Removal of Phenol from Oil/Gas Wastewater
by Catalytic Supercritical Water Treatment

A thesis presented to
the faculty of
the Russ College of Engineering and Technology of Ohio University

In partial fulfillment
of the requirements for the degree
Master of Science

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April 2016
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This thesis titled
Removal of Phenol from Oil/Gas Wastewater
by Catalytic Supercritical Water Treatment

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Abstract

DE SILVA, CHAMARA L., M.S., April 2016, Chemical Engineering

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The U.S. oil/gas industry generates over 21 billion barrels of produced water annually [1]. This wastewater stream contains a host of components including suspended solids, dissolved solids, and hydrocarbons [2]. This waste stream represents a significant beneficial resource if reused to offset other water consumption demands. However, many beneficial reuse applications have strict hydrocarbon limits [3].

Oxidation of hydrocarbons in supercritical water media provides an effective removal technique allowing wastewater reuse. In order to quickly and effectively remove hydrocarbons in supercritical water a heterogeneous catalyst is needed. In this study, an MnO₂ catalyst on a TiO₂ support was synthesized and evaluated for removal of phenol in supercritical water. Synthesized catalysts were characterized using temperature programmed reduction, pulse chemisorptions and X-ray powder diffraction. Catalyst activity for phenol conversion was evaluated in a continuous packed bed reactor at supercritical water conditions, while analyzing vapor and liquid products. Evaluated process variables included free O₂ concentration and the catalyst Mn loading. Both variables had positive effects on phenol conversion. The process reached complete destruction of phenol at an O₂ level of 500% of the stoichiometric O₂ for complete oxidation. Increase in catalyst Mn loading increased its active sites concentration enhancing the contribution of heterogeneous reaction kinetics for phenol supercritical
water oxidation (SCWO); however a saturation limit appeared to be reached as Mn loading is further increased. A part of the Mn composition appeared to be unable to create active sites on the catalyst due to interactions with TiO₂. A phenol conversion of 70% was reached at 12% (w/w) Mn in the catalyst with 100% excess O₂.
I dedicate this thesis to my dear parents, Quintus Silva and Kumuduni Samarabandu. Their encouragements, background support and love kept my courage to complete this work successfully.
Acknowledgements

I would like to give my deepest appreciation to my academic advisor, Dr. Jason Trembly, for guiding me throughout my graduate studies. His immense support including advice, suggestions and financial support allowed the research to move forward while developing myself as an engineering professional.

My kind acknowledgements also goes to the committee members, Dr. David Young, Dr. Natalie Kruse and Dr. Marc Singer for their valuable time and insight. Their guidance in the planning of my research helped narrow my focus resulting in a better quality product.

My special thanks also goes to Mr. Shyler Switzer, Dr. Wen Fan and Mr. David Ogden for providing me with immense technical and analytical support. Their workshop and analytical training, equipment purchasing support, advice, safety reviews and troubleshooting support were extremely important during the fabrication and the operation of the experimental apparatus.

In addition, I am also thankful to Mr. Tom Johnson for his help in developing the controls for the experimental apparatus used in this work. Further, I would like to acknowledge my fellow graduate and undergraduate students for their help and support during my time at Ohio University.
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Acronyms

\( C_{GE} \) : Carbon to Gas Efficiency

\( C_{GE_{cat}} \) : Carbon to Gas Efficiency in the presence of catalyst

\( C_{GE_{hom}} \) : Carbon to Gas Efficiency in the absence of catalyst

\( a_{CO2} \) : Concentration of CO\(_2\) in gas product stream (ppmw)

\( a_{CO} \) : Concentration of CO in gas product stream (ppmw)

\( a_{H2} \) : Concentration of H\(_2\) in gas product stream (ppmw)

\( a_{in\_Phenol} \) : Concentration phenol in feed water stream (ppmw)

\( a_{out\_Phenol} \) : Concentration phenol in liquid product stream (ppmw)

\( C_{out\_gas} \) : Total carbon flow rate in gas product stream (mg/hr)

\( C_{out\_Phenol} \) : Total carbon flow rate as phenol in liquid product stream (mg/hr)

\( C_{out\_non\_Phenol} \) : Total carbon flow rate as non-phenols in liquid product stream (mg/hr)

\( C_{in} \) : Total carbon flow rate into the system (mg/hr)

\( V_{Ar} \) : UHP grade Ar injection rate to the product stream via MFC-101 (sccm)

\( V_{m\_STP} \) : Molar volume of Ar at standard temperature & pressure (ml/mol)

\( M_c \) : Molecular weight of carbon (mg/mol)

\( M_{phenol} \) : Molecular weight of phenol (mg/mol)

\( F \) : Fluid flow rate at room temperature (=8 \times 10^{-3} \text{ L/min controlled by HPLC pump})

\( SA_{Act} \) : Active surface area (m\(^2\)/g)

\( D_{met} \) : Percent metal dispersion (%)

\( N_{surface} \) : Number of active metal atoms on catalyst surface

\( N_{total} \) : Number of active metal atoms in catalyst sample

\( m_l \) : Mass of Mn solution (g)

\( SV_p \) : Specific pore volume of catalyst support (cm\(^3\)/g)

\( m_s \) : Measured catalyst support mass (g)

\( \rho_l \) : Density of Mn solution (g/cm\(^3\))

\( L_{cat} \) : Length of catalyst bed (cm)

\( t_r \) : Residence time (s)

\( V_R \) : Volume flow rate at reactor conditions (cm\(^3\)/s)
\( A_{\text{In}} \) : Internal flow cross section area in reactor perpendicular to main flow (cm\(^2\))

\( PCV \) : Phenol conversion (%)

\( n_{O_2,\text{ac}} \) : \( O_2 \) molar flow rate into the reactor (mol/s)

\( n_{O_2,\text{st}} \) : Stoichiometric \( O_2 \) molar flow rate for complete combustion (mol/s)

\( \text{BET} \) : Brunauer, Emmett and Teller surface area measurement methodology

\( V_s \) : Total adsorbed \( O_2 \) volume at STP in a pulse chemisorption experiment (cm\(^3\))

\( SW \) : Sample weight used for pulse chemisorption (g)

\( SF \) : Stoichiometric factor for \( O_2 \) chemisorption

\( A_{\text{MnO}_2} \) : Molecular cross section of \( \text{MnO}_2 \) (m\(^2\))

\( F_{\text{Mn}} \) : Fraction of Mn in catalyst (w/w)

\( M_{\text{Mn}} \) : Molar mass of Mn (g/mol)

\( r_{\text{cat}} \) : Heterogeneous reaction rate \((\text{mol}_{\text{phenol}}/\text{g}_{\text{cat}} \cdot \text{s})\)

\( n_{\text{phenol \ in}} \) : Phenol molar flow rate into the reactor (mol/s)

\( m_{\text{cat}} \) : Catalyst mass used in the reactor (g)
Chapter 1: Introduction

1.1. Background

Today, wastewater treatment receives significant attention in a wide range of industries, from oil/gas to food and beverages. It has been estimated that the United States uses 1.4% of its electrical generation on water and wastewater treatment and distribution, at a cost of $4 billion per year [5]. The water and wastewater treatment chemicals market has a globally forecasted Compound Annual Growth Rate (CAGR) of 4.5% from 2013 to 2018, indicating the significance of water treatment requirements in the near future [6].

Of the toxic compounds frequently encountered in industrial wastewater, phenol raises particular concerns. The U.S. Environmental Protection Agency (EPA) has defined eleven phenolic compounds, as priority pollutants in industrial and municipal wastewaters [6]. The EPA-defined human health water quality criteria value for phenol is 10 mg/L [7]. Phenol is a major pollutant in wastewater streams from petroleum, petrochemical, pharmaceutical, steel, dye synthesis, pulp and paper, and coal gasification industries [8, 9]. These industries comprise approximately 30% of the water and wastewater treatment equipment market worldwide [10].

Oil and gas wells have been and are increasingly becoming an even greater source of wastewater containing organics due to the development of U.S. unconventional shale plays [14]. Shale plays are developed using a combination of horizontal drilling with hydraulic fracturing. Once completed, such wells generate flowback water, which can be reused in subsequent hydraulic fracturing jobs, and produced water generated along with the hydrocarbons. More than 1,500 gallons of produced water can be generated from every 1,000 cubic feet of natural gas produced [16]. According to statistics prepared for the Groundwater Protection Council, the U.S. oil/gas industry generated 21.1 BBL of produced water in 2012 [75]. Analysis of produced water samples generated by Marcellus shale wells indicates the water contains over 100 organic compounds with total concentrations ranging from 0.5 to 20 ppm. Phenol and pyridine are the main semi-volatile compounds found in the produced water streams [15]. The primary method of managing produced water is to truck it to Class II salt water disposal (SWD) wells, where it is injected deep below the surface into saline aquifers to avoid contamination of fresh water.
1.2. Current Phenol Removal Methodologies

Methods used for phenol removal from wastewater include both non-destructive and destructive techniques. Adsorption, distillation, extraction, and membrane separation processes are the main representatives of non-destructive techniques. Activated carbon is a common adsorbent used in the industry. However, regeneration of used activated carbon significantly reduces its activity. Issues associated with extraction processes include subsequent solvent regeneration requirements, which increase costs [11]. Membrane separation processes are easily scalable and are low energy consumers; however, fouling caused by colloids is a common limitation [13]. As destructive processes, oxidation and biological degradation are popular in the field [11]. Oxidation is being investigated using oxygen, other chemicals (O₃, Cl₂, H₂O₂, etc.), and electrochemical-based techniques [11]. The possibility of generating hazardous wastes by adding pollutants such as chlorinated organic compounds to the environment limits the use of oxidation-based techniques. Furthermore, in the case of using O₂ in compressed air as the oxidant, maintaining a homogeneous oxidant concentration in the reactor is a significant challenge [12].

1.3. Supercritical Water Treatment Processes

Supercritical water (SCW) treatment has received recent attention for removal of phenol in waste streams. SCW treatment uses the non-polar characteristics of water above its critical point (374 °C, 22.1 MPa), allowing water, oxidant gases, and non-polar hydrocarbons to form a single phase [18]. In typical phenol supercritical water oxidation (SCWO) processes, an oxidant (typically O₂ or air) is introduced into the water stream. This increases operational costs by demanding compressed oxidant gases. Alternatively, SCW reforming processes without oxidants, requiring temperatures within the range of 500 to 700 °C, have been investigated [19, 20]. In general, this process is identified as supercritical water gasification (SCWG) in the literature. However, effective use of a catalyst has the potential to lower both reactor temperature and oxidant concentration, thereby reducing treatment costs.
1.4. Research Objectives

This proposed work evaluates the use of a heterogeneous MnO2-based catalyst with a liquid oxidant to destroy phenol at SCW conditions. This thesis consists of three objectives.

1.4.1. Catalyst Synthesis and Characterization

The first objective is to synthesize and characterize MnO2 catalysts supported on TiO2. Supported MnO2 catalysts were synthesized using an incipient wetness impregnation (IWI) method, with Mn loadings of 3, 6, and 12 % (w/w). For characterization, active metallic surface area (AMSA), percent metal dispersion (Dmet), and temperature programmed reduction (TPR) profiles were determined for all three catalysts using a Micromeritics Autochem II chemisorption analyzer.

1.4.2. Effect of O2 Concentration on Phenol Conversion

The second objective is to evaluate the effect of free O2 concentration on phenol conversion with the supported MnO2 catalyst. A catalyst with 6 % (w/w) Mn were used to evaluate the effect of free O2 concentration on phenol oxidation in SCW. In addition, trials without catalyst were completed to elucidate homogeneous phenol oxidation kinetics. Phenol conversion (PCV: Equation 1-2) and Carbon to Gas Efficiency (CGE: Equation 1-1) were determined for each experiment.

\[ C_{GE} = \frac{c_{out\_gas}}{c_{in}} \times 100\% \]  
\[ PCV = \frac{a_{in\_phenol} - a_{out\_phenol}}{a_{in\_phenol}} \times 100\% \]

1.4.3. Effect of Mn Loading on Phenol Conversion

The third objective is to evaluate the effect of Mn loading of an MnO2/TiO2 catalyst on phenol conversion in SCWO. An O2 concentration that produced a CGE of approximately 50 % from Objective 2 was used in these experiments to clarify the catalyst loading effect. PCV and CGE were determined for SCWO experiments using MnO2/TiO2 catalysts with Mn loadings of 3, 6, and 12 % (w/w).
Phenol is an aromatic organic compound that is moderately soluble in water. Some of the important physical properties of phenol are given in Table 2.1. It is the simplest compound containing a hydroxyl group attached to an aromatic ring. Hydrogen bonding between the hydroxyl oxygen atoms and hydroxyl hydrogen atoms of neighboring molecules is responsible for phenol’s water solubility [21]. Also, phenol’s aromatic structure and associated resonance make it a very stable compound and difficult to decompose [17]. This makes phenol a stable product formed in many organic reformation processes. Further, since the phenoxide ion is a stable form, an H⁺ ion can easily escape from the —OH group of phenol, producing phenoxide, resulting in phenol’s acidity. This acidity can shift the pH in groundwater streams. Phenol is a major pollutant found in wastewater from many industries, including petroleum refineries, petrochemical industries, pharmaceutical industries, steel industries, dye synthesis units, pulp and paper industries, and coal gasification industries [8, 9]. A number of techniques are used for phenol removal from wastewater. Some techniques are under research and development, while others are used by industry.

Table 2.1: Phenol Structure and Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₆H₅OH</td>
</tr>
<tr>
<td>Molecular structure</td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>94.11 g/mol</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>9.3 g/100 ml</td>
</tr>
<tr>
<td>Vapor pressure at 25 °C</td>
<td>0.3513 mmHg</td>
</tr>
<tr>
<td>Acidity in water (pKa)</td>
<td>9.89</td>
</tr>
<tr>
<td>Melting point</td>
<td>40.9 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>181.75 °C</td>
</tr>
</tbody>
</table>
2.1.1. Non-destructive Techniques

2.1.1.1. Adsorption Processes

Adsorption is a popular technique used for removal of phenol from waste streams. Activated carbon (AC) is mainly used as the adsorbent. AC’s high porosity and ability to support surface polymerization of phenol makes it attractive for this application. AC adsorption is feasible for removal of phenol at concentrations as low as 2 ppm [22]. Factors such as pH, temperature, and presence of electrolytes affect the adsorption rate and capacity [11, 22], and the process can be optimized considering these conditions. However, some active sites on AC tend to adsorb phenol irreversibly [23] by chemisorption. Even though the presence of dissolved O\textsubscript{2} in the stream can improve the adsorption capacity, it also increases the irreversible chemisorption of phenol [24]. Regeneration is possible via heated steam, hot water, or heated nitrogen. However, these regenerative processes add additional operational complexities and costs while also reducing the adsorption capacity of AC by oxidation or attrition [11].

Other than AC, polymeric resins, modified aluminas, synthetic zeolites, and clay materials such as bentonite and perlite have been used for phenol adsorption [11, 25]. Most of the polymer-based materials adsorb phenols physically, and therefore regeneration is easier compared to AC [26]. Zeolites can be synthetically produced for selective adsorption. Hot air treatments and chemical treatments such as ethanol are typically used for regenerating synthetic adsorbents [11]. However, the adsorption capacities of these materials are lower than that of AC [27]. Moreover, the majority of polymeric resin adsorbents are temperature sensitive, demanding high control over temperature during adsorption and regeneration cycles. In addition, fixed bed adsorption processes face a reduction of efficiency because a part of the bed is regenerated. Furthermore, the regeneration process continuously produces waste materials, creating disposal management issues.

2.1.1.2. Distillation Processes

Since the boiling points of water and phenol are dissimilar, distillation may be used for phenol separation. Fractional distillation is mainly used for separation of completely miscible components. At room temperature, phenol-water mixtures with approximately 10
to 70 % (w/w) phenol are completely miscible. However, miscibility limits expand with temperature. Therefore, for most phenol-water mixtures, fractional distillation is required for phenol separation [28]. However, in water-rich mixtures, steam stripping is used. In this case, steam is used to separate phenol [11]. Bartak et al. [29] used simultaneous steam distillation and extraction processes to pre-concentrate phenol to facilitate a phenol detection technique for water sample analysis. It has been reported that complete separation is possible at a commercial scale over temperatures ranging from 90 to 180 °C [30]. This will allow phenol to be created as a by-product instead of producing wastes. However, the distillation-based processes are energy intensive. For an integrated process, distillation and stripping steps will be required [11] to reach complete separation requiring a high operating temperature and a greater degree of control and maintenance.

2.1.1.3. Extraction Processes

Solvent extraction is a technique that has been used to remove phenols from wastewater in both continuous and batch processes. In this particular technique, phenol is allowed to diffuse into an organic solvent based on the solubility equilibrium of phenol within water and the solvent. Hydrocarbons such as toluene, benzene, cyclohexane, n-hexane, and ethyl benzene, as well as organic acetates, ketones, and esters, are used as the solvent [11, 31]. Every solvent extraction process is followed by a solvent recovery step to separate phenol from the solvent. Distillation, biological treatment, and adsorption techniques are generally used for solvent recovery [9, 32]. Since phenol can be recovered without destruction, the phenol product can be beneficially reused. It has been reported that extraction processes can be profitable at phenol concentrations higher than 10,000 ppm [31]. An on-site trial phenol extraction plant developed by Yang et al. to treat coal gasification wastewater has been able to remove more than 93 % of the phenol [33].

However, at lower phenol concentrations, solvent extraction is unlikely to be economically attractive. Due to solubility equilibrium limitations, some solvents may not be applicable. In this case, the applicable solvents can be more expensive. Furthermore, the requirement of subsequent unit operations for solvent recovery increases operational costs. In addition, vacuum-steam stripping is typically used to recover residual solvents in the water phase after the extraction. These steps are also typically completed at the same
temperature as the extraction column [32]. Maintaining required temperatures, flow rates, and construction costs of the solvent recovery columns results in economic disadvantages for such extraction processes.

2.1.2. Destructive Techniques

In certain situations, phenol removal in waste streams is achieved by completely changing the molecular structure of phenol. This can be accomplished through destruction into smaller molecules or synthesis into larger molecules to facilitate convenient separation [11]. Many destruction processes for phenol removal are useful at low phenol concentrations, as recovery methodologies will be inefficient [17, 65].

2.1.2.1. Oxygen Based Oxidation

As for the techniques involving destruction of phenol, oxidation and gasification methodologies are most prominent. The most common oxidant is air. Wet air oxidation (WAO) is a popular established oxidative phenol destruction technique as given in equation 2-1. Operating conditions for WAO typically range from 180 to 315 °C and 2 to 15 MPa [34]. The technique has been improved with use of homogeneous and heterogeneous catalysts to reduce phenol oxidation temperature. Cations of transition metals such as Fe and Cu are usually used as homogeneous catalysts [11]. Heterogeneous catalysts are more attractive since they often don’t require a catalyst separation step. Precious metals such as Pt and Ru are often used as active materials for these catalysts. However, O₂ dissolution in water is a major limitation in WAO techniques. Because of this, the reactor pressure has to be increased to provide a higher O₂ partial pressure for effective phenol oxidation. Stable low molecular intermediates such as acetic acid and formic acid are produced during phenol oxidation. These intermediates are difficult to remove at the typical WAO operating temperatures [11]. To overcome these issues, operating conditions above water’s critical point are used.

\[
C_6H_5OH + O_2 \rightarrow CO_2 + H_2O
\]

Eq. 2-1
2.1.2.2. Chemical Oxidation

In addition to O$_2$, H$_2$O$_2$ and O$_3$ have also been used as phenol oxidation species. These chemical oxidants can facilitate phenol conversions at considerably lower temperatures than WAO. In a previous work, use of O$_3$ resulted in complete conversion of 200 ppm of phenol at 20 °C [32]. H$_2$O$_2$ is an easily handled oxidant with a high capacity for oxidation, which also provides environmentally friendly operation. Chemical oxidation-based phenol destruction processes have been studied with catalyst involvement facilitating fast conversion via free radical reaction pathways [36]. However, low molecular weight compounds, such as quinones and oxalic acid, remain as oxidation products. In this case, further steps are required to remove those products. Further, the cost of chemical oxidants creates a significant disadvantage for this particular method.

2.1.2.3. Electrochemical Oxidation

Electrochemical oxidation processes are sometimes used to break down aromatic organic compounds. Oxidizing agents are produced via a cathodic or anodic reaction. Anodically produced chlorine and hypochlorite have been used for the oxidation reactions, as cathodically produced H$_2$O$_2$ [37, 38]. In addition, transition metal ions such as Ag$^+$, Co$^{3+}$, and Fe$^{3+}$ can be used in the solution to produce hydroxyl radicals (OH·), which can enhance reformation of organic pollutants [11]. However, the addition of metal ions into the solution for this purpose creates more complications by demanding metal ion removal processes. Sometimes, direct anodic oxidation is completed by producing hydroxyl radicals on the electrode itself, resulting in organic oxidation [39]. In the latter case, metal ions are not required, but the electrodes have to be specifically designed to allow hydroxyl radical adsorption. Overall, the cost of electrodes limits the practicality of this technique.

2.1.2.4. Biological Destruction Processes

Aerobic digestion of organic compounds has been a technique of interest in recent years. Certain bacteria and fungi species are capable of destroying phenol in waste streams [40, 41]. For the aerobic digestion, O$_2$ supply is a critical parameter [42]. In order to produce O$_2$ effectively, agitation and aeration is typically completed in the fluid stream. However, other contaminants present in the water can significantly limit the range of microbial species that can be used. Cells can be killed by high concentrations of phenol,
and this limits the application of this technique [11]. High O₂ demand will add more operating costs to the system [40]. Finally, separation of dead cells and microbial metabolites will require additional unit operations, while failure in the process can add biological hazards to the waste streams.

A summary of techniques used for phenol removal from wastewater is given in Table 2.2.

**Table 2.2: Alternative Methods for Phenol Removal from Wastewater**

<table>
<thead>
<tr>
<th>Process</th>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-destructive processes</td>
<td>Adsorption processes</td>
<td>• Selective separation</td>
<td>• Process complexity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Complete separation</td>
<td>• Energy intensive</td>
</tr>
<tr>
<td></td>
<td>Distillation processes</td>
<td>• Phenol recoverable as byproduct</td>
<td>• High maintenance costs</td>
</tr>
<tr>
<td></td>
<td>Extraction processes</td>
<td>• Ease in scale-up</td>
<td>• High construction costs</td>
</tr>
<tr>
<td>Destructive processes</td>
<td>Oxygen-based oxidation</td>
<td>• Small process footprint with catalyst</td>
<td>• Low O₂ solubility in water</td>
</tr>
<tr>
<td></td>
<td>Chemical oxidation</td>
<td>• Applicable at low concentrations</td>
<td>• Creates additional contaminants</td>
</tr>
<tr>
<td></td>
<td>Electrochemical oxidation</td>
<td>• Continuous processing capability</td>
<td>o Excess reactants</td>
</tr>
<tr>
<td></td>
<td>Biological destruction</td>
<td></td>
<td>o Metal ions</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>o Partial oxidation products</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Expensive oxidation agents</td>
</tr>
</tbody>
</table>
2.2. Supercritical Water Reforming of Organic Compounds

2.2.1. Supercritical Water

Fluids exist at different states depending on their temperature and pressure. A water phase diagram indicating these states is given in Figure 2.1. When the temperature and pressure of water are above its critical values (374 °C, 22.1 MPa), it is said to be in a supercritical state. As water reaches the supercritical region, it undergoes drastic property changes, creating a medium denser than gases with a lower viscosity than liquids. In addition, polar characteristics of water decrease at this region due to a diminution in hydrogen bonding. The combination of water properties at this state produces a useful medium for reactions requiring multiphase reactants.

![Figure 2.1: Phase Diagram of Water](image)

2.2.2. Supercritical Water Gasification (SCWG)

The supercritical water environment is used to break down heavy organic compounds into gases and low molecular weight compounds. This can be utilized in both energy production via H₂, CH₄, etc. and in wastewater treatment applications. Good transport properties of supercritical water allow for a homogenized reaction medium, facilitating higher reaction rates. SCWG has been investigated as both a catalytic and a non-catalytic process. Catalysts used are often heterogeneous in nature. In this case, the
high diffusivity of supercritical water is useful in preventing coke formation on catalyst surfaces and avoiding mass transfer limitations of heterogeneous reactions [44].

In a majority of the related literature, methanol and glycerol have been of interest for destruction via SCWG [45-48]. Bennekom et al. [45] investigated the effects of residence time, temperature, and presence of catalyst on the conversion of feed compounds. They suggested that ionic reaction pathways are dominant around the critical temperature, leading to intermediate organic compounds, while higher temperatures enhance free radical pathways, allowing for more gaseous products. DiLeo et al. [47] utilized kinetic studies to compare the use of a Ni catalyst to the non-catalytic conditions for SCWG of methanol. At 500 to 550 °C, conversions were not high enough to determine meaningful kinetic rates.

Biomass is a popular type of feedstock used in SCWG for H₂ production. D.C. Elliot [49] reviewed catalysts used for biomass gasification in supercritical water. His important findings will be discussed in an upcoming section. Yanik et al. [50] investigated SCWG of cotton stalk and corncob in the presence of K₂CO₃, Raney nickel, and a set of clay materials. They suggested that effective use of catalysts can produce significant amounts of H₂ from these biomass at temperatures near 500 °C.

Several researchers attempted to apply SCWG for phenol destruction. Savage and Huelsman [51] conducted batch experiments for catalyzed and non-catalyzed phenol gasification under supercritical conditions. They observed that with a phenol feed of 5 % (w/w), only about 5 % (mol/mol) conversion can be reached without catalysts at 500 °C. Further studies identified dibenzofuran and benzene as primary products of the phenol gasification reaction, while a range of other products appear to have been derived from these compounds as secondary products [19]. A SCWG reaction network proposed by Savage and Huelsman is given in Figure 2.2. A wide range of organic compounds observed in the liquid product stream implies that the phenol reformation process occurs as a complex chain of reactions. Stable intermediate compounds formed within this chain limit the gasification efficiency. When SCWG is applied for wastewater treatment, effective conversion with increased gas production facilitates easy separation of a significant amount of organic carbon from the water stream. In order to reach useful conversions at temperatures lower than 500 °C, a catalyst is needed.
2.2.3. Supercritical Water Oxidation (SCWO)

Organic reforming reactions in supercritical water are sometimes completed in the presence of an oxidant. Often the O$_2$ becomes the oxidant, which is supplied via compressed air, compressed O$_2$ or H$_2$O$_2$. In general, the extra cost associated with supplying O$_2$ into the supercritical reactor results in a higher conversion at lower temperatures compared to SCWG, resulting in better overall treatment costs. In addition, the SCWO process utilizes the non-polar characteristics of water at these conditions to homogenize non-polar O$_2$ molecules at a lower O$_2$ partial than what is used in typical WAO processes. Also, when a heterogeneous catalyst is used, the high diffusivity of supercritical water minimizes mass transfer limitations of O$_2$ molecules transported to the active sites.

Many investigations focused on SCWO have proven that use of a catalyst significantly improves reformation of organic compounds in the water. Catalytic SCWO processes have been investigated with various organic compounds, including phenol and benzene [18, 52-54]. Selection of these compounds has been influenced by their stability in wastewater streams. Sometimes, acetic acid has been a choice, since it is a stable intermediate formed during oxidation [55].
Our current interest, phenol, was selected by several researchers due to its relative inertness and possibility of being a stable intermediate in reaction pathways that may produce undesirable organic products and char. Savage and Thornton [56] investigated the effect of temperature, pressure, and residence time for non-catalyzed oxidation of phenol in a plug flow reactor at supercritical and near critical conditions. They claimed that the range of organic compounds found in the liquid products indicates the complexity of the reaction pathways of the phenol reformation process. Further research used a CARULITE 150 catalyst consisting of Cu, Zn and Co oxides [18]. This investigation was completed over the temperature range of 380 to 430 °C. In the presence of the catalyst, the reaction kinetics were determined to be first order with respect to phenol conversion. However, Krajnc et al. evaluated the kinetics for phenol conversion using a similar catalyst over the temperature range of 400 to 440 °C, and their results followed the Langmuir-Hinshelwood formula for phenol conversion [17]. Furthermore, they observed a range of organic acids in liquid products for non-catalytic reactions, while only formic and acetic acids were produced as organic acids for catalytic reactions. This was explained as the result of heavy organic acids being adsorbed onto active sites and of their further destruction into smaller molecules.

Figure 2.3 illustrates reaction pathways for ring opening, dimers formation and overall complete combustion reaction occurs during SCWO [76, 82]. In order to improve conversion with more selectivity toward gaseous products than liquid products, a proper understanding of catalytic reaction kinetics and innovative catalyst materials is needed. In order to achieve this goal, an effective comparison of various catalysts under these conditions is required.
Ring opening reaction:

\[ C_6H_5OH + O_2 \rightarrow C_6H_5\dot{O} + H\dot{O}_2 \]

\[ H_2O + O_2 \rightarrow \dot{O}H + H\dot{O}_2 \]

Overall complete SCWO:

\[ C_6H_5OH + O_2 \rightarrow CO_2 + H_2O \]

Dimer formation:

Figure 2.3: Suggested Pathways for SCWO [76, 82]

2.3. Catalysts Used in Supercritical Media

Use of catalysts in organic oxidation in SCW media significantly improves the conversion rates and reduces operating temperature. In order to effectively improve the
process, catalytic activity and stability are important. Both heterogeneous and homogeneous catalysts have been evaluated by researchers.

2.3.1. Heterogeneous Catalysts

2.3.1.1. Catalytic Activity

Metal oxides or metals supported on carrier materials are typically used as heterogeneous catalysts. Noble metals and transition metal oxides are generally introduced as the active component of heterogeneous catalysts. Ding et al. [57] reported that correlating physicochemical properties for these materials, including redox potential, acid-base characteristics, oxygen adsorption, and surface structure, with the catalytic activity facilitates the selection of catalyst active materials. They further mention that oxides of V, Zn, Cu, Mn, Cr, Ni, Zr, Ti and Al and noble metals have favorable catalytic activities for SCWO processes. According to the generally accepted reaction mechanism, oxygen in the metal oxide lattice or oxygen adsorbed on the catalyst surfaces generates phenoxy radicals to initiate ring opening reaction pathways [58, 76]. Figure 2.3 above illustrates a reaction pathway for SCWO from the literature [76].

2.3.1.2. Catalyst Stability

However, stability limits the use of above materials in supercritical media. When supported metal catalysts are used, the crystal size of active metals can be increased over time with exposure to supercritical environments [59-61]. This will reduce the active surface area, causing catalyst deactivation. This process is identified as sintering [60, 62]. For this reason, growth of crystal size should be an effective indicator of stability for supported metal catalysts. Phase changes of metal oxide catalysts can also reduce catalytic activity. Bennekom et al. [59] identified a phase change of ZrO₂ from monoclinic to tetragonal under SCW conditions over three hours with a reduction of catalytic activity. Also, phase changes in catalyst support materials affect the metal dispersion and thereby reduce catalytic activity. Frisch et al. [61] observed phase changes of titania rutile and γ-Al₂O₃ into titania anatase and α-Al₂O₃, respectively, during their batch experiments in supercritical media. Changes of overall catalyst material from the amorphous to the crystalline phase have been reported in previous work for catalysts consisting of transition metals or metal oxide mixtures [59, 61]. These changes have significantly decreased the
conversion of organic compounds. When metals are used as the catalyst in their reduced form, metal oxidation can occur, impeding the catalyst’s performance. In particular, Ni has a tendency to form NiO in SCW environments, and NiO has significantly lower catalytic activity than Ni in reforming organic compounds [62]. Further, Pt can convert into its oxide or hydroxide form when used in SCWO processes [57]. Moreover, the leaching of metal ions into supercritical water can be a considerable stability issue for heterogeneous catalysts. Metal oxides reacting with water to form metal hydrates will cause this issue. Cr, Pb, V and Cu are susceptible to undergoing leaching in supercritical media [57]. Not only can this add heavy metal contaminants to the water, but it can also cause catalyst deactivation and ultimately the collapse of the structure of the material. In addition, metals with low melting points will create metal agglomerates at critical temperatures, causing a significant reduction of surface area. Due to this reason, low melting point metals such as Cs, P, Pt, Re, and Se will not be suitable for this application [57]. Based on literature studies on material stabilities in SCW environments, Ding et al. [57] suggest oxides of Ce, Mn, Fe, Co and Zn as suitable active materials for catalysts and oxides of Ti, Zr, Al and Hf as stable catalyst support materials.

2.3.1.3. Use of Promoters

In order to enhance the activity and stability of heterogeneous catalysts, researchers have used promoters. Transition metals such as Co, Mo, W, Fe and Sn have previously been used as promoters [57, 62]. These metals are located in between active metal crystals on the catalyst surface and resist the agglomeration of active metal crystals, maintaining the metal dispersion. Furthermore, promoters can improve the mechanical strength of the material. If the promoter is catalytically active for the particular reaction, it will enhance the reaction rate.

2.3.2. Homogeneous Catalysts

Homogeneous catalysts have been used for oxidizing organic compounds at elevated temperatures and pressures. Yang et al. used Cu$^{2+}$ and Mn$^{2+}$ salts as homogeneous catalysts to oxidize p-chlorophenol in supercritical water. They observed a moderate increase in oxidation rate with the use of the catalyst compared to the non-catalyzed reaction [53]. They also found corrosion products of reactor material acting as
homogeneous catalysts in the reaction mixture. Bennekom et al. [59] reported that alkali salts can act as catalysts for glycerol oxidation. If alkali salts can catalyze phenol oxidation, these salts, which are typically present in industrial wastewater, can be used in the phenol destruction process. However, homogeneous catalysis has been of less interest to researchers in recent years as further concerns have arisen regarding separation of the catalysts from the reaction mixture or contamination of the water product with catalytic metal ions.

2.3.3. Summary of Catalysts

A summary of the catalyst materials used in supercritical media for hydrocarbon destruction is provided in Table 2.3.
<table>
<thead>
<tr>
<th>Active Material(s)</th>
<th>Support(s)</th>
<th>Feedstock(s)</th>
<th>Concentration</th>
<th>Process</th>
<th>Temperature</th>
<th>Conversion/C\textsubscript{GE} range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu, Zn, Co oxides</td>
<td>-</td>
<td>Phenol</td>
<td>510-1900 ppm</td>
<td>Continuous SCWO</td>
<td>400-440 °C</td>
<td>Conversion: 34-93%</td>
<td>[17]</td>
</tr>
<tr>
<td>MnO\textsubscript{2}, CuO</td>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>Phenol</td>
<td>15-307 ppm</td>
<td>Continuous SCWO</td>
<td>380-430 °C</td>
<td>Conversion: 70-100%</td>
<td>[18]</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>Guaiacol, phenol</td>
<td>1.6%(w/w)</td>
<td>Batch SCWG</td>
<td>400-700 °C</td>
<td>Conversion: 100% within 10-30 min</td>
<td>[63]</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>Phenol, glycine</td>
<td>5%(w/w) Phenol 10%(w/w) Glycine</td>
<td>Batch SCWG</td>
<td>500-600 °C</td>
<td>Conversion: 100% within 15-60 min</td>
<td>[20]</td>
</tr>
<tr>
<td>Na\textsubscript{2}CO\textsubscript{3}(aq)</td>
<td>-</td>
<td>Phenol</td>
<td>77%(w/w)</td>
<td>Continuous SCWG</td>
<td>300-480 °C</td>
<td>Conversion: 15-75%</td>
<td>[64]</td>
</tr>
<tr>
<td>Pt, MnO\textsubscript{2}</td>
<td>Al\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}</td>
<td>Pyridine</td>
<td>420 ppm</td>
<td>Continuous SCWG</td>
<td>365-440 °C</td>
<td>Conversion: 20-100%</td>
<td>[65]</td>
</tr>
<tr>
<td>Ni, Mo</td>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>Hexylbenzene n-Hexadecane</td>
<td>31%(w/w)</td>
<td>Batch SCWO</td>
<td>400 °C</td>
<td>NG</td>
<td>[66]</td>
</tr>
<tr>
<td>Ni</td>
<td>ZrO\textsubscript{2}</td>
<td>Polyethylene glycol (PEG)</td>
<td>2000 ppm</td>
<td>Continuous SCWG</td>
<td>390 °C</td>
<td>C\textsubscript{GE} 16-60%</td>
<td>[67]</td>
</tr>
<tr>
<td>Ni, Mg</td>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>Glucose</td>
<td>9%(w/w)</td>
<td>Batch SCWG</td>
<td>400 °C</td>
<td>C\textsubscript{GE} 40-75%</td>
<td>[68]</td>
</tr>
<tr>
<td>Ni</td>
<td>La\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}</td>
<td>Glycerol</td>
<td>5%(w/w)</td>
<td>Continuous SCWG</td>
<td>450-574 °C</td>
<td>Conversion: 70-100%</td>
<td>[46]</td>
</tr>
<tr>
<td>Pt, Ni, Cu</td>
<td>CeZrO\textsubscript{2}, ZrO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}</td>
<td>Glycerol</td>
<td>10%(w/w)</td>
<td>Continuous SCWG</td>
<td>375-700 °C</td>
<td>Conversion: 20-100%</td>
<td>[59]</td>
</tr>
<tr>
<td>Ni</td>
<td>ZrO\textsubscript{2}, MgO</td>
<td>Glycerol</td>
<td>5-45%(w/w)</td>
<td>Continuous SCWG</td>
<td>600-800 °C</td>
<td>Conversion: 99-100%</td>
<td>[44]</td>
</tr>
</tbody>
</table>
**Table 2.3: (continued)**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Al$_2$O$_3$</th>
<th>Feedstock</th>
<th>Feedstock Composition</th>
<th>Reaction Process</th>
<th>Reaction Temperature</th>
<th>C$_{\text{GE}}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt, Ni</td>
<td></td>
<td>Glycerol</td>
<td>2.5-20%(w/w)</td>
<td>Continuous SCWG</td>
<td>380-500 °C</td>
<td>15-100%</td>
<td>[69]</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>Glucose, acetic acid</td>
<td>22%(w/w) Glucose 0.24%(w/w) Phenol 0.6%(w/w) Acetic</td>
<td>Continuous SCWG</td>
<td>600 °C</td>
<td>C$_{\text{GE}}$100%</td>
<td>[70]</td>
</tr>
<tr>
<td>Ni, K$_2$CO$_3$, trona, red mud</td>
<td>-</td>
<td>Biomass (cotton stalk, corn cob)</td>
<td>5.5%(w/w)</td>
<td>Batch SCWG</td>
<td>500 °C</td>
<td>NG</td>
<td>[50]</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>-</td>
<td>Acrylonitrile</td>
<td>0.4-0.65%(w/w)</td>
<td>Continuous SCWO</td>
<td>400-500 °C</td>
<td>Conversion: 93.6-100%</td>
<td>[71]</td>
</tr>
<tr>
<td>Cu$^{+2}$ (aq), Mn$^{+2}$ (aq)</td>
<td>-</td>
<td>P-chlorophenol</td>
<td>64-1157 ppm</td>
<td>Continuous SCWO</td>
<td>400 °C</td>
<td>NG</td>
<td>[53]</td>
</tr>
</tbody>
</table>

*Note: NG = Not Given, C$_{\text{GE}}$ = Carbon to Gas Efficiency*
Chapter 3: Experimental Procedure

This chapter describes the experimental apparatus and procedures as well as the analytical methodologies that were used to fulfill the proposed thesis objectives.

3.1. Catalyst Synthesis

In order to fulfill the thesis objectives, metal oxide catalysts (MnO$_2$ supported on TiO$_2$) were synthesized with Mn loadings of 3, 6, and 12 % (w/w). The incipient wetness impregnation (IWI) technique was used in catalyst synthesis.

3.1.1. Catalyst Support Preparation

TiO$_2$ was selected as the catalyst support due to its high stability [57] and catalytic activity for reforming selected organic compounds under SCW conditions [72]. For this study, porous TiO$_2$ material ST 3*119® in 3 mm pellet form, obtained from Saint-Gobain NorPro, was used as the catalyst support. Pellets were crushed using a Retsch ZM200 mill and sieved for twenty-five minutes to obtain TiO$_2$ particles between mesh sizes of 35 and 120 (125 to 500 µm). This sieved product is referred to as catalyst support for the remainder of the document. The particle size range of the catalyst support was determined using a Mastersizer particle size analyzer. The particle size distribution of the sieved support is shown in Figure 3.1.

![Particle Size Distribution](image)

**Figure 3.1: TiO$_2$ - ST 3*119® Catalyst Support Particle Size Distribution**

Further, support pore volume was determined using BET methodology. Samples were first degassed at 20 µmHg for 60 minutes followed by a heating cycle at 350 °C for
240 minutes. Next, the samples were cooled to -197 °C using liquid N₂ and an N₂ adsorption isotherm was generated via injection of N₂ at saturation pressure ratios between 0.01 to 1 and quantification of the adsorbed N₂. Using the isotherm data, the total surface area and the total pore volume were determined using BET and BJH methods, respectively. Table 3.1 presents physical properties of the catalyst support.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>TiO₂ (Anatase)</td>
</tr>
<tr>
<td>Mean particle size-D₅₀</td>
<td>200 µm</td>
</tr>
<tr>
<td>Packing density</td>
<td>0.958 g/cm³</td>
</tr>
<tr>
<td>Total surface area</td>
<td>47.5 m²/g</td>
</tr>
<tr>
<td>Specific pore volume</td>
<td>0.26 cm³/g</td>
</tr>
<tr>
<td>Average pore diameter</td>
<td>22 nm</td>
</tr>
</tbody>
</table>

### 3.1.2. Impregnation

The objective of the IWI method was to add a sufficient amount of Mn(NO₃)₂ solution to fill the pores of the catalyst support. Aqueous Mn nitrate was used as the impregnation media to deposit Mn onto the catalyst support. A Mn(NO₃)₂ solution with a concentration of 4 M was prepared. The density of this solution was measured using a volumetric flask.

A mass of catalyst support between 25 and 30 g was measured and added to an evaporating dish, and its total pore volume was calculated based on properties shown in Table 3.1. To determine the mass of solution to add to the catalyst support, Equation 3-1 was used. This resultant mass value of solution was measured into a weigh boat, poured onto the catalyst, mixed using a spoonula, and allowed to dry overnight in a fume hood. Depending upon the target Mn loading, this procedure was repeated.

\[ m_i = SV_p \times m_S \times \rho_i \]  
Eq. 3-1
3.1.3. Drying and Calcination

The impregnated catalyst sample was dried in a laboratory oven at 105 °C until constant weight was achieved. Subsequently, the sample was calcined in a furnace at 300 °C for three hours using a temperature ramp of 2 °C/min. Mn(NO₃)₂ was expected to decompose to MnO₂ releasing NOₓ at temperatures above 250 °C.

Calcined catalyst was crushed using a mortar to break the clumps formed during the calcination process. Bulk density of three samples from the catalyst was measured by weighing the mass of a known volume using a volumetric cylinder. Whenever the standard deviation of bulk density was more than 10% of the average, the crushing and bulk density measurement process was repeated.

3.2. Catalyst Characterization

To fulfill Objective 1, each of the synthesized MnO₂/TiO₂ catalysts was characterized. Temperature programmed reduction (TPR) and active metallic surface area (AMSA) analysis were performed to characterize the materials.

3.2.1. Temperature Programmed Reduction (TPR)

Temperature Programmed Reduction (TPR) analyses were completed to determine the peak reduction temperatures of the catalysts that characterize the Mn phases. The TPR analyses were performed using a Micromeritics Autochem 2920. During operation, Mn oxides were expected to reduce according to the pathway given in Equation 3-2 [73] under a continuous temperature ramp. H₂ was the reducing agent. Parameters used for TPR experiments are given in Table 3.2.

\[
\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO} \quad \text{Eq. 3-2}
\]

A thermal conductivity detector (TCD) signal was recorded during reduction. The signal data was plotted against temperature, and the observed peaks indicated peak reduction temperatures for various Mn phases contained in the material. The reduction peaks can be associated with the steps in the reaction pathway in Equation 3-2.
Table 3.2: TPR Settings for MnO\textsubscript{2} Catalyst on TiO\textsubscript{2} in Autochem 2920

<table>
<thead>
<tr>
<th>Setting</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2} flow rate</td>
<td>2 ml/min</td>
</tr>
<tr>
<td>He flow rate</td>
<td>18 ml/min</td>
</tr>
<tr>
<td>Temperature ramp</td>
<td>10 °C/min</td>
</tr>
<tr>
<td>Sample size</td>
<td>30-40 mg</td>
</tr>
</tbody>
</table>

3.2.2. Pulse Chemisorption

Pulse chemisorption experiments were conducted using O\textsubscript{2} to determine AMSA and the \(D_{\text{met}}\) of catalysts using a Micromeritics Autochem 2920. According to preliminary TPR analyses for the MnO\textsubscript{2}/TiO\textsubscript{2} catalyst, the highest reduction peak was observed around 250 °C, and no reduction peaks were observed below this temperature. Based on this information, it was reasonably assumed that this peak represented MnO\textsubscript{2} reduction. Therefore, a pre-reduction was completed at this temperature prior to pulse chemisorption. Afterwards, O\textsubscript{2} and He were used as the chemisorbed (loop gas) and carrier gases, respectively. While the catalyst sample was purged with He, O\textsubscript{2} pulses were injected in periodic episodes. Chemisorption of O\textsubscript{2} on the active sites was quantitatively detected by the TCD signal via change of O\textsubscript{2} concentration in the exhaust. Parameters used for pulse chemisorption experiments are given in Table 3.3.
Table 3.3: Pulse Chemisorption Settings for MnO₂ catalyst on TiO₂ in Autochem

<table>
<thead>
<tr>
<th>Setting</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-reduction gas</td>
<td>H₂</td>
</tr>
<tr>
<td>Pre-reduction temperature</td>
<td>250 °C</td>
</tr>
<tr>
<td>Pre-reduction time</td>
<td>3 hr</td>
</tr>
<tr>
<td>Pre-reduction temperature ramp</td>
<td>10 °C/min</td>
</tr>
<tr>
<td>Sample size</td>
<td>0.4 – 0.5 g</td>
</tr>
<tr>
<td>Loop gas</td>
<td>O₂</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He</td>
</tr>
<tr>
<td>Carrier gas flowrate</td>
<td>50 ml/min</td>
</tr>
<tr>
<td>Pulse chemisorption gas composition</td>
<td>10% O₂ in He</td>
</tr>
<tr>
<td>Loop volume</td>
<td>0.5715 ml</td>
</tr>
<tr>
<td>Pulse chemisorption temperature</td>
<td>45 °C</td>
</tr>
</tbody>
</table>

3.2.2.1. Active Metallic Surface Area (AMSA)

During the pre-reduction period of pulse chemisorption experiments, the MnO₂ phase should be reduced. The reduced phase is responsible for the O₂ chemisorbed during loop gas injection. This O₂ volume was detected via a TCD element. With this data, AMSA was calculated using Equations 3-3 and 3-4. A stoichiometric factor (SF) of 1 has been used for calculations.

\[
N_{Surface} = \left( \frac{V_g}{22414} \right) \times SF \times 6.123 \times 10^{23} \quad \text{Eq. 3-3}
\]

\[
SA_{Act} = N_{Surface} \times A_{MnO₂} \quad \text{Eq. 3-4}
\]

3.2.2.2. Percent Metal Dispersion (D_{met})

D_{met} is a measure of the amount of Mn in the catalyst that is catalytically active. It was calculated using Equation 3-3, 3-5 and 3-6.
\[ N_{total} = \frac{SW \times F_{Mn}}{55} \quad \text{Eq. 3-5} \]

\[ D_{met} = \frac{N_{surface}}{N_{total}} \times 100\% \quad \text{Eq. 3-6} \]

3.2.3. X-Ray Diffraction

X-ray diffraction tests were completed using an Ultima IV X-Ray Diffractometer. Samples of around 1 g from 3, 6 and 12 % (w/w) Mn catalysts were tested using a scanning rate of 1 °/min within a Bragg angle range of 10–70°. XRD patterns were analyzed for TiO2 and MnO2 phase identification and crystallite sizes using PDXL software.

3.3. Performance Testing

Supercritical Water Oxidation (SCWO) experiments were conducted to evaluate the catalytic performance of MnO2/TiO2 catalysts and to fulfill Objectives 2 and 3. A detailed standard operating procedure and safety evaluation report for the experimental apparatus are provided in Appendix C and Appendix D.

3.3.1. Experimental Apparatus

A piping and instrumentation diagram (PID) for the experimental apparatus is provided in Figure 3.2. The flow rate of a model solution containing selected organics was controlled using a Prep 100 HPLC pump (P-100). System pressure was controlled using a manual Swagelok® spring loaded back pressure regulator. Experiments were conducted using an 8 ml/min solution flow rate. The stream was heated to its supercritical condition via heaters HX-100 and HX-130 and sent through the packed catalyst bed in the reactor (V-110). The product stream underwent condensation by HX-120 followed by gas/liquid separation in V-130.
Figure 3.2: SCWO Unit PID
3.3.2. Packed Bed

A schematic of the packed bed inside V-110 is shown in Figure 3.3. The reactor was a vertical tube (316SS). To minimize tube wall kinetic effects, an internal non-porous alumina tube with an internal diameter of 0.5 inch was used. The packed bed was retained inside the alumina tube using two 40 micron porous stainless steel frits. This bed consisted of three layers. The middle layer consisted of the catalyst, and the other layers were composed of an inert-mesh size 80 silicon carbide (SiC). A thermocouple located at the inlet of the catalyst bed was used to control the temperature of the catalyst layer. For each trial, a new packed bed was installed in the reactor. Length of the catalyst layer (Layer 2—Figure 3.3) was varied to reach the expected residence time inside the reactor. Catalyst bed length was calculated using Equation 3-7. Maintaining the same total reactor tube length, the desired catalyst bed length was created by adjusting the lengths of Layers 2 and 3 (Figure 3.3).

![Figure 3.3: Packed Bed Reactor Schematic](image-url)
\[ L_{\text{cat}} = \frac{L_r \times V_R}{A_{\text{in}}} \]  
Eq. 3-7

3.3.3. Model Solution

The water composition used in the experimentation is provided in Table 3.4. The wastewater of focus in this study is produced water from oil/gas wells. This wastewater has hundreds of volatile and semi-volatile organic compounds [15]. For simplification, the proposed water composition used in this study consisted of 20 ppmw phenol, which is greater than the maximum amount of semi-volatile and non-volatile organic compounds found in wastewater generated by Marcellus shale wells [15]. To account for the dissolved solids contents of produced water, salts were added. The salt content of the feed water was adjusted to prevent precipitation, which would plug the reactor and impact phenol oxidation kinetics.

Table 3.4: Proposed Model Water Composition for SCWO experimentation

<table>
<thead>
<tr>
<th>Ion/ species</th>
<th>Concentration</th>
<th>Source(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>20 ppm</td>
<td>Phenol (≥99%)</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>500 ppm</td>
<td>NaCl (≥99.2%)</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>90 ppm</td>
<td>MgCl(_2).6H(_2)O (≥98%)</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>80 ppm</td>
<td>CaCl(_2) (≥96%)</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>1180 ppm</td>
<td>NaCl, MgCl(_2).6H(_2)O, CaCl(_2)</td>
</tr>
</tbody>
</table>

3.3.4. Gas Sample Analysis

The gas product stream of the reactor system was continuously analyzed using a Cirrus 2 mass spectrometer (MS). Due to the small concentration of phenol, a gas product stream larger than the sampling rate of the mass spectrometer (20 SCCM) could not be expected at complete conversion. Therefore, ultra-high purity (UHP) Ar was injected at a flow rate of 100 SCCM into the product stream prior to the separator (V-130). This created a diluted gas product stream with a sufficient flow rate for MS sampling with concentrations greater than its detection limits (100 ppb).
The MS provides signals corresponding to each molecular mass in the mass spectrum. Upon preliminary trials, dominant gases expected in the gaseous product stream were H₂, CO₂, and CO. The mass spectrometer signal was calibrated to determine instantaneous concentrations of these gases based on their signal. Concentration plots against elapsed time were developed for each trial. The results will be discussed in Chapter 4. Using these plots for each gas, average concentration for the steady state time period was calculated with standard deviation.

3.3.5. Liquid Sample Analysis

To verify the phenol concentration in the feed solution, 5 ml samples were collected from V-100 (Figure 3.2) in crimp top glass vials before and after each trial. During steady state operation, three 5 ml samples were collected to quantify the phenol concentration in the liquid product stream. To identify steady state operation during the trial, 10 ml liquid samples were collected every 10 minutes and analyzed for total dissolved solids (TDS) using an Oakton portable TDS meter until the TDS content was observed to be constant.

After each trial, liquid samples were analyzed via a coupled Trace GC Ultra gas chromatograph and Trace ISQ mass spectrometer (GC-MS) using manual sample injection. This sample analysis was preceded by analysis of a set of standards to develop a calibration curve, which facilitated determination of phenol concentrations. Each sample analysis was completed in triplicate and an average phenol concentration with a standard deviation was determined.

3.3.6. Mass Balance Methodology

Carbon fed to the reactor was found in three product forms: gaseous phase (C_{out, gas}), unreacted liquid phase phenol (C_{out, phenol}), and other liquid phase carbon forms (C_{out, non-phenol}). Total carbon input to the system (C_{in}) was calculated using Equation 3-8, while phenol and gaseous carbon species exiting the reactor were quantified using Equations 3-9 and 3-10.

\[
C_{in} \left( \frac{mg}{min} \right) = a_{in, phenol} (ppm) \times F \left( \frac{l}{min} \right) \times \frac{M_c \times 6}{M_{phenol}}
\]

Eq. 3-8
\[ C_{\text{out, gas}} \left( \frac{mg}{min} \right) = (a_{CO2} (ppm) + a_{CO} (ppm)) \times \frac{V_{Ar} (scm)}{10^6 \times V_{m, STP} (mL/mol)} \times M_c \left( \frac{mg}{mol} \right) \quad \text{Eq. 3-9} \]

\[ C_{\text{out, phenol}} \left( \frac{mg}{min} \right) = a_{out, phenol} (ppm) \times F \left( \frac{L}{min} \right) \times \frac{M_c \times 6}{M_{phenol}} \quad \text{Eq. 3-10} \]

For the calculations, \( a_{CO2}, a_{CO}, a_{out, phenol}, \) and \( a_{in, phenol} \) were obtained from liquid and gas sample analysis results. \( V_{Ar} \) was recorded in the data log of the trial. Using these results, a carbon balance was performed using Equation 3-11 to calculate \( C_{\text{out, non-phenol}} \).

\[ C_{in} \left( \frac{mg}{min} \right) = C_{\text{out, gas}} \left( \frac{mg}{min} \right) + C_{\text{out, phenol}} \left( \frac{mg}{min} \right) + C_{\text{out, non-phenol}} \left( \frac{mg}{min} \right) \quad \text{Eq. 3-11} \]

In addition, Carbon to Gas Efficiency (\( C_{GE} \)) and phenol conversion (\( PCV \)), as defined in Equations 3-12 and 3-13, were determined as indicators of catalytic performance.

\[ C_{GE} = \frac{C_{\text{out, gas}}}{C_{in}} \times 100\% \quad \text{Eq. 3-12} \]

\[ PCV = \frac{a_{in, phenol} - a_{out, phenol}}{a_{in, phenol}} \times 100\% \quad \text{Eq. 3-13} \]
Chapter 4: Results and Discussion

This chapter presents and discusses catalyst characterization and performance evaluation results to fulfill the thesis objectives. Each objective will be reviewed, followed by discussions of results associated with each respective objective.

4.1. Catalyst Synthesis and Characterization

The first objective was to synthesize and characterize an MnO₂ catalyst supported on TiO₂. Catalysts were synthesized using the IWI method with Mn loadings of 3, 6, and 12% (w/w). The AMSA and Dₘₑₜ were determined for each catalyst, along with their TPR profiles. Key deliverables to fulfill this objective include TPR profiles for each catalyst and plots of AMSA and Dₘₑₜ with Mn loading. In addition, XRD patterns are provided for each catalyst to confirm catalyst phases present and approximate crystallite sizes.

4.1.1. Temperature Programmed Reduction (TPR)

TPRs were performed with catalysts impregnated with 3, 6, and 12% (w/w) Mn. In addition, TPRs were obtained for MnO₂ and the TiO₂ support as described in 3.2.1. The TPR profiles are shown in Figure 4.1. The TPR results were used to determine the lowest associated MnO₂ peak reduction temperature for use in the AMSA and Dₘₑₜ analyses. MnO₂ can undergo a series of reduction steps as in Equation 3-2. Figure 4.1 doesn’t indicate any peaks for the TiO₂ support over the investigated temperature range, indicating that all shown peaks are associated with reduction of manganese oxide phases. Each catalyst investigated in this study possesses two clear reduction peak ranges. The lower peaks range from 240 to 280 °C and the higher peaks range from 350 to 420 °C. Ramesh et. al. [77] suggest such a two-step reduction consisting of bulk MnO₂ to Mn₃O₄ followed by Mn₃O₄ to MnO (Equation 4-1). In contrast, the TPR results of Ettireddy et al. [73] show three to four reduction peaks for an MnO₂ catalyst on TiO₂ support synthesized using the wet solution impregnation method. Three of its reduction steps are associated with the sequence highlighted in Equation 3-2, along with reduction of Mn⁴⁺ incorporated into the TiO₂ lattice. The TPR profiles in this study are more aligned with a two-step reduction sequence (Equation 4-1) indicating the presence of bulk MnO₂, with less bridging with the TiO₂ support. The IWI method used for catalyst synthesis in this study could explain the contrast between these results and those of Ettireddy et al. [73]. In the IWI method, the
capillary action of water transports Mn$^{2+}$ into the support pores, trapping air bubbles that, when evacuated, push Mn$^{2+}$ back toward the pore entrance, possibly forming bulk MnO$_2$. In contrast, in the wet impregnation method, air trapping is avoided, allowing better Mn$^{2+}$ distribution/bridging within the pore, resulting in smaller MnO$_2$ crystals [80]. Further, peak intensity increases with Mn loading, resulting from greater H$_2$ consumption associated with Mn content.

$$\text{MnO}_2 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$$ \hspace{1cm} Eq. 4-1

$$\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$$ \hspace{1cm} Eq. 3-2

Figure 4.1: TPR Profiles for TiO$_2$ Supported MnO$_2$ Catalyst; 20 SCCM of 10% H$_2$ in He, 10 °C/min Ramp, 30–40 mg Sample Size

Moreover, for a supported metal catalyst, reduction temperature could be affected by bridging between the catalyst and the support [78]. As Mn content decreases, MnO$_2$ particle size on TiO$_2$ should decrease, maximizing the percentage of the Mn$^{4+}$ inserted into the TiO$_2$ lattice. The bond energy of the bridging Mn$^{4+}$ may be lower than that of the bulk
MnO₂, decreasing the reduction temperatures at lower Mn loadings. This is supported by the results in this study, indicating a decrease in peak reduction temperatures as Mn loading decreases. Moreover, diffusion limitations of H₂ into MnO₂ sites [73] could also support the observed peak reduction temperature drift. However, diffusion limitations are unlikely as the crystalline sizes were very small, as discussed in Section 4.1.3. Based on the MnO₂ reduction temperatures from TPR curves, a pre-reduction temperature of 280 °C was selected for pulse chemisorption analyses to ensure partial reduction of the MnO₂ active sites for CO adsorption.

4.1.2. Pulse Chemisorption

Pulse chemisorption experiments were performed with catalysts impregnated with 3, 6, and 12% (w/w) Mn, as described in Section 3.2.2. Results including AMSA and Dₘₑₜ are provided in Figure 4.2 and Figure 4.3, respectively. Each data point represents the average of two pulse chemisorption tests with the propagated error for one standard deviation.

Figure 4.2: Active Metal Surface Area (AMSA) for TiO₂ Supported MnO₂ catalyst; Pulse Chemisorption at 45° C, 50 SCCM Carrier Gas (He) Flow, 10% O₂ in He Loop Gas, 0.5715 ml Loop Volume, 1 atm Pressure, 0.4–0.5 g sample size
Except for the 3% (w/w) Mn case, error in both plots was less than 5%. The greater error associated with the 3% (w/w) Mn case was attributed to its lower AMSA and $D_{\text{met}}$ values compared to the instrumental error. The error were calculated using the standard deviation of the two trials. Therefore the smaller error margins confirm the homogeneity of the materials.

Figure 4.2 shows that AMSA increases with increasing Mn loading. This suggests that within the range of 3 to 12% (w/w) Mn, the support may not have been entirely covered with MnO$_2$ (i.e, a MnO$_2$ monolayer was not formed on the TiO$_2$ surface over the investigated Mn loading range). A study by Ettireddy et al. [73] observed the same trend for an impregnated MnO$_2$ catalyst on TiO$_2$. The authors provided a similar explanation for the trend. However, as saturation of the TiO$_2$ surface is reached, AMSA should reach a limiting value. This characteristic is likely beginning to be observed in these results with decreasing AMSA gradient with Mn loading. If Mn loadings higher than 12% (w/w) are tested, one could reach monolayer coverage and start forming bulk MnO$_2$ on the surface. This could avoid further increase of AMSA with Mn loading. From an applications point of view, an extended plot would be useful to determine the maximum effective Mn loading for the catalyst.

**Figure 4.3**: Percent Metal Dispersion ($D_{\text{met}}$) for TiO$_2$ Supported MnO$_2$ catalyst; Pulse Chemisorption at 45 °C, 50 SCCM Carrier Gas (He) Flow, 10% O$_2$ in He Loop Gas, 0.5715 ml Loop Volume, 1 atm Pressure, 0.4–0.5 g sample size
According to Figure 4.3, $D_{\text{met}}$ is also observed to increase with Mn loading, further supporting the fact that a complete MnO$_2$ monolayer on TiO$_2$ has not been formed within the investigated Mn loading range. Specifically, a portion of the Mn atoms likely bonds directly to the TiO$_2$ lattice, preventing them from creating active sites on the catalyst [73]. As Mn loading increases, more of the Mn atoms would contribute to form this inactive layer, while still adding to the Mn weight of the sample. This would produce an increasing trend in the $D_{\text{met}}$ plot. If the Mn loading were further increased, one would observe a maximum in the $D_{\text{met}}$ plot at the monolayer coverage, followed by a decreasing trend driven by bulk MnO$_2$ formation. This information aligns well with the pulse chemisorption results of Ettireddy et al. [73].

4.1.3. X-Ray Diffraction

XRD analyses were also completed in this study to identify crystalline phases present in the material. Each analysis produced an XRD pattern showing the peaks characteristic to the solid materials present in the catalyst. PDXL software was used to identify the crystalline phases matching the peaks in the XRD patterns and determine their average crystallite sizes. XRD results are shown in Figure 4.4 and Table 4.1.

Table 4.1: Average Crystalline Sizes from XRD results; 1 °/min angular speed, ≈0.1g

<table>
<thead>
<tr>
<th>Mn Loading</th>
<th>Average Crystalline Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12%</td>
<td>22</td>
</tr>
<tr>
<td>6%</td>
<td>7</td>
</tr>
<tr>
<td>3%</td>
<td>&lt;5*</td>
</tr>
</tbody>
</table>

*MnO$_2$ peaks are not detected at very low Mn loadings due to too smaller crystal sizes
In Figure 4.4, peaks characteristic to TiO$_2$ are labeled as “T” and peaks characteristic to MnO$_2$ are labeled as “M.” For all the catalysts, TiO$_2$ peaks are sharp enough to easily identify and the combination of its peaks was characteristic of a TiO$_2$ anatase phase. This confirms that our porous anatase TiO$_2$ support material didn’t undergo any phase changes during the synthesis process.

Conversely, MnO$_2$ phase intensity increased with Mn loading, as MnO$_2$ isn’t discernable in the 3% (w/w) sample, but is clearly indicated in the 12% (w/w) sample. This increasing trend of MnO$_2$ peak intensity against Mn loading was also observed by Ettireddy et al. [73] for a TiO$_2$ supported MnO$_2$ catalyst. Their results indicated the absence of MnO$_2$ peaks up to Mn loadings of 11% (w/w). The authors suggest the presence of highly dispersed MnO$_2$ crystallites or Mn$^{4+}$ ions inserted into the TiO$_2$ lattice, causing the absence of MnO$_2$ peaks at lower Mn loadings. In addition, thin MnO$_2$ films could also yield low peak intensity.

Based on PDXL XRD pattern analysis, these MnO$_2$ peaks were characteristic of the pyrolusite phase of MnO$_2$. In Table 4.1, average crystallite size of this MnO$_2$ phase
almost doubles as the Mn loading is doubled from 6 to 12% (w/w). However, 3% (w/w) Mn was not sufficient to effectively determine an average crystallite size due to the reasons discussed above.

4.2. Effect of O₂ Concentration on Phenol Conversion

The second objective of this thesis was to evaluate the effect of free O₂ concentration on phenol conversion with the supported MnO₂ catalyst. To fulfill this objective, catalysts impregnated with 6% (w/w) Mn were used in the experimental trials. Trials were conducted at RO₂% values of 0, 100, and 500%, with the O₂ stoichiometric ratio (RO₂%) defined by Equation 4-1.

\[
R_{O₂\%} = \frac{n_{O₂, ac}}{n_{O₂, st}} \times 100\% \quad \text{Eq. 4-1}
\]

In addition, SCWO trials without a catalyst and with RO₂% values of 0, 100, and 500% were completed to elucidate the influence of homogeneous kinetics. Each case was replicated to ensure the consistency of the results. Deliverables to fulfill this objective include carbon balances, PCVs, and C_GE for each trial. This information is used to draw relationships between free O₂ concentration and the conversion of phenol to both liquid and gas products, as well as to determine an approximate RO₂% range to meet target phenol conversions.

4.2.1. Effect of Free O₂ Concentration on Product Carbon Distribution

As described in Sections 3.3.4 and 3.3.5, the composition and phenol content of the product gas and liquid fractions were determined for each trial. A representative gas concentration plot used to determine steady state gas compositions from a trial with RO₂% of 500% and a catalyst with 6% (w/w) Mn loading is provided in Figure 4.5. Gas concentration plots for all of the O₂ concentration trials are presented in Appendix A. Further, Table 4.2 shows the measured phenol compositions for the investigated O₂ concentrations.
Figure 4.5: Gas Analysis Results; SCWO Trial 6, 5s Residence Time, 382 °C Reactor Temperature, MnO₂ on TiO₂ catalyst, 6% (w/w) Mn, 500% RO₂%

Table 4.2: Phenol Feed and Product Stream Concentrations with O₂ Concentration and 6% (w/w) Mn on TiO₂

<table>
<thead>
<tr>
<th>Trial Number</th>
<th>RO₂%</th>
<th>Phenol Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Feed Stream</td>
</tr>
<tr>
<td>1</td>
<td>0%</td>
<td>18.3 ± 0.4</td>
</tr>
<tr>
<td>2</td>
<td>100%</td>
<td>19.2 ± 1.6</td>
</tr>
<tr>
<td>3</td>
<td>500%</td>
<td>17.5 ± 1.1</td>
</tr>
<tr>
<td>4</td>
<td>0%</td>
<td>19.3 ± 0.4</td>
</tr>
<tr>
<td>5</td>
<td>100%</td>
<td>19.5 ± 2.3</td>
</tr>
<tr>
<td>6</td>
<td>500%</td>
<td>19.5 ± 0.6</td>
</tr>
</tbody>
</table>

The mass balance methodology, discussed in Section 3.3.6, was applied to the results to determine the carbon composition in the form of non-phenol compounds (Table 4.3) (C_{out\_non-phenol}) in the liquid product stream for each experiment. Product carbon
distributions from the trials are provided in Figure 4.6. $C_{\text{out\_gas}}$, $C_{\text{out\_phenol}}$ and $C_{\text{out\_non-phenol}}$ are the average values of the replicated trials for each O$_2$ concentration.

![Carbon Product Distribution for O$_2$ Concentration Trials; 5s Residence Time, 382 °C Reactor Temperature, MnO$_2$ on TiO$_2$ catalyst, 6% (w/w) Mn, 0–500% RO$_2\%$

The ultimate goal of the SCWO process is to maximize the carbon to gas conversion in order to facilitate easy removal of organic carbon from the feed stream. Therefore, a higher portion of gaseous carbon in the products is preferred. $C_{\text{out\_gas}}$ increases with RO$_2\%$, indicating an increase in the rate of the phenol reformation reaction.

The significant non-phenol liquid products yielded in the presence of O$_2$ (100% and 500%) indicate the formation of stable intermediate products. Qualitative analyses were conducted using GC-MS to identify the intermediate compounds. Non-phenol products found in the liquid product stream are summarized in Table 4.3. However, the
concentration of each compound was not quantified, as only the yield of non-phenol liquid products was of interest.

Many of the compounds in Table 4.3 have benzene rings. The absence of aliphatic compounds suggests that when aromatic ring opening occurs, the product is more likely to undergo complete dissociation. Therefore, one may hypothesize that aromatic ring opening reactions are the rate limiting step in regard to phenol oxidation. Furthermore, some of the compounds in Table 4.3 include multiple benzene rings. This indicates the presence of reactions among phenol molecules and their aromatic derivatives within the reaction mixture other than the phenol degradation reactions.

Interestingly, a negligible portion of non-phenol liquid products is found in the absence of O₂, while this portion significantly increases for 100 and 500% RO₂% levels. This could be a result of differing pathways between supercritical water gasification (SCWG) and SCWO. Savage et al. (2013) have investigated the kinetics and reaction pathways for phenol gasification in supercritical water [19].
Table 4.3: Non-Phenol Liquid Products

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5-biphenyl diol</td>
<td><img src="image" alt="2,5-biphenyl diol" /></td>
</tr>
<tr>
<td>3-hydroxydiphenyl ether</td>
<td><img src="image" alt="3-hydroxydiphenyl ether" /></td>
</tr>
<tr>
<td>Dibenzofuran</td>
<td><img src="image" alt="Dibenzofuran" /></td>
</tr>
<tr>
<td>m-chlorophenol</td>
<td><img src="image" alt="m-chlorophenol" /></td>
</tr>
<tr>
<td>2,3,6-trichlorobenzaldehyde</td>
<td><img src="image" alt="2,3,6-trichlorobenzaldehyde" /></td>
</tr>
</tbody>
</table>

4.2.2. Effect of Free O₂ Concentration on $C_{GE}$

Using Equation 1-1 with gas and liquid sample analysis results, $C_{GE}$ values were calculated for each trial. $C_{GE}$ with $R_{O₂%}$ is shown in Figure 4.7, with results in the absence and presence of the catalyst provided. Each data point represents the average $C_{GE}$ of the trial replicates for each case, including propagation of error with one standard deviation.
In Figure 4.7, homogeneous kinetics are represented by the non-catalytic data. These results demonstrate that a portion of the phenol conversion is associated with homogeneous reactions taking place within the supercritical fluid. Phenol conversion that can be attributed to the Mn-based catalyst is caused by the difference in conversion between the non-catalytic and catalytic cases. This contribution of heterogeneous kinetics aligns with the reaction mechanisms reviewed by Ding et al. In the presence of a metal oxide catalyst, oxygen can involve the reaction as an adsorbed species, creating an ionic environment favorable for the oxidation reactions [57]. Moreover, the surface adsorbed O$_2$ population of the catalyst should increase with total O$_2$ concentration in the system, enhancing the contribution of heterogeneous kinetics. This explains the difference between the catalytic and non-catalytic case increases with RO$_2\%$, demonstrating the catalyst’s value in phenol reforming and oxidation.
4.2.3. Effect of Free $O_2$ Concentration on PCV

Using Equation 1-2 along with liquid sample results, PCV values were calculated for each trial, as shown in Figure 4.8. Each data point represents the average PCV of the trial replicates for each case, including propagation of error within one standard deviation.

PCV represents the percentage of phenol converted in the feed stream to either gas or liquid phase products. Therefore, the PCV is more of an indicator of the rate of initiating the phenol oxidation reaction chain. In both non-catalytic and catalytic cases, PCV reaches 100% at an $R_{O2\%}$ of 500%. However, the non-catalytic and catalytic $C_{GE}$ values at this oxygen value are 32 and 54%, respectively.

In Figure 4.8, the non-catalytic (homogeneous) data lies below the catalytic (heterogeneous) data, especially around 100% $R_{O2\%}$ where intermediate conversions are observed. With this information, it may be discerned that heterogeneous kinetics makes a measurable contribution toward initiating phenol destruction. Furthermore, both data sets have positive slopes with respect to $O_2$ concentration, implying $O_2$ concentration has a
positive order. However, both homogeneous and heterogeneous reactions appear to have non-linear reaction rates with respect to O₂ concentration. The limited data set associated with this study does not allow the determination of detailed kinetic rate coefficients.

4.2.4. Effect of Free O₂ Concentration on Heterogeneous Reaction Rate

The SCWO process examined here is focused for use in organic-containing wastewater treatment applications. However, the lab-scale reactor used here has technical limitations of catalyst loadings and residence time. Nevertheless, phenol conversion reaction rates may be determined, which allows for preliminary design. Heterogeneous reaction rates were determined based on experimentally measured conversions. Moreover, the objective of this treatment technique is to convert hydrocarbons into gaseous products; as such, reaction rates based on C_{GE} will be a better performance indicator to use in process scale-up. These reaction rates were determined using Equation 4-2 considering the error propagation of the replicates for each O₂ concentration. Results are given in Figure 4.9.

\[ r_{cat} = \frac{n_{phenol \, \text{in}} \times (C_{GE\,\text{cat}} - C_{GE\,\text{hom}})}{m_{cat}} \]

Eq. 4-2

Figure 4.9: Heterogeneous Reaction Rates for O₂ Concentration Trials; Complete Phenol Oxidation Reaction, 5s Residence Time, 382 °C Reactor Temperature, MnO₂ on TiO₂ catalyst, 6% (w/w) Mn, 0–500% RO₂%
The kinetic studies of Savage et al. [79] revealed that in the presence of both bulk TiO₂ and bulk MnO₂, the SCWO process can reach a phenol to gas conversion rate of up to the order of $10^{-7} \text{mol}_{\text{phenol}}/\text{g}_{\text{cat}} \cdot \text{s}$ with an RO₂% level of 230% and residence times comparable to our study. The difference could have been driven by the differences between phenol concentrations (300 ppm vs. 20 ppm) or in the total amount of accessible catalyst (bulk catalyst vs. supported). Further, it may be discerned that the reaction rate is not linear with respect to O₂ concentration, further confirming the higher order of the reaction with respect to O₂.

4.3. Effect of Catalyst Mn Loading on Phenol Conversion

The third objective of this thesis is to evaluate the effect of catalyst Mn loading on phenol conversion in SCWO. To fulfill this objective, SCWO trials were completed with catalysts containing 3, 6, and 12% (w/w) Mn. If an R₀₂% of 0% or 500% was used for these experiments, the phenol conversion would not allow the effect of Mn loading to be discerned. To clearly distinguish the trends of phenol conversion against Mn loading, a moderate R₀₂%, 100%, was used for this set of experiments. An SCWO trial without catalyst at the selected R₀₂% was also completed. Each trial was replicated to ensure the consistency of the experimental data. Deliverables to fulfill this objective include carbon balance results for each trial and plots of PCV and C_GE with Mn loading. The results were used to draw relationships between Mn loading, catalyst properties, and phenol conversion to determine a catalyst Mn loading range necessary to meeting process needs.

4.3.1. Effect of Mn Loading on Product Carbon Distribution

Similar to O₂ concentration experiments, gas concentration plots and liquid sample analysis results were used to analyze the effect of catalyst Mn loading. Gas concentration plots for this set of trials are given in Appendix B. Phenol composition results for Mn loading trials are given in Table 4.4.
Table 4.4: Phenol Feed and Product Stream Concentration Results with Mn Loading and 500% RO2%

<table>
<thead>
<tr>
<th>Trial Number</th>
<th>Mn Loading</th>
<th>Phenol Concentration (ppm)</th>
<th>Feed Stream</th>
<th>Product Stream</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3%</td>
<td>19.3 ± 2.8</td>
<td>8.0 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6%</td>
<td>19.2 ± 1.6</td>
<td>6.4 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>12%</td>
<td>19.9 ± 1.5</td>
<td>4.9 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>3%</td>
<td>19.3 ± 0.1</td>
<td>7.9 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6%</td>
<td>19.5 ± 2.3</td>
<td>6.5 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>12%</td>
<td>20.7 ± 0.4</td>
<td>5.4 ± 0.4</td>
<td></td>
</tr>
</tbody>
</table>

The same method that was described in Section 4.2.1 was used with the results to determine the carbon composition in the form of non-phenol compounds (C_{out\_non-phenol}) in the liquid product stream for each experiment. Carbon product distribution with respect to catalyst Mn loading is shown in Figure 4.10. C_{out\_gas}, C_{out\_phenol}, and C_{out\_non-phenol} are the average values of the replicated trials for each O_2 concentration.
In Figure 4.10, carbon in all three forms is observed in significant portions for all the tested Mn loadings. The portions of $C_{\text{out non-phenol}}$ indicate the presence of non-phenol liquid products, introduced in Table 4.3. A gradual increase in gaseous products is observed with the increase of Mn loading. This is expected, since the active site population is increased with Mn loading according to AMSA results in Section 4.1.2. However, the portion of phenol carbon seems to minimally decrease, indicating that initiation of the phenol destruction reaction is less sensitive to Mn loading. According to the phenol SCWO reaction pathways studied by Savage et al., the initiation reactions may form non-phenol cyclic products such as benzene and dibenzofuran [19], followed by secondary reactions to break the benzene ring and completely oxidize them into gases. Based on this hypothesis and the above observation, catalyst active sites in this study may be utilized more for the oxidation of the intermediate non-phenol cyclic products rather than for catalyzing the initiating reaction.
4.3.2. Effect of Mn Loading on $C_{GE}$

$C_{GE}$ values were calculated for each Mn loading using Equation 1-1 and are provided in Figure 4.11. $C_{GE}$ without catalyst is indicated by the continuous dashed line. Each data point represents the average $C_{GE}$ of the replicates for the particular case considering the error propagation with one standard deviation.

![Figure 4.11: CGE Plot for Mn Loading Trials; 5s Residence Time, 382 °C Reactor Temperature, 500% Ro2%, MnO2 on TiO2 catalyst, 3–12% (w/w) Mn](image)

The results in Figure 4.11 indicate increasing Mn loading results in greater $C_{GE}$, with an increase from 15.8 to 29.3% over the evaluated Mn loading range. As the non-catalytic $C_{GE}$ data was acquired using inert SiC packed bed instead of the catalyst, the results also infer that the TiO$_2$ support may also have a measurable impact on catalytic activity. To ensure this, pure TiO$_2$ support can be tested for SCWO. In literature, Savage et al. (2000) [79] have studied the use of Bulk TiO$_2$ for SCWO of phenol and reached a phenol conversion of approximately 25% with a residence time of 7.5 s.
$C_{GE}$ tends to increase with Mn loading. This aligns with the results in Section 4.2.2 regarding the contribution of heterogeneous kinetics to the SCWO reaction via adsorbed $O_2$ on catalyst active sites. In fact, the increasing number of active sites with increasing Mn loading, as seen in our AMSA results (Section 4.1.2), increases the contribution of heterogeneous kinetics. However, at an $R_{O2\%}$ of 100%, the highest $C_{GE}$ achieved was approximately 30% in the presence of a 12% Mn catalyst. Further, the rate of increase of $C_{GE}$ appears to decrease as Mn content increases. These observations indicate that the gain of $C_{GE}$ with the increase of Mn loading within the range of 3 to 12% (w/w) is limited. This could be the result of increasing Mn loading, causing larger Mn crystallites instead of greater active site population. However, the IWI synthesis technique used in this study will be more challenging at higher Mn loadings, as more impregnation cycles will be required when using a saturated impregnation solution, resulting in higher synthesis costs. One could use other synthesis techniques, such as co-precipitation and wet impregnation [80], to reach higher Mn loadings and thus to further investigate the effect of catalyst Mn loading on phenol conversion.

4.3.3. Effect of Mn Loading on PCV

PCV values were calculated using Equation 1-2 and are shown in Figure 4.12. PCV in the absence of the catalyst is indicated by the continuous dashed line. Each data point represents the average PCV of the replicates for the particular case considering the error propagation with one standard deviation.
In the absence of the catalyst, PCV is nearly 50%, indicating that homogeneous kinetics succeed in initiating nearly 50% of phenol conversion. However, the figure indicates only a slight increase of PCV with Mn loading, indicating the effect of MnO$_2$ sites on PCV is limited.

With 12% of Mn loading, PCV reaches 75% and the trend appears to dampen, indicating a saturation limit. This limit could be expected due to the saturation of active site population on the support. The same behavior existed in the AMSA plot in Figure 4.2 and could be observed in these SCWO experiments if Mn loading were further increased. Overall, at first glance, PCV appears not to be as sensitive to Mn loading as to O$_2$ concentration, since PCV did not reach 100% for any of the Mn loading trials. However, it is worthwhile to quantitatively compare the heterogeneous reaction rates for the two parameters. Further, as an alternative to increasing O$_2$ concentration and Mn loading, one could attempt increasing operating temperature and/or residence time to increase phenol conversion.
4.3.4. Effect of Free Mn Loading on Heterogeneous Reaction Rate

Heterogeneous reaction rates for phenol to gas conversion were determined using Equation 4-2. Non-catalytic results used in the calculation had an $R_{O2\%}$ of 100%. The heterogeneous reaction rates determined from this study are summarized in Figure 4.13.

![Figure 4.13: Heterogeneous Reaction Rates for Mn Loading Trials; Complete Phenol Oxidation Reaction, 5s Residence Time, 382 °C Reactor Temperature, 500% $R_{O2\%}$, MnO$_2$ on TiO$_2$ catalyst, 3–12% (w/w) Mn](image)

It is clear that heterogeneous reaction rate increases with Mn loading. This confirms that MnO$_2$ contributes to heterogeneous reaction kinetics even though some of the Mn atoms may have interactions with the TiO$_2$ support lattice. Active MnO$_2$ sites at lower Mn loadings could be created via bulk MnO$_2$ crystals formed near TiO$_2$ pore openings, due to accelerated drying during the catalyst synthesis [80].

Reaction rates in Figure 4.13 are of the order of $10^{-10} mol_{phenol}/gas_{cat}\cdot s$. In Section 4.2.4, the work of Savage et al. was discussed [79], which produced total reaction rates in the order of $10^{-7} mol_{phenol}/gas_{cat}\cdot s$. Our explanations in Section 4.2.4 on the basis of phenol concentration difference also apply for these results. The maximum
reaction rate achieved with an R\textsubscript{O2} of 500\% and 6\% Mn loading was $(10.68 \pm 2.24) \times 10^{-10}$ \textit{mol\textsubscript{phenol}/g\textsubscript{cat}.s}. Here, at an R\textsubscript{O2} of 100\% with 12\% (w/w) Mn loading, the reaction rate was nearly identical. This calls for an evaluation of the economic and technical limitations of increasing reactor O\textsubscript{2} concentration and catalyst Mn loading in order to better compare the parameters.

In Figure 4.13, although Mn loading is progressively increased, the heterogeneous reaction rate does not increase at the same rate. This could be due to the saturation of the TiO\textsubscript{2} support surface with MnO\textsubscript{2}, as discussed in previous sections. However, more data points will be required to verify the saturation. If the Mn loading is further increased, the reaction rate will reach its limiting value due to bulk MnO\textsubscript{2} formation. However, formation of internal pores, increasing MnO\textsubscript{2} surface area in bulk MnO\textsubscript{2}, may change this pattern. Oshima et al. [81] revealed that internal mass transfer limitations come into play at these conditions over porous MnO\textsubscript{2}.
Chapter 5: Conclusions

5.1. Catalyst Characterization

Evaluation of the TPR profiles indicates that the MnO₂ catalyst derived by the IWI technique undergoes a two-step reduction pathway with H₂, as shown in Equation 4-1. TPR peak reduction temperatures slightly increase with Mn loading, indicating that the reduction temperatures are affected by Mn⁴⁺ bridging with the TiO₂ lattice. The effect of H₂ diffusion limitations in the MnO₂ particles is believed to be limited due to the small crystallite sizes. Mn loadings below 12% (w/w) were not sufficient to saturate the TiO₂ surface to form a MnO₂ monolayer, as indicated by Dmet results showing increasing metal dispersion from 3 to 12% (w/w).

5.2. Effect of O₂ Concentration

Increasing O₂ concentration was beneficial in the destruction of phenol in supercritical water. The opening of the aromatic ring may be the rate-limiting step in oxidative phenol destruction, as non-phenol aromatic compounds were found in the product stream while aliphatic intermediate products were not found. More complex products, such as dibenzofuran, 2,5-biphenyl diol, and 3-hydroxydiphenyl ether, are formed by reactions between phenol and aromatic intermediate products in the oxidative atmosphere. However, such products were not observed in the absence of O₂, indicating a different initiating phenol conversion pathway.

Differences between phenol conversion in the presence and absence of catalyst at the same RO₂% level indicate that the heterogeneous catalyst has a measurable impact on the SCWO reaction. The catalyst facilitates the SCWO reaction via absorbed O₂ on the catalyst surface. Increasing O₂ concentration resulted in greater surface adsorbed O₂ population, thereby increasing the reaction rate. As a result, PCV reached 100% at an RO₂% of 500%. Reaction rates observed using the MnO₂ catalyst in the SCWO environment were on the order of 10⁻¹⁰ molphenol/gcat·s.

5.3. Effect of Mn Loading

Phenol conversion attributed to heterogeneous reaction kinetics increases with Mn loading. This is a result of greater catalyst active site population with increased Mn loading. However, the trend dissipates due to increasing MnO₂ particle size at higher Mn
loadings, which results in a proportionally lower AMSA. Alternative catalyst synthesis methods will be needed to effectively increase Mn loading beyond 12% (w/w), as the IWI synthesis method becomes ineffective at higher Mn loadings due to the requirement of more impregnation cycles with saturated impregnation solutions.

The rate of increase in PCV with Mn loading was lower when compared to C_{GE}, indicating that the catalyst sites were more active toward hydrocarbon oxidation as compared to the initiation reactions of SCWO, which form non-phenol cyclic products such as benzene and dibenzofuran. The highest heterogeneous reaction rates for complete oxidation achieved with an increase of R_{O2}\% up to 500\% and Mn loading up to 12\% (w/w) were nearly identical. A techno-economic analysis of the two parameters will be required to identify optimal operating conditions.
Chapter 6: Recommendations

During the course of this study, a lab-scale packed bed reactor capable of operating at supercritical water conditions was designed, fabricated, and operated to evaluate the performance of TiO$_2$ supported MnO$_2$ catalysts for the removal of phenol from oil/gas wastewater. During the course of these studies, methods to improve both the SCWO process and catalyst performance were identified. This chapter provides a summary of recommendations to consider for future studies.

At Mn loadings up to 12% (w/w), a monolayer of MnO$_2$ on the TiO$_2$ support was not obtained, as indicated in the metal dispersion plot shown in Figure 4.3. Higher Mn loadings could be investigated to identify the Mn loading required to create a monolayer on the TiO$_2$ support. As Mn loading is further increased, the active metallic surface area (AMSA) of the catalyst would reach saturation with monolayer formation, followed by bulk MnO$_2$ formation. Using such results, the catalyst composition could be optimized to minimize process costs.

Non-phenol aromatic liquid products such as dibenzofuran and 2,5-biphenyl diol were identified in this study. Additional analytical methods such as high-performance liquid chromatography (HPLC) could be incorporated to quantify such product concentrations. Accounting for these non-phenol liquid products would allow for a more detailed carbon balance to be completed, allowing a carbon loss term to be included. This carbon loss term could be used to account for potential coke formation on catalyst surfaces.

This thesis reports the results of a screening study to determine the effect of O$_2$ concentration and Mn loading on phenol conversion. To allow for detailed reactor design studies to be completed, a more detailed experimental program is recommended that evaluates the effects of residence time and temperature in addition to $R_{O2\%}$ and Mn loadings at suggested factor levels of 5 to 60s, 382 to 450 °C, 0 to 500% (R$_{O2\%}$), and 0 to 50% (w/w) (Mn loading), respectively. This data will allow phenol conversion kinetic rates to be developed, allowing activation energy concentration orders to be determined. A design of experiment (DOE) routine should be implemented to minimize the number of trials required to complete the study.
To integrate the described recommendations, several experimental apparatus improvements should be incorporated. First, the reactor tube needs to be extended, allowing greater SCWO residence times. In this case, a multi-point thermocouple should be considered to track the temperature at several points along the reactor length. Further, the heating capacity of reactor pre-heaters (HX-100, HX-101) needs to be increased, allowing for higher reactor temperatures. Reactor temperatures of at least 450 °C will facilitate more comparisons to existing SCWO literature results.

Finally, it is recommended to develop a process simulation and techno-economic assessment so that a sensitivity study may be completed. This sensitivity study should focus on evaluating the effects of important process parameters (such as O₂ concentration, O₂ source, Mn loading, etc.) on wastewater treatment costs. Results from this study will allow an optimized process design to be developed.
References


Appendix A: Gas Sample Analysis Results - Objective 2

Figure A-1: Gas Analysis Results; SCWO Trial 1, 5s Residence Time, 382 °C Reactor Temperature, MnO$_2$ on TiO$_2$ catalyst, 6% (w/w) Mn, 0% RO$_2$%

Figure A-2: Gas Analysis Results; SCWO Trial 2, 5s Residence Time, 382 °C Reactor Temperature, MnO$_2$ on TiO$_2$ catalyst, 6% (w/w) Mn, 100% RO$_2$%
Figure A-3: Gas Analysis Results; SCWO Trial 3, 5s Residence Time, 382 °C Reactor Temperature, MnO₂ on TiO₂ catalyst, 6% (w/w) Mn, 500% RO₂%

Figure A-4: Gas Analysis Results; SCWO Trial 4, 5s Residence Time, 382 °C Reactor Temperature, MnO₂ on TiO₂ catalyst, 6% (w/w) Mn, 0% RO₂%
Figure A-5: Gas Analysis Results; SCWO Trial 5, 5s Residence Time, 382 °C Reactor Temperature, MnO₂ on TiO₂ catalyst, 6% (w/w) Mn, 100% RO₂%

Figure A-6: Gas Analysis Results; SCWO Trial 6, 5s Residence Time, 382 °C Reactor Temperature, MnO₂ on TiO₂ catalyst, 6% (w/w) Mn, 500% RO₂%
Appendix B: Gas Sample Analysis Results – Objective 3

Figure B-1: Gas Analysis Results; SCWO Trial 7, 5s Residence Time, 382 °C Reactor Temperature, MnO₂ on TiO₂ catalyst, 3% (w/w) Mn, 100% RO₂%

Figure B-2: Gas Analysis Results; SCWO Trial 8, 5s Residence Time, 382 °C Reactor Temperature, MnO₂ on TiO₂ catalyst, 12% (w/w) Mn, 100% RO₂%
Figure B-3: Gas Analysis Results; SCWO Trial 9, 5s Residence Time, 382 °C Reactor Temperature, MnO₂ on TiO₂ catalyst, 3% (w/w) Mn, 100% RO₂%

Figure B-4: Gas Analysis Results; SCWO Trial 10, 5s Residence Time, 382 °C Reactor Temperature, MnO₂ on TiO₂ catalyst, 12% (w/w) Mn, 100% RO₂%
Appendix C: Standard Operating Procedure

Institute for Sustainable Energy and the Environment (ISEE)

Standard Operating Procedure for "Packed bed catalytic reactor system"

Document Number:
SOP_Packed bed catalytic reactor system_141202

Last Updated:
12/02/2014

Contributor(s):
Chamara De Silva
I. Purpose/Scope of Work

The Packed Bed Catalytic Reactor System (PBCRS) shown in Figure 2.1 is used to evaluate performance of heterogeneous catalysts under supercritical water environments. This document provides a standard operating procedure for the PBCRS. Procedures detailed in this SOP include catalyst loading, feed water tank and condenser preparation, reactor system start-up, operation, shutdown, and emergency shutdown.

II. Test System Description

The PBCRS, located in Stocker 045A, is used to evaluate performance of heterogeneous catalysts used for reforming organic compounds dissolved in water under supercritical conditions. A Pipe & Instrumentation Diagram (P&ID) for the experimental apparatus is provided in Figure 2.2. A model solution containing selected organics is pressurized and heated up to reach its supercritical region and then sent through the packed catalyst bed, V-110 (Figure 2.1). Maximum limits of equivalent Toluene concentration, reactor temperature (TE-104) and operating pressure are 3.5% (w/w), 400 °C and 3500 psi respectively. Product stream is condensed and gas and liquid phases are separated. Gas and liquid phases of the product stream are then analyzed for composition for each trial. After the trial, V-110 is dismantled and used catalyst material is analyzed for crystallinity and composition.

Figure 2.1: Packed bed catalytic reactor system (PBCRS)
Figure 2.2: PBCRS P&ID
III. Personal and Project Site Preparations

Exact locations of all the safety equipment, tools/analytical equipment and supplies are labeled in respective laboratories.

A. Required Personnel Training (include everything)

<table>
<thead>
<tr>
<th>No.</th>
<th>Operator Training</th>
<th>Offered by:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OSHA Laboratory Chemical Hygiene Training</td>
<td>EHS - Ohio</td>
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<tr>
<td>2</td>
<td>Plan for Excellence, Safety, and Operation (PESO)</td>
<td>CHO - ISEE</td>
</tr>
<tr>
<td>3</td>
<td>Shop Tool Usage Guidelines</td>
<td>CHO – ISEE</td>
</tr>
<tr>
<td>4</td>
<td>Analytical Instruments Usage Guidelines</td>
<td>CHO – ISEE</td>
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</tbody>
</table>

B. Required Safety Equipment

<table>
<thead>
<tr>
<th>No.</th>
<th>Safety Equipment</th>
<th>Purpose</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Splash goggles</td>
<td>Protect operators’ eyes during chemical measurements and dosing</td>
<td>Stocker 045 Main Lab</td>
</tr>
<tr>
<td>2</td>
<td>Safety glasses</td>
<td>Protect operators’ eyes while inspecting the experiment</td>
<td>Stocker 045 Main Lab</td>
</tr>
<tr>
<td>3</td>
<td>Nitrile gloves</td>
<td>Prevent skin contact with chemicals while handling</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>4</td>
<td>Laboratory safety coat</td>
<td>Protect operators’ clothing and body during chemical measurement and dosing</td>
<td>Stocker 045 Main Lab</td>
</tr>
<tr>
<td>5</td>
<td>Exposure fume hood 9855</td>
<td>Protect operator from volatile chemicals during feed water preparation</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>6</td>
<td>Insulated gloves</td>
<td>Protect operator from high temperature surfaces</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>7</td>
<td>Work gloves</td>
<td>Protect operators hand while handling equipment</td>
<td>Stocker 045 Main Lab</td>
</tr>
</tbody>
</table>
### C. Required Tools /Analytical Equipment

<table>
<thead>
<tr>
<th>No.</th>
<th>Tools/Analytical Equipment</th>
<th>Purpose</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mettler Toledo AX504 Balance, accuracy of 0.1mg.</td>
<td>Weigh catalyst for loading</td>
<td>Stocker 045A</td>
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<tr>
<td>2</td>
<td>Mettler Toledo CarePac S, certified mass set.</td>
<td>Verify proper operation of the balance.</td>
<td>Stocker 045</td>
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<tr>
<td>3</td>
<td>OAKTON Instruments Portable Meter Kit (TDS meter included)</td>
<td>Measure total dissolved solids (TDS) of feed water samples</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>4</td>
<td>Spoonulas, Stainless Steel, 7¼” x 3</td>
<td>Transfer salts and catalysts from containers during weighing</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>5</td>
<td>Polypropylene (PP) funnel, 3” opening 58° short stem</td>
<td>Load catalysts into V-110</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>6</td>
<td>Erlenmeyer Flasks 125 ml, x 2</td>
<td>Solution containers for TDS measurements</td>
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<td>7</td>
<td>Wash Bottle, 0.5 gal</td>
<td>Contain distilled water to clean glassware</td>
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<tr>
<td>8</td>
<td>Glass Beakers, 600 ml x 3</td>
<td>Collect excess liquid during liquid sampling</td>
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<tr>
<td>9</td>
<td>Step ladder</td>
<td>Access elevated sections of the apparatus</td>
<td>Stocker 045A</td>
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<tr>
<td>10</td>
<td>Crescent wrench, 12” x 2</td>
<td>Install and dismantle V-110 from the apparatus</td>
<td>Stocker 045D</td>
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<tr>
<td></td>
<td>Description</td>
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<td>--------------------------------------------------</td>
<td>---------------------------------------------------</td>
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<tr>
<td>11</td>
<td>9/16” Wrench</td>
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<td>Pack the catalyst inside V-110</td>
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<td>Phillips head screwdriver</td>
<td>Install and remove C-HX110</td>
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<td>Wire brush</td>
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<td>4L PP beaker</td>
<td>Transfer water into condenser (HX-120) shell</td>
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<td>HDPE pails, 10 gal x2</td>
<td>Handle water during system flushing</td>
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<tr>
<td>19</td>
<td>Box cutter</td>
<td>Cut insulation to uncover V-110</td>
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<tr>
<td>20</td>
<td>Flashlight</td>
<td>View inside V-110 during catalyst loading</td>
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<td>21</td>
<td>Polyethylene syringe without tip, 25 ml</td>
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<td>22</td>
<td>Plastic drying tray, 12” x 18”</td>
<td>Avoid water spills during V-110 dismantlement</td>
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### Required Supplies

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<td>Weighing boats</td>
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<td>Stocker 045A</td>
</tr>
<tr>
<td>2</td>
<td>Disposable polypropylene vials (120 ml)</td>
<td>Collect and store water samples</td>
<td>540</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>3</td>
<td>Paper towels</td>
<td>Dry the TDS and hold analytical tools clean</td>
<td>2 rolls</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>4</td>
<td>Extran MN 01 Powder detergent</td>
<td>Labware cleanup</td>
<td>500g</td>
<td>Stocker 045A</td>
</tr>
</tbody>
</table>

**Vial crimper, 11 mm**

Crimp and seal the liquid samples

**ORION 2 STAR pH Benchtop PH probe**

Measure pH of during distilled water flushing

**CGA 580 gas regulators, x 2**

Regulate Nitrogen and Argon delivery pressures

**CGA 350 gas regulator**

Regulate Hydrogen delivery pressure

**5/16-18 bolts with nuts, x 4**

Support PBCRS safety shield
<table>
<thead>
<tr>
<th></th>
<th>Description</th>
<th>Use</th>
<th>Quantity</th>
<th>Stocker</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Plastic closed lid container, 1 gal</td>
<td>Contain distilled water to clean V-100</td>
<td>4</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>6</td>
<td>Clean white papers, (A4 size)</td>
<td>Hold used catalyst during V-110 unloading</td>
<td>30</td>
<td>Stocker 045 Main lab</td>
</tr>
<tr>
<td>7</td>
<td>¼” OD transparent tube, 12” long</td>
<td>Retain TE-104 straight during catalyst loading</td>
<td>1</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>8</td>
<td>¼” ID flexible polyvinyl chloride (PVC) tube, 6 ft</td>
<td>Drain water during PBCRS washing</td>
<td>1</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>9</td>
<td>¼” OD polypropylene (PP) tube, 6 ft</td>
<td>Flush distilled water through PBCRS</td>
<td>1</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>10</td>
<td>Aluminum foil tape, 2” width</td>
<td>Cover V-110 insulations</td>
<td>50 yds.</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>11</td>
<td>Very high temperature flexible fiberglass insulation, 1” thick</td>
<td>Insulate V-110 inlet</td>
<td>5 ft²</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>12</td>
<td>Crimp top vials, 10 ml</td>
<td>Contain liquid samples that need to be preserved</td>
<td>100</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>13</td>
<td>Crimp top caps, 11 mm</td>
<td>Close and seal liquid samples that need to be preserved</td>
<td>100</td>
<td>Stocker 045A</td>
</tr>
</tbody>
</table>
### E. Required Services (include electrical, gas, water, etc.)

<table>
<thead>
<tr>
<th>No.</th>
<th>Services</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.0UHP grade Argon</td>
<td>Increase outlet gas stream content during operation</td>
</tr>
<tr>
<td>2</td>
<td>Water (distilled)</td>
<td>Process fluid</td>
</tr>
<tr>
<td>3</td>
<td>Electricity (208VAC, 15A, Single phase)</td>
<td>PBCRS power supply</td>
</tr>
<tr>
<td>4</td>
<td>Electricity (120VAC, 20A, 1P) (two outlets)</td>
<td>PBCRS Computer power supplies (PC-045A-3 and PC-045A-2)</td>
</tr>
<tr>
<td>5</td>
<td>Hydrogen, industrial grade</td>
<td>Reduce catalyst materials for activation (only nickel based catalysts)</td>
</tr>
<tr>
<td>6</td>
<td>Nitrogen, industrial grade</td>
<td>Purging PBCRS</td>
</tr>
<tr>
<td>7</td>
<td>Water (direct tap line)</td>
<td>Condenser cooling water</td>
</tr>
<tr>
<td>8</td>
<td>Drainage</td>
<td>Cleaning V-100 and glassware</td>
</tr>
</tbody>
</table>

### F. Required Procedures (as referenced within this document)

<table>
<thead>
<tr>
<th>No.</th>
<th>Procedures/ Manuals</th>
<th>Server / Physical Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Prep 100 Dual Piston Pump manual</td>
<td>Stocker 045 Main Lab</td>
</tr>
<tr>
<td>2</td>
<td>Instruction Manual, COND 6+ Conductivity/Temp, TDS 6+ TDS/Temp, Salt 6+ Salinity/Temp</td>
<td>Stocker 045 Main Lab</td>
</tr>
<tr>
<td>3</td>
<td>NewClassic Balances MS-S/MS-L Models Operating Instructions</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>4</td>
<td>Swagelok tube fitters manual</td>
<td>Stocker 045A</td>
</tr>
<tr>
<td>No.</td>
<td><strong>Operator(s)</strong></td>
<td><strong>Purpose</strong></td>
</tr>
<tr>
<td>-----</td>
<td>--------------------------------------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Minimum one operator</td>
<td>Startup and perform experiment (Attended operation only)</td>
</tr>
<tr>
<td>2</td>
<td>Minimum one additional person</td>
<td>Staying within the lab 045 (not necessarily involved in PBCRS operation)</td>
</tr>
</tbody>
</table>

**G. Required Operators and/or Technical Assistance**
Note: Labware used in this procedure must be clean before use and washed with detergent and water followed by a distilled water rinse after use. Washed labware may be placed on a drying rack. Dry glassware from the drying rack may be used in the following procedure. Distilled water required for the procedure can be obtained from ‘PBCRS DI water’ container in Stocker 045A. Operator must coordinate with the ISEE analytical chemist to verify the availability of all the analytical instruments used in this procedure. All the labels used in the procedure are illustrated in the P&ID (Figure 2.2) and/or index at the end.

IV. Catalyst unloading/loading

This is the procedure to unload the used catalyst from the previous trial and load the synthesized and characterized catalyst sample into the packed bed reactor for the next trial. Operator may use the wrench set and ¼” and ¾” Tee wrenches as necessary. Make sure PBCRS is left at rest for at least 2 hour since the last shutdown, in order to ensure the system is at room temperature. Follow the guidelines of “Swagelok Tube Fitters Manual” during assembling/dissembling of Swagelok fittings.

4.1 Required Safety Preparations

1. Refer to MSDS sheets for catalysts and inert material used in the trial.
   
   Note: Refer to Standard Test Method (STM) for catalyst and inert materials.

2. Wear nitrile gloves, safety glasses, dust mask and laboratory coat before handling chemicals and insulation materials.

4.2 V-110 dismantlement

1. Make sure PS-2 (refer to index) on the wall is at ‘OFF’ position.

2. Unscrew and remove the four sets of 5/16 nuts and bolts on top of the PBCRS safety shield (Figure 4.1).

3. Remove the safety shield from PBCRS by lifting it up along its guiders (Figure 4.1) and store it in the “PBCRS safety shield storage area”.

4. Disconnect TE-102, TE-103 and TE-104 connectors (Figure 4.1A).

5. Unplug C-HX110 (Figure 4.1A).

6. Remove insulation and aluminum foil between HX-100 and V-110 using the box cutter to cut the aluminum foil.

7. Carefully cut the aluminum foil around V-110 insulation and remove the front half of the insulation.
   
   Note: Cut should be parallel to the frame of PBCRS and V-110 should appear as in Figure 4.2B after removing insulation.

8. Carefully loosen and unwind HX-110-Section A (Figure 4.2B).

9. Loosen the plug 1/4P1 (Figure 4.1A) using 9/16 wrench and ¼” tee wrench.
   
   Note: Use a plastic flat drying tray underneath the plug to avoid water spills.

10. Loosen 1/4N1 and 1/4N3 (Figure 4.2B) using 9/16 wrench and ¼” tee wrench.

11. Install 1/4P1 back using the same wrenches.

12. Loosen CL2-V110 (Figure 4.2B) using a Phillips head screwdriver to unscrew its nuts.

13. Carefully remove V-110 assembly together with its components between 1/4N1 and 1/4N3 together with HX-110 (Figure 4.2B).

14. Invert the assembly over the nearest sink allowing water trapped inside the assembly to
drain out.

15. Attach the inverted assembly to the bench vise at 3/4T1 as in Figure 4.1B.

16. Unwind and remove HX-110 from the assembly completely.

Figure 4.1 A): Heated zone of PBCRS; B): Dismantling/assembling V-110

Figure 4.2 A): V-110 internal assembly; B): V-110 assembly and its components
17. Place a clean piece of paper, a glass rod, and a spoonulet in the fume hood 9855.
18. Assemble a ring stand inside the fume hood.
19. Loosen 3/4N1 (Figure 4.2B) using a 12” Crescent wrench.
20. Remove V-110 together with 3/4T2 and TE-104 from 3/4T1 and transfer it into the fume hood.
   Note: Hold V-110 vertically during removal. Make sure neither the quartz frit fixed inside 3/4T1 nor any of the catalyst material inside V-110 fall off. Rest of the unloading procedure must be performed inside fume hood.
21. Using finger, make sure the ceramic tube inside V-110 is rotatable independently from its SS tube wall.
22. Close V-110 open end tightly using thumb.
23. Turn the assembly upside down.
24. Loosen the thumb allowing ceramic tube to come out of SS 304 tube with catalyst materials packed inside it.
   Note: Make sure your thumb avoids catalyst leaking from the ceramic tube.
25. Carefully transfer the material inside the ceramic onto the paper.
   Note: If different materials are present in layers inside V-110 along its axis (Figure 4.2A), operator must be careful enough to minimize mixing between the three material layers. Use the glass rod as necessary to push the materials out of the ceramic tube in order to achieve this.
26. Transfer a sample with maximum possible size from each layer into a separate sample container using a clean spoonulet labeling them using “ISEE Naming Procedure_140820”.
27. Measure the weight of the quartz frit using Mettler Toledo AX504 Balance and record the reading in the lab notebook.
28. Clean the ceramic tube and V-110 using a wire brush.
29. Dump the dirty papers into the nearest trash receptacle.
30. Clean and return the tools.
31. Loosen 3/4T1 from bench vise.
32. Store the dismantled components of V-110 in ‘PBCRS Storage Area’ in Stocker 045A unless the catalyst for next trial is ready to use.
   Note: Throughout the procedure, any spills of catalyst materials must be collected into a Polypropylene (PP) container, label and disposed according to “Chemical Inventory Guidelines_140521”.

4.3 V-110 installation
1. Assemble a ring stand inside fume hood 9855.
2. Make sure Mettler Toledo AX504 Balance located in inside fume hood 9855 is level by observing the bubble on the bubble level lies within its circled area. If not level, adjust the balance level via leg screws as necessary.
3. Plug-in the balance to the nearest power outlet and allow a 10 minute warm-up period before checking for calibration.
4. Using the certified mass set with tweezers verify proper balance calibration by placing the 2g calibrated mass on the four corners and the center of the span while observing the digital scale. The scale should display 2.0000 g if the balance is calibrated properly.

*Note: Sliding glass case on the balance should be closed before accepting a reading. Wave your finger over motion sensor of the balance as necessary to open/close the glass case.*

5. Once the balance is validated, carefully return the 2g mass to its packaging.

6. Repeat steps 4-5 with 50g calibrated mass. Validate as needed.

*Note: Repeat steps 1-4 above whenever you use the balance after an unattended day in the laboratory.*

7. Transfer the appropriate catalyst sample container (Refer to STM) from its storage cabinet to near the balance.

8. Place a weigh boat onto the balance and tare.

9. Transfer the catalyst mass value for ‘Layer 1’ (Figure 4.2A, Refer to STM) into the weigh boat using a clean spoonulet and record the mass in laboratory notebook.

10. Label the weigh boat using the materials’ layer number inside V-110 given by STM.

11. Return the catalyst sample container.
12. Repeat steps 6-10 for materials in each layer (Figure 4.2A) based on STM.
13. Transfer a flash light, a piece of ¼” OD transparent tube, a clean glass rod, a spoonulet and a short stem 4” glass funnel onto the fume hood.
14. Attach V-110 (already attached with 3/4T2 and TE-104), onto the ring stand inside fume hood at 3/4T2 as shown in Figure 4.3A. Adjust the ring stand height as necessary.
15. Insert the cleaned ceramic tube into V-110.
16. Insert the transparent tube into TE-104 node inside ceramic tube. Use the flash light if needed (Figure 4.3).
17. Fill the material measured for top most layer of V-110 (refer to STM) into the ceramic tube using a clean funnel (Figure 4.3).
   Note: Use inserted transparent tube to hold thermocouple node along the center axis of V-110.
18. Carefully take off the transparent tube.
19. Pack the filled material inside V-110 using the glass rod. Use the flash light as necessary. Do not allow TE-104 node to dislocate out from the center axis.
20. Repeat steps 15-18 for the remaining material layers according to the layout given in STM.
   Note: ¼” OD transparent tube may not necessary for the layer(s) beyond half way along V-110.
21. Measure the weight of the quartz frit to be installed inside 3/4T1 using the Balance.
22. Attach 3/4T1 (attached with TE-103 and ¼” piece of tube to run between HX-100 and V-100-Figure 4.1B) into V-110 and tighten 3/4N1 up to finger tight.
Note: Make sure the quarts frit inside 3/4T1 seats properly inside the tee fitting as shown in Figure 4.2A.

23. Detach the assembly from the ring stand and transfer to the bench vise.
24. Attach the assembly to the vise from 3/4T1 same as in Figure 4.1B.
   Note: Make sure branches of 3/4T1 and 3/4T2 are directing opposite to each other.
   Adjust the tee fittings as necessary.
27. Wrap HX-110-Section B helically upward around V-110.
   Note: Make sure tape is in well contact with the tube wall and its turns don’t overlap.
28. Secure the remaining string of HX-110-Section B around 3/4T2.
29. Secure one tie string of HX-110-Section A around 3/4T1.
30. Remove the assembly from the bench vise and transfer it to PBCRS.
31. Secure the V-110 assembly within CL1-V110 and CL2-V110 (Figure 4.2B).
32. Secure and tighten 1/4N1 and 1/4N2 using the 9/16 wrench.
33. Tighten CL2-V110 using the cross head screwdriver.
34. Wrap HX-110-Section A around ¼” tubing between HX-100 and V-100.
35. Secure HX-110 remaining tie string around 1/4T1 (Figure 4.2B).
36. Cover V-110 using the front half of its insulation.
37. Insulate fittings between HX-100 and V-100 using very high temperature flexible fiberglass insulation and aluminum foil.
38. Connect C-HX110, TE-103 and TE-104 to respective connectors as labeled.
39. Clean and return the tools and glassware.

V. V-100 and HX-120 preparation

Operator has to coordinate with the laboratory technician to make sure the availability of utility gases (Industrial grade N2 and H2, and UHP grade Ar) in Stocker 045, prior to prepare V-100. Make sure the labeling machine is loaded with a sticker cartridge prior to starting of this section.

5.1 Required Safety Preparations
1. Refer to MSDS sheets available at chemical storage shelf 045A-4 for all the chemicals used for feed water preparation (Refer to STM).
2. Wear nitrile gloves, splash goggles and laboratory coat before handling chemicals.

5.2 V-100 Cleaning
1. Place an HDPE pail on the floor near PBCRS.
2. Close HV-101 (Figure 5.1).
3. Disconnect the John Guest fitting of the piece of polypropylene (PP) tube connected to downstream of HV-101.
4. Connect a ¼” OD PP drain tube to HV-101, placing its open end into the pail.
5. Open HV-101 draining contents of V-100 into the pail.
Note: V-100 may need to be tilted towards HV-101 to drain contents from the bottom of the vessel.

6. Dump the contents in the pail into the nearest sink.  
7. Wash the pail with tap water.  
8. Disconnect PP drain tube.  
9. Transfer V-100 and a 125ml Erlenmeyer flask to the nearest trench drain (in 045D).  
10. Fill two 1 gal plastic containers with distilled water.  
11. Open V-100 lid and rinse V-100 thoroughly using distilled water from a plastic container, draining into the trench drain. Open HV-100 as necessary.  

12. Collect a sample from the wash concentrate into the Erlenmeyer flask.  
13. Measure the total dissolved solids (TDS) of the sample using OAKTON Instruments Portable Meter Kit. Note: Use OAKTON TDS meter Instructions manual for detailed instructions.  
14. Repeat steps 11-13 until TDS meter reads a value less than 5 ppm. Collect more distilled water into containers as necessary.  
15. Collect one more sample from wash concentrate and measure for pH using ORION 2 STAR pH Benchtop PH probe.  
16. Repeat steps 11 and 15 until pH value reaches 7±0.5.  
17. Drain the water out of V-100 completely.  
18. Locate V-100 on the table near PBCRS and make sure HV-101 is closed.  
19. Clean and return glassware and supplies.
5.3 V-100 installation
Operator has to prepare and transfer the feed water solution into V-100 as per Standard Test Method (STM).
1. Make sure V-100 lid is closed.
2. Connect the free end of the PP line in the upstream of HV-102 (Figure 5.1), into HV-101.
4. Label a 10ml crimp top vial using ISEE Naming Procedure_140820 to indicate as feed water solution sample.
5. Collect a water sample into the vial from SP-101 by opening HV-102 until the vial overflows with the sample.
   Note: Use paper towels to avoid the table being wet.
6. Secure and crimp a crimp top cap on the vial using the 11 mm vial crimper.
7. Store the sample in ‘Catalyst trials sample storage area’.

5.4 Condenser preparation
1. Make sure HX-120 shell side outlet tube is directed to the sink nearest to PBCRS (Figure 5.2).
2. Connect HX-120 shell side inlet tube to the water outlet nearest to PBCRS (Figure 5.2).
3. Place a step ladder on the floor near PBCRS.

![Figure 5.2: HX-120](image)

4. Fill a 4L PP beaker with tap water.
5. Pour the water into HX-120 shell (Figure 5.2).
6. Repeat steps 4-5 until HX-120 shell side overflows from its outlet.
7. Return the step ladder and the beaker.
VI. Turning on PBCRS

6.1 Required Safety Preparations
1. Wear safety glasses while working Stocker 045A.

6.2 Turning on PBCRS
1. Put PS-2 on the wall to ‘ON’ position.
2. Open PBCRS control box using the cross head screwdriver to unlock the door.
3. Put PS-1 (Figure 6.1B) to its ‘Up’ position.
4. Turn on the battery backup (Figure 6.1) by pressing its “Power” button and holding until ‘beep’ noise comes.
5. Turn on the computer, PC-045A-3 (nearest computer to PBCRS).
6. Verify proper networking between computer and PBCRS via the blinking LED at the Ethernet cable port inside ‘Control Box’ (Figure 6.1B).
7. Wait for at least 2 minutes and double click on the ‘LabVIEW interface_PBCRS’ icon on the desktop to open the GUI.
8. Verify proper wiring connections by observing non-zero values in temperature and pressure indicators on GUI (Figure 6.2).
9. Close the control box.
10. Enter the required data logging time interval in seconds in the ‘Data Log Interval’ text box on GUI (Figure 6.2).
    Note: Unless otherwise specified, data logging interval is to be 10s.
11. From the ‘Data Log Menu’, select ‘Select File Location’ and locate the file path to be ‘Desktop/PBCRS’ using ISEE Sample Naming Procedure 140820.
12. Position PBCRS safety shield by sliding it along its guiders (Figure 4.1).
13. Install the four sets of 5/16 nuts and bolts to the safety shield by hand by aligning the holes on top surface of the shield and safety shield supports.

Figure 6.1A): PBCRS control box exterior; B): PBCRS control box interior
Figure 6.2 : GUI ‘Control’ tab
VII. Catalyst activation

This procedure is performed only for the catalysts that need to be activated by reducing with hydrogen (Refer to STM).

7.1 Required Safety Preparations
1. Wear safety glasses while working Stocker 045A.
2. Attach ‘HOT’ caution onto PBCRS safety shield before start heating up.

7.2 Catalyst activation
1. Turn HV3-103 (Figure 7.1), HV3-101 and HV3-102 (Figure 7.3) into ‘Reducing Gas’ direction.
2. Enter high temperature values as provided by STM to the respective text boxes on ‘High Temps’ frame of PBCRS GUI.
3. Click ‘OK’ button.
4. Select ‘N2’ from ‘MFC 101’ drop down menu.
5. Click on the ‘Calibration’ tab (Figure 6.3).
6. Enter the PID gains as provided by STM to the appropriate text boxes.
7. Click ‘OK’ button.
8. Make sure HV3-FBR2-1 and HV3-FBR2-2 (Figure 7.2) are open to ‘PBCRS’ direction.
9. Open FR-102 and FR-103 completely by turning them counterclockwise (Figure 7.2) all the way.

Figure 7.1: P-100
Figure 7.2: H\textsubscript{2} and N\textsubscript{2} supply setup

Figure 7.3: MFC-101 (MFC-101, HV3-101,102)

Figure 7.4 A): Stocker 045A N\textsubscript{2} supply system; B): Stocker 045C H\textsubscript{2} supply system
10. Open N2FR-101 completely by turning it counterclockwise (Figure 7.4A).
12. Close and adjust N2FR-101 until N2PI-101 indicates a value 100 psi greater than the reducing delivery pressure defined by STM.

13. Open BPR-101 all the way by turning its valve counterclockwise.

14. Open HV-104 (Figure 7.5).

15. Adjust FR-102 until PI-105 indicates the reducing delivery pressure defined by STM.

16. Place a 600 ml glass beaker underneath SP-102 (Figure 7.6).

17. Open HV-105 (Figure 7.6).


19. Wait until dripping of water from SP-102 stops. Operator may observe the gauge glass on V-130 to (Figure 7.6) determine when the V-130 (and there by the whole system) would be completely aerated and stop its water dripping.

20. Close HV-105 and dump the water collected in the beaker into the nearest sink.

21. Reach H2 supply unit (Figure 7.4) in 045C lab.

22. Repeat steps 10-12 for H2 supply unit (Figure 7.4) with equivalent valves.

23. Wait for at least 10 minutes.

24. Open HV-103 (Figure 7.5).


26. Adjust SPR-101 to set ‘MFC 102 OUT’ value on GUI to its desired flow rate (refer to STM).

27. Enter 150 (°C) to both ‘Preheater Control’ and ‘Reactor Control’ text boxes on GUI (Figure 6.2).

Note: We shall call these ‘preheater control set point’ and ‘reactor control set point’ respectively.

28. Click ‘ON/OFF’ buttons of ‘Preheater Control’ and ‘Reactor Control’ on GUI.

29. Select TE-102 and TE-104 from the list down menus of Graph 1 and 2 respectively (Figure 6.2).

30. Wait until TE-104 settles within ±10°C around preheater control set point.

31. Increase preheater and reactor set points by 50°C.

32. Repeat steps 30-31 until TE-102 reaches its operating temperature (refer to STM).

33. Enter the desired operating temperature for TE-104 (refer to STM) onto ‘Reactor Control’ text box on GUI.

34. Once TE-104 reaches its set point, allow system to run for a reducing time period as given in STM.

35. Repeat step 28.

36. Wait until TE-104 to drops below 50°C.

37. Set ‘MFC 102 OUT’ value on GUI to zero using SPR-101.

38. Close H2V-101 (inside H2 supply unit- Figure 7.4B) and then close HV-103.

39. Wait for at least 10 minutes.

40. Set MFC-101 flow rate to 0 SCCM.

41. Close N2V-101 and N2V-102 and then close HV-104.
VIII. Startup

In this section, P-100 will be primed followed by flushing the PBCRS with the prepared water medium. After, pressure and temperatures will be increased to the desired levels by the operator using the GUI and a real time DAC program. Operator has to make sure the supplementary components for gas analysis are turned on with settings defined by STM prior to the startup.

8.1 Required Safety Preparations
1. Wear safety glasses while working Stocker 045A.
2. Display ‘HOT’ caution sign near PBCRS before start heating up.

8.2 P-100 Priming
1. Turn HV3-103 into ‘Feed Water’ direction (Figure 7.1).
2. Place a 5 gal empty pail on the floor near PBCRS.
3. Connect ¼” ID flexible PVC tube to SP-102 and direct its free end into the pail.
4. Open HV-105.
5. Turn P-100 power switch “ON”.
6. Press “MODE” key until P-100 LED1 (Figure 7.1) is lit.
7. Use arrow keys to increase the display value in P-100 to 10 ml/min.
   Note: Steps 6-7 set the flow rate of P-100.
8. Connect a syringe to prime valve of P-100.
9. Press “RUN/STOP” button to start P-100 allowing water to be sucked into the syringe from the prime valve.
10. Turn prime valve 1-2 turns counterclockwise.
11. After collection of a minimum of 20 ml into the syringe, Close the prime valve and dump water in the syringe into the pail.
12. Press “RUN/STOP” button to stop P-100.

8.3 Introducing water media to PBCRS
1. Enter temperature interlock values as provided by STM into the respective text boxes on ‘High Temps’ frame of PBCRS GUI (Figure 6.2).
2. Click ‘OK’ button.
3. Click on the ‘Calibration’ tab (Figure 6.3).
4. Enter PID gains as provided by STM into the appropriate text boxes.
5. Click ‘OK’ button.
6. Click on ‘Control’ tab.
7. Press “MODE” button of P-100 until P-100 LED3 (Figure 7.1) is lit.
8. Use arrow keys to set display value to 4000 psi.
9. Press “MODE” button of P-100 until P-100 LED4 (Figure 7.1) is lit and make sure display value is 0 psi.
   Note: Steps 7-9 set and confirm the higher and lower outlet pressures of P-100.
10. Open BPR-101 all the way by turning its valve counterclockwise.
11. Press “RUN/STOP” button of P-100 to start the flow.
12. Select “PT-101” from the list down menu of Graph 1 (Figure 6.2).
13. Press ‘PRIME’ button on P-100.
14. Collect a water sample to an Erlenmeyer flask (125 ml) from SP-101.
15. Measure the TDS of the sample using OAKTON Instruments Portable Meter Kit.
16. Once water starts draining out continuously from SP-102, repeat steps 14-15 for SP-102.
17. Repeat step 16 until TDS reaches a value within 10% of the value from step 15.
18. Press “RUN/STOP” button to stop P-100.
19. Close HV-105
20. Disconnect the tube on SP-102.
21. Dump the water collected in the pail into the nearest trench drain.
22. Clean and return the tube, glassware and the pail.
23. Set P-100 flow rate to the desired value given by STM using steps 6-7 in section 8.2.
24. Press “RUN/STOP” button of P-100.

8.4 PBCRS Liquid sampling
1. Place the labeling machine, a 10 ml crimp top vial, a 11 mm crimp top cap, 11 mm
crimper and a 600ml beaker near PBCRS.
2. Holding the crimp top vial underneath SP-102, open HV-105 and allow the water
sample inside V-130 to collect into the vial. Use paper towels on the table underneath
SP-102 to avoid the table being wet.
3. Close HV-105 as the vial starts overflowing.
4. Secure and crimp a crimp top cap on the vial opening using the vial crimper.
5. If V-130 doesn’t empty by steps 2-4, empty the remaining water inside V-130 into the
600 ml glass beaker in the same way.
7. Label the sample using ISEE Naming Procedure_140820.
8. Place the sample in storage 045A-4 in “Catalyst trials sample storage area”.
9. Return the labeling machine.
   Note: Section 8.4 must be repeated in time periods defined by STM until PBCRS is
   shutdown. Empty the 600ml beaker as necessary.

8.5 Pressurizing PBCRS
1. Close BPR-101 slowly by turning its regulator valve clockwise until PT-101 and PT-
102 readings just start rising on Graph 1.
2. Close BPR-101 by half a turn.
3. Wait until PT-101 settles within ±50psi of its apparent average value in Graph 1.
4. Repeat steps 2-3 until pressure reaches the operating pressure provided by STM.
   Note: Use quarter turns for BPR-101 instead of half turns at pressures within ±10% of
   the operating pressure.

8.6 Process gas supply
1. Turn HV3-101 and HV3-102 into ‘Process Gas’ direction.
2. Open FR-101 completely by turning it counterclockwise all the way.
3. Open ARV-101 (Figure 8.1) by turning the valve counterclockwise.
4. Adjust FR-101 until PI-104 indicates 50 psi (Figure 8.1).
5. Select ‘Ar’ from ‘MFC 101’ drop down menu on GUI.


Figure 8.1: UHP Ar bottle and its regulator

### 8.7 Heating up PBCRS

*Note: Operator should adjust BPR-101 as necessary during the heating up process, to maintain PT-101 within ±1% around the operating pressure.*

1. Make sure HX-120 outlet tube (Figure 5.2) is directed to the sink nearest to PBCRS.
2. Open and adjust HV-106 until the desired flow rate is observed in FI-101 in GPM (Figure 5.2).
3. Repeat steps 27-33 in section 7.2 with operating temperatures for catalytic reforming defined in STM.

*Note: System is considered as reached steady state once TE-104 settles within ±2°C around its operating temperature.*
IX. Operation

9.1 Required Safety Preparations
1. Wear safety glasses while working in Stocker 045A.

9.2 Running the trial
1. Carefully adjust BPR-101 as necessary to maintain PT-101 within ±1% around the operating pressure (refer to STM). Use Graph 1 in GUI to observe changes in PT-101. *Note: Turn the valve in BPR-101 as slowly as possible when adjusting the pressure.*
2. Repeat section 8.4 in time periods defined by STM for liquid sampling.
3. After every one hour of operation, collect a sample from SP-101, label and preserve in a crimp top vial in the same way. *Note: Trial must be continued at this steady state for the trial length given by the STM.*

X. Handling Emergency Situations

10.1 Steam Leakage
Steam leakages can be identified by a vapor jet with sound from fittings most likely within the tubing between TE-102 and TE-105. Do not approach a steam leakage point.

1. Turn the circuit breaker number ‘15’ on 045A Electrical panel (“PANEL GLP”, Figure 10.1) to ‘OFF’ position.
2. Allow PBCRS to cool down by losing its heat and pressure.
3. Contact a technician or supervisor immediately.

Figure 10.2: Stocker 045A electrical panel
10.2 Fire

Note: Do not attempt to fight the fire.

1. Review a ‘Ohio Coal Research Center (OCRC) Safety Response Guidelines’ document available at an accessible point in Stocker 045 Main Lab or 045D (Figure 10.2) prior to commencing back the experimentation.
2. Evacuate the lab as soon as possible.

10.3 Power failure

ITWDES can instantly stop its operation due to power failure in Stocker 045A. This can be caused by an error in the electric power distribution system internal or external to Stocker 045A. System must be cooled to 50 °C before the system may be restarted after recovery of power.

1. Turn PS-02 to ‘OFF’ position.

Note: If PS-02 is not reachable due to electric spark or anything, operator may turn off the circuit breaker number ‘15’ on 045A Electrical panel (Figure 10.1).
2. MFC-101 set point to zero.
3. Close ARV-101 (Figure 8.1).
4. Contact the ‘University Facilities Management Work Center’ (740-593-2911) to know an estimated time period for the power outage.
5. Inform a supervisor and a laboratory technician.
6. Once power is back, repeat steps 3-9 in section 6.2 to turn on PBCRS.
7. Contact a supervisor regarding continuation or dismissal of the trial.
8. Wait until all the temperature readings are below 50 °C.
9. If the trial is to be continued, repeat sections 8.4 through 8.7 to restart PBCRS.

10.4 Over temperature

Any of the measured process parameters exceeding safety margins (refer to STM) will trigger an automatic shutdown sequence in the DAC program with an error message on the “Warning” window (Figure 6.2). This will turn off both HX-100 and HX-110.

1. Read the error message displayed on GUI and inform a supervisor and a laboratory technician about the error.
2. Wait until all the temperatures drop below 50°C.
   *Note: This can take more than 3 hours depending on the situation.*
3. MFC-101 set point to zero.
4. Close ARV-101 (Figure 8.1)
5. Slowly open BPR-101 (counterclockwise) and wait until ITWDES pressure drops below 200 psi.
6. Press “RUN/STOP” button of P-100.
7. Contact a supervisor regarding continuation or dismissal of the trial.
8. If the trial is to be continued, repeat sections 8.4 through 8.7 to restart PBCRS.

XI. Shutdown

*Liquid samples must be taken from the outlet stream (use Section 8.4) after every sampling time period (refer to STM) until the pump it turned off (step 12) in this section.*

11.1 Required Safety Preparations

1. Wear safety glasses while working Stocker 045A.

11.2 Shutting down PBCRS

1. Click on the ‘Control’ tab of GUI.
2. Click the ‘Preheater Control’ and ‘Reactor Control’ ‘ON/OFF’ buttons on GUI.
3. Make sure ‘TE-104’ is selected from drop down list of Graph 2 on GUI.
4. Repeat steps 6 in section 8.6 to change MFC-101 set point to zero.
5. Turn ARV-101 counterclockwise all the way.
7. Allow PBCRS to circulate water medium until TE-104 drops below 100°C.
8. Turn BPR-101 one turn counterclockwise.
9. Wait until PT-101 settles within ±50 psi of its apparent average in Graph 1 on GUI.
10. Repeat steps 8-9 until PT-101 drops below 100psi.
11. Allow TE-104 to drop below 50°C.
12. Press the ‘RUN/STOP’ button of P-100 to pause water circulation.
13. Remove and return the ‘HOT’ caution sign.
14. Select ‘Stop data log’ from ‘Data log Menu’ drop down list in GUI.
15. Close HV-106.
16. Disconnect HX-120 shell side inlet tube from its water supply line and direct the tubes’ free end into the nearest sink.
17. Fill a clean pail with at least 4 gal of distilled water.
18. Place the distilled water pail on the floor near PBCRS.
19. Place an empty pail near the distilled water pail.
21. Disconnect the piece of PP tube of SP-101 from HV-102 (Figure 5.1).
22. Connect a ¼” OD PP drain tube to HV-102.
23. Immerse the free end of the PP tube in distilled water in pail.
24. Connect ¼” ID PVC drain tube to SP-102 and direct its free end into the empty pail.
26. Press the ‘RUN/STOP’ button of P-100 to start water circulation.
27. Press ‘PRIME’ button on P-100.
28. Repeat steps 14-15 of section 8.3 for SP-102 until TDS meter reads less than 10 ppm.
29. Collect a sample from SP-102 and measure for pH repeatedly until pH reaches 7±0.5.
30. Press ‘RUN/STOP’ button to stop P-100.
32. Disconnect the two drain tubes connected to HV-102 and SP-102.
33. Connect SP-101 PP tube back into HV-102 open end.
34. Dump the water in the pails into the nearest trench drain.
35. Clean the pails and drain tubes using distilled water.
36. Uninstall PBCRS safety shield (steps 2-3, Section 4.2).
37. Open PBCRS control box.
38. Turn PS-01 off.
39. Turn PS-02 to ‘OFF’ position.
40. Turn off the battery backup by pressing its “Power” button and holding until ‘beep’ noise comes.
41. Reinstall the PBCRS safety shield.
Index

- ARV-101: Argon shutoff valve located in 5.0 UHP grade Ar bottle.
- BPR-101: PBCRS back pressure valve.
- CV-101: Check valves
- C-HX-110: HX-110 power connector.
- FI-101: Condenser cooling water flow indicator.
- FR-103: N2 gas flow regulator valve located on FBR#2.
- H2PI-101: H2 delivery pressure gauge at H2 supply unit.
- HV-101: V-100 outlet valve
- HV-102: SP-101 valve
- HV-103: H2 shutoff valve
- HV-104: N2 shutoff valve
- HV-105: SP-102 valve
- HV-106: Condenser cooling water supply valve
- HV3-101: 3 way valve to switch between N2 and Ar sources for MFC-101.
- HV3-102: 3 way valve to switch MFC-101 outlet towards PBCRS feed stream and product stream.
- HV3-103: 3 way valve to switch PBCRS inlet to feed water and reducing gas.
- HV3-FBR2-1: 3 way valve on FBR#2 directing H2 supply towards PBCRS.
- HV3-FBR2-2: 3 way valve on FBR#2 directing N2 supply towards PBCRS.
- HX-100: Preheater
- HX-110: Reactor heat tape.
- HX-120: Condenser
- MFC-101: Mass flow controller for N2 and Argon.
- N2FR-101: N2 gas flow regulator valve at N2 supply unit.
- N2PI-101: N2 delivery pressure gauge at N2 supply unit.
- N2V-101: N2 shutoff valve located in industrial grade N2 bottle.
- N2V-102: N2 shutoff valve on N2 supply unit.
- P-100: PBCRS HPLC pump
- PI-101: Pressure gauges
- PRV-101: Reactor upstream pressure relief valve.
- PRV-102: Reactor downstream pressure relief valve.
- PS-01: PBCRS main power switch inside control box.
- PS-02: 208V power supply switch located on the wall near PBCRS.
- PT-101: PBCRS upstream pressure transducer.
- PT-102: PBCRS downstream pressure transducer.
• SP-101: PBCRS upstream liquid sample port
• SP-102: PBCRS downstream liquid sample port
• SPR-101: MFC-102 set point controller (set point regulator)
• TE-101: 106 Thermocouples
• V-100: Feed water tank
• V-110: Reactor
• V-120: Separator
• 1/4T1: ¼” tee fitting at HX-100 outlet
• 1/4N1: ¼” Swagelok nut on 1/4T1 (Figure 4.2B)
• 1/4N2: ¼” Swagelok nut at V-110 inlet (Figure 4.2B)
• 1/4N3: ¼” Swagelok nut at V-110 outlet (Figure 4.2B)
• 3/4T1:T2 ¾” tee fittings on V-100
• 3/4N1:N2 ¾” Swagelok nuts on 3/4T1 and 3/4T2 (Figure 4.2B)
Appendix D: Safety Evaluation Report

Institute for Sustainable Energy
and the Environment (ISEE)

Safety Evaluation Report
for
"Packed Bed Catalytic Reactor System"

Document Number:
SER_Packed bed catalytic reactor system_141202

Last Updated:
12/02/2014

Contributor(s):
Chamara De Silva

Initial Safety Certification - Failure Mode and Effects Analysis Worksheet
(Adapted from Cincinnati Machine PFMEA)
I. Name / Description of Test System, including SOP\(^1\): (include photos of system and location)

The PBCRS, located in Stocker 045A, is used to evaluate performances of heterogeneous catalysts used for reforming organics dissolved in water under supercritical conditions. A P&ID for the experimental apparatus is provided in Figure 2.2. A model solution containing selected organics is pressurized and heated up to reach its supercritical region and then sent through the packed catalyst bed, V-110. Product stream is condensed and gas and liquid phases are separated. During the trial, samples are collected from gas and liquid phases of product stream which are then analyzed for composition. After the trial, V-110 is dismantled and used catalyst material is analyzed for crystallinity and composition.

| Key Contact / Phone | Chamara De Silva  
|                     | (740) 274-9736 | Date of Initial FMEA  
|                     |                | 11-13-2014 | Date of Initial System Demonstration  
|                     |                | 11-13-2014 |  
| Location:           | Stocker 045 | Safety Review Board Approval / Date  
| SOP name:           | SOP_Packed bed catalytic reactor system _141117 | Other Approval (if required) |  
|                     | STM name(s):  
|                     | STM_Catalytic Reforming_141117 |  
|                     | STM_Catalyst Synthesis by Impregnation_141117 |  
|                     | STM_Catalyst Synthesis by coprecipitation_141117 |
II. Hazard Identification Discussion

(Details for the "description of test subsystem or operating procedure" and "potential failure mode") columns.

*Note the procedure used to identify all potential hazards, including who was involved and what was done to insure completeness. All aspects and modes of operation of the system must be evaluated, including system setup, actual testing, post-test cleanup, etc. Strive to design your system and procedures to completely avoid dangers whenever possible. For guidance, review the design for safety guidelines, especially with respect to avoidance, protection and warnings.*

PBCRS was designed fabricated at ISEE research facility under the inspection of design engineer, David Ogden. Use of proper PPE during fabrication was regularly inspected by Shyler Switzer. Potential hazards and issues were discussed together with the P&ID at weekly update meetings held on at Stocker 252, based on the update presentations given by Chamara De Silva. The weekly update meetings were occurred with the participation of Dr. Jason Trembly, Shyler Switzer and David Ogden. Based on the recommendations raised during meetings, necessary modifications were done to the system as necessary. System was pressure tested at 4000 psi using CO₂ with the involvement of David Ogden to ensure absence of leakages prior to shakedown tests. After the installation, a complete shakedown test was run by Chamara De Silva based on the ESER document approved by Dr. Jason Trembly. Proper functioning and control of heaters under operating conditions was ensured during the shakedown test. An additional hazard identification discussion was held on 21st October with the participation of post doctorial researcher Swapnil Fegade and graduate student Xiao Dong in front of PBCRS. Chemicals involved in the experiments were evaluated using respective MSDS sheets. Based on the recommendations during safety discussions, Chamara De Silva developed the Standard Operating Procedure (SOP), to ensure safety during the whole life cycle of an experimental trial.

III. SUPPORTING EXPERIMENTAL SER’s

<table>
<thead>
<tr>
<th>ESER name</th>
<th>Starting Date</th>
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### IV. Hazard 1 (Exposure to chemicals)
1. FMEA description and ratings for Hazard 1

<table>
<thead>
<tr>
<th>Categorize: Identify test subsystem or section of SOP</th>
<th>Potential Failure Mode</th>
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<tbody>
<tr>
<td>Catalyst loading/unloading, Feed water preparation</td>
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<thead>
<tr>
<th>Potential Effect of Failure (Severity)</th>
<th>Initial Evaluation</th>
<th>After Action Results</th>
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Ni(NO$_3$)$_2$ has carcinogenic effects and it’s toxic to lungs and the nervous system; Skin/eye contact of Phenol can result in irritation or blindness; Birth defects and cancer risk by Toluene.

<table>
<thead>
<tr>
<th>Potential Cause(s) / Mechanism(s) of Failure (Probability of occurrence)</th>
<th>Probability of detection</th>
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Spills/splashes during catalyst synthesis, loading/unloading and water media preparation; Spills/splashes during V-100 dosing; Spills/splashes during liquid sample collection and handling.

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<tr>
<th>Current Control Detection / Prevention (Probability of detection)</th>
<th>Probability of detection</th>
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Wear respirator to avoid catalyst material get in contact with mouth and nose; Preparation of water media inside fume hood; Use of PP vials with closed lids for sample handling; Use of splash goggles and nitrile gloves while preparing feed water solutions.

<table>
<thead>
<tr>
<th>Risk Priority Number</th>
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<thead>
<tr>
<th>Recommended Action</th>
<th>Person Responsible &amp; Completion Date</th>
<th>Action Taken</th>
</tr>
</thead>
<tbody>
<tr>
<td>Move catalyst loading/unloading procedure to inside of fume hood and therefore respirator is not necessary</td>
<td>Chamara De Silva</td>
<td>Changes in SOP to Move catalyst loading/unloading procedure to inside of fume hood and analytical balance moved to inside of fume hood.</td>
</tr>
</tbody>
</table>
2. Include some discussion/justification for the rating for severity (SEV)

Ni(NO_3)_2 has carcinogenic effects and it’s toxic to lungs and the nervous system. High dose of Toluene can cause birth defects. Serious eye contact of Phenol can cause blindness. This severity never changes although the actions are taken to minimize exposure.

3. Include some discussion/justification for the rating for probability of occurrence (OCC)

Probability of exposure to catalyst is reduced by moving catalyst loading/unloading procedure to inside of fume hood. Very low concentrations of Toluene and Phenol are used (<50 ppm) for water media. Closed lid plastic container ensures absence of spills of organics containing samples. Sample handling is done using PP vials with lids and samples are small as 50 ml.

4. Include some discussion/justification for the rating for probability of detection (DET)

Spills of catalyst materials can occur only inside fume hood. Any spills of pure volatile organics can be seen inside fume hood. MSDS sheets are referred before handling the chemicals;

5. Recommended actions: Make specific recommendations for action and include some discussion of the alternatives that were considered.

6. Notes on Actions taken:

V. Hazard 2 (Rupture/leak of high pressure component)

1. FMEA description and ratings for Hazard 2

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<tr>
<th>Categorize: Identify test subsystem or section of SOP</th>
<th>Potential Failure Mode</th>
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<td>Initial Evaluation</td>
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<tr>
<td>Potential Effect of Failure (Severity)</td>
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<td></td>
<td>E</td>
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<td>V</td>
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<tr>
<td>Cuts/ burns on skin around critical areas by exposure to high pressure steam</td>
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<tr>
<td>Potential Cause(s)/Mechanism(s) of Failure (Probability of occurrence)</td>
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<tr>
<td>Reactor over temperature; Preheater over temperature; Faulty component; Improper installation; Failure of control system;</td>
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<td>Current Control Detection / Prevention</td>
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*(Probability of detection)*

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<tr>
<th>Embedded LabVIEW controlling program; Designed with high safety margins;</th>
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**Risk Priority Number**

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<table>
<thead>
<tr>
<th>Recommended Action</th>
<th>Person Responsible</th>
<th>Action Taken</th>
</tr>
</thead>
<tbody>
<tr>
<td>Install a safety shield in front of the reactor.</td>
<td>Chamara De Silva</td>
<td>Installed a removable polycarbonate safety shield.</td>
</tr>
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</table>

2. Include some discussion/justification for the rating for severity (SEV)

Exposure to steam at 3500 psi can cause a severe injury. However severity doesn’t change with introduction of safety shield.

3. Include some discussion/justification for the rating for probability of occurrence (OCC)

System is leak tested for design pressure prior to installation. But V-110 is replaced after every trial. Loss of concentration of technician during V-110 installation can cause incomplete tightening of fittings. However, SOP guides operator during V-110 installation. Probability of occurrence is further reduced by Labview controlling system.

4. Include some discussion/justification for the rating for probability of detection (DET)

HX-100 and HX-110 are over designed with safety factors of 2.5. The Steam leaks are detectable via sound and/or steam jet appeared. With the safety shield, any damage to operator by a steam leak is controlled. Also Operator can still see the steam jet through the polycarbonate shield.

5. Recommended actions: Make specific recommendations for action and include some discussion of the alternatives that were considered.

6. Notes on Actions taken:
VI. Hazard 3 (Gas leakage)

1. FMEA description and ratings for Hazard 3.

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<th>Categorize: Identify test subsystem or section of SOP</th>
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<td>Catalyst activation</td>
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<table>
<thead>
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<th>Potential Effect of Failure (Severity)</th>
<th>Initial Evaluation</th>
<th>After Action Results</th>
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<tr>
<td>Skin burn injuries and equipment damage by fire</td>
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<th>Potential Cause(s) / Mechanism(s) of Failure (Probability of occurrence)</th>
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<tr>
<td>Current Control Detection / Prevention (Probability of detection)</td>
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<td>Indication of any gas flow changes by mass spectrometer connected to PBCRS</td>
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<thead>
<tr>
<th>Recommended Action</th>
<th>Person Responsible &amp; Completion Date</th>
<th>Action Taken</th>
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</thead>
<tbody>
<tr>
<td>Use a H₂ and N₂ mixture instead of pure H₂ for activation.</td>
<td>Chamara De Silva</td>
<td>Use 10% H₂ in N₂ for catalyst activation.</td>
</tr>
</tbody>
</table>

2. Include some discussion/justification for the rating for severity (SEV)

A hydrogen leakage can cause a fire in the lab if an ignition source is present near leak point. Use of 10% H₂ is less severe than pure H₂. Even though Lower explosive Limit (LEL) of H₂ is 4%, but this case is in the absence of Oxygen.

3. Include some discussion/justification for the rating for probability of occurrence (OCC)

Hydrogen supply line runs all around Stocker 045 laboratory. However, since valves are used to control the gas flows, no changes are done to fittings on gas lines once they are installed and leak tested. Also H₂ flow rate is as low as 10 ml/min.

4. Include some discussion/justification for the rating for probability of detection (DET)

A leakage starts during the operation is reflected by concentration changes in mass spectrometer.

5. Recommended actions: Make specific recommendations for action and include some discussion of the alternatives that were considered.
6. Notes on Actions taken:

VII. Hazard 4 (Burns from high temperature components)

1. FMEA description and ratings for Hazard 4

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<tr>
<th>Categorize: Identify test subsystem or section of SOP</th>
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<table>
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<th>Potential Effect of Failure (Severity)</th>
<th>Initial Evaluation</th>
<th>After Action Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skin burns</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>V</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Potential Cause(s) / Mechanism(s) of Failure (Probability of occurrence)</th>
<th>Initial Evaluation</th>
<th>After Action Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact with reactor; Contact with pre-heater; Contact with heated plumbing;</td>
<td>6</td>
<td>3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Current Control Detection / Prevention (Probability of detection)</th>
<th>Initial Evaluation</th>
<th>After Action Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use of HOT caution sign;</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Risk Priority Number</th>
<th>Initial Evaluation</th>
<th>After Action Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>P</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>180</td>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Recommended Action</th>
<th>Person Responsible &amp; Completion Date</th>
<th>Action Taken</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use a safety shield in front of the reactor</td>
<td>Chamara De Silva</td>
<td>Installed a polycarbonate safety shield avoiding operator getting touch with heated components</td>
</tr>
</tbody>
</table>

2. Include some discussion/justification for the rating for severity (SEV)

Skin contact of heated components can cause skin burns. However, insulation surface temperature of preheater and reactor are less than 60 °C.

3. Include some discussion/justification for the rating for probability of occurrence (OCC)

Tubing from reactor outlet to condenser inlet is not insulated to enhance cooling by heat loss prior to condenser. Preheater and reactor are covered with insulation. Safety shield avoids operators hands getting closer to heated components.
4. Include some discussion/justification for the rating for probability of detection (DET)

HOT caution sign makes operator and visitors aware of the hazard.

5. Recommended actions: Make specific recommendations for action and include some discussion of the alternatives that were considered.

6. Notes on Actions taken:

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**VIII. Hazard 5 (Electric shock)**

1. FMEA description and ratings for Hazard 5

<table>
<thead>
<tr>
<th>Categorize: Identify test subsystem or section of SOP</th>
<th>Potential Failure Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Box, 208V power supply</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Initial Evaluation</strong></td>
<td><strong>After Action Results</strong></td>
</tr>
<tr>
<td><strong>Potential Effect of Failure</strong></td>
<td><strong>S</strong></td>
</tr>
<tr>
<td>(Severity)</td>
<td><strong>E</strong></td>
</tr>
<tr>
<td>Electric shock / Electrocution</td>
<td><strong>V</strong></td>
</tr>
<tr>
<td><strong>Potential Cause(s) / Mechanism(s) of Failure</strong></td>
<td><strong>O</strong></td>
</tr>
<tr>
<td>(Probability of occurrence)</td>
<td><strong>C</strong></td>
</tr>
<tr>
<td>Damaged shielding or insulation; Water exposed to electrical circuit; Operator error or access to Control Box; Component short; External wiring covered with finger molds.</td>
<td><strong>3</strong></td>
</tr>
<tr>
<td><strong>Current Control Detection / Prevention</strong></td>
<td><strong>D</strong></td>
</tr>
<tr>
<td>(Probability of detection)</td>
<td><strong>E</strong></td>
</tr>
<tr>
<td>Proper guidance in SOP in opening and closing the Control Box; Main switch and fuses installed within the electric circuit.</td>
<td><strong>T</strong></td>
</tr>
<tr>
<td><strong>Risk Priority Number</strong></td>
<td><strong>R</strong></td>
</tr>
<tr>
<td></td>
<td><strong>P</strong></td>
</tr>
<tr>
<td></td>
<td><strong>N</strong></td>
</tr>
<tr>
<td></td>
<td><strong>108</strong></td>
</tr>
<tr>
<td></td>
<td><strong>54</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Recommended Action</th>
<th>Person Responsible &amp; Completion Date</th>
<th>Action Taken</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use finger molds to cover external wiring</td>
<td>Chamara De Silva</td>
<td>Used finger molds to run external wiring</td>
</tr>
</tbody>
</table>

2. Include some discussion/justification for the rating for severity (SEV)

An AC power outlet with 208VAC and 20A is used.
3. Include some discussion/justification for the rating for probability of occurrence (OCC)

SOP guides operator to open the Control Box only twice in the whole procedure. Finger molds enclose and protect external electrical wires.

4. Include some discussion/justification for the rating for probability of detection (DET)

Operator can detect any water spills near Control Box. However, any damages to insulation are hidden by finger molds.

5. Recommended actions: Make specific recommendations for action and include some discussion of the alternatives that were considered.

6. Notes on Actions taken: