$(\epsilon_A = Pa/V_L)$

ϵ_D = sparge gas isothermal expansion power per unit volume of clear liquid $W \cdot m^{-3}$

μ = liquid viscosity, $Pa \cdot s$

ρ = liquid density, $kg \cdot m^{-3}$

ρ_G = gas density, $kg \cdot m^{-3}$

σ = liquid surface tension, $N \cdot m^{-1}$

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Manuscript received September 27, 1976; revision received May 11, and accepted May 18, 1977.

A Simplified Model of Electro-Aerodynamic Atomization

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This study represents an attempt to provide an analytical description of the atomization process of a liquid by the combined action of an electrostatic field and a parallel air stream that creates waves on the liquid surface.

The physical phenomenon is extremely complicated, and the theoretical description given is a simplified one. The opposing molecular and electrical forces which occur at the liquid surface whenever an electric charge concentrates on the surface of the liquid could be responsible for the disintegration of the liquid volume into numerous electrically charged droplets. Analyzed like this, the problem seems particularly simple; however, the case under consideration presents the additional complication of an air stream that will atomize the liquid even if there is no electric field.

From the previous consideration, it can be concluded that the model we are trying to develop will have to be based on two factors: hydrodynamics of perturbed liquid surfaces and the characteristics of electrical conduction in liquids. When we take into account the complexity of the phenomenon under study, gross approximations must be made in constructing a theoretical model.

This work is an extension of a work originally published by Mayer (1961), and the modification sought is one that will allow the consideration of electrostatic field effects on the atomization process.

MATHEMATICAL MODEL

The forces acting on a planar liquid surface are assumed to affect the perturbations in such a way that motion is restricted to the coordinate normal to the liquid surface. If the fluid surface is perturbed by small cosine waves, the equation of the surface can be taken as

$$z = z_o \cos(\omega t) \cos\left(\frac{2\pi x}{\lambda}\right) \qquad (1)$$

Let us assume that $\epsilon_L > \epsilon_o$; this assumption leads to the following expressions for the electric fields if E_o is the field outside the liquid at a distance where it is not perturbed by the surface instabilities, and the liquid molecules are rapidly oriented:

$$E_{z_o} = \frac{2\pi}{\lambda} E_o z_o e^{-\frac{2\pi z}{\lambda}} \cos\left(\frac{2\pi x}{\lambda}\right) \cos(\omega t) + E_o \quad z > 0 \qquad (2)$$

$$E_{zL} = \frac{\epsilon_o}{\epsilon_L} \frac{2\pi}{\lambda} E_o z_o e^{\frac{2\pi z}{\lambda}} \cos\left(\frac{2\pi x}{\lambda}\right) \cos(\omega t) + \frac{\epsilon_o}{\epsilon_L} E_o \quad z < 0 \qquad (3)$$

Remembering that the forces in a field are given by the product charge times field and that the charge at the surface is given by

$$q_{\text{surface}} = \epsilon_o \left(1 - \frac{\epsilon_o}{\epsilon_L}\right) E_{z_o} = \epsilon_L \left(1 - \frac{\epsilon_o}{\epsilon_L}\right) E_{zL} \qquad (4)$$

We can estimate the electrostatic forces acting at the liquid surface.

If the expressions for electrostatic field are used, the electrostatic pressure equation can be obtained. The following expression results upon neglecting the terms that include z_o^2 and terms that are independent of surface perturbation. Thus, the electrostatic pressure that tends to enhance the perturbation becomes

$$P_E = \epsilon_o \left(1 - \frac{\epsilon_o}{\epsilon_L}\right)^2 E_o^2 \, z_o \frac{2\pi}{\lambda} \cos\left(\frac{2\pi x}{\lambda}\right) \cos(\omega t) \tag{5}$$

The value of the angular frequency ω can be determined by calculating the forces that act on the fluid surface in the z direction (normal to liquid surface). For equilibrium at the fluid surface, the difference between the inertial pressures is set equal to the difference between the surface tension pressure and the electrostatic pressure.

The pressure difference due to surface tension can be expressed as

$$\Delta P_\sigma = \left| \frac{\partial^2 z}{\partial x^2} \right| \sigma \tag{6}$$

The pressure difference due to inertial effects has been demonstrated by Lamb (1945) to be

$$\Delta P_I = (\rho + \rho_L)\, \omega^2 z_o \frac{\lambda}{2\pi} \cos\left(\frac{2\pi x}{\lambda}\right) \cos(\omega t) \tag{7}$$

If the difference between the inertial pressure is set equal to the difference between the surface tension pressure and the portion of the electrostatic field that tends to enhance the surface perturbation, we may find by straightforward algebraic manipulation a solution for the angular frequency of oscillation as

$$\omega = \left[\frac{\left(\frac{2\pi}{\lambda}\right)^3 \sigma - \epsilon_o \left(1 - \frac{\epsilon_o}{\epsilon_L}\right) E_o^2 \left(\frac{2\pi}{\lambda}\right)^2}{\rho + \rho_L} \right]^{1/2} \tag{8}$$

Equation (8) becomes

$$\omega = \left(\frac{2\pi}{\lambda}\right)^{3/2} \left[\frac{\sigma_{\text{eff}}}{\rho + \rho_L}\right]^{1/2} \tag{9}$$

if in the previous equation an effective surface tension is defined as

$$\sigma_{\text{eff}} = \sigma - \epsilon_o \left(1 - \frac{\epsilon_o}{\epsilon_L}\right) E_o^2 \left(\frac{\lambda}{2\pi}\right) \tag{10}$$

Physically effective surface tension can be interpreted as the net result of the opposing effects of the cohesive surface tension forces and the disrupting forces created by the repulsive forces between like charges at molecular level. It has been previously suggested by Straubel (1954) and Graf (1962) that electrostatic field effects can be associated with disruptive forces generated by the electrical charging of the liquid. A previous experimental and theoretical study by Burayev and Vereschagin (1972) demonstrated that in electrostatic atomization the electric field necessary to cause disruption in the liquid mass increases as the liquid surface tension increases.

A previous study by Jones and Thong (1971) has expressed the idea that electrostatic fields at the liquid surface are a controlling factor in electrostatic atomization.

A prediction of average droplet sizes in high velocity air stream atomization accounting for both surface tension and air velocity effects has been published by Mayer (1961). This analysis can be modified to account for the additional effects of electrostatic forces by the use of the effective surface tension defined in Equation (8). The derivation of Mayer's analysis and its modification in this manner are given as follows.

Mayer's analysis was based on the assumption that droplet sizes are a function of both rate of change of surface wave amplitude and wave velocity. Lamb (1945) used Jeffreys' expression (1924, 1925) for wind pressure effects to account for the rate of change of wave amplitude in surface disturbances and obtained the following expression:

$$\frac{d\alpha}{dt} = \alpha \left[\frac{\beta\rho(V - c)^2}{2\sqrt{\rho_L \, \sigma_{\text{eff}}}} \sqrt{\frac{2\pi}{\lambda}} - 2\frac{\mu_L}{\rho_L}\left(\frac{2\pi}{\lambda}\right)^2 \right] \tag{11}$$

This equation used by Mayer was obtained from an approximate energy balance in which surface phenomena were neglected in comparison with the kinetic and potential energy of the wave, viscous work, and the dynamic effects of the wind. Equation (11) may also be assumed to be valid in high velocity atomization in the presence of an electrostatic field, since it is assumed that electrostatic forces produce surface effects only. The wave velocity of a system of traveling waves is considered by Lamb (1945*b*) to be

$$c = \frac{\omega\lambda}{2\pi} \tag{12}$$

Substituting Equations (12) and (10) into Equation (11) and neglecting c in comparison with V, we get

$$\frac{d\alpha}{dt} = \alpha \left[\frac{\beta \rho V^2}{2\sqrt{\rho_L \, \sigma_{\text{eff}}}} \sqrt{\frac{2\pi}{\lambda}} - 2\frac{\mu_L}{\rho_L}\left(\frac{2\pi}{\lambda}\right)^2 \right] \tag{13}$$

It is also assumed that the air density is negligible when compared to the liquid density to obtain the previous equation, which can be expressed as

$$\frac{d\alpha}{dt} = \frac{\alpha}{\tau} \tag{14}$$

where

$$\frac{1}{\tau} = \frac{\beta \rho V^2}{\sqrt{2 \rho_L \, \sigma_{\text{eff}}}} \left(\frac{2\pi}{\lambda}\right)^{1/2} - 2\frac{\mu_L}{\rho_L}\left(\frac{2\pi}{\lambda}\right)^2 \tag{15}$$

In view of the fact that the surface waves will grow or diminish according to the sign of τ, the waves maintained by the wind effect will be greater than the minimum which is obtained when $(1. / \tau) = 0$:

$$\frac{\beta \rho V^2}{2\, \sigma_{\text{eff}}^{1/2}} - 2\frac{\mu_L}{\sqrt{\rho_L}}\left(\frac{2\pi}{\lambda}\right)^{3/2} = 0 \tag{16}$$

Equation (16) can be solved to obtain values of λ_{min}.

The following atomization mechanism has been postulated by Mayer (1961): "When the wind induced wave of length λ has grown to an amplitude α comparable with, λ, the crest of the wave is eroded as a ligament from which droplet of a size proportional to λ are formed, where F is independent of λ but possibly dependent on fluid parameters."

$$d_o = F \cdot \lambda \tag{17}$$

Levich (1962) gives support to the idea that jet atomization produces droplets of sizes proportional to the wavelengths of the disturbed surface. It has been considered reasonable by Vonnegut and Neubauer (1952) to assume that in electrostatic fields the droplet formation should occur from crests of the waves. In electrostatic atomization there is a preferential migration of charges to surface protuberances as stated by Thong and Weinberg (1971). These ideas also give support to the thought that droplet formation occurs from the crest of the surface waves, since the maximum concentration of electric charges and minimum valve of effective surface tension will occur at these points.

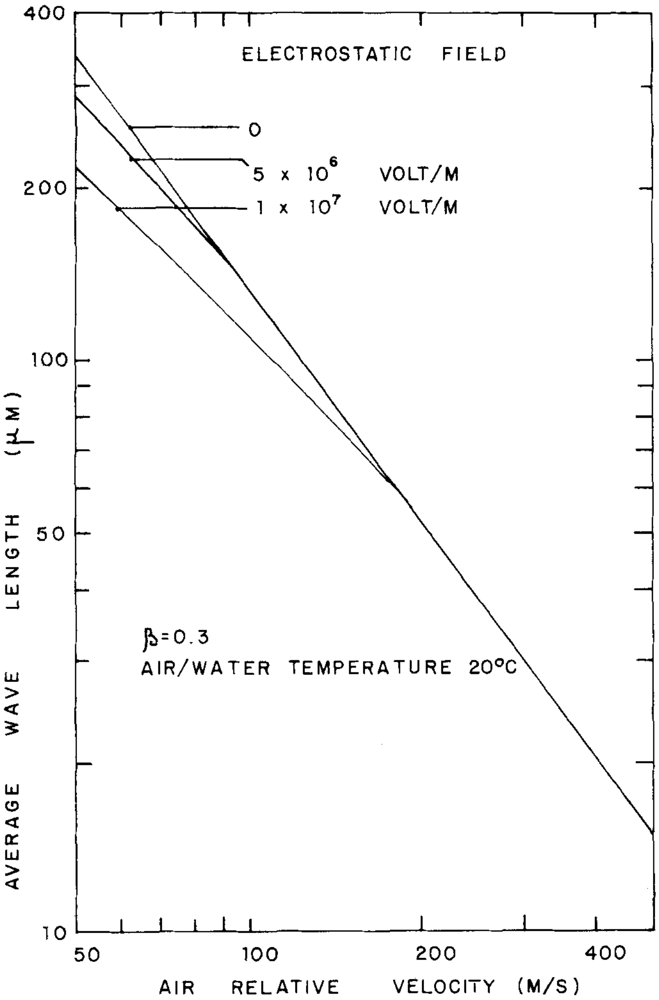

Fig. 1. Average wavelength as a function of air relative velocity and electrostatic field.

Mayer (1961) took a wavelength distribution function of the form

$$N(\lambda) = 1./(\tau\lambda^2) \tag{18}$$

so it follows from Equation (17) that

$$\bar{d}_o = F\,\bar{\lambda} \tag{19}$$

where $\bar{\lambda}$ is determined from

$$\bar{\lambda} = \frac{\displaystyle\int_{\lambda_{\min}}^{\lambda_{\max}} \frac{d\lambda}{\lambda\tau}}{\displaystyle\int_{\lambda_{\min}}^{\lambda_{\max}} \frac{d\lambda}{\lambda^2\tau}} \tag{20}$$

The values of $\lambda_{\min}$ can be obtained from Equation (16), and the value of $\lambda_{\max}$ is obtained from Equation (10) by setting the value of the effective surface tension to zero.

Since this analysis is an extension of Mayer's work, it is important to notice that if we take an electrostatic field equal to zero, the maximum wavelength becomes infinite, the effective surface tension is then liquid surface tension, and the whole set of results reported by Mayer is reproduced.

Figure 1 presents the average wavelength as the dependent variable for an air-water system. In order to solve explicitly the equations that describe λ, a value of the sheltering parameter β of 0.3 was used as suggested by Mayer (1961) and Lamb (1945c). Bearing in mind that the ratio ϵ_o/ϵ_L is a constant for a given system, we assume that the water is a perfect conductor without loss of generality.

CONCLUDING REMARKS

The addition of an electrostatic field to an atomization process, where there is a finite velocity difference between the liquid being atomized and the air surrounding it, produces a reduction in the wavelength of the surface perturbations and, in view of the atomizations mechanism accepted, a reduction in the average droplet size of the spray.

The electrostatic field influence becomes reduced as the velocity difference between the air and liquid face increases, and at high relative velocities the effect of the electrostatic field becomes negligible. Theoretically it is possible to increase the electrostatic field so as to produce droplet size reduction at any velocity; however, there is a practical limit set by the maximum field that can be sustained before electrical breakdown occurs.

ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr. I. Smith of the City University of London and Drs. P. Lychaa and J. Castillo both of Universidad del Zulia, Maracaibo, Venezuela.

NOTATION

c = wave velocity
E_o = unperturbed electric field
E_{z_o} = electric field in z direction in free space
E_{z_L} = electric field in z direction in liquid
F = configuration factor
P_E = electrostatic pressure
P_σ = surface tension pressure
P_I = pressure due to inertial effects
q_{surface} = surface electric charge
t = time
V = velocity difference between liquid and air
x, y, z = rectangular coordinates
z_o = surface perturbation at $t = 0$

Greek Letters

α = wave amplitude
β = sheltering parameter
ϵ_L = liquid electric permittivity
ϵ_o = free space electric permittivity
λ = wavelength
$\lambda_{\max}$ = maximum wavelength
$\lambda_{\min}$ = minimum wavelength
μ_L = liquid viscosity
μ = air viscosity
ρ = air density
ρ_L = liquid density
τ = reciprocal of time modulus
ω = angular frequency of oscillation
σ = liquid surface tension

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Manuscript received November 9, 1976; revision received January 18, and accepted January 25, 1977.

Kinetics of the Reaction Between Tungsten Trioxide and Carbon Tetrachloride

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Under proper experimental conditions, tungsten trioxide reacts with chlorine or chloridizing reactants giving two volatile oxichloridized products: WO_2Cl_2 and $WOCl_4$. The former is a light yellow solid melting at 226°C and decomposing before reaching boiling point; the latter melts at 211°C and boils at 227.5°C.

As proposed in the literature (for example, Li and Wang, 1956; Papa, 1968), these reactions could prove to be helpful in the tungsten trioxide purifying processes.

Calderon et al. (1969) studied the kinetics of reaction between tungsten trioxide and chlorine with carbon. Our aim was to investigate the kinetics of the reaction between tungsten trioxide and carbon tetrachloride.

Thermodynamic investigations on the system, carried out by Funaki and Uchimura (1962) and by Castro Luna and Rivarola (1971), show that the main possible reactions are

$$WO_3(s) + CCl_4(g) \rightleftarrows WOCl_4(g) + CO_2(g) \quad (1)$$

$$2WO_3(s) + CCl_4(g) \rightleftarrows 2WO_2Cl_2(g) + CO_2(g) \quad (2)$$

$$WO_3(s) + CCl_4(g) \rightleftarrows WO_2Cl_2(g) + COCl_2(g) \quad (3)$$

The system is very complex, and it is necessary to simplify it in order to elaborate a reasonably simple model. Thus, the three equations shown above can be summed up as

$$A(g) + b\,B(s) \rightleftarrows \text{gaseous products} \quad (4)$$

THEORY

If we consider that our spherical pellets of WO_3 have an initial porosity ϵ_o, the reaction with CCl_4 vapor will take place simultaneously on the outer and inner surfaces. As the reaction goes on, the porosity and surface areas will change.

The starting point is a mass balance for A and B. Assuming that our solid is isotropic, and considering that we are working with spherical pellets, we get

$$\epsilon \frac{\partial C_A}{\partial \theta} = \nabla (D_A \nabla C_A) - r_A \quad (5)$$

$$-\frac{\partial C_B}{\partial \theta} = b\,r_A \quad (6)$$

If we assume that under our experimental conditions the reaction is irreversible, the rate equation can be written as

$$r_A = k\,a_i\,C_A{}^{\gamma} \quad (7)$$

With the following additional hypotheses: the gaseous reactant instantaneously achieves the pseudo steady state, the system is isothermal, and the gaseous reactant is totally consumed near the outer pellet surface, Equations (5), (6), and (7) can be solved as proposed by Williams et al. (1970). Thus, the following equations are obtained:

$$M\,\theta = 3\,(1 - R^*) + 2\,P \ln R^* \quad (8)$$

$$1 - X_B = R^{*3} - P\,R^{*2} \quad (9)$$

where

$$M = \left[\,1 + \frac{1-\alpha_o}{\alpha_o}\,\frac{h^+}{h_o}\right] \frac{b\,k\,C_{As}{}^{\gamma}}{L_o C_{B_o}} \quad (10)$$

$$P = \frac{\gamma+1}{2}\,\frac{h^+}{h_o} \quad (11)$$

and h_o is represented by

$$h_o = L_o \left[\,\frac{\gamma+1}{2}\,\frac{k\,a_{i_o}\,C_{As}{}^{\gamma-1}}{D_{A_o}}\,\right]^{0.5} \quad (12)$$

and h^+ is a factor defined by