Method of Liquid Inactivation by Supercritical Ozone

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ABSTRACT

Ozone is a tri-atom molecule with powerful oxidizing ability and decay to oxygen with a half-life of approximately thirty minutes. Although the precise mechanisms of ozone disinfection are not firmly established, the effectiveness is already well documented. Elevating ozone into supercritical state allows better mixing with liquid by narrowing density differences. Utilizing the virtue ozone and supercritical fluid (SFC) is viable to extend its application. Here, we review the previous method for generating supercritical ozone/carbon dioxide mixture, and then propose a novel method to obtain supercritical ozone for liquid inactivation and other applications.

Keywords: supercritical, ozone, inactivation, green chemistry

1 INTRODUCTION

When a substance is taken to its specific critical temperature, T_c, and pressure, p_c, and is unable to be condensed to liquid by pressure alone, it exists in a so called supercritical fluid (SCF) state. Critical temperature and pressure are usually defined as the maximum pressure at which a gas can be converted to a liquid by an increase in temperature, and the maximum temperature at which a liquid can be converted to gas by an increase in pressure, respectively. The vaporization curve ends at the critical point in a pressure-temperature diagram. At a temperature above the critical point, the vapor and liquid have the same density. The critical parameters for some common fluids in analytical studies can be found in the literature [1], in particular, T_c = 31.3 ◦C and p_c = 7.38 MPa for the most common SCF (CO_2). Supercritical CO_2 (sc CO_2) is widely used because of its convenient critical parameters, low cost, and safety aspects (low toxicity, nonexplosive).

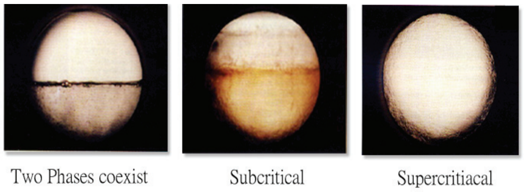

Figure 1 : Transition of the interface of different states

At the supercritical state, the interface between liquid and gas is undetermined as in figure 1. The physical properties of a SCF are intermediate between those of a typical gas or liquid. For example, the diffusivity of a SCF is intermediate between a liquid and a gas and the viscosity is similar to a gas. The density of a SCF can be changed by varying the applied pressure on the fluid and can range between that exhibited by a gas to liquid-like values when the fluid is compressed at high pressures. As the density of a SCF is typically 100–1000 times higher than that of a gas and more comparable to that of a liquid, molecular interactions can be strong owing to short intermolecular distances. Consequently, the solvating properties are similar to those of liquids, but with significantly lower viscosities and higher diffusion coefficients. The viscosity is 1-2 orders lower and the diffusion coefficients is 1-2 orders higher in SCF compared with liquid result in a significantly enhanced mass transfer of solutes in applications such as disinfection and extraction with SCF than in conventional extractions with liquids. Higher pressure at constant temperature increases density and solvating power, whereas higher temperature at constant pressure decreases density and hence solvating power. In short, a SCF is essentially as a solvent with continuously adjustable solvent power.

Ozone is a powerful oxidant and decay to oxygen with a half-life of approximately 30 minutes. Although the precise mechanism of ozone disinfection is not firmly established, the effectiveness is already well documented [2]. The self-decomposing property makes it more eco-friendly in comparison to other sterilant like formaldehyde and peracetic acid. Ozone as a gas sterilant is useful for surface disinfection, however, liquid inactivation is not suitable due to gas/liquid mass transfer limitation. Elevating ozone to supercritical state is viable to enhance the mixing by reducing the density difference. The critical parameters for ozone are 55 atm and -12°C, ie., ozone and carbon dioxide mixture is in the supercritical state while operated in the condition of $scCO_2$. Utilizing the benefits of ozone and SCF is viable to extend the application of SCF (figure 2).

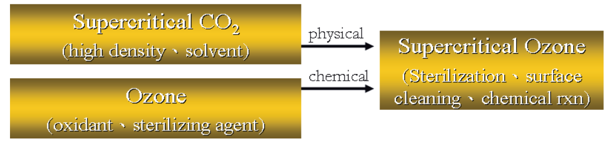

Figure 2 : Utilizing the benefits of both SCF and ozone is viable to extend their application

2 SUPERCRITICAL OZONE

In previous studies, researchers apply supercritical ozone mainly on the photoresist cleaning of solid surfaces, decomposing large molecules into smaller ones and then removed by solvated in supercritical fluid. The same technique can be adopted in disinfection. The followings are few documented supercritical ozone methods.

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2.1 Ozone Booster Method

Supercritical ozone environment can be built-up by adopting ozone booster is sketched in figure 3[3]. The approach including placing a contaminated wafer in a high pressure reactor vessel and treating the wafer with supercritical or near supercritical ozone built-up by the booster is especially useful in removing patterned photoresist from a wafer, removing residual small particles, and precision drying semiconductor wafers that have undergone various lithographic processes. The method is straightforward, however, some drawbacks exist, such as:

1. Ozone compatible booster is expensive, and leakage might arise safety issues.
2. Higher operational and maintenance cost.
3. A large ozone generator is needed to supply sufficient ozone.
4. Unable to monitor the ozone concentration while operating at high pressure.

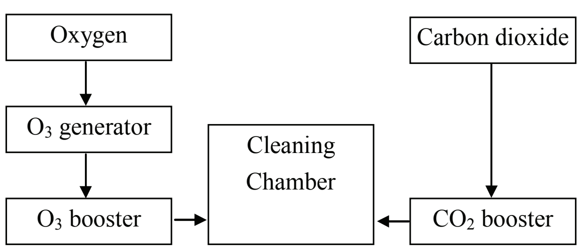

Figure 3: Supercritical ozone obtained by utilizing boosters.

2.2 Ozone Absorbent Method

Ozone in the fluid is absorbed in the absorbing bed under pressure and desorbed by another high pressure fluid such carbon dioxide to obtained high pressure ozone mixture (figure 4) [4]. Two absorbing beds are designed to absorb in one and desorb in another alternatively to generate continuous supercritical ozone. The supercritical fluid is utilized for the application of surface cleaning or disinfection. The following drawbacks are addressed.

1. High operating cost due to the complexity of absorbing bed.
2. Impurities in the beds might shuffle with ozone mixture and result in subsequent pollution.
3. Ozone concentration is unable to monitor under high pressure [5].
4. The decay of absorbent might diminish the amount of ozone.

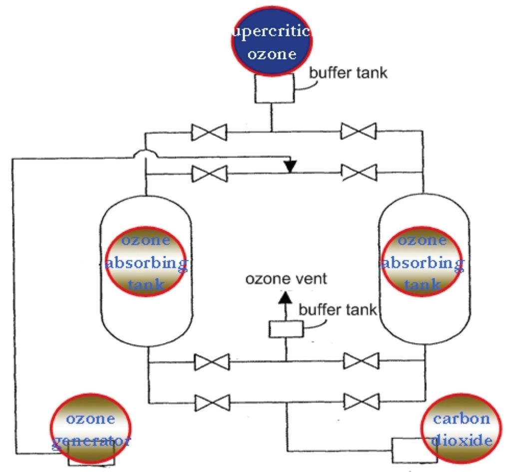

Figure 4: Supercritical ozone obtained by absorption /desorption mechanism

2.3 Ozone Pretreatment Method

Post-etch residue, including photoresist remnants, anti-reflective coatings and other materials used for patterning a substrate can be removed by supercritical fluid with ozone pretreatment [6]. Two reaction chambers are constructed in series to decompose larger organic compounds by ozone in the first, and then the smaller molecules are transferred to the second for dissolution by supercritical fluid. Figure 5 is the flowchart of surface cleaning with $scCO_2$ pretreated by ozone.

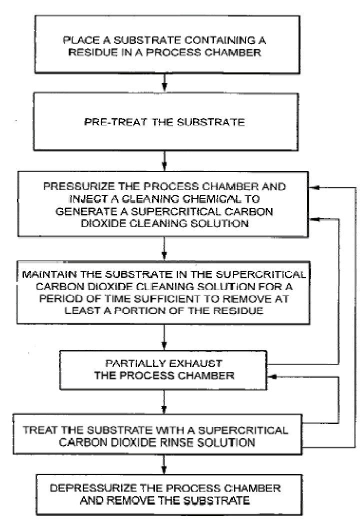

Figure 5: Method of surface cleaning with $scCO_2$ pretreated by ozone

Similarly, some characteristics is summarized as,

1. Pretreated with ozone and clean by scCO2.
2. Two reaction chambers and a transfer device are needed, increase devices complexity.
3. Larger ozone generator is necessary to provide sufficient ozone concentration.

3 ENRICH OZONE CONCENTRATION BY CIRCULATION

Sealing materials with less anti-oxidation ability are aged much faster in concentrated ozone environment, and it often results in serious leakage and fails to build up supercritical state. Pressurizing concentrated ozone will make it even worse. To avoid the leakage, one principle is to enrich ozone concentration under ambient condition by circulation instead of pressurizing ozone directly. The proposed system for producing supercritical ozone comprising a inactivation chamber, an ozone generator, a circulating pump, and an ozone analyzer is sketched in figure 6. The ozone-circulating device is coupled to the ozone generator and the ozone analyzer to draw the gas in the chamber at atmospheric pressure, taking the gas to flow through the ozone generator so as to convert oxygen in the gas into ozone. The gas with higher ozone concentration is then driven back to the chamber. Such a circulation process can continuously increase the ozone concentration in the reactor to enrich the ozone environment [7]. Because the concentration of ozone is increased under atmospheric pressure, the leakage issue caused by the erosion of high pressure ozone can be avoided. Using a simple ozone generator to produce ozone can prevent generated ozone from containing impurities, and allows the system to have a simple structure and low manufacturing cost.

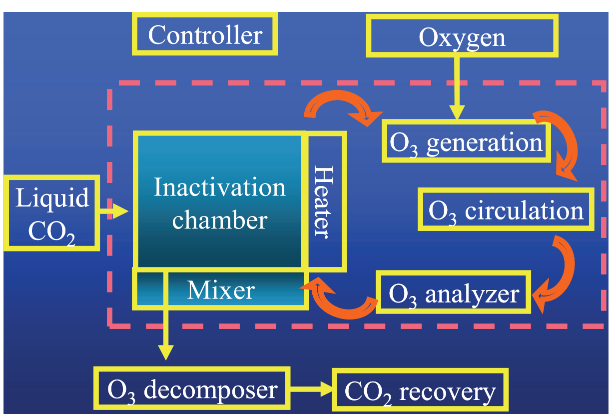

Figure 6: Sketch of the apparatus of inactivation by Supercritical ozone

Introducing the liquid carbon dioxide into the reactor to pressurize the interior of the reactor to above 70 bars and raising the temperature to 30 °C can achieve the supercritical state for CO_2/ozone mixture. The system for producing supercritical ozone needs only a single reactor so that the system has a simple structure, low manufacturing cost and a space-saving advantage.

The reactor can be connected with a temperature regulation device for controlling the temperature of the interior of the reactor. The temperature regulation device comprises a heater, a cooler, and a temperature controller. The PID temperature controller controls the heating and cooling to achieve constant temperature control.

The system for producing supercritical ozone may further comprise a stirrer, which is used when a stirring operation is required. For example, the supercritical ozone and non-sterile liquid can be mixed using the either a magnetic stirrer or mechanical stirrer.

As the flowchart in figure 7, the solution is first input into the chamber where ozone concentration is monitored and enriched by continuous circulation. When the designed concentration is achieved, liquid carbon dioxide is connected to build up the supercritical fluid environment. The solution and the supercritical fluid with closer densities can have better contact by mixing to accomplish liquid inactivation. After a certain inactivation time, fluid pressure is released slowly to avoid solution flow out, ozone is decomposed into oxygen and carbon dioxide is recovered. The ozone decomposer can comprise activated carbon or catalyst such as manganese dioxide to decompose ozone, and a heater can also be managed to decompose ozone by heat.

Consequently, the advantages of this method comparing to the others include low cost, higher safety, no contamination issue, and ozone concentration is measurable in operation.

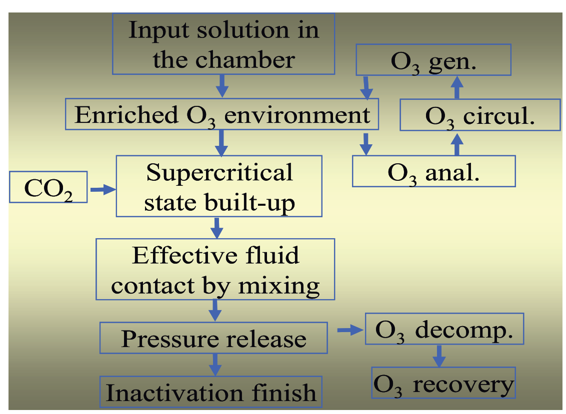

Figure 7: Supercritical ozone inactivation flowchart

Table 1: Comparison of supercritical ozone techniques

Item	O_3 enriched by circulation	O_3 booster	O_3 absorbent	O_3 pretreatment
Fluid	ozone	Ozone	Ozone	CO2
Ozone enrich method	Ozone circulation	Ozone booster	Ozone absorber	Ozone generator
Equip. complexity	Simple	Complex	Complex	Complex
Generator scale	Small	Large	Large	Large
Ozone leakage	No	Yes	No	-
Cost	Low	High	High	Low
Concentration	Medium	High	Medium	-
Safety	High	Low	Medium	High
Ozone measurement	Easy	Hard	Hard	Easy
Application	Sterilization Cleaning	Sterilization Cleaning	Cleaning	Cleaning
Pollution	Low	Low	High	Low
Stability	High	Medium	Low	high

4 CONCLUSIONS

Ozone is a powerful oxidant and able to operate under supercritical state to accomplish liquid inactivation by mixing with supercritical fluid. In the paper, we review several methods including using ozone booster and ozone absorbent to enrich ozone concentration in accompanying carbon dioxide to achieve supercritical ozone environment, and propose a ozone concentration enrichment approach by circulation to avoid possible leakage and contaminants for liquid inactivation.

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