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Mass Flow Controlled Evaporation System

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Abstract. In many (CVD-) processes, there is an increasing demand for delivering reactants as near liquid vapours. Controlling vapours, however, is often a delicate matter. The proven method is the well known "bubbler" system, with its inherent problems: poor stability and poor reproducibility, due to the extremely high sensitivity for changes in temperature. The system described in this paper is an evaporation system, based on mass flow controllers. The vapour is controlled in the liquid phase; thus the amount of vapour is controlled, stable and reproducible, independent of temperature or pressure. Special attention is given to the new possibilities that come into reach with this system, e.g. fluids with very low vapour pressures which are unstable at high temperatures and mixtures can be evaporated properly in this system.

1. INTRODUCTION

In CVD processing there is a growing tendency to use liquid precursors instead of gases. This means that the fluid to be dosed is a liquid, but it has to be in vapour phase for the reaction. The use of liquid precursors is popular, because many liquid precursors are less harmful, less flammable, less corrosive or less poisonous, than gaseous ones. Many liquid precursors give better results in CVD processes. In MOCVD, Metal Organic CVD, a gaseous precursor for the wanted metal is often not available.

The flow control of gases can easily be realised with gas mass flow controllers. For the (liquid) vapour dosage, the subject is more complex. Bubbler derived systems are commonly used in this field, but the performance is poor. There is an urgent need for a system that can control vapour, out of a liquid in a stable, reproducible and flexible way.

Bronkhorst High-Tech BV develop and produce mass flow equipment. One of their products is the liquid flow controller for small liquid flows. Based on this instrument, an evaporator system was developed, the CEM: The Controlled Evaporation, Mixing system.

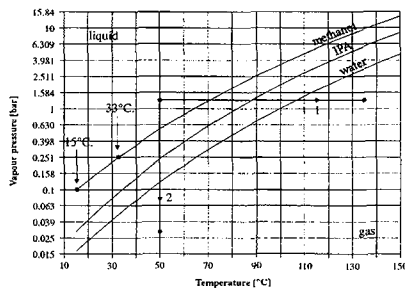


Figure 1a. Vapour pressure lines of some fluids

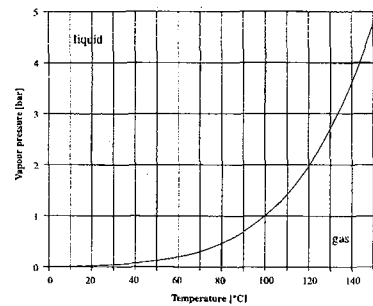


Figure 1b. The vapour pressure line of water (linear pressure scale)

2. THEORETICAL BACKGROUND

In figure 1a, the vapour pressure line of some liquids, including water are plotted.

The transition from liquid to gas can basically be realized in two ways, by rising the temperature (see (1) in figure 1a) or by lowering the pressure (see (2) in figure 1a).

Rising the temperature is straightforward, it is illustrated in daily life in boiling water. Decreasing pressure can be done in two ways: the system pressure can be decreased, simply by pumping down the vessel. But another way is to decrease the (partial) pressure of the fluid by diluting the fluid at constant pressure. Again in daily life this can be seen from water vapour in surrounding air at ambient conditions. So with a boiling point of 100°C, water can beyond doubt, be in the vapour state at ambient conditions.

The shape of the vapour pressure function, plotted on a logarithmic pressure axis is globally the same for most fluids, see figure 1a. The difference is a shift in the temperature axis.

The relation between temperature and vapour pressure is rather sharp. Small variations in the temperature give relatively large deviations in the vapour pressure. This can be seen in the vapour pressure line of figure 1b, where for the pressure, the linear scale is used. In this way, the presentation of figure 1a, with a log scale for the pressure is commonly used, as it gives a rather straight line.

For the transition of a fluid from liquid into gas, the vaporisation energy ΔH_{vp} , is needed. In table 1, the vaporization energy of some liquids is given. As can be seen, the vaporization energy per mole of a liquid is fairly constant. This is the reason why the vaporization per gram of water (a light molecule) takes much energy.

	M (g)	ΔH_{vp} (kJ/mol)	ΔH_{vp} (kJ/kg)
Water	18	46.134	2563
Iso-propyl Alcohol IPA	60.1	42.780	713
Methanol	32.04	39.953	1247

Table 1. The vaporization energy of some liquids.

Example: Deliverance of methanol (vapour) mixed with O₂ for an combustible mixture.

Properties of Methanol: M= 32.04 g
 $\Delta H_{vp} \approx 40$ kJ/mol
 Vapour pressure @ 20 °C is approximately 130 mbar.

Process parameters: Pressure is atmospheric.
 Temperature of vaporisation is room temperature: approx 20 °C.
 Vapour flow = nominal 150 g/h.

1. The (carrier) gas flow needed

For complete vaporisation at 20 °C, the partial pressure of Methanol has to be lower than 130 mbar. So at 20 °C and atmospheric pressure, the ratio (mol) between gas and vapour must be higher than

$$\frac{1013}{130} \approx 7.8$$

This means that at 150 g/h 4.7 mol/h, at least

$$\frac{7.8 \cdot 4.7}{60} \cdot 22.4 \approx 13.7 \text{ l}_n/\text{min gas (O}_2\text{)}$$

is needed for complete vaporization.

2. Energy needed for the vaporization

Mass flow = 150 g/h \approx 0.0013 mol/s, and with $\Delta H_{vp} \approx$ 40 kJ/mol, the vaporization energy per second for this flow is: 52 J/s (W).

Remark: From the vapour pressure curve, see figure 1a, it can be seen that with only a small rise in temperature, far less carrier gas is needed for complete vaporization. At 33 °C, the vapour pressure is 2.5 times higher than at 15 °C, so 2.5 times less gas is needed.

3. BUBBLER BASED SYSTEMS

In the field of liquid dosing, the bubbler is a well known instrument. Most of the used systems are somehow derived from the bubbler concept. See figure 2.

A bubbler is a vessel filled with the liquid that has to be evaporated and dosed. The liquid is evaporated by heating it with a temperature controlled heater device.

The pressure in the bubbler is defined by the temperature of the liquid. The relation between vapour pressure and temperature is very sensitive. See figure 1. As a result, the vapour flow too is very sensitive for temperature changes. The bubbler can be used with- or without carrier gas. See figure 2a, 2b and 2c.

Figure 2. The Bubbler

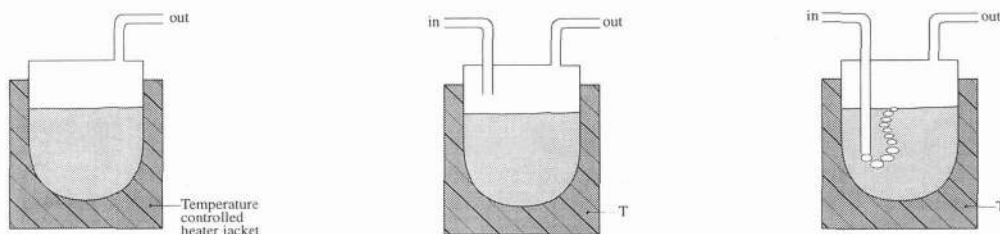


Figure 2a. Without carrier gas.

Figure 2b. Carrier gas over the liquid.

Figure 2c. Carrier gas through the liquid.

3.1. The bubbler concept (see figure 3)

In the bubbler system where no carrier gas is used, two types can be classified:

Figure 3a. The bubbler with a (manual) restriction in the outlet. The flow is controlled by the temperature (implies vapour pressure) and the flow restriction.

Figure 3b. The bubbler with a mass flow controller controlling the vapour in the outlet.

An other series of bubbler systems are based on the use of carrier gas. Again the temperature of the bubbler is controlled to achieve a certain constant vapour pressure in the vessel.

Three types can be distinguished:

Figure 3c. Vapour flow is controlled by the carrier gas flow.

Figure 3d. Vapour flow is controlled by the carrier gas flow and the pressure in the bubbler is held constant.

Figure 3e. In the system of figure 3e the thermal conductivity of the carrier gas which flows into the bubbler is compared with the conductivity of the saturated carrier gas that leaves the bubbler. The change in conductivity is a measure for the vapour content in the flow. The vapour flow can be controlled with this signal by controlling the carrier gas flow and/or the temperature of the bubbler.

The different configurations of the bubbler mentioned above are a result of the many ways of optimisation of the bubbler concept to achieve stable vapour flow. In all bubbler configurations, the vapour flow is directly related to the supply (vapour) pressure in the vessel. This pressure depends on the temperature according to the vapour pressure line. See figure 1b.

The main problems with bubbler systems, poor reproducibility and instability of the flow are a result of the sharp sensitivity of the vapour pressure to temperature.

3.2. Optimization of the bubbler

The temperature control can be optimized by measuring the temperature more accurately or by stirring the fluid.

Controlling a stable vapour flow can be optimized when the absolute pressure in the vessel in a system with carrier gas is controlled by a pressure controller. See figure 3d. When the pressure of the bubbler is held constant, at constant temperature of the bubbler, then the ratio gas/vapour is constant and the vapour can be controlled by the carrier gas flow.

In some cases, corrections for the level of the fluid in the bubbler are made. The flow depends on the level of the fluid because the vapour pressure changes, when the fluid becomes less pure, or when the fluid disintegrates. Also, the pick up rate of the carrier gas changes by changing liquid level.

The variation sketched in figure 3b, where a mass flow controller is used to control the pure vapour, is rather attractive. Stable, flexible flow control and good precision can be realized. But in this system, substantial limitations are present:

1. The precursor has to be at high temperature to get high (vapour) pressure.
2. The temperature of the mass flow controller and downstream tubing must be high, to prevent recondensation.
3. The flows are restricted because of 1 and 2.

The high temperatures for the liquid and for the mass flow controller cause problems because a precursor can disintegrate when kept on high temperature for a long time. Mass flow controllers for high temperature are expensive, delicate and subsequently often not very precise and repeatable. The electronics have to be located out of the instrument, away from the heated zone.

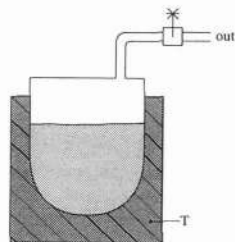


Figure 3a. Restriction in outlet

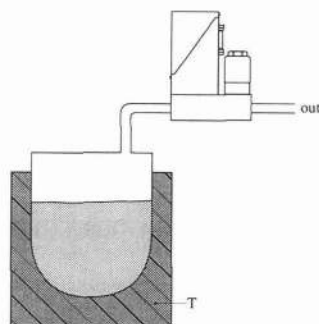


Figure 3b. Mass flow controller in the outlet

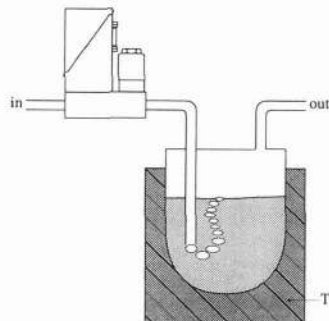


Figure 3c. The vapour flow is controlled by the carrier gas flow.

4. THE CEM, CONTROLLED EVAPORATION AND MIXING SYSTEM (see the photo)

The design of the CEM is essentially different from the bubbler. It is a vapour delivery system, based on a liquid mass flow controller.

The precursor is controlled in its natural (liquid) state, at ambient conditions, and consequently evaporated in a continuous way with the aid of a carrier gas. See figure 4. The liquid flow controller consists of a thermal mass flow meter and a liquid flow valve. The flowmeter is for small liquid flows, in ranges of 1 g/h to 500 g/h. Many of the CVD processes use vapour flows in this flow range.

In the CEM system, liquid, controlled by the liquid flow controller, is transported into the heat exchanger by the carrier gas. Here the vaporization takes place. The temperature of the heater is controlled. In this way, the temperature of the vapour may be chosen between ambient temperature and 140 °C. Special attention is paid to the continuity of the vapour flow and the (time) response of the system. The liquid leaving the liquid control valve is immediately dragged away into the heated zone by the carrier gas. The inner volume of the mixing chamber is minimised. Therefore, the response of the system is mainly defined by the response of the liquid- and gas mass flow controllers of the CEM.

The temperature and pressure are no critical parameters in the CEM system, these parameters are only boundary conditions. The temperature of vaporisation for instance, has to be under the vapour pressure line, it is not critical at all.

4.1. Boundary conditions for the CEM system

A. The physical conditions e.g.: partial pressure and temperature in the evaporator must be chosen so that the state of the fluid is a vapour.

B. The vapour flow is limited by the maximum power available in the heater. (for the moment, some 100 Watt)

C. The system always needs a minimum flow of (carrier) gas, to lead the liquid into the heated evaporation zone.

A special type of the CEM is realised by controlling the vapour direct into a low pressure system with a regular liquid flow control valve. No carrier gas is involved here. However, this system is considerably limited. This is caused by the disturbance of the vapour flow as the vaporisation is not smoothly (explosive expansion from boiling effect). The maximum flow is limited by the heat transport to the place of vaporization, this is the outlet of the liquid flow valve. The maximum flow is limited to some 20 g/h of most liquids, and to only 5 g/h water.

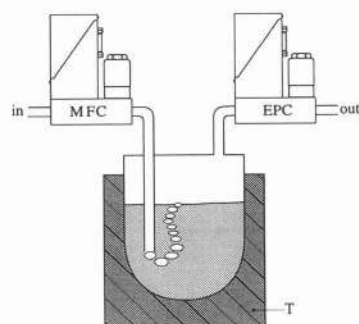


Figure 3d. The pressure in the bubbler is held constant, by an electronic pressure controller.

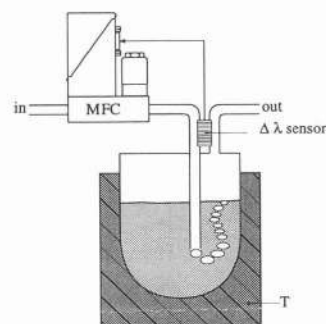
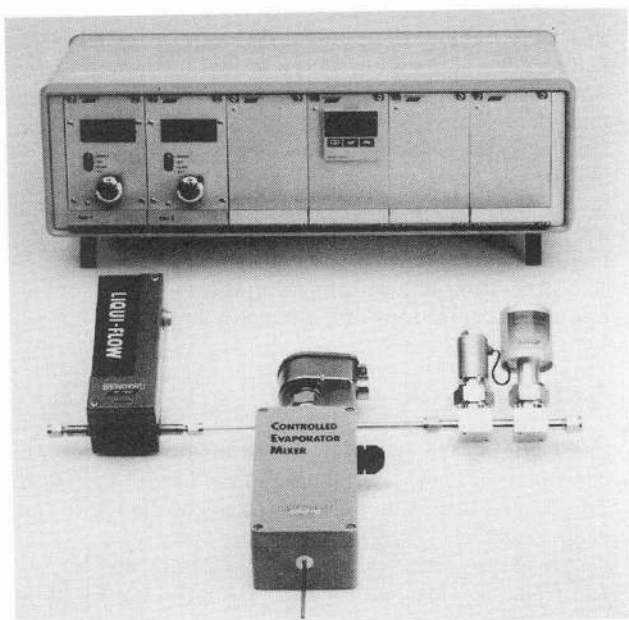


Figure 3e. The vapour flow is controlled by a thermal conductivity sensor



5. COMPARISON OF THE CEM WITH THE BUBBLER SYSTEMS

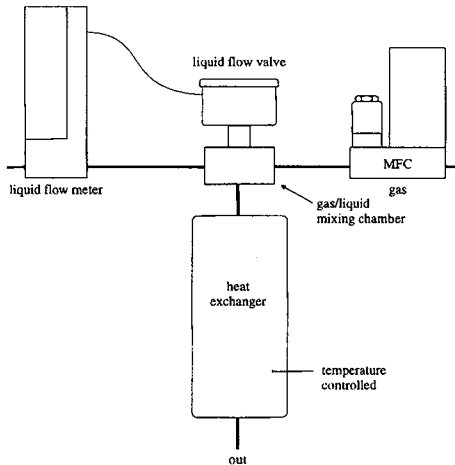


Figure 4. The CEM.

In the CEM, the flow rate is not critical for T and p. So the stability is high, the flow is stable and repeatable. The flows are adjustable with the flow controllers. With the CEM, the mixing ratio (mass or mole) can be controlled directly, and the ratio can be adjusted easily. The system response is rather fast compared to the bubbler. The pick-up rate is usually higher in the CEM.

In the CEM, the working temperature is reduced. The vaporization temperature is lower than in the bubbler and the temperature of the liquid can remain at room temperature while in a bubbler the temperature of the liquid is often high for a long period.

A disadvantage of the CEM might be that the delivery of the liquids may be restricted to the use of the bubbler. The liquids are usually delivered in Quartz (bubbler) vessels. For the CEM, a certain pressure on the supply vessel is needed for the liquid flow controller. The pressure that may be put on these

Quartz containers is limited. It can also be stated that the bubbler system is attractive due to the simplicity of the design. The performance of the CEM, however, is incomparably superior.

With the CEM approach, also new opportunities are created.

It is possible to evaporate mixtures now. In a bubbler based system this is not possible because the fluid with the highest vapour pressure will evaporate first.

Another new feature of this system is the possibility to evaporate at pressures (much) higher than atmospheric, as long as the physical conditions are not violated.

6. APPLICATIONS

In a large number of applications, water is evaporated. Generating a certain humidity, but also delivering water vapour for an oxidation step in the silicon processing can be the aim.

The delivery of Tri-chloro-ethane (or Trans-LC nowadays), for scrubbing a Quartz reactor in an inter-deposition CVD processing step.

Dosing Cupra-select, or a mixture containing Cupra-select, in a CVD process.

Delivering $TiCl_4$ vapour for various purposes. Titanium is deposited in APCVD processes for hard layers or corrosive resistant layers, but $TiCl_4$ is also used as a precursor in a Laser Enhanced CVD process. (Laser writing of Titanium.)

Fuel mixed with air for combustion experiments.

The generation of a certain calibration mixture for calibration of analysis systems; for instance ppm or ppb concentrations of Toluene in air.

7. CONCLUSION

In the High-Tech approach of vapour flow delivery, the vapour flow is being measured and controlled in the liquid phase and the carrier gas is only an assisting medium.

This results in substantial advantages of the CEM system, compared with the bubbler related evaporators.

Fast response time, repeatability, accuracy and low working temperature are the main advantages while also new possibilities come within reach such as evaporating at high pressures and evaporating of mixtures.

With this system, a second generation evaporation system has been born.