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Supercritical Water Gasification of Municipal Sludge: A Novel Approach to Waste Treatment and Energy Recovery

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1. Introduction

Municipal sewage sludge is often heavily moisture-laden, containing moisture well in excess of 95 w/w% (Fytili & Zabaniotou, 2008; Harrison et al., 2006; Hong et al., 2009). Annual U.S. sludge volume is estimated to be between 500 million and 1.5 billion wet tons, resulting in the need to remove between 130 and 400 billion gallons of water from it for treatment and disposal. This dewatering process expends 80% of the total electricity used by a wastewater treatment facility (Bernardi et al., 2010; Demirbas, 2011b; Fytili & Zabaniotou, 2008; USEPA, 2009), representing an average of 150 billion KWh of electricity each year, at an approximate cost of $6 billion, or ~4% of the total annual U.S. electricity use (CSS, 2011; Kim & Parker, 2008).

Nascent technologies that use the entrained water of the sludge itself have been studied and developed in order to overcome the expense and complexity of dewatering municipal sludges (Savage, 2009). Water, when raised simultaneously to very high temperatures and pressures, becomes one of the most promising solvation media for rapid gasification and complete destruction of aqueous, organic wastes. As temperature and pressure increase, water approaches what is known as the "critical point" (≥374.2°C and 22.1 MPa), above which water becomes "supercritical". This chapter discusses recent developments of using water and elevating its temperature and pressure to near and above supercritical conditions (Figure 1) for the treatment and disposal of municipal sewage sludge.

Supercritical water's unique abilities to quickly dissolve and gasify organic compounds in sludge without dewatering are presented (Kalinci et al., 2009). Furthermore, adding catalysts or oxidants to supercritical water can intensify the reaction, substantially reducing operating costs by creating self-sustaining conditions that can lead to energy recovery and

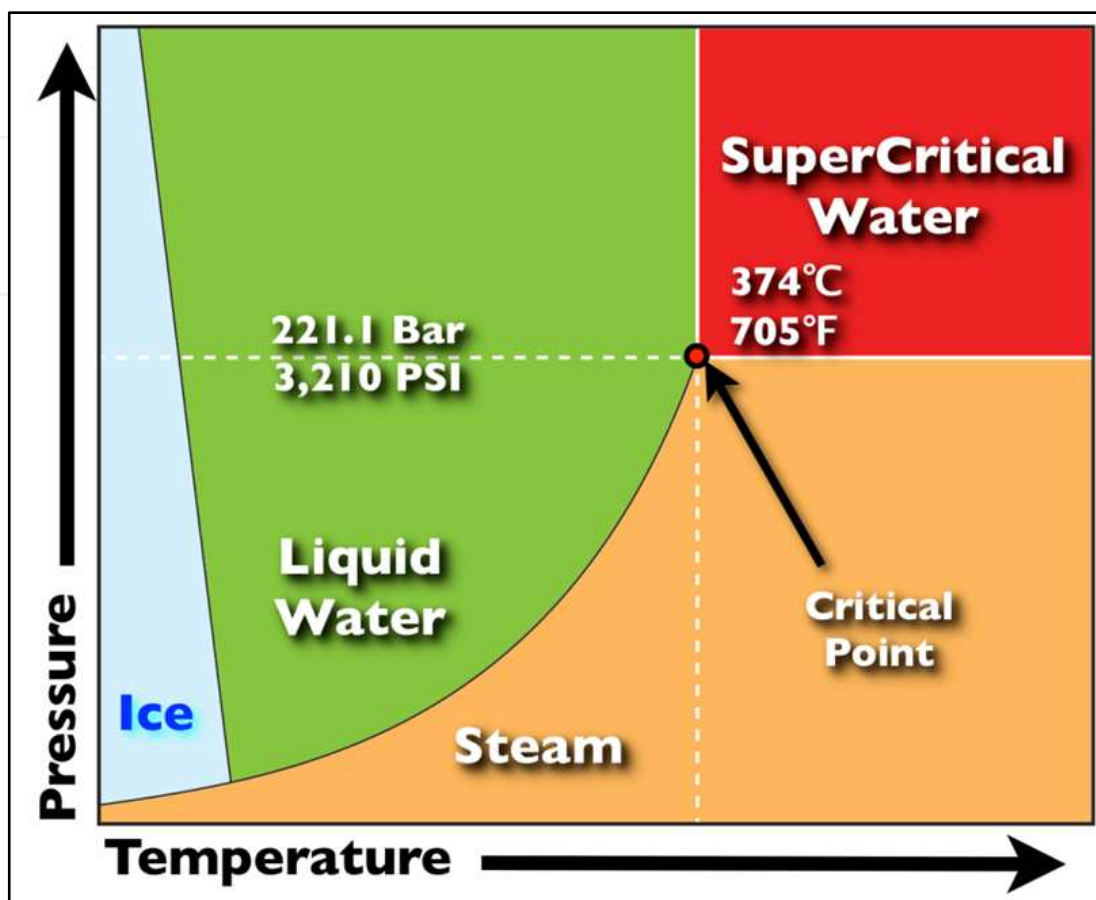short residence times, as compared to more conventional sludge disposal methods, including incineration.

Figure 1. Phases of Water.

The chapter reviews supercritical-water research that addresses various sludge destruction advantages as well as known challenges. The review highlights forays and attempts at commercialization of supercritical water systems for wet-waste destruction and discusses the nascent industrial aspects of the technology and the challenges of creating a commercially viable plant.

1.1. Wastewater sludge

Sewer systems in the U.S. transport over 14.6 trillion gallons of municipal wastewater to ~17 thousand public wastewater facilities each year (CSS, 2011; Fytili & Zabaniotou, 2008). The facilities are designed to collect, remediate, and dispose of human and commercial wastes within an established regulatory framework (Chun et al., 2011; Demirbas, 2011b; Fytili & Zabaniotou, 2008; Svanström et al., 2004; USEPA, 2009). Sewage that enters wastewater treatment facilities gets processed and separated into two products. One is clean water, which is the primary objective of municipal facilities. The other is the leftover waste, generically known as sewage sludge (Abelleira et al., 2011).

Sludge is the most ubiquitous wet waste generated by humans (Abelleira et al., 2011). The U.S. Environmental Protection Agency (EPA) last estimated U.S. sewage-sludge production in 1998 at 6.9 million dry tons (USEPA, 1999b). Unconfirmed estimates dating back as far as 1982, however, put total U.S. sewage sludge volume much higher at nearly 20 million dry tons with an additional comparable amount of other industrial sludges (Gloyna & Li, 1993; Svanström et al., 2004).

All sewage sludge from modern wastewater treatment plants is potentially harmful to human health by design and is designated as a pollutant by the Clean Water Act (Harrison et al., 2006; Mathney, 2011; NASNRC, 1996, 2002; USEPA, 2009). When sewage undergoes treatment, the solids, along with a myriad of entrained hazardous and harmful pollutants and pathogens, are removed from the water and concentrated into sludge (Bernardi et al., 2010; Hong et al., 2009; Snyder, 2005; USEPA, 1999a, 2009). Consequently, the physical properties and chemical constituents of sludges vary widely, depending on the source and treatment of the sewage. Generally, however, sewage sludge is treated as a homogenous, non-standardized slurry of materials, consisting mainly of human metabolic and food wastes as well as varying amounts of industrial, agricultural, and medical wastes (Harrison et al., 2006; Hong et al., 2009).

1.1.1. Sewage sludge composition & regulatory framework

All sewage sludge produced in the U.S. contains varying concentrations of three types of harmful pollutants: 1) heavy metals, 2) hazardous organic compounds, and 3) pathogenic microorganisms. Safely managing these hazardous compounds and pollutants has proven challenging (NASNRC, 2002; USEPA, 2009).

1.1.1.1. Heavy metals

Heavy metals ubiquitously entrained in sludge pose serious and well-documented public health and environmental risks (Babel & del Mundo Dacera, 2006; Bag et al., 1999; Beauchesne et al., 2007; Dimitriou et al., 2006; Fjällborg et al., 2005; Fytianos et al., 1998; Goyal et al., 2003; Hooda, 2003; Kidd et al., 2007; McBride, 2003; Pathak et al., 2009; Reddy et al., 1985; Sánchez-Martín et al., 2007; USEPA, 2009). The EPA, however, limits sludge regulations to only ten (i.e., arsenic, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc) of the high-risk, hazardous, bioaccumulating, and leaching metals (Babel & del Mundo Dacera, 2006; Dean & Suess, 1985; Harrison et al., 1999; McBride, 2003; Pathak et al., 2009; Sánchez-Martín et al., 2007; USEPA, 2002b, 2009). Reviews detailing heavy metal prevalence in sludge and related health concerns can be found elsewhere (Babel & del Mundo Dacera, 2006; Bag et al., 1999; Harrison et al., 1999; McBride, 2003; Pathak et al., 2009; Sánchez-Martín et al., 2007; Snyder, 2005).

1.1.1.2. Hazardous organic compounds

Hazardous organic compounds commonly found in sewage sludge matrices are many and varied, including endocrine disrupters, pharmaceuticals, polybrominated fire retardants,

polychlorinated biphenyls, carcinogens, pesticides, household chemicals, solvents, and dioxins (Costello & Read, 1994; Gómez et al., 2007; Hale et al., 2001; McBride, 2003; NASNRC, 2002; Qi et al., 2010; Rulkens, 2008; Santos et al., 2010; Sipma et al., 2010; Snyder, 2005; Stasinakis et al., 2008; Zorita et al., 2009). Hazardous pollutants are ubiquitous in sewage sludge. The EPA studied sewage sludges from wastewater facilities across the U.S. and found large amounts of hazardous materials in all of the sludges (USEPA, 2009). Many organic compounds in sludge do not break down quickly in the environment and are often highly mobile, resulting in widespread harmful, organic-compound distribution (Guo et al., 2009; Kulkarni et al., 2008; Leiva et al., 2010; Rulkens, 2008). Consequently, human exposure to some harmful organic compounds from sewage sludge (e.g., dioxins) is considered pervasive and chronic (Kulkarni et al., 2008). Only about 110 organic chemicals (of fewer than 130 total chemicals) are on EPA's antiquated priority pollutant list, and there is no regulatory requirement to monitor any of those in sewage sludge (Clarke & Smith, 2011; Deblonde et al., 2011; Eriksson et al., 2008; Harrison et al., 2006; Hospido et al., 2010; Petrovic' et al., 2003; Verlicchi et al., 2010).

The proliferation of new pollutants in sewage sludge is also a growing concern. The number of organic chemicals is increasing rapidly, now well in excess of 100 thousand. Very few of the pollutants noted to be commonly present in sludge, including low-grade, radioactive residues in medical wastes, have been studied in detail either in terms of prevalence or harmful effects (Eriksson et al., 2008; Fytili & Zabaniotou, 2008). Even though their effects on environment and human health are largely unknown, these "emerging pollutants" fall outside EPA regulatory status (Deblonde et al., 2011; NASNRC, 2002; Tsai et al., 2009). Furthermore, there have been no major updates to the EPA's priority pollutant list in almost three decades (Harrison et al., 2006; Mathney, 2011; Snyder, 2005).

1.1.1.3. Pathogens

Pathogen loads in sewage sludge are almost universally high and pose a communicable disease hazard (NASNRC, 2002; Reilly, 2001; USEPA, 2009). The pathogens are a result of normal, human metabolic wastes as well as additional loading from medical effluents (Arthurson, 2008; Deblonde et al., 2011; Lewis et al., 2002; Mathney, 2011; Reilly, 2001; Straub et al., 1993; USEPA, 2009; Verlicchi et al., 2010). There are fewer than two dozen pathogens (e.g., fecal coliforms, Salmonella, enteric viruses, and parasites) monitored in sewage sludge (Mathney, 2011; NASNRC, 2002; Reilly, 2001; Snyder, 2005; USEPA, 2000, 2002b, 2003), and many dangerous pathogens (e.g., prions) are neither affected by sewage treatment nor detected by standard analytical methods (Gale & Stanield, 2001; NASNRC, 2002; Peterson et al., 2008b; Saunders et al., 2008; Smith et al., 2011; Snyder, 2005).

Despite considerable controversy surrounding potential sludge hazards, there has been disturbingly little critical inquiry into the environmental effects and human health risks of traditional sludge disposal methods (Deblonde et al., 2011; Mathney, 2011; Nature, 2008; Tollefson, 2008). Nonetheless, some EPA goals (albeit with no specified implementation horizon) indicate that very high destruction requirements (up to 99.9999%) may become standard for some compounds, along with totally enclosed treatment facilities (Lavric et al.,

2005; Veriansyah & Kim, 2007). If such regulatory standards are ever implemented, the feasibility and suitability of conventional sludge disposal techniques will be subject to increased scrutiny (Demirbas, 2011b; Veriansyah & Kim, 2007).

1.2. Sludge processing & disposal

Despite improvements in wastewater cleaning technology and expansion of centralized wastewater services to meet the needs of most of the U.S. population, sludge disposal has historically been, and continues to be, the weak link in the wastewater treatment process (Demirbas et al., 2011; Fytili & Zabaniotou, 2008; Harrison et al., 2006; NASNRC, 1996, 2002). Ocean dumping was a preferred sludge disposal method for the last couple of centuries (Chun et al., 2011; Snyder, 2005), but it was banned in the 1990s by both U.S. and international law due to the high level of harmful pollutants in the sludge and the adverse effect on marine organisms (Abbas et al., 1996; Costello & Read, 1994; Harrison et al., 2006; Snyder, 2005). The loss of ocean-dumping drove most municipalities to embrace either agricultural land application or thermal destruction (viz., incineration) as their primary sludge-disposal routes, with a small percentage using landfilling or composting (Lavric et al., 2006). Current sludge disposal methods, and associated regulations, are outgrowths of the need for municipalities to find a viable solution for treating or disposing large amounts of concentrated harmful pollutants resulting from wastewater treatment. Disposal choice is influenced by economics, public policy, and regional environmental conditions (Cappon, 1991; Rulkens, 2008).

1.2.1. Land application

Agricultural land application is the most commonly used and most controversial of the sludge disposal methods, but has gained favor due to the simple-bottom-line cost. Potential hazards of applying sludge to croplands were noted early on in the adoption of land-application practices. Using material laden with harmful organic compounds in food and forage cultivation makes land application problematic both in terms of operational costs and, more importantly, public health concerns (Borán et al., 2010; CSS, 2011; Demirbas et al., 2011; Eriksson et al., 2008; Fytili & Zabaniotou, 2008; Harrison et al., 2006; NASNRC, 1996, 2002). Specifically, potential food-crop contaminant uptake and subsequent human-food-chain contamination are legitimate concerns (Cappon, 1991). Despite the well-documented, undesirable properties of sewage sludges for agricultural purposes, most communities continue to favor sludge land application over other disposal methods (Beauchesne et al., 2007; Beck et al., 1995; McBride, 2003). The proponents of sludge land application argue that harmful-organic-compound behavior in soils from sludge application is reasonably well understood and that there will be negligible detrimental health and environmental impacts (McBride, 2003).

1.2.2. Thermal destruction

Thermal destruction (i.e., incineration) offers a year-round, all-weather sludge disposal option, albeit an energy-intensive and thus increasingly expensive option. Many large cities

in the colder northern climates use incineration, with more than 200 sewage-sludge incinerators (fluidized-bed and multiple hearth configurations) in use nationwide (Sloan et al., 2008). High water content (along with associated high enthalpy demand) poses the main thermodynamic impediment to cost-effective thermal sludge destruction. During the destruction process, all of the energy released from the sludge, and essentially all of the incinerator fuel, is consumed to boil off water (Demirbas, 2011b; Dijkema et al., 2000; Fytili & Zabaniotou, 2008). Furthermore, sludge must initially be dewatered to a "sludge cake" consistency with moisture content below 85% prior to feeding into the incinerator. Once in the incinerator, the sludge cake must be further dewatered thermally to ~35 w/w% moisture before the material itself can actually begin to thermally combust (Abuadala et al., 2010). Dewatering is expensive, and as energy costs continue to rise, drying processes are becoming increasingly prohibitive (Weismantel, 2001).

Dry pyrolysis and gasification face similar thermoeconomic efficiency limitations to incineration, in that high-moisture levels in sludge cause ignition and combustion problems (Demirbas et al., 2011; Dogru et al., 2002). Specifically, traditional gasification technologies encounter operational air:fuel ratio and gas:ventilation mobility problems when the feedstocks exceed 30% moisture content, and sewage-sludge moisture content generally needs to start at less than 15% to serve as a proper feedstock for gasifiers (Dogru et al., 2002). Plus, fuels produced require significant additional cleaning due to the presence of heavy metals and incomplete destruction of harmful organic compounds (Dogru et al., 2002). Indeed, traditional thermal technologies do destroy hazardous organic compounds, but only up to a point. Incineration-derived slag, for example, still contains all of the heavy metals, up to 30% of the original hazardous organic compounds, and additional secondary combustion compounds (Dogru et al., 2002; Fytili & Zabaniotou, 2008). Most contemporary thermal options are prohibitively costly due to high capital investment and increasingly stringent, air-quality permitting and compliance standards (Chun et al., 2011; Fytili & Zabaniotou, 2008). Thermal destruction also meets with considerable, unfavorable public opinion due to the air-borne release of metal emissions and harmful gases (Abbas et al., 1996; Adegoroye et al., 2004; Lavric et al., 2006). Intense public protests of new permits alone have derailed some incinerator permitting efforts (Sloan et al., 2008; Weismantel, 1996).

1.2.3. Landfill disposal

Landfilling (i.e., burial) of sludge is used as a disposal method by many municipalities, often in an effort to avoid expensive regulatory incineration restrictions and to sidestep the greater scrutiny of land application. Nonetheless, landfilling also has a host of problems, including decreased landfill life, increased landfill odor, and increased landfill leachate volume and toxicity. Leachate is a ubiquitous product of landfills, wherein excess water percolates through landfill waste layers, freeing organic compounds from the waste and carrying them away concentrated in leachate. The high water content of sewage sludge is known to escalate leachate volume from landfills (Demirbas et al., 2011). Furthermore, the degradation and conversion of organic compounds in landfilled sludge is usually

incomplete (Ejlertsson et al., 2003), and metabolites can be generated that are even more hazardous than their parent compounds, with the secondary organic pollutants also collecting in the leachate (Oleszczuk, 2008). The composition of leachate is complex, environmentally reactive (with very high COD values: above 60K mg/L), and difficult to treat via conventional methods (Wang et al., 2011). Landfill leachate is a noted health and environmental threat, and harmful compounds in sewage sludge exacerbate the problem (Demirbas et al., 2011). A rise in tipping fees, decreased availability of economic landfill sites, and a move toward sustainable solutions has begun to sour municipal fondness for landfilling (Abbas et al., 1996).

1.2.4. Composting

Non-industrial composting of agricultural wastes dates back thousands of years to ancient Rome, Greece, and Israel for agricultural recycling, and has now gained some recent traction as a recycling method for modern organic wastes including sewage sludge (Epstein, 1997; Gajalakshmi & Abbasi, 2008; Hubbe et al., 2010; Kumar, 2011). Industrial composting processes are used to convert sewage sludge into "marketable fertilizer" products and ostensibly reduce sludge volume and organic pollutants (Oleszczuk, 2008). Nonetheless, under U.S. Department of Agriculture (USDA) branding regulations, sludge-derived compost cannot legally be labeled as "Certified Organic", limiting its market potential (USDA, 2011).

There are many composting methods. The simpler composting approaches of mixing sludge with other organic wastes and letting them react with microorganisms are relatively low-tech, inexpensive, slow, odorous, and invariably require large footprints and relatively dry and warm weather conditions for outdoor operations (USEPA, 2002a). More complex approaches often use thermally accelerated, composting processes, commonly known as in-vessel, thermal drying, which produce agricultural "pellets" from sewage sludge at faster processing times in a reduced footprint (Gajalakshmi & Abbasi, 2008; Hubbe et al., 2010; Kumar, 2011; Turovskiy & Mathai, 2005; USEPA, 2002a). A number of municipalities use in-vessel, thermal drying, but the high-temperature, pelletizing process generates secondary, hazardous organic metabolites similar to landfilling, but at a much accelerated rate (Farrell & Jones, 2009; Fytili & Zabaniotou, 2008; Kumar, 2011; Oleszczuk, 2008). High-temperature, in-vessel composting increases mobility and bioavailability of the metabolites, which by extension can significantly contaminate and toxify soil faster (Oleszczuk, 2008). Pellet production costs often exceed $400 per dry ton (and can approach $1,000 per dry ton), but many communities end up landfilling all or part of their pellets due to limited market demand (Sloan et al., 2008). Several reviews have evaluated the advantages and disadvantages of different composting technologies (Farrell & Jones, 2009; Gajalakshmi & Abbasi, 2008; Hubbe et al., 2010; Kumar, 2011; Phillips, 1998; USEPA, 2002a).

1.2.5. Carbonization

Carbonization of the sludge into a solid, fuel-like product is a competing energy recovery option that can be performed for considerably lower cost than compost-pellet production

due to elimination of the nuanced need to maintain a marketable fertilizer product. There are a number of competing carbonization conversion processes seeking commercialization that rely on drying and various woody-biomass or coal combinations (Chen et al., 2011; Roy et al., 2011). Some seek stand-alone fuel status, while others function on the expectation of using carbonized sludge as a co-firing fuel supplement with coal at concentrations less than 5 w/w% (Abbas et al., 1996; Roy et al., 2011; Rulkens, 2008). Reviews of sludge-derived, carbonized, solid fuels can be found elsewhere (Maier et al., 2011; Roy et al., 2011).

1.2.6. Regulatory & institutional framework

Municipalities' sludge-disposal difficulties, accompanied by the vexing problems of harmful compound removal, have not been lost on EPA regulators. Historically, regulation has been leniently "tailored" to municipal sludge-disposal needs, only regulating ten metals (i.e., As, Cd, Cr, Cu, Pb, Hg, Mo, Ni, Se, and Zn) and zero organic chemicals (Harrison et al., 1999, 2006; Mathney, 2011; McBride, 2003; Snyder, 2005). Indeed, metal toxin levels legally allowed in sewage sludge applied to croplands or included in sludge compost are several times higher in some cases than levels allowed at superfund sites (Harrison et al., 2006). The EPA has even opted to forgo extending sludge regulations to dioxins (at any level) or any other organic pollutant in sludge (Harrison et al., 2006). Many scientists and other federal agencies point out that EPA assessments for metals, hazardous organic compounds, and pathogens may significantly underestimate risks (Harrison et al., 2006; Mathney, 2011; McBride, 2003; NASNRC, 2002; Nature, 2008; Oleszczuk, 2008; Snyder, 2005; Tollefson, 2008; USDA, 2011). The National Academies of Science, a U.S. District Court, numerous scientists, and the EPA's own Inspector General have openly cast doubt on the quality, objectivity, and integrity of the research upon which the EPA has relied for sludge-disposal policy formulation (Alaimo, 2008; Dominy, 2009; Tollefson, 2008; USEPA, 1999b, 2000, 2002b). No labeling or disclosure is required for compost made from sewage sludge, and very few consumers are aware of the hazards posed by the products (Harrison et al., 2006; USEPA, 2000, 2002b).

Numerous researchers and institutions have noted that in order to fully evaluate sludge safety and risks, it is necessary to go well beyond the EPA's minimalist, chemical analyses and actually combine those with genuine ecotoxicological criteria (Abbas et al., 1996; Chun et al., 2011; Leiva et al., 2010; McBride, 2003; NASNRC, 1996, 2002; Nature, 2008; Oleszczuk, 2008; Snyder, 2005; Tollefson, 2008). There is even growing concern that in the very near future, traditional management options will be unable to handle the increasing sludge quantities (Bernardi et al., 2010). Furthermore, externalized environmental and health costs are beginning to marginalize existing and well-established, sludge disposal methods. In terms of public health risk, the National Academies of Science's National Research Council has expressed concern about the use of sludge-based materials (NASNRC, 1996, 2002). This concern was echoed in a lead editorial in the journal Nature:

> In what can only be called an institutional failure spanning more than three decades … there has been no systematic monitoring program to test what is in the sludge. Nor has

there been much analysis of the potential health effects among local residents — even though anecdotal evidence suggests ample cause for concern (Nature, 2008).

As a result, new processing technologies capable of destroying all organic compounds, including hazardous, pathogenic, and recalcitrant organic compounds, at levels in excess of 99.99%, is of paramount importance for protecting environmental and human health.

2. Hydrothermal decomposition & conversion

Chemical compounds in sludge can be converted by several methods into various forms of energy and energy carriers (Rönnlund et al., 2011). Thermal decomposition methods have been developed over the last two decades into aqueous analogs, namely supercritical water gasification (SCWG), catalytic supercritical water gasification (CSCWG), and supercritical water oxidation (SCWO) (Catallo & Comeaux, 2008; Kruse, 2009; Toor et al., 2011; Veriansyah & Kim, 2007). These hydrothermal decomposition methods use supercritical (≥374.2°C and 22.1 MPa) or near-supercritical states as the destruction medium for sludge. Many of these techniques have been repeatedly demonstrated in laboratory experiments to thoroughly destroy wet wastes such as sewage and oily sludges with efficiencies exceeding 99% (Cao et al., 2011). This high level of destruction is possible due to supercritical water's unique properties that change from standard phases, to allow for solvation of organic substances, diffusivity into solid materials and modified reactivity, leading to the degradation of organic substances into carbon dioxide, carbon monoxide, water, and thermal energy in a single reactor system (Byrd et al., 2008; Savage, 2009; Weiss-Hortala et al., 2010).

Particularly relevant to the destruction of sludge wastes is that water, under supercritical conditions, changes from a polar solvent to a non-polar solvent as the transition between subcritical and supercritical occurs (Byrd et al., 2008; Sato et al., 2003; Savage, 2009). Consequently, hydrocarbons and organics become highly miscible in water above supercritical conditions (Byrd et al., 2008). Due to the increased temperatures and pressures of these systems, the dissolved organics begin thermochemical decomposition above the critical points (Figure 2).

Supercritical water behaves like a "non-ideal" gas, wherein solute molecules in contact with the fluid will interact and react at a faster rate than would be the case with either true liquids or gases (Hyde et al., 2001). Vapor pressure of solutes, based on polarity, will increase for organic molecules and decrease for inorganic compounds, resulting in solvation enhancement for sludge-entrained organics (Sato et al., 2003; Savage, 2009). Local density enhancements resulting from electrostatic and van der Waal effects also have a role in solubility (Brennecke & Chateauneuf, 1999; Marrone et al., 2004). Localized densities surrounding solute increase well above densities throughout most of the fluid due to eddy effects, aggregation, and nucleation around solute molecules (Hyde et al., 2001). Extensive reviews of supercritical water properties can be found elsewhere (Brunner, 2009a; Dinjus & Kruse, 2007; Hauthal, 2001; Hyde et al., 2001; Kruse, 2008; Kruse & Dinjus, 2007a, 2007b;

Loppinet-Serani et al., 2010; Machida et al., 2011; Noyori, 1999). The most important advantage of supercritical-water, hydrothermal destruction systems is that aqueous sludges do not require any pre-treatment or drying steps in order for the thermochemical conversion process to occur, resulting in efficient material transfer and economically beneficial characteristics (Duan & Savage, 2011), which can be further enhanced by modifying the system for production of H_2, the addition of catalysts, or energy recovery.
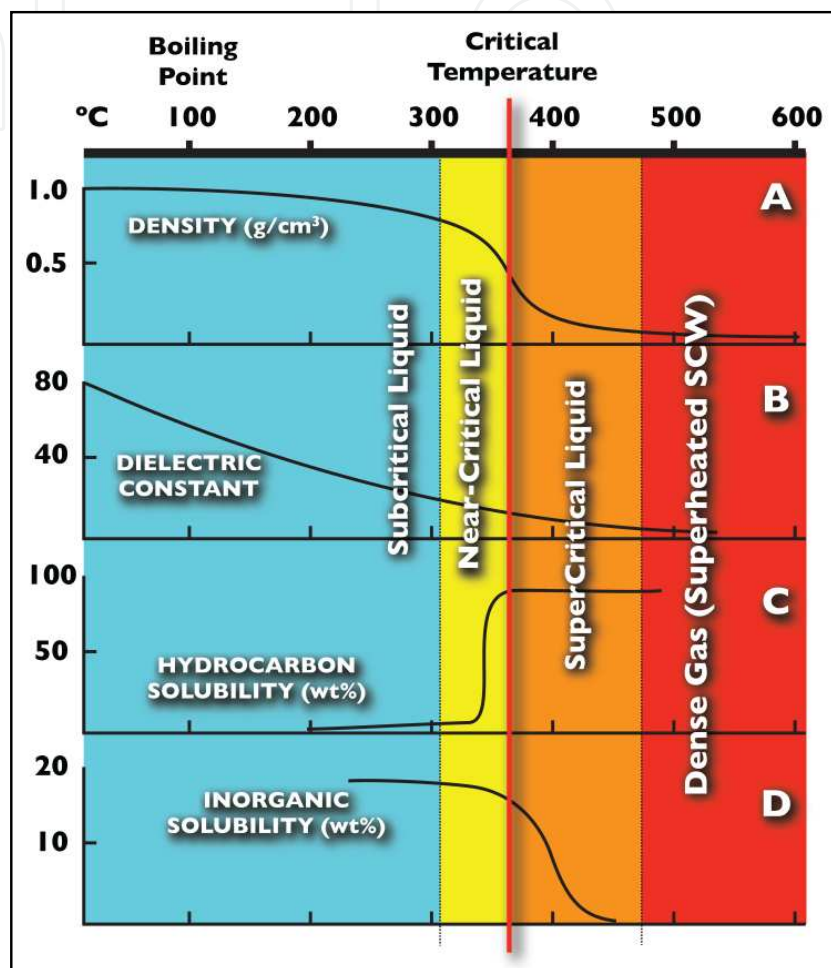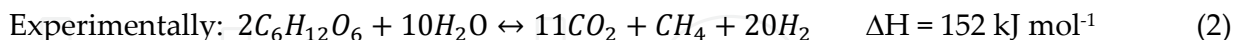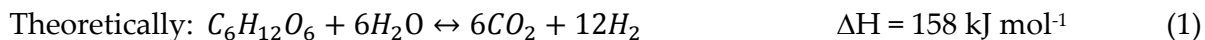

Figure 2. Properties of Water in Subcritical, Near-Critical, and Supercritical Conditions, Adapted from (Zhang et al., 2010).

2.1. Supercritical Water Gasification

Supercritical water gasification (SCWG) technologies have been developed into solutions to wet-waste, wet-biomass, and aqueous-sludge destruction (Savage, 2009). The primary objective of SCWG, however, is similar to conventional thermal gasification, in that SCWG is typically used for the production of fuel or chemicals, with waste stream elimination only a secondary consideration. Nonetheless, the various properties of supercritical water enable supercritical-water gasification to quickly destroy wet biomass and organic aqueous wastes while efficiently producing H_2 and C1 rich gases. Supercritical water gasification product-composition studies using actual sludge are limited and expected supercritical product

yields are variable (Afif et al., 2011; Cao et al., 2011). The assumed, basic expected, reaction kinetics (using glucose as a model compound) are represented by the formulas (1-2) listed below (Gasafi et al., 2007; Schmieder et al., 2000):

$$\text{Theoretically: } C_6H_{12}O_6 + 6H_2O \leftrightarrow 6CO_2 + 12H_2 \qquad \Delta H = 158 \text{ kJ mol}^{-1} \qquad (1)$$

$$\text{Experimentally: } 2C_6H_{12}O_6 + 10H_2O \leftrightarrow 11CO_2 + CH_4 + 20H_2 \qquad \Delta H = 152 \text{ kJ mol}^{-1} \qquad (2)$$

However, a review of studies reported that product gas composition under both catalytic and non-catalytic conditions approximate values of H_2: 40%-60%, CO_2: 30%-70%, CH_4: 15%-25%, and CO: 5%-30%, with non-catalytic conditions favoring CO production over CH_4 (Afif et al., 2011). The H_2 and CO gaseous streams can be recombined into liquid hydrocarbon fuels via Fischer-Tropsch or similar catalytic reforming systems (Demirbas, 2007), allowing for sludge to become a second-generation biofuel feedstock (Demirbas, 2011a; Demirbas et al., 2011).

The SCWG process dates back to the late 1970s, with incremental improvements in processing and reactor design, but very little reactor and reaction modeling taking place since (Elliott, 2008; Jessop et al., 1999; Modell, 1977; Modell et al., 1982; Savage, 2009). Like other SCW systems, SCWG can convert wet biomass directly, thereby avoiding high-energy drying processes associated with conventional thermochemical gasification (Hao et al., 2005) leading to similar chemical end-products. Unlike traditional gasification options, most SCWG can demonstrate an energy balance that can yield self-sufficient processing, positively addressing the high-moisture content of very wet wastes such as sewage and oily sludges.

Water simultaneously fulfills multiple roles in the SCWG process. Initially, water serves as the solvent for hydrolysis reactions, which quickly depolymerizes the major biomass sludge components (e.g., polysaccharides and fatty acids) into simpler structures like fructose, glucose, and short-chain organic acids (Di Blasi et al., 2007). The gasification reaction progresses beyond hydrolysis, wherein high-temperature water pyrolyzes those simple sugars and organic products to produce H_2-rich fuel gas and carbon oxides (Elliott, 2008). The H_2 bonds in supercritical water are weak, which means that, during water-gas shift reactions, the water can act as a H_2 donor, thereby increasing H_2 and O_2 availability and the corresponding H_2 yield (Yuan et al., 2006). The increase in O_2 availability can facilitate weak exothermic reactions, which improve process efficiency. Under supercritical conditions, water's hydrolysis solvation characteristics quickly give way to a secondary role as a reactant as well as a H_2 source (Han et al., 2008). Numerous studies have shown the potential role of SCWG for H_2 production from a variety of wet-waste feedstocks including sludge, with H_2 yields increasing by 80% from 330°C subcritical conditions at 380°C supercritical conditions (Demirbas, 2009; Xu et al., 2009; Yan et al., 2009).

Understanding how water molecules interact at supercritical conditions is helpful to predict surface-bound, transition-state species and the reaction energetics (Savage, 2009).

Supercritical water's solvation and dilution characteristics suppress tar and coke formation by preventing polymerization of double-bond intermediates, mainly by spatial distancing and reduced collisions between reactant molecules (Kruse & Dinjus, 2007a).

Surplus H_2 availability also positions supercritical water as the natural upgrading medium for oily sludges, coal pitch, and petroleum coke (Han et al., 2008). Prevailing dogma, however, asserts that H_2-production costs via SCWG of wet biomass (e.g., sludge) are several times higher than the costs of H_2 production via steam CH_4 or natural gas reforming (Balat et al., 2009; Demirbas, 2007). The H_2-production argument is based solely on fuel (viz., H_2) as the cost reference point. When nested within the revenue framework of waste disposal as the primary objective, secondary H_2 fuel conversion costs via SCWG is actually estimated to be a full two magnitudes less than that of natural gas reforming (Gasafi et al., 2008). The conversion costs are constant, regardless of the feedstock origin. However, the bottom-line product production costs are also largely driven by feedstock production and extraction costs, which in the case of natural gas have dropped significantly as a result of shale-based, strata fracturing (a.k.a. "fracking"), albeit fraught with controversy (DiPeso, 2011; Mooney, 2011).

2.2. Catalytically augmented supercritical water

Supercritical-water, fuel-gas production can be catalytically enhanced. The addition of a small quantity of catalyst to the SCWG process enhances gasification efficiency much like in conventional thermochemical gasification, especially at low reaction temperatures (Zhang et al., 2010). Adding catalysts intensifies SCWG reaction kinetics under milder conditions, and in the process, improves the efficiency of the water-gas shift reaction, promoting higher gas yields and a reduced yield of unwanted products (Elliott, 2008; Sınag et al., 2004). Catalysts also intensify hydrolysis liquefaction processes via flash pyrolysis that produces a liquid condensate in the dissolved supercritical water (Penninger & Rep, 2006). The flash-pyrolysis condensate is then readily converted in supercritical water into a H_2-rich gas, which further suppresses char and tar formation and reduces operating costs (Calzavara et al., 2005; Penninger & Rep, 2006; Sınag et al., 2004; Toor et al., 2011).

Catalytic SCWG studies can be divided into two categories based on the types of catalyst used: supported and unsupported catalysis (Lee, 2011). Supported catalysts can include the Noble metals (viz., Ru, Rh, Pd, Ir, and Pt) or lower-cost, common metals (viz., Re, Sn, Pb, W, Mo, Zn, Cr, and Ni) (Chang et al., 1993). Supported catalysts usually consist of various metals (including oxides and ores) dispersed on fixed-bed supports or particles made of ceramic, carbon, or metal oxide (Ding et al., 1996; Lee, 2011). High-performance ceramics (e.g., Al_2O_3, ZrO_2, SiO_2, Si_3N_4, Ce_2O_3, and TiO_2) have been used as supports for catalysts in SCW (Azadi et al., 2011; Ding et al., 1996; Lee, 2011). All of these ceramics are, however, subject to thermal creep at much lower temperatures than when exposed to high-temperature gases, thereby allowing the supported catalyst particles to contact each other, then sinter, weld, or polish, rendering them inactive (Bermejo & Cocero, 2006b; Hyde et al.,

2001). Ceramic supports also serve as nucleation points for salts, which can quickly plug reactors and deactivate the catalysts (Aki & Abraham, 1999; Brunner, 2009a). In some cases, as with silicon-based supports, erosion through solvation in water may occur (Cocero, 2001; Marrone & Hong, 2009). Unsupported catalysts are not fixed in the reactor and can include water-dissolved alkali salts (e.g., KOH, NaOH, Na_2CO_3, and K_2CO_3) in addition to the same metals as those used on fixed supports (Li et al., 2011; Lu et al., 2010; Schmieder et al., 2000). Reactive characteristics of unsupported catalysts are typically higher than supported catalysts (Anglada et al., 2011). An additional advantage of unsupported catalysts is that they can carry salts out of the reactor as the catalyst particles pass through the system (Anglada et al., 2011).

Metal catalysts have been well documented at promoting water-gas shift reactions, methanation, and hydrogenation reactions (Yoshida & Oshima, 2004). Four metals (viz., Ru, Rh, Pt and Ni) have received the greatest amount of attention in the literature. Ruthenium is reported to perform better than either Rh or Pt, in promoting SCWG H_2 production (Azadi & Farnood, 2011; Balat et al., 2009; Byrd et al., 2008; Chakinala et al., 2010; Chang et al., 1993; D'Jesús et al., 2006; Ding et al., 1996; Fang et al., 2008; Hao et al., 2005; Izumizaki et al., 2005; Izumizaki et al., 2008; Krajnc & Levec, 1994; Sato et al., 2011; Sato et al., 2003), especially when supported on TiO_2. Ruthenium commands a lower market price than Rh or Pt, making it an attractive option (Elliott, 2008; Guo et al., 2007; Izumizaki et al., 2005). Ruthenium is also reported to be more easily recovered for reuse than either Rh or Pt (Izumizaki et al., 2005).

Compared to Noble metals, including Ru, Rh, and Pt, Ni is a low cost material capable of catalyzing conversion at high rates with relatively low temperatures without sacrificing H_2 yields (Antal et al., 2000; Calzavara et al., 2005; Matsumura et al., 2002; Xu et al., 1996). Nickel catalysts have been reportedly effective at cracking tar into smaller, volatile fractions and promoting water-gas shift reactions, methanation, and hydrogenation reactions. Nickel can resist deactivation due to polishing and sintering if properly supported on TiO_2 or non-oxide ceramic substrates (viz., silicon carbide or carbon) (Azadi & Farnood, 2011; Marrone & Hong, 2009; Youssef et al., 2010a). Certain forms of Ni, including reduced Ni or skeletal Ni, commonly known as "Raney", have become a primary focus due its high porosity and surface area, which results in a high number of reactive sites and gasification efficiencies above 93% in SCWG laboratory-scale systems (Afif et al., 2011; Elliott, 2008).

Three alternatives to metal and salt catalysts have been identified: carbon catalysts, synergistic catalysts, and *in-situ* catalysts. Carbon can be used as either a catalyst or as a catalyst support (Antal et al., 2000). The conversion efficiencies of carbon due to increased temperature from partial-oxidation reactions can be on par with metals and alkali salts for H_2 and CO_2 production (Kruse et al., 2000; Matsumura et al., 2002; Rönnlund et al., 2011; Xu et al., 2009). Carbon is very stable in supercritical water, especially when H_2 gas is present (Calzavara et al., 2005). Plus, carbonaceous materials are common and relatively inexpensive, meaning that even the need for large catalyst volumes should still be economically feasible (Matsumura et al., 2002). Synergistic catalysts are formed by

combining metals with relatively inexpensive alkali salts, creating a highly reactive surface, with less overall catalyst used, resulting in a higher H_2 output with reduced CH_4 production (Bernardi et al., 2010; Elliott, 2008). Carbon and ceramic (e.g., Al_2O_3, ZrO_2, and CeO_2) catalyst supports have also been shown to have significant synergistic effects on catalytic effectiveness, increasing gas yield by as much as five-fold and non-linearly altering the gas fraction (Elliott, 2008; Minowa & Inoue, 1999). Catalytic reactivity is often strongly influenced by characteristics of the dispersion on a support and the support itself (Azadi & Farnood, 2011). The common support for metal catalysts, zirconia, actually doubled H_2 yield from SCWG processing (Guo et al., 2007; Watanabe et al., 2003). Carbon and the rutile form of TiO_2 have shown similar catalytic promoter effects when used as supports for metal catalysts (Chakinala et al., 2010; Elliott, 2008). It is known, however, that soluble salts and insoluble metals catalytically react in different ways (mainly solubilization, mineralization, and oxidation), and a number of researchers have pointed out that there is no straightforward explanation in the literature for the kinetic mechanisms governing these synergistic processes (Azadi & Farnood, 2011; Bernardi et al., 2010; Lu et al., 2010). Catalytic *in-situ* effects resulting from sludge-entrained inorganic species have been studied as alternatives to conventional catalysts (Lee, 2011). This approach makes use of the antisolvent effect of supercritical water, wherein catalytically active salts and metals present in the sludge matrix actually produce catalyst precursors on the fly, such as activated carbon and trace reactive metals (Marques et al., 2011). The *in-situ* propagation of catalysts could rapidly form a supersaturation of nano-scale, semi-homogenous catalyst particles that promote gasification of the matrix (Gadhe & Gupta, 2007; Levy et al., 2006; S1nag et al., 2011).

2.3. Catalyst effect on chars & tars

Employing catalysts pushes total SCWG efficiency up to 98% by converting a high proportion of char and tar to gas products (Calzavara et al., 2005; Xu et al., 2009). Tars and sulfur edicts commonly released from sludge during gasification also present a threat to long-term catalyst stability (Afif et al., 2011; Elliott, 2008; Izumizaki et al., 2005; Yoshida & Oshima, 2004; Zhang et al., 2011). Tarry deposits and sulfur poisons dramatically impact metal catalyst effectiveness and resulting gas yield volume, even though they have little discernable effect on gas fraction and composition (Afif et al., 2011; Lee, 2011). Some catalyst regeneration was evident with the flushing of sulfur-poisoned catalysts with subcritical water (at 250-300°C), which removed up to 75% of the sulfur (Elliott, 2008). Water can activate or deactivate metal-catalyzed reactions via autoxidation (García-Verdugo et al., 2004). Regeneration effects can be augmented via the addition of an oxidant, such as H_2O_2 (Elliott, 2008). Deactivation effects, however, can be extensive and irreversible due to unique interactions between the catalyst and water (Ding et al., 1996).

2.4. Catalyst stability & sintering

Catalysts under harsh SCW conditions are subject to numerous morphological challenges affecting reactivity, lifecycle, stability, and economical operation (Ding et al., 1996; Elliott,

2008; van Rossum et al., 2009). Harsh SCW conditions demand more durable catalyst materials than gaseous operations (Ding et al., 1996). Significant loss of catalyst surface area, interstitial space, and chemically active sites result from numerous phenomena, including hydrothermal sintering, friction welding, friction polishing, thermal glazing, support creep, and aqueous dissolution (Aki & Abraham, 1999; Hao et al., 2005).

High temperatures alone are insufficient to cause significant catalyst sintering problems (Hao et al., 2005). Raney Ni shows a high resistance to heat in a gaseous atmosphere (Afif et al., 2011; Hao et al., 2005). Nickel has been noted to resist deactivation due to polishing and sintering when supported on TiO_2 or non-oxide ceramics such as silicon carbide or carbon (Azadi & Farnood, 2011; Marrone & Hong, 2009; Youssef et al., 2010a). If there is no proper support, as with Raney Ni, sintering can occur even after short-term operation (Hao et al., 2005; Lee, 2011). Raney Ni deactivates due to accretional crystal growth resulting from hydrothermal sintering (Afif et al., 2011; Elliott, 2008). Furthermore, the effect of the hydrothermal sintering was measured to be six-fold higher under exposure to hydrothermal treatment (380°C) than was observed at the same temperature in a gas atmosphere (Afif et al., 2011). Even when stabilized by Ru doping, Raney Ni sintered rapidly at 400°C (Elliott, 2008). Development of hydrothermally stable supports continues to be an area of active research and development efforts (Xu et al., 2009).

2.5. Supercritical Water Oxidation (SCWO)

Supercritical water oxidation (SCWO) is closely related to SCWG, both in terms of kinetics and technology. The objective of SCWO, however, is to oxidatively destroy organic compounds in water (Bermejo & Cocero, 2006b; Jing et al., 2008). The technology was originally developed nearly 30 years ago at the Massachusetts Institute of Technology for NASA, back when it was thought there would be a human colony on the moon and a need for a single system to treat and purify water was a priority (Bubenheim & Wydeven, 1994; Modell, 1977; Modell et al., 1982; Slavin & Oleson, 1991; Sloan et al., 2008; Svanström et al., 2004; Svanström et al., 2005).

Applications of SCWO technology ensued in the defense industry, where it was perfected as a destruction method for the most dangerous organic compounds in the world (Crooker et al., 2000; Onwudili & Williams, 2006; Savage, 2009; Veriansyah & Kim, 2007). The U.S. Department of Defense (DOD) developed SCWO into a viable technology specifically in support of the 1993 International Chemical Weapon Convention (Marrone et al., 2005; Savage, 2009; Veriansyah & Kim, 2007; Veriansyah et al., 2007). Currently, SCWO is used on a regular basis by the U.S. Army and U.S. Air Force to destroy nerve gas, biological weapons, and other dangerous munitions (Crooker et al., 2000; Onwudili & Williams, 2006; Savage, 2009; Veriansyah et al., 2005). The U.S. Navy has developed compact SCWO units for ship-board, hazardous waste treatment in order to comply with national and international waste discharge standards (Crooker et al., 2000; Veriansyah & Kim, 2007; Veriansyah et al., 2005).

The SCWO technology functions as a hydrothermal analog to incineration, thermochemically destroying wet wastes, such as sewage sludge, that are rich in organic compounds and residues (Onwudili & Williams, 2006). The SCWO process functions in much the same way as SCWG, but it is taken a step further by adding a strong oxidant (e.g., O_2, H_2O_2, or $KMnO_4$) in order to completely oxidize organic compounds dissolved in the supercritical water (Anglada et al., 2011; Castello & Fiori, 2011; Guo et al., 2007; Youssef et al., 2010a). Under highly oxidizing conditions, carbon compounds are quickly converted into carbon oxides (CO_2 and CO), H_2 is converted to H_2O, and the active oxidation process results in the exothermic release of energy (Abelleira et al., 2011; Castello & Fiori, 2011; Guo et al., 2007; Mahmood & Elliott, 2006; S1nag et al., 2004; Svanström et al., 2004). Notably, the biomass destruction rate efficiency using H_2O_2 in supercritical water has been shown to be 16-fold higher (based on free molar O_2 mass) than injected O_2, which by extension makes the effective oxidative cost of H_2O_2 less than $1/5^{th}$ that of injected O_2 (D'Jesús et al., 2005).

The unique reaction media provided by SCW is important, because it induces almost zero, inter-phase mass transfer limitations (Byrd et al., 2008; Letellier et al., 2010). Consequently, SCW operates in a homogeneous phase where O_2 (or other oxidants) availability becomes high. Oxygen, therefore, dissolves faster in supercritical water than in subcritical water. As water transitions into the supercritical state, it becomes a strong oxidant further enhancing the process. Depending on the quantity of oxidants introduced, partial-oxidation reactions occur in the working fluid, actually heating itself *in-situ* rather than relying on an external reactor heater. The resultant internal heating by the working fluid itself (i.e., water) dramatically lowers the transport phenomena resistance, and thus produces high efficiencies for heat-transfer and gasification processes inside the reactor (Calzavara et al., 2005). High transfer efficiencies are the primary drivers behind the very short residence times (i.e., <1sec) and smaller reactor volumes characteristic of SCWO systems (Letellier et al., 2010). The overall chemical transformations achieve complete organic destruction (>99.99%) while producing essentially no char, tar, or NO_x (Du et al., 2010; Mahmood & Elliott, 2006).

2.6. Effects of temperature, pressure, & residence time

Temperature, pressure, and residence time have been noted to be the most important variables for modifying supercritical reaction conditions (Brunner, 2009a; Elliott, 2008). Optimal supercritical conditions can be experimentally derived and aided by models to induce the ideal combination of temperature, pressure, and residence time (Soria et al., 2008). System optimization, however, involves maximizing the desired output (energy or organic destruction), while reducing reaction times to minutes or seconds versus the hours required for similar results in subcritical water (Gloyna & Li, 1993).

Temperature is considered the most sensitive variable in SCWG processes, with 600°C serving as an often-cited, optimal target temperature due to associated high conversion rates (D'Jesús et al., 2006; Elliott, 2008; Susanti et al., 2010). When temperature was increased in SCWG, for example, from 601°C to 676°C, CH_4 yield was reduced and H_2 yield doubled

(Susanti et al., 2010). A similar, inverse effect was observed as temperature declined. A drop in temperature from 600°C to 500°C during the SCWG process resulted in an overall decline in gasification efficiency from 98% to 51% (Elliott, 2008). Substantial changes either side of 600°C were evident in CSCWG as well, suggesting that it too has a narrow effective temperature range (Antal et al., 1995; Brunner, 2009a; Izumizaki et al., 2008; Jessop et al., 1999). The CSCWG process achieved unacceptably low efficiencies when temperatures declined far below 600°C, and carbon catalyst decomposition occurred when temperatures increased far above 600°C (Antal et al., 1995; Xu et al., 2011; Xu et al., 1996).

Short residence times (<1 min) and high organics destruction efficiencies (>99.99%) occur during gasification and oxidative reactions at supercritical operating conditions above 600°C (Cao et al., 2011; Du et al., 2010). Furthermore, when temperatures are above 600°C, reactions can take as little as a few milliseconds (Augustine & Tester, 2009; Bermejo et al., 2011; Cabeza et al., 2011; Narayanan et al., 2008; Wellig et al., 2009). Longer residence time can improve gasification thoroughness, but there is also an inverse relationship between temperature and reaction completeness, dropping from a few minutes below 600°C to a few seconds above 600°C (Cao et al., 2011). The optimal temperature threshold for SCWG (i.e., 600°C) has been shown to be on the low side of the rapid-conversion range for higher concentration biomass in the absence of a catalyst or strong oxidant (Afif et al., 2011; Antal et al., 1995; Xu et al., 2011; Xu et al., 1996). Without a catalyst or oxidant, temperatures more in the range of 800°C are required for rapid conversion (Afif et al., 2011; Guo et al., 2007; Izumizaki et al., 2008). Conversely, water just below the critical temperature (375°C) has been shown to be highly effective for gasification when performed with active catalysts when primarily targeting CH_4 (vs H_2) production (Elliott, 2008). However, at temperatures more than about 20°C below the critical temperature, all gasification ceases, with or without catalyst, resulting in only hydrolysis and solvation reactions (Elliott, 2008).

While both temperature and reaction times seem to consistently be straightforward influences on reducing organic content, several studies indicate that pressure variations have more subtle and complex effects on conversion efficiency and gas product fraction (Brunner, 2009a; Cui et al., 2009; D'Jesús et al., 2006; Guo et al., 2007). Supercritical water reactions have been demonstrated to be very stable. Temperature profiles represent a quasi-constant plateau near the critical conditions, and there is little or no reaction effect from pressure variations above a threshold point (Dutourníe & Mercadier, 2005). Nonetheless, the limited reaction effect from pressure could be attributed to the fact that high pressure stabilizes reaction energetics (Dutourníe & Mercadier, 2005). Similarly, the potential for complex pressure effects should not be ignored because water properties including density, dielectric constant, and ion product increase with pressure (Guo et al., 2007). Higher ionic reaction rates can restrain free-radical reactions (Guo et al., 2007). These complex pressure effects can be used to fine tune the chemical composition of the solvent and control gas composition and yield (Savage, 2009). Specifically, pressure has little or no influence on reaction rate, but it does affect solvent density (Brunner, 2009a). Density also has little effect on gasification efficiency above the critical point, but can have significant affects on gas

fraction characteristics (Brunner, 2009a). High pressures, and correspondingly higher densities, favor CH_4 production and inhibit H_2 production (Brunner, 2009a).

2.7. Char & tar formation

Substantial amounts of char and condensable volatile tars form during hydrothermal decomposition of sludge, especially in the absence of catalysts or oxidants (Afif et al., 2011; Azadi et al., 2011). Sewage sludge is highly prone to char and tar formation due to the presence of high levels of condensable volatile materials, which favor the production of cyclic compounds (Adegoroye et al., 2004; Dogru et al., 2002; Onwudili & Williams, 2006). Char and tar formation can severely impair carbon gasification efficiency, which is a common and persistent problem with both traditional, dry gasification and hydrothermal gasification (Chuntanapum & Matsumura, 2010). Even under supercritical conditions, if the thermal kinetics are not high enough, wet biomass (including sludges) can dehydrate and then polymerize into tarry condensates prior to hydropyrolytic liquefaction (Azadi & Farnood, 2011; Matsumura et al., 2005; Onwudili & Williams, 2006). The exact influence of SCW reaction kinetics on tar formed during biomass gasification is largely unknown beyond the general benefits of higher temperatures and higher heating rates (Adegoroye et al., 2004; Kruse, 2009; Matsumura et al., 2005).

Chars and tars are difficult to gasify and once formed, act as persistent barriers to complete gasification (Afif et al., 2011; Calzavara et al., 2005; Chuntanapum & Matsumura, 2010). If not properly handled, chars and tars can quickly plug SCW reactors in as little as one hour of operation (Calzavara et al., 2005; Chuntanapum & Matsumura, 2010; Jin et al., 2010). Slow, reaction-heating rates and low reaction temperatures accelerate char and tar formation (Azadi & Farnood, 2011; Jin et al., 2010). Thus, in the absence of catalytic promoters, char and tar formation is especially problematic during process startup, wherein the reaction relies on external heating (Azadi & Farnood, 2011; Jin et al., 2010). The preheating of reactor and heat-up zones where feedstocks first enter has been noted as a possible solution to char and tar formation, buildup, and plugging (Antal et al., 2000; Elliott, 2008). Despite the fact that SCWG processes produce less char and tar, the lower reactor volume and small diameter typical of SCW systems are still vulnerable to plugging (Calzavara et al., 2005). Even if plugging is avoided, char formation can still cause a cascading loss of carbon gasification efficiency (Chuntanapum & Matsumura, 2010).

Nevertheless, char and tar formation in SCW is usually considerably less than that in low-pressure processes, largely due to higher water solubility, intensified kinetics, high heat, and mass transport properties (Byrd et al., 2008; Calzavara et al., 2005; Chuntanapum & Matsumura, 2010). Plus, hydrolysis and hydropyrolysis reactions in SCW quickly dissolve sludge educts before they can dehydrate, thus suppressing polymerization of cleavage products and tar formation (Gasafi et al., 2007). Although small quantities of an oxidant can produce partial oxidation, catalysts appear to be the key for reliably achieving both char and tar avoidance and selectivity for efficient H_2 production (Balat et al., 2009; Calzavara et al., 2005; Ding et al., 1996).
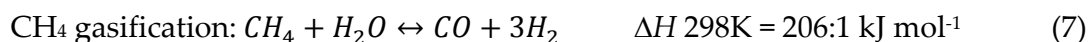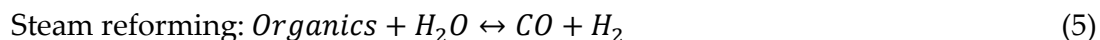
3. Reactor, kinetics, & design considerations

Supercritical-water reaction kinetics and effective reactor engineering are inextricably linked. New reactors, able to withstand harsh SCW operating conditions, are needed for SCWG technology to advance from laboratory and emerging status to genuine commercial operations (Yoshida et al., 2003). Most commercial and industrial applications require that engineering designs and materials overcome corrosion and plugging problems and that systems operate on a continuous duty cycle (Azadi et al., 2011; Elliott, 2008; Guo et al., 2007). Some common, SCW-reactor considerations are presented here, while extensive and detailed reviews can be found elsewhere (Bermejo et al., 2005a, 2005b, 2009; Calzavara et al., 2004; Fauvel et al., 2003, 2005; Lieball et al., 2001; Machida et al., 2011; Marrone & Hong, 2009; Mitton et al., 2000; Peter, 2004; Tan et al., 2011; Veriansyah et al., 2009; Wellig et al., 2005; Yoshida & Matsumura, 2009).

Continuous-flow reactor systems provide the most suitable options for real-world applications, because they offer plant expansion flexibility and versatile, industrial scale-up (Guo et al., 2007; Veriansyah & Kim, 2007). There are several categories of reactor designs, including in-line tubular systems, transpiring-wall (both tubular and vessel), and pressure vessel setups (Azadi et al., 2011; Elliott, 2008). Basic choices of system configuration require a complete understanding of how water molecules interact with each other at supercritical conditions and how reactants influence catalyst-surface adsorption and desorption events (Feng et al., 2004; Matsumura et al., 2005; Savage, 2009).

Even when water's transport properties can be predicted, thermodynamic phase equilibria are still handicapped by varying real-world, compositions of reactant educts and the presence of inorganic salts (Bermejo & Cocero, 2006b). Furthermore, the sequential and simultaneous progression of hydrolysis, pyrolysis, steam-reforming, and water-gas shift reactions in supercritical gasification chemistry are complex and have yet to be comprehensively described beyond speculative assumptions based largely on limited observations and first-order kinetics (Calzavara et al., 2005; Kruse, 2009; Matsumura et al., 2005; Sato et al., 2004; Vogel et al., 2005).

Designing reactor energy flows requires clearly definable equilibrium relationships (Feng et al., 2004; Gassner & Maréchal, 2009). The characterization of inherently arbitrary reactor feed equilibria, however, is complicated by thermodynamic mechanics of fluid mechanics, heat transfer, mass transfer, kinetics, and phase behavior (Hodes et al., 2004). Modeling, predicting, and defining these thermodynamic mechanisms is difficult, and there is no straightforward explanation in the literature for SCW reaction kinetic mechanisms (Azadi & Farnood, 2011; Bermejo & Cocero, 2006b; Bernardi et al., 2010; Hodes et al., 2004; Lu et al., 2010). The assumed, basic reaction kinetics are represented by the formulas (3-8) listed below (Chun et al., 2011; White et al., 2011):

$$\text{Hydrolysis: } Organics \xrightarrow{K_1} Sugars \xrightarrow{K_2} Degradation\ Products \tag{3}$$

$$\text{Pyrolysis: } Organics \xrightarrow{K_1} \text{"Active" } Organics \xrightarrow{K_2} Volatiles\ or\ Chars \tag{4}$$

$$\text{Steam reforming: } Organics + H_2O \leftrightarrow CO + H_2 \tag{5}$$

$$\text{Steam gasification: } C + H_2O \leftrightarrow CO + H_2 \qquad \Delta H \text{ 298K = 132 kJ mol}^{-1} \tag{6}$$

$$\text{CH}_4 \text{ gasification: } CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H \text{ 298K = 206:1 kJ mol}^{-1} \tag{7}$$

$$\text{H}_2\text{O-CO shift: } CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H \text{ 298K = -41:5 kJ mol}^{-1} \tag{8}$$

All of the reactions are assumed to use a first-order rate constant that obeys the Arrhenius equation (9) in which k_{io} serves as a pre-exponential factor, with A as acid concentration (wt%) raised to the power m_i, E_i as the activation energy, and R and T as gas constant and temperature, respectively (Jacobsen & Wyman, 2000):

$$k_i = k_{io} \times A^{m_i} \times e^{-\frac{E_i}{RT}} \tag{9}$$

Attempts to develop detailed understanding of the reaction kinetics have so far been limited and isolated, relying primarily on *in-situ* diagnostics gleaned through direct visual/optical observations and indirect nuclear radiographic observations. Visually observing reactions is advantageous when compared to drawing surrogate reactant samples, in that direct observations support real-time, kinetic diagnostics and operational integrity (Hunter et al., 1996). Direct observations of small-scale, transparent reactors (e.g., diamond anvil cells or quartz capillary tubes) allow reactions to be seen, photographed, and quickly halted if necessary (Azadi & Farnood, 2011; Fang et al., 2008; Hashaikeh et al., 2007; Maharrey & Miller, 2001; Peterson et al., 2008a; Sasaki et al., 2000; Vogel et al., 2005). Larger scale systems have been directly observed via optical, laser Raman spectroscopy through sapphire reactor viewing ports in order to capture finite details of the reaction progress, fluid mechanics, reactant destruction completeness, and oxidation efficiencies (Chuntanapum & Matsumura, 2010; García-Verdugo et al., 2004; Hunter et al., 1996; Koda et al., 2001; Rice et al., 1996). Indirect, nuclear radiography accomplishes the same result as optical Raman spectroscopy, but does not require viewing-port reactor modifications (Peterson et al., 2008a, 2008b, 2010). Consequently, radiography is more flexible than direct observation, because reaction observations can be made from different angles independent of reactor design (Peterson et al., 2008b).

Supercritical-water reaction educts will ultimately be determined exclusively by thermodynamic kinetics (Savage, 2009). The exact influence of SCW reaction kinetics is largely unknown beyond the general benefits of higher temperatures and higher heating rates (Adegoroye et al., 2004; Kruse, 2009; Matsumura et al., 2005; Vogel et al., 2005). Newer reaction-observation techniques show promise for developing an understanding of the missing, critical kinetics needed for comprehensive modeling of SCWG reactions (Vogel et al., 2005). Reaction observation techniques (particularly Raman spectroscopy), nonetheless, are not widely used, are limited to methodological studies, and have no comprehensive kinetics models based on them (Hunter et al., 1996; Rice et al., 1996). Existing observation studies have, however, partially confirmed the assumptions that endothermic, acid-catalyzed hydrolysis reactions quickly dissolve sludge educts before they can dehydrate,

resulting in complete solubilization and liquefaction early in the process (Brunner, 2009b; Koda et al., 2001; Peterson et al., 2008a). The rapid endothermic, hydrothermal-pyrolytic decomposition of liquefied organic materials appears to progress concurrently with hydrolysis, reaching completion within seconds to minutes (Brunner, 2009b; Peterson et al., 2008a). Partial oxidation of the pyrolyzed compounds drives the pyrolysis and gasification reaction exothermically (Koda et al., 2001; Kruse & Vogel, 2010; Peterson et al., 2008a; Vogel et al., 2005). The disintegration of sludge under SCW conditions results in the formation of hydrolysis products, including volatile fatty acids, phosphorous compounds, dissolved biodegradable organics, gases (i.e., CO and CO_2), and H_2O (Rulkens, 2008). Due to the lack of a well-established Equation of State (EOS) for SCW and any form of biomass, very few studies have systematically investigated the complexities of reaction progress or even heat transfer to reactants in supercritical reactors, and a comprehensive description of reaction kinetics is unlikely to evolve in the absence of an EOS (Azadi et al., 2011; Bermejo et al., 2007; Yoshida et al., 2004).

Supercritical-water reaction kinetics and effective reactor engineering may very well be inextricably linked, but the connections are largely unknown. Consequently, rather than designing systems to accommodate any particular reaction progression or kinetics, progress in SCW reaction-kinetics engineering has largely relied on trial-and-error to solve corrosion and scaling problems (Hodes et al., 2004; Marrone et al., 2004). Efforts to design SCW systems continue in the absence of clearly defined models of reaction kinetics, and progress is reflected by the many successful industrial applications of SCW (notably, General Atomics, Foster Wheeler, and Chematur Engineering) (Bermejo & Cocero, 2006b).

Mixtures of supercritical water and sludge can be thought of as dynamic systems, wherein regions may predictably or transiently exist (Savage, 2009). An increase in organic content, for example, shifts the critical point of the mixture further from that of pure water (Savage, 2009). Despite well-documented SCW effectiveness for gasification, data is very limited for phase behavior of sludge-decomposition (Fang et al., 2008). Consequently, a number of broad assumptions and logical leaps must be made to model supercritical reactor conditions (based on either *Peng-Robinson* or *Anderko-Pitzer* EOSs), including volume translation corrections to reproduce densities (Bermejo & Cocero, 2006b; Bermejo et al., 2007; Vogel et al., 2005).

3.1. Corrosion influence on reactor design

Corrosion has historically impeded SCW commercialization due to limited reactor life (Barner et al., 1992; Hodes et al., 2004). Metal corrosion in SCW systems is driven, in part, by water's own natural solvation characteristics and is largely localized to areas where water drops below the critical point (Marrone & Hong, 2009). Water in the near-critical region actually exhibits maximum corrosion effects (Marrone & Hong, 2009). Just below the critical point, water's fast kinetics from high temperatures, high pressures, and natural acidity are particularly taxing on metals (Marrone & Hong, 2009). Escalated corrosive severity of near-

critical water means that components used in preheating and cool-down are typically more susceptible to corrosion than the reactor itself (Marrone & Hong, 2009).

Reactor-specific corrosion problems often result from the fact that supercritical water cannot solvate charged (polar) species. Precipitation of polar species (i.e., inorganic salt) can form subcritical-water "microenvironments" between salt deposits on reactor walls and the reactor's internal metal surface (Hodes et al., 2004; Marrone & Hong, 2009). The highly saline and acidic, subcritical water in the microenvironments ultimately leads to severe and localized, reactor-wall corrosion (Hodes et al., 2004; Marrone & Hong, 2009). Consequently, reactor corrosion is a particular concern when alkali-salt catalysts are used or when high-salt-content sludges are processed (Lee, 2011).

Oxidative, metal corrosion results from supercritical water's high O_2 availability and correspondingly high electrochemical potential (Marrone & Hong, 2009). Corrosion prevention often requires the use of expensive alloys capable of withstanding high temperatures and pressures (Toor et al., 2011). Materials such as advanced Ni-based alloys (Inconel 625 or Hastelloy C276) and Ti alloys can suppress corrosion losses. Nickel-based alloys resist aqueous corrosion by forming a passivated and impermeable oxide surface coating that prevents corrosive solvent contact with the underlying metal, which protects the metal from further corrosion (Lee, 2011).

A separate, but related issue, is that corrosion-resistant, high-Ni-content reactor alloys (viz., Inconel and Hastelloy alloys) exert a catalytic influence on gasification chemistry (Afif et al., 2011; Antal et al., 2000; Chakinala et al., 2010; D'Jesús et al., 2006). This phenomenon has become commonly known as the "wall effect" (Sınag et al., 2004), wherein the reactor-wall alloys promote water-gas shift activity in SCW conditions (Chakinala et al., 2010). There has been considerable work with reactor alloys in an attempt to control and promote these catalytic effects (Afif et al., 2011). The fabrication of a fixed-bed catalyst from the same Inconel material used in the reactor, for example, increased gasification efficiency four-fold (Ding et al., 1998).

Corrosion in SCW is species-specific, targeting and selectively dissolving chromium's passivating oxide layer, thereby exposing the underlying alloy to further attack (D'Jesús et al., 2006; Marrone & Hong, 2009). Specific corrosive activity is discernable with process effluent analysis. Effluent laden with Ni, Cr, and Mo would indicate that corrosion is stripping those metals from the reactor wall (Sınag et al., 2004). One advantage of corrosion dynamics in SCW processes is that, even if corrosion occurs, the gas products are almost completely free of any corrosive substances, because the corrosive educts remain in the liquid phase (Kruse, 2009). Consequently, unlike dry processes, extensive cleaning of the SCW-produced fuel gases is typically not necessary (Kruse, 2009). Also, the metal embrittlement resulting from H_2 exposure in dry gasification is not a major problem in SCW processes (Kruse, 2009).

Transpiring-wall reactors are recent developments designed to avoid high temperatures near the walls and flush away corrosive salts with a thin film of subcritical water (Lavric et

al., 2006). The reaction chamber consists of a porous inner wall through which clean water continuously flows, creating a thin film of subcritical water (Figure 3). A second outer wall contains high pressure water that is never exposed to the extreme temperatures or corrosive effects of the reaction working fluid (Bermejo & Cocero, 2006a). The transpiring-wall approach allows one reactor wall to contain the pressure while the other wall endures exposure to the corrosive effects. This arrangement potentially allows for lower temperature operating conditions, less-extensive and costly containment alloys, and lower capital costs (Elliott, 2008).
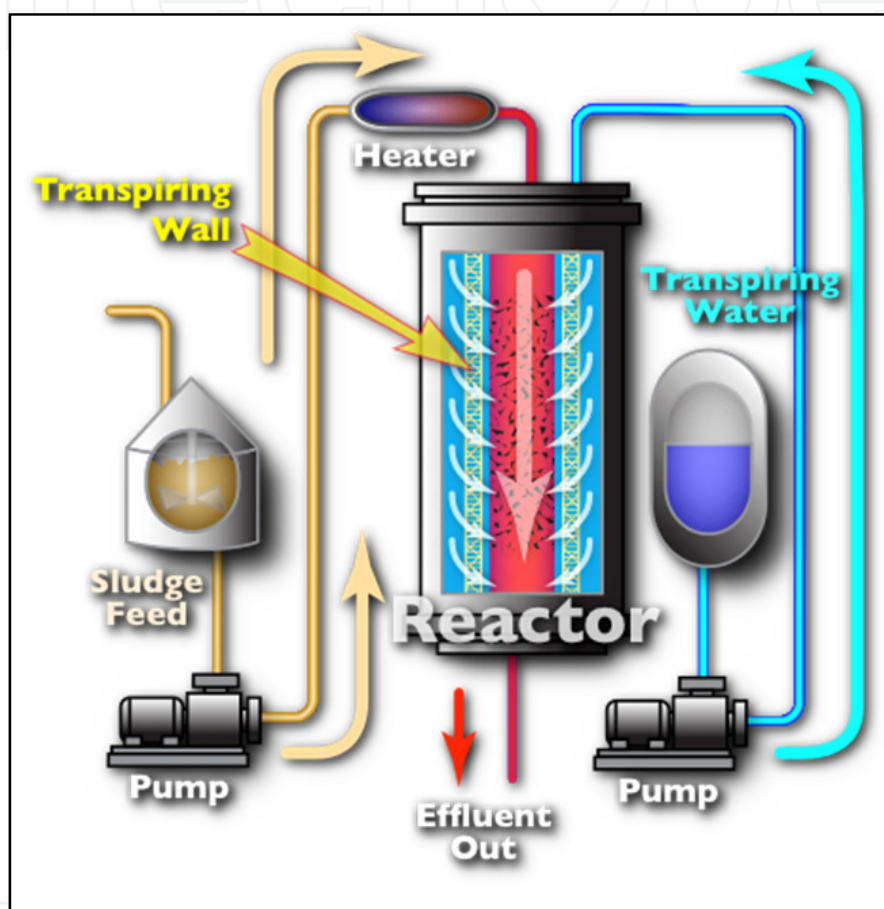

Figure 3. Transpiring Wall Reactor.

3.2. Salt precipitation & scaling influence on reactor design

Salts are pervasive and abundant in sludge (Brunner, 2009b; Elliott, 2008; Kruse et al., 2010). Waste-dissolved salts can precipitate and, if not controlled, eventually block SCW reactors (Brunner, 2009a, 2009b; Demirbas, 2011a; Marrone et al., 2004). Salt precipitation persistently complicates SCW systems (Du et al., 2010), thereby impeding widespread commercialization due to inherent practical difficulties of scale buildup, fouling, and corrosion (Cocero et al., 2003; Hodes et al., 2004). Salt handling represents one of the greatest remaining technical challenges for development of SCW biomass gasification processes at commercial scales (Hodes et al., 2004; Kruse et al., 2010). Salt precipitation and control are briefly discussed

here, but reviews of the subject can be found elsewhere (Hodes et al., 2004; Kruse et al., 2010; Leusbrock et al., 2010; Marrone et al., 2004; Príkopský et al., 2007; Schubert et al., 2010a, b, 2012; Xu et al., 2010).

The low, dielectric constant of SCW reduces the salt-dissolving power of SCW to nearly zero (Figure 2), which results in the formation of solid precipitates (Brunner, 2009a, 2009b; Demirbas, 2011a; Marrone et al., 2004). Salt precipitation is particularly common in the preheating sections of SCW systems, due to steep concentration gradients as liquid water transitions to SCW, and mineral ions release from sludge matrices (Bermejo & Cocero, 2006b; Hodes et al., 2004; Penninger & Rep, 2006). Sludge-entrained, acidic solutions also precipitate educt salts during neutralization at the end of the SCW process (Hodes et al., 2004). Therefore, low solubility results in rapid salt precipitation immediately after sludge enters, and salts also precipitate as the effluent exits (Elliott, 2008; Marrone et al., 2004). Salt precipitation and plugging is particularly challenging with fixed-catalyst beds, which serve as both bottlenecks to velocity and ready nucleation sites for salt (Elliott, 2008; Kruse, 2009).

Numerous reactor designs, some paired with dedicated salt-separation equipment, have been proposed and studied (Brunner, 2009a; Du et al., 2010). Transpiring-wall reactors provide a nuanced use of liquid water to flush salt from the system (Bermejo & Cocero, 2006a; Lavric et al., 2006). A more common method, however, is a brute-force approach using high fluid velocities in tubular reactors such as AquaCat® and AquaCritox® processes developed by Chematur (Bermejo & Cocero, 2006b; Marrone et al., 2004). Tubular reactors are designed with small tube diameters in order to maintain high fluid velocity (Bermejo & Cocero, 2006b). The high fluid velocities overcome salt nucleation and agglomerate adhesion via high shear forces, in combination with scouring effects of entrained inorganic solids such as sand (Marrone et al., 2004). Tubular reactors have become the overwhelming technology of choice for commercial applications in part because of their salt control advantages (Barner et al., 1992; Bermejo & Cocero, 2006b; Brunner, 2009a; Cabeza et al., 2011; Matsumura et al., 2005). Well over 80% of the industrial applications of supercritical treatment of industrial wastewaters use tubular reactors coupled with a countercurrent heat exchanger for increased efficiency (Vadillo et al., 2011; Vogel et al., 2005).

Salt-control, maintenance duty has become a significant SCW implementation consideration, requiring frequent and costly shutdowns for cleaning (Hodes et al., 2004; Marrone et al., 2004). Some commercial entities (e.g., Chematur and SCFI) have developed a design workaround to the shutdown problem with parallel redundant systems, so that one unit can be in operation while a second unit is in cleaning mode (Bermejo & Cocero, 2006b). In addition to this reactor design solution, a variety of additive "magic sauces" have been developed to mitigate salt precipitation. These mixtures are comprised of "Type-1" salts (e.g., K_3PO_4 or KNO_3) that are sometimes supplemented with very finely ground abrasives (Marrone et al., 2004; Yoshida et al., 2003). Under supercritical water conditions, the Type-1 salts remain liquid and are not very "sticky" to metal, thereby acting as both solvating and nucleating agents for "Type-2" sticky salts such as $NaCl$ and Na_2SO_4 (Marrone & Hong, 2009; Yoshida et al., 2003). Entrained inert solids also act as additional nucleating media for

Type-2 salts and as a scouring and polishing media for reactor walls (Kruse, 2009; Marrone et al., 2004). The resulting mixture forms a eutectic with a melting point less than the operating temperature at the system pressure (Bermejo & Cocero, 2006b; Hodes et al., 2004). The resulting molten-salt blend will flow more easily through the reactor. Abrasive solids have very high surface areas (1,000 times higher than polished reactor walls) and exert much higher van der Waal and electrostatic attraction on the salt than the metal walls themselves (Marrone et al., 2004).

The liquid-salt phases are consistent with density eddies or "local density augmentations" often observed in supercritical fluids and are related to the isothermal compressibility of the supercritical state (Brennecke & Chateauneuf, 1999; Hyde et al., 2001). The localized densities cluster together and are perpetuated by van der Waals forces (Brennecke & Chateauneuf, 1999; Hyde et al., 2001; Marrone et al., 2004). Consequently, a dense, liquid slurry of "good" salts forms and abrasives constantly "clean" and clear the reactor of the "bad, sticky" salts.

3.3. Sludge dewatering & water retention

A critical consideration for the apparatus setup is the degree to which the sludge can be pumped into the reactor, which is primarily limited by viscosity from biomass solids content. Preheating sludge slurries allows higher solid concentrations, because increased temperature and pressure, even when well below the critical point, decrease sludge viscosity (Abelleira et al., 2011; Xu et al., 1996). Reduced viscosity is likely due to biomass liquefaction as a result of accelerated hydrolysis (Abelleira et al., 2011).

Beyond reaction kinetics, sewage sludge is mostly water, and dewatering has been a key focus of transportation logistics, with less water reflecting lower transport costs (Weismantel, 2001). Most estimates put the moisture content of sewage sludge at well above 95% for liquid sludge and nearly 90% for dewatered, semi-solid sludge cake (Fytili & Zabaniotou, 2008; Harrison et al., 2006; Hong et al., 2009). One reason for the difficulty in dewatering sludge is the presence of macromolecules and extracellular polymeric substances, as well as large quantities of cellular bacteria (Abelleira et al., 2011; Xu et al., 1996). Polymeric, cellular substances impede ion movement and thus promote water retention (Abelleira et al., 2011). When pre-heated to about 150°C at relatively low pressure (about 10 bar), walls of sludge-entrained cellular bodies are destroyed, thus decreasing sludge viscosity and making the cell contents more available to catalytic, oxidative, and thermal degradation (Abelleira et al., 2011). Preheating the wet organic feedstock with heat recycled from the hot reaction gases is also important in terms of reaching a self-sustaining, process threshold (Abelleira et al., 2011; Cocero, 2001; Cocero et al., 2002; Guan et al., 2011; Matsumura et al., 2005).

3.4. Energy recovery

The advantage of SCW is that much of the process energy investment can be recovered from the hot effluent at supercritical temperatures and reused to preheat the wet, organic feedstock (Guan et al., 2011). Recycling heat from the hot effluent through heat exchangers

back to the incoming, pressurized feedstock achieves a positive energy balance and acceptable system efficiency, which is critical to overcoming the high enthalpy of water (Abelleira et al., 2011; Cocero, 2001; Cocero et al., 2002; Matsumura et al., 2005). Preheating temperature (to well above the critical point 375°C) can also be a very important optimization (or simulation) consideration, especially when dealing with dilute or low-heating-value feedstocks (Barner et al., 1992; Cocero, 2001; Cocero et al., 2002). High preheating demand can be offset by supplementing the feed stream with a liquid, high-heating-value "fuel" such as waste oils or discarded organic solvents from industrial processes (Barner et al., 1992; Cocero, 2001; Cocero et al., 2002).

Even though supercritical water exhibits excellent heat and mass transfer properties, making use of those properties is a much higher technical challenge than other oxidation processes such as incineration (Bermejo & Cocero, 2006a; Cocero, 2001). External preheating through heat exchangers is usually necessary to initiate the reaction process, but can be discontinued once oxidative, exothermic reaction kinetics occur (Abelleira et al., 2011; Bermejo & Cocero, 2006a). Heat exchanger inefficiencies often negate high heat production, thereby undermining overall process efficiency (Yoshida et al., 2003). Heating rate is strongly related to reactor flow rate, which by extension defines heating duty length (Azadi et al., 2011). As flow rates decline, an increase in external heating has little impact on the temperature profile along the reactor (Azadi et al., 2011).

3.5. Potential

Until a sustainable sludge destruction solution is found, the sludge disposal problem will continue to grow with increasing population, rather than dissipate (Lavric et al., 2006). Application of sewage sludge on agricultural land has become socially unacceptable due to the fact that it is increasingly regarded as an unsafe and insecure handling route (Eriksson et al., 2008; Fytili & Zabaniotou, 2008; Harrison et al., 2006; Mathney, 2011; McBride, 2003; Snyder, 2005; USEPA, 2000, 2002b). Relying on agricultural and horticultural options as a disposal route for sewage sludge is simply not a valid, long-term solution by a whole host of sustainability and safety measures (Alaimo, 2008; Angenent et al., 2004; Arthurson, 2008; Booth et al., 2010; Costello & Read, 1994; CSS, 2011; Deblonde et al., 2011; Dijkema et al., 2000; Duić et al., 2011; Farré & Barceló, 2003; Fodor & Klemes, 2011; García-Serna et al., 2007; Harrison et al., 1999, 2006; McBride, 2003; NASNRC, 2002; Nature, 2008; Phillips, 1998; Smith et al., 2011; Snyder, 2005; Tollefson, 2008; USEPA, 2002a, 2009). Furthermore, public policy and regulations governing sludge disposal methods are beginning to reflect the growing public recognition that sewage sludge is more appropriately treated as hazardous waste than as fertilizer (Veriansyah & Kim, 2007; Youssef et al., 2011). Beyond the fact that sludge disposal regulations are becoming increasingly stringent worldwide, land available for waste disposal has also become more limited (Youssef et al., 2011). Driven by all these issues, sewage sludge is prime for capitalizing on a paradigm shift in the municipal wastewater industry.

Adoption of a new paradigm requires critically questioning the benefits of continuing with existing sludge disposal methods, and doing so will ultimately lead to dramatic technological developments, with SCW processes providing a viable alternative (Dijkema et al., 2000; Domínguez et al., 2006; Youssef et al., 2011). The hydrothermal decomposition of municipal wastewater solids would shift the view of sewage sludge as a costly disposal problem to that of a valuable, sustainable energy source. The U.S. annually consumes 4% of total national electricity just separating water from sludge (CSS, 2011; NASNRC, 2002; Phillips, 1998). Destroying sewage sludge *in-situ* would mean that municipalities would not have to dewater the sludge, thereby gaining massive, immediate financial savings, while simultaneously addressing a critical and vexing wastewater management problem (Fytili & Zabaniotou, 2008).

3.6. Commercial forays & missteps

Supercritical water processes have been used in the defense industry for over 30 years, but their use in the biofuels and wastewater industries dates back only a decade. Current SCW commercialization efforts focus in two main areas: 1) biomass (including coal) gasification and 2) municipal waste destruction. Applications, aside from the military, have been limited so far to demonstration units. Detailed performance reports from those demonstration units are scarce, with correspondingly even fewer review articles (Brunner, 2009a; Crooker et al., 2000; Onwudili & Williams, 2006; Savage, 2009; Veriansyah & Kim, 2007; Veriansyah et al., 2005; Xu et al., 2012). The engineering challenges discussed previously (viz., corrosion and salt precipitation) have been limiting factors to SCW commercialization (Brunner, 2009a). Efforts to commercialize SCW have been made by only a handful of companies, including Foster Wheeler, General Atomics, EcoWaste Technologies, Chematur Engineering, HydroProcessing, SuperWater Solutions, and Supercritical Fluids International (Bermejo & Cocero, 2006b; Bermejo et al., 2009; Marrone et al., 2004; Xu et al., 2012). Notably, much of the work by those companies has been limited to SCWO and funded by defense-industry contracts, with only more recent developments focused on municipal waste and energy (Bermejo et al., 2009).

Foster Wheeler developed several full-scale SCWO projects for multiple branches of the U.S. Armed Forces. Their systems were based on transpiring-wall reactor designs for the destruction of U.S. Army munitions. Sandia National Laboratories continues to operate one of Foster Wheeler's systems (Veriansyah & Kim, 2007). Foster Wheeler successfully tested the same system on halogenated solvents for the U.S. Navy as well as nerve agent hydrolysates (e.g., HD, GB, and VX) and propellants (Veriansyah & Kim, 2007).

General Atomics tested very similar systems to those of Foster Wheeler for comparable defense-industry purposes (Veriansyah & Kim, 2007). General Atomics took their designs a step further with a full-scale design for chemical weapons demilitarization as well as operational, compact SCWO systems for U.S. Navy shipboard-waste destruction.

EcoWaste Technologies designed and built the world's first commercial SCWO plant for Huntsman Chemical in 1994. The plant was a tubular reactor system constructed for the

destruction of organic wastes produced on-site at Huntsman's Austin Research Laboratories (Bermejo & Cocero, 2006b; Veriansyah & Kim, 2007; Xu et al., 2012). The system was able to operate at about half the cost of incineration, even without integrated energy recovery (Veriansyah & Kim, 2007).

Chematur Engineering acquired a world-wide licensing agreement in 1995 for the EcoWaste SCWO process developed for Huntsman Chemical, in order to further develop the process in Europe and elsewhere (Bermejo & Cocero, 2006b; Bermejo et al., 2009; Mahmood & Elliott, 2006; Veriansyah & Kim, 2007). Chematur developed the SCWO process into an integrated energy production and waste destruction system, which they marketed under the trade name AquaCritox®. Chematur built two pilot plants, one in Europe and one in Japan for Shinko Pantec (Bermejo & Cocero, 2006b; Bermejo et al., 2009; Mahmood & Elliott, 2006; Veriansyah & Kim, 2007). Chematur constructed a full-scale SCWO facility for Johnson Matthey in the UK (Bermejo et al., 2011; Bermejo & Cocero, 2006b).

HydroProcessing built a full-scale, tubular SCWO unit in 2001 specifically for sewage sludge destruction in Harlingen, Texas (Bermejo & Cocero, 2006b; Bermejo et al., 2009; Griffith & Raymond, 2002; Marrone et al., 2004; Sloan et al., 2008; Svanström et al., 2004; Veriansyah & Kim, 2007; Weismantel, 2001; Xu et al., 2012). The Harlingen system was touted as the first U.S. SCWO system dedicated to sewage sludge and operated for about four years achieving very high destruction efficiencies (Bermejo & Cocero, 2006b; Bermejo et al., 2009; Griffith & Raymond, 2002; Marrone et al., 2004; Sloan et al., 2008; Svanström et al., 2004; Veriansyah & Kim, 2007; Weismantel, 2001; Xu et al., 2012). However, the system ultimately failed due to inadequate pump durability and insufficient flow velocities, which resulted in salt precipitation, corrosion, and plugging (Bermejo & Cocero, 2006b; Bermejo et al., 2009; Marrone et al., 2005; Sloan et al., 2008; Xu et al., 2012).

SuperWater Solutions began jointly developing a pilot-scale, SCWO system with the City of Orlando, Florida in 2007. The high-velocity, tubular reactor system is designed to destroy sewage sludge (Sloan et al., 2008). Reported pilot runs of the system indicate that high velocities have been able to keep solids in suspension, thus eliminating clogging caused by inorganic solids (Sloan et al., 2008). Development apparently is continuing, and additional details are not available.

Supercritical Fluids International purchased all intellectual property rights to the AquaCritox® technology from Chematur in 2007 (Bermejo et al., 2009; Marrone & Hong, 2009). Supercritical Fluids International has further refined the process into a sewage sludge destruction system with integrated, electrical generation and value-added production (e.g., CO_2, phosphorus, and silica) (Bermejo et al., 2009). The AquaCritox® system appears to be the only fully integrated and turn-key system currently available for commercial sale. The basic flow schematic for the AquaCritox® system is shown (Figure 4).

Supercritical reactor sizes (sufficient for 99.99% decomposition of biomass) can be commercially scaled down by orders of magnitude, making such systems suitable for much smaller physical footprints as long as viable salt precipitation control mechanisms are

deployed. Scalability could facilitate the location of conversion systems at the source of wet waste production, enabling on-site use of the energy contained in the waste streams while simultaneously avoiding waste storage and transportation. The successful process intensification of wet-biomass conversion into an energy-efficient and sustainable pathway has many potential markets and public benefits.
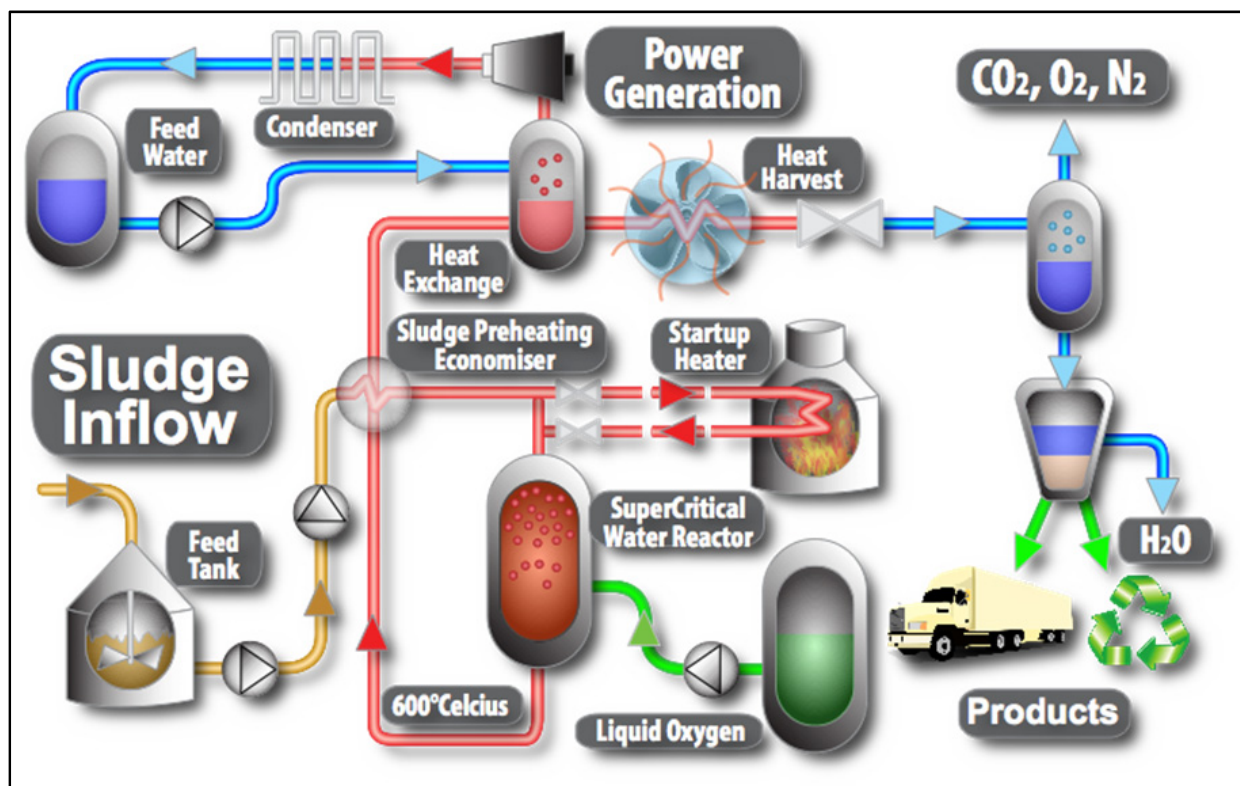

Figure 4. AquaCritox® System Flow Schematic, Adapted from (SCFI, 2012).

4. Conclusion

Solutions to contemporary, waste-management and energy problems are becoming universally multi-objective (Klemes & Stehlík, 2006). Important considerations include reductions in energy consumption and associated costs, while simultaneously stemming harmful pollutant releases. Ideally, wastewater treatment facilities would produce clean water effluent, operate at net-plus energy, and have near-zero pollutant releases to the environment (Münster & Lund, 2010; Villar et al., 2012; Weismantel, 1996). Currently, wastewater treatment facilities do produce clean water, but only at immense energetic and environmental expense. Municipalities collectively spend about $6 billion annually in the U.S. just reducing the moisture content of sewage sludge (CSS, 2011; Kim & Parker, 2008; USEPA, 2009). After moisture reduction, the millions of tons of still-moisture-laden sludge are then typically dried, at great expense, prior to disposal by conventional methods (Abuadala et al., 2010; Borán et al., 2010; CSS, 2011; Demirbas et al., 2011; Eriksson et al., 2008; Fytili & Zabaniotou, 2008; Harrison et al., 2006; Kruse et al., 2000; NASNRC, 1996, 2002). The disposal of the increasingly pollutant-laden and voluminous

leftover sludge is also expensive and is becoming more problematic. Sewage sludge contains heavy metals, harmful organic compounds, and pathogens that are potentially hazardous to human and environmental health. Consequently, current disposal methods are increasingly unpopular with the public. It is likely that climbing wastewater-related energy costs, coupled with more stringent environmental regulations, will ultimately lead to the adoption of new wastewater processing and sludge disposal techniques (Dutourníe & Mercadier, 2005).

Given that sewage sludge is mostly water, hydrothermal decomposition via supercritical water gasification (SCWG) is viewed as a promising technology for sustainable sludge disposal. The unique properties of supercritical water enable SCWG to quickly destroy wet biomass such as sludge while efficiently producing marketable byproducts (e.g., heat, H_2, and CO-rich fuel gases) (Kalinci et al., 2009). Adding catalysts or oxidants to SCWG (i.e., CSCWG or SCWO) can further reduce operating costs by creating self-sustaining reactions under milder conditions with even shorter residence times.

As a research area, the number of SCW-related studies has grown exponentially during the last 10 years. Much of this research is focused on the technological SCW limitations, notably reactor corrosion and plugging, which seems to be nearly resolved (Bermejo et al., 2009; Calzavara et al., 2005; Marrone & Hong, 2009). Many supercritical-water techniques have been repeatedly shown to thoroughly destroy wet wastes such as sewage and oily sludges. Most SCW technologies, nonetheless, remain relatively new and untested beyond laboratory applications, relegating SCW systems to emerging-technology status (Youssef et al., 2010b). Likewise, SCW designs are somewhat niche-based, with few flexible enough to deal with the wide range of mixed wastes generated by municipalities and industry. Commercial viability sets a very high bar for an emerging technology to clear, and, so far, no SCW systems have yet reached the bar of true commercialization in the wastewater industry (Savage, 2009).

The destruction of sewage *in-situ*, without separating the water from the sludge offers the best potential for sustainable wastewater processing. Furthermore, sewage has a relatively high energy content in the form of organic matter and can be used to produce renewable energy (Chen et al., 2011; Fodor & Klemes, 2011). The annual energy entrained in U.S. sewage sludge is estimated at 1.5 Quads. The *in-situ* destruction of sewage sludge via SCW processes would help municipalities gain massive and immediate financial savings, while simultaneously addressing a critical and vexing wastewater management problem (Fytili & Zabaniotou, 2008). The widespread use of hydrothermal decomposition of municipal wastewater solids would shift the view of sewage sludge as a costly disposal problem to that of a valuable, sustainable energy source (Tsai et al., 2009). Supercritical-water technologies (particularly SCWO) can be integrated into existing wastewater treatment facilities as bolt-on, end-of-pipe systems (Bermejo et al., 2009; Brunner, 2009a; Cocero Alonso et al., 2002; Gloyna & Li, 1993), and might very well be the panacea for municipal sewage sludge.

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Addendum

Research publication trends

The annual trend in the number of published studies provides a suitable proxy of the importance of promising research areas (Savage, 2009). The amount of supercritical water (SCW) research has grown at a near-exponential rate since 1988 (Figure 5A). Data were collected using a Web of Science search for "supercritical water". The data were plotted biennially, and a trend line was fitted to the growth curve. Despite the fact that SCW research dates back to the 1970s, there were only a total of 22 hits from the Web of Science database prior to 1988.

The amount of supercritical water gasification (SCWG) research has grown at a near-exponential rate since 1996, and shows no signs of slowing (Figure 5B). The proportion for the larger category of supercritical water research is still relatively small (23.1%), but is poised to lead supercritical water research in the next two or three years. Data were collected using a Web of Science search for "supercritical water" and "gasif*". The data were plotted biennially, and a trend line was fitted to the growth curve. There were a total of ten search hits from the Web of Science database prior to 1998. Catalytic supercritical water gasification (CSCWG) research is one of the newest areas of study within the scope of supercritical water science. Interest in CSCWG has grown considerably over the past two decades, with most of the research taking place in the last ten years (Azadi & Farnood, 2011). Indeed, the amount of CSCWG research has grown exponentially since 2000, and shows no signs of slowing down (Figure 5C). The data were collected using a Web of Science search of articles with the terms "supercritical water", "gasif*", and "cataly*". The data were plotted biennially, and a trend line was fitted to the growth curve. There were a total of only five search hits from the Web of Science database prior to 2000. Catalytic gasification now makes up a full two thirds of the SCWG research, and if the growth rate continues, it is likely that CSCWG will increase its current 15.4% proportion of all supercritical water research. The most prevalent message from recent works is that CSCWG

shows great scientific promise as well as notable technologic and commercialization feasibility for hydrogen production from biomass (Calzavara et al., 2005). Supercritical water oxidation (SCWO) research dates back a bit further than either SCWG or CSCWG, but most of the research occurred as greater interest developed at universities, national laboratories, and government agencies in the late 1980s (Barner et al., 1992). Despite its early beginnings, SCWO now has only a slightly larger percentage of overall supercritical water research (27.8%) than SCWG (23.1%). The amount of SCWO research grew rapidly from about 1988, and continues to grow (Figure 5D) but at a much more moderate rate than either SCWG or CSCWG. The data were collected using a Web of Science search for "supercritical water" and "oxida*". The data were plotted biennially, and a trend line was fitted to the growth curve. There were a total of only three search hits from the Web of Science database prior to 1988.
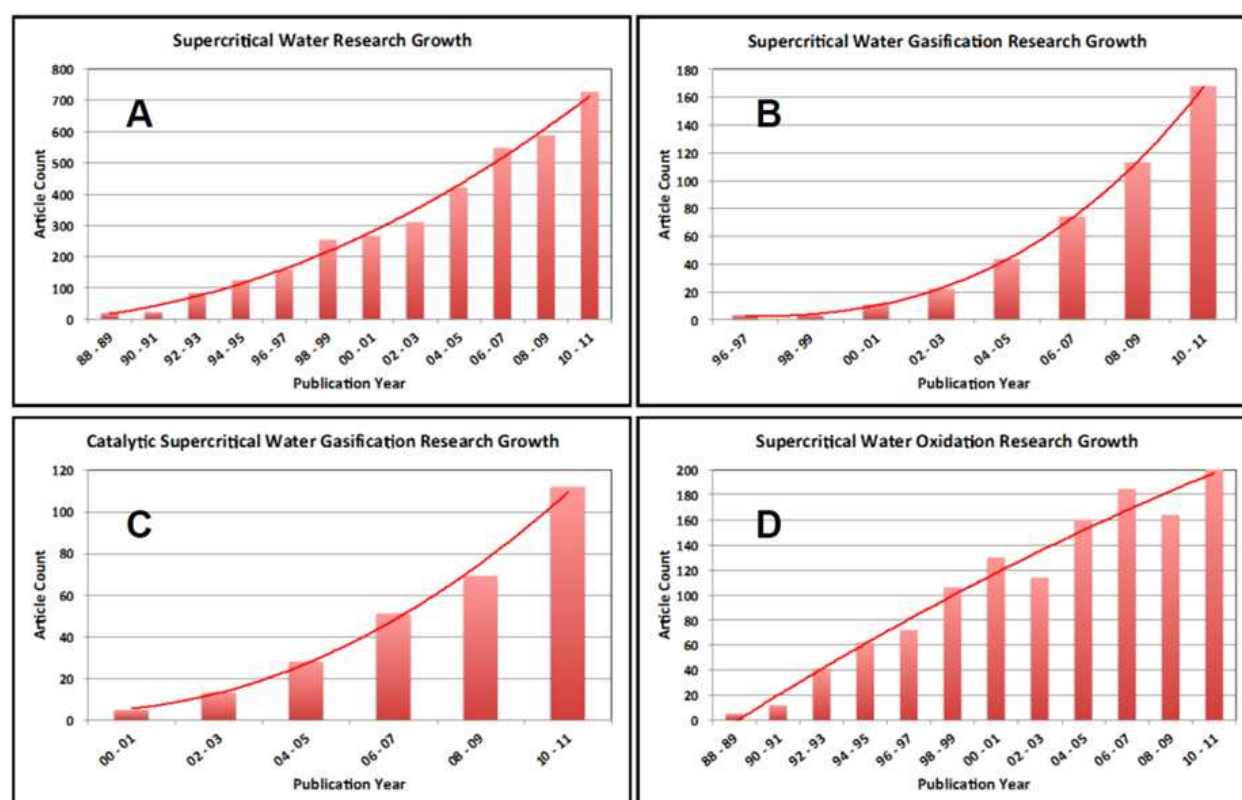

Figure 5. Supercritical Water Research Publication Trends.

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