

## MODELLING AND OPTIMISATION OF LOW SOLIDS WASTE TREATMENT PROCESSES

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*Dulux Australia* is a subsidiary of the multinational chemical company *ICI* and is the largest paint manufacturer in Australia. To increase paint production capacity it will be necessary for the company to implement more effective methods of cleaning and waste disposal at the manufacturing site. Paint is a substance composed of resins and pigments which are initially suspended in a mixture of liquid solvents. In this form the paint must be stored in sealed containers to prevent evaporation of volatile solvents. The liquid paint can be applied by brush or spray to a wood or metal surface where it subsequently dries to provide a durable protective coating. The resins are used for surface adhesion, the liquid solvents allow easy application of the paint and are sufficiently volatile to promote quick drying, and the pigments provide colour. Since colour is a particularly important characteristic it is essential that the tanks in which the paint is manufactured are scrupulously cleaned between batches. The cleaning process generates a large amount of liquid waste from which the solvents can be recovered by distillation. Unfortunately the high temperatures normally required to recover the less volatile solvents can result in baking of solid waste onto the walls of the container. In this article we propose a simple model for the distillation process and show that boiling temperatures can be lowered by reducing the pressure in the container. In particular we show that the required pressure reduction can be achieved using a condenser, provided that the heat exchange capacity of the condenser matches the heat exchange capacity of the boiler at the desired boiling temperature. In this way we suggest that baking of solid waste onto the container walls can be avoided. Since both the boiler and the condenser used for this process by *Dulux Australia* are vacuum rated it may be possible for the company to implement the proposed operation with only minor modifications to the current equipment.

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## 1. Introduction

In this section we review the current waste recovery process and discuss some of the associated problems.

### 1.1 A brief description of the waste recovery process

The tanks used for paint manufacture by *Dulux Australia* need to be carefully cleaned after each batch of paint is produced. The resultant liquid waste consists of up to eight different solvents and contains solid particles of paint and resin. After the waste is allowed to settle the upper layer, containing less than ten percent solids, is pumped into a Brighton still. The still is heated by superheated steam in a steam jacket around the vessel and a vacuum pump is used to reduce the pressure inside the still. The solvents are thereby distilled and are subsequently recovered. The distillation process is continuous with more waste added from time to time but the process must be stopped periodically to remove residual waste. The residue from the Brighton still contains a high percentage of solid material and is treated by a different process known as the Dusol process. The Dusol vessel is heated by a steam jacket in the same way as the Brighton still but in normal operation also allows superheated steam to be injected directly into the mixture by internal sparges. In this case a solvent and water mixture is distilled. The solvent is recovered after condensation while the water is returned to the Dusol vessel. The Dusol process is not continuous and is operated at atmospheric pressure. The solid waste that remains after completion of the process is used as landfill.

### 1.2 Problems associated with the current operation

The current operation has resulted in overloading of the Brighton still and under utilisation of the Dusol vessel. To overcome this imbalance *Dulux Australia* has proposed that the Dusol operation be modified to allow low-solids waste to be treated in the Dusol vessel. Some trials have already been conducted and two specific problems have arisen. If the steam sparges are used then the total amount of waste water produced at the site increases beyond the maximum disposal capability. If the steam sparges are not used then the high temperatures needed to recover the less volatile solvents cause solid waste to bake onto the sides of the Dusol vessel. This requires an expensive and time-consuming cleaning operation. The company asked MISG 97 to consider the possible benefits associated with a modified Dusol process that would avoid the above mentioned problems. In particular they asked us to model the distillation process and to consider the effect of reducing the pressure in the Dusol vessel.

## 2. The MISG investigation

In this section we describe the particular problems investigated during the MISG, we present the main results of our investigations and make several recommendations that could improve the waste treatment procedure.

### 2.1 The particular problems

The MISG team began by proposing a model of the boiling process in the Dusol vessel for a one-component solvent with no solid waste. The proposed model is nothing more than an idealised model of the boiling process for a pure liquid. The model uses two ordinary differential equations to describe the conservation of mass and energy and thereby relates the vaporisation of the liquid to the heat transfer capacity of the vessel and in turn to the temperature difference between the steam in the steam jacket and the liquid in the container. An analytic solution to the differential equations was obtained and this solution has been used to calculate the time taken to complete the boiling process. By incorporating Antoine's law, an empirical law relating the boiling temperature of the liquid to the pressure in the container, the solution has also been used to determine what happens to the boiling temperature and to the time taken to complete the boiling process when the pressure in the container is reduced.

The model of the boiling process for a one-component solvent was then extended to a model for a two-component solvent. Although the team did not attempt to find an analytic solution to the extended problem an elementary numerical scheme can be used to obtain a suitable solution. Further extension to a multiple solvent model is easy and an elementary numerical scheme could again be used to obtain a solution.

The most important part of the MISG investigation was the development of a model for the distillation of a one-component solvent at reduced pressure. The MISG team proposes that the Dusol vessel and the condenser be connected in such a way that the entire distillation process takes place in a sealed chamber. Once boiling has commenced the distillation chamber will fill with vaporised solvent and air will be vented from the chamber. The chamber should then be sealed from the atmosphere and the condenser should be turned on. If the heat-exchange capacity of the condenser initially exceeds the heat-exchange capacity of the boiler then vapour will be removed from the chamber and the pressure will fall. This will cause the boiling temperature to fall and this in turn will mean a higher temperature gradient between the steam jacket and the boiling liquid. As a result the heat-exchange capacity of the boiler will increase. At

the same time, as the temperature in the distillation chamber falls, the heat-exchange capacity of the condenser will decrease. Eventually it seems likely that a balance will be reached and that the distillation process will operate at a lower pressure and a lower temperature. The model for this process is essentially an extension of the original model for the boiling of a one-component solvent and includes additional algebraic equations to describe the heat exchange process in the condenser. We can again obtain an analytic solution for the extended system of differential and algebraic equations and can again calculate the time taken to complete the boiling process. We can also calculate the equilibrium boiling temperature. Antoine's law is used to find the pressure in the distillation chamber. A schematic diagram of the Dusol vessel and the condenser for the proposed distillation operation is shown in Figure 1. The diagram shows a pressure valve between the Dusol vessel and the condenser. This valve is essentially a safety valve and should be used to control the pressure drop in the Dusol vessel when the condenser is first turned on. A sudden pressure drop could cause an explosive vaporisation of the solvent.

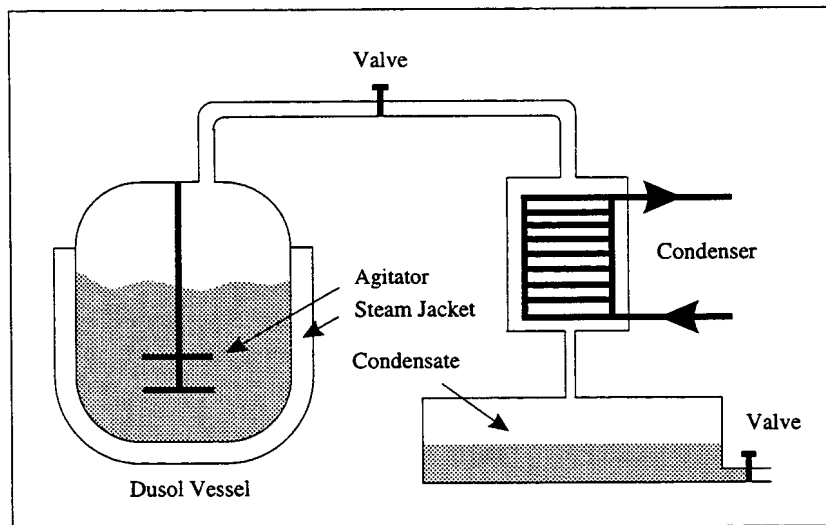


Figure 1: A schematic diagram of the Dusol vessel and the condenser for the proposed distillation operation.

The distillation model for a one-component solvent is easily extended to a distillation model for a two-component solvent and once again it seems that this model could be solved using a suitable numerical scheme.

### 3. The main results

#### 3.1 Notation

To explain the main results we use the following notation:

- $M = M(t)$  is the mass of the liquid at time  $t$ ;
- $U$  is the heat transfer coefficient of the steam jacket on the Dusol vessel;
- $A$  is the effective heat transfer area between the steam jacket and the liquid in the Dusol vessel;
- $T_s$  is the temperature of the steam in the steam jacket;
- $\lambda$  is the latent heat of vaporisation of the liquid;
- $T_b$  is the boiling temperature of the liquid;
- $T = T(t)$  is the temperature of the liquid at time  $t$ ; and
- $c$  is the specific heat of the the solvent.

#### 3.2 Explanation of the main results

We use the fundamental principles of heat transfer to derive a system of elementary equations that describe the vaporisation process for a one-component solvent and we present schemes for the analytic and numerical solution of these equations. We show how the analysis can be extended to provide a basic model for a more complicated mixture of solvents and we comment on the implications of our theoretical models.

For the vaporisation of a one component solvent we show that the time taken to reach the boiling temperature is

$$t_0 = \frac{cM(0)}{UA} \log \left[ \frac{T_s - T(0)}{T_s - T_b} \right] \quad (1)$$

and the additional time taken to complete the boiling process is given by

$$t_1 - t_0 = \frac{\lambda[M(t_0) - M(t_1)]}{UA(T_s - T_b)}. \quad (2)$$

Note that no boiling occurs for  $0 \leq t \leq t_0$  and so  $M(t_0) = M(0)$ . If, for the sake of argument, the boiling temperature  $T_b$  could be lowered to the extent

that  $T_s - T_b$  were doubled then the time taken to reach the boiling temperature would be reduced significantly with the actual change in  $t_0$  given by

$$\Delta t_0 = (-1) \frac{cM(0)}{UA} \log 2 \approx (-0.69) \frac{cM(0)}{UA}. \quad (3)$$

We can see from (2) that the additional time taken to complete the boiling process would be nearly halved. The boiling temperature could be lowered by installing a vacuum pump but our model of a coupled system for the distillation of a one-component solvent shows that it may be more effective to use the condenser to lower the pressure in the distillation chamber. From a quasi steady-state analysis we argue that the distillation time is now given approximately by

$$t_1 - t_0 = \frac{\lambda[M(t_0) - M(t_1)]}{UA(T_s - T_{b,e})} \quad (4)$$

where  $T_{b,e}$  is the lowered equilibrium boiling temperature for the solvent. Since the quasi-steady-state analysis assumes a constant rate of mass transfer which is equal to the final equilibrium rate  $m_{v,e}$  and since  $m_{v,e}$  is always greater than the actual distillation rate  $m_v$  the true distillation time will lie somewhere between the first estimate (2) and the second estimate (4). Nevertheless we emphasise that the total cycle time will be significantly reduced. A preliminary simulation of the coupled system using parameter values for water has shown that the numerical solution of the equations is consistent with our theoretical analysis and that a significant reduction in boiling point can be expected.

The MISG team believes that the analysis of the one-component solvent is particularly important in so far as it can be used to provide a good model for recovery of the least volatile solvent. If the distillation process is designed so that the least volatile solvent is recovered at a suitably lowered boiling temperature then it should follow that all other solvents will be inadvertently recovered.

### 3.3 The MISG recommendations

As a result of our investigations the MISG team believes that the recovery of solvents can be considerably improved if:

- the Dusol container is modified so that the waste recovery process can be operated at reduced pressure; and
- the Dusol container and the condenser are coupled so that the condenser can be used to lower the pressure in the Dusol vessel.

We believe that the company should undertake a pilot program to verify the preliminary conclusions from our theoretical analysis. In conducting this program we recommend:

- that a series of trials be conducted on a coupled system with low volumes of solvent to determine appropriate control strategies;
- that the pressure and temperature in each vessel should be continuously monitored;
- that the heat exchange capacity of the condenser should be set at zero initially and should be gradually increased to ensure a properly controlled pressure decrease in the boiler; and
- that pressure valves be inserted as appropriate to prevent any sudden pressure drop and associated possible explosive vaporisation of liquid in the boiler.

### 3.4 Further work

From a practical viewpoint we need to test the observed behaviour of the system against the predicted theoretical behaviour of the model. In those cases where the observed behaviour and the predicted behaviour agree in principle the tests will allow us to determine appropriate values for the important parameters. The development of suitable numerical solution techniques for the various differential and algebraic equations is also an area where further work could be done.

From a theoretical point of view there are two clearly defined problems that could be studied. In the first place it is obvious that the proposed distillation process can be formulated as a control problem. The basic control variables are the rate of steam flow into the steam jacket and the rate of coolant flow through the condenser. These variables control the respective heat exchange capacities that determine the rate of distillation. Is it possible to determine a stable control procedure that will avoid a sudden drop in pressure and a possible explosive vaporisation of liquid in the boiler? Is the state of the system controllable? Can we construct a suitable cost function and determine an optimal control policy that minimises this cost? In the second place it would be interesting to consider the possible development of an analytic solution to the two-component distillation model.

## 4. Vaporisation of a one-component solvent

In this section we describe the vaporisation process for a one-component solvent.

### 4.1 Notation

We use the following notation:

- $N = N(t)$  is the number of moles of the liquid at time  $t$ ;
- $w$  is the molar mass of the liquid;
- $M = M(t) = N(t)w = Nw$  is the mass of the liquid at time  $t$ ;
- $n_v = n_v(t)$  is the molar vaporisation rate of the liquid at time  $t$ ;
- $m_v = m_v(t) = n_v(t)w = n_v w$  is the mass vaporisation rate of the liquid at time  $t$ ;
- $\rho$  is the density of the liquid;
- $U$  is the heat transfer coefficient of the steam jacket on the Dusol vessel;
- $A$  is the effective heat transfer area between the steam jacket and the liquid in the Dusol vessel;
- $T_s$  is the temperature of the steam in the steam jacket;
- $\lambda$  is the latent heat of vaporisation of the liquid;
- $T_b$  is the boiling temperature of the liquid;
- $T = T(t)$  is the temperature of the liquid at time  $t$ ;
- $P = P(t)$  is the vapour pressure in the Dusol vessel at time  $t$ ; and
- $c = c(P)$  is the specific heat of the the solvent at pressure  $P$ .

### 4.2 The basic equations

We assume that the liquid solvent contains only a single component. The rate of heat transfer from the steam to the liquid is directly proportional to the temperature difference. The temperature of the liquid rises until the boiling temperature is reached at time  $t_0$ . The liquid then begins to boil and boiling



continues until time  $t_1$  when the process is stopped. With pure solvent the process could continue until the liquid was completely vaporised but in practice the solvent contains dissolved material and it is necessary to stop the process when the mass of liquid reaches a minimum acceptable value. During the first phase when  $t \leq t_0$  we assume that the entire heat transfer is used to raise the temperature of the liquid and that no vaporisation occurs. During the second phase for  $t_0 \leq t \leq t_1$  we assume that the temperature of the liquid remains constant and that the heat transfer is used only to supply the latent heat required for vaporisation.

In each phase we have two basic equations for mass balance and energy balance. In the case of a single component solvent it is convenient to write these equations in terms of mass. We will assume that the effective area of heat transfer remains constant. In general the equations will be

$$\frac{dM}{dt} = -m_v \quad (5)$$

for the mass balance and

$$cM \frac{dT}{dt} = UA(T_s - T) - m_v \lambda \quad (6)$$

for the energy balance. When  $0 \leq t \leq t_0$  we assume  $m_v = 0$  and hence

$$\frac{dM}{dt} = 0 \quad (7)$$

and

$$cM \frac{dT}{dt} = UA(T_s - T) \quad (8)$$

from which it follows by elementary calculus that

$$M = M(0) \quad (9)$$

and

$$T_s - T = [T_s - T(0)] e^{-UA t / M(0)c}. \quad (10)$$

In particular we note that  $M(t_0) = M(0)$ . By using the boundary condition  $T(t_0) = T_b$  we obtain

$$t_0 = \frac{cM(0)}{UA} \log \left[ \frac{T_s - T(0)}{T_s - T_b} \right]. \quad (11)$$

For  $t_0 \leq t \leq t_1$  we assume that  $T = T_b$  is constant with

$$\frac{dM}{dt} = -m_v \quad (12)$$

and

$$m_v \lambda = UA(T_s - T_b) \quad (13)$$

and hence it follows that

$$M = M(t_0) - \frac{UA}{\lambda}(T_s - T_b)(t - t_0). \quad (14)$$

By setting  $t = t_1$  we obtain

$$t_1 - t_0 = \frac{\lambda[M(t_0) - M(t_1)]}{UA(T_s - T_b)}. \quad (15)$$

The equations (10) and (14) are supported in principle by experimental observations. From equations (11) and (15) we can argue that the batch cycle time  $t_1$  will be reduced if we can reduce the boiling temperature  $T_b$ . This could be accomplished by reducing the pressure in the Dusol vessel. The relationship between the liquid boiling temperature and the pressure in the vessel is given explicitly by Antoine's law

$$\log P = \alpha - \frac{\beta}{T_b + \gamma} \quad (16)$$

where  $P$  is the pressure in the vessel and  $\alpha$ ,  $\beta$  and  $\gamma$  are solvent dependent constants.

### 4.3 The modified basic equations

Note that in reality the heat transfer area will decrease with time as the liquid is vaporised. We will show that the previous analysis can be modified to take this into account and that a similar conclusion is reached. The analysis for the first phase with  $0 \leq t \leq t_0$  is not changed because no vaporisation occurs and the contact area  $A(t) = A(0)$  remains constant. During the second phase for  $t_0 \leq t \leq t_0^*$  the level of liquid solvent in the container falls but until the level falls to the top of the steam jacket at time  $t_0^*$  the previous analysis remains valid with the contact area still given by  $A(t) = A(0)$  for  $t_0 \leq t \leq t_0^*$ . Thereafter the contact area decreases and a modified analysis should be used until the process is stopped at time  $t_1$ . The details of the modified analysis are given in the appendix.

## 5. Vaporisation of a two-component solvent

In this section we consider the vaporisation of a solvent with two components.

## 5.1 Notation

We use the following additional notation:

- $N_i = N_i(t)$  is the number of moles of component  $i$  in the liquid at time  $t$ ;
- $w_i$  is the molar mass of component  $i$ ;
- $M_i = M_i(t) = N_i(t)w_i = N_i w_i$  is the mass of component  $i$  in the liquid at time  $t$ ;
- $n_v = n_v(t)$  is the molar vaporisation rate of the liquid at time  $t$ ;
- $x_i = x_i(t)$  is the mole fraction of component  $i$  in the liquid at time  $t$ ;
- $P_i = P_i(t)$  is the vapour pressure of component  $i$  in the liquid at time  $t$ ;
- $\lambda_i$  is the latent heat of vaporisation of component  $i$ ;
- $T_{b,i}$  is the boiling temperature of component  $i$ ;
- $T_b$  is the boiling temperature of the liquid;
- $c_i = c_i(P)$  is the specific heat of component  $i$  in the liquid at constant pressure  $P$ ; and
- $y_i = y_i(t)$  is the mole fraction of component  $i$  in the vapour at time  $t$ .

## 5.2 The basic equations

The temperature of the solvent rises until the initial boiling temperature of the mixture is reached at time  $t_0$ . The boiling temperature can be calculated using Raoult's law. To find the boiling point  $T_b = T_b(t)$  at time  $t$  we solve

$$x_1 P_1 + x_2 P_2 = P \quad (17)$$

where  $x_1 = x_1(t)$  and  $x_2 = x_2(t)$  are the mole fractions given by

$$x_1 = \frac{N_1}{N_1 + N_2} \quad \text{and} \quad x_2 = \frac{N_2}{N_1 + N_2} \quad (18)$$

of the two components in the liquid mixture and where the vapour pressures  $P_1 = P_1(T_b)$  and  $P_2 = P_2(T_b)$  of the two components are determined by Antoine's formula

$$\log P_i = \alpha_i - \frac{\beta_i}{T_b + \gamma_i} \quad (19)$$

for each  $i = 1, 2$ . If we assume that the boiling temperatures for the two separate components are given by  $T_{b,i}$  for each  $i = 1, 2$  with  $T_{b,1} < T_{b,2}$  then there is a unique solution to equation (17) with  $T_{b,1} < T_b < T_{b,2}$  and  $P_1 > P > P_2$ . The composition of the vapour is calculated from the equations

$$y_i P = x_i P_i \quad (20)$$

for each  $i = 1, 2$ . It is clear from these equations that  $y_1 > x_1$  and  $y_2 < x_2$  and hence the molar fraction  $x_1(t)$  is a decreasing function while the molar fraction  $x_2(t)$  is an increasing function. Thus the molar fraction of the higher boiling point component increases and hence the boiling temperature  $T_b$  increases. The evolution of the system is also governed by the mass balance equations

$$\frac{dN_i}{dt} = -n_v y_i \quad (21)$$

for each  $i = 1, 2$ , and the energy balance equation

$$(c_1 w_1 N_1 + c_2 w_2 N_2) \frac{dT_b}{dt} = UA(T_s - T_b) - n_v (w_1 \lambda_1 x_1 + w_2 \lambda_2 x_2). \quad (22)$$

### 5.3 A method for the approximate solution of the basic equations

Let us consider the approximate solution of the basic equations on an interval  $[t, t + \Delta t]$  using an elementary difference scheme. If  $N_i$  is known at time  $t$  then we know  $x_i$  for each  $i = 1, 2$  and we can use the equations (17) and (19) to calculate  $T_b$ . We use equation (20) to find  $y_i$  for each  $i = 1, 2$  and we use the equations

$$\Delta N_i = -n_v y_i \Delta t \quad (23)$$

and

$$\Delta T_b = \frac{UA(T_s - T_b) - n_v (w_1 \lambda_1 x_1 + w_2 \lambda_2 x_2)}{c_1 w_1 N_1 + c_2 w_2 N_2} \Delta t \quad (24)$$

to find  $\Delta N_i$  for each  $i = 1, 2$  and  $\Delta T_b = \Delta T_b(n_v)$  in terms of the unknown parameter  $n_v$ . We can now substitute these values into the equation

$$(P_1 \Delta x_1 + x_1 \Delta P_1) + (P_2 \Delta x_2 + x_2 \Delta P_2) = 0 \quad (25)$$

with

$$\Delta x_1 = \frac{(N_1 y_2 - N_2 y_1) n_v \Delta t}{(N_1 + N_2)^2} = -\Delta x_2 \quad (26)$$

and

$$\Delta P_i = \frac{P_i \beta_i \Delta T_b}{(T_b + \gamma_i)^2} \quad (27)$$

to give

$$(P_1 - P_2) \frac{(N_1 y_2 - N_2 y_1) n_v}{(N_1 + N_2)^2} \Delta t + \left\{ \frac{P_1 \beta_1 x_1}{(T_b + \gamma_1)^2} + \frac{P_2 \beta_2 x_2}{(T_b + \gamma_2)^2} \right\} \Delta T_b(n_v) = 0 \quad (28)$$

from which we can calculate  $n_v$ . Now we can use equation (23) to determine  $\Delta N_i$  for each  $i = 1, 2$ . Finally we calculate the new values  $N_i(t + \Delta t) = N_i + \Delta N_i$  for each  $i = 1, 2$  and the solution is complete. This step can be repeated on subsequent time intervals.

## 6. A coupled system for distillation of a one component solvent

In this section we consider the distillation of a solvent with one component where the Dusol vessel and the condenser are connected so that vaporisation and condensation take place in a distillation chamber where the pressure is determined by the balance between the two processes.

### 6.1 Notation

We use the following additional notation:

- $U'$  is the overall heat transfer coefficient of the condenser;
- $A'$  is the heat transfer area of the condenser;
- $h_f$  is the heat transfer coefficient between the thin film of condensate and the condenser wall;
- $k$  is the thermal conductivity of the condensate;
- $g$  is the acceleration due to gravity;
- $\mu$  is the dynamic viscosity of the liquid;
- $d_o$  is the outside diameter of the condensation tube;
- $U_w$  is the heat transfer coefficient of the condenser wall;
- $T_w = T_w(t)$  is the temperature of the condenser wall at time  $t$ ;
- $T_c$  is the temperature of the coolant;
- $m_{v,e}$  is the mass vapourisation rate at equilibrium; and
- $T_{b,e}$  and  $T_{w,e}$  are equilibrium temperatures.

## 6.2 The basic equations

The vaporisation process becomes more efficient if the pressure in the Dusol vessel can be reduced. This can be accomplished by installing a vacuum pump or more effectively by isolating the Dusol vessel and the condenser from the atmosphere once vaporisation has commenced and all air has been expelled from the system. The condenser then acts as a vacuum pump for the coupled system and reduces the boiling temperature  $T_b$  as time passes. The mass balance in the vessel is given by

$$\frac{dM}{dt} = -m_v \quad (29)$$

and the energy balance in the vessel can be written as

$$cM \frac{dT_b}{dt} = UA(T_s - T_b) - m_v \lambda. \quad (30)$$

The energy balance in the condenser can be expressed in two different ways. The overall balance takes the form

$$m_v \lambda = U' A' (T_b - T_c) \quad (31)$$

where  $U'$  is the mean overall coefficient of heat transfer. Alternatively we can consider an energy balance between the thin film of condensate and the condenser wall and an energy balance between the condenser wall and the coolant. These energy balance equations are discussed in Section 10-18 of Perry and Chilton (1973). In the first place the energy balance between the thin film of condensate and the condenser wall is determined by the equation

$$m_v \lambda = h_f A' (T_b - T_w) \quad (32)$$

where the coefficient of heat transfer is given by

$$h_f = \frac{c_f}{(T_b - T_w)^{1/4}} \quad (33)$$

and  $c_f$  is determined by Nusselt's formula

$$c_f = \kappa \left[ \frac{k^3 \rho^2 g \lambda}{\mu d_o} \right]^{1/4} \quad (34)$$

with  $\kappa$  a known positive constant. The Nusselt formula was originally obtained by a thermo-fluid flow analysis of an idealised laminar film and has been found to give surprisingly good results in practice. In the second place the energy balance between the condenser wall and the coolant is given by

$$h_f A' (T_b - T_w) = U_w A' (T_w - T_c). \quad (35)$$

The quantities  $U_w$  and  $T_c$  are known. The equations (33) and (35) can be used to show that  $T_w$  is determined implicitly for each  $T_b$  by the unique solution  $T_w \in (T_c, T_b)$  to the equation

$$T_w + \left[ \frac{U_w(T_w - T_c)}{c_f} \right]^{4/3} = T_b \quad (36)$$

and now the equations (31), (32), (33) and (35) can be used to show that  $U'$  is also uniquely determined by  $T_b$  according to the formula

$$\frac{1}{U'} = \frac{1}{U_w} + \frac{(T_b - T_w)^{1/4}}{c_f}. \quad (37)$$

The equations (29), (30), (31), (36) and (37) form a closed set of non-linear equations which can be solved to find  $T_b$ ,  $M$ ,  $m_v$ ,  $T_w$  and  $U'$ .

### 6.3 Approximate solution of the basic equations using an elementary finite difference scheme

We consider the approximate solution of the basic equations on an interval  $[t, t + \Delta t]$  using an elementary difference scheme. We suppose that  $T_b$  is known at time  $t$ . Since  $T_c$  is a known constant we can use equations (36) and (37) to determine  $T_w$  and  $U'$ . We can calculate  $m_v$  from (31) and can also calculate  $\Delta M$  and  $\Delta T_b$  from the formulae

$$\Delta M = -m_v \Delta t \quad (38)$$

and

$$\Delta T_b = \left[ \frac{UA(T_s - T_b) - m_v \lambda}{cM} \right] \Delta t. \quad (39)$$

Thus we find  $M(t + \Delta t) = M(t) + \Delta M$  and  $T_b(t + \Delta t) = T_b(t) + \Delta T_b$ . This calculation can be repeated on subsequent time intervals. The boiling temperature will decrease if  $UA(T_s - T_b) < m_v \lambda$  and will increase if  $UA(T_s - T_b) > m_v \lambda$ . The corresponding pressure  $P$  is given by Antoine's formula (16).

The graphs shown in Figure 2 and Figure 3 were obtained by numerical solution of the equations for the coupled system using parameter values for water and nominal heat transfer capacities for the boiler and the condenser. For the purposes of the graphs we have chosen to measure mass in kilograms, temperature in degrees Celsius and time in minutes.

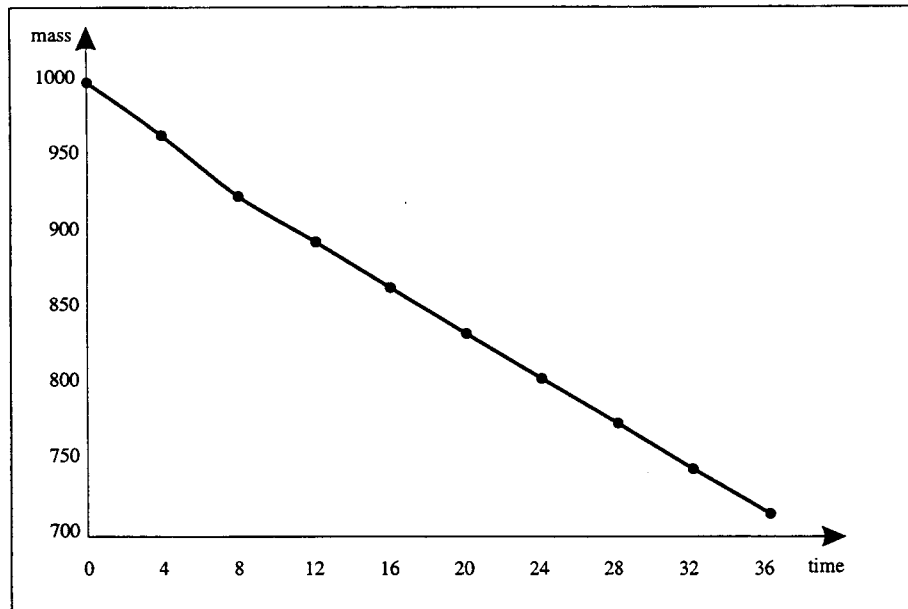


Figure 2: Graph of mass against time for simulated operation of the coupled system.

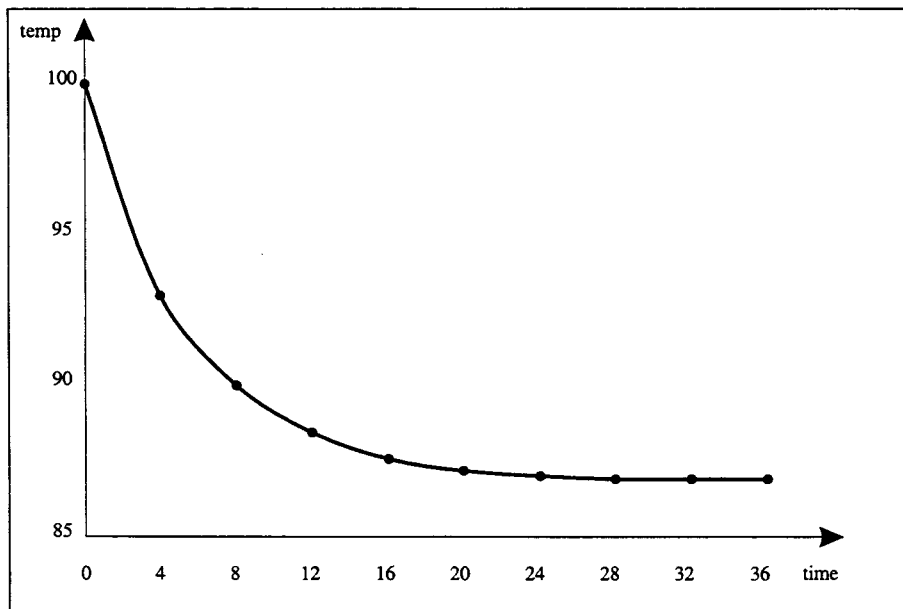


Figure 3: Graph of temperature against time for simulated operation of the coupled system.



## 6.4 The equilibrium temperatures

The equilibrium boiling temperature  $T_{b,e}$  and the equilibrium wall temperature  $T_{w,e}$  can be found by setting

$$m_v \lambda = UA(T_s - T_{b,e}) \quad (40)$$

and by using the additional equations

$$m_v \lambda = \frac{A'(T_{b,e} - T_c)}{\left[ \frac{1}{U_w} + \frac{(T_{b,e} - T_{w,e})^{1/4}}{c_f} \right]} = c_f A'(T_{b,e} - T_{w,e})^{3/4} = U_w A'(T_{w,e} - T_c) \quad (41)$$

to obtain the non-linear algebraic equations  $F(T_{w,e}) = T_{b,e}$  and  $G(T_{b,e}) = T_{w,e}$  where

$$F(T_w) = T_w + \left[ \frac{U_w(T_w - T_c)}{c_f} \right]^{4/3} \quad (42)$$

and

$$G(T_b) = T_b - \left[ \frac{UA(T_s - T_b)}{c_f A'} \right]^{4/3}. \quad (43)$$

It is obvious that  $F(T_c) = T_c$  and  $G(T_s) = T_s$ . Furthermore it can be seen that  $F'(T_w) < 1$  when  $T_w < T_c$  and  $F'(T_w) > 1$  when  $T_w > T_c$  and also that  $G'(T_b) > 1$  when  $T_b < T_s$  and  $G'(T_b) < 1$  when  $T_b > T_s$ . Therefore  $F(T_w) > T_w$  for all  $T_w \neq T_c$  and  $G(T_b) < T_b$  for all  $T_b \neq T_s$ . If we set

$$H(T_b) = F(G[T_b]) \quad \text{and} \quad K(T_w) = G(F[T_w]) \quad (44)$$

then  $H(T_c) < T_c$ ,  $K(T_c) < T_c$ ,  $H(T_s) > T_s$  and  $K(T_s) > T_s$ . It follows that there exist solutions  $T_{b,e}$  and  $T_{w,e}$  in the interval  $(T_c, T_s)$  to the equations  $H(T_b) = T_b$  and  $K(T_w) = T_w$ . The solutions are unique because  $H'(T_b) > 1$  and  $K'(T_w) > 1$  and they are related by the equations  $F(T_{b,e}) = T_{w,e}$  and  $G(T_{w,e}) = T_{b,e}$  which show that  $T_c < T_{w,e} < T_{b,e} < T_s$ . The solutions can be found using convergent iterations defined by

$$H(T_b^{(n+1)}) = T_b^{(n)} \quad \text{and} \quad K(T_w^{(n+1)}) = T_w^{(n)} \quad (45)$$

with  $T_b^{(0)} = T_s$  and  $T_w^{(0)} = T_c$ . Alternatively we could use these iterations in the form

$$F(T_w^{(n+1)}) = T_b^{(n)} \quad \text{and} \quad G(T_b^{(n)}) = T_w^{(n)} \quad (46)$$

starting from  $T_b^{(0)} = T_s$  to produce decreasing sequences  $\{T_b^{(n)}\}$  and  $\{T_w^{(n)}\}$  or starting from  $T_w^{(0)} = T_c$  to produce increasing sequences  $\{T_b^{(n)}\}$  and  $\{T_w^{(n)}\}$ . The iteration is illustrated in Figure 4.

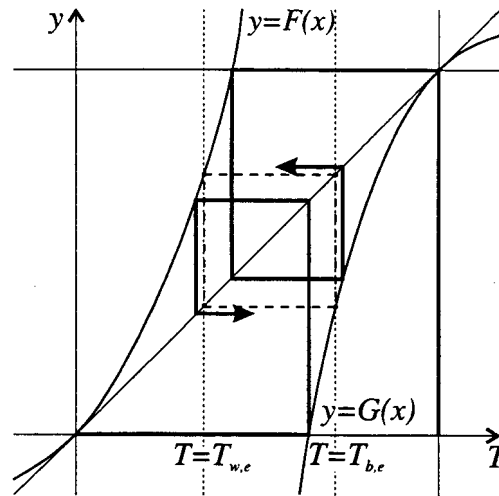


Figure 4: Determination of the equilibrium temperatures.

### 6.5 A quasi-steady-state solution

It is intuitively reasonable to assume that the distillation process reaches a quasi-steady-state and that the mass vaporisation rate approaches a corresponding constant value. If we assume that  $m_v = m_{v,e}$  for  $t_0 \leq t \leq t_1$  where  $t_1$  is the time at which distillation is completed and that  $M(t_1) = 0$  then

$$M = M(t_0) - m_{v,e}(t - t_0) \quad (47)$$

and

$$t_1 - t_0 = M(t_0)/m_{v,e} \quad (48)$$

and substitution into (30) shows that

$$\frac{dT_b}{UA(T_s - T_b) - m_{v,e}\lambda} = \frac{dt}{c[M(t_0) - m_{v,e}(t - t_0)]} \quad (49)$$

which is easily solved to give

$$\left| \frac{UA(T_s - T_b) - m_{v,e}\lambda}{UA[T_s - T_b(t_0)] - m_{v,e}\lambda} \right|^{cm_{v,e}/UA} = 1 - \frac{m_{v,e}(t - t_0)}{M(t_0)} \quad (50)$$

for  $t_0 \leq t \leq t_1$ . Since  $M(t_1) = 0$  it follows from equation (30) that

$$m_{v,e}\lambda = UA(T_s - T_{b,e}) \quad (51)$$

and we can rewrite the solution (50) in the form

$$\left[ \frac{T_b - T_{b,e}}{T_b(t_0) - T_{b,e}} \right]^{c(T_s - T_{b,e})/\lambda} = \frac{t_1 - t}{t_1 - t_0} \quad (52)$$

for  $t_0 \leq t \leq t_1$ . For convenience we have assumed that  $T_b(t_0) \geq T_b \geq T_{b,e}$ . We will show in the remainder of the section that this assumption is reasonable and that a rigorous analysis can be used to support the above intuitive procedure.

## 6.6 Exact solution of the basic equations

The original equations can be solved exactly by separating the variables. It is necessary to reformulate the problem in terms of the wall temperature  $T_w$  and to calculate the boiling temperature  $T_b = F(T_w)$  from  $T_w$  wherever necessary. From the equations (29) and (30) it follows that

$$cM \frac{dT_b}{dM} = (-1) \frac{UA(T_s - T_b)}{m_v} + \lambda \quad (53)$$

and by using equations (32), (33) and (43) this becomes

$$cM \frac{dT_b}{dM} = \lambda \left[ 1 - \frac{UA(T_s - T_b)}{c_f A' (T_b - T_w)^{3/4}} \right]. \quad (54)$$

By using the relationship (36) in the form  $T_b = F(T_w)$  the differential equation can be rewritten as

$$cM F'(T_w) \frac{dT_w}{dM} = \lambda \left\{ 1 - \left[ \frac{F(T_w) - K(T_w)}{F(T_w) - T_w} \right]^{3/4} \right\} \quad (55)$$

and we can now separate the variables to give

$$\frac{dM}{M} = \frac{cF'(T_w)dT_w}{\lambda D(T_w)} \quad (56)$$

where

$$D(T_w) = 1 - \left[ \frac{F(T_w) - K(T_w)}{F(T_w) - T_w} \right]^{3/4} \quad (57)$$

and hence the solution is given by

$$\log \left[ \frac{M}{M(t_0)} \right] = \int_{T_w(t_0)}^{T_w} \frac{cF'(T)dT}{\lambda D(T)} \quad (58)$$

provided  $D(T) \neq 0$  for all  $T$  in the interval of integration. We note that  $D(T_{w,e}) = 0$  with  $D(T) < 0$  for  $T < T_{w,e}$  and  $D(T) > 0$  for  $T > T_{w,e}$  and

that  $D'(T_{w,e}) > 0$ . Since  $F(T)$  and  $D(T)$  are analytic near  $T = T_{w,e}$  it follows that

$$\log \left[ \frac{M}{M(t_0)} \right] = \int_{T_w(t_0)}^{T_w} \left[ \frac{p}{(T - T_{w,e})} + r(T) \right] dT \quad (59)$$

where

$$p = \frac{cF'(T_{w,e})}{\lambda D'(T_{w,e})} = \frac{c[(T_{w,e} - T_c) + \frac{4}{3}(T_{b,e} - T_{w,e})](T_s - T_{b,e})}{\frac{4}{3}\lambda[(T_s - T_c) + \frac{1}{3}(T_{b,e} - T_{w,e})]} \quad (60)$$

and  $r(T)$  is analytic near  $T = T_{w,e}$ . It is easy to see that

$$0 < p < \frac{3}{4} \frac{c(T_s - T_{b,e})}{\lambda}. \quad (61)$$

Therefore the solution  $M = M(T_w)$  can be written in the form

$$M = M(t_0) \mathcal{R}(T_w) \left[ \frac{T_w - T_{w,e}}{T_w(t_0) - T_{w,e}} \right]^p \quad (62)$$

where  $\mathcal{R}(T_w) > 0$  and  $\mathcal{R}[T_w(t_0)] = 1$ . Thus  $M = 0$  if and only if  $T_w = T_{w,e}$  with either  $T_w(t_0) \leq T_w \leq T_{w,e}$  or else  $T_w(t_0) \geq T_w \geq T_{w,e}$ . For the sake of argument we will presume where necessary that the latter situation prevails.

## 6.7 Calculation of the distillation time

We will now show that  $T_w \rightarrow T_{w,e}$  as  $t \rightarrow t_1$  where  $t_1$  is the finite time at which distillation of the solvent is completed. In fact we will show that the previous solution can be used to find the time  $t = t(T_w)$  to reach a specified wall temperature  $T_w$ . By once again using the relationship (36) in the form  $T_b = F(T_w)$  and by using similar arguments to those used above we can separate the variables in equation (30) to give

$$\frac{cM(T_w)F'(T_w)dT_w}{c_f A' E(T_w)} = -dt \quad (63)$$

where

$$E(T_w) = [F(T_w) - T_w]^{3/4} - [F(T_w) - K(T_w)]^{3/4} \quad (64)$$

and hence the solution is given by

$$\int_{T_w(t_0)}^{T_w} \frac{cM(T)F'(T)dT}{c_f A' E(T)} = -(t - t_0) \quad (65)$$

provided  $E(T) \neq 0$  for all  $T$  in the interval of integration. In the manner of our previous analysis we note that  $E(T_{w,e}) = 0$  with  $E(T) < 0$  for  $T < T_{w,e}$

and  $E(T) > 0$  for  $T > T_{w,e}$  and that  $E'(T_{w,e}) > 0$ . Since  $F(T)$  and  $E(T)$  are analytic near  $T = T_{w,e}$  it follows that

$$\int_{T_w(t_0)}^{T_w} \left[ \frac{T - T_{w,e}}{T_w(t_0) - T_{w,e}} \right]^p \left[ \frac{q}{(T - T_{w,e})} + s(T) \right] dT = -(t - t_0) \quad (66)$$

where

$$q = \frac{cM(t_0)\mathcal{R}(T_{w,e})F'(T_{w,e})}{c_f A' E'(T_{w,e})} > 0 \quad (67)$$

and  $s(T)$  is analytic near  $T = T_{w,e}$ . By evaluating this integral we obtain our solution in the form

$$\mathcal{S}(T_w) \left[ \frac{T_w - T_{w,e}}{T_w(t_0) - T_{w,e}} \right]^p - \mathcal{S}[T_w(t_0)] = -(t - t_0) \quad (68)$$

where  $\mathcal{S}(T_w)$  is analytic near  $T = T_{w,e}$ . This shows that the total distillation time  $(t_1 - t_0)$  is a finite time given by

$$t_1 - t_0 = \mathcal{S}[T_w(t_0)] \quad (69)$$

and that  $T_w = T_{w,e}$  when  $t = t_1$ . Now it is convenient to write the solution as

$$\mathcal{X}(T_w) \left[ \frac{T_w - T_{w,e}}{T_w(t_0) - T_{w,e}} \right]^p = \frac{t_1 - t}{t_1 - t_0} \quad (70)$$

where  $\mathcal{X}(T_w) = \mathcal{S}(T_w)/\mathcal{S}[T_w(t_0)]$  for  $t_0 \leq t \leq t_1$ . Note that  $\mathcal{X}[T_w(t_0)] = 1$ .

## 6.8 The dependence of mass on time

From the solutions in (62) and (70) we can see that

$$M = \mathcal{Y}(T_w)M(t_0) \left[ \frac{t_1 - t}{t_1 - t_0} \right] \quad (71)$$

and

$$m_{v,e} = \left. \frac{dM}{dt} \right|_{t=t_1} = \frac{\mathcal{Y}(T_{w,e})M(t_0)}{\mathcal{S}[T_w(t_0)]} \quad (72)$$

where  $\mathcal{Y}(T_w) = \mathcal{R}(T_w)/\mathcal{X}(T_w)$  and  $\mathcal{Y}[T_w(t_0)] = 1$ . Now we can write

$$M = \mathcal{Y}(T_w)M(t_0) - \left[ \frac{\mathcal{Y}(T_w)}{\mathcal{Y}(T_{w,e})} \right] m_{v,e}(t - t_0) \quad (73)$$

and

$$t_1 - t_0 = \frac{\mathcal{Y}(T_{w,e})M(t_0)}{m_{v,e}} \quad (74)$$

to compare the exact solutions with the earlier intuitive formulae.

## 7. A coupled system for distillation of a two-component solvent

In this section we consider the distillation of a solvent with two components where the Dusol vessel and the condenser are connected so that vaporisation and condensation take place in a distillation chamber where the pressure is determined by the balance between the two processes.

### 7.1 Notation

We use the following additional notation:

- $x = x(t) = (x_1(t), x_2(t)) = (x_1, x_2)$  is the molar composition vector for the liquid at time  $t$ ;
- $y = y(t) = (y_1(t), y_2(t)) = (y_1, y_2)$  is the molar composition vector for the vapour at time  $t$ ;
- $Q_i = Q_i(t)$  is the partial pressure of component  $i$  in the vapour at time  $t$ ;
- $T_d = T_d(t)$  is the condensation temperature of the vapour at time  $t$ ;
- $h_f = h_f(y)$  is the heat transfer coefficient between the thin film of condensate and the condenser wall;
- $k = k(y)$  is the thermal conductivity of the condensate; and
- $\mu = \mu(y)$  is the dynamic viscosity of the condensate.

### 7.2 The basic equations

Once again we isolate the Dusol vessel and the condenser from the atmosphere when vaporisation has commenced and all air has been expelled from the system. As before we use the basic equations (17), (18), (19), (20), (21) and (22) to determine the boiling point  $T_b$  of the liquid in the vessel. The pressure  $P$  is no longer constant and is determined by a balance between the vaporisation process and the condensation process. The overall energy balance in the condenser takes the form

$$n_v(w_1\lambda_1y_1 + w_2\lambda_2y_2) = U' A'(T_d - T_c) \quad (75)$$

where  $U'$  is the mean overall coefficient of heat transfer. Alternatively we can consider an energy balance between the thin film of condensate and the condenser

wall and an energy balance between the condenser wall and the coolant. In the first place the energy balance is determined by the equation

$$n_v(w_1\lambda_1y_1 + w_2\lambda_2y_2) = h_f A'(T_d - T_w) \quad (76)$$

where the coefficient of heat transfer is given by

$$h_f = \frac{c_f}{(T_d - T_w)^{1/4}} \quad (77)$$

and  $c_f$  is determined by Nusselt's formula

$$c_f = \kappa \left[ \frac{k^3 \rho^2 g \lambda}{\mu d_o} \right]^{1/4} \quad (78)$$

where  $\kappa$  is a known positive constant and where  $\lambda = \lambda(y)$  is given by

$$\lambda(y) = \frac{w_1\lambda_1y_1 + w_2\lambda_2y_2}{w_1y_1 + w_2y_2}. \quad (79)$$

In the second place the energy balance is given by

$$h_f A'(T_d - T_w) = U_w A'(T_w - T_c). \quad (80)$$

It is necessary to balance the vapour pressures using the equation

$$x_1 P_1 + x_2 P_2 = y_1 Q_1 + y_2 Q_2 \quad (81)$$

which is Raoult's law where

$$\log Q_i = \alpha_i - \frac{\beta_i}{T_d + \gamma_i} \quad (82)$$

is determined by Antoine's law for each  $i = 1, 2$ .

## A The Appendix

### A1 The modified basic equations for distillation of a one-component solvent

We will let  $h = h(t)$  denote the height of the surface of the liquid solvent with the final height  $h(t_1)$  and we will assume that the container is cylindrical in shape for  $h \geq h(t_1)$ . For  $t_0^* \leq t \leq t_1$  the contact area  $A = A(t)$  at height  $h$  is given by

$$A = 2\pi r[h - h(t_1)] + A(t_1) \quad (83)$$

where  $A(t_1)$  is the final contact area and the mass  $M = M(t)$  of liquid is calculated from

$$M = \pi r^2 [h - h(t_1)] \rho + M(t_1) \quad (84)$$

where  $\rho$  is the density of the liquid. When  $t = t_0^*$  the height at the liquid surface is equal to the height at the top of the steam jacket and so

$$h(t_0^*) - h(t_1) = \frac{A(t_0^*) - A(t_1)}{2\pi r} \quad (85)$$

where we note that  $A(t_0^*) = A(t_0) = A(0)$  and

$$M(t_0^*) = \pi r^2 [h(t_0^*) - h(t_1)] \rho + M(t_1). \quad (86)$$

From the original analysis using equation (15) with  $t_1$  replaced by  $t_0^*$  and  $M(t_1)$  replaced by  $M(t_0^*)$  we have

$$t_0^* = t_0 + \frac{\lambda [M(t_0) - M(t_0^*)]}{UA(t_0)(T_s - T_b)}. \quad (87)$$

The equations for mass balance and energy balance in the region  $t_0^* \leq t \leq t_1$  are given by

$$\frac{dM}{dt} = -m_v \quad (88)$$

and

$$m_v \lambda = UA(T_s - T_b) \quad (89)$$

from which it follows that

$$\frac{d}{dt} [h - h(t_1)] + \frac{2U}{\lambda \rho r} [h - h(t_1)] = -\frac{UA(t_1)}{\lambda \pi r^2 \rho} (T_s - T_b). \quad (90)$$

By using the initial condition (85) we obtain the solution

$$h - h(t_1) = \left\{ \frac{A(t_0^*)}{2\pi r} - \frac{A(t_1)}{2\pi r} [1 - (T_s - T_b)] \right\} e^{-2U(t-t_0^*)/\lambda \rho r} - \frac{A(t_1)}{2\pi r} (T_s - T_b) \quad (91)$$

for  $t_0^* \leq t \leq t_1$ . It follows that

$$t_1 = t_0^* + \frac{\lambda \rho r}{2U} \log \left[ 1 + \frac{A(t_0^*) - A(t_1)}{A(t_1)(T_s - T_b)} \right] \quad (92)$$

which gives the natural first order approximation

$$t_1 - t_0^* \approx \frac{\lambda \rho r [A(t_0^*) - A(t_1)]}{2UA(t_1)(T_s - T_b)} = \frac{\lambda [M(t_0^*) - M(t_1)]}{UA(t_1)(T_s - T_b)}. \quad (93)$$



## Acknowledgements

The moderators, Phil Howlett and Colin Thompson, were assisted by Michael Sparrow and Brian Harlow from *Dulux Australia*, and by John Andrews, Derek Chan, Des Hill, Paul Livingstone, Chuck Miller, Erich Olbrich and Michael Peake. Particular thanks are due to Derek Chan who suggested that the condenser could be used to lower the pressure in the boiler and to Erich Olbrich who supplied most of the specific information about the heat exchange equations for the condenser. We are also indebted to Erich for running the numerical simulations of the distillation process sketched in Figure 2 and Figure 3. Finally we wish to acknowledge the valuable role played by John Andrews and Erich Olbrich in providing sound engineering advice to the research team.

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