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Entropy analysis in spray cooling for dosing water injection

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Abstract. Spraying water in air improves air-cooling capacity, which then relies on the evaporation of water. Even for small drop sizes, literature reports that the evaporation remains limited inside the spray and below saturation limits. In this article, we describe the evolution of thermodynamic quantities in a mixture of air and evaporating liquid water. A complete and coherent formulation is used to express enthalpy, entropy and chemical potential. At constant enthalpy, we show that the chemical equilibrium corresponds to an intermediate state in which droplet evaporation is not complete and entropy is maximum under certain conditions. Results are compared with some experimental values measured in a wind tunnel downstream of a spray. The calculated values are consistent with observations. Cooling efficiency is discussed for the various parameters, which are the amount of water, air temperature and ambient humidity. Then, the numerical approach is inverted in order to forecast the amount of water needed to reach a target cooling temperature. This numerical approach is used to set water flow depending on inlet flow conditions and cooling objectives.

1. Introduction

Misting cooling is a process consisting in spraying droplets of water into a flow of air to cool either air or water. Widely used to refresh surrounding air in summer, misting is also practiced in air treatment processes, for humidification purposes or to cool heating elements such as air conditioning condensers.

Sensitive to climatic conditions, effectiveness of misting has been widely studied, for example by Guan et al. in [1] to estimate its cooling potential in different regions of Australia. The work of Farmahani-Farahani et al. in [2] and [3] complete this analysis by describing exergy yields of mistcooling. Unlike Santos et al. in [4], which obtains exergy efficiencies close to 1, Farmahani-Farahani et al. report more moderate exergy efficiencies. The differences lie in definitions of exergy yields and their various formulations, which were analyzed in detail by Ratlamwala and Dincer in [5]. Indeed, the efficiency of evaporative processes, either energetic or exergetic, depends on whether it is based on saturation temperatures or enthalpies.

While the various parameters that influence evaporative yields have been studied, such as



air/water ratio in Lemouari et al. [6], droplet size and nozzle position in Tissot et al. [7], distance in Montazeri et al. [8], few theoretical elements allow a prior-test estimate about evaporative efficiency. However, experimental observations suggest that air/water mixture introduced in stream rapidly reach an equilibrium state from which evaporation becomes slow although vapour content is far from saturation ([7], [9], [10]). Numerical simulations confirm evaporative blockage, which results from mechanical, thermal and chemical balances occurring in air-water mixture ([8], [11]).

The exergetic approach offer a clear distinction between the 3 mechanisms involved during evaporation in mixtures to predict cooling efficiency. Sometimes, efficiency is also related to deviation from ideality or gradients within the mixture, affecting evaporation rate, like, Smrekar et al. in [12]. In this article, they use entropy and its topological distribution to optimize the cooling efficiency of a cooling tower. Mixing operations are also involved in chemical potential but are seldom used. Here, we assume the ideality of the mixture which corresponds well to a spray of small droplets. In this article, the detailed expressions of enthalpy, chemical potential and pressure are used to study the entropy of the mixture as well as mechanical, chemical and thermal equilibria. The chemical equilibrium coincides under certain conditions with the maximum entropy and is expressed from the operating conditions. It is shown that the chemical equilibrium agrees fairly well with experimental measurements. It is used to obtain an upper bound for cooling, related to partial evaporation, allowing to dose the corresponding sprayflow rate.

2. Model of mistcooling in wind tunnel

2.1. Process and hypothesis

A mixture of air and liquid water undergoes conversion processes that involve thermal (cooling), mechanical (gas pressure, fragmentation and mixing of droplets), and chemical (evaporation) transfers between the phases and the components of mixture before reaching the equilibrium ([5],[13]). When mixing spray and air inside a wind-tunnel, transformations occurs in a space spatially constrained by the pipe's geometry: the transformations are therefore isochoric as long as the tunnel's section does not vary. The mixing is also supposed perfect: since the velocities of the phases are homogeneous, time and space are directly connected by the flow rate of air and water masses. We can therefore use a stationary or quasi-static approach to describe the thermo-chemical evolution of the mixture as it moves along the duct. The liquid-gas interface is then represented by the molar concentrations, which means a small size of the droplets (molar scale). Since the mix is not at equilibrium in its initial state, the evaporation of the liquid water occurs spontaneously. Chemical (evaporation), thermal (cooling)and mecanical (pressure) transfers in the environment are coupled.

2.2. Input data

Humid air (ai) is introduced in wind-tunnel and liquid water (wl) is injected using nozzle spraying droplets with a very small diameter. Air flowrate V_g (m^3/s), temperature T_{ai} (K), pressure P_g (Pa) and humidity P_{wg}/P_g (%) are given, as well as water flowrate m_{wl} (kg/s) and temperature T_{wi} (K). Molar flowrates (mol/s) are deduced from flowrates using molar mass of components (\bar{M}_i kg/mol) and the total molar flowrate is constant:

$$n_t = \sum_i n_i = n_{as} + n_{wg} + n_{wl} = n_{as} + (n_{wg} + x) + (n_{wl} - x) \quad (1)$$

$n_g = n_{as} + n_{wg}$ referred to the gaseous molar rate (mol/s) introduced in the wind-tunnel and additional features about liquid-vapour transfer are used:

$$L_{vap} = h_{wg}^0(T_0) - h_{wl}^0(T_0) \quad C_{p,vap} = C_{p,wg}(T_0) - C_{p,wl}(T_0) \quad S_{vap} = S_{p,wg}^0(T_0) - S_{p,wl}^0(T_0)$$

$$C_{p,m} = \frac{n_{as} \cdot C_{p,as} + n_{wg} \cdot C_{p,wg} + n_{wl} \cdot C_{p,wl}}{n_t} \quad T_m = \frac{(n_{as} \cdot C_{p,as} + n_{wg} \cdot C_{p,wg}) \cdot T_{ai} + n_{wl} \cdot C_{p,wl} \cdot T_{wi}}{n_t C_{p,m}}$$

The fluid is made of two components (dry air as and water w), water being in liquid wl and vapour wg phases. The Gibbs-Duhem relation states that the degree of freedom for the mixture made of $n=2$ components and $p=2$ phases is 2 at equilibrium. Thus, state variables are written using 2 variables T_m (mixture temperature) and x molar rate of evaporated water (mol/s). After fragmentation of liquid, water droplets are mixed into the gaseous flow to obtain an assumed perfect and homogeneous mixture. Then, evaporation starts and x moles of water changes from liquid to vapour phase while temperature decreases. Air and water masses are conserved but water amount in each phase varies. Thermodynamic functions related to evaporation in the mixture are given in the following.

2.3. Enthalpy, chemical potential and entropy of mixture

2.3.1. Enthalpy The system is described with terms related to mechanical (pressure), thermal and chemical equilibrium. Fluid internal energy dU is $-P.dV + T.dS + (\mu_{wg} - \mu_{wl}).dx$ whereas its enthalpy dH is $V.dP + T.dS + (\mu_{wg} - \mu_{wl}).dx$ ([14]). Each of these terms are detailed in Table 1. Enthalpy is the sum of elemental enthalpies weighted by molar rates and its differential form is stated with reference to a standard state ([14]). This latest is defined by $P_0 = 101\,325$ Pa and $T_0 = 298$ K, with humid air containing n_{wg} moles of water vapour coexisting with n_{wl} moles of liquid water. Formation enthalpies, entropies and calorific values are given by thermodynamic tables ([15]). Calorific values are supposed constant and no thermal gradient exists between phases when temperature changes from mixing temperature down to final equilibrium temperature.

Table 1: Enthalpy, pressure, entropy and chemical potential equations (W)

	dH	$V.dP$	$T. [dS]$	$(\mu_{wg} - \mu_{wl}).dx$
Chemical	$(L_{vap} + C_{pvap} \cdot \Delta T) \cdot dx$		$T. [S_{vap} + C_{pvap} \cdot \log \frac{T}{T_0}] \cdot dx$	$(L_{vap} + C_{pvap} \cdot \Delta T) \cdot dx$ $-T. (S_{vap} + C_{pvap} \cdot \log \frac{T}{T_0}) \cdot dx$
Mechanical		$RT \cdot dx$	$T. [-R \cdot dx]$	$+RT \cdot \log \frac{n_t}{n_t - x}$ $+RT \cdot \log \frac{n_{vap} + x}{n_g + x}$ $+RT \cdot \log \frac{P}{P_0}$
Thermal	$(n_t \cdot C_{p,m} + x \cdot C_{p,vap}) \cdot dT$	$R(n_g + x) \cdot dT$	$T. [(n_t \cdot C_{p,m} + x \cdot C_{p,vap}) \cdot dT/T]$ $-T. [(n_g + x) \cdot R \cdot dT/T]$	
Other			$-T. [\mu_0 dx/T]$	μ_0

2.3.2. Pressure The ideal gas law is used to described pressure ($P = (n_g + x).R.T/V_g$) where R ($J/(mol.K)$) is the ideal gas constant and V_{ai} the constant volume (rate m^3/s) of tunnel. Hence, the impact of liquid on pressure is neglected. As initial condition differs from the standart state, flowing work (W) is needed to transfer fluids (mainly air), which is written at standart pressure:

$$\delta W = -P_O.(V - V_0) = n_g.R.(T_m - T_0) \quad (2)$$

This open system is isenthalpic, so dU is $-V.dp - PdV$. Therefore, pressure change related to cooling $V.dp$ are added to flowing work δW into internal fluid energy.

2.3.3. Chemical potential Some thermochemistry is reminded here in order to link our formulae with usual expressions used for moist air. Like enthalpy, chemical potential is defined up to a constant. For the reactive pure components (liquid and vapour water), it is related to entropy and enthalpy by:

$$\mu_i^{pure} = h_i(T) - T.S_i(T) = h_i^0(T_0) - T.S_i^0(T_0) + C_{p,i}. \left[T - T_0 - T. \log\left(\frac{T}{T_0}\right) \right] \quad (3)$$

In mixture, component concentrations modify potential, what is written for an ideal gas (vapour) and a very dilute ideal solution (droplets):

$$\begin{aligned} \mu_{wg}(T, P, c_{wg}) &= \mu_{wg}^{pure}(T) + R.T \log \frac{P}{P_0} + R.T \log \frac{P_{wg}}{P} \\ \mu_{wl}(T, P, c_{wl}) &= \mu_{wl}^{pure}(T) + R.T \log c_{wl} \end{aligned}$$

Change of chemical potential in a reactive mixture is generally written $\Delta_r\mu = \Delta_r\mu^0 + R.T \log Q_r$ which is also $R.T. \log(K(T)/Q_r)$. Indeed, the equilibrium constant $K(T)$ is more often used than $\Delta_r\mu^0(T)$. $K(T)$ depends on temperature, according to a relation written with $\log(K) = A - B/T$. By comparing these 2 expressions, parameters of equilibrium constant are expressed by $A = S_{vap}/R$ and $B = L_{vap}/R$. Hence, entropy and enthalpy of formation are related to equilibrium constant for the evaporation process.

Concentrations are related to the reactive quotient Q_r , which rates product over reactant concentrations in monophasic. Here, dilution ratio is needed for liquid water and partial pressure for water vapour. With only moist air, $Q_r = P_{wg}/P_O$ is egal to equilibrium constant $K(T)$, which leads directly to the saturation law for moist air if $P_{wg} = P_{sat}$.

In diphasic mixture, liquid water impacts dilution ratio of ideal solution $R.T. \log((n_{wl} - x)/n_t)$ whereas air humidity is involved in partial pressure for vapour $R.T. \log((n_{wg} + x)/(n_g + x))$. These both terms modify chemical equilibrium. Thermochemistry analysis reveals that adding liquid water improves evaporation whereas adding water vapour reduces it. Dry air does not change equilibrium position.

Chemical potential is defined up to a constant which is assessed while observing that no evaporation occurs if initial mixture temperature equals air dew point temperature T_{dp} . The chemical potential is null at $x=0$. Then, the first two lines in Table 1) are equal to $R.T_{dp}. \log(n_{wg}/n_g)$, which is air saturation. This is injected in the potential equation to assess μ_0 , which sizes in fact the disequilibrium involved by mixing.

$$\mu_0 = RT_m. \log \frac{n_{wl}}{n_t} \cdot \frac{T_0}{T_m} \quad (4)$$

Chemical potential in Table 1 implicitly contains saturation law for moist air through entropy and enthalpy formation. The main change of our expression, compared to usual expressions in exergetic litterature (e.g. [16],[17],[13]) lies in introducing concentration for liquid water. Thermochemistry analysis indicates that this term has an impact on the local chemical equilibrium inside wind tunnel but it is cancelled in exergy. This is because the equilibrium is stated with respect to the environment (infinite air volume), where a complete evaporation up to air saturation is reached.

2.3.4. Entropy Like enthalpy, mixture entropy is the sum of component entropies, to whom a production term is added. The production term includes diffusion terms (liquid dilution and partial pressure changes) included in the chemical potential. Thus, such an entropic expression, found in Table 1, make up for pressure $V.dP$ and chemical variations, as needed to cancel $V.dP + T.dS + (\mu_g - \mu_l).dx$ and get a constant enthalpy.

3. Isenthalpic vaporisation and chemical equilibrium

3.1. Evaporation at constant enthalpy

Evaporative cooling is a chemical conversion at constant enthalpy, which is described by cancelling the first column of Table 1.

$$\frac{dT}{L_{vap} + C_{p,vap} \cdot (T - T_0)} = \frac{-dx}{n_m \cdot C_{p,m} + x \cdot C_{pvap}} \quad (5)$$

The differential is integrated between initial mixing without evaporation and local conditions given by $[T_m, T]$ for temperatures and $[0, x]$ for moles of evaporated liquid. This gives:

$$T = \frac{n_m \cdot C_{p,m} \cdot T_m - x \cdot (L_{vap} - C_{p,vap} \cdot T_0)}{n_m \cdot C_{p,m} + x \cdot C_{pvap}} \approx T_m - x \cdot \frac{L_{vap} + C_{pvap}(T_m - T_0)}{n_m \cdot C_{p,m}} \quad (6)$$

Temperature drop is linked to endothermic reaction for vaporisation. At the first order, the relation is approximated by the line whose slope is $\beta = (L_{vap} + C_{pvap}(T_m - T_0))/(n_t \cdot C_{p,m})$. Equation 6 represented on Figure 1, with circles for the whole expression and by the line for the approximation. The imperceptible difference ascertains that the linear approximation can be further used.

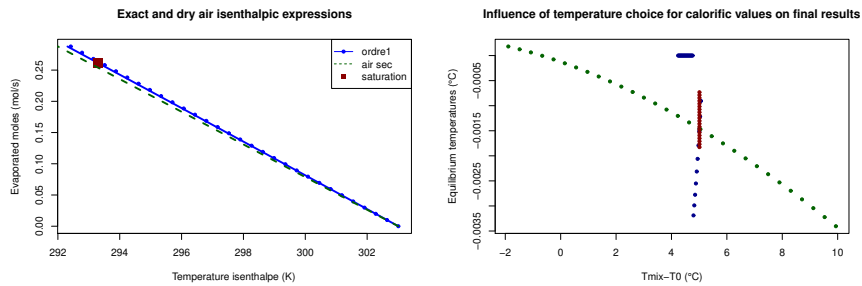


Figure 1: On the left, temperature according to liquid evaporation moles using present- and air- enthalpy approximation and on the right, equilibrium temperature gradient using calorific values assessed at T_{air} or T_0 .

3.2. Chemical equilibrium

Table 1 ensures cancelling terms for enthalpy, when assessed from entropy, pressure and chemical potential. It also emphasizes that chemical equilibrium corresponds to entropy maximum only if pressure terms are cancelled. Equilibrium equation is reached when $\mu_g - \mu_l$ equals zero, which is written in Equation 7 using only x , amount of liquid moles that are evaporated. For given initial conditions, equation root is numerically solved using R software ([18]). Root of Equation 7 expresses the amount of evaporated water at chemical equilibrium and is used to derive other quantities, like temperature with Equation 6.

$$0 = \left[S_{vap} + C_{pvap} \cdot \log \frac{T_m - \beta \cdot x}{T_0} \right] - \beta \cdot \frac{n_t \cdot C_{p,m} + x \cdot C_{pvap}}{T_m - \beta \cdot x} - R \log \left(\frac{n_{wg} + x}{n_g} \frac{n_t}{n_{wl} - x} \frac{T_m - \beta \cdot x}{T_0} \right) - R \frac{T_m}{T_m - \beta \cdot x} \log \left(\frac{n_{wl}}{n_t} \frac{T_0}{T_m} \right) \quad (7)$$

3.3. Setting water injection

The aim is to cool air down to target temperature, T_{target} which is necessarily between mixing and adiabatic saturation temperatures. Setting water with this objective means that target temperature equals equilibrium temperature. Molar conservation implies $n_t = n_g + n_{wl}$, where liquid water moles (n_{wl} (mol/s)) is unknown. Assuming same temperature T_i for air and water at inlet, the isenthalpic equation expresses now the relation between moles to evaporated and physical mixture properties:

$$x = -(T_{target} - T_i) \cdot \frac{L_{vap} + C_{p,vap} \cdot (T_i - T_0)}{n_g \cdot C_{p,g} + n_{wl} \cdot C_{p,wl}} \quad (8)$$

Combined with equilibrium equation 7, the following equation is obtained and depends only on injected liquid moles:

$$0 = S_{vap} + (C_{p,vap} - R) \cdot \log \frac{T_{target}}{T_0} - \frac{L_{vap} + C_{p,vap} \cdot (T_i - T_0)}{T_{target}} + C_{p,vap} \cdot \frac{T_{target} - T_i}{T_{target}} - R \cdot \log \left(\frac{n_{wg} + \alpha \cdot (n_g \cdot C_{p,g} + n_{wl} \cdot C_{p,wl}) \cdot (n_g + n_{wl})}{n_{wl} - \alpha \cdot (n_g \cdot C_{p,g} + n_{wl} \cdot C_{p,wl})} \cdot \frac{n_g + n_{wl}}{n_g} \right) - R \cdot \frac{T_i}{T_{target}} \cdot \log \left(\frac{n_{wl}}{n_g + n_{wl}} \cdot \frac{T_0}{T_{target}} \right) \quad (9)$$

Where $\alpha = -(T_{target} - T_i) / (L_{vap} + C_{p,vap} \cdot (T_i - T_0))$. Here again, an equation solver is used to extract root of equation 9 defining the amount of water needed to get sufficient evaporation at chemical equilibrium for cooling air down to target temperature.

4. Results

4.1. Reference case

A reference case, corresponding to detailed inlet conditions in Table 2 is used for sensitivity analysis. These conditions are used to study the impact of temperature used in the assessment of calorific values (see Figure 1 on right). It shows that final equilibrium temperature weakly changes with the various C_p values.

Table 2: Input data in the reference case

T_{ai} °C	HR_a (%)	P_{ref} Pa	V_{gaz} m^3/s	m_{wl} kg/s	T_{wl} °C
30	40	101 325	1	0.004	20

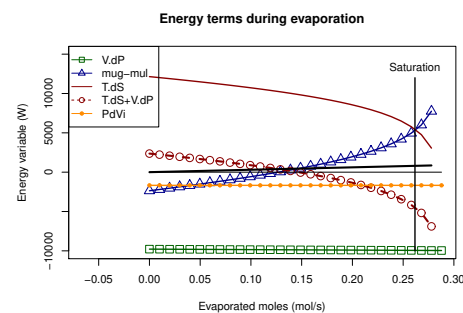


Figure 2: Energy variations along the evaporation process

4.2. Impact of evaporation on energy variables

Energy terms in Table 1 are computed for the reference case with varying the amount x of evaporated moles, which is represented on Figure 2. The orange line represents flowing work

for fluid, which is constant over evaporation process. The green line, used for the pressure term, is much more negative than flowing work but stays also quite constant over evaporation process: mixture pressure decreases with temperature in the wind-tunnel and its derivative is quite constante, showing the small effect of molar changes in gas. Chemical potential, in blue, is negative at starts, as needed for spontaneous reaction, but becomes zero in the middle, blocking there the evaporation reaction. Chemical potential curve intersects entropy curve in red at adiabatic saturation: there, these two terms balances pressure variation. But this state can not be achieved spontaneously as evaporation is blocked before. The black curve is the sum of pressure, entropy and chemical terms, which is enthalpy and stays near zero along the x-axis. The small slope is attributed to the first order approximation. Entropy derivative is positive at starts, showing mixture entropy increase when beginning evaporation. If pressure terms are removed from entropy expression, curve with red circle is obtained and then chemical equilibrium matches pseudo-entropy maximum. If entropy derivative is not zero, evaporative cooling can not be adiabatic unless pressure derivative is zero. Or pressure contribution in entropy derivative represent mechanical irrversibilities that should not be included in heat related to entropy. Such irrversibilities could also explain pressure drop and additionnal work needed at fan in evaporative systems.

4.3. Studying the chemical equilibrium

Chemical equilibrium is reached before adiabatic saturation in our reference case. As equilibrium depends on mixing conditions, Figure 3 shows equilibrium positions in the psychrometric chart for various operating conditions.

The green dotted line is for inlet air temperature variations, the red dotted one is obtained by changing air humidity at inlet and the blue dotted one by changing liquid flowrate. Solide lines represent the related evolution of the equilibrium. Cross of the three curves is the solution for the reference case. While increasing air temperature, evaporation rate is increased as showed by the humidity ratio of the green curve. If air humidity is increased, the cooling effect is reduced since the equilibrium temperature rises on the red curve. Increasing water flowrate improves cooling on the blue curve close to the isenthalpic curve.

The gap between air isenthalpic and blue curves arises from water temperature: the more water, the more precooling effect of mixing. This shifts the real origin of isenthalp (mixing temperature) on left. A graphic method is also proposed here for approaching chemical equilibrium: the violet exponential curve, passing through $[T_{dp}, y_{ai} = n_{wg} \cdot \bar{M}_{wg} / (m_{as} \cdot \bar{M}_{as})]$ and $[T_{ai}, y_{twc} = y_{ai} + n_{wl} \cdot \bar{M}_{wl} / (m_{as} \cdot \bar{M}_{as})]$ intersects air isenthalpic curve close to equilibrium solution.

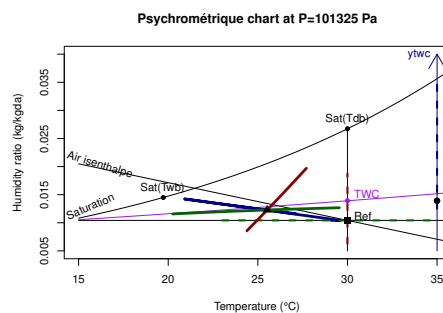


Figure 3: Chemical equilibrium in psychrometric chart for various inlet conditions

4.4. Comparison between modelled and observed data

On Figure 4, measurements of spraying in wind-tunnel found in [7] are reported. Green and blue marks are used for the two positions of measurements, made for several inlet conditions. These pairs of measurements reveals evaporation blocking. In red are reported calculated chemical equilibrium by solving Equation 7, that is independant of positions or time. Red triangles are computed assuming standart atmospheric pressure in the wind tunnel because pressure measurements are not specified in the paper. Computed solutions always overestimates cooling in almost all conditions: our estimate is a majorant of

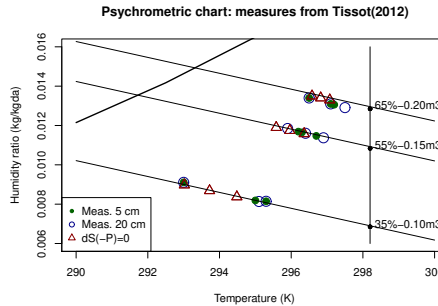


Figure 4: Comparison of calculated chemical equilibrium and measurements published in Tissot(2012)

librium and measurements published in Tissot(2012). However, evaporated fluxes matches quite well measurements and calculation gives a correct magnitude for cooling efficiency according to operating changes. A lot of imperfections (droplet size, non ideal mixing) could explain why the chemical optimum is not completely achieved in experiments.

4.5. Setting water injection according to cooling objectives

Equation 7 sizes a correct majorant for cooling air with spray in wind tunnels for various inlet conditions. So the inverted Equation 9 may be used to size minimal spray flowrate needed to ensure a target temperature in cooling. Figure 5 shows the cooling effect obtained at chemical equilibrium for various water flowrates (reference case for other variables).

Cooling, shown with the black curve, is increased when rising spray flowrate. If the flowrate exactly matches vapour needs to obtain adiabatic saturation ($m_{wl,sat}(T_{wb})$), cooling is around 5°C when cooling potential (orange curve) is above 10°C. Evaporation always stays uncomplete and excess water is needed to increase cooling. But even if equilibrium temperature is lowered by increasing spray flowrate, evaporation rate (red curve) decreases. The more water injected, the more cooling but also the more unused water.

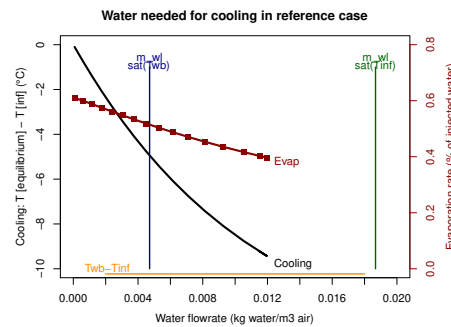


Figure 5: Cooling reached at chemical equilibrium according to injected liquid water flowrate

Cooling slowly converges near adiabatic saturation when water flowrate tends to saturation flowrate at air temperature $m_{wl,sat}(T_{air})$.

5. Conclusion

This article aims to study thermodynamic variables in misted air used for evaporative cooling. Expressions of enthalpy, chemical potential and entropy are detailed for an ideal mixture of

air and liquid water in an isochoric conversion. Analysis of the mixture chemical potential shows that evaporation of droplets occurs spontaneously in air. But evaporation reaction ends before reaching adiabatic saturation, in a state which corresponds in fact to a local chemical equilibrium. This chemical equilibrium varies as a function of operating conditions and a graphical method is proposed to approximate this position in the psychrometric diagram. Position of chemical equilibrium is found to be a reliable upper bound, compared to experimental measurements about spraying in wind-tunnels. Uncertainties on spray cooling efficiency does not lie in evaluating the physical properties of fluids but rather in mixing imperfections. The thermochemical analysis thus offers a method for dosing the water to inject in order to cool air while accounting for evaporative blockage. Results also show that the evaporative cooling is either isenthalpic or adiabatic, but not both, except by considering that mechanical irreversibilities associated with the pressure terms in the entropy are not integrated in heat. Further work is needed to study adiabaticity of evaporative cooling and requires additional measurements of pressure.

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