Supercritical Water Oxidation (SCWO) Technology an Alternative to the Conventional Wastewater Treatment Plant

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Abstract *— Clean water is essential for human survival. One issue to be face is the impact of wastewater treatment on water sources. Is essential to bring alternative solution for the wastewater treatment. There are many technologies regarding wastewater treatment, but over the years, the day to day practice have shown that the technologies associated with this are complicated, expensive and are no strangers to facing issues. For example; operational efficiency, cost, sustainability and the possible waste, between others. One new technologies applied to the wastewater treatment is called Supercritical Water Oxidation (SCWO for its initials). SCWO is the destruction of wastewater is performed beyond the critical temperature (374.2 ℃) and critical pressure (22.1 MPa) of water. During SCWO the wastewater and the added oxidants become homogenous, so that the oxidative ability increases and the pollutants are oxidized quickly. In simple words, oxidation means burning. For that reason, upon this technology waste is burned in presence of oxygen. But the reaction is performed in a high-temperature, high-pressure reactor using supercritical water as a process fluid. SCWO is a powerful technology to treat hazardous wastewaters with many advantages. However, this has two main weaknesses as salt deposition and corrosion.*

Key Terms *— SCWO, Supercritical Water, Water Contamination, WWTP.*

INTRODUCTION

According to the World in Data organization developed by the Oxford Martin School, from 1750 to 1980 the world population increased 2.1%.

Figure 1 presents the annual population growth rate (red line) overlaid with the total world population (blue zone), for the 1750-2010 period and includes a projection up to 2100.

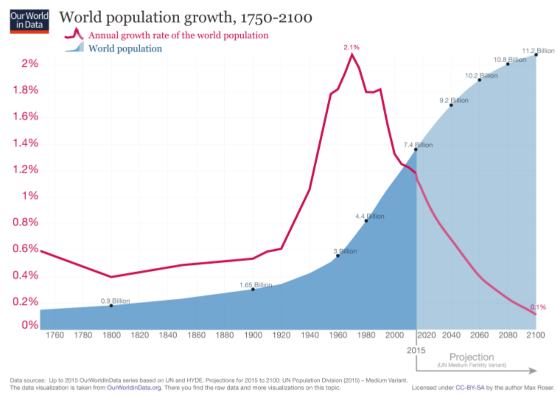

Figure 1
World Population Growth from 1760-2100

Over the years, population growth has impacted the sustainability of the world resources and direct impacted the environment, specially the water resources. Meaning by standability the balance between the society, economy an environment. In other words, what the society need, what can be afforded but without negatively impact the world.

Many studies have established a direct relationship between population growth and environment degradation because more individuals claim more resources and produce more waste. Evidently one of the challenges of a growing population is to develop and stablish new technology to overcome the environmental problems.

The water demand has grown significantly over the last years because of the households, agriculture activities, industrialization this as a direct impact of the population growth. For that reason, water resources management is the key to meet the growing population demands. As well, is essential to prevent and stop further degradation of water sources and put in place the necessary technologies to clean up polluted waters.

Supercritical Water Oxidation is an advance wastewater treatment and an alternative for the conventional wastewater treatment techniques. In order to understand this advance treatment is important to explain some chemistry.

SUPERCRITICAL FLUIDS

A substance has three phases; solid, liquid and gas. Depending on the temperature and pressure of the substance is the phase. As shown in figure 2, phase diagram of water, as the temperature increase (high temperatures) but the pressure remains relatively constant the water is in gas phase (steam). In the other hand, if the temperature remains relatively low and constant but the pressure increase the water is in solid phase (ice).

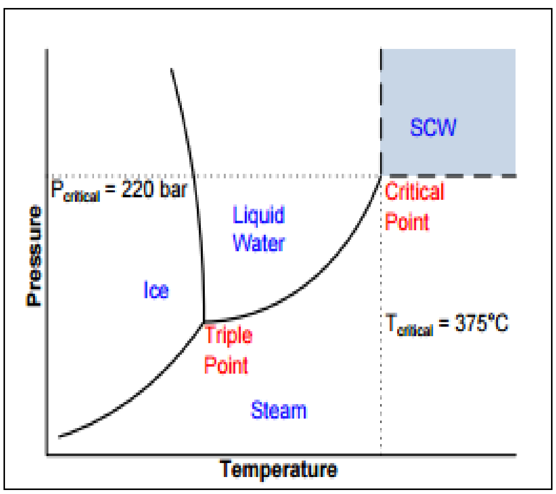

Figure 2
Phase Diagram of Water Showing Supercritical Water Conditions

Though, if the temperature and pressure increase, the water is in liquid phase (known as water). The triple point is the temperature and pressure at which the three (3) phases (solid-liquid-gas) of water coexist in thermodynamic equilibrium.

Nevertheless, as is shown in figure 2, there is a zone call the Critical Zone, mark in the graph as SCW which means Supercritical Water.

A supercritical fluid is a substance at which its temperature and pressure is above its critical point. The supercritical zone is characterized by the incapacity to distinguish whether the substance is a liquid or a gas. For instance, supercritical fluids (SCF) do not have a definite phase.

Supercritical Fluids are useful for science due to its characteristics [1]-[2]. For example, supercritical fluids:

- have the diffusion coefficient 10-100 times more than normal liquid fluid, which is beneficial to mass transfer and heat exchange.
- are compressible, slight change of temperature or pressure will cause great change of its density, and impacts its dissolving ability.
- can lead to reactions, which are difficult or even impossible to achieve in conventional solvents.
- have solvent power similar to light hydrocarbons for most of the solutes
- the fluids are commonly miscible with permanent gases (e.g. N_2 or H_2) and this leads to much higher concentrations of dissolved gases than can be achieved in conventional solvents.

As can be seen, supercritical fluids have properties between those of a gas and a liquid. Table 1 presents the critical properties for some components, which are commonly used as supercritical fluids.

Table 1
Critical Properties of Various Solvents [3]-[4]

Solvent	Molecular Weight (g/mol)	Critical Temperature (K)	Critical Pressure (atm)	Critical Density (g/cm^3)
Carbon Dioxide (CO_2)	44.01	304.1	72.8	0.469
Water (H_2O)	18.015	647.096	217.75	0.322

Table 1 (continue)
Critical Properties of Various Solvents [3]-[4]

Solvent	Molecular Weight (g/mol)	Critical Temperature (K)	Critical Pressure (atm)	Critical Density (g/cm^3)
Methane (CH_4)	16.04	190.4	45.4	0.162
Ethane (C_2H_6)	30.07	305.3	48.1	0.203
Propane (C_3H_8)	44.09	369.8	41.9	0.217
Ethylene (C_2H_4)	28.05	282.4	49.7	0.215
Propylene (C_3H_6)	42.08	364.9	45.4	0.232
Methanol (CH_3OH)	32.04	512.6	79.8	0.272
Ethanol (C_2H_5OH)	46.07	513.9	60.6	0.276
Acentone (C_3H_6O)	58.08	508.1	46.4	0.278
Nitrous Oxide (N_2O)	44.013	306.57	72.5	0.452

These unique characteristics of the supercritical fluids has aroused scientific interest to apply it into wastewater treatment technology.

SCWO

Supercritical water has been investigated as a means of destroying toxic wastes, and as an unusual synthesis medium. Under standard temperature and pressure (STP), water is a polar solvent that can dissolve electrolyte (e.g. salts) but hardly can dissolve gases and organics as well at STP water density slightly changes with pressure. On the supercritical conditions, the physical proprieties of water change. Density is less than that of the liquid; viscosity is the same as the gas, diffusivity is between the liquid and the gas.

Nevertheless, at supercritical state (Supercritical Water) small change of temperature will cause a big decrease of density. At the critical point the density of water is 0.322 g/cm^3, this means that supercritical water is a good solvent for non-polar organic molecules, due to its low viscosity and relative permittivity (dielectric constant) and deprived hydrogen bonding.

In essence, supercritical water has high dissolve ability for non-polar organics, while significantly low for inorganic matter, causing precipitation of inorganic substance. With this characteristic supercritical water is completely miscible with gases (e.g. carbon dioxide, air, nitrogen) [5].

For that, supercritical water will oxidize the pollutants in the water because SFW is a good solvent for organics and oxygen. In other word, during this process when water hydrogen bonds are broken, water molecules can dissolve chemicals that were previously insoluble. When oxygen is present, the organic component of biomass undergoes an exothermic oxidation reaction in SCW which converts the biomass into carbon dioxide vapor and releases heat [6]. This is called supercritical water oxidation (SCWO).

Simplifying the process the wastewater and an oxidant enter a reactor at supercritical conditions and the total organic compounds (TOC) are dissolved. The output area carbon dioxide, water and other, depending upon the reactor conditions and process efficiency. See figure 3 for more details.

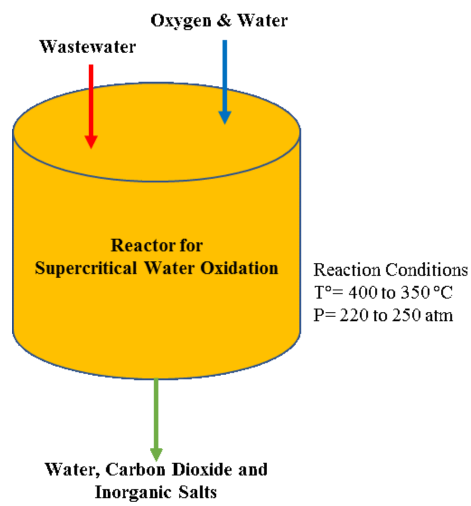

Figure 3
SCWO Reactor Inputs / Outputs

According to some studies with the proper temperature, pressure and reactor residence time almost any pollutant can be completely destroyed by SCWO with residence time less than 1 minute [7].

ADVANTAGES OF SCWO

Table 2 Shows come disadvantage of non-conventional wastewater treatment technologies in comparison to the SCWO.

Table 2
Wastewater Treatment Technologies Comparison

Non-Conventional Wastewater Treatment Technologies	Disadvantage compare to SCWO
wet oxidation	problems of incomplete oxidation due to insufficient oxygen dissolved in water and VOC-containing emitted exhaust
incineration method	pre-treatment of compressed dehydration consumes much energy and the high temperature reaction tends to form NOx

According to many studies, some advantages of the SCWO are the following:

- Complete conversion of toxic compounds - Water, organic compounds, oxygen or oxidants become homogeneous in one single phase, avoiding two-phase reaction.
- The oxidation speed of organic compounds is fast and reaction time is short, facilitating adiabatic operation and total recycle off waste heat.
- Oxidation of organic compounds is complete, eliminating the need for secondary treatment of exhaust.
- Negligible NO_x and SO_2 production.
- Under supercritical conditions, sewage sludge will combust, releasing energy as heat.
- Process stability and Control.
- Contained process.

The supercritical water oxidation process, requires a big quantity of energy, but this can be recover during the steam production process as show in figure 4. For that reason, the economic inversion can be returned.

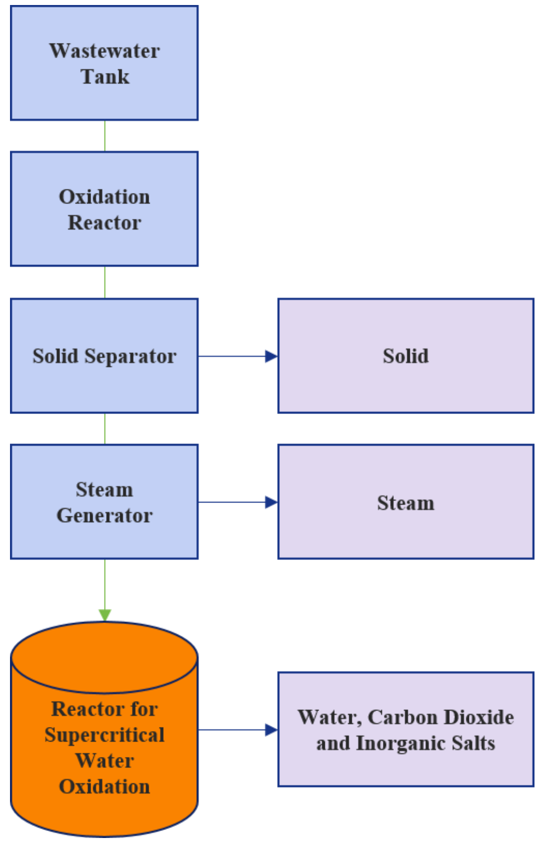

Figure 4
Typical Process of the Supercritical Water Oxidation

DISADVANTAGE OF SCWO TECHNOLOGY

SCWO has two major limitations corrosion and salt deposits [7]. Yet, this technology provides a powerful alternative to treat hazardous and toxic organic wastes without the concomitant production of noxious byproduct, as might be experienced with combustion based technologies.

Moreover, substances that contains no carbon (inorganic substances) are not soluble in supercritical water and tend to form precipitates, see figure 5 for a visual representation. Some effluents Substances as halogens (e.g. Fluorine, chlorine, bromine, iodine and astatine) and sulfur will form strong acids, which are very corrosive. In the other hand, studies have shown that there are ways to treat those waste; by removing halogens and dissolved salts; and/or by design a SCWO Reactor that can handle the halogens.

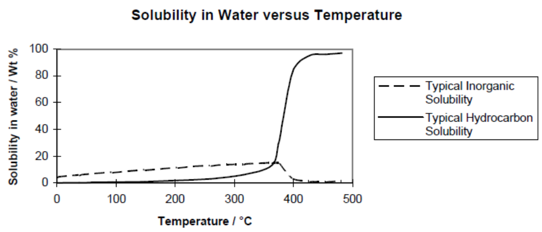

Figure 5
Solubility in Water versus Temperature a Case Study [7]

Consequently, a wastewater treatment plant using the SCWO technology will need to use a strong corrosion resistant materials which will make more expensive the Plant. Additionally, the usage of high pressures and temperatures will require some safety precaution equipment's (e.g. rupture disk), impacting the cost of the Plant.

LOOKING TO THE FUTURE [8]-[9]

The Department of Civil and Environmental Engineering in Duke University in North Carolina, USA has been researching about a prototype to treat fecal sludge using the Supercritical Water Oxidation Reactor. In their research, they study the feces and urine chemical composition to stablish the conversion efficiency and factors. The table 3 below present the composition of feces and urine and the conversion of feces input to energy output.

Table 3
Chemical Composition of Feces and Urine

Feces Composition (For 70-520 g/day) with 80% moisture	
Fats	5-25%
Carbohydrates	10-30%
Nitrogen Materials	2-3%
Minerals	5-8%
Bacteria and Bacteria Debris	10-30%
Conversion to Energy	1.6 MJ per day

Urine Composition (0.6-1.1 L/day)	
Organic Salts	38%
Urea	36%
Organic Compounds	13%
Ammonium Salts	13%
Conversions Energy	440 Wh/day

Duke University constructed an *Omni Processor for Fecal Waste*, a sanitation for the urban poor prototype, using the SCWO technology. Their prototype will treat the waste 1200 people that will can be converted to 450 to 530 kWh/day. The figure 6 show their prototype.

Figure 6
Supercritical Sanitation System Prototype

This study successfully demonstrated that the supercritical water oxidizes the organics in seconds resulting in heat creation and CO_2. During this process, they use air as an oxidant ant place a heat and energy recovery, to make a sustainable system. A process flow diagram is show in the following figure 7 and the typical run of this process will look like the following figure 8.

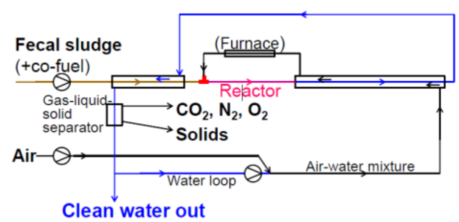

Figure 7
Process Flow Diagram of Duke University Prototype

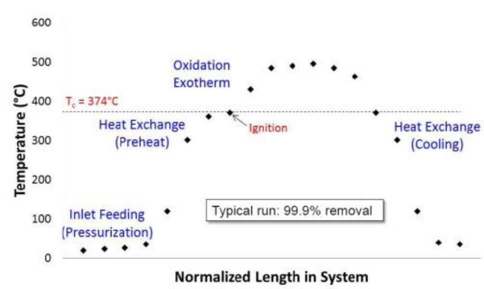

Figure 8
Typical Run of the Prototype

This study show the potential of SCWO in wastewater treatment. Their study validates a removal of 99.97% can be achieved, this means that this process produces clean water without odor, Sox or NOx, a common issue for conventional wastewater treatment technologies. Besides, SCWO achieves both waste treatment and pathogen control fast. In the other hand this study mentioned that many challenges remain, including slurry pumping, long term operation (plugging and corrosion) and process economy.

CONCLUSION

Last decades the population exploitation of natural resources including the water has increase dramatically. For that reason, is crucial to search for advance water treatment technologies that can be cost-effective. Likewise, treatment of toxic and dangerous wastes has become a trending topic for environmental protection.

This paper has compile a literature background that present the process SCW as the reaction medium, and an oxidant such as air, O_2 or NO_3. Put towards high temperature and pressure. Organic waste and metals are oxidized to inert species. Oxidized to CO_2 and water along with a release of energy. Some researchers agree that this process is rapid and a complete reaction, has a total conversion of organics to CO_2, water and N_2 and halogens converted to the corresponding mineral acids. Moreover, without harmful by-products. As well this reaction is considered without exhaust gas cleaning requirements, is a continuous operation and enclosed process.

For those facts, supercritical water oxidation is an alternative to treat wastewaters. This advance technology combine pressure and temperature like reaction activator. In other words, the pressure moves the reaction equilibriums between the phases, allowing an intimate contact between organic matter and oxidant, while the temperature increases the kinetics of the reactions.

According to many studies and references listed on this project all subject matter experts agrees that the supercritical water oxidation technology provides a powerful alternative to treat hazardous and toxic organic wastes in an efficient and effective way. However, given the process parameters necessary to achieved the supercritical water (high temperatures and pressures), this technology present some concerns in the process cost necessary to operate a wastewater treatment plan with this technology.

I think that this technology is a good option of private companies as pharmaceuticals and other industries that have private wastewater treatment plant with high quantities of organic compounds. Besides, these industries could make good use of the steam and other products generated by this technology.

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