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Improving run-time stability with aerosol jet printing using a solvent add-back bubbler

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Abstract

Aerosol jet printing is a non-contact process capable of printing on conformal and flexible surfaces. Aqueous or solvent nano-inks are pneumatically atomized under nitrogen. The atomizing gas flow through the atomization cup leads to evaporation and removal of volatile solvent(s). As the ink solid loading fraction increases with the loss of solvent during atomization, the rheological changes eventually lead to instabilities in print output. A potential solution to this problem is to moisten the incoming atomizing gas with a solvent add-back system. In this study, neat co-solvent solutions of ethanol and ethylene glycol at 85 : 15 and 30 : 70 mixing ratios were atomized using nitrogen flow rates ranging from 600 to 1 000 $cm^3 \cdot min^{-1}$ (ccm, cubic centimeters per minute). It was observed that ethanol, being the more volatile solvent, was depleted from the neat solution at a much higher rate than ethylene glycol. When nitrogen gas was passed through a bubbler prior to atomization, an excessive amount of ethanol was returned to the neat solution. The solvent loss rate from an ethanol rich neat solution (80 %) was higher compared to an ethylene glycol rich neat solution. Perfecting the solvent add-back rate to an ink will enable longer print runs in a manufacturing environment.

Keywords: aerosol jet printing, direct write, ink stability, solvent evaporation rate

1. Introduction and background

Direct-write (DW) printing refers to a class of additive manufacturing processes in which inks or pastes are digitally deposited in any desired geometric pattern onto a substrate of interest. Substrate examples could include molded plastic parts, 3D printed parts, composite panels, etc. Direct-write printing is rapidly gaining importance in several industries. For example, significant weight reductions are possible when electrical traces are printed onto or even within a non-planar component surface instead of using externally routed wires and connectors (Kessler et al., 2009). Printed antennas that conform to non-planar surfaces provide tremendous flexibility in location, number, and size of antennas (Deffenbaugh et al., 2013). A broad spectrum of electronic components such as ring oscillators (Ha et al., 2013), thin film transistors (Jones et al., 2010), and hydrogen sensors (Liu et al., 2012) can be printed directly on a wide-variety of substrates, regardless of whether or not the substrate is planar.

Whereas conventional lithography processes have much higher feature resolutions than current DW printing technologies, DW processes are able to deposit a much wider array of materials. Practically speaking, any nano-material that can be synthesized in ink form can be DW printed. For example, solid oxide fuel cells employing yttria-stabilized zirconia (YSZ) electrolyte layers and YSZ-nickel oxide composite anodes have been aerosol jet printed (Sukeshini et al., 2012). Specifically, aerosol jet printed poly(3-hexylthiophene) (P3HT) polymer semiconductor inks for use in printed transistors was reported by Kim et al. (2013). Aerosol jet printing was also used to deposit biologically active inks (Grunwald et al., 2010).

When used in printed electronics applications, DW processes are also attractive from an environmental perspective. Rather than plating copper, conductive inks (e.g. copper, silver, gold, etc.) can be selectively printed thereby minimizing material use and hazardous waste disposal.

For any relatively new manufacturing technology, the transition from a research and development environment to a production environment is largely dictated by factors such as cost, throughput, and process stability and repeatability. This paper specifically focuses on run-time printing stability on a production scale aerosol jet printing platform when using co-solvent blended ink systems that have, in many cases, vastly different boiling points or evaporation rates.

1.1 Aerosol jet printing

1.1.1 Process fundamentals

Aerosol Jet (AJ) printing is a DW printing technique for depositing a pre-set pattern or layout (Hon, Li and Hutchings, 2008). It is capable of producing fine pitch structures below 50 µm using nano-ink suspensions with particle sizes up to a recommended maximum of approximately 700 nm and with an ink viscosity range from 0.7 to 2 500 mPa·s (Goth, Putzo and Franke, 2011). The AJ process steps are illustrated in Figure 1, and typical process parameters are given in Table 1. A fluid can be atomized in the reservoir either pneumatically with nitrogen gas or ultrasonically. The maximum wet droplet diameter is typically on the order of 2 to 5 µm (Mahmud et al., 2010).

Although AJ printing has been used for numerous interesting applications produced in very small quantities, the process as a manufacturing option has not been widely studied. Hoerber et al. (2011) studied the effect of process parameters on printed line width and thickness. They observed that the line width increased with increases in atomization and sheath flow rates. Also, line width and height increased when the number of print passes was increased. Conversely, line width decreased when the translation speed increased.

Sukeshini et al. (2010) studied the effect of varying the nozzle stand-off distance and virtual impactor exhaust flow rate values. It was observed that for the YSZ ink used in the study, the amount of material deposited increased to a maximum; and then, decreased as virtual impactor exhaust flow rate was increased. Several studies determined a process parameter window that influences the line quality, electrical properties and adhesion of AJ printed silver lines (Verheecke et al., 2012; Mahajan, Frisbie and Francis, 2013).

1.1.2 Current aerosol jet challenges

For AJ printing to be a viable production tool, run-time stability will depend on a consistent ink composition. Many inks are colloidal dispersions in a solvent (single solvent or co-solvent). Surfactants are optionally included to lower the ink surface tension, and dispersants are often used to prevent particle coagulation.

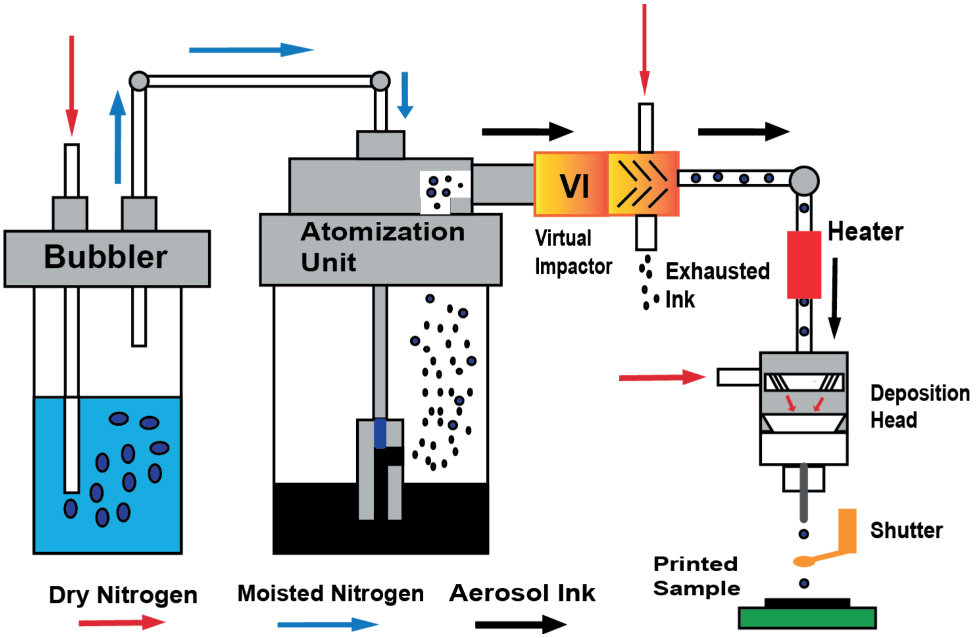

Figure 1: Schematic representation of the aerosol jet printing process

Table 1: Aerosol jet printing process parameters

Process Parameter	**Units**	**Recommended Range**
Atomization Flow Rate	$m^3 \cdot s^{-1}$	8.33×10^{-6} to 20.0×10^{-6}
Virtual Impactor Flow Rate	$m^3 \cdot s^{-1}$	6.67×10^{-6} to 18.3×10^{-6}
Sheath Gas Flow Rate	$m^3 \cdot s^{-1}$	0.50×10^{-6} to 1.67×10^{-6}
Tube Heater Temperature	°C	20 to 90
Platen Temperature	°C	20 to 90
Nozzle Diameter	µm	100, 150, 200, 250, 300
Nozzle Stand-Off Distance	mm	3 to 10

During atomization, nitrogen gas flow over the ink surface causes preferential loss of high volatile components through evaporation. Preferential component loss will create changes in the physical ink properties. The high vapor pressure (low boiling point) solvent removal rate would depend on the dry atomizing gas flow rate (nitrogen gas flow rate) over the solvent, and the component fractional vapor pressure as illustrated in Equation 1.

$$Q_V = Q_{N2} \cdot \frac{P_V}{P_T \cdot P_V} \qquad [1]$$

where Q_v is the flow rate of solvent vapors ($m^3 \cdot s^{-1}$), Q_{N2} is the flow rate of atomizing gas ($m^3 \cdot s^{-1}$), P_T is the total pressure (kPa), and P_v is the vapor pressure (kPa) of volatile solvent component.

With a 69 kPa (10 psi) atomization cup pressure, Figure 2 illustrates the simulated loss of ethanol (P_v) from the atomizing cup via evaporation at different nitrogen flow rates and temperatures using Equation 1. Antoine's equation was used to calculate the partial pressure due to ethanol as a function of temperature. To illustrate, a common solvent blend used in aerosol jet printing are ethanol and ethylene glycol mixtures. In comparison, ethanol has a low normal boiling point (78.4 °C) and higher normal vapor pressure (5.95 kPa) than ethylene glycol (197.1 °C and 0.0075 kPa, rescpetively). Ethylene glycol loss during atomization, therefore, is approximately 0.1 % that of ethanol. Consequently, in co-solvent inks containing both low and high vapor pressure constituents, one can effectively focus on the high vapor pressure solvent component when trying to control ink stability. As shown in Figure 2, the expected rate of solvent transfer with the atomization gas, and therefore solvent loss in the atomization cup, increases significantly with both carrier gas flow rate and temperature.

We propose to control solvent loss by feeding the atomizing gas through a bubbler system prior to the atomizing cup as seen in Figure 1. The idea was that moist atomizing gas will "add back" solvent into the atomizing cup. We are not aware of any research using such an add-back method. The aim of this paper, therefore, was to study the impact of this solvent add-back approach by monitoring the solvent blend composition during atomization over time while holding the atomization cup temperature constant at 23 °C.

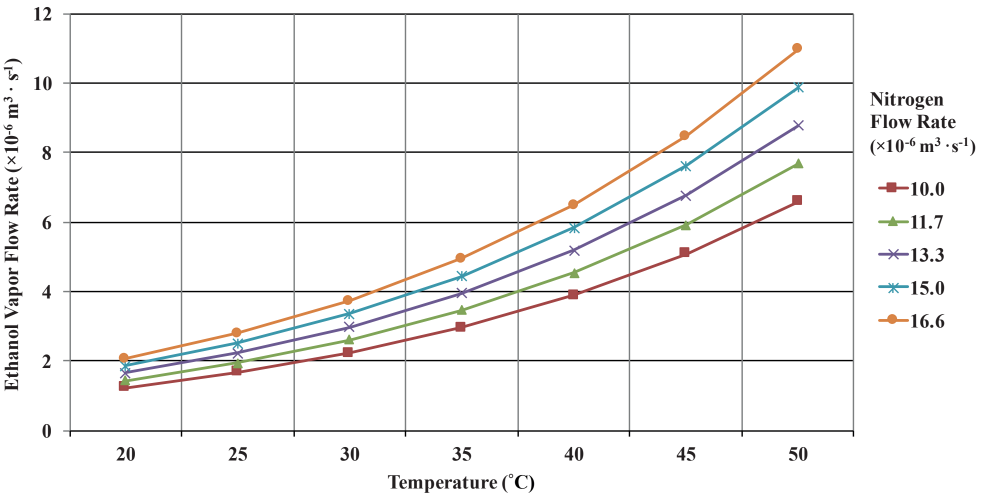

Figure 2: Simulated ethanol loss from the atomization cup as a function of different nitrogen flow rates and atomization cup temperatures

2. Materials and methods

All experiments were conducted using an Optomec Aerosol Jet system equipped with two pneumatic atomizers. A bubbler add-back system, as seen in Figure 1, contains ethanol, the more volatile solvent component (vide infra). Nitrogen gas was bubbled through the solvent, thereby transferring solvent vapor. The saturation state, of the more volatile component, in the atomization cup will depend on flow rate and cup temperature. In this study, atomization cup temperature was kept constant at approximately 23 °C.

In order to study AJ ink stability as a function of process parameter values, two types of neat co-solvent solutions of ethylene glycol (higher boiling point, lower vapor pressure) and ethanol (lower boiling point, higher vapor pressure) were prepared. No pigment components were added in this study. The co-solvent blend is used in a number of commercial nano-inks, and was therefore a representative co-solvent system of practical significance. The less volatile ink blend consisted of 30 % mass fraction of ethanol and 70 % mass fraction of ethylene glycol. The more volatile ink blend consisted of 85 % mass fraction of ethanol and 15 % mass fraction of ethylene glycol. These two inks were AJ printed over an extended period of time (210 minutes or 3.5 hours) at different atomization flow rates ranging from 10.0×10^{-6} $m^3 \cdot s^{-1}$ to 16.6×10^{-6} $m^3 \cdot s^{-1}$. Experiments were conducted without the solvent add-back system, and then again, with the solvent add-back system. Samples of the neat solutions were extracted from the atomization cup at 30 minute time intervals in order to determine the stability of the neat solution as measured by the relative proportions of the two co-solvents.

The relative ethanol and ethylene glycol proportions, in a given sample, were determined by measuring the refractive indices on an Abbe Refractometer. Using the rule of mixtures, the percentage of ethanol in any sample can be determined using Equation 2 in order to quantitatively determine the rate at which the more volatile ethanol solvent was being lost during atomization.

$$\textit{Mass fraction of Ethanol} = \frac{RI_{EG} - RI_{S}}{RI_{EG} - RI_{Eth}} \times 100\ (\%) \qquad [2]$$

where RI_{EG} is the refractive index of ethylene glycol (measured value = 1.43854), RI_{S} is the refractive index of the extracted ink sample, and RI_{Eth} is the refractive index of ethanol (measured value = 1.36163).

3. Results and discussion

3.1 Ink stability without solvent add-back

Figures 3 and 4 show results of experiments for the low volatility and high volatility inks, respectively, run without the solvent add-back system.

Figures 3 and 4 clearly demonstrate a substantial ethanol loss in a relatively short amount of time (3½ hours) when atomization was done with dry nitrogen gas. For the 30 % ethanol ink, nearly half of the ethanol was lost in just three hours of printing. The high vapor pressure solvents (e.g. ethanol) allow aerosol ink droplets to rapidly dry on the substrate. As high vapor pressure co-solvent is depleted in the ink, the drying speed and surface energy of the ink changes – sometimes dramatically. As the drying time of printed lines increases due to loss of high vapor pressure co-solvents in the atomizing cup, the printed lines have time to both (1) spread out and form wider traces; or, (2) retract into discontinuous beads resulting from a surface tension increase. These printed fluid and drying dynamics are common for many print processes using liquid inks. For example, an ink containing 85 % ethanol would have a starting surface tension of about 23 $mN \cdot m^{-1}$ (data not shown). Upon complete ethanol loss in co-solvent ink, the surface tension would match that associated with ethylene glycol (47.7 $mN \cdot m^{-1}$) resulting in a dynamic increase in contact angle with the substrate. Practically speaking, this means that the quality of the printed lines, as indicated by line width, thickness, and overspray, will change as the high vapor pressure solvent is depleted. Figures 3 and 4 point towards a strong need for an alternative approach to atomization with high vapor pressure co-solvent blends. The aforementioned solvent add-back system was a relatively simple low-cost approach.

3.2 Ink stability with solvent add-back

In order to quantitatively assess the solvent add-back system effectiveness on ink stability, a second set of experiments were run using the solvent add-back system (see Figure 1). The bubbler contained the more volatile ethanol since the rate of evaporation of ethylene glycol at room temperature is substantially lower than that of ethanol. Figures 5 and 6 show results of experiments for the 30 % and 85 % ethanol inks at 10.0×10^{-6} $m^3 \cdot s^{-1}$ (low flow) and 16.6×10^{-6} $m^3 \cdot s^{-1}$ (high flow) nitrogen atomization flow rates, respectively. The dry nitrogen (no solvent add-back) results are also plotted for comparison.

Figure 5 shows ethanol concentration for the low ethanol (30 % mass fraction) solution. The ideal outcome would be a horizontal line indicating that the ethanol concentration remains constant over the 3½ hours of

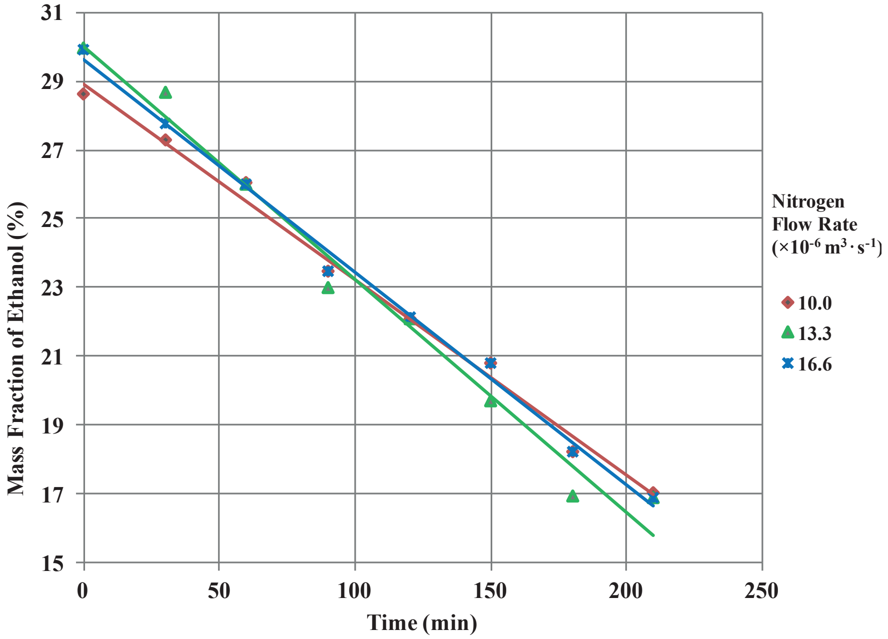

Figure 3: Mass fraction of ethanol versus time plot for atomization a 30 % ethanol 70 % ethylene glycol co-solvent mixture without the bubbler add-back system

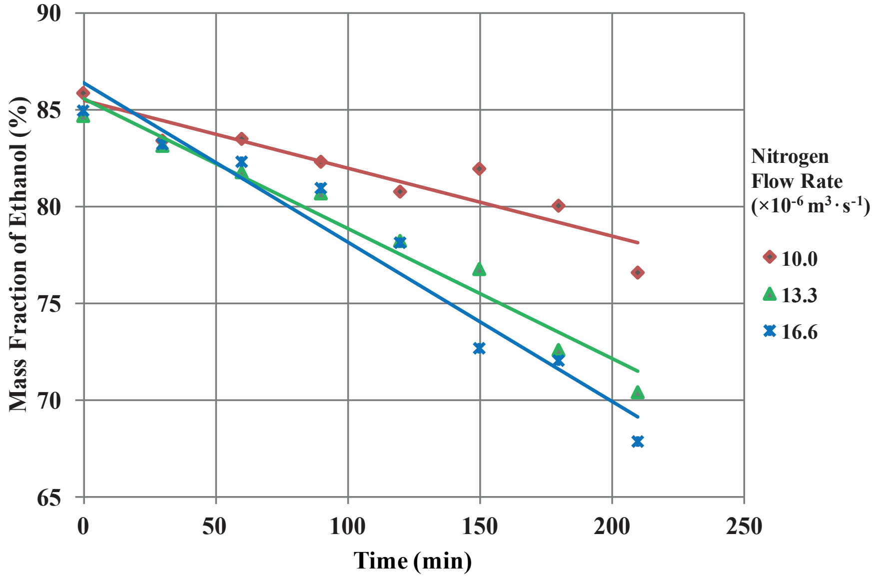

Figure 4: Mass fraction of ethanol versus time plot for atomization of 85 % ethanol 15 % ethylene glycol co-solvent mixture without bubbler add-back

atomization. As opposed to the trends observed without an add-back system, Figure 5 illustrates that the ethanol concentration actually increased with each flow condition using a bubbler. Clearly, the rate of ethanol addition to the atomization cup was greater than ethanol loss from the cup. Possibilities to be explored further are differences in the ethanol evaporation rates, in the two cups, due to differential flow rate anomalies; or, ethanol partial pressure depression created by the mixed solvent system used in the atomization cup. Figure 6 illustrates a similar trend for the high (85 %) ethanol ink solution. As expected, the ethanol loss rate with dry nitrogen was greatest at high atomization flow rates (16.6 $m^3 \cdot s^{-1}$ or 1 000 cubic centimeters per minute). When the solvent add-back bubbler technique was used, the ethanol concentration was nearly consistent with run-time.

Since it appears that a simple solvent add-back technique was able to compensate for the loss of low boiling point solvent during atomization is promising. Figure 5, however, points to the need for further development work to overcome excessive solvent add-back.

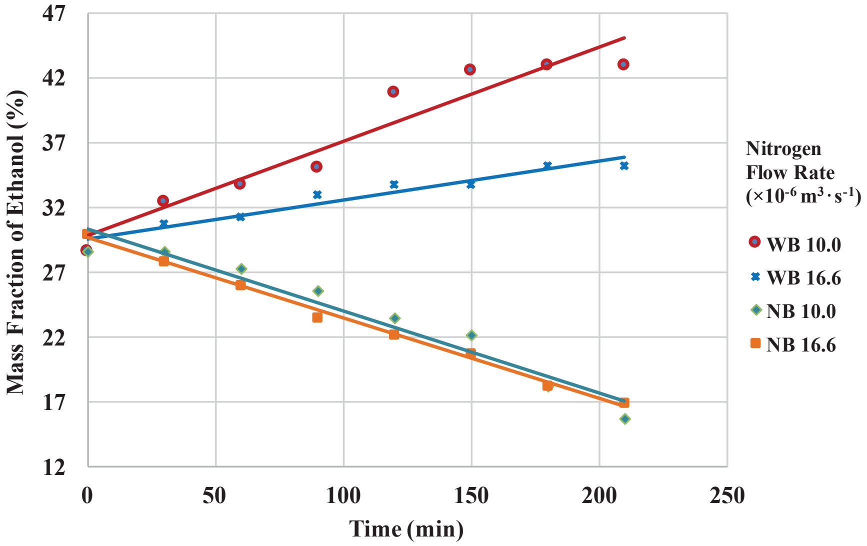

Figure 5: Mass fraction of ethanol versus time plot for atomization of 30 % ethanol 70 % ethylene glycol co-solvent mixture with (with bubbler; WB) and without (no bubbler; NB) the solvent add-back

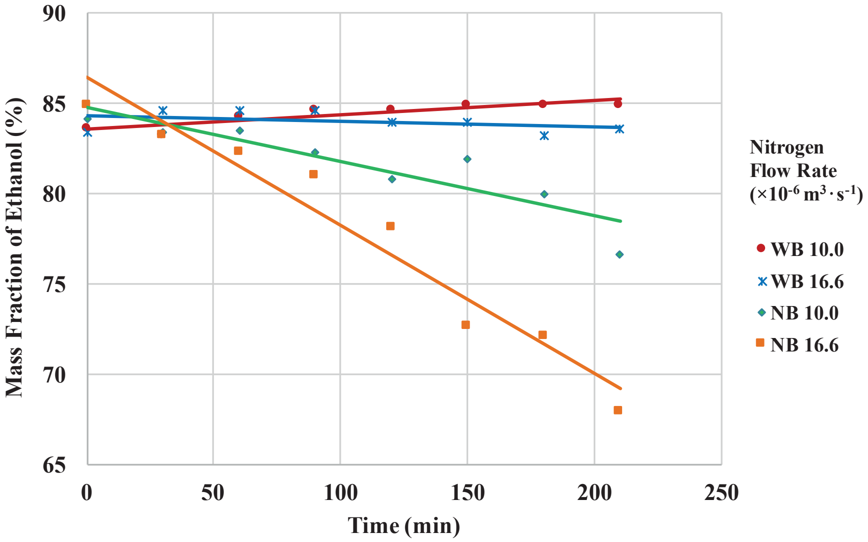

Figure 6: Mass fraction of ethanol versus time plot for atomization of 85 % ethanol 15 % ethylene glycol co-solvent mixture with (WB) and without (NB) the solvent add-back

4. Conclusions

Many ink formulations, used in AJ printing, use blends of low and high boiling point co-solvents. In some applications, slow drying inks that flow out and form a continuous coating are desired; whereas, other applications call for fast drying inks used to print narrow lines and/or features with high aspect ratios.

Depending upon the application, the low boiling point solvent composition may range from just a few percent up to nearly 100 %. This paper has demonstrated that AJ printing with dry nitrogen gas leads to rapid loss of low boiling point, high evaporation rate, solvent(s). As the ink concentrates, the nanoparticle loading fraction increases, and the wetting and spreading ink behaviour may dramatically change. Ultimately, inks with high concentrations of low boiling point solvents may become unprintable due to a rapid shift to the higher boiling point solvent concentration. A potential solution to this problem is to add solvent back into the atomizing cup through the use of a bubbler.

The solvent add-back method uses a bubbler to moisten the nitrogen gas before it enters the atomizing cup. This study has shown that the bubbler solvent add-back approach has the potential to overcome excessive co-solvent concentration change with low boiling point (high vapor pressure) rich solvent components. It is, however, also possible to overcompensate solvent addition when the concentration of low boiling point solvent is relatively low.

In studying Figure 5, one can envision that a blend of dry and moist nitrogen gas, in the correct ratios, will lead to continuous printing with a constant ethanol concentration. In ongoing future work, we will present new results demonstrating the effects of mixing these two mass flow conditions – dry and vapor-rich carrier gas flows. Two mass flow controllers may be needed to independently control the ratios of dry and wet nitrogen in order to maintain equilibrium.

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