A NOVEL APPROACH TOWARDS THE STUDY OF FLAMES IN SUPERCRITICAL WATER

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ABSTRACT

Supercritical water (SCW) is an effective medium for the breakdown of complex organic molecules in presence of oxygen, making it an ideal green solvent for waste remediation. The incineration of complex organic molecules under normal conditions leads to the formation of intermediate pollutant molecules such as dioxins and furans that have negative impacts on living organisms and the environment. In contrast, the oxidation of organic compounds in SCW flameless mode has gained extensive attention. The presence of flames in supercritical water enhances the oxidation rates of complex molecules and results in the production of CO_2 and water vapor. In this study, flames were generated in a portable supercritical water oxidation facility designed by NASA at Glenn Research Center, USA. The production of flames in supercritical water increased the temperature and reactivity of the combustion environment oxidizing the organics in milliseconds. However, the ignition and stability of flames were influenced by flame temperature, oxidant temperature and injection flow rate. This paper explores new insights about the flame oxidation of organics to permanent gases in supercritical water.

INTRODUCTION

Supercritical fluids have properties of both liquids and gases, which makes them superior to the conventional organic solvents. They find wide range of applications in many chemical processes such as microfluidics, fuel cells, biomass and waste gasification [1-3]. Of all the supercritical fluids, CO_2 and H_2O are known to be non-flammable and cheaply available. The critical point of a fluid and the operating parameters of supercritical process decide the option of choosing a fluid. The critical point of water (374°C and 22.1 MPa) favours the degradation of many organic compounds to simple molecules [4]. Supercritical water (SCW) completely dissolves the organics, making it suitable for use as an attractive medium for oxidation, gasification, pyrolysis and liquefaction of complex organic materials for the purpose of waste remediation [5-7]. Applying SCW for oxidation of organics is the most effective way for environment [8, 9].

Supercritical water oxidation (SCWO) is considered as a non-flame wet-oxidation process for waste disposal but with the presence of an organic solvent (e.g., alcohols) and oxidant (e.g., air or oxygen), ignition takes place to form flames in SCW. The generation of flames in SCW is found to oxidize the recalcitrant organic molecules in milliseconds [10].

However, the process of flame generation in SCW is acute, demanding appropriate operating conditions [11]. In the initial step, an organic solvent is mixed with water at supercritical conditions. In the next step, an oxidant is injected at a specified flow rate which is responsible for igniting the flames. These flames are termed as hydrothermal flames because of their generation in SCW. The temperature of flames could reach 2000°C. It is strongly dependant on air-to-fuel ratio.

A complete knowledge of hydrothermal flame behavior helps in finding its application for the upgrading of tars and heavy crude oils which are difficult to crack [12]. In addition, hydrothermal flames have found applications in thermal spallation of drilling of hard-rocks deep in the well [13]. The thorough understanding of hydrothermal flames is necessary for designing reactors to process noxious wastes through SCWO. Operating parameters such as reactor temperature, pressure, feed concentration and type of oxidant along with its flow rate and temperature have been reported to impact the production of hydrothermal flames.

Organic solvents such as methanol and iso-propanol have been mostly used as fuels for production of flames in SCW [10, 14]. The feed solution is composed of a minimum concentration of the organic solvents with water. Air or oxygen can be used as the oxidant, although air is regarded as safer to handle compared to oxygen which at high temperatures and pressures poses flammable risks. Air temperature plays a prominent role in the generation of flames in SCW [11]. The ignition of a SCW mixture might be delayed when low temperatures of air are employed into the reactor [8, 12]. An insufficient air for the combustion of organics in SCW leads to form significant amounts of CO as an indication of incomplete combustion. An increase in air temperature increases flame temperatures in the reactor. The oxidation rates are enhanced to a greater extent in the presence of hydrothermal flames due to the highly reactive environment. For the ignition of flames, the operating parameters should be above the auto-ignition temperature of the fuel [15].

At present, there are only a few studies on the generation of hydrothermal flames in supercritical conditions. With this objective to extend our understanding, a portable supercritical water oxidation facility, designed by National Aeronautics and Space Administration (NASA) at Glenn Research Center in Cleveland, USA has been used to generate the flames in SCW. This paper provides various insights about the oxidation of recalcitrant organic compounds to permanent gases with the aid of such mobile SCW units.

MATERIALS AND METHODS

In this study, we attempt to elucidate the breakdown of a wide range of organic compounds including polycyclic aromatic hydrocarbons (e.g., naphthalene and anthracene) and phenyl-ring components such as azobenzene, which are toxic for the environment and challenging to degrade. The major objective of the research is to completely denature these intricate compounds to innocuous molecules through the generation of hydrothermal flames.

A mobile SCWO unit designed by NASA at Glenn Research Center in Cleveland was used for the production of flames in SCW. The reactor has capabilities of treating the aircraft carrier wastes accumulated in the space shuttles. Previous works by NASA in similar SCWO reactors at Glenn Research Center have largely focused on space and extra-terrestrial application in relation to the gravitational effects on the thermo-physical processes occurring in medium [16]. The reactor is currently being used in the Department of Earth and Space Science Engineering at Lassonde School of Engineering in York University, Canada in collaboration with NASA.

The NASA SCWO set-up used in this study is shown in Figure 1. The set-up consists of a high pressure reactor, high pressure bottle cylinders for N_2 and air, piston accumulator, heat exchangers, heaters, gear pump, air booster, high pressure automatic valves, orifice meter valve and high temperature thermocouples. The potential organic solvents for use as co-fuel with SCW in the reactor are methanol, ethanol, butanol, acetone and iso-propanol. The oxidant for use is air, as pure O_2 at high temperatures and pressure is extremely flammable.

The set-up is purged by N_2 before commencement of the experiments for the purpose of reactor cleaning. After cleaning, the reactor and its associated lines are evacuated by creating vacuum. The pressure difference between the atmosphere and the vacuum forces the feed solution into the reactor and the lines. Air booster was used to pressurize the system. The pressure in the system was regulated by piston-accumulator. The excess pressure during experiments was reduced by micro-metering valve. The oxidant pressure is maintained close to 5000 psi, greater than the reactor pressure of 3500 psi. The flow-rate of the oxidant can be set by orifice valve which is located before reactor in the injection line. The oxidant is preheated before injection with the help of tape heaters.

There are two heaters to heat the reactor, both placed at the reactor’s polar ends (i.e., top and bottom). The temperature of the reactor and tape heater are monitored and controlled. The high temperature thermocouples are used to measure flame temperatures. By maintaining the operating parameters above the auto-ignition conditions of the feed solution, ignition of hydrothermal flames is achieved. The liquid and gas products are collected at their respective outlets, which are further analysed through various analytical instruments such as gas chromatography (GC), Fourier Transform-Infra Red (FT-IR) and Raman spectroscopy. The remaining effluents are cooled with two heat exchangers which are located at the exit of the reactor.

FINDINGS AND FUTURE APPLICATIONS

At present, significant research is underway in studying the degradation of polycyclic aromatic hydrocarbons using the NASA SCWO reactor. A few notable works by NASA were performed in similar reactors to understand the wet-oxidation of a spacecraft wastes [17], sub- and supercritical water oxidation of CELSS (controlled ecological life support systems) [18], and SCWO of polystyrene [19] and lignocellulosic biomass [20].

Regardless of the feedstock, its particle size influences the SCWO [21]. Hence, a smaller particle size feedstock is optimal to provide a higher surface area for the hydrothermal cracking to simple compounds. The effect of particle size and distribution on the SCWO of polystyrene beads [19] and wheat straw [20] has been extensively investigated by researchers in NASA with similar set-ups under a range of high temperatures and pressures.

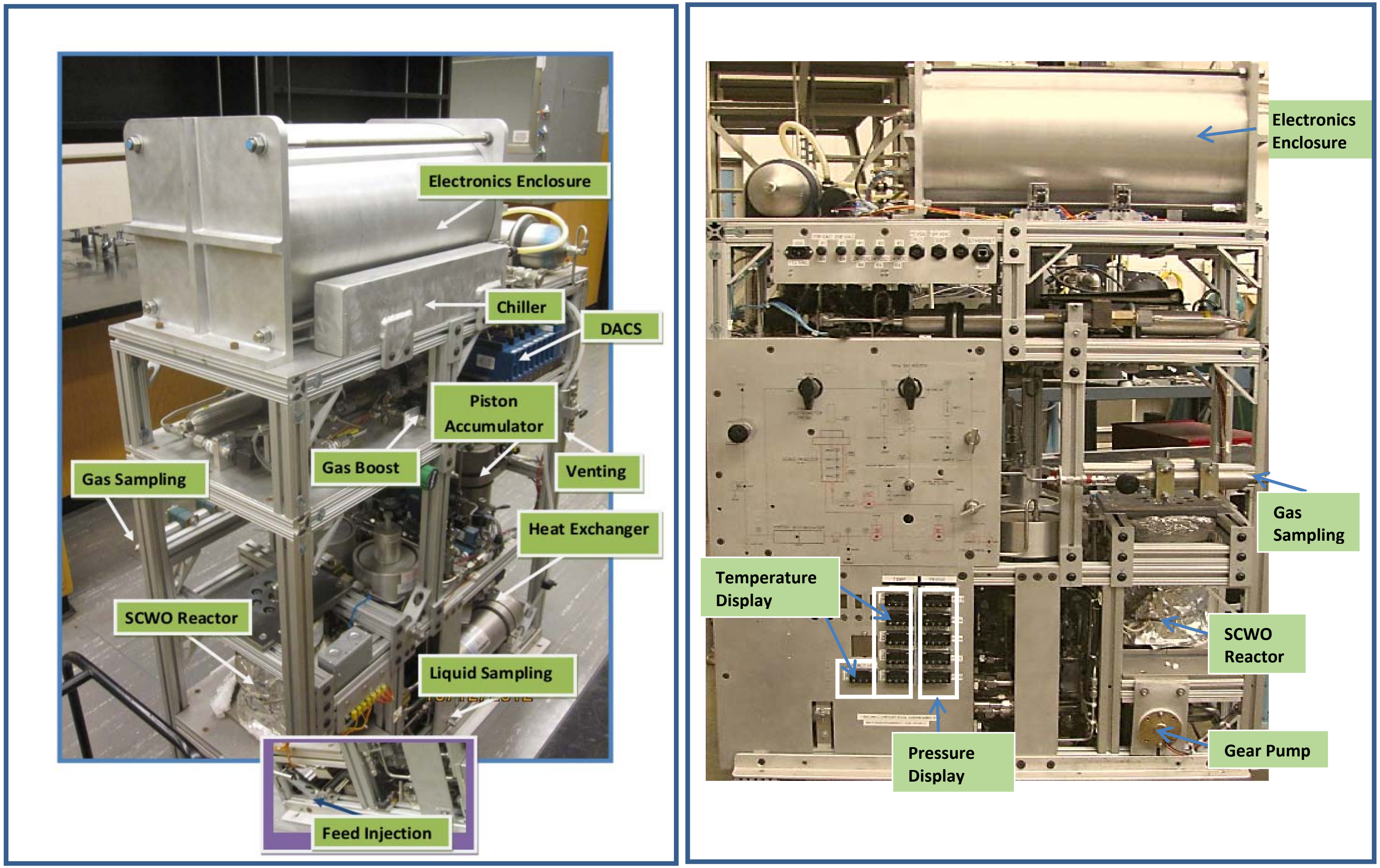

Figure 1: Side and front view of the mobile NASA SCWO reactor.

Gravitational force is one of the key factors that influence the performance of SCWO reactors. As initially designed for long-duration space missions by NASA, the effect of gravity on SCWO was studied in two different modes, namely premixed and diffusion-limited modes [22]. In premixed mode, the reactants are brought to supercritical conditions simultaneously, whereas in diffusion-limited mode one of the reactants (usually the oxidizer) is injected into the reactor after the bulk fluid attains supercritical conditions. In order to quantify the gravitational effects on hydrothermal mixing and reactant/oxidizer injection in SCWO reactor, a zero gravity facility was created at NASA's Glenn Research Center in Ohio [23]. The free-fall experiments in zero gravity were carried out within 5.2 seconds in the NASA's drop tower facility that comprised of a 480 mL high pressure reactor along with accessory parts for studying SCWO reactions either in continuous flow mode or batch mode.

The behavior of flames and temperature profiles in SCW at zero gravity (0-g) is not similar to that of ground level experiments (1-g). For the ignition to happen in any of the above mentioned modes (i.e., premixed- and diffusion-limited) a proper approach of oxidant injection and its distribution with fuel needs to be investigated. The ignition of hydrothermal flames is different due the buoyant forces that are present in 1-g level but absent at 0-g level. The previous test results inform that the axial temperature distribution in 0-g and 1-g is similar at the injection point where the inertial forces are predominant. The thermocouple readings which were placed axially with the oxidizer inlet imply that temperature profile in 0-g is nearly 4 times than that of 1-g [23]. In addition, the average temperature rise in 0-g has been found to be double than 1-g. The cooling rates are also found to be different in 0-g and 1-g environments. For example, the cooling rates in 0-g are nearly half of that in 1-g experiments. These findings indicate that buoyancy has a major impact on the behavior of flames in SCW.

The buoyant forces need to be thoroughly understood both in 1-g and 0-g for the efficient design of SCW systems. The complexities arising due to the presence and absence of buoyant and induced forces have to be evaluated for the application of SCWO in space research. The radial and axial temperature profiles depend on the thermal distribution, reactant mixing, oxidizer injection, chemical kinetics, diffusivities of the components and their transport properties. The current research on SCW flames in NASA includes impact of these parameters on flame ignition and stability, combustion in 1-g and 0-g modes, reaction chemistry and simulation models [16].

In collaboration with NASA, our research program at York University is focused on studying the ignition of hydrothermal flames along with their stability and propagation. The influence of inertial and buoyant forces on axial temperature distribution, reactant mixing with the oxidant and the thermal distribution of energy is under investigation.

CONCLUSIONS

Supercritical water oxidation in presence of flames has been found to be an effective way of noxious waste including space and terrestrial waste conversion. Thorough understanding of the flame characteristics both in ground level and zero gravity is essential for applying supercritical water oxidation in treating spacecraft-generated waste materials. The efficiency of hydrothermal flames mainly depends on the thermal distribution and reactant mixing both in ground level and zero gravity. Hydrothermal flames enhance the oxidation rates further decreasing the reaction times to milliseconds. Moreover, the harmful intermediates which are formed during incineration could be completely decomposed to simple gases in the presence of hydrothermal flames. Supercritical water oxidation studies reveal that the impacts of oxidant temperature and fuel concentration are crucial for the generation of flames.

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