

Reduction of Thermodynamic Losses in a Supersonic Nucleating Steam Nozzle by Spraying Water Droplets

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Abstract. *During the course of expansion of steam in turbines, the vapour first supercools and then nucleates to become a two-phase mixture. Formation of the liquid phase causes thermodynamic and aerodynamic losses in steam turbines. In this study, the treatment is a one-dimensional, non-equilibrium flow in a steady Laval nozzle. In this paper, the changes in the rate of nucleation, entropy, pressure and other parameters of the two-phase flow, subjected to spraying the liquid droplets close to the nozzle's throat, are investigated. By injecting the water droplets into a supersonic condensing flow, the thermodynamic loss is considerably decreased.*

Keywords: *Two-phase flow; Convergent-divergent nozzle; Nucleation.*

INTRODUCTION

The fluid temperature in LP turbines decreases due to the steam expansion. Therefore, the superheat vapour crosses the saturation line and enters the two-phase region. Due to the high velocity of the steam flow, it is still single-phase, which is called supercooled vapour. This situation continues to the Wilson point, where the supercooled steam cannot continue and the fluid starts nucleating. The subcooled vapour loses its latent heat and liquid droplets with small diameter forms. The nucleation model presented in this research is a homogenous one. In this kind of nucleation, condensation occurs without any impurity or surfaces [1,2]. In the supersonic region, if the flow is heated, its velocity decreases and its pressure increases. Therefore, we have condensation shock (or pressure rise) [3] which increases the flow entropy. It is found that this shock disappears by spraying water droplets close to the nozzle's throat. In this case, vapour condensation occurs mainly on the surface of the sprayed droplets,

the subsequent nucleation is negligible and the formed droplets begin to grow.

The presence of a liquid phase within the turbine causes the following losses [3-8]:

- A) Thermodynamic losses: Losses that are caused by internal heat transfer within the fluid. When the flow is sufficiently supercooled, the condensing molecules give up latent heat to the droplets but the bulk of this energy has to be returned to the vapour. Therefore, the temperature difference between the phases causes an irreversible process.
- B) Aerodynamic losses: Losses that occur due to aerodynamic shock and its effects on the boundary layers.
- C) Mechanical losses or erosion: Droplet impingement on the blades, which damages the steam turbine blades.

NON-EQUILIBRIUM CONDENSATION MODEL

Nucleation is investigated in thermodynamic and kinetic aspects and various models are presented in the field of nucleation, such as those reported in the literature [1,2,9-11].

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Droplet Formation

The change of Gibbs free energy for a mass, m_r , from a supercooled vapour at constant pressure and temperature that forms a liquid droplet at the same pressure and temperature can be calculated in four stages, in the absence of magnetic and electrical fields:

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4,$$

$$\begin{cases} \Delta G_1 \text{ (isothermal expansion term)} \\ \Delta G_2 \cong 0 \text{ (vapour phase change)} \\ \Delta G_3 \cong 0 \text{ (isothermal compression term)} \\ \Delta G_4 \text{ (formation of droplet from bulk phase)} \end{cases}$$

$$\Delta G = \Delta G_1 + \Delta G_4 = -m_r RT_G \ln \left(\frac{P}{P_s(T_G)} \right) + 4\pi r^2 \sigma_r. \quad (1)$$

Based on the thermodynamic equilibrium, there is a minimum radius, r^* (the critical radius), that must be attained in order to form a stable nucleus from supersaturated vapour. For this condition, the Gibbs free energy of formation of a critical cluster is denoted as ΔG^* . By differentiating Equation 1, with respect to r , the critical radius, (r^*), and ΔG^* are obtained as follows:

$$\Delta G^* = \frac{16\pi\sigma_r^3}{\rho_L RT_G \ln[p/p_s(T_G)]}, \quad (2a)$$

$$r^* = \frac{2\sigma_r}{\rho_L RT_G \ln[p/p_s(T_G)]}. \quad (2b)$$

Droplets with a radius smaller than r^* have a tendency to evaporate by losing their molecules and by decreasing their Gibbs free energy. If the radius is greater than r^* , the droplet will grow in the vapour phase.

Nucleation Rate Equation

Even within the body of a superheated vapour, molecular clusters are continually formed and disrupted by the statistical fluctuations. The statistically steady state population, n_g , of clusters containing g molecules is given by Boltzmann's relation:

$$n_g = n_1 \exp \left[\frac{\Delta G}{KT_G} \right], \quad (3)$$

where n_g and n_1 are the numbers per unit volume of g -mers and monomers, respectively. ΔG is the free energy required to form a g -mers and K is the Boltzmann constant. If the rate of condensation and evaporation from a cluster are denoted by C and E , respectively, then the equilibrium equation can be written as:

$$n_g C_g = n_{g+1} E_{g+1}. \quad (4)$$

In a supersaturated vapour, the processes of cluster formation and disruption are similar, but if the clusters exceed the critical size, they encounter a favorable ΔG gradient and tend to grow.

The steady state described by Equation 4 is no longer applicable because the rates at which the clusters grow and decay are no longer balanced. To signify the difference, the symbol f_g is used to denote the concentration of g -mers under these conditions. The net rate per unit volume, J_g , at which g -mers grow to $(g+1)$ -mers, is termed the nucleation current and can be expressed as:

$$J_g = C_g f_g - E_{g+1} f_{g+1}. \quad (5)$$

As given in Appendix C, for the constant nucleation current, it may be as follows:

$$J_g \int_{g=1}^{g^*} \frac{dg}{C_g n_g} = \int_{g=1}^{g^*} -d \left(\frac{f_g}{n_g} \right) = 1, \quad (6)$$

where C_g is proportional to r^2 and it is a slowly varying function. n_g may be written in terms of n_{g^*} , using Equation 3, and $\Delta(G-G^*)$ may be expanded using the Taylor series about $(g-g^*)$. With some assumptions as explained in Appendix C, Equation 6 may be written as:

$$J_{st} = \frac{C_{g^*} n_g \exp(-\Delta G^*/KT_G)}{(2\pi K_G T/\zeta)^{1/2}}, \quad (7)$$

where:

$$\zeta = - \left[\frac{\partial^2 \Delta G}{\partial g^2} \right]_{G=G^*}.$$

The above reasoning, in general, is true at low and high pressures. The only terms which can be affected by the virial coefficient in further developing the analysis are ζ and C_{g^*} .

ζ is obtained by double differentiation of Equation 1. To avoid the introduction of the virial coefficient, ζ can be written in terms of density as follows:

$$\zeta = \frac{2}{9} \left[\frac{36\pi}{\rho_L^2} \right]^{\frac{1}{3}} \frac{J_{st}}{(g^*)^2}. \quad (8)$$

C_{g^*} is evaluated from the kinetic theory in terms of density:

$$C_{g^*} = q \frac{4\pi r^{*2}}{m} \rho \sqrt{\frac{RT_G}{2\pi}}, \quad (9)$$

where m is the mass of one molecule and q is the condensation coefficient defined as the fraction of molecules that collide with the surface and condense.

Combining Equations 7 to 9, the nucleation rate equation is given as:

$$J_{st} = q \sqrt{\frac{2\sigma_r}{m^3 \pi}} \frac{\rho_G^2}{\rho_L^2} \exp \left[-\frac{16\pi\sigma^3}{\rho_L R T_G \ln [p/p_s(T_G)] / K T_G} \right], \quad (10)$$

where:

$$m = \frac{4}{3} \pi r^3 \rho_L g.$$

In the present investigation, the nucleation theory adopted is the classical result, subject to the refinements by Courtney and Kantrowitz [3] as follows:

$$J_{Ka} = \left(1 + \frac{q_c \rho_G}{\alpha_r} \left(\frac{R T_G}{2\pi} \right)^{0.5} \left(\frac{L^2}{R T_G^2} - \frac{L}{2 T_G} \right) \right)^{-1} \\ \times \sqrt{\frac{2 N^3}{\pi}} \frac{q P^2 \sqrt{\sigma_r}}{\rho_L (R T_G)^2} \exp \left[\frac{-16\pi N \sigma_r^3}{3 \rho_L^2 (R T_G)^3 \left\{ \ln \left(\frac{P}{P_s(T_G)} \right) \right\}^2} \right]. \quad (11)$$

Droplet Growth Equations

Once droplets form, they increase in size as vapour molecules condense on their surfaces. Released energy in condensation leads to a rise in the droplet temperatures, and thus the droplets become hotter than the surrounding vapour during the condensation. The growth is then governed mainly by the mass flow towards a droplet and energy flux away from it. In a pure vapour, however, due to the release of a very high latent heat in the rapid condensation zone, the droplet growth is dominated by the thermal transfer rate. The energy conservation law can be formulated as:

$$\frac{dr}{dt} \left(\frac{4}{3} \pi r^3 \rho_L L \right) = \alpha 4 \pi r^2 (T_L - T_G), \quad (12)$$

where α is the coefficient of heat transfer from a droplet with radius r to the surrounding vapour. Therefore, the droplet growth rate can be calculated if both α and T_l are known:

$$\frac{dr}{dt} = \frac{1}{\rho_L L} \alpha (T_L - T_G). \quad (13)$$

The Knudsen number, Kn , plays a key role in the coefficient of heat transfer, due to the wide range of droplet radii. The Knudsen number is the ratio of the mean free path, $\bar{l}$, of vapour molecules to the droplet diameter:

$$Kn \equiv \frac{\bar{l}}{2r}. \quad (14)$$

For the heat transfer coefficient, an empirical relation was presented in 1964 by Gyarmathy [2]:

$$\alpha_{\text{empirical}} = \frac{\lambda}{r(1 + 3.18 Kn)}. \quad (15)$$

He also suggested the following equation for liquid temperature [3]:

$$T_L = T_G + \left[1 - \frac{r^*}{r} \right] [T_s(p) - T_G]. \quad (16)$$

Bakhtar and Zidi presented a semi-empirical relation for droplet growth as explained in reference [3]:

$$\frac{dr}{dt} = \frac{Kn}{Kn + 0.375} \frac{q_c}{q_c S_c} \left(\frac{R}{2\pi} \right)^{1/2} \\ \times [\rho_G \sqrt{T_G} - \rho_s(T_L, r) \sqrt{T_L}]. \quad (17)$$

Main Flow Equations

By considering the steady one-dimensional flow over an incremental distance, dx , along the channel, the fundamental equation of flow can be written as:

$$\frac{d\rho_G}{\rho_G} + \frac{dA}{A} + \frac{du}{u} + \frac{dW_L}{W - W_L} = 0, \quad (18)$$

where W is the overall mass flow rate.

State Equations

$$\frac{P}{\rho_G R T_G} = 1 + B_1 \rho_G + B_2 \rho_G^2 + B_3 \rho_G^3 + B_4 \rho_G^4 + B_5 \rho_G^5, \quad (19)$$

where B parameters are virial coefficients; these are functions of temperature as given in Appendix A.

$$\frac{dP}{P} - X \frac{d\rho_G}{\rho_G} - Y \frac{dT_G}{T_G} = 0, \quad (20)$$

where:

$$X = \frac{\rho_G}{P} \left(\frac{\partial P}{\partial \rho_G} \right)_{T_G} \\ = \frac{1 + 2B_1 \rho_G^2 + 3B_2 \rho_G^2 + 4B_3 \rho_G^3 + 5B_4 \rho_G^4 + 6B_5 \rho_G^5}{1 + B_1 \rho_G^1 + B_2 \rho_G^2 + B_3 \rho_G^3 + B_4 \rho_G^4 + B_5 \rho_G^5}, \\ Y = \frac{T_G}{P} \left(\frac{\partial P}{\partial T_G} \right)_{\rho_G} \\ = 1 + \frac{\rho_G T_G}{1 + B_1 \rho_G^1 + B_2 \rho_G^2 + B_3 \rho_G^3 + B_4 \rho_G^4 + B_5 \rho_G^5} \\ \times \left[\frac{dB_1}{dT_G} + \rho_G \frac{dB_2}{dT_G} + \rho_G^2 \frac{dB_3}{dT_G} + \rho_G^3 \frac{dB_4}{dT_G} + \rho_G^4 \frac{dB_5}{dT_G} \right].$$

Mach Number

The speed of sound in a single phase gas is:

$$a = \sqrt{\frac{\gamma P}{\rho_G}}. \quad (21)$$

Thus:

$$Z = \text{Ma}^2 = \frac{u^2}{\left(\frac{\gamma P}{\rho_G}\right)}. \quad (22)$$

Differentiating Equation 22 leads to:

$$\frac{dZ}{Z} = \frac{2d\text{Ma}}{\text{Ma}} = 2\frac{du}{u} + \frac{d\rho_G}{\rho_G} - \frac{dP}{P}. \quad (23)$$

Momentum Equation

Considering the flow as a whole, the change in momentum of the system across dx can be written as:

$$AdP + A \frac{f\rho_G u_G^2}{2D_e} dx = -d[W_G u_G + W_L u_L]. \quad (24)$$

Expanding this equation, denoting $dW_G = -dW_L$ and dividing by $A \times P$, considering $\frac{(u_G - u_L)}{AP} dW_L$ small, in comparison with others and re-arranging results in:

$$\begin{aligned} \frac{dP}{P} = & -\frac{f\rho_G u_G^2}{2P} \frac{dx}{D_e} - \frac{(W - W_L)u_G}{AP} \frac{du_G}{u_G} \\ & - \frac{W_L u_L}{AP} \frac{du_L}{u_L}. \end{aligned} \quad (25)$$

Energy Equation

Considering the flow of energy into and out of the control volume and assuming the heat loss through the sides of the duct to be small, the energy equation can be written as:

$$d \left[(W - W_L) \left(h_G + \frac{u^2}{2} \right) + W_L \left(h_L + \frac{u^2}{2} \right) \right] = 0. \quad (26)$$

Since the phase change occurs within the control volume, the term $dW_L(h_G - h_L)$ will appear while expanding this equation. It represents the heat released to or absorbed from the flow by condensation onto or evaporation from the droplets. Having considered the released energy associated with the phase change, the bulk of the vapour may then be regarded as a perfect gas, for which the term dh_G can be replaced by $C_p dT_G$. Substituting this into Equation 26, denoting $(h_G - h_L)$ by L , considering the term $\frac{u_G^2 - u_L^2}{2}$ small compared to

L , neglecting $W_L dL$, dividing throughout by $MC_p T_G$ and rearranging results in:

$$\begin{aligned} \frac{dT_G}{T_G} = & - \left(1 - \frac{W_L}{W} \right) \frac{u_G^2}{C_p T_G} \frac{du_G}{u_G} + \frac{L}{C_p T_G} \frac{dW_L}{W} \\ & - \frac{W_L}{W} \frac{u_L^2}{C_p T_G} \frac{du_L}{u_L}. \end{aligned} \quad (27)$$

Equations 20, 23, 25 and 27 can be solved for the four unknowns $\frac{dT_G}{T_G}$, $\frac{dP}{P}$, $\frac{du}{u}$ and $\frac{d\rho_G}{\rho_G}$ providing that $\frac{du_L}{u_L}$, $\frac{dA}{A}$ and $\frac{dW_L}{W_L}$ are known as explained in [3].

SPRAYING WATER DROPLETS INTO THE SUPERSONIC TWO-PHASE FLOW

In order to calculate the flow variables in the , the flow in the converging part is studied in the dry-form and the Mach number is assumed to be one at the physical throat.

In the divergent part, the flow crosses the saturation line, and so the two-phase flow equations are used. Therefore, all the figures of the variables related to the wet flow such as the nucleation and droplet diameters are prominent only after the throat, but the other variables are plotted for the whole nozzle axial length in dry and wet flows.

The rate of spraying or injecting the liquid droplets just after the throat (or before nucleating the vapour phase) is calculated by giving the wetness fraction and droplet diameter.

Assuming that the mass of vapour phase is decreased by the same amount as the mass of sprayed droplets, the number of droplets can be varied by changing the wetness fraction for a given diameter.

Calculating the Interaction Between the Sprayed and New Droplets

There are two kinds (groups) of droplet inside each element of Δx . Group (a) includes the droplets formed and grown within the element in the case of a considerable rate of nucleation (Figure 1). Group (b) includes the droplets formed in the upstream of the element entrance, which grow within the element of Δx . In the element of Δx , the time of Δt is divided by n to give a suitable time scale (δt):

$$\Delta t = \frac{\Delta x}{u}, \quad \delta t = \frac{\Delta t}{n}. \quad (28)$$

Depending on the formation time of new droplets, they grow with r^* size and the mass of the liquid phase related to the droplets of Group (a) at the time of

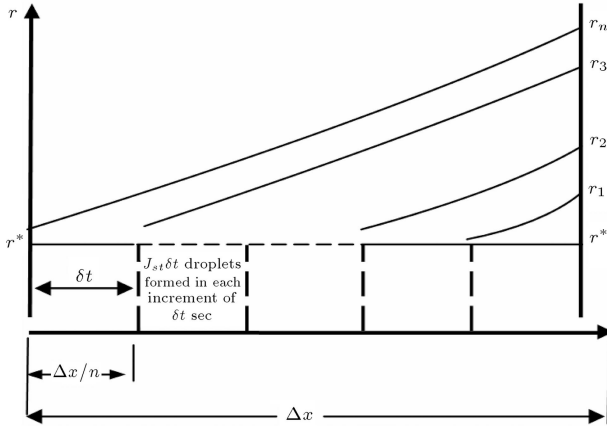


Figure 1. Growth of new droplets within the element.

nucleation is calculated as:

$$W_L(a) = J_{st}\delta t(AU)\frac{4}{3}\pi \times \left[\rho_L \frac{r^{*3}}{2} + \rho_{L1}r_1^3 + \rho_{L2}r_2^3 + \cdots + \rho_{Ln}\frac{r_n^3}{2} \right]. \quad (29)$$

Taking the number of droplets in Group (b) as N_i , if r_i is the mean input radius and r_e is the mean output radius of the element, the net mass of the grown droplets within the element of Δx is equal to:

$$W_L(b) = N_i \frac{4}{3}\pi (\rho_{Le}r_e^3 - \rho_{Li}r_i^3). \quad (30)$$

It should be noted that, in this research, the droplets of Group (b) are initially sprayed and then new droplets are produced in the nucleation zone.

The total mass of the injected and formed droplets in the element of Δx is:

$$W_L = \frac{4}{3}\pi N_i r_i^3 \rho_{Li} + W_L(a) + W_L(b),$$

$$N = N_i + J_{st}\Delta t(A\Delta x). \quad (31)$$

In order to decrease the calculation complexity, the mean diameter and temperature of the droplets at the end of the element of Δx are used as inputs for the next element.

Using the method of a mean square root, the droplet radius at the end of the element is determined as:

$$S = 4\pi N_i r_e^2 + J\delta t(A\Delta x)4\pi \left[\frac{r^{*2}}{2} + r_1^2 + \cdots + \frac{r_n^2}{2} \right],$$

$$\bar{r} = \left(\frac{S}{4\pi N} \right). \quad (32)$$

Calculations continue for other elements using this method.

Results and Discussion

In this study, the diameter of the sprayed droplets is assumed to be $1 \mu\text{m}$, the initial pressure $P = 198576 \text{ Pa}$ and initial temperature $T = 405.6 \text{ K}$. In a certain radius, the higher rate of spraying droplets gives more droplets and, therefore, greater surfaces are provided for the condensation of vapour. Since Gibbs free energy of condensation on the surface is less than that of the nucleation, it is expected that the nucleation will decrease. From Figure 2, it is concluded that:

$$J_{\text{wetness}=0.01} < J_{w=0.0001} < J_{w=0}. \quad (33)$$

As discussed in gas dynamics, the pressure locally increases because of heat transfer to the supersonic flow. Since the nucleation is reduced at higher rates of injection, less latent heat is given to the vapour flow and, therefore, the losses are decreased due to a reduction in the condensation shock strength (see Figure 3). For this condition, based on Rayleigh flow, the Mach reduction is smaller. In Figure 4, these results are compared.

$$\text{Mach}_{\text{wetness}=0.01} > \text{Mach}_{w=0.0001} > M_{w=0}. \quad (34)$$

In steam turbines, the purpose is to transform the flow enthalpy to kinetic energy. Fortunately, spraying droplets into a wet steam flow prevent the decrease of fluid velocity or kinetic energy. Another result of injecting water droplets is that, although a liquid phase is added to the flow, the wetness fraction relative to the non-sprayed cases at the end of nozzle is decreased by 1% as shown in Figure 5. The main reason for this reduction in the wetness fraction is the decrease of nucleation rate.

As expected, the more droplets are sprayed, the less is the heat given to the supersonic flow and,

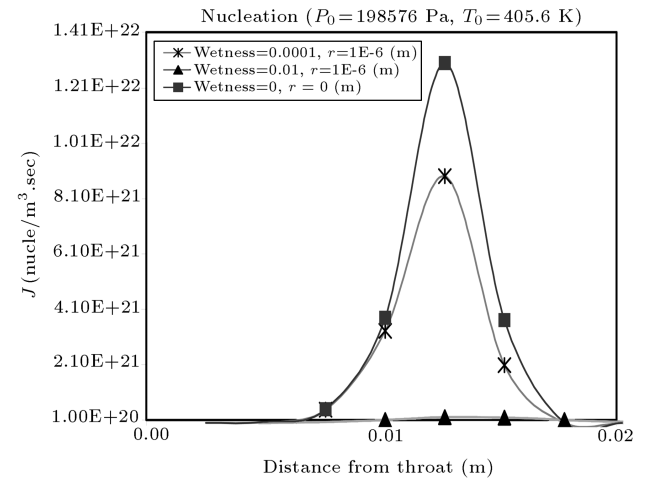


Figure 2. Effect of spraying on nucleation (radius is constant).

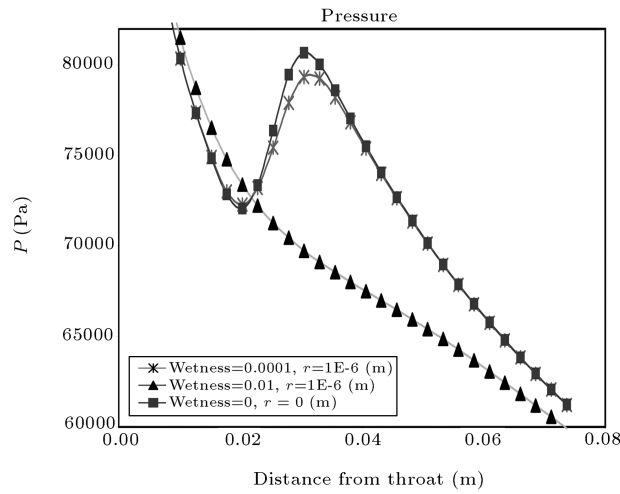


Figure 3. Effect of spraying on pressure changes (radius is constant).

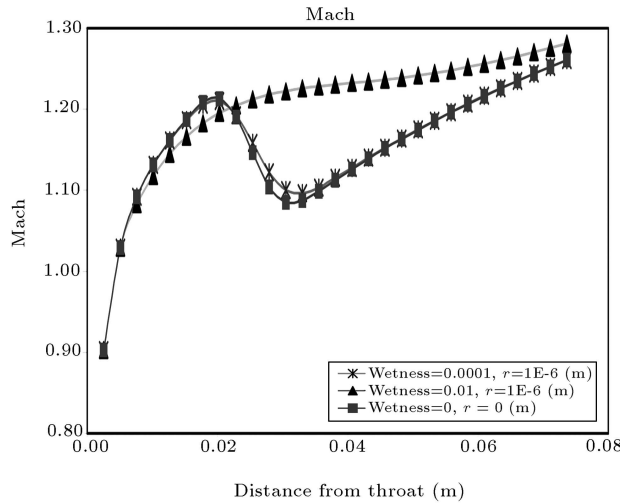


Figure 4. Effect of spraying on Mach number (radius is constant).

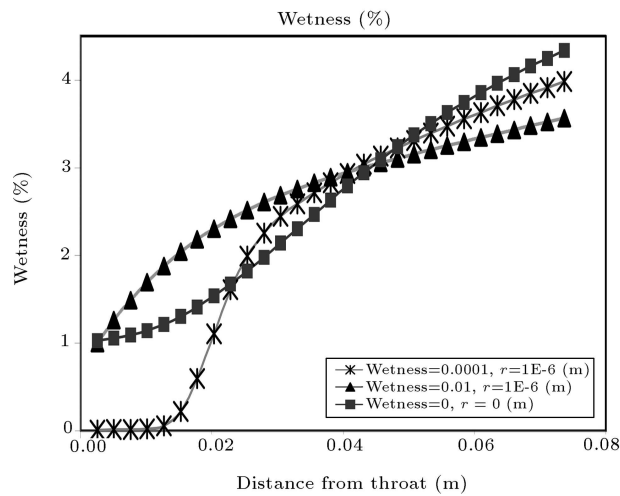


Figure 5. Effect of spraying on wetness (radius is constant).

therefore, the increased temperature is smaller for both droplets and vapour as shown in Figure 6.

It is observed that spraying droplets reduces the degree of supercooling or supersaturating ratio such that entropy, in the case of injecting droplets, is much lower than that of the case without spray as seen in Figure 7.

The wasted energy or thermodynamic loss is calculated using the values of entropy and temperature in each step as shown in Figure 8.

It should be mentioned that all of these solutions are performed for a constant inlet wetness fraction, but the radii of the sprayed droplets are changed. In this case, for the same wetness, as the radius is smaller, the numbers of droplets are increased and, therefore, larger surfaces are provided for the vapour to condense. As a result, the rate of nucleation decreases considerably as shown in Figure 9.

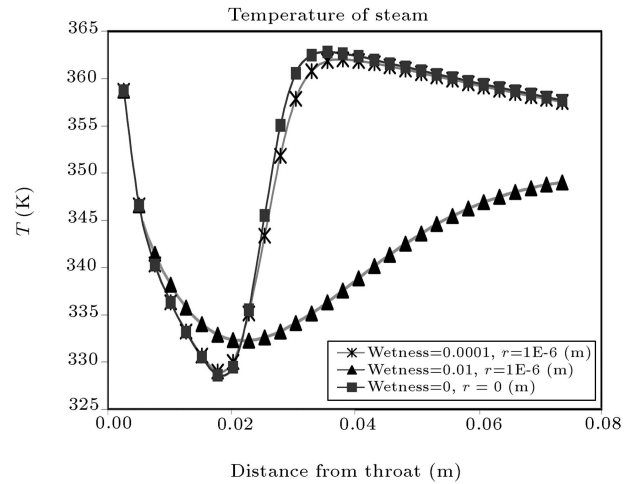


Figure 6. Effect of spraying on vapour temperature changes (radius is constant).

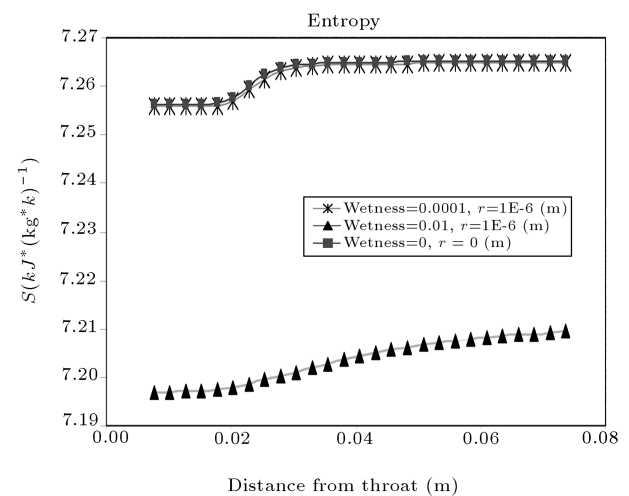


Figure 7. Effect of spraying on entropy change (radius is constant).

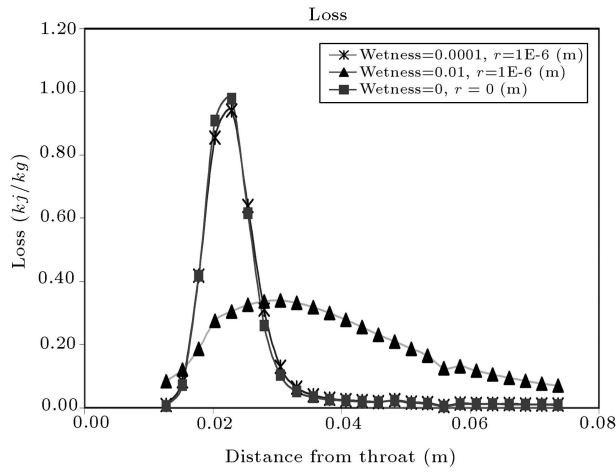


Figure 8. Effect of spraying on thermodynamic losses (radius is constant).

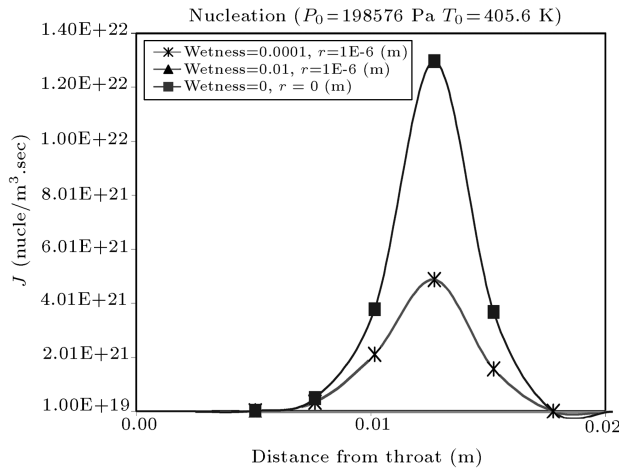


Figure 9. Effect of spraying droplets on nucleation (wetness is constant).

Comparisons with Experimental Results

In the experiment carried out by Pouring [12], steam with a few degrees of superheat was supplied by the central power station. The supply lines were purged and heated for several hours before conducting experiments to ensure equilibrium conditions. Dry steam, which was produced on passage through the electric, is superheated. The degree of superheat could be controlled precisely after particles were sprayed into the nozzle. In Figures 10a and 10b, the calculated pressure distributions are compared to those of the experiment reported by Pouring. As observed in both figures, the trend of pressure reduction in the critical zone or the rapid condensation region is similar to theory and experiments.

CONCLUSION

The results obtained in this study show that spraying

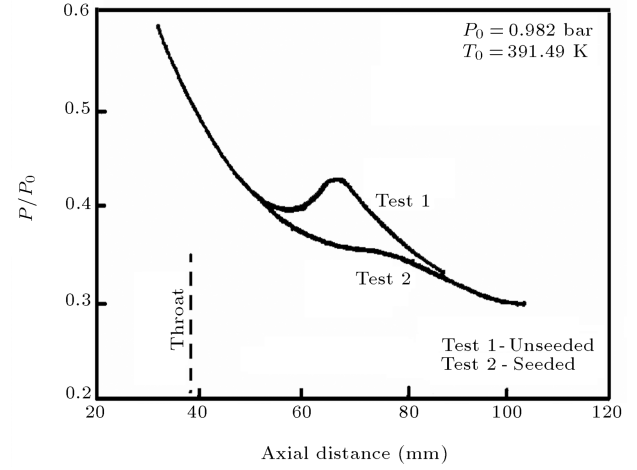


Figure 10a. Experimental results presented by Pouring [12].

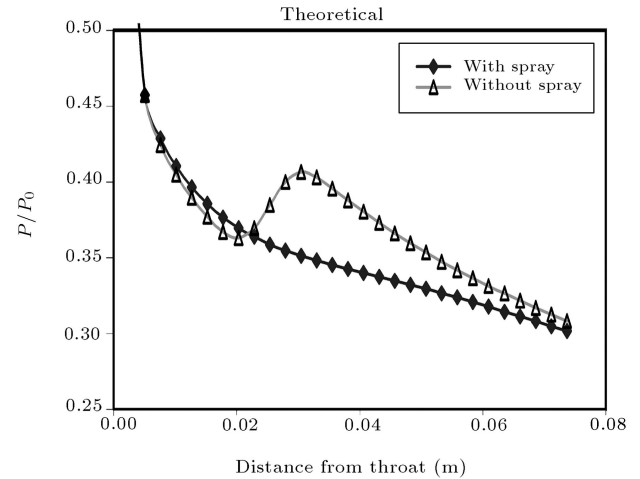


Figure 10b. Comparison of pressure distribution in the case with and without spraying droplets.

droplets into the two-phase flow can:

1. Remove the condensation shock and its effects (there is no decrease in velocity or increase in pressure;
2. Decrease the thermodynamic losses due to less entropy generation;
3. Reduce the wetness fraction at the outlet.

Therefore, by spraying the droplets in steam turbines, the thermodynamic losses of a two-phase flow can be considerably reduced.

NOMENCLATURE

A	area
C_p	specific heat at constant pressure
D_e	equivalent diameter
f	friction factor

ΔG	change in Gibbs free energy
J	rate of formation of critical droplets per unit volume and time
Kn	Knudsen number
L	latent heat
Ma	mach number
m_r	mass of droplet
P	vapour pressure
$P_s(T_G)$	saturation pressure at T_G
Q	condensation coefficient
R	gas constant for water vapour
r	radius of droplet
S	supersaturation ratio $[P/P_s(T_G)]$
T	temperature
$T_s(P)$	saturation temperature at P
ΔT	degree of supercooling $[T_s(P) - T_G]$
T	time
U	velocity
v	specific volume
W	total mass flow rate
X	distance along duct axis
X, Y	functions of temperature and density in equation of state
α_r	coefficient of heat transfer
γ	isentropic component
μ_G	kinematic viscosity of vapour
ζ	dryness fraction
ρ	density of mixture
λ	coefficient of thermal conductivity
σ	surface tension
$\rho_s(T_L, r)$	density corresponding to saturation pressure at temperature T_L over a surface of curvature r
Sc	Schmidt number

Subscripts

G	vapour phase
L	liquid phase
0	stagnation condition
r	radius of a droplet
s	saturation

Superscripts

*	critical droplet
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APPENDIX A

The Virial Coefficients of Vukalovich State Equation

$$B_1 = -\frac{e}{GT} - \phi_1 + b, \quad B_2 = -b\phi_1 + 4\phi_1^2\phi_2,$$

$$B_3 = 32b\phi_1^2\phi_2, \quad B_4 = 0, \quad B_5 = -4n\phi_1^2\phi_2,$$

where:

$$\phi_1 = \frac{CG}{TW_1}, \quad \phi_2 = 1 - \frac{K}{TW_2},$$

and:

$$e = 63.2, \quad b = 0.00085, \quad C = 0.3900 \times 10^6,$$

$$G = 47.053, \quad K = 22.7, \quad n = 0.355 \times 10^{-7},$$

$$m_1 = 1.968, \quad m_2 = 2.957,$$

$$W_1 = (3 + 2m_1)/2, \quad W_2 = (3m_2 - 4m_1)/2.$$

APPENDIX B

The Thermodynamic Properties

$$h = pv - RT^2 \left(\frac{1}{v} \frac{dB_1}{dT} + \frac{1}{2v^2} \frac{dB_2}{dT} + \frac{1}{3v^3} \frac{dB_3}{dT} + \frac{1}{4v^2} \frac{dB_4}{dT} + \frac{1}{5v^5} \frac{dB_5}{dT} \right) + 1.111177T$$

$$+ 3.55878 \times 10^{-4} T^{-2} - \frac{6991.96}{T} + 2070.54,$$

$$s = R + 0.30773 + 1.111177 \ln T + 7.11756$$

$$\times 10^{-4} T - \frac{3495.98}{T^2},$$

$$C_v = \frac{\partial}{\partial T}(h - pv)_v,$$

$$C_p = C_v - \frac{T \left(\frac{\partial p}{\partial T} \right)_v^2}{\left(\frac{\partial p}{\partial v} \right)_T},$$

$$R = 0.46151 \text{ kJ/kg.k}.$$

APPENDIX C

Derivation of the Nucleation Rate Equation

n_g : Number of cluster containing g molecules per unit volume in equilibrium vapour.

f_g : Number of cluster containing g molecules per unit volume in supercooled vapour.

C_g : Rate of condensation $\left(g \xrightarrow{C_g} g+1 \right)$.

E_g : Rate of evaporation $\left(g \xrightarrow{E_g} g-1 \right)$.

In the equilibrium condition, rate of condensation must be equivalent to rate of evaporation, so the number of

clusters containing g molecules must be constant.

$$\left. \begin{array}{l} g \xrightarrow{C_g} g+1 \\ g \xleftarrow{E_{g+1}} g+1 \end{array} \right\} \Rightarrow n_g C_g = n_{g+1} E_{g+1}. \quad (C1)$$

In the supercooled vapour, there is a non-equilibrium condition so:

Growth rate of cluster containing g molecules = (Rate of condensation cluster containing g molecules) – (Rate of evaporation cluster containing $g+1$ molecules):

$$\left. \begin{array}{l} g \xrightarrow{C_g} g+1 \\ g \xleftarrow{E_{g+1}} g+1 \end{array} \right\} \Rightarrow J_g = f_g C_g - f_{g+1} E_{g+1}. \quad (C2)$$

Then, the growth rate of cluster containing $g-1$ molecules is:

$$\left. \begin{array}{l} g-1 \xrightarrow{C_{g-1}} g \\ g-1 \xleftarrow{E_g} g \end{array} \right\} \Rightarrow J_{g-1} = f_{g-1} C_{g-1} - f_g E_g. \quad (C3)$$

Therefore, the total growth rate of cluster containing g molecules is as follows:

$$\left. \begin{array}{l} g-1 \xrightarrow{C_{g-1}} \\ g+1 \xleftarrow{E_{g+1}} \end{array} \right\} \boxed{g} \left. \begin{array}{l} \xrightarrow{C_g} g+1 \\ \xleftarrow{E_g} g-1 \end{array} \right\} \quad (C4)$$

Use Equation C4 to obtain:

$$\frac{\partial f_g}{\partial t} = \overbrace{(f_{g-1} C_{g-1} + f_{g+1} E_{g+1})}^{\text{input}} - \overbrace{(f_g C_g + f_g E_g)}^{\text{output}},$$

$$\frac{\partial f_g}{\partial t} = \overbrace{(f_{g-1} C_{g-1} - f_g E_g)}^{J_{g-1}} - \overbrace{(f_g C_g - f_{g+1} E_{g+1})}^{J_g},$$

$$\frac{\partial f_g}{\partial t} = J_{g-1} - J_g = -\frac{J_g - J_{g-1}}{\Delta g} = -\frac{\partial J_g}{\partial g},$$

$$\Delta g = 1. \quad (C5)$$

Divide Equation C2 by $n_g C_g$ to give:

$$\frac{J_g}{n_g C_g} = \frac{f_g C_g}{n_g C_g} - \frac{f_{g+1} E_{g+1}}{n_g C_g}. \quad (C6)$$

Substitute $n_{g+1} E_{g+1}$ from Equation C1 into Equation C6:

$$\begin{aligned} \frac{J_g}{n_g C_g} &= \frac{f_g C_g}{n_g C_g} - \frac{f_{g+1} E_{g+1}}{n_{g+1} E_{g+1}} = \frac{f_g}{n_g} - \frac{f_{g+1}}{n_{g+1}} \\ &= -\frac{\partial}{\partial g} \left(\frac{f_g}{n_g} \right). \end{aligned} \quad (C7)$$

Use Equations C5 and C7 to get:

$$\begin{aligned}
 \frac{\partial f_g}{\partial t} &= -\frac{\partial J_g}{\partial g} = -\frac{\partial}{\partial g} \left[-n_g C_g \frac{\partial}{\partial g} \left(\frac{f_g}{n_g} \right) \right] \\
 &= \frac{\partial}{\partial g} \left[n_g C_g \frac{\partial}{\partial g} \left(\frac{f_g}{n_g} \right) \right] \Rightarrow \frac{\partial f_g}{\partial t} \\
 &= \frac{\partial}{\partial g} \left[n_g C_g \frac{\partial}{\partial g} \left(\frac{f_g}{n_g} \right) \right]. \tag{C8}
 \end{aligned}$$

To obtain an expression for J_{st} , Equation C8 is written

for a series of cluster sizes in the range of $1 < g < g^+$, where g^+ is much larger than g^* .

The assumptions for obtaining Equation 7 are as follows:

- a) C_g is taken out of the integral and is given a mean value, say as C_{g^*} , then the integral is carried out;
- b) With very little loss of accuracy, the limits of integral is changed from $-\infty$ to $+\infty$.