CONTROL IN SUPERCRITICAL WATER OXIDATION SYSTEMS USING AN EQUILIBAR BACKPRESSURE REGULATOR

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ABSTRACT

A technical challenge in continuous supercritical water systems is control of backpressure. Our team at Duke University and the University of Missouri operate two supercritical water oxidation units, one on a laboratory scale and one on a pilot scale. Here, we document the design and corresponding qualitative results of the backpressure regulation systems in the SCWO units, specifically the use of different diaphragm materials in a diaphragm operated backpressure regulator, as produced by Equilibar, LLC. Depending upon the diaphragm material and thickness, there seems to be a tradeoff between the diaphragms' sealing ability and their longevity. The observations below could be useful for applications in which backpressure control is needed other than just supercritical water systems.

BACKGROUND

Supercritical Water Oxidation of Biomass: At temperatures above 375°C (710°F) and 220 bar (3,200 psi), water becomes supercritical. Figure 1 at right shows a phase diaphragm of water. Biomass (organics) and oxygen are readily soluble in supercritical water (SCW) and conditions allow rapid processing of biomass. When oxygen is present, the organic component of biomass undergoes an exothermic oxidation reaction in SCW which converts the biomass into carbon dioxide (CO_2) vapor and releases heat. This is called supercritical water oxidation (SCWO). It is easy to see why such a process would be useful in treating low value or hard-to-handle biomass and other wastes.

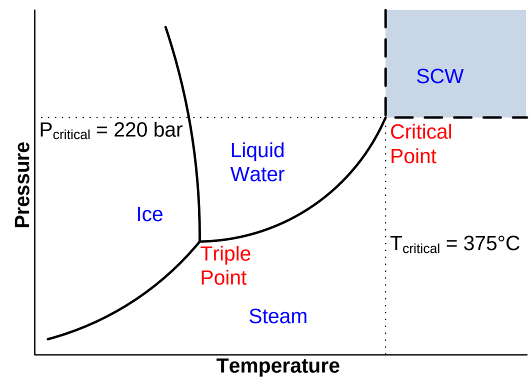


FIGURE 1. Phase diagram of water showing supercritical water conditions.

The SCWO Process: Our team at Duke University and the University of Missouri is developing SCWO technology and currently operate a laboratory scale unit (Missouri) and a pilot scale unit (Duke). Figure 2 shows the process flow diagram of the depressurization subsystem of the SCWO unit at Duke. Leaving the reactor and heat exchangers (which are not shown in Fig. 2) is a three phase mixture of permanent vapor (CO_2, N_2, O_2), liquid (water) and low concentrations of suspended solids (inorganic ash and salts). In the first high pressure vessel, the liquid (and solid) phase is separated from the vapor phase. The liquids drain into a second high pressure vessel in which the solids are filtered. The water is depressurized using capillary tubing. The solids are removed intermittently. The vapor in the first vessel is depressurized through a backpressure regulator (BPR).

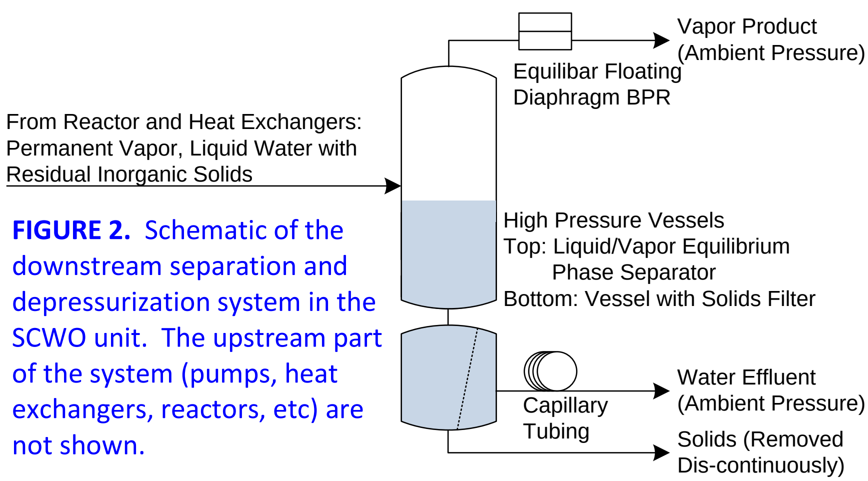


FIGURE 2. Schematic of the downstream separation and depressurization system in the SCWO unit. The upstream part of the system (pumps, heat exchangers, reactors, etc) are not shown.

Pressure Control Issues

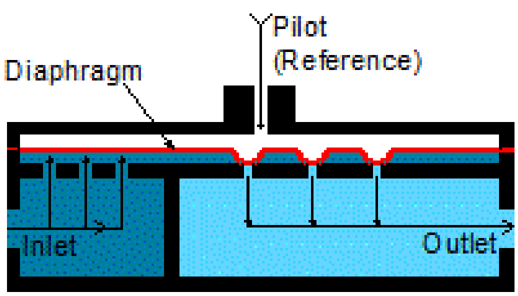
Importance of Uniform Pressure: During SCWO, it is important to maintain a constant pressure above the critical pressure of water so that the reacting fluid remains fully in the supercritical phase. Fluctuating pressure could result in phase changes which could hinder or completely stop the reaction and require shut down. The SCWO system is designed such that the pressure in the entire system is maintained by the backpressure regulator.

Sources of Pressure Fluctuation: The SCWO system has two potential sources or pressure fluctuation that need to be dampened by the backpressure regulator: (1) pulsation of the pumps; and (2) exothermic heat of reaction. The biomass pump and the water pump both use a piston and are subject to large pressure changes between the suction and stroke of each cycle. The exothermic heat of reaction causes changes in density down the length of the reactor. Because the biomass feed in non-homogenous, the heat of reaction is not uniform and causes additional pressure fluctuations. Some of this variation is absorbed by the vapor and supercritical fluid in the system. The remainder is mitigated by the backpressure regulator.

BACKPRESSURE REGULATION

Continuous supercritical water systems require reliable backpressure control. It is desirable to use backpressure regulators to depressurize the fluid (vapor, liquids, and residual solids) for operational simplicity. However, there is not a backpressure regulator commercially available that can withstand continuous operation at pilot or industrial scale flow rates due to excessive wear and potential cavitation effects when depressurizing liquids with suspended solids. In the SCWO unit at Duke, a backpressure regulator is used to only depressurize the vapor phase as shown in Figure 2. However, back pressure regulators are still susceptible to excessive wear even when only contacting vapors.

FIGURE 3. Cross sectional sketch of the research series backpressure regulator. Taken from www.equilibar.com.



In the SCWO units at Duke and Missouri, we use Equilibar Research Series backpressure regulators with floating seal support, as detailed at www.equilibar.com and in US Patent 6,886,591 and shown in Figure 3. In Figure 3, it is implied that the inlet is the high pressure fluid and the outlet is at low (often ambient) pressure. Figure 4 shows a picture of the backpressure regulator used in the Duke SCWO unit.

Below we report observational results using different diaphragms in the backpressure regulators. The maximum c_v of the Duke BPR is 0.58 and of the Missouri BPR is 0.10. The results presented here are mostly qualitative and give observational insights into potentially successful designs. In this report, we only document the use of metal diaphragms. Polymer diaphragms are not an option for this application because of the potentially very hot fluid temperatures. Table 1 lists the different diaphragms that were tested.

FIGURE 4. Left Picture: The BPR as installed in the Duke SCWO unit. High pressure fluid enters from the left and leaves at ambient pressure on the right. The smaller process line entering from the top is the charged pressure applying force to the floating diaphragm. Right Picture: The BPR with the top and diaphragm removed.

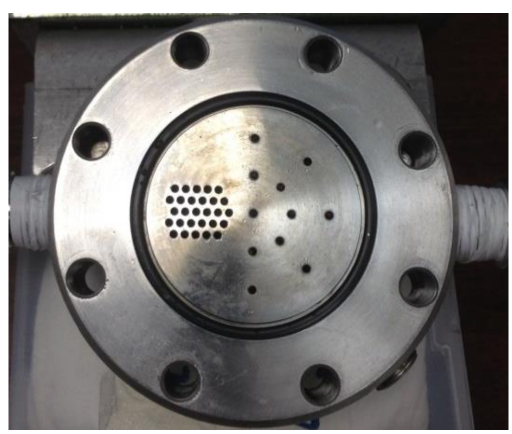


TABLE 1. A list of the different diaphragms, in order of increasing elasticity modulus, tested in the SCWO units at Duke and Missouri.

Diaphragm	Material	Elasticity Modulus (psi)	Hardness (Rockwell)	Thickness (in)

1	Titanium, Grade 5 (Ti)	6.1×10^6	C30	0.032"
2	Bronze 510	17.5×10^6	B92	0.032"
3	Stainless Steel 316 (SS316)	29×10^6	B88	0.01" and 0.032"

RESULTS

Below are pictures of several diaphragms used in the SCWO units at Duke and Missouri. Because of the experimental nature of the investigation, the diaphragms were exposed to a range of conditions. To date, the most used diaphragm has a little over 30 hours of operation, and more experience and operational time is needed to draw definitive conclusions. It should be noted that higher temperatures than reported below are expected in future experimentation. In the lab scale SCWO unit (Missouri), a floating seal backpressure regulator was used to depressurize the liquid phase effluent, which was mostly water but also contained low concentrations of inorganic, insoluble, suspended particles (ash and salts) remaining from the SCWO reaction. Because of the damage to the diaphragms in the Missouri unit, we did not expose any of the thicker diaphragms shown below in the pilot unit (Duke) to solids and minimized the amount of water depressurized through the floating seal backpressure regulator. The thinner diaphragms (0.01", called SS8 below) were provided by Equilibar; the thicker diaphragms (0.032") were fabricated in-house at Duke.

Figure 5a. Top view of a SS8 diaphragm used in the Missouri SCWO unit. Diaphragm was exposed to liquid phase effluent in a lab scale SCWO unit without prior filtering of residual solids. It appears as if the accelerating solids through the backpressure regulator caused the damage to the diaphragm, as flow rates were estimated to be too low to show signifiant caviation effects.

Material:	SS 316
Thickness:	0.01"
Operational Time:	20 hours
Flow Rate:	0.015 - 0.025 gpm
Fluid:	Water (no filtering)
Pressure Range:	3400 - 3600 psi
Temperature Range:	20 - 25°C

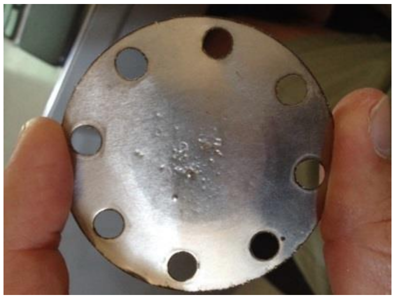


Figure 5b. Top view of a SS8 diaphragm used in the Duke SCWO unit. Diaphragm was primarily exposed to air, but also some liquid water. The diaphragm burst after about 5 hours of operation (center indentation is punctured, may not be visible in picture).

Material:	SS 316
Thickness:	0.01"
Operational Time:	5 hours
Flow Rate:	0.10 - 0.25 gpm water, 10-20 scfm air
Fluid:	Air and Water
Pressure Range:	3600 - 3700 psi
Temperature Range:	5 - 15°C

Figure 5c. Top and bottom view of a SS8 diaphragm used in the Duke SCWO unit. Diaphragm did not burst, but showed clear signs of wear after only 2 hours of operation with only vapor.

Material:	SS 316
Thickness:	0.01"
Operational Time:	2 hours
Flow Rate:	14-32 scfm
Fluid:	Air
Pressure Range:	3600 - 3700 psi
Temperature Range:	5 - 15°C

Figure 5d. Top and bottom view of a stainless steel diaphragm, thicker than the standard SS8, used in the Duke SCWO unit. This thicker stainless steel diaphragm was only subjected to 2 hours of pressure testing, and showed some signs of fatigue.

Material:	SS 316
Thickness:	0.032"
Operational Time:	2 hours
Flow Rate:	14-32 scfm
Fluid:	Air
Pressure Range:	3600 - 3700 psi
Temperature Range:	5 - 15°C

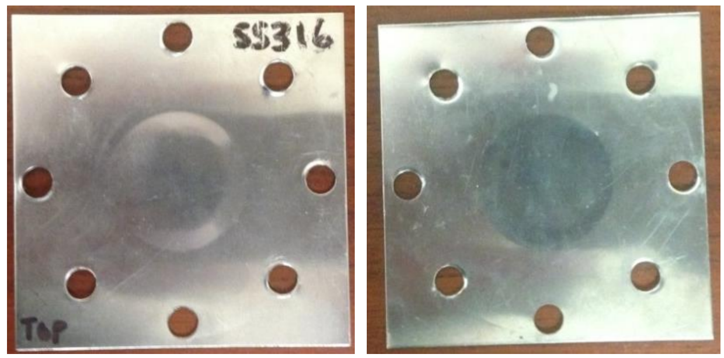


Figure 5e. Top and bottom view of a bronze diaphragm used in the Duke SCWO unit. Diaphragm was made in-house, after consulting with Equilibar on this research applicat. The diaphragm has shown no signs of wear after over 30 hours of operation. In the bottom view, it looks as if the diaphragm is showing indentations similar to above in Figure 5c; these are just dis-colorations and not actual indentations in the metal.

Material:	Bronze 510
Thickness:	0.032"
Operational Time:	30 hours
Flow Rate:	14-32 scfm
Fluid:	Air
Pressure Range:	3600 - 3700 psi
Temperature Range:	5 - 50°C

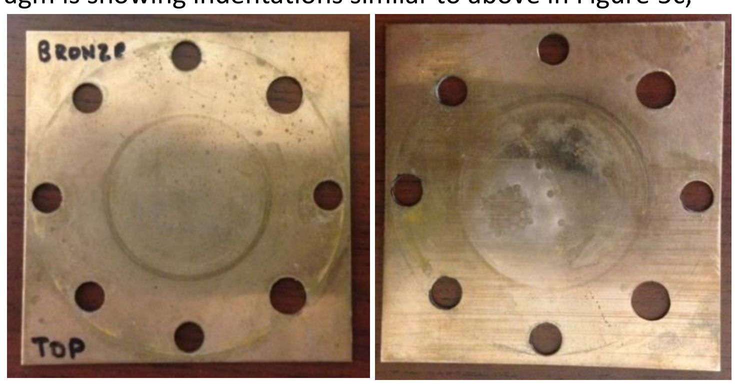
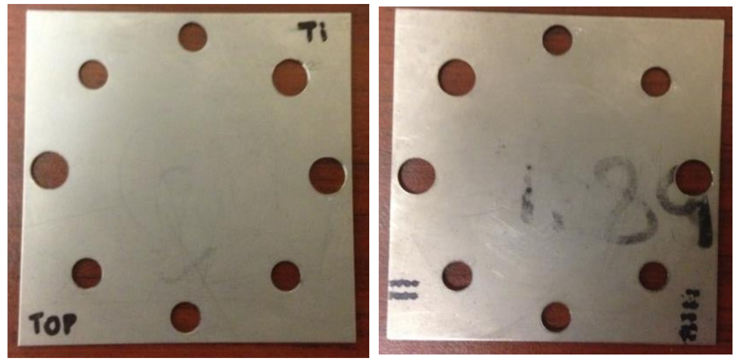


Figure 5f. Top and bottom view of a titanium diaphragm used in the Duke SCWO unit. Diaphragm was made in-house, and has shown no signs of wear after over 12 hours of operation.

Material:	Titanium 5
Thickness:	0.032"
Operational Time:	12 hours
Flow Rate:	14-32 scfm
Fluid:	Air
Pressure Range:	3600 - 3700 psi
Temperature Range:	5 - 30°C



DISCUSSION

It should be noted that the results shown here have been generated with only limited operational time, and maximum expected temperatures of the fluid in contact with the back pressure regulators has not been reached. Below are some noteworthy observations.

1. *Thickness:* In general, thicker diaphragms do not create as perfect of a seal as thinner diaphragms, however, thicker diaphragms appear to last longer. This is supported by comparing the thinner stainless steel diaphragms in Figures 5b and 5c to the thicker stainless steel diaphragm of Figure 5d. In the pilot scale SCWO plant, some leakage is acceptable and thus, longevity is more important than the ability to form a perfect seal, and so diaphragms of 1/32" have been and will continue to be used for most experimentation.
   Thicker diaphragms have less flexibility relating to the third power of the thickness. Therefore the diaphragm has more difficulty flexing to seal over the orifice at lower flow rates. Equilibar recommends keeping the working flow in the diaphragm active range for better performance. The active range is defined as the range of flows corresponding to the max c_v *of the unit to the minimum* c_v *limited by the diaphragms ability to hold pressures at low flows.*
2. *Elasticity Modulus:* Looking at Figure 3 above, it can be seen that the sealing surface is caused by a slight deformation in the diaphragm, and can be seen visually in the pictures in Figures 5b and 5c. Thus, the diaphragms with lower elasticity moduli (and thus less rigidity) are able to form better seals. However, these less rigid materials might also be expected to fatigue and fail much faster than a material with higher elasticity modulus, although operation with bronze and titanium diaphragms (lower elasticity modulus than stainless steel) has not shown any increased sign of wear. Note that these statements are conjectural, as we have not operated long enough to draw conclusions.
3. *Hardness:* For similar reasons as with the elasticity modulus, diaphragms from with high hardness do not form as perfect of seals as materials with less hardness. It is unknown if there is a correlation between hardness and longevity, as high hardness can also be correlated with brittleness. However, due to elevated fluid temperatures during normal operation of the SCWO plant, it is unlikely that any of the metals tested will experience brittleness.

Of the diaphragms tested above, the thin (0.01") stainless steel diaphragms were able to form a perfect seal at 4,000 psi (no detectable leakage), whereas the thick (0.032") stainless steel, bronze, and titanium diaphragms did not form a perfect seal. There was a noticeable leak at 4,000 psi with the thicker diaphragms; however, the leak was not quantifiable with the equipment in the SCWO unit (detection limits are limited to minimum recordable flow of 0.1 scfm). In our system, this small amount of leakage is acceptable in exchange for the increased reliability and life of the diaphragm.

CONCLUSIONS AND FUTURE WORK

Because of energy and operational issues, it is generally accepted that supercritical water oxidation systems need to be operated continuously while minimizing down time for maintenance in order to profit from the benefits of the technology. To achieve continuous operation, reliable backpressure regulators are needed. It seems that Equilibar backpressure regulators could be capable of continuously depressurizing vapor products of SCWO, and only require periodic replacement of the diaphragms. However, it is clear that these same backpressure regulators cannot continuously handle liquids, especially liquids with residual amounts of inorganics solids such as after oxidation of biomass in supercritical water. Future work should revolve around improving the diaphragm to create an effective backpressure regulation system that can continuously depressurize all three phases of the effluent of SCWO of biomass continuously.

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