flow characteristics were scaled appropriately.

5.4.7 *Effect of Mixing Section Flow Rate*

For the seventh, and final, parametric study the effect that additional ambient temperature water to the top, or exit, of the mixing section had on VO₂ particles was studied by varying the flow rate of Pump 3. The precursor concentration was held constant at 0.01187 M using a 1:4 molar ratio, and the flow rate of Pump 1 and 2 was kept constant at 10 and 115 mL·min⁻¹, respectively. For the first experiment, H1, both Pump 3 and Pump 4 were set to 10 and 9 mL·min⁻¹, to repeat experiment F1 which itself was a repeat of the optimum conditions defined in experiment E1. For the second experiment, H2, Pump 4 was not used, so as to repeat experiment F3. Then, for the third and fourth experiments, Pump 3 was not used to see if there was a noticeable difference in VO₂ properties. The results from experiments are shown in **Table 5-7**.

Table 5-7. Experiments in Study 7: Mixing Section Flow Rate (Pump 3) Effect on VO₂ nanoparticles synthesized in a CHFS reactor - Experimental Parameters, Residence Time, Re, DLS and XRD Material Characterization

Exp.	Total/ Pump 3/ Pump 4 Flow Rate (mL·min ⁻¹)	Average Temperature (°C)		Residence Time (s)			DLS			XRD Phase
		T4	T5	Mixing Section	Reactor Section	Total	Re	MI	MN	
H1	144/ 10/ 9	438.2	387.6	0.24	1.05	1.29	12,496	78.9	44.5	-
H2	135/ 10/ 0	427.5	386.9	0.24	1.15	1.39	11,635	94.2	57.8	M
H3	125/ 0/ 0	435.1	390.0	0.23	1.14	1.37	11,020	96.8	55.6	M
H4	125/ 0/ 0	439.3	394.9	0.21	1.04	1.25	11,225	80.1	56.2	-

From this experiment set, H1 confirmed for the second time the repeatability of the optimum set of conditions defined in the fourth study, E1. Experiment H2 confirmed the repeatability of nanoparticle size results and crystallinity via XRD confirming M-phase. The residence time between H2 and H3 is also about the same at 1.37 s, due to the temperature of the scH₂O being increased, to 435.1°C. This resulted in lower density of the colloidal solution and faster velocity. This third experiment (H3), where Pump 3 was turned off so only Pump 1 and Pump 2 contributed to the total system flow rate, produced nanoparticles with similar intensity average particle sizes as in the H1, but with an increased number average size of 55.6 nm; more than 10 nm larger than when Pump 3 is turned on. This suggests that the additional flow rate does in fact have an effect on the nanoparticle size, acting to decrease the number average. The residence time between H2 and H3 was also about the same at 1.37s, due to the temperature of the scH₂O being increased, to 435.1°C, resulting in lower density of the colloidal solution and faster velocity. The increase of temperature for H3 decreased the Re to 11,020, showing again that there exists a balance of the flow characteristics in the reactor which yields a given synthesized result. For the fourth and final experiment (H4), all parameters of H3 are used, with the exception to the temperature of the scH₂O, which is further increased to 439.3 °C to observe any additional temperature effects on the VO₂ particles. As a result, H4 presented a slightly lower DLS intensity

average particle size of 80.1 nm, but the number average particle size remained virtually unchanged at 56.2 nm. From these four experiments, it could be concluded that, although not enough sample from H1 is recovered to measure the phase composition, Pump 3 is an important factor to increase overall system flow rate and Re which in turn help to reach the goal of VO_2 nanoparticles less than 50 nm in diameter. It is thought however, that since H2 obtained pure M-phase at T4 and T5 temperatures below that of H1, that M-phase would likely be attainable in H1 as well. There may also be other uses for employing Pump 3 including adding a capping agent to make the nanoparticles, but such study is beyond the scope of this chapter.

5.5 CONCLUSIONS

This chapter revealed that the single-step continuous hydrothermal flow synthesis (CHFS) reactor can adjust multiple parameters instantaneously, giving unique advantages over the conventional multi-step batch-methods. Seven parametric studies focusing on understanding the roles of flow rates, temperature, precursor concentration, and composition helped determine the optimal conditions to synthesize VO_2 nanoparticles ranging in size from 45-350 nm and in either the M- or A-phase. For the specific goal of ultrasmall nanoparticles suitable for applications like smart window films, the CHFS reactor manufactured VO_2 M-phase nanoparticles with average diameter below 50 nm with precise control. At elevated colloidal solution reaction temperatures between 390-395°C, full conversion of the 50 nm VO_2 nanoparticles from A- to M-phase is achieved when a 1:4 vanadium pentoxide to oxalic acid dihydrate molar ratio for precursor concentration of 0.01187 M $[V^{4+}]$ and a total system flow rate between 125-135 mL·min⁻¹ for a total residence time between 1.23-1.50s and Re between 11,000-12,500 was used. CHFS reactors demonstrate a promising potential to manufacture VO_2 nanoparticles with reliable control of size, shape, and crystallinity.

Chapter 6. SUMMARY AND FUTURE WORK

6.1 SUMMARY AND RESEARCH CONTRIBUTIONS

This dissertation presents several contributions to the application of supercritical phase fluids for scalable nanomaterial synthesis. A matrix of simulations gives insight into how the selection of equation of state (EoS) models impact supercritical phase fluid simulation accuracy which can aid in reactor design and optimization. A new continuous flow reactor using supercritical carbon dioxide as a heating and mixing medium is developed and applied to the synthesis of two metal-organic framework (MOF) nanomaterials across a range of reactor parameters. Finally, the first single-step synthesis of pure M-phase VO₂ nanoparticles is achieved using a continuous flow supercritical water reactor.

Chapter 2 presents a 99-case matrix simulated near the critical point to inform how EoS selection impacts accuracy. The simulation matrix covers four EoS: Ideal Gas Law, Peng-Robinson, Soave-Redlich-Kwong, Span-Wagner, at isobaric conditions with two inlet temperatures, four wall temperatures, and eleven Reynolds numbers. Large variations in thermophysical properties led to thermal and momentum behavior far more complicated than found in non-critical fluids. These effects make EoS of lower accuracy like the Ideal Gas Law and the commonly used Peng-Robinson and Soave-Redlich-Kwong cubic EoS inaccurate. Thus, using the Ideal Gas Law for numerical simulations near the critical point is not recommended. Compared to the high-fidelity SW EoS, cubic EoS's underestimates Nu values by up to 38%, and cubic EoS underestimates C_D values by 18-42%. Regarding the computational cost of EoS selection, high accuracy Span-Wagner EoS requires half the number of iterations of medium accuracy cubic EoS

while adding only 17% wall-time to simulations. Thus, the computational cost should not significantly deter applying this higher accuracy EoS to future numerical simulations. These findings pave the way for robust and scalable simulation solutions in the supercritical phase.

Chapter 3 details the analysis, design, and operation of an innovative approach for rapidly producing MOFs in an environmentally friendly and scalable continuous scCO₂ flow reactor. The approach successfully synthesized the zirconium-based MOF UiO-66 at a production rate of 104 g·h⁻¹ with a reaction time of under three seconds. This research contribution verifies the feasibility of the conceptualized continuous scCO₂ flow synthesis reactor method. The contribution also encourages the continued exploration of using scCO₂ in a continuous flow reactor for sustainable and scalable MOF synthesis.

Chapter 4 expanded on the research in Chapter 3 by making modifications to the original reactor design, which allowed for increased insight into the thermodynamic and kinetic environment in the reactor. In turn, a second MOF, the copper-based MOF HKUST-1, was successfully synthesized. The modified continuous scCO₂ flow reactor success in synthesizing pure HKUST-1 across three different pressures, six different temperatures, and four different CO₂ mole fractions. High quality materials were synthesized at all conditions, which establishes the robustness of the synthesis method. Four sets of experiments showed very good repeatability for both particle size and porosity. Additionally, this synthesis method proved to repeatably result in high-quality HKUST-1 MOF materials with a maximum BET surface area of over 2,389 m²·g⁻¹. Thus, the new scalable synthesis method presented in Chapters 3 and 4 can enable the widespread integration of MOFs into commercial applications like energy storage devices, targeted drug delivery, and gas capture.

Chapter 5 utilized the established continuous flow supercritical water reactor method to synthesize the metal-oxide nanomaterial VO₂. The research contributed new knowledge to how continuous flow supercritical water reactors can be used for high-throughput analysis to tune VO₂ nanoparticle's crystalline phase, shape, and size. Specifically, seven parametric studies focus on understanding the role of residence time, temperature, precursor concentration, and molar concentration to outline the optimal conditions to synthesize VO₂ nanoparticles ranging in size from 45-350 nm and in either the M- or A-phase. The parameters presented through the work can be used to synthesize uniform M-phase VO₂ nanoparticles applicable to thermochromic smart window films for which the world can benefit.

6.2 FUTURE DIRECTIONS

Future directions of for the work described in this dissertation could include developing a simulation model that incorporates the heat transfer, mass transfer, and fluid dynamics occurring in counter-current mixing sections using supercritical fluids as a heating and mixing medium. Creating an accurate model would require first the measurement of the properties of the fluids of interest in syntheses, such as N, N-dimethylformamide (DMF), and binary mixtures, such as CO₂-Ethanol. Then, a high-fidelity equation of state (EoS) would have to be created and selected for such a simulation as errors here could limit the accuracy of results, as shown in Chapter 2. Experimental validation of the model can be completed with thermocouple placement like those described in Chapter 4 and Chapter 5.

Another future direction could be investigating the synthesis of other nanomaterials at different conditions within the continuous flow reactor systems. Additional MOFs that could be valuable to investigate include the zinc-based MOF, MOF-5, given its ultrahigh porosity applicable for hydrogen gas storage.²⁵⁷ Different conditions to be investigated include lower

temperatures than studied in this dissertation. For reactors using scCO₂, decreasing the temperature to as low as 35 °C would still allow for carbon dioxide to maintain in the supercritical phase. Given that continuous flow reactors using supercritical fluids can operate across a range of temperatures and pressures, studying synthesis in this way could deliver the large datasets necessary for artificial intelligence and machine learning computational analysis.

Lastly, a future direction of the research could entail including *in operando* characterization techniques into the reactor, such as Raman spectroscopy or X-ray diffraction. *In operando* Raman spectroscopy has been applied by our research group in continuous flow supercritical water gasification reactors to provide kinetic information about the formation and decomposition of alcohols and organic compounds.^{145, 258, 259} *In operando* Raman spectroscopy applied to the subject of continuous flow nanomaterial synthesis described in this dissertation could provide valuable insight into synthesis kinetics and possibly reaction pathways.

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APPENDIX A

c	Fitting constant for convective heat transfer
C_D	Drag coefficient
c_p	Specific heat at constant pressure, $J \cdot kg^{-1} \cdot K^{-1}$
d	Diameter of cylinder, m
F_D	Drag force
g	Gravitational acceleration, $m \cdot s^{-2}$
h	Heat transfer coefficient, $W \cdot m^{-2} \cdot K^{-1}$
k	Thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$
ℓ	Length of mixing section, m
m	Mass, kg
m	Fitting constant for convective heat transfer
$\dot{m}$	Mass flow rate, $kg \cdot s^{-1}$; $(\rho \cdot V)$
P	Pressure, MPa
q'	Heat flux per unit length, W
T	Temperature, K
U	Free-stream velocity, $m \cdot s^{-1}$
v	Velocity magnitude, $m \cdot s^{-1}$
V	Volume, m^3

Greek Symbols

Δ	Change
β	Volumetric thermal expansion coefficient
$\mathcal{D}$	Mass diffusivity, $m^2 \cdot s^{-1}$
ρ	Density, $kg \cdot m^{-3}$
μ	Dynamic viscosity, $Pa \cdot s$
ω	Acentric factor

Non- Dimensional Numbers

Gr	Grashof number; $\left(\frac{d^3 \cdot \rho \cdot g \cdot \Delta \rho}{\mu^2} \right)$
Le	Lewis number; $\left(\frac{Sc}{Pr} \right)$
Nu	Nusselt number, $\left(\frac{h \cdot d}{k} \right)$
Pe	Peclet number; $(Re \cdot Sc)$
Pr	Prandtl number; $\left(\frac{\mu \cdot c_p}{k} \right)$

Re	Reynolds number; $\left(\frac{\rho \cdot v \cdot d}{\mu}\right)$
Sc	Schmidt number; $\left(\frac{\mu}{\rho \cdot \mathcal{D}}\right)$
Sh	Sherwood number; $\left(\frac{h \cdot d}{\mathcal{D}} = (4 + 1.21 \cdot Pe^{2/3})^{1/2}\right)$

Superscripts

*	Nondimensional value
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Subscripts

1	Inner inlet pipe
2	Outer inlet pipe
b	scCO ₂ bubble
cr	Critical
f	Film
o	Free-stream fluid
pc	Pseudocritical
r	Reduced
w	Wall

Abbreviations

BPR	Back Pressure Regulator
CO ₂	Carbon Dioxide
EoS	Equation of State
DMF	N, N- Dimethylformamide
H ₂ O	Water
IGL	Ideal Gas Law
liq.	Liquid phase
PR	Peng-Robinson
PXRD	Powder X-Ray Diffraction
rpm	Rotations Per Minute
sc	Supercritical
scCO ₂	Supercritical carbon dioxide
scH ₂ O	Supercritical Water
SRK	Soave-Redlich-Kwong
SW	Span-Wagner
v.	Vapor phase

APPENDIX B

Details on Vapor-Liquid Equilibrium (VLE) solubility extrapolation

Table S1. Experimental Vapor-Liquid Equilibrium (VLE) data for Carbon Dioxide-N,N-Dimethylformamide system reported by Duran-Valencia *et al.*¹⁷²

T [K]	P [MPa]	Mole Fraction	
		xCO ₂ (liquid)	yCO ₂ (vapor)
293.95	0.56	0.0962	0.9993
293.95	1.03	0.1691	0.9996
293.95	1.51	0.2402	0.9997
293.95	1.99	0.3088	0.9997
293.95	2.45	0.3694	0.9997
293.95	3.12	0.461	0.9998
293.95	3.57	0.5256	0.9998
293.95	4.02	0.6031	0.9997
293.95	4.51	0.6832	0.9997
293.95	4.85	0.7723	0.9997
293.95	5.04	0.8627	0.9997
293.95	5.13	0.8823	0.9997
313.05	0.43	0.0528	0.9976
313.05	1.22	0.1414	0.9989
313.05	1.86	0.2062	0.999
313.05	3.02	0.3165	0.9993
313.05	3.87	0.398	0.9992
313.05	5.03	0.5075	0.9992
313.05	5.63	0.5672	0.999
313.05	6.92	0.7194	0.9983
313.05	7.51	0.8137	0.9977
338.05	0.43	0.0345	0.991
338.05	1.09	0.0861	0.995
338.05	2.18	0.1641	0.9976
338.05	3.23	0.2395	0.998
338.05	4.29	0.3037	0.998
338.05	5.34	0.3712	0.9979
338.05	6.2	0.4233	0.9978
338.05	8.09	0.5385	0.9962
338.05	8.97	0.5921	0.9957
338.05	9.91	0.6583	0.9933
338.05	11.05	0.7422	0.9874
338.05	11.51	0.7894	0.9836

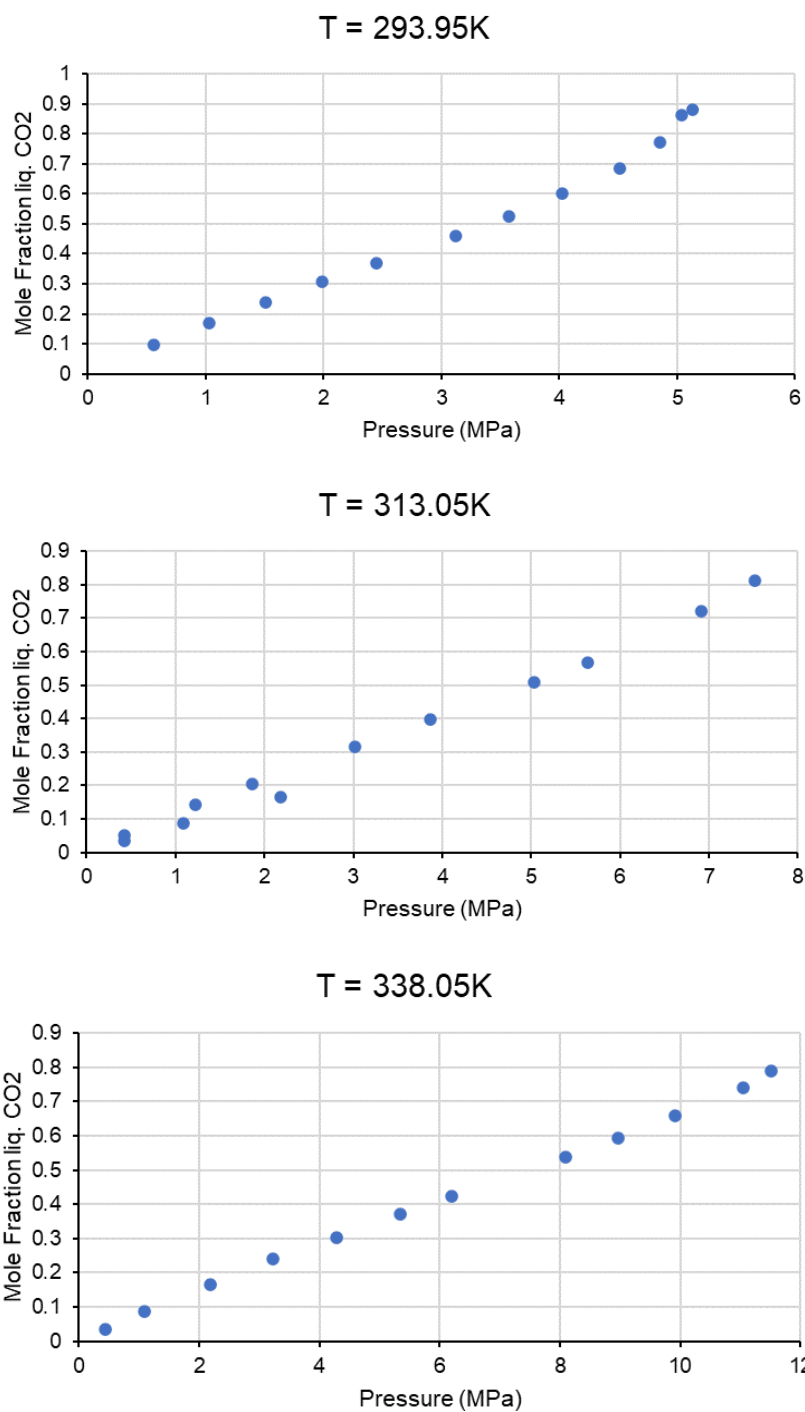


Figure S1. Plots of the total pressure versus the liquid phase CO₂ mole fraction at (top) T=293.95K (middle) T=313.05K and (bottom) T=338.05K from Duran-Valencia *et al.*¹⁷²

Note: Liquid phase CO₂ data was used because vapor phase CO₂ data showed that it mainly consisted (>98%) of vapor phase CO₂, and no vapor phase DMF.

The Lewis Randall rule¹⁸⁰ was used to calculate the fugacity of the CO₂ in the liquid phase at four pressures (1, 2, 3, 4 MPa) for each of the three temperatures.

$$f_{\text{CO}_2,\text{g}} = x_{\text{CO}_2} f_{\text{CO}_2,\text{f}}$$

At elevated pressure, the fugacity of CO₂ in the vapor phase deviates from the measured pressure, so estimation of the corrected fugacity value was completed. The vapor phase fugacity of the CO₂ was calculated from the known temperature and pressure using a generalized fugacity coefficient chart. Then the known value of x_{CO_2} can be used to calculate $f_{\text{CO}_2,\text{f}}$ (**Table S2**).

Table S2. Overview of fugacity coefficients at known temperature and pressure and in turn corrected fugacity value for vapor phase CO₂

	Fugacity Coefficient			Fugacity, MPa		
Temperature, K	293.95	313.05	338.05	293.95	313.05	338.05
Pressure, MPa						
1	0.95	0.98	1	0.95	0.98	1
2	0.92	0.94	0.96	1.84	1.88	1.92
3	0.85	0.89	0.94	2.55	2.67	2.82
4	0.82	0.85	0.92	3.28	3.40	3.68
6		0.83	0.86		4.98	5.16
8			0.82			6.56
10			0.76			7.6

The liquid phase fugacity values were then calculated using the vapor phase fugacity values and the liquid phase CO₂ mole fraction via the Lewis Randall rule (**Table S3**).

Table S3. Overview of liquid phase CO₂ mole fraction via Lewis Randall rule and liquid phase fugacity

	X _{CO₂} (interpolated from data plots)			Liquid Phase Fugacity, MPa		
Temperature, K	293.95	313.05	338.05	293.95	313.05	338.05
Pressure, MPa						
1	0.19	0.12	0.095	5.000	8.167	10.526
2	0.32	0.22	0.16	5.750	8.545	12.000
3	0.45	0.31	0.23	5.667	8.613	12.261
4	0.60	0.42	0.29	5.467	8.095	12.690
6		0.62	0.42		8.032	12.286
8			0.545			12.037
10			0.68			11.176

The results show that, as expected, the liquid phase fugacity values appear to be independent of total pressure.

We next use the Claperyon-Clausius temperature dependence to extrapolate the liquid phase fugacity to 393 K. This entails a plot of $\ln(f_{\text{CO}_2,f})$ vs. $1/T$ for the four pressures for which we have full temperature data (**Figure S2**).

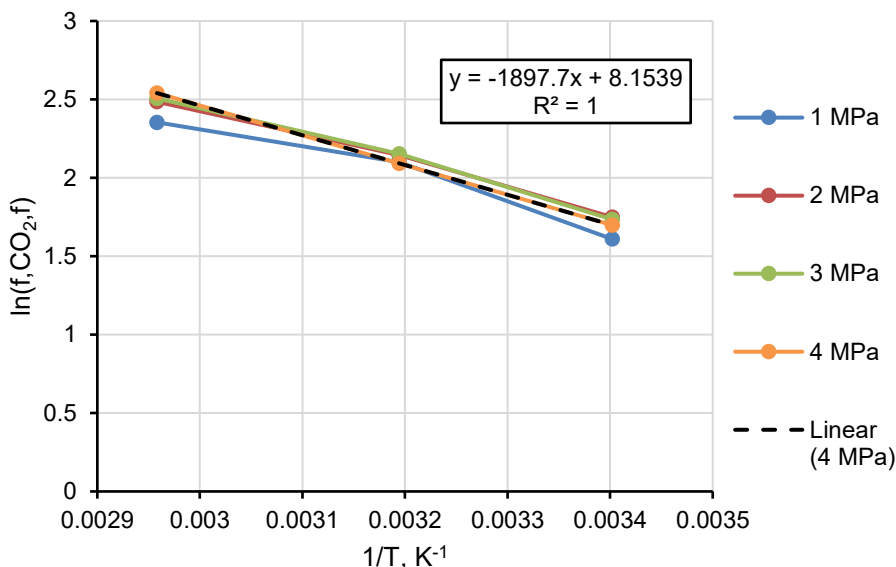


Figure S2. Plot of the fugacity versus temperature at four pressures.

A linear regression for the 4MPa data produced the fit shown below:

$$\ln(f, \text{MPa}) = 8.1539 - 1897.7/T(\text{K})$$

Inserting the target temperature (393K) produced $f_{\text{CO}_2,f} = 27.8\text{MPa}$.

At 393K and 10MPa, the fugacity coefficient for CO₂ is 0.96, which is used in the Lewis Randall rule

$$f_{\text{CO}_2,g} = x_{\text{CO}_2} f_{\text{CO}_2,f} \text{ or } (0.96)(10 \text{ MPa}) = x_{\text{CO}_2}(27.8\text{MPa})$$

results in the equilibrium mole fraction of CO₂ in the liquid phase as $x_{\text{CO}_2} = 0.345$. The resulting equilibrium mole fraction of 0.345 equals an equilibrium mass fraction of 0.2408g of CO₂ in the liquid DMF.

Method and calculations of energy consumption for UiO-66 MOF synthesis

Density, ρ ($\text{kg}\cdot\text{m}^{-3}$), and specific heat, c_p ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$), values from NIST Refprop¹⁴².

1st law of thermodynamics energy balance equation reduces to: $E=q=m\cdot c_p\cdot\Delta T$

Given:

- Continuous flow MOF synthesis reactor operates for one hour
- $20\text{mL}\cdot\text{min}^{-1}$ volumetric flow rate, $\dot{v}$ where $\dot{v} = \frac{\dot{m}}{\rho}$ where $\dot{m}$ is mass flow rate
- H_2O enters pump at room temperature and atmospheric pressure (298K, 0.101MPa)
 - Density H_2O at 298K, 0.101MPa is $1007.6\text{kg}\cdot\text{m}^{-3}$
- CO_2 enters pump from cold bath temperature and pressure (266K, 3.45MPa)
 - Density CO_2 at 266K, 3.45MPa is $971.02\text{kg}\cdot\text{m}^{-3}$
- scH_2O reactor operating temperature is 673K
- hydrothermal reactor operating temperature is 418K
- scCO_2 reactor operating temperature is 398K

Results:

- Total volume flowing through reactor in the one hour of operation is ($20\text{mL}\cdot\text{min}^{-1} \times 60\text{min}\cdot\text{h}^{-1} = 1200\text{mL}$)
- Mass of CO_2 is 1166g
- Mass of H_2O is 1209g
- scH_2O change in temperature, $\Delta T = 673\text{K} - 298\text{K} = 375\text{K}$
- hydrothermal change in temperature, $\Delta T = 418\text{K} - 298\text{K} = 120\text{K}$
- scCO_2 change in temperature, $\Delta T = 273\text{K} - 393\text{K} = 120\text{K}$
 - The initial temperature is above the pumped temperature because it is assumed that heat from the surroundings increases the fluid temperature as it flows from the pump exit to the inlet of the heating section

Energy required (in kJ) to raise the solvent (H_2O or CO_2) to operating temperature:

- For scH_2O – 3,037.52kJ
- For hydrothermal – 603.41kJ
- For scCO_2 – 393.13kJ

Method and calculations of DMF waste created for 100g UiO-66 MOF

Quantifying amount of waste produced in different continuous flow UiO-66 MOF synthesis methods by amount of DMF used to synthesize 100g of UiO-66. Does not count DMF used for post processing including non-synthesis reactor cleaning (i.e. continuous flow microwave synthesis reportedly used DMF to pump remainder of reagents through the microwave oven). For DMF quantities it was assumed that solid precursors are well mixed and fully dissolved in liquid precursor with negligible change in volume and ideal mixing occurs between liquid phase precursors.

Table S4. Breakdown of DMF used in synthesis of UiO-66 MOF by continuous flow microwave, solvothermal, and scCO₂ reactors.

Continuous Flow MOF Synthesis Method	Approximate Amount of DMF Used in Synthesis (mL)	Amount UiO-66 Synthesized (g)	Reference
Microwave	392 [†]	17.51	80
Solvothermal	20	0.28 [‡]	75
scCO ₂	100	8.71	this work

[†]Calculated from reference's supplementary information

[‡]Calculated from reported reaction run time of 10min and production rate of 1.68g·hr⁻¹

[†]Approximate amount of DMF used for continuous flow microwave synthesis (scaled-up synthesis method) ⁸⁰:

1. Zr-metal precursor stock solution of 13.98g ZrCl₄ + 103mL Acetic Acid + 26mL water + 271mL DMF for 400mL total
 - a. Solution is ~ (271/400=) 67.75% DMF
 - b. Flow rate of 5.05mL·min⁻¹ for 66 min → 333.3mL solution
 - c. Amount of DMF is: (333.3·0.6775=) 225.8mL DMF
2. BDC organic precursor stock solution of 9.97g H₂BDC + 200mL DMF
 - a. Solution is 100% DMF
 - b. Flow rate of 2.52mL·min⁻¹ for 66 min → 166.32mL solution
 - c. Amount of DMF is: 166.32mL DMF
3. Total amount of DMF used/waste created (226+166=) 392mL DMF

For 100g of UiO-66 MOF by continuous flow synthesis method:

- Microwave: 100g/17.51g=5.711 → 392mL DMF · 5.711 = 2,338.7mL DMF
- Solvothermal: 100g/0.28g = 357.14 → 20mL DMF · 357.14 = 7,143mL DMF
- scCO₂: 100g/8.71g = 11.48 → 100mL DMF · 11.48 = 1,148 mL DMF

APPENDIX C

Archival Publications

7. **Rasmussen, E. G.**, Kramlich, J., Novosselov, I., (2021) “Continuous Flow Synthesis of High-Quality HKUST-1 MOF in Supercritical Carbon Dioxide”, *In Preparation*
6. **Rasmussen, E. G.**, Tran, M., Shevchenko, E., Li, J., (2021) “High-throughput Screening of Vanadium (IV) Oxide via Continuous Hydrothermal Flow Synthesis Reactor”, *Under Review*, doi: 10.33774/chemrxiv-2021-kl74l
5. **Rasmussen, E. G.**, Yellapantula, S., Martin, M., (2021) “How equation of state selection impacts accuracy near the critical point: Forced convection supercritical CO₂ flow over a cylinder”, *The Journal of Supercritical Fluids*, 171,105141. doi: 10.1016/j.supflu.2020.105141
4. **Rasmussen, E. G.**, Kramlich, J., Novosselov, I., (2020) “Scalable Continuous Flow Metal Organic Framework (MOF) Synthesis Using Supercritical CO₂ ”, *ACS Sustainable Chemistry and Engineering*, 8 (26), 9680-9689. doi: 10.1021/acssuschemeng.0c1429
3. Martin, M., **Rasmussen, E. G.**, Yellapantula, S., (2019) “Nonlinear Heat Transfer from Particles in Supercritical Carbon Dioxide near the Critical Point”. *Journal of Thermal Science and Engineering Applications*, 12(3). doi:10.1115/1.4045222
2. Pinkard, B. R., Gorman, D. J., **Rasmussen, E. G.**, Kramlich, J. C., Reinhall, P. G., Novosselov, I. V. (2019). Kinetics of formic acid decomposition in subcritical and supercritical water—a Raman spectroscopic study. *International Journal of Hydrogen Energy*, 44(60), 31745-31756. doi: 10.1016/j.ijhydene.2019.10.070
1. Pinkard, B. R., Gorman, D. J., Tiwari, K., **Rasmussen, E. G.**, Kramlich, J. C., Reinhall, P. G., Novosselov, I. V. (2019). “Supercritical water gasification: practical design strategies and operational challenges for lab-scale, continuous flow reactors” *Heliyon*, 5(2), e01269. doi: 10.1016/j.heliyon.2019.e01269

Technical Conference Podium Presentations

3. **Rasmussen, E.G.**, Martin, M.J., Yellapantula, S., Kramlich, J., Novosselov, I., "Effects of Equations of State Selection in Numerical Simulations of Supercritical Carbon Dioxide" APS Division of Fluid Dynamics (Seattle, WA) November 25, 2019.
2. **Rasmussen, E.G.**, Kramlich, J., Novosselov, I., "Continuous Hydrothermal Synthesis of Catalytic Metal Oxide Nanoparticles in Supercritical Water" MRS Fall Meeting-ET08: Emerging Materials and Characterization for Catalysis (Boston, MA) November 28, 2018.
1. **Rasmussen, E.G.**, Yellapantula, S., Martin, M. J., “Comparison of Multiple Equations of State in Numerical Simulation of Supercritical Carbon Dioxide Flow Around a Heated Cylinder” Rocky Mountain Fluid Mechanics Research Symposium (Boulder, CO) August 14, 2018.

APPENDIX D

1. U.S. Provisional Patent Application No. 62/892,340 filed 08/27/2019;
Entitled: “Continuous Synthesis of Porous Coordination Polymers in Supercritical Carbon Dioxide”; Inventors: Elizabeth G. Rasmussen, John C. Kramlich, Igor V. Novosselov
2. W.O. Provisional Patent Application No. 2021/086483 A2 filed 08/27/2020;
Entitled: “Continuous Synthesis of Porous Coordination Polymers in Supercritical Carbon Dioxide”; Inventors: Elizabeth G. Rasmussen, John C. Kramlich, Igor V. Novosselov

APPENDIX E

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