

Removal of phenol from oil/gas produced water using supercritical water treatment with TiO₂ supported MnO₂ catalyst



Chamara L. De Silva^{a,1}, Ravinder K. Garlapalli^{b,1}, Jason P. Trembly^{a,b,c,*}

^a Department of Chemical and Biomolecular Engineering, Ohio University, Athens, OH 45701, USA

^b Institute for Sustainable Energy and the Environment, Ohio University, Athens, OH 45701, USA

^c Department of Mechanical Engineering, Ohio University, Athens, OH 45701, USA

ARTICLE INFO

Article history:

Received 4 October 2016

Received in revised form 3 December 2016

Accepted 13 December 2016

Available online 20 December 2016

Keywords:

Produced water
Supercritical water
Phenol
Oxidation
MnO₂ catalyst

ABSTRACT

MnO₂ catalyst supported on TiO₂ was synthesized and evaluated for removal of phenol in supercritical water. Synthesized catalysts were characterized using temperature programmed reduction, pulse chemisorption, and X-ray powder diffraction. Catalyst activity for phenol conversion was evaluated in a continuous packed bed reactor at supercritical water conditions by analyzing gaseous and liquid products. Process variables evaluated include O₂ stream concentration and Mn catalyst loading. Both variables had positive effects on phenol conversion. The process achieved complete conversion of phenol at oxygen ratio of 5 based on complete phenol combustion stoichiometry. Increasing catalyst Mn loading increased its active site concentration, enhancing the contribution of heterogeneous reaction kinetics for supercritical water oxidation (SCWO) of the phenol. A phenol conversion of 70% was reached at 12% (w/w) Mn in the catalyst with oxygen ratio of 1.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

In today's world, 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 the electricity generated on water and wastewater treatment and distribution, at a cost of \$4 billion per year [1]. Oil and gas wells have been and are increasingly becoming greater sources of wastewater containing organics due to the development of U.S. unconventional shale plays [2]. Shale plays are developed using a combination of horizontal drilling with hydraulic fracturing that generate flowback water, and produced water. More than 1500 gallons of produced water can be generated from every 1000 ft³ of natural gas produced [3]. According to statistics prepared for the Groundwater Protection Council, the U.S. oil/gas industry generated 21.1 billion barrels of produced water in 2012 [4]. The primary method of managing produced water is to transport the waste to Class II salt water disposal (SWD) wells, where it is injected deep below the surface into saline aquifers.

Analysis of produced water samples generated by Marcellus shale wells indicates the presence of 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 [5]. Phenol is also a major pollutant in wastewater streams from petroleum, petrochemical, pharmaceutical, steel, dye synthesis, pulp and paper, and coal gasification industries [6], it is chosen to be the model compound in present study.

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 [7]. Membrane separation processes are easily scalable and are low energy consumers; however, fouling caused by colloids is a common limitation [8]. As destructive processes, oxidation and biological degradation are popular in the field [7]. Oxidation is being investigated using oxygen, other chemicals (O₃, Cl₂, H₂O₂, etc.), and electrochemical-based techniques [7]. The possibility of generating hazardous wastes by adding pollutants such as chlorinated organic compounds to the environment limits the

* Corresponding author at: Department of Chemical and Biomolecular Engineering, Ohio University, Athens, OH 45701, USA.

E-mail address: trembly@ohio.edu (J.P. Trembly).

¹ C. L. De Silva and R. K. Garlapalli equally contributed as first authors.

use of some oxidation-based techniques. Chemical oxidation processes such as ozone, ozone with UV, ozone with hydrogen peroxide, photolysis and UV/H₂O₂, Fenton's reagent, and photocatalysis have been studied for elimination of recalcitrant chemicals present in wastewater. It was reported that Fenton reagent was found to be the fastest for phenol degradation. However, costs associated with chemical oxidation can be expensive and often be prohibitive for wastewater treatment [9]. Furthermore, in the case of using compressed air as the oxidant, maintaining a homogeneous oxidant concentration in the reactor is a significant challenge [10].

One approach to overcome these issues is to perform catalytic oxidation reactions in supercritical water (SCW). SCW treatment has received a lot of attention for removal of phenol in waste streams [11]. 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. In typical supercritical water oxidation (SCWO) processes applied to phenol, 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 have been investigated in absence of oxidants [12,13]. However, these reforming processes require higher temperatures (500–700 °C) increasing costs and process energy demand. Effective use of a catalyst has the ability to lower both reactor temperature and oxidant concentration, reducing treatment costs.

Several groups of researchers have examined the use of heterogeneous catalysts such as CuO/ZnO/CoO supported on porous cement [14]; MnO₂/CeO₂, V₂O₅/Al₂O₃ [15]; CuO/Al₂O₃ [16], Carulite 150, a commercial catalyst [11], bulk TiO₂ [17] and bulk MnO₂ [18] for phenol oxidation and reported enhanced phenol conversions and reaction rates under supercritical conditions. The catalysts not only increased phenol conversion, but also increased the selectivity of phenol conversion to CO₂ and reduced the yield of organic byproducts. Ding et al. [19] reported that correlating physicochemical properties of catalyst materials, including redox potential, acid-base characteristics, oxygen adsorption, and surface structure, with the catalytic activity facilitates the selection of catalyst active materials. Enhanced reaction rates and selectivity at milder conditions continues to motivate research into catalytic SCWO, which appears to offer a route to improved SCWO process economics. For this reason, process conditions slightly above the critical conditions of water (T = 381.2 °C, 24.1 MPa) was chosen to evaluate the reaction rate and selectivity.

The work presented here investigates the use of TiO₂ supported MnO₂ catalyst for SCWO of phenol. In this work, the catalysts were characterized using TPR and pulse chemisorption techniques to predetermine variations of reduction temperature profiles and active surface area with Mn loading. The effects of both Mn loading and O₂ concentration in the supercritical water on phenol removal effectiveness and selectivity towards gas conversion were evaluated.

2. Experimental

2.1. Catalyst synthesis

TiO₂ supported MnO₂ catalysts were synthesized using incipient wetness impregnation (IWI) technique. Porous TiO₂ (anatase phase) 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 to obtain TiO₂ particles between mesh sizes of 35 and 120 (125–500 μm). Further, support pore volume was determined using BET methodology and a Micromeritics ASAP 2020.

A 4M Mn(NO₃)₂ (≥97.5%, Acros organics) solution was introduced into a measured support mass (approximately 25–30 g) with a volume equal to its total pore volume. The mixture was allowed to dry overnight in a fume hood followed by drying in a laboratory oven at 105 °C until constant weight, followed by calcination at 300 °C for three hours using a temperature ramp of 2 °C/min. The catalyst was then crushed using a mortar and pestle to break agglomerates formed during the calcination process.

2.2. Catalyst characterization

H₂ temperature programmed reduction (TPR) analyses were performed using a Micromeritics Autochem 2920. A sample size of 30–40 mg and a temperature ramp of 10 °C/min were used in the TPR with 10% H₂ in He at a total flow rate of 20 cm³min⁻¹.

Pulse chemisorption experiments were conducted using O₂ to determine active metallic surface area (AMSA) and the percent metal dispersion (D_{met}) in a Micromeritics Autochem 2920. A sample size of 0.4–0.5 g was used. A pre-reduction was completed with H₂ at 300 °C for three hours prior to each pulse chemisorption experiment to ensure the active MnO₂ phase was reduced. He (Helium) at a flow rate of 50 cm³min⁻¹ was used as the carrier gas and 10% O₂ in He was used as the loop gas with a loop volume of 0.5715 ml. Pulse chemisorptions were completed at 45 °C.

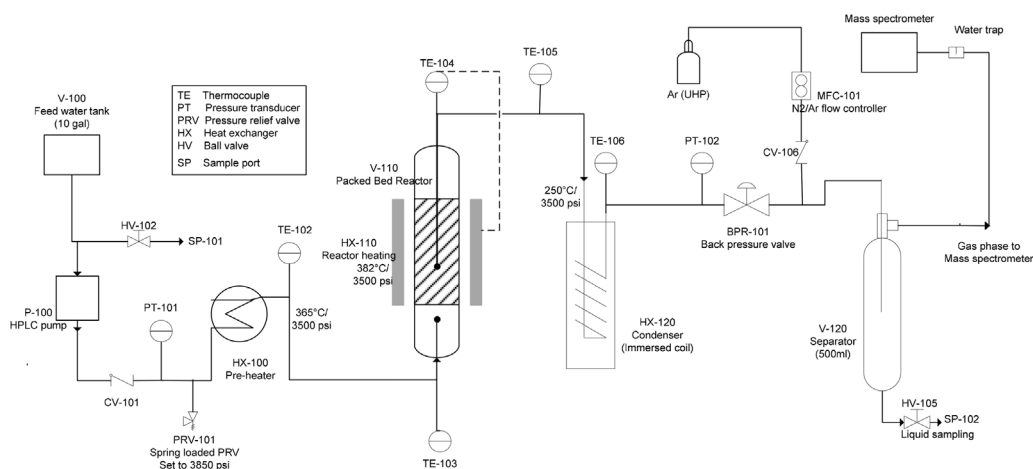


Fig. 1. Supercritical water experimental apparatus P&ID.

Download English Version:

<https://daneshyari.com/en/article/6477395>

Download Persian Version:

<https://daneshyari.com/article/6477395>

[Daneshyari.com](https://daneshyari.com)